

Diesel Emission Control – Sulfur Effects (DECSE) Program

Phase I Interim Data Report No. 3:

**Diesel Fuel Sulfur Effects on
Particulate Matter Emissions**

November, 1999

**Sponsored by:
The U.S. Department of Energy
Engine Manufacturers Association
Manufacturers of Emission Controls Association**

The test program and subsequent data analysis represents a collaborative effort of a technical work group consisting of representatives from the U.S. Department of Energy, National Laboratories, Engine Manufacturers Association, and Manufacturers of Emission Controls Association. The work group prepared this report using methods believed to be consistent with accepted practice. All results and observations are based on information available using technologies that were state-of-the-art at the time of this effort. To the extent that additional information becomes available, or factors upon which analyses are based change, the findings could subsequently be affected.

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List of Acronyms

APG – Absolute pressure gauge
CDPF – Catalyzed diesel particulate filter
CFM – Cubic feet per minute
CO – carbon monoxide
CO₂ – carbon dioxide
CR-DPF – continuously regenerating diesel particulate filter
cpsi – cells per square inch
DECSE – Diesel Emission Control-Sulfur Effects
DOC – diesel oxidation catalyst
DPF – diesel particulate filter
EGR – exhaust gas recirculation
EMA – Engine Manufacturers Association
EO – engine-out
FEP – fuel economy penalty
FEV – FEV Engine Technology
H₂ – hydrogen
HC – hydrocarbon(s)
HSDI – high-speed, direct injection
MECA – Manufacturers of Emission Controls Association
N₂ – nitrogen
NO_x – oxides of nitrogen
NREL – National Renewable Energy Laboratory
NVH – noise-vibration harshness
OEM – original equipment manufacturer
ORNL – Oak Ridge National Laboratory
OTT – Office of Transportation Technologies
PDP-CVS – Positive Displacement Pump-Constant Volume Sampler
PM – particulate matter
ppm – parts per million
R&D – research and development
RTD – Resistive thermal device
SO₂ – sulfur dioxide
SO₃ – sulfur trioxide
SOF – soluble organic fraction
TPM – total particulate matter
TWC – three-way catalyst

Executive Summary

ES.1 DECSE Objective

The Diesel Emission Control–Sulfur Effects (DECSE) program is a joint government/industry program that studies the impact of diesel fuel sulfur levels on emission control systems. The use of these systems could lower emissions of oxides of nitrogen (NO_x) and particulate matter (PM) from on-highway trucks in the 2002-2004 model years. The program's systems-level approach will serve to enhance our collective knowledge base on engines, diesel fuels, and emission control technologies. The results will (1) guide industry in developing products with lower emissions, and (2) add to the technical base for government decisions about regulating diesel fuel's sulfur content.

Phase 1 of the program was designed to meet the following objectives:

- (A) Evaluate the effects of varying the fuel's sulfur content on the emission reduction performance of four emission control technologies
- (B) Measure and compare the effects of up to 250 hours of aging on selected devices for multiple levels of fuel sulfur content.

Four emission control technologies are being tested in Phase 1: (1) NO_x adsorbers, (2) diesel particulate filters (DPFs), (3) lean-NO_x catalysts, and (4) diesel oxidation catalysts (DOCs). The devices include commercially available technologies as well as state-of-the-art technologies that are being developed. The sulfur contents in the test fuels are nominally 3, 16 (NO_x adsorber only), 30, 150, and 350 parts per million (ppm). The engines being tested are currently available models that were selected to provide a representative source of diesel exhaust and various exhaust temperature profiles to challenge the emission control devices. Important characteristics of the exhaust stream are exhaust flow rate, stream temperature, and concentrations of NO_x, hydrocarbons (HC), carbon monoxide (CO), and PM.

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

The results of this program to date have been organized into separate reports describing different aspects of the four technologies. Previous Interim Reports may be found on www.ott.doe.gov/decse. This report covers the effects of diesel fuel sulfur level on particulate matter emissions.

ES.2 Diesel Oxidation Catalyst

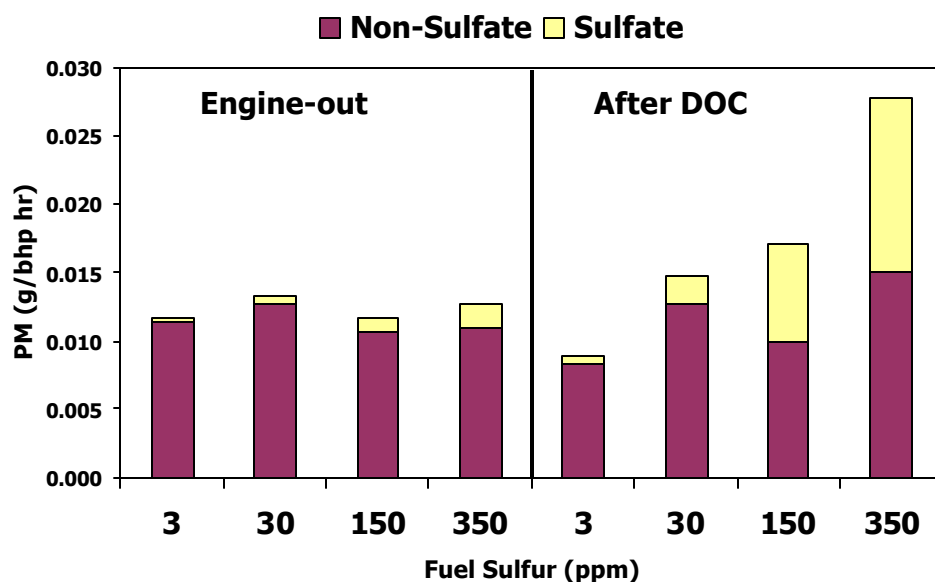
Diesel oxidation catalysts reduce HC, CO, and PM emissions in engine exhaust by oxidation over precious metal catalysts. PM is lowered by oxidation of the soluble organic fraction (SOF) of diesel

PM. Catalyst selection is based on the exhaust temperature requirement. West Virginia University (WVU) is conducting aging and evaluation of the DOC. Engines used in this program were selected to represent reasonable extremes in operation. The Cummins ISM370 represents a typical heavy-duty line-haul truck engine that meets 1999 certification requirements. Aging sequences were conducted using fuels with each of the following nominal fuel sulfur levels: 3, 30, 150, and 350 ppm.

This interim report covers PM emissions data on the high temperature catalyst. Post-catalyst emission measurements are compared to engine-out measurements (with the same fuel and operating conditions) to determine PM reduction efficiencies and relative PM composition.

Results for the Navistar T444E are pending data analysis. For the Cummins ISM370, engine-out and catalyst-out PM emissions, including analysis for sulfate fraction, were measured on the 4-mode OICA cycle, at OICA mode 2 (peak torque), and on the heavy-duty FTP (exhaust temperature range = 270°C – 518°C).

Figure ES-1 illustrates results from OICA Mode 2 (peak torque). At this high exhaust temperature (518°C), engine-out PM emissions are largely independent of fuel sulfur, but catalyst-out emissions show a very strong sulfur effect. With 3-ppm fuel, catalyst-out emissions are 0.009 g/bhp hr but increase to 0.027 g/bhp hr with the 350-ppm fuel. Compositional analysis confirms that a large fraction of this difference can be attributed to an increase in sulfate content. At this condition engine-out sulfate conversion is approximately 2%. The DOC increases this sulfate conversion to 10%. This conversion level is relatively low due to the low precious metal content of the catalyst formulation.



(Catalyst inlet temperature = 518°C)

Figure ES-1: OICA Mode 2 (Peak Torque) PM emissions – Cummins ISM 370 – DOC

In order to examine effects of transient operation, catalyst evaluations were performed over the heavy-duty FTP. In this study, PM emissions over the heavy-duty FTP varied independent of fuel sulfur level for both engine-out and catalyst-out emissions. Compositional analysis of the PM determined that a very small fraction of the total PM was sulfate, even when run with the 350-ppm sulfur fuel. Catalyst inlet temperature over the heavy-duty FTP is quite low, averaging 239°C over the cycle. These temperatures are too low to produce significant amounts of sulfate with this catalyst formulation.

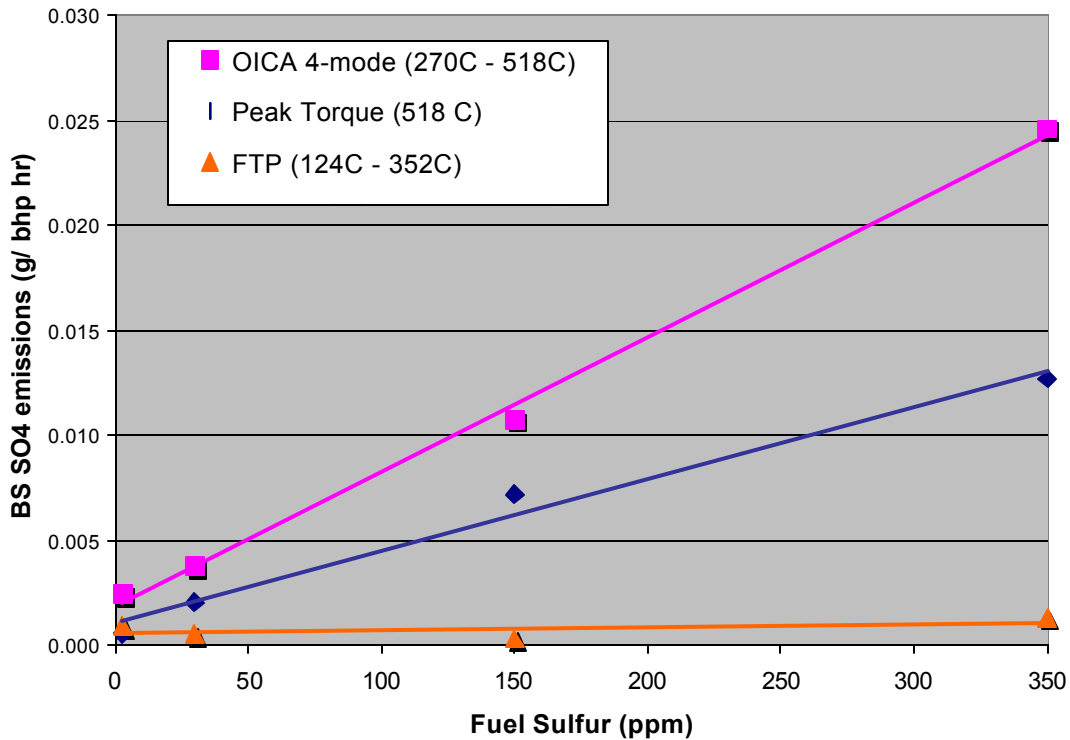


Figure ES-2: Summary of Catalyst-out Sulfate Emissions as a Function of Fuel Sulfur Level—Cummins ISM370- DOC (catalyst inlet temperature)

Conclusions

- Under certain operating conditions, DOCs can increase PM emissions above engine-out emissions due to an increase in sulfate fraction. The magnitude of this increase is directly proportional to the amount of sulfur in the diesel fuel. This sulfate increase counteracts the SOF reduction benefit of the DOC.
- Catalyst-out sulfate conversion with a DOC is temperature dependent and varies with operating condition: 1% over the heavy-duty FTP, 8% at peak torque, and 15% over a 4-mode steady-state composite test.

ES.3 Lean-NO_x Catalyst

Lean-NO_x catalysts reduce diesel NO_x emissions with the assistance of a supplemental HC reducing agent (such as diesel fuel) under a lean (oxygen-rich) exhaust condition. Lean-NO_x catalysts can be divided into two different groups: low-temperature (170E– 300EC) and high-temperature (350E– 600EC). Low-temperature catalysts are primarily composed of precious metals, such as platinum (Pt); high-temperature catalysts are mainly composed of base metal components, such as metal/zeolite (Cu-ZSM) catalysts. In addition to the temperature effect, other parameters also affect catalyst performance: HC and NO_x concentration (and HC/NO_x ratio), space velocity, precious-metal (or base-metal) loading, fuel sulfur level, HC speciation, and flow distribution. If diesel fuel is used as the reductant, the type of sulfur components and the level of fuel vaporization also affect the catalyst performance. In this interim report, the effect of diesel sulfur level on sulfate formation by the given high-temperature lean-NO_x catalyst is summarized and discussed.

PM and sulfate (SO₄) emission data from the lean-NO_x evaluation tests are presented in Figure ES-3 and ES-4. The reported sulfate portion does not include the bound water. Also, the reported PM and SO₄ values only came from the primary particulate filters. Figure ES-3 depicts the comparison between the engine-out data and the catalyst-out results from the OICA 4-mode test cycle. The high-temperature lean-NO_x catalyst sulfate emissions (catalyst-out) were higher than that of the engine baseline (engine-out) with the 150- and 350-ppm sulfur fuels. The higher the diesel sulfur level, the higher the sulfate (SO₄) emission level. This result implies that the high-temperature lean-NO_x promotes sulfate (SO₄) formation. The experimental results at the OICA mode 2 (peak torque) are displayed in Figure ES-4. Once again, the catalyst-out sulfate emissions were higher than that of the engine-out with the 150- and 350-ppm sulfur fuels. At this high temperature (~518°C), the percentage of sulfate in the TPM was higher than that of the OICA 4-mode test cycle for both engine-out and catalyst-out data. The high temperature lean-NO_x catalyst showed no propensity to make sulfate with a diesel sulfur level of less than 30-ppm.

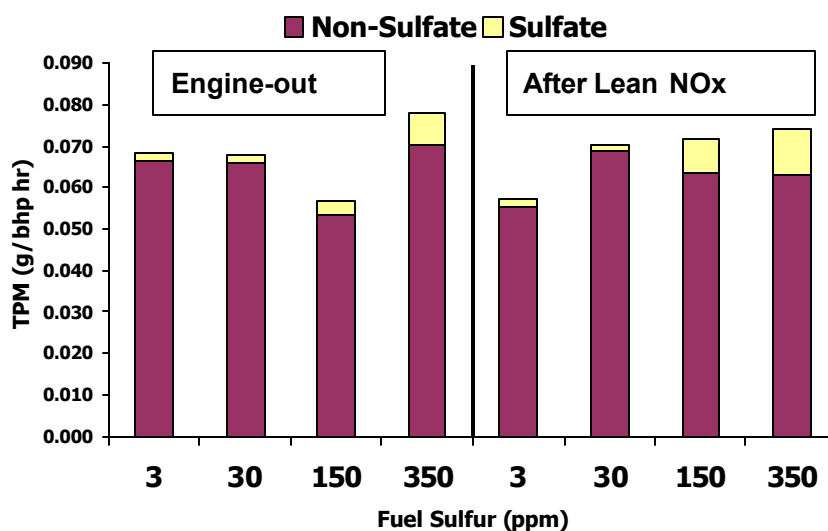


Figure ES-3. Comparison of SO₄ emissions between converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, OICA 4-mode composite)

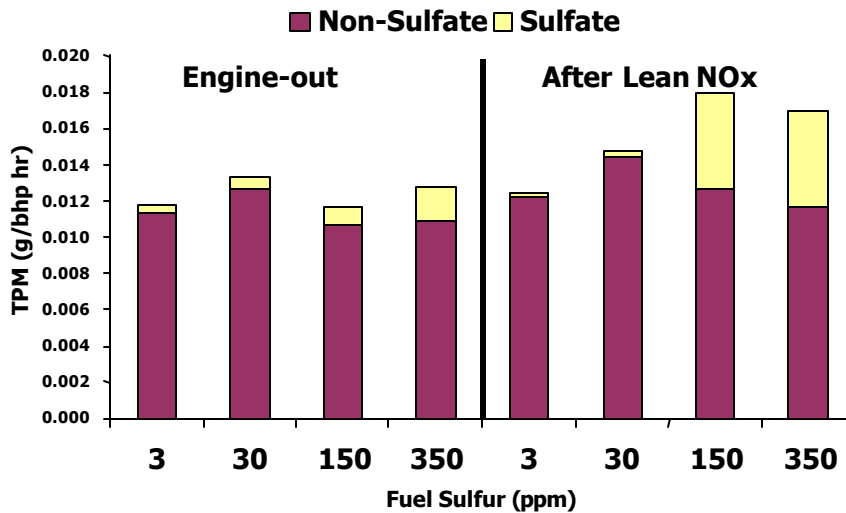


Figure ES-4. Comparison of SO₄ emissions between converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, OICA Mode 2)

Conclusions

- With 150- and 350-ppm sulfur fuels, the engine-out sulfate emissions increased by a factor of 2 to 5 compared to the levels observed with 3-ppm sulfur fuel. With the high-temperature lean-NO_x catalyst, the post-catalyst sulfate emissions increased by a factor of 10 to 20.
- With the high exhaust temperature (~518°C) at OICA mode 2, the percentage of sulfate in TPM was higher than that of the OICA 4-mode test cycle for both engine-out and catalyst-out data.

ES.4 Continuously Regenerating Diesel Particulate Filter and Catalyzed Diesel Particulate Filter

The CR-DPF and CDPF represent two general approaches to passive regeneration of DPFs. Passive regeneration is preferred, as opposed to active regeneration, because passive regeneration offers significant fuel consumption savings, lower system cost and is less complex.

The CR-DPF and CDPF were designed to remove PM from the engine exhaust stream. In each device, PM was removed from the exhaust stream by collecting on a filter, which in these cases are ceramic wall-flow elements. Unlike other diesel emissions control devices, primary removal of the targeted pollutant (PM) is fixed by the physical characteristics of the filter medium and is relatively unaffected by the engine operating conditions. The critical issue, instead, is the cleaning or regeneration of the DPF (by oxidation of the collected PM) to prevent DPF from plugging.

The CR-DPF accomplishes this filter regeneration by continuously generating NO₂ from engine-emitted NO over a diesel oxidation catalyst placed upstream of the DPF. NO₂ has been established as a more effective low-temperature oxidizing agent for diesel PM than oxygen. Sulfur in the exhaust (originated from the fuel and lubricant), however, can be oxidized over the CR-DPF,

forming sulfates, which are measured as PM. Sulfur oxides also compete for the critical NO and NO₂ reaction, making the regeneration characteristics less effective.

The CDPF accomplishes the DPF regeneration by using a catalyst coating on the DPF element to promote oxidation of the collected PM using available oxygen in the diesel exhaust. Sulfur in the exhaust can be oxidized over the CDPF to form sulfates. Exhaust-gas temperature and fuel-sulfur level are critical factors that affect the performance of both types of DPFs (CR-DPF and CDPF)

Engineering Test Services (ETS) in Charleston, South Carolina, has been contracted to conduct the DPF test program. A Caterpillar 3126 engine rated at 205 kW (275 horsepower) and equipped with electronic controls was used for the tests. The 3126 engines are typically used for applications that result in relatively low temperature exhaust (e.g. below 300°C). For such applications, regeneration of the DPF at low temperature is critical to proper operation of the emissions control system and hence the engine operation (maintaining a low back pressure by not allowing PM to build up continuously on the filter). Because fuel sulfur is expected to affect the filter regeneration temperature, these low temperature applications are an excellent test of the effects of fuel sulfur.

The two DPF technologies chosen for the program, CR-DPF and CDPF, underwent (1) emissions tests over steady state and the 13-mode OICA for PM and selected gases, and (2) experiments to measure the effect of fuel sulfur level on the regeneration temperature required by the filter devices. When operating on 3-ppm sulfur fuel with either of the DPF devices, overall particulate reductions in excess of 90% are observed. However, as the nominal sulfur level of the fuel is increased to 30-ppm, 150-ppm, and finally to 350-ppm a corresponding increase in the total particulate emissions are observed (see figure ES-5).

At the 150-ppm nominal sulfur test point an apparent 0% reduction in PM is seen. The results of the particulate compositional filter analysis show that the SOF and carbon fractions of the particulate have been largely removed and an equivalent mass of sulfate has been generated. At the 350-ppm nominal test point the total PM has increased by roughly a factor of two over baseline engine emissions.

Conclusions

- Fuel sulfur* has significant effects on PM emissions. Both DPFs were effective in reducing PM emissions (95% over the OICA cycle) when using fresh catalysts with 3-ppm sulfur fuel. With 30-ppm sulfur fuel, the PM reduction efficiencies for the fresh catalysts dropped to 72 and 74% for the CR-DPF and CDPF, respectively. At the 150-ppm sulfur test point, PM reductions were near zero.
- The conversion efficiency of fuel sulfur to sulfate particulate over the 13-mode OICA cycle appears to be approximately 40% to 50%.
- Results to date show that the DPF regeneration temperatures (at which the collected PM is oxidized to prevent plugging) are higher when testing with the 30-ppm fuel. Additional testing is planned with the 150-ppm and 350-ppm fuels.

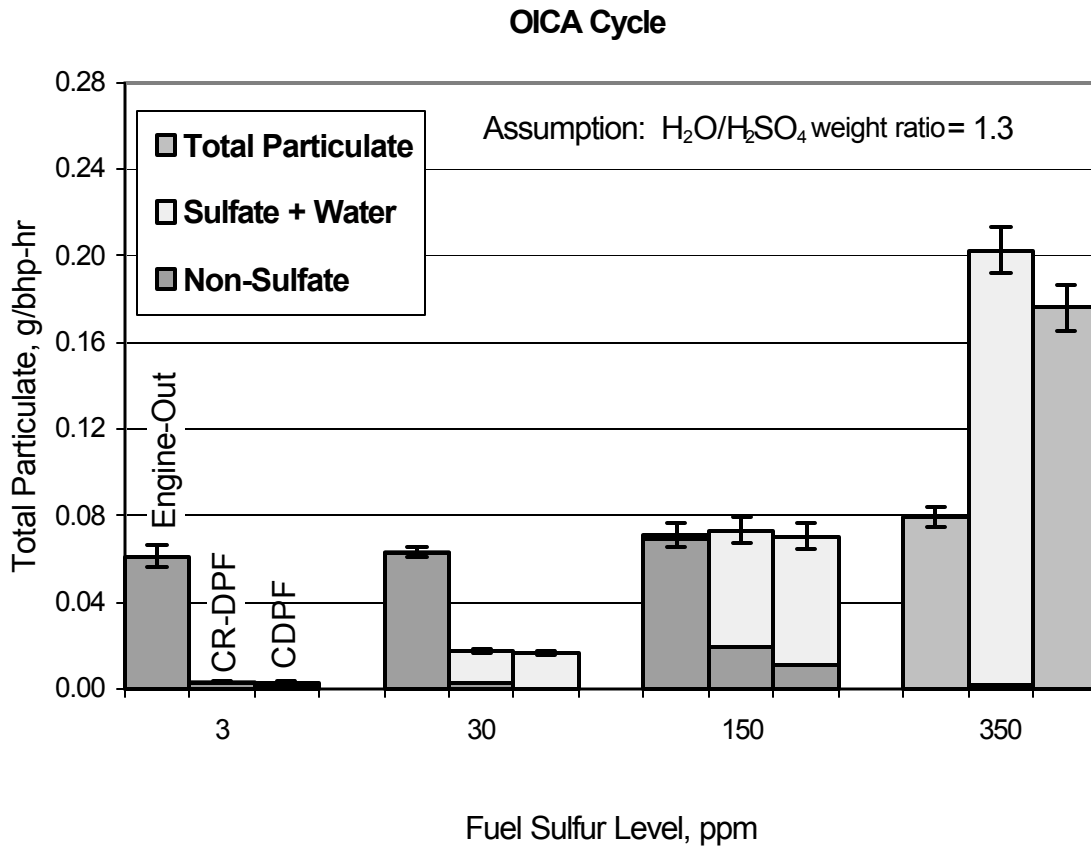


Figure ES-5. Effect of Fuel Sulfur Level on OICA Cycle PM

ES.5 NO_x Adsorber Catalyst

The results reported in the Phase 1 Interim Report No. 2 (Oct 99) showed how adsorber catalyst performance was affected by sulfur level for three different fuel sulfur levels. This report uses the same data base to examine how the fuel sulfur level affected exhaust particulate, both at the engine and catalyst outlets.

The NO_x adsorber catalyst functions by first storing NO_x during the lean exhaust conditions typical of diesel engine operation and then in a briefly rich condition reducing the stored NO_x to N₂ over three-way catalyst materials. The adsorber has a strong affinity for sulfur; SO₂ in the exhaust undergoes reactions forming sulfates on the catalyst adsorbent that are extremely stable. As a result, in time, sulfur in the exhaust will block the NO_x adsorption sites and reduce its NO_x conversion effectiveness.

Given these characteristics, analysis of the test data indicates that, as shown in Figure ES-6, the total particulate material (TPM) at the catalyst outlet was in the same range and nearly constant for the three fuel sulfur levels for the duration of testing. The catalyst-out TPM represents up to an 80% reduction in engine-out TPM. The engine-out TPM has a large soluble organic fraction (SOF), much of which is removed by the adsorber catalyst. This removal is not degraded by catalyst aging.

Furthermore, results showed that sulfates in the particulate material at the catalyst outlet were undetectable, consistent with the adsorber's strong sulfur affinity. This was also true for the test duration and at all sulfur levels.

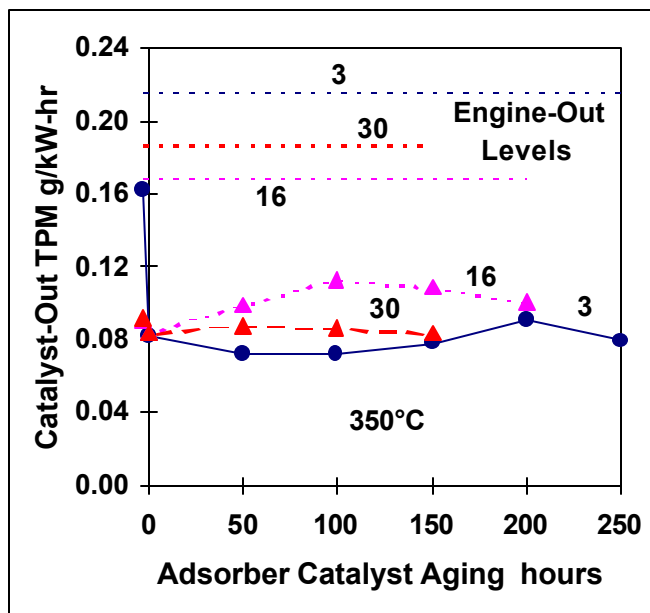


Figure ES-6. Adsorber catalyst total particulate material during aging

Conclusions

- NO_x adsorber catalysts significantly reduce engine-out TPM and SOF emissions across the full temperature range of operation, with the highest efficiencies in the low temperature regimes.
- The ability of the adsorber catalyst to reduce engine-out TPM and SOF does not degrade with catalyst aging, up to 250 hrs.
- No fuel sulfur affects are apparent for TPM, SOF or non-SOF across the range of analysis temperature or during adsorber catalyst aging up to 250 hours
- With fuel sulfur levels up to 30-ppm, adsorber catalysts apparently do not cause elevated sulfate releases into the atmosphere, consistent with the sulfur-adsorbing chemical process inherent in the NO_x adsorber catalyst.

Section 1

Introduction

1.1 *DECSE Objective*

A joint government/industry test program, “Diesel Emission Control – Sulfur Effects” (DECSE), is in progress to determine the impact of diesel fuel sulfur levels on emission control systems that could be implemented to lower emissions of nitrogen oxides and particulate matter from on-highway trucks in the 2002-2004 model year.

The program, spanning calendar year 1999, is being conducted by the U.S. Department of Energy’s (DOE) Office of Heavy Vehicle Technologies within DOE’s Office of Transportation Technologies; the National Renewable Energy Laboratory (NREL); Oak Ridge National Laboratory; manufacturers of heavy-duty engines under the Engine Manufacturers Association (EMA); and manufacturers of emission control systems under the Manufacturers of Emission Controls Association (MECA).

To date, the work group has issued two interim data reports:

- DECSE Program Phase 1 Interim Data Report No. 1 (Lean-NO_x Catalysts, Diesel Oxidation Catalysts, Continuously Regenerating – Diesel Particulate Filters, and Catalyzed Diesel Particulate Filters); August 1999.
- DECSE Program Phase 1 Interim Data Report No. 2: NO_x Adsorber Catalysts; October, 1999.

In this same timeframe, the U.S. Environmental Protection Agency (EPA) issued an Advanced Notice of Proposed Rulemaking (ANPRM) indicating their considerations to set “new quality requirements for diesel fuel to enable the use of a new generation of emission control technologies for diesel engines” [64 Fed. Reg. 26142; May 13, 1999]. Stakeholder input in response to the ANPRM, including the results from the DECSE program, will be considered as the agency drafts a Notice of Proposed Rulemaking (NPRM) which will likely be released early in 2000.

In conjunction with the diesel fuel ANPRM, EPA issued an NPRM [64 Fed. Reg. 26003; May 13, 1999; the “Tier 2 Proposal”] which proposes extremely stringent standards on NO_x and PM emissions from passenger cars, light-duty trucks, minivans, and sport utility vehicles as well as requirements that would mandate lower sulfur gasoline. Additionally, the agency is expected to publish an NPRM covering new heavy-duty emissions standards that could go into effect as early as 2007. Both the Tier 2 regulations and these new heavy-duty diesel standards are not approachable without improved engine, fuel, and emissions control device technologies working in concert. It is in this spirit that the DECSE program was initiated.

1.2 Fuel Sulfur Impact on Emissions

Sulfur from fuel and to some extent the engine lubricant has implications on the emissions from both catalyst and non-catalyst equipped engines. There are two distinct emissions impacts:

- deterioration of catalytic converter performance due to deactivation (poisoning) of catalyst sites by sulfur.
- formation of sulfate laden particulate matter.

These effects have been the subject of much study and are extensively documented in the literature [1-11]. While the DECSE program independently addresses each mechanism, this report will specifically address the latter.

In 1993, on-highway diesel fuel sulfur levels were reduced to 500 ppm. This mandated sulfur reduction enabled manufacturers of heavy-duty diesel engines to meet the 1994 particulate matter emission standard of 0.1 g/bhp hr. Another step-change improvement in PM emissions would likely require associated reductions in fuel sulfur.

Diesel exhaust contains sulfur dioxide (SO_2) formed during the combustion of sulfur from diesel fuel and lubricating oil. A fraction of this SO_2 is oxidized in the exhaust to form SO_3 , which rapidly hydrates to form sulfate and is emitted as particulate matter (thus contributing to total PM in certification testing). The degree of conversion is dependent to a great extent on the exhaust temperature and the presence of a catalyst. Figure 1.2-1 illustrates the strong temperature dependence of the SO_3/SO_2 equilibrium ratio. It is clear that increasing temperature favors the production of SO_3 . While engine-out SO_2 conversion rates are in the range of 1-3%, post-catalyst conversion rates can escalate to 60-70% under certain operating conditions. In the absence of much lower sulfur diesel fuels, introduction of high efficiency NO_x and hydrocarbon reduction catalysts would come at the expense of higher PM emissions resulting from the high fraction of sulfate in the particulate matter.

The new heavy-duty engine emission certification protocol has become very comprehensive, requiring testing under the HD transient Federal Test Procedure (FTP), as well as a 13-mode steady-state Supplemental Emissions Test. In addition, compliance is required at any point in a Not-To-Exceed (NTE) zone (See Figure 1.2-2). The evaluation modes and a portion of the NTE zone extend into the high load regime making converter performance under high exhaust temperatures critical. It is under these high exhaust temperature conditions that the catalytic conversion of sulfate is a maximum. With these factors in mind, this report summarizes data and conclusions pertaining to PM emissions in the DECSE program.

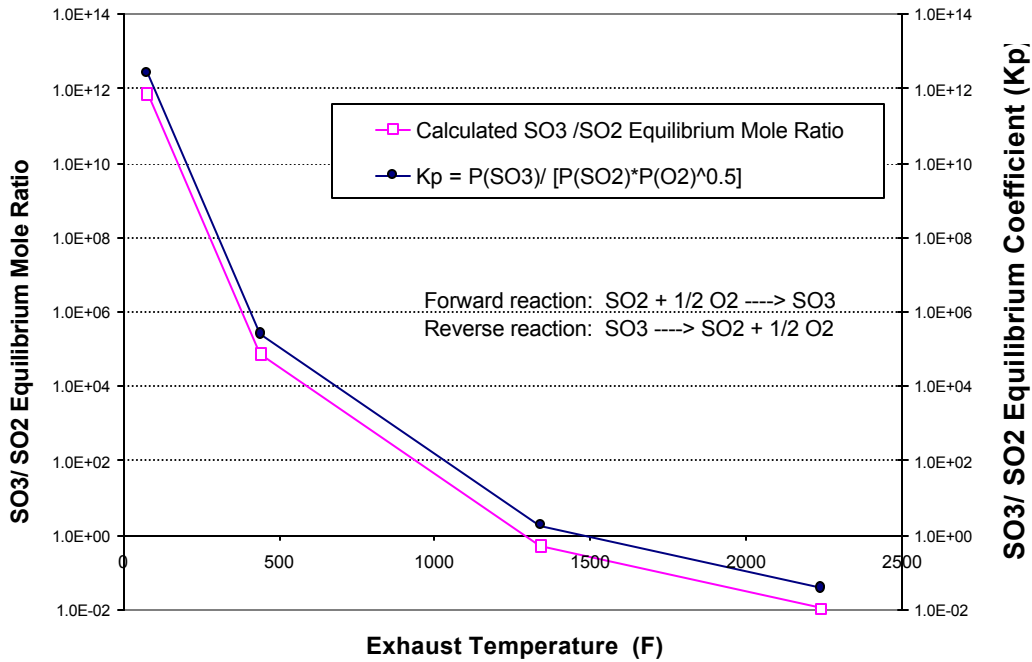


Figure 1.2-1: Calculated SO₃/SO₂ Equilibrium Ratio based on K_p Coefficient (assumes ideal gas behavior, 8% O₂, 1 atm absolute pressure)

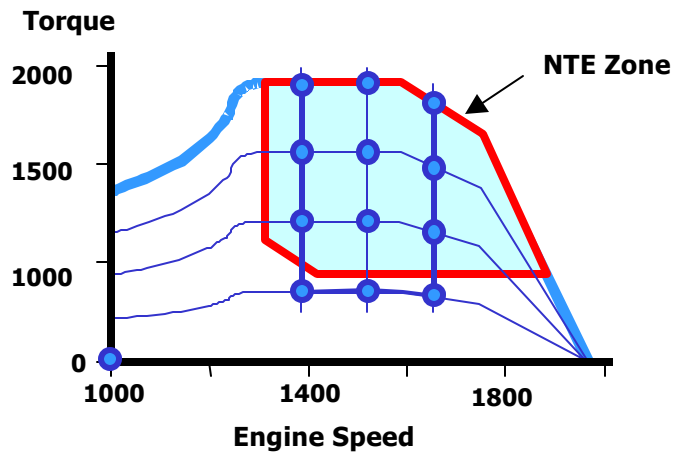


Figure 1.2-2: Example engine map displaying steady-state Supplemental Emissions Test points and Not-To-Exceed zone.

Section 2

Diesel Oxidation Catalyst

2.1 Technology Overview

2.1.1 Principle of DOC Operation

DOCs reduce HC, CO, and PM emissions in engine exhaust by oxidation over precious metal catalysts. PM is lowered by oxidation of the soluble organic fraction (SOF) of diesel PM. Catalyst selection is based on the exhaust temperature requirement. Catalysts highly loaded with precious metal are active at lower temperatures and can provide increased reductions. However, at higher exhaust temperatures, the higher the loading, the more vulnerable the catalyst is to sulfate production (as a result of the oxidation of SO₂ to SO₃). Therefore, lower precious metal loadings may be desirable.

2.1.2 Experimental

WVU is conducting aging and evaluation of the DOC. Engines used in this program were selected to represent reasonable extremes in operation. The Cummins ISM370 represents a typical heavy-duty line-haul truck engine that meets 1999 certification requirements. Results from the Navistar engine are pending analysis and will not be reported here. The Navistar T444E (7.3L, V8) engine represents lighter-duty (and thus lower-exhaust temperature) operation. Aging sequences were conducted using fuels with each of the following fuel sulfur levels: 3, 30, 150, and 350 ppm. Shell Rotella T 15W40, a widely used commercially available lubricating oil, was used in all phases of the DECSE program.

The test beds were equipped with a dual exhaust arrangement with a flow divider capable of splitting the exhaust flow equally between the two branches. This allows the DOCs and lean-NO_x catalysts to be aged on the same engine (one on each leg). Special non-catalyzed substrates were canned (installed in metal housings) for installation in one leg of the flow to maintain the flow balance while the other technology is being evaluated in the opposite branch. Table 2.1-1 describes each of the DOCs under study.

Table 2.1-1. DOC Specification

Catalyst Type	Pt Loading (g Pt / ft ³)	Substrate Size OD x Length (cm)	Volume Liters	#of Substrates	Cell Density (cps)	Converter Size OD x Length (cm)
High-Temperature	2	19.1 x 15.9	4.50	1	400	20.3 x 66.0
Low-Temperature	>50	17.8 x 11.8	2.92	1	400	19.1 x 40.6

Note: Catalysts were sized to handle half of the engine's exhaust flow.

2.1.3 Test Procedure

2.1.3.1 Testing Summary

Evaluations were conducted on the ISM370 engine equipped with fresh (unaged) diesel oxidation catalysts. Both engine-out and catalyst-out evaluations were completed. Performance was evaluated by measuring PM, CO, and HC emissions over the heavy-duty FTP and 4 modes (modes 2, 3, 10, and 11) selected from the OICA mode cycle (illustrated in Figure 2.1-1). A single PM filter was collected across the 4 modes.

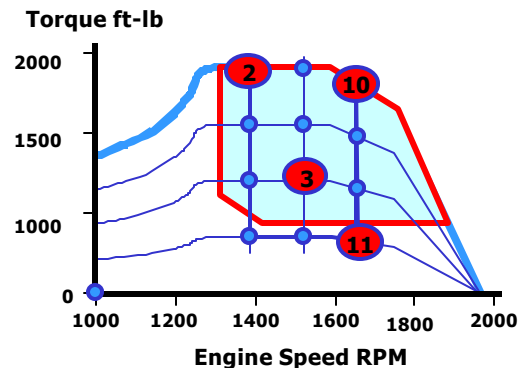


Figure 2.1-1. Test points utilized from the OICA 13-mode test cycle

Previous testing has shown that at high-load, low-speed conditions, the conversion of SO_2 to SO_3 is accentuated, resulting in an increase in PM because of the higher sulfate content. To explore this effect in the DECSE program, a separate evaluation was conducted on mode 2 of the OICA test cycle.

Test engines were broken in per manufacturer specifications. Catalysts were “degreened” for 10 hours of operation on the 4-mode aging sequence. Catalyst performance was evaluated and compared with engine-out (EO) emissions levels with each of the 4 fuels (nominally 3-, 30-, 150-, 350-ppm sulfur). Emissions measurement (THC, CO, NO_x , CO_2 , SO_2 , and PM) tests were conducted. Only PM results are presented here. Details of the PM sampling system follow.

2.1.3.2 Particulate Matter Sampling System

Engine exhaust is ducted to the mouth of a stainless steel full scale dilution tunnel through insulated piping. The dilution air and exhaust mixture is drawn through the dilution tunnel by a constant volume sampler (CVS) and controlled by critical flow venturies. The tunnel flow rate is corrected to standard temperature and pressure using an RTD and APG upstream of the critical flow venturies. A slip stream sample of the dilution air and exhaust mixture is drawn through a secondary dilution tunnel. A mass flow controller controls the sample flow rate and adjusts it in proportion to the flow rate in the primary dilution tunnel. Secondary dilution air can be added to the secondary dilution tunnel to maintain a maximum of 52°C filter face temperature. If secondary dilution air is added, the flow rate is also controlled in proportion to the flow rate in the primary dilution tunnel. PM Samples are drawn through a primary and secondary 70-mm Palflex TX40H120 filters.

When performing steady state testing such as the NAV-9 or 4-mode OICA, a bypass system was devised to allow for PM sampling during specified data collection periods. The bypass system allows the sample to pass through the mass flow controllers continuously, eliminating delays associated with starting and stopping the sample flow during the steady state mode.

2.1.3.3 Heavy Duty FTP Cycle on the Cummins ISM Engine

The high temperature DOC is evaluated over the Federal Test Procedure (FTP) cycle on a Cummins ISM 370 engine. The exhaust is split into two streams. Half of the exhaust flows through the catalyst under evaluation and into the full flow dilution tunnel. The other half of the exhaust is directed through an identically canned non-catalyzed brick prior to being vented from the engine test cell. During catalyst testing on the Cummins ISM engine, the nominal dilution tunnel flow rate is set to 1400 cfm. A slipstream of the diluted exhaust is drawn into the secondary dilution tunnel and through two 70-mm filters in series. The flow rate of diluted exhaust drawn through the 70-mm filters is nominally 5–6 cfm. No secondary dilution air is required during the transient cycle in order to keep the filter face temperature below 52°C as required by CFR 40 part 86 Subpart N. Each filter is conditioned in an environmental chamber at 25°C and 50% relative humidity for a period of 8 hours and pre-weighed prior to being exposed to engine exhaust. Following the test the filters are again conditioned for 8 hours and post-weighed.

A daily background (tunnel blank) 70-mm filter pair is collected. During collection of the background filter, the full flow dilution tunnel is operated at 1400 cfm and a secondary sample flow rate of 5–6 cfm is maintained for a period of 20 minutes. No secondary dilution air is added during collection of the background filter. The filters are conditioned and weighed before and after the background sample is collected and the total flow of sample through the filter is recorded via a flow totalizer.

The brake specific PM emission is calculated according to equations outlined in the CFR 40 Part 86.

$$P_{MASS} = (V_{MIX} + V_{SF}) \left[\frac{P_F}{V_{SF}} - \left(\frac{P_{BF}}{V_{BF}} [1 - (1/DF)] \right) \right]$$

P_{MASS} = Mass of particulate emitted per test

V_{MIX} = Total dilute exhaust volume corrected to standard conditions.

V_{SF} = Total volume of sample removed from primary dilution tunnel corrected to standard conditions

P_F = Mass of particulate on sample filter (primary +secondary)

P_{BF} = Net weight of particulate on background filter

V_{BF} = Volume of sample passed through background filter corrected to standard conditions

DF = Dilution Factor = $13.4 / [\text{CO}_{2\text{ppm}} + \text{HC}_{\text{ppm}} + \text{CO}_{\text{ppm}}] * 10^{-4}$

For double dilution systems:

$$V_{SF} = V_{AV} - V_{AP}$$

V_{AV} = Volume of double diluted sample passing through particulate filter corrected to standard conditions

V_{AP} = Volume of secondary dilution air corrected to standard conditions

$$PM = P_{MASS}/Bhp-Hr$$

2.1.3.4 Four Mode Steady State Cycle on the Cummins ISM Engine

The high temperature lean-NO_x and DOC are evaluated over a 4-mode fully stabilized steady state cycle derived from the OICA 13-mode cycle. A single 70-mm particulate filter pair is collected. The full flow dilution tunnel is operated at a nominal flow rate of 1400 cfm and the secondary sample flow rate drawn through the 70-mm filters is maintained at 5-6 cfm nominally. During the steady state cycle the exhaust temperature and emissions are allowed to stabilize prior to sampling gaseous emissions and particulate emissions. The stabilization period is approximately 20 minutes. During the stabilization period the secondary sample flow bypasses the 70-mm filters. Gaseous and particulate emissions are sampled during the last 2-3 minutes of each 20-minute mode. The sample times vary from mode to mode according to the weighting factors prescribed in a subset of the European Stationary Cycle (ESC) as specified in Annex III of the European Economic Community (EEC) Euro III standard (amendment to Directive 88/77/EEC, see Table 2.1-2). During the prescribed sampling period, the exhaust is passed through the 70-mm filters. No dilution air was added to the secondary dilution tunnel during the OICA 4-mode steady state test. Typical filter face temperatures are also shown in Table 2.1-2.

$$PM = \frac{P_{MASS}}{\sum BhpHr_i * WF_i}$$

where BhpHr_i is the brake horsepower hour of each mode and WF_i are the weighting factors mode.

Table 2.2-1: Sulfate Conversion

Test Cycle	Catalyst Inlet Temp (°C)	Sulfate Conversion (%)
OICA 4-mode	270°C – 518°C	15%
OICA Mode 2 (Peak Torque)	518°C	8%
FTP	124°C – 352°C	1%

2.1.3.5 Soluble Organic Fraction (SOF) and Sulfate Measurement

SOF Determination. The exposed particulate sampling filters are conditioned for >18 hrs at constant relative humidity (RH) and temperature at the analytical laboratory and weighed. The filters are then extracted with supercritical CO₂ under proprietary time and temperature conditions. The extracted filters are then re-conditioned for >18 hrs at constant RH and weighed. The SOF is then the simple difference between the pre-extraction weight and the post-extraction weight.

Sulfate and Nitrate Determination. After weighing, the filters are rolled into a cylinder, put in 15 ml centrifuge tubes with 10 ml triple distilled water and agitated for one minute. The centrifuge tubes are then put in a rack in a 90°C water bath for 30 minutes. After removal from the bath, the tubes are agitated for one minute, and the supernatant filtered into a sample vial. The samples are then analyzed immediately or refrigerated for analysis in less than 24 hrs.

The filtered extracts are analyzed for SO_4^- and NO_3^- by ion chromatography (IC) using standard IC methods for anions. Peak identification is based on retention times compared to standard sulfate solutions. An autosampler is used for convenience and vials containing check standards are inserted among the sample vials. A standard curve is developed from the results for standards at 0.25, 0.50, 1.0, 5.0, and 10 ug/ml. Peak height is used for quantitation, and minimum quantifiable level of 0.05 ug/ml has been established. Typical standard curves have a correlation coefficient, r^2 , of 0.999 or better. The sample concentrations are then calculated from the regression equation for the standards. If a sample is more concentrated than the standard curve, dilutions are used to bring the sample within the limits. More than one dilution level is used for the same sample to check for accuracy of the dilution. The concentrations are multiplied by the total volume 10 ml of extract to obtain the total mass of dry SO_4^+ on a sample filter. The dry SO_4^+ number is reported. Actual sulfate contribution to the PM mass weight is higher because of water associated with the ion. For comparison of PM sulfate generation between fuels, however, the dry SO_4^+ number is adequate.

Blank filters are treated in the same way as exposed filters, and a filter blank is included in each batch of analyses. Blank levels of SO_4^+ have been extremely low, ranging from 2-8 ug/filter for SO_4^+ and 0-4 ug/filter for NO_3^- . Blank filter SOF is typically <10 ug. The SO_4^+ and NO_3^- masses on samples are corrected for the blank values before calculation of brake specific emission of sulfate and nitrate.

2.2 Diesel Oxidation Catalyst Results

This interim report covers PM emissions data from a DOC equipped Cummins ISM370 and a Navistar T444E with each of the four DECSE fuels (nominally 3-ppm, 30-ppm, 150-ppm, 350-ppm sulfur). Post-catalyst emission measurements are compared to engine-out measurements (with the same fuel and operating conditions) to determine PM reduction efficiencies and relative PM composition. At this point, analysis of the secondary PM filter is incomplete and will not be reported here. While this exclusion may alter the magnitude of the results, analysis of the primary filters allows for accurate trend analysis and does not mask the sulfur effects under study. A more complete analysis will be included in the final DECSE report.

2.2.1 Cummins ISM370 Results

Engine-out and catalyst-out PM emissions, including analysis for sulfate fraction, have been measured on the 4-mode OICA cycle, at OICA mode 2 (peak torque), and on the heavy-duty FTP. Figure 2.2-1 summarizes the results of these measurements over the OICA 4-mode composite (exhaust temperature range = 270°C – 518°C). Total PM emissions vary insignificantly over this cycle as a function of fuel sulfur level, both with and without a DOC; however, increasing the fuel sulfur level results in larger fraction of sulfate in the PM. Reductions in the soluble organic fraction of the PM are countered by the associated increase in sulfate, resulting in no net change in total PM over this operating cycle.

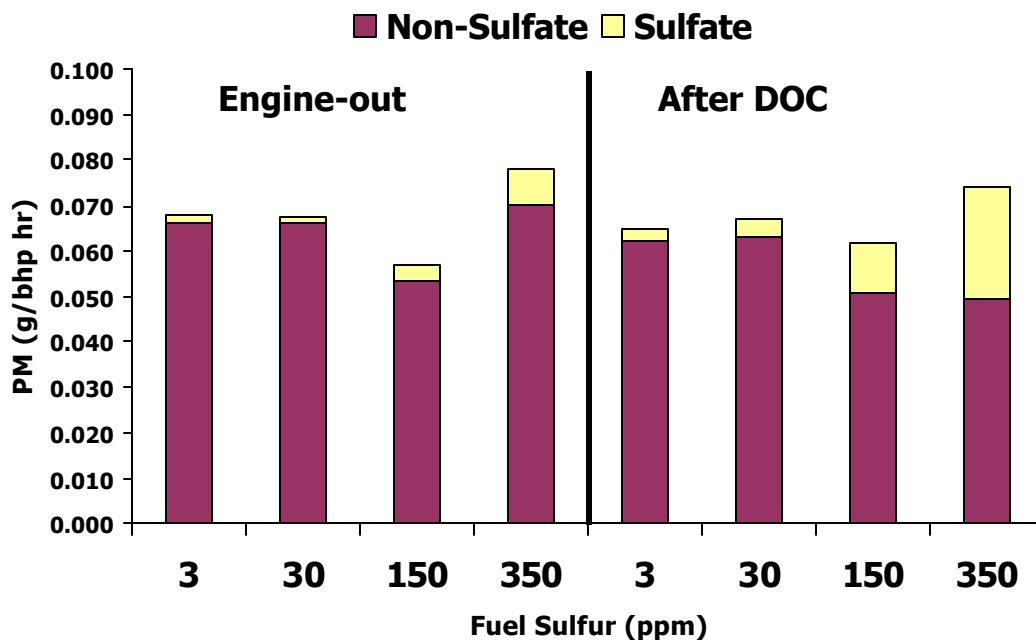


Figure 2.2-1: OICA 4-mode composite PM emissions – Cummins ISM370 – DOC
(Catalyst inlet temperature range = 270°C – 518°C)

Figure 2.2-2 illustrates results from OICA Mode 2, which was run in addition to the 4-mode composite. At this high exhaust temperature (518°C), engine-out PM emissions are largely independent of fuel sulfur, but catalyst-out emissions show a very strong sulfur effect. With 3-ppm fuel, catalyst-out emissions are 0.009 g/bhp hr but increase to 0.027 g/bhp hr with the 350-ppm fuel. Compositional analysis confirms that a large fraction of this difference can be attributed to an increase in sulfate content. At this condition engine-out sulfate conversion is approximately 2%. The DOC increases this sulfate conversion to 10%. This conversion level is relatively low due to the low precious metal content of the catalyst formulation.

The previous analyses looked at PM emissions during steady-state operating cycles. In order to examine effects of transient operation, catalyst evaluations were performed over the heavy-duty FTP. These results are presented in Figure 2.2-3. In this study, PM emissions over the heavy-duty FTP varied independent of fuel sulfur level for both engine-out and catalyst-out emissions. Compositional analysis of the PM determined that a very small fraction of the total PM was sulfate, even when run with the 350-ppm sulfur fuel. Catalyst inlet temperature over the heavy-duty FTP is quite low, peaking at 352°C and averaging 239°C over the cycle. These temperatures are too low to produce significant amounts of sulfate with this catalyst formulation.

Figure 2.2-4 provides a summary of sulfate production as a function of sulfur in the fuel for each of the three operating conditions studied. In these tests, sulfate conversion was highest (15%) during the OICA 4-mode composite, 8% at peak torque, and 1% over the heavy-duty FTP.

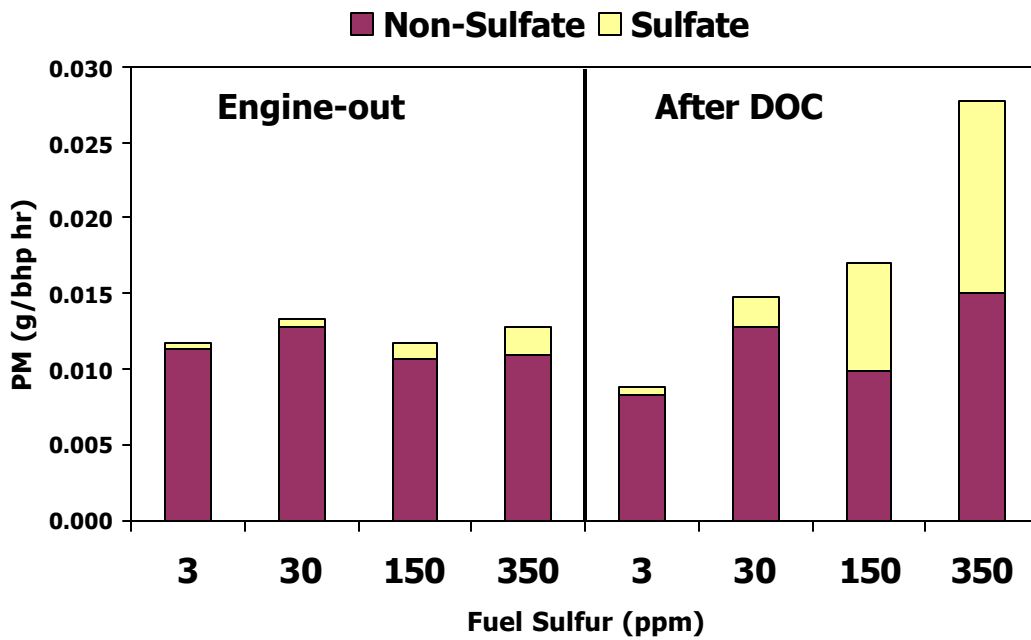


Figure 2.2-2: OICA Mode 2 (Peak Torque) PM emissions – Cummins ISM 370 – DOC (Catalyst inlet temperature = 518°C)

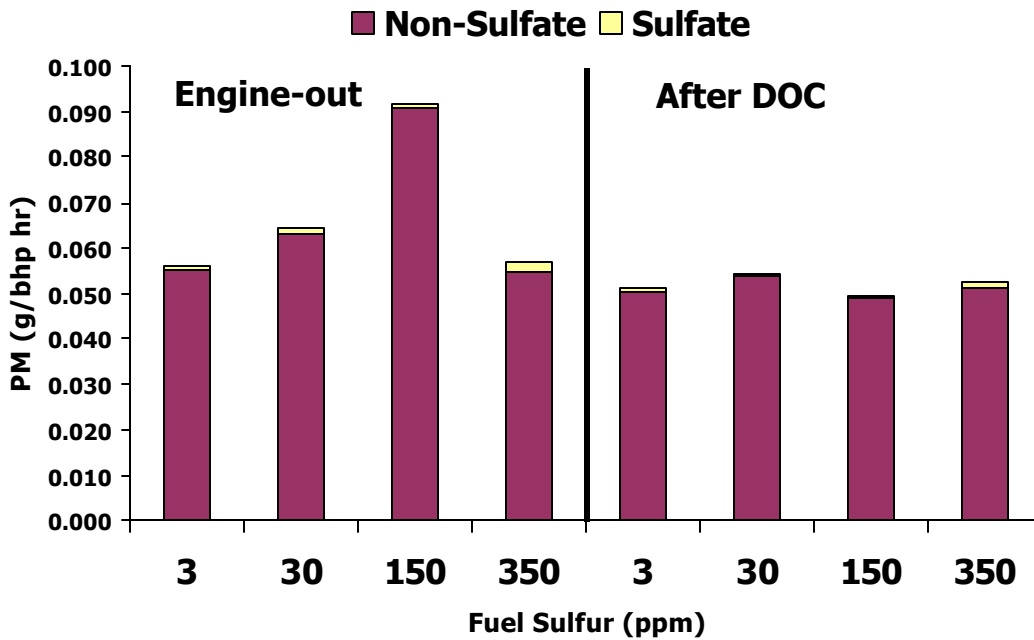


Figure 2.2-3: FTP PM emissions – Cummins ISM370 – DOC (Catalyst inlet temperature range = 124°C – 352°C, Avg. = 239°C)

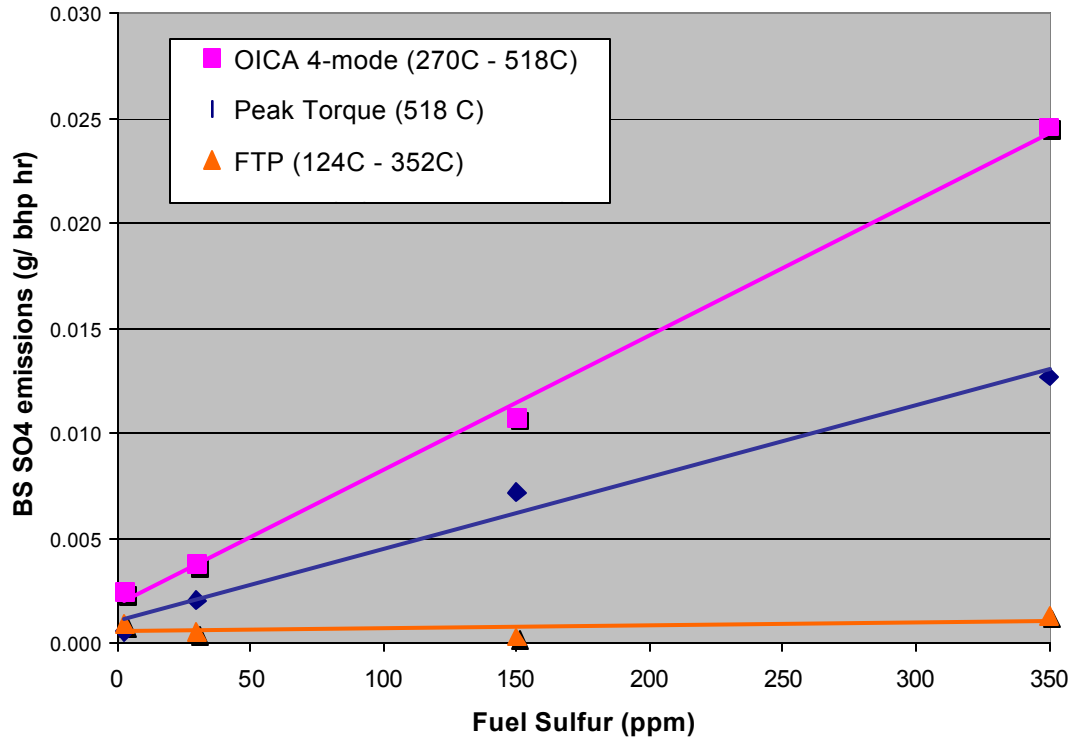


Figure 2.2-4: Summary of Catalyst-out Sulfate Emissions as a Function of Fuel Sulfur Level—Cummins ISM370- DOC (catalyst inlet temperature)

2.2.2 Navistar T444E Results

This section is pending data analysis.

2.2.3 Conclusions

- Under certain operating conditions, DOCs can increase PM emissions above engine-out emissions due to an increase in sulfate fraction. The magnitude of this increase is directly proportional to the amount of sulfur in the diesel fuel. This sulfate increase counteracts the SOF reduction benefit of the DOC.
- Catalyst-out sulfate conversion with a DOC is temperature dependent and varies with operating condition: 1% over the heavy-duty FTP, 8% at peak torque, and 15% over a 4-mode steady-state composite test.

Section 3

Lean-NO_x Catalyst

3.1 Technology Overview

Lean-NO_x catalyst technology includes one type of catalyst that can be used to reduce diesel NO_x emissions with the assistance of a supplemental HC reducing agent (such as diesel fuel) under a lean (oxygen-rich) exhaust condition. Lean-NO_x catalysts can be divided into two different groups: low-temperature (170E– 300EC) and high-temperature (350E– 600EC). Low-temperature catalysts are primarily composed of precious metals, such as platinum (Pt); high-temperature catalysts are mainly composed of base metal components, such as metal/zeolite (Cu-ZSM) catalysts. In addition to the temperature effect, other parameters also affect catalyst performance: HC and NO_x concentration (and HC/NO_x ratio), space velocity, precious-metal (or base-metal) loading, fuel sulfur level, HC speciation, and flow distribution. If diesel fuel is used as the reductant, the type of sulfur components and the level of fuel vaporization also affect the catalyst performance.

Lean-NO_x catalyst technology has been developed over several years. However, there has been no systematic investigation of the effect of diesel sulfur level on the performance of lean-NO_x catalysts until the DECSE Interim Report No.1 (August, 1999). As a continuation of the DECSE program, this report will be mainly focused on the sulfate (PM) formation issue by a given lean-NO_x catalyst under certain engine operating conditions. Please refer to the DECSE Interim Report No.1 for a more detailed description on lean- NO_x catalyst technologies.

In this interim report, effect of diesel sulfur level on sulfate formation by the given high-temperature lean-NO_x catalyst is summarized and discussed.

3.2 Experimental

Testing is being conducted at West Virginia University (WVU). Two Navistar T444E (7.3L, V8, 99 MY) engines and two Cummins ISM 370 (11L, 99 MY) engines are being used for this test program. One engine of each type is being used for the catalyst aging process, and the other two are being used for the catalyst evaluation. The T444E engine is generating exhaust for evaluating the low-temperature lean-NO_x catalyst. Likewise, the ISM 370 engine is generating exhaust for evaluating the high-temperature lean-NO_x catalyst.

In regard to the reductant fuel injection (fuel injected into the exhaust to provide a reductant), two sets of fuel-injection systems (with a fluid-metering pump and an air-atomized injection nozzle) were assembled: one for the aging engine, and one for the evaluation engine. The fuel-injection nozzle is located 20 to 24 inches from the catalyst inlet. The reductant fueling rate (for a given mode) was optimized for NO_x reduction while HC and PM slippage were controlled.

Catalyst manufacturers provided the low-temperature lean-NO_x catalytic converters (precious-metal catalyst) and high-temperature lean-NO_x catalytic converters (base-metal catalyst). According to information provided by MECA, specifications for the lean-NO_x catalysts are presented in Table 3.1.

Table 3.1. Lean-NO_x Catalyst Specification

Catalyst Type	Formulation	Substrate Size OD x Length (cm)	# of Substrates	Volume (liters)	Cell Density (cps)	Converter Size OD x Length (cm)
High-temperature	Base metal/ Zeolite	26.7 x 15.2	1	8.5	400	27.3 x 51.4
Low-temperature	Precious metal	17.8 x 12.7	2	6.4	400	19.1 x 55.9

Note: Catalysts were sized to handle half of the engine's exhaust flow.

All the catalysts were degreened for 10 hours with 3-ppm sulfur fuel. There was no reductant fuel injection during the catalyst degreening process.

To evaluate the high-temperature lean-NO_x catalyst, four test modes (2, 10, 3, and 11) were selected from the OICA test cycle to comprise a special 4-mode test cycle. The total mode time was fixed at 20 minutes for each selected test mode. Sampling time was assigned to each test mode according to the mode-weighting factor. To properly control the THC and CO slippage rate, the secondary fueling rate for a given test mode was optimized. The compromise was made between the NO_x reduction efficiency and the THC and CO slippage rate. As designed, the overall secondary fueling rate is about 4% of the total engine fuel consumption.

Only one single PM filter set (primary and secondary) is being used for a special 4-mode test cycle. According to the definition of the OICA test cycle, the weighting factors were applied to determine the sampling time for a given test mode. The catalyst evaluation conditions are summarized in Table 3.2.

In addition to the special 4-mode test cycles, two high-temperature modes (mode 2 of the OICA test cycle and mode 9 of the Nav-9 test cycle) were specifically selected for examining the effect of fuel sulfur level on sulfate (PM) formation by a lean-NO_x catalyst. Individual PM sample is being collected (10 minutes) during an individual mode test.

Table 3.2. High-Temperature Lean-NO_x Catalyst Evaluation Modes (Four OICA Modes)

OICA Mode #	Engine Speed (rpm)	Engine Torque (Nm)	Catalyst Inlet Temp. (EC)	NO_x (g/bhp-hr)	Mode Time (seconds)	Sampling Time (seconds)	Reductant Fueling (%)
11	1884	339	270	6.53	1200	100	0
3	1573	815	375	6.37	1200	100	0
10	1884	1353	444	6.12	1200	200	3.3
2	1261	1692	518	6.09	1200	150	7.5

Please refer to the DECSE Interim Report No.1 for more detailed information with regard to the lean-NO_x catalyst experimental conditions.

3.3 Particulate Sampling and Breakdown Analysis

WVU is carrying out the DECSE program for both lean-NO_x and DOC catalyst evaluations in the same engine Laboratory. Please refer to the DOC section (Section 2.1.3) for the PM sampling conditions.

3.4 Particulate Mass Calculations

For the same reason described in Section 3.3, please refer to the DOC section (Section 2.1.3) for the PM mass conditions under different engine test conditions.

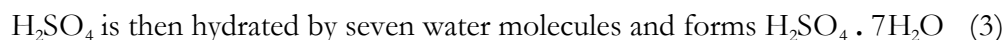
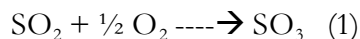
3.5 Results and Discussion

3.5.1. Effect of diesel sulfur level on high-temperature lean-NO_x catalyst

As discussed earlier, this interim report is focused on evaluating the effect of diesel sulfur level on sulfate formation by certain aftertreatment devices. The effect of diesel sulfur level on deactivation of lean-NO_x catalysts will be reported. In this section, the test results of the fresh high-temperature lean-NO_x catalyst (zero aging hours) will be presented and discussed.

Generally speaking, lean-NO_x catalysts are temperature sensitive. The operating temperature of the high-temperature lean-NO_x catalyst ranged between 360°C and 600°C as expected. With regard to the four selected OICA modes (11, 3, 10 and 2), mode 11 is out of the temperature window of the given catalyst, mode 3 is at the low edge of the window; and modes 10 and 2 are within the window (as shown in Table 2.2). At mode 3, the development work showed that the small amount of secondary fuel injection had little effect on NO_x reduction, but created THC and CO slippage. Therefore, both modes 11 and 3 were kept as passive modes without injecting any secondary fuel. For mode 10 and mode 2, the optimal secondary fueling rates were 3.3% and 7.5%, respectively. The effect of diesel sulfur level on NO_x reduction efficiency has already been discussed in the DECSE Interim Report No.1.

Diesel fuel sulfur is oxidized to SO₂ during internal engine combustion. The sulfate formation process in diesel exhaust can be simply described as follows:



The hydrated sulfate, with its weight contribution to TPM, is about 2.3 times the analyzed sulfate (SO₄) weight. In the case of particulate matter a high proportion of sulfate, such as the emissions from a DOC, one could expect this number to be much higher. The hydrated sulfate will continue to absorb water almost indefinitely. Obviously, the ambient humidity and temperature have an effect on the sulfate hydration process.

The high-temperature lean-NO_x catalyst does have the potential to make sulfate (or PM) if the diesel fuel sulfur level is high enough to provide a suitable SO₂ concentration. Kinetically, the higher the catalyst temperature, the higher the sulfate-making rate would be for a given catalyst. However, the SO₂ conversion rate can be limited by the chemical equilibrium of SO₂ and SO₃ at a given reaction temperature (see Figure 1.2.1). In general, within the diesel catalyst inlet temperature range (250°F to 1100°F), the SO₂ conversion is kinetically controlled. A suitable catalyst will escalate SO₂ conversion at higher exhaust temperatures.

The TPM and sulfate (SO₄) emission data, according to the chemical breakdown analysis conducted by ORNL, are presented in Figure 3.1 and 3.2. Bear in mind that the reported sulfate portion does not include the hydrated water. Furthermore, due to the time constraint, the reported TPM and SO₄ values only came from the primary particulate filters. Figure 3.1 depicts the experiment results from the OICA 4-mode test cycle. A comparison between the engine-out data and the catalyst-out data is shown in the figure. As indicated, the high-temperature lean-NO_x catalyst sulfate emissions (catalyst-out) were higher than that of the engine baseline (engine-out) with the 150- and 350-ppm sulfur fuels. The higher the diesel sulfur level, the higher the sulfate (SO₄) emission level was.

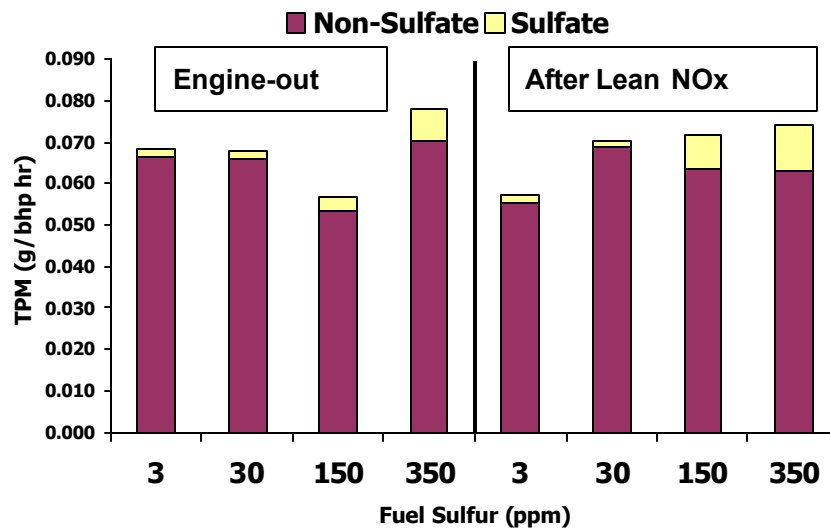


Figure 3.1. Comparison of SO₄ emissions between converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, OICA 4-mode composite)

This result implies that the high-temperature lean-NO_x promotes sulfate (SO₄) formation. Likewise, the experimental results at the OICA mode 2 (peak torque condition) are displayed in Figure 3.2. Once again, the catalyst-out sulfate emissions were higher than that of the engine-out with the 150- and 350-ppm sulfur fuels. At this high temperature (~518°C), the percentage of sulfate in the TPM was higher than that of the OICA 4-mode test cycle for both engine-out and catalyst-out data (see

Table 3.3). The high temperature lean-NO_x catalyst showed no propensity to make sulfate with a diesel sulfur level of less than 30ppm.

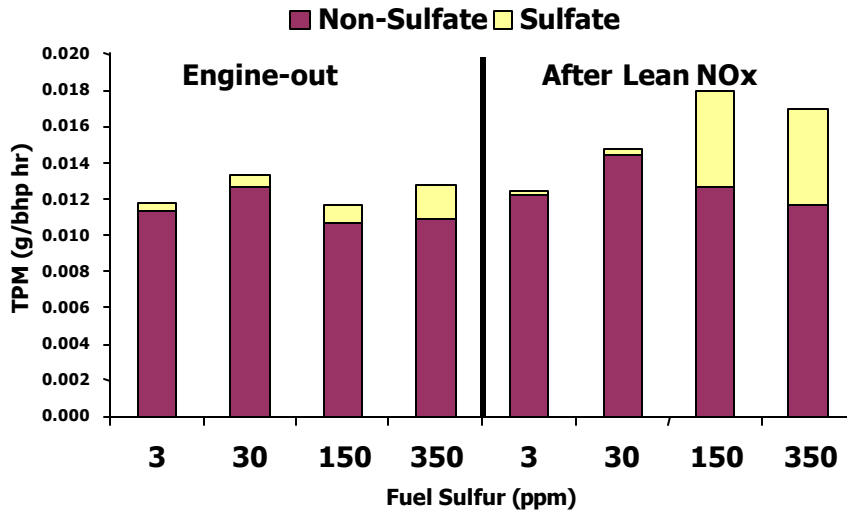


Figure 3.2. Comparison of SO₄ emissions between converter-out and engine-out with the fresh high-temperature lean-NO_x catalyst (Cummins ISM engine, OICA Mode 2)

Table 3.3. Sulfate Percentage in Total Particulate Matter (TPM) with High Sulfur Diesel Fuels

Nominal Fuel sulfur Level (ppm)	OICA 4-mode (Engine-out) SO ₄ % in TPM	OICA 4-mode (Catalyst-out) SO ₄ % in TPM	OICA Mode 2 (Engine-out) SO ₄ % in TPM	OICA Mode 2 (Catalyst-out) SO ₄ % in TPM
150	6.23%	11.0%	8.36%	29.4%
350	10.1%	15.0%	15.0%	30.8%

To further investigate the sulfate formation capability of the given high temperature lean-NO_x catalyst, the engine-out sulfate emission data was subtracted from the catalyst-out sulfate emission data, for a given test condition. Then the sulfate generated purely by the lean-NO_x catalyst as plotted versus the diesel sulfur level in Figure 3.3. Interestingly enough, it was observed that the brake-specific sulfate formation by the catalyst was apparently independent of the given engine test conditions. More test data will be generated and analyzed in the near future before providing a meaningful explanation on this interesting phenomenon.

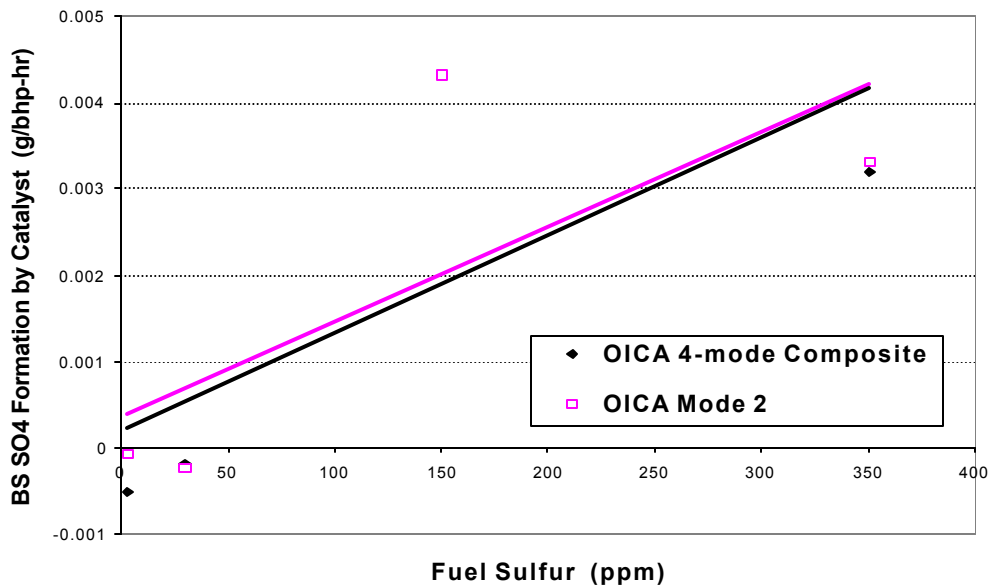


Figure 3.3. Comparison of sulfate (SO_4) formations by the fresh high-temperature lean- NO_x catalyst under two different engine test conditions (Cummins ISM engine)

3.6 Conclusions

- Diesel sulfur level may have an effect on PM emissions from the high-temperature lean- NO_x catalyst. With 3-ppm sulfur fuel, PM reduction efficiency (based on the 4-mode composite test) was statistically significant at 16%. However, with high sulfur fuels, there was an increase in PM (compared to engine-out emissions), or the reduction efficiency was not statistically significant. This suggests the formation of PM by the lean- NO_x catalytic converter with high sulfur fuels.
- With 150- and 350-ppm sulfur fuels, the engine-out sulfate emissions increased by a factor of 2 to 5 compared to the levels observed with 3-ppm sulfur fuel. With the high-temperature lean- NO_x catalyst, the post-catalyst sulfate emissions increased by a factor of 10 to 20. Higher sulfate emissions increase the overall PM emissions.
- With the high exhaust temperature ($\sim 528^\circ\text{C}$) at OICA mode 2, the percentage of sulfate in TPM was higher than that of the OICA 4-mode test cycle for both engine-out and catalyst-out data.
- The brake-specific sulfate formation by the given lean- NO_x catalyst was apparently independent of the given engine test conditions. More test data will be generated and analyzed in the near future before providing a meaningful explanation to this phenomenon.

Section 4

Continuously Regenerating Diesel Particulate Filter and Catalyzed Diesel Particulate Filter

4.1 Technology Overview

The CR-DPF and CDPF represent two general approaches to passive regeneration of DPFs. Passive regeneration is preferred, as opposed to active regeneration, because passive regeneration offers significant fuel consumption savings, lower system cost and is less complex.

The CR-DPF and CDPF were designed to remove PM from the engine exhaust stream. A schematic diagram of the DPF system configurations used for this study is provided in Figure 4.1-1. In each device, PM was removed from the exhaust stream by collecting on a filter, which in these cases are ceramic wall-flow elements. Unlike other diesel emissions control devices, primary removal of the targeted pollutant (PM) is fixed by the physical characteristics of the filter medium and is relatively unaffected by the engine operating conditions. The critical issues, instead, is the cleaning or regeneration of the DPF (by oxidation of the collected PM) to prevent DPF from plugging.

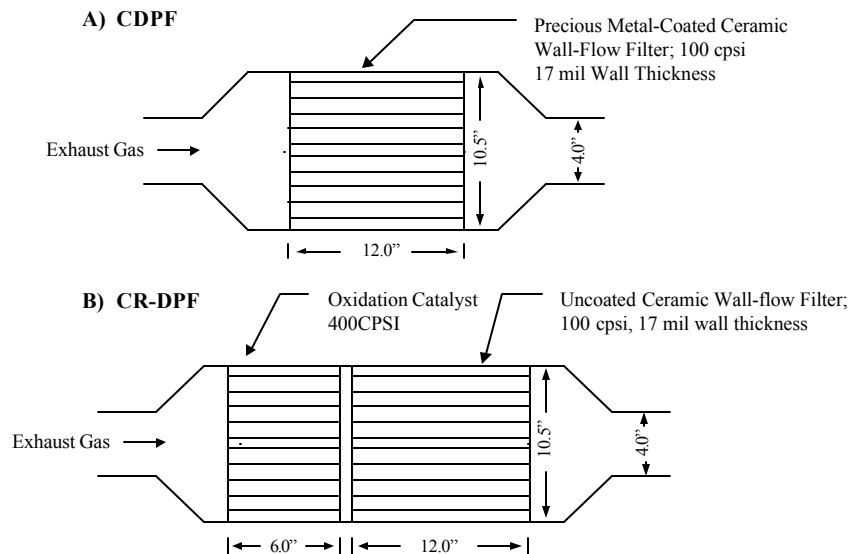


Figure 4.1-1. Schematic diagram of DPF system configurations

The CR-DPF accomplishes this filter regeneration by continuously generating NO_2 from engine-emitted NO over a diesel oxidation catalyst placed upstream of the DPF. NO_2 has been established as a more effective low-temperature oxidizing agent for diesel PM than oxygen. Sulfur in the exhaust (originated from the fuel and lubricant), however, can be oxidized over the CR-DPF, forming sulfates, which are measured as PM. Sulfur oxides also compete for the critical NO and NO_2 reaction, making the regeneration characteristics less effective.

The CDPF accomplishes the DPF regeneration by using a catalyst coating on the DPF element to promote oxidation of the collected PM using available oxygen in the diesel exhaust. Sulfur in the exhaust can be oxidized over the CDPF to form sulfates.

Exhaust-gas temperature and fuel-sulfur level are critical factors that affect the performance of both types of DPFs (CR-DPF and CDPF).

4.2.1 Experimental

Engineering Test Services (ETS) in Charleston, South Carolina, has been contracted to conduct the DPF test program. A Caterpillar 3126 engine rated at 205 kW (275 horsepower) and equipped with electronic controls was used for the tests. The 3126 engines are typically used for applications that result in relatively low temperature exhaust (e.g. below 300°C). For such applications, regeneration of the DPF at low temperature is critical to proper operation of the emissions control system and hence the engine operation (maintaining a low back pressure by not allowing PM to build up continuously on the filter). Because fuel sulfur is expected to affect the filter regeneration temperature, these low temperature applications are an excellent test of the effects of fuel sulfur.

4.2.1 Particulate Sampling System at ETS

Dilution air and total engine exhaust is mixed and drawn through an 18-inch diameter stainless steel dilution tunnel by a positive displacement pump constant volume sampler (PDP-CVS). The tunnel flow rate is corrected to standard temperature and pressure using temperature and pressure measurements upstream of the PDP-CVS. ETS uses a double dilution method for the particulate sampling outlined in the CFR 40 Part 86, Subpart N.

The emission sampling zone temperature in the primary dilution tunnel is maintained at 375 °C or less. Gaseous emission samples are taken at this sampling point. For particulate sampling, an exhaust sample is taken at this point to be diluted a second time for use in determining particulate emissions. The secondary dilution system is used to maintain the double-diluted exhaust stream at a temperature of 52 °C or less at the PM filter face. A mass flow controller controls the sample and secondary dilution flows to a constant rate through the PM filter pair. PM samples are drawn through primary and secondary 90-mm Pallflex filters (TX40H120).

When performing OICA and steady state emissions testing, a bypass system is used to allow for PM sampling during specified data collection periods. The bypass system allows for continuous flow through the mass flow controllers eliminating delays associated with starting and stopping the sample flow during each mode.

4.2.2 OICA and Steady state Cycles

The PM sampling for the OICA cycle is automated to collect PM using a single filter method. The PM sampling duration at each mode is weighted by time to the weighting factor of the OICA cycle. The total sampling time for the 13-mode OICA is 20 minutes. The 13-mode speed and torque targets were determined using data from an 8 rpm per second full load performance curve. During the OICA and steady state cycles the exhaust temperature and emissions were allowed to stabilize

for 5 minutes prior to sampling gaseous and particulate emissions. During the stabilization period the secondary sample flow bypasses the 90-mm filters.

Table 4.2.2-1 presents the gaseous and PM sampling time for the 13-mode OICA cycle. Table 4.2.2-2 presents the gaseous and PM sampling time for the steady state mode conditions.

Table 4.2.2-1. Gaseous and PM Sampling time for 13-mode OICA Cycle

Mode	Engine Speed	Percent Load, (%)	Weighting Factor	Stabilization time, (seconds)	Sampling time, (seconds)	Mode length, (seconds)
1	idle	-	0.15	300	180	480
2	A	100	0.08	300	96	396
3	B	50	0.1	300	120	420
4	B	75	0.1	300	120	420
5	A	50	0.05	300	60	360
6	A	75	0.05	300	60	360
7	A	25	0.05	300	60	360
8	B	100	0.09	300	108	408
9	B	25	0.1	300	120	420
10	C	100	0.08	300	96	396
11	C	25	0.05	300	60	360
12	C	75	0.05	300	60	360
13	C	50	0.05	300	60	360
		Total	1	3900	1200	5100

Table 4.2.2-2. Gaseous and PM Sampling time for Steady State modes

Mode	Engine Speed (rpm)	Engine load (%)	Stabilization Mode (seconds)	Sample Time (seconds)
Torque Peak	1440	100	300	1200
Road Load	1783	75	300	1200

The nominal primary dilution tunnel flow rate is set to 1600 scfm. The flow rate of diluted exhaust drawn through the 90-mm filters is nominally set to 4–5 scfm and the secondary dilution air is set to 2-3 scfm. The filters are conditioned in an environmental chamber at 21 °C and 50% relative humidity for a period of 8 to 48 hours and pre-weighed prior to being exposed to engine exhaust. Following the test, the filters are again conditioned for 8 to 48 hours for post-weight.

The brake specific PM emission is calculated according to equations outlined in the CFR 40 Part 86, Subpart N (as shown in 2.1.3.3). Since primary and secondary dilution air is filtered, the background PM is not routinely measured.

4.3 Results

Essentially all of the sulfur entering the combustion chamber of a diesel engine, no matter the source or chemical compound, will exit the engine as sulfur dioxide (SO_2). It has been observed in past engine tests (without catalysts) that a small fraction (typically 1% to 3%) of the fuel sulfur is converted to sulfate through the diesel combustion process. However, in the presence of a precious metal catalyst, a fraction of the SO_2 in the exhaust will be oxidized to form sulfate which, with its associated water, is collected and measured as a component of diesel particulate emission.

The data obtained in this study, substantiates the past findings. When operating on 3-ppm sulfur fuel with either of the DPF devices, overall particulate reductions in excess of 90% are observed. However, as the sulfur level of the fuel is increased to 30-ppm, 150-ppm, and finally to 350-ppm a corresponding increase in the total particulate emissions are observed (see figure 4.3-1). Although absolute emission levels vary somewhat by engine operating mode (weighted OICA cycle, peak torque, or a steady state simulated road load), the overall trend is quite consistent.

At the 150-ppm sulfur test point an apparent 0% reduction in PM is seen. Subsequent analysis of the particulate filter samples shows that the SOF and carbon fractions of the particulate have been largely removed and an equivalent mass of sulfate has been generated. At the 350-ppm test point the total PM has increased by roughly a factor of two over baseline engine emissions.

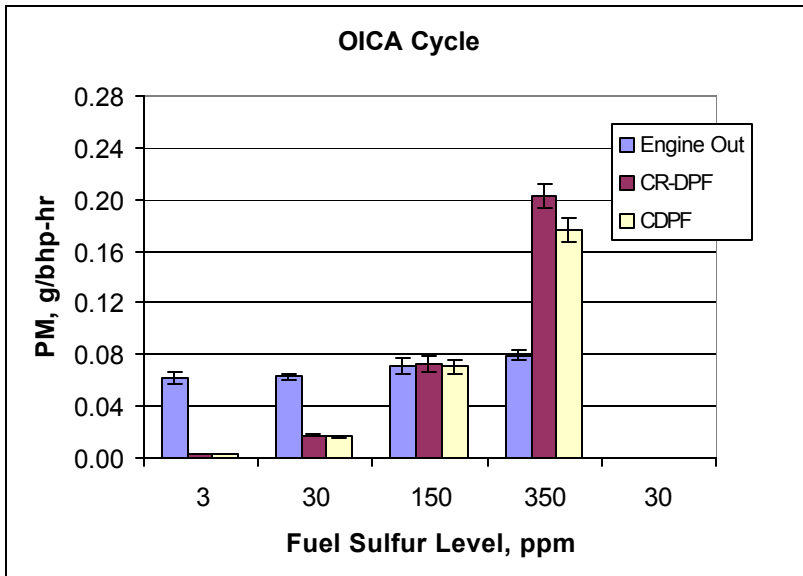
Particulate compositional analysis was conducted by ETS. As an independent check, the compositional analysis was also performed by the Oak Ridge National Laboratory on two particulate filter samples obtained from the OICA cycle test with the CR-DPF device and the 350-ppm sulfur fuel. The results are presented in Figure 4.3-2. The analysis results confirm that the increase in the total particulate matter with increased fuel sulfur level is mainly due to the increase in sulfate-make.

When plotted as a function of fuel sulfur level (see figure 4.3-3), the measured “dry” sulfate particulate emissions over the 13-mode OICA cycle show a linear relationship. Both devices (CR-DPF and CDPF) show similar trends.

Sulfate emissions were calculated for various fuel sulfur levels assuming 40%, 50% and 60% conversion of fuel sulfur to sulfate. These calculated values are shown superimposed as reference lines on figure 4.3-3. An assumed values for BSFC (0.355 g/bhp-hr) was used for these calculations.

From these results it appears that approximately 40% to 50% of the available sulfur was converted to sulfate over these devices. Since the catalytic oxidation of sulfur dioxide is a function of temperature, this sulfur conversion value applies only to this engine operating over this specific cycle. Sulfur conversion over the HDD Transient Cycle, for instance, because of the lower average exhaust temperature would undoubtedly be somewhat less than the 40% to 50% seen over the 13-mode OICA cycle.

This same data, plotted on an expanded scale is shown in figure 4.3-4. The implications of these data are fairly clear. Fuel sulfur, even in the range below 50-ppm has a very significant impact on the emissions performance of both the CR-DPF and CDPF.



	Peak Torque	Road Load
CR-DPF		
Engine RPM	1,440	1,783
Torque, ft-lb	772	541
Filter inlet T, °C	585	457
CDPF		
Engine RPM	1,440	1,783
Torque, ft-lb	780	541
Filter inlet T, °C	547	433

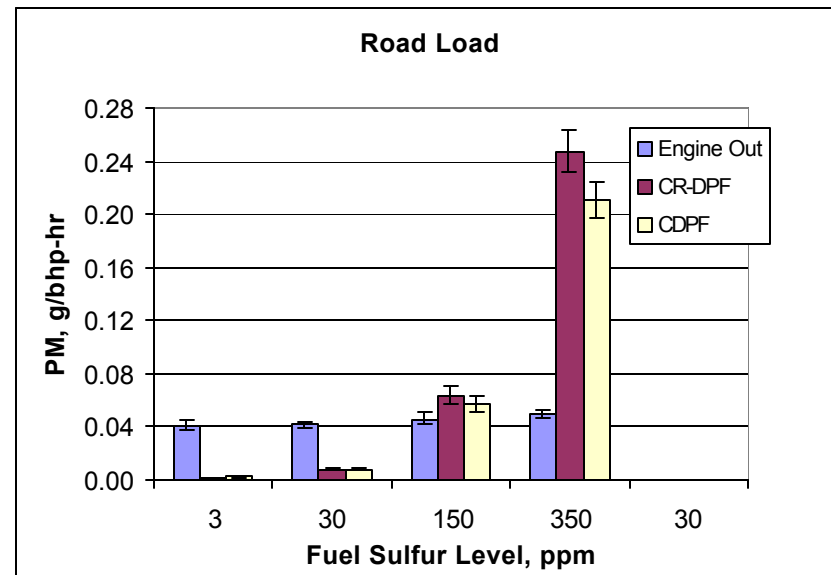
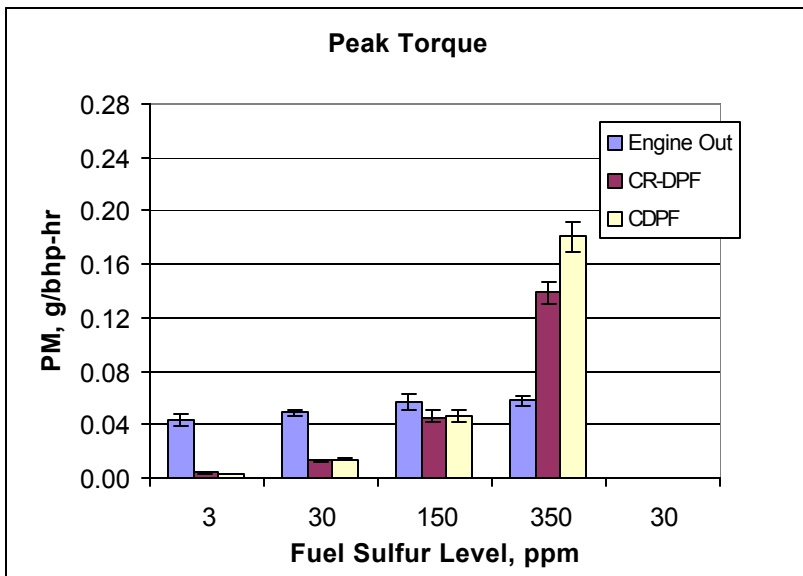


Figure 4.3-1. Effect of fuel sulfur level on PM emissions

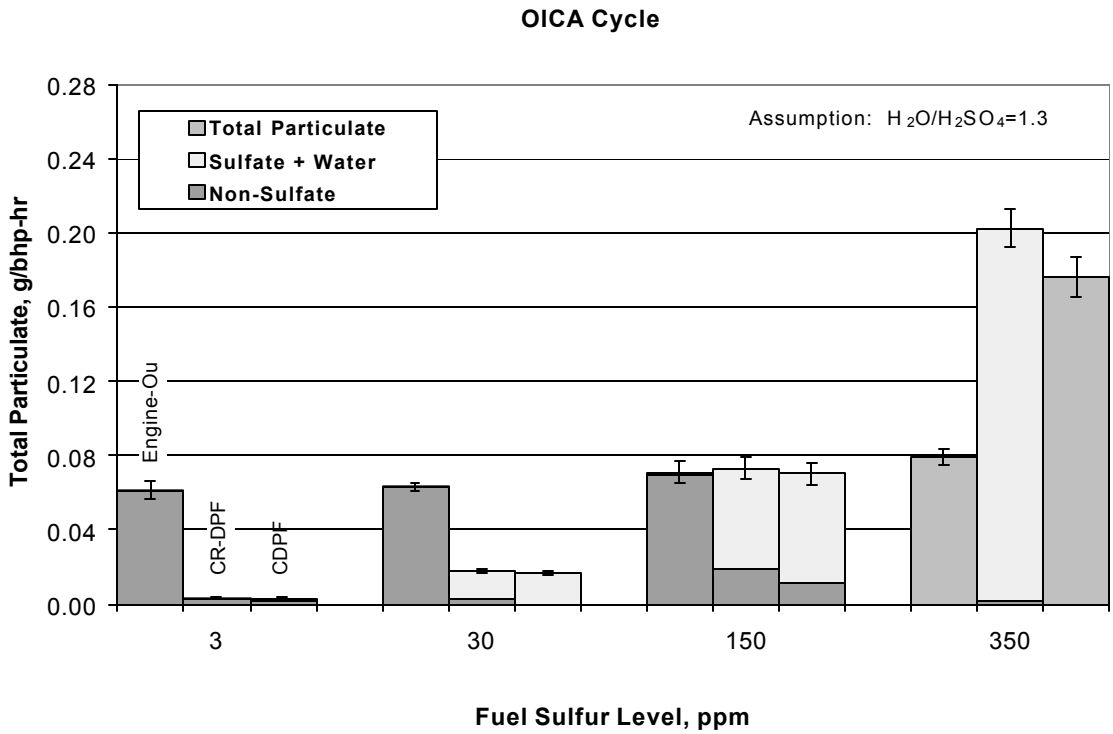


Figure 4.3-2. Effect of fuel sulfur level on total on total PM and sulfate emissions

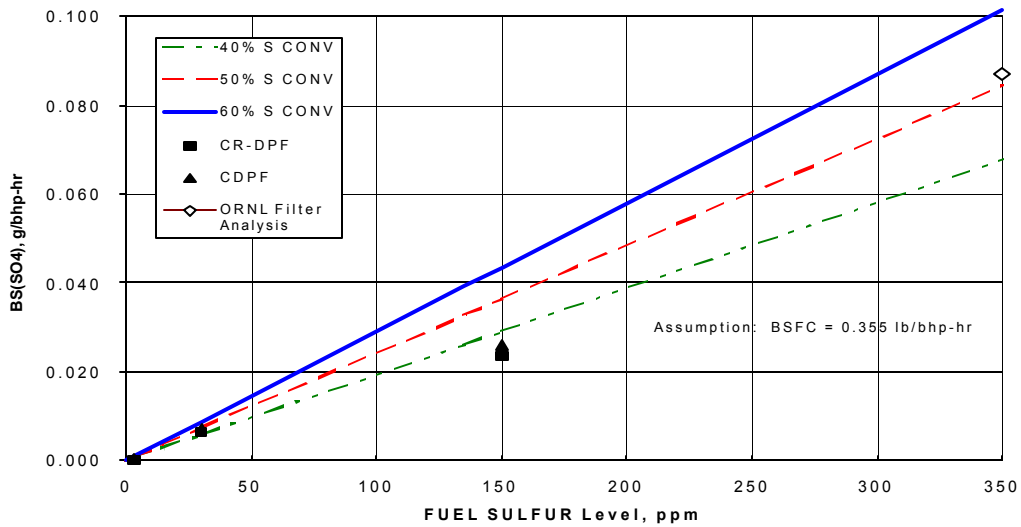


Figure 4.3-3. Effect of fuel sulfur on OICA cycle particulate emission

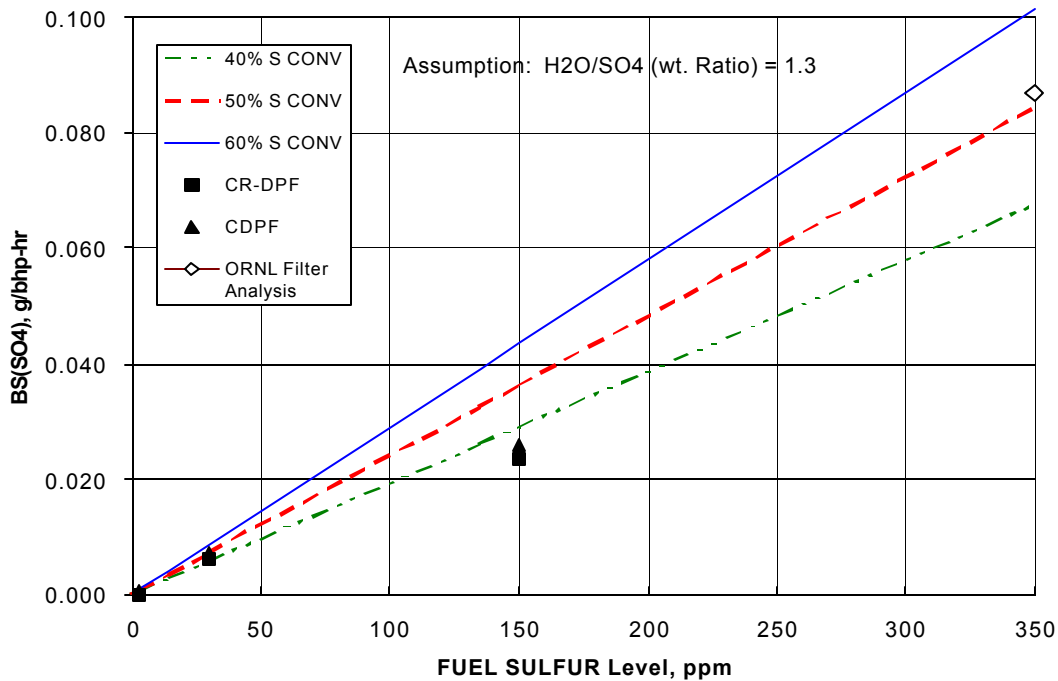


Figure 4.3-4. Effect of fuel sulfur on OICA cycle particulate emissions

The balance point temperature (BPT) is a very critical measure of the survivability of a diesel particulate filter system. In a typical application the diesel engine spends a considerable fraction of time running at conditions such that the exhaust temperature is below that required for effective filter regeneration. Therefore, any increase in the balance point temperature reduces the safety margin for filter survival. As shown by figure 4.3-5 regeneration (or in-situ cleaning) of the diesel particulate filters was negatively impacted by increasing fuel sulfur level. In general, the BPT increased 20-25°C when changing from 3-ppm to 30-ppm sulfur fuel.

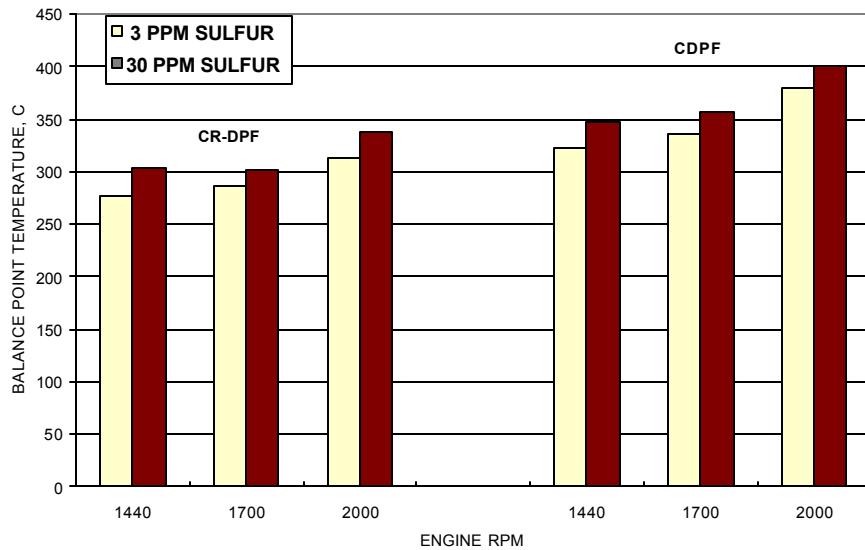


Figure 4.3-5. Effect of fuel sulfur on balance point temperature

4.4 Conclusions

The two DPF technologies chosen for the program, CR-DPF and CDPF, underwent (1) emissions tests for PM and selected gases, and (2) experiments to measure the effect of fuel sulfur level on the regeneration temperature required by the filter devices. The tests to date have resulted in the following conclusions:

- Fuel sulfur has significant effects on PM emissions. Both fresh DPFs were effective in reducing PM emissions (95% over the OICA cycle) when used with 3-ppm sulfur fuel. With 30-ppm sulfur fuel, the PM reduction efficiencies of the fresh catalysts dropped to 72% and 74% for the CR-DPF and CDPF, respectively. At the 150-ppm sulfur test point, PM reductions were near zero.
- The conversion efficiency of fuel sulfur to sulfate particulate over the 13-mode OICA cycle appears to be approximately 40% to 50%.
- Results to date show that the DPF regeneration temperatures (at which the collected PM is oxidized to prevent plugging) are higher when testing with the 30-ppm fuel. Additional testing is planned with the 150-ppm and 350-ppm fuels.

Section 5

NO_x Adsorber Catalysts

5.1 Program Overview

The results reported in the Phase 1 Interim Report No. 2 (Oct 99) showed how adsorber catalyst performance was affected by sulfur level for three different sulfur levels. This report uses the same data base but will only cover how the fuel sulfur levels affected exhaust particulate material.

A brief overview of the test is provided first. For more detail the reader is directed to the full Interim Report which can be found at <http://www.ott.doe.gov/decse>.

5.1.1 Principle of Operation

The NO_x adsorber catalyst was conceived to overcome the problem of creating a chemical reducing reaction in the oxygen-rich diesel exhaust gas atmosphere. A NO_x adsorber catalyst functions by first converting NO in the exhaust to NO₂. The NO₂ is then stored as a nitrate under the lean exhaust conditions typical of diesel engine operation. Bringing the exhaust briefly to a rich condition allows for the release of the stored NO_x and, under these rich conditions, the catalyst is capable of performing the reactions typical of a three-way catalyst (TWC) and reduces the NO_x to N₂.

In order to perform these functions, an adsorber must contain two principal catalytic components, a NO_x adsorbent and the catalytic materials used in a TWC. The adsorbent used is typically an alkali or alkaline earth carbonate and the catalytic materials used in a TWC include precious metals which are responsible for both converting NO to NO₂ under lean conditions and NO_x to N₂ under rich conditions.

In a NO_x adsorber catalyst, however, any SO₂ in the exhaust undergoes reactions that are analogous to those of NO_x and alkali and alkaline earth sulfates are formed. Unlike their corresponding nitrates, these sulfates are extremely stable. It has been shown in the literature (e.g., SAE paper numbers 1999-01-1285 and 982594) that desulfurization of the catalyst would require rich exhaust conditions and temperatures exceeding 600°C, a temperature outside the normal range of engine operation. As a result, in time, SO₂ in the exhaust will block the NO_x adsorption sites and reduce its NO_x conversion effectiveness.

5.1.2 Experimental Approach

The DECSE experiment was designed to address the following questions:

What is the effect of fuel sulfur level on:

- NO_x adsorber catalyst NO_x conversion efficiency
- Rate of deactivation of the adsorber catalyst
- Production of sulfate

Again, this report will provide results specific to fuel sulfur effects on the exhaust PM, including sulfates.

Engine. The engine had been modified previously for NO_x adsorber operation by the single bidder, FEV Engine Technology. It is a modern, 1.9-liter, I4, high-speed, direct-injection (HSDI) engine rated at 81 kW at 4,200 rpm and uses a common-rail injection system. Through a combination of inlet throttling, exhaust gas recirculation (EGR), and fuel-injection modifications, the engine allows rich/lean operation without affecting driveability. Although the engine management system is not completely refined, it is representative of a system with production potential.

Fuel and Oil. Phillips Chemical supplied nominal 3-ppm and 30-ppm fuel. FEV blended these two fuels to produce the 16-ppm fuel. Shell Rotella T 15W40 engine oil was used. Oil and fuel samples were routinely collected and submitted for analysis.

Catalyst. The NO_x adsorbent material was supported on a single 14.4 cm-diameter by 15.2 cm-long, 400-cpsi ceramic substrate for a total volume of 2.5 liters. The catalyst contains a precious metal formulation incorporating Pt, Pd, and Rh. Each of the substrates is housed in a stainless steel shell measuring 15.2 cm in diameter by 66 cm in length, including 15.2 cm-long by 7.6 cm in diameter inlet and outlet pipes.

The catalysts were sized to result in a maximum space velocity of 50,000 hours⁻¹ at the 3000-rpm engine test speed. Pairs of adsorber catalysts (denoted a/b) were tested in parallel. The samples were identified as 3a, 3b, 16a, 16b, 30a, 30b, S3, and S4, to track which fuel sulfur level the catalyst was tested with. (Adsorber catalysts S3 and S4 were spare adsorber catalysts used for engine management calibration revision.)

PM Measurements. FEV collected particulate material on filters (47 mm dia. Teflon-impregnated glass fiber TX40H120WW) using a mini-dilution tunnel that could sample the exhaust before or after the adsorber catalysts. Collected filter samples were analyzed for total particulate material (TPM), by mass gain on the filter, for soluble organic fraction (SOF), by Soxhlet extraction with dichloromethane, and for inorganic sulfate, by aqueous extraction and ion chromatography. The filter analyses were performed by a local FEV subcontractor and reported at the end of the test program. In addition, a smoke meter was operated behind the adsorber catalyst to monitor, predominately, black smoke produced by the engine.

Since the focus of the test program was to assess the NO_x conversion abilities of the NO_x adsorber catalyst as a function of fuel sulfur level, only an abbreviated schedule of PM filter measurements was requested by the technical committee. Baseline (engine-out) filter samples of TPM were collected during the initial mapping performed 2.5 engine-hours before the zero-hour aging evaluation. The same was done with the adsorber catalyst at each sulfur level. These measurements were performed across each of the nine temperatures from 150 to 550°C. The baseline emissions levels were assumed to be invariant, so no further baseline emissions were monitored. During aging, the catalyst-out particles were sampled at 0, 50, 100, 150, 200 and 250 hours for the 350°C temperature point ONLY.

Unfortunately, the 350°C PM measurement point used during aging is the same temperature where the minimum in the NO_x conversion occurred, as a result of the faulty engine management calibration. Despite this concern, the impact of the calibration problem on PM interpretation appears to be minimal based on the PM trends versus temperature shown in the top two rows of figures in 5.2-1; the engine and catalyst out PM show no unusual trend at the 350C point.

The collected filter samples were weighed to determine TPM by weight gain, a portion of each filter was used for the SOF determination and the remainder was used for the sulfate determination. Single filters were collected for each measurement, hence no duplicate filter information is available.

5.1.3 Test Procedure

All testing was conducted at 3,000 engine rpm. Two adsorber catalysts were tested simultaneously to increase statistical confidence in the results. Engine exhaust flow was configured to provide equal flow through each catalyst. Testing followed a five-step sequence:

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

Steps in the sequence are described below.

Degreening. Each set of adsorber catalysts was first thermally stabilized by ten hours of operation at 400°C. The engine control system was set to operate lean-only (normal diesel operation). A substitute, low-sulfur (3 ppm) base fuel was used to expedite work since test fuel was not yet available.

Rich/Lean Time Optimization. The rich/lean engine management system was calibrated with the times selected for rich and lean operation meant to maximize NO_x conversion, with a constraint that fuel consumption penalty was not to exceed 4%. The 4% fuel consumption penalty was selected to provide a basis of comparison with the lean-NO_x catalyst technologies also being evaluated in the DECSE program. The program average fuel consumption penalty was 2.9%.

Performance Mapping. Adsorber catalyst performance maps were developed for each of the three sulfur level fuels. The maps show NO_x conversion between 150 and 550°C in 50°C increments.

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

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

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

Periodic Measurement During Aging. NO_x conversion was measured for each set of samples at 50-hour intervals during aging tests to track their performance. Measurements were conducted using the same test procedure as that used for mapping. A catalyst was defined to have failed when measurements showed that the NO_x conversion average over the temperature range had dropped by 50% or more from the fresh value. The 3 ppmS adsorber catalyst systems achieved the full 250 hour objective but the 16 ppmS systems achieved 200 hours and the 30 ppmS systems achieved 150 hours.

5.1.4 Special Requirements

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

The engine and test cell fuel systems were flushed and filters changed at the start of testing with each fuel to avoid contamination. Engine oil and filters were also changed to avoid possible fuel dilution effects.

5.2. Results of the PM Measurements

Sulfate was never observed in the PM analyses above the detection limit of 0.02 mg/filter, or roughly 1% of the TPM. Thus, there are only two fractions to the TPM: soluble organic fraction (SOF) and non-SOF (elemental carbon (soot) + sulfate + inorganic + water). All of the PM results are displayed in Figure 5.2-1.

The engine-out results are shown in the top two plots of Figure 5.2-1. The engine-out TPM is high (3 g/kW-hr at 150°C) for the low-load points of 150 and 200°C, but is much lower (0.3 g/kW-hr) from 250 to 550°C and is relatively constant, with only a slight fall-off apparent with increasing temperature. The engine-out TPM is >90% SOF at 150 - 200°C, 50-60% SOF from 250 to 450°C, and only 20-30% SOF at 500 and 550°C. This trend most likely represents vaporization of some of the organic material from the TPM as the exhaust temperature increases. The SOF fraction of the TPM is on the high side compared to that normally observed for heavy duty diesel TPM, which is generally about 30% SOF. The non-SOF, or soot, portion of the TPM increases as a percentage of the TPM, as the SOF decreases, but the soot emission rate increases by only about a factor of two from low to high temperature (low to high engine load). Being a very small mass component, the soot measurements are more 'noisy', or more variable, than are the TPM or SOF results. There are no apparent effects of the fuel sulfur level on the engine-out TPM, SOF or non-SOF emission rates for the mapping studies as a function of temperature.

The catalyst-out results are shown in the middle two plots of Figure 5.2-1. The adsorber catalyst is very effective at removing the SOF (90 to 50% removal, decreasing with increasing temperature)

from the TPM, especially at low temperatures. The catalyst-out TPM is only about 0.15 g/kW-hr over the 250 to 550°C temperature range, and, in this range, the SOF is only about 0.03 g/kW-hr. The reductions in TPM and SOF are a result of oxidation of some of the adsorbed hydrocarbons in the TWC portion of the adsorber catalyst during lean operation. There is even an indication that, at least up to 300°C, a portion of the soot, or non-SOF, may also be removed across the adsorber catalyst, a possibility that could result from reaction between soot carbon and adsorbed NO_x. There are no apparent effects of the fuel sulfur level on the catalyst-out TPM, SOF or non-SOF emission rates for the mapping studies. The failure to detect sulfates in the TPM indicate that, at least at these relatively low fuel sulfur levels, NO_x adsorber catalysts do not generate excess sulfate from SO₂ oxidation, at least sulfate that is released from the adsorber catalyst. Sulfate release should be monitored during desulfurization of the NO_x adsorber catalysts, when those studies are performed.

The aging effects on the PM emission rates are shown in the bottom two plots of Figure 5.2-1. The 350°C SOF fraction was large (95%) for fresh adsorber catalyst, falling off to as low as 10% for aged systems. The catalyst-out TPM, the SOF and the non-SOF showed no dependence on fuel sulfur level, with the possible exception of the non-SOF with, age at 350°C. There are differences between the 3 ppmS non-SOF aging and the 16 and 30 ppmS non-SOF aging, but they do not correlate with the fuel sulfur level. The TPM was about 0.08 g/kW-hr and did not vary with aging or with fuel sulfur level. The SOF decreased from 0.03 g/kW-hr with fresh systems, to about 0.02 g/kW-hr at 250 hours aging, with no apparent differences by fuel sulfur level. The non-SOF tended to increase with aging, starting at 0.05 g/kW-hr and reaching asymptotic limits of about 0.07 g/kW-hr midway in the aging process.

The spare adsorber catalysts with the revised engine management calibration were monitored for PM emissions during mapping from 150 to 550°C but no aging studies were performed. The TPM, SOF and non-SOF were virtually indistinguishable from the catalyst-out results in the middle of Figure 5.2-1 for adsorber catalysts with the initial engine management calibration for the three sulfur levels evaluated.

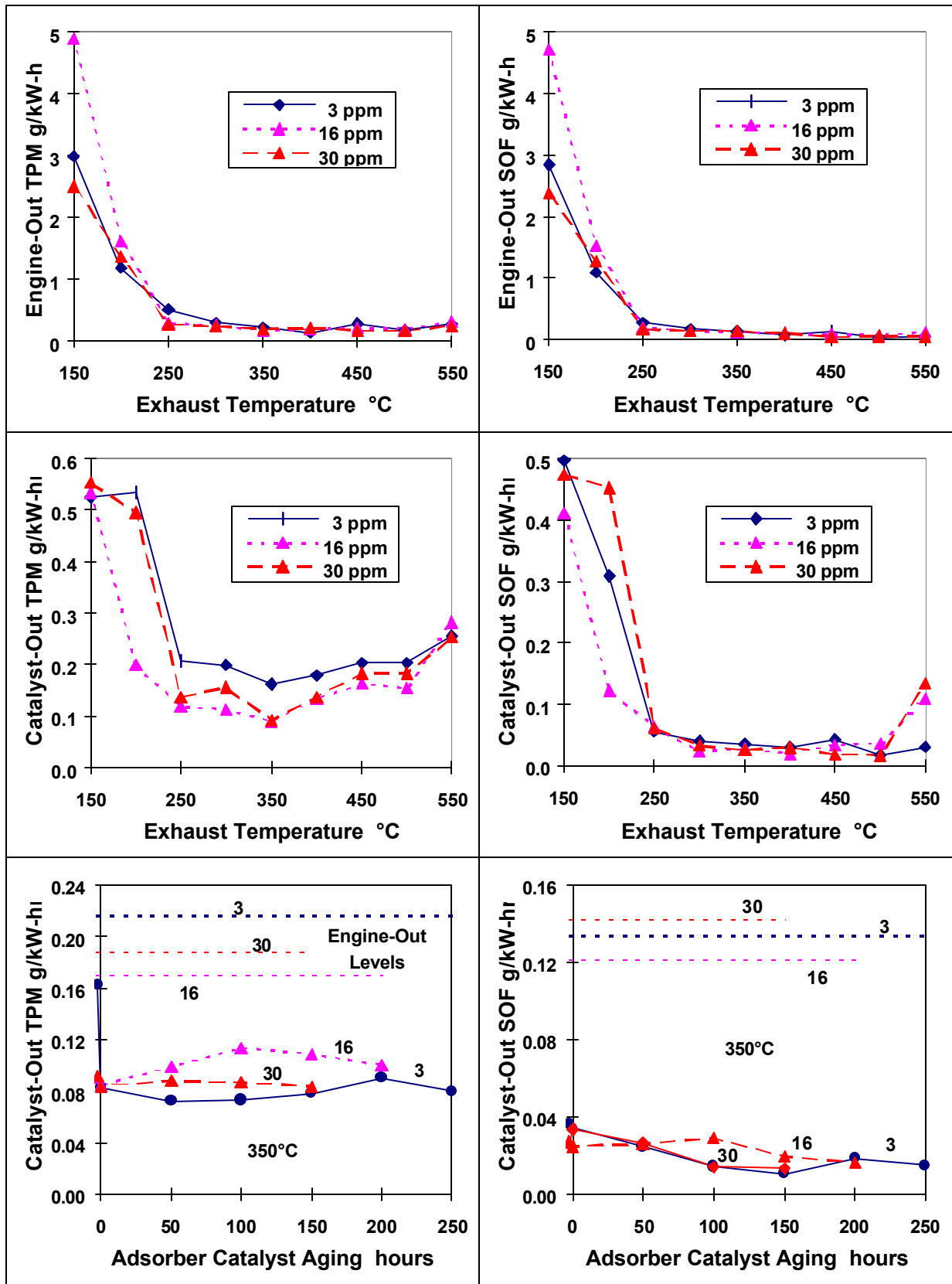


Figure 5.2-1. TPM and SOF dependence on fuel sulfur, temperature and aging

5.3 Conclusions Regarding the PM Measurements

- NO_x adsorber catalysts significantly reduce engine-out TPM and SOF emissions across the full temperature range of operation, with the highest efficiencies in the low temperature regimes.
- The ability of the adsorber catalyst to reduce engine-out TPM and SOF does not degrade with catalyst aging, up to 250 hrs.
- No fuel sulfur affects are apparent for TPM, SOF or non-SOF across the range of analysis temperature or during adsorber catalyst aging up to 250 hours
- With fuel sulfur levels up to 30-ppmS, adsorber catalysts apparently do not cause elevated sulfate releases into the atmosphere, consistent with the sulfur adsorbing chemical process inherent in the NO_x adsorber catalyst.

REFERENCES

1. J. C. Wall and S. K. Hoekman, "Fuel Composition Effects on Heavy-Duty Diesel Particulate Emissions", SAE 841364, 1984.
2. J. C. Wall, S. A. Shimpi, and M. L. Yu, "Fuel Sulfur Reduction for Control of Diesel Particulate Emissions", SAE 872139, 1987.
3. N. J. Khatri, J. H. Johnson, and D.G. Leddy, "The Characterization of the Hydrocarbon and Sulfate Fractions of Diesel Particulate Matter", SAE 780111, 1978.
4. Manufacturers of Emission Control Association. "The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems", Manufacturers of Emission Controls Association, Washington, DC, 1997.
5. Manufacturers of Emission Control Association. "The Impact of Sulfur in Diesel Fuel on Catalytic Emission Control Technologies", Manufacturers of Emission Controls Association, Washington, DC, 1999.
6. Manufacturers of Emission Control Association. "Demonstration of Advanced Emission Control Technologies Enabling Diesel Powered Heavy-Duty Engines to Achieve Low Emissions Levels", Manufacturers of Emission Controls Association, Washington, DC, 1999.
7. G. Hunter, J. Scholl, F. Hibbler, S. Bagley, D. Leddy, D. Abata, and J. Johnson, "The Effect of an Oxidation Catalyst on the Physical, Chemical, and Biological Character of Diesel Particulate Emissions", SAE 810263, 1981.
8. J. E. Thoss, J. S. Rieck, and C. J. Bennett "The Impact of Fuel Sulfur Level on FTP Emissions - Effect of PGM Catalyst Type", SAE 970737, 1997.
9. G. Smedler, et. al., "Diesel Catalysts for Europe Beyond 1996", *Automotive Engineering*, October, 1995.
10. R. J. Farrauto, J. J. Mooney, "Effects of Sulfur on Performance of Catalytic Aftertreatment Devices", SAE 920557, 1992.
11. D. Dou, and O. H. Bailey, "Investigation of NO_x Adsorber Catalyst Deactivation", SAE 982594, 1998.