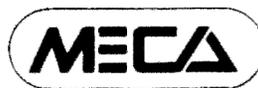


# **THE IMPACT OF GASOLINE FUEL SULFUR ON CATALYTIC EMISSION CONTROL SYSTEMS**

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**Manufacturers of Emission Controls Association**

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## **I. EXECUTIVE SUMMARY**

Catalytic emission control systems, used on passenger cars since 1975, have played a key role in substantially reducing exhaust pollutants from motor vehicles. Exhaust emission control is influenced not only by the emission control system, but by engine design and fuel quality as well. Since 1975, catalyst technology and engine designs have continued to advance dramatically. Changes in fuel quality, most notably eliminating lead in gasoline and reducing gasoline sulfur levels, have also contributed to achieving very low vehicular emissions. Currently the U.S. federal gasoline sulfur limits (30 ppm sulfur average) lag the gasoline sulfur limits found in California, the European Union, Japan, and South Korea (20 ppm sulfur cap in California, 10 ppm sulfur cap for the EU, Japan, South Korea).

Sulfur in gasoline inhibits the emission control performance of catalyst technology. A variety of factors influence the degree of this impact and the extent to which it is reversible. These factors include the sulfur level in the gasoline, the catalyst composition, the catalyst design, the catalyst location, the type and control of fuel metering, the engine calibration, and the manner in which the vehicle is operated.

Recent studies have shown that the effect of sulfur inhibition has a greater impact on the emission control systems of vehicles designed to meet SULEV-type standards and that the effects of sulfur may not be completely reversible on these vehicles. While catalyst manufacturers are continuing design efforts to reduce the effects of sulfur on catalyst technology, the growing body of technical information strongly indicates that reducing the sulfur level in gasoline would have a significant benefit to the emission control performance of past, current and future emission control systems.

MECA supports the adoption of U.S. federal gasoline fuel sulfur specifications that are in line with sulfur limits currently in place in California: a gasoline sulfur cap in the range of 20-25 ppm and a national average of 10 ppm or lower. The change should be brought about as quickly as possible, although adequate lead-time should be provided to implement these changes and the limits should include compliance flexibility strategies similar to those used in the past to facilitate cost effective compliance.

## **II. BACKGROUND**

Catalytic emission control systems have been used on U.S. gasoline passenger cars since the 1975 model year - first oxidation catalysts (OC) and then, since the early 1980s, three-way conversion (TWC) catalysts. For over 30 years, the closed loop TWC system has dominated as the most efficient automobile exhaust emission control system. This system consists of front and rear oxygen sensors, a three-way catalytic converter, an electronic control unit (ECU), and a controllable fuel metering unit. The system provides very good fuel economy and engine performance, as well as the simultaneous control of hydrocarbons (HC), carbon monoxide (CO)

and oxides of nitrogen (NO<sub>x</sub>) exhaust emissions. It is used on virtually all gasoline passenger cars and light-duty trucks sold around the world.

Exhaust emission control is influenced by engine design and fuel quality. The engine, the emission control system, and the fuel are essential components of the engine exhaust control system. Engines and the emission control systems have continued to develop as improvements in gasoline fuel quality have occurred.

## **Catalyst Technology Advances**

The automotive catalyst industry has improved three-way catalyst performance to over 98% efficiency by utilizing improved formulations, high cell density substrates and layered coating architectures. The new catalyst designs are more durable and thermally resistant, lasting for well over 150,000 miles. Today's catalysts can be formulated to survive harsh hydrothermal environments found in the exhaust, including temperatures of up to 1100°C in accelerated aging tests. Development work continues to further improve catalyst technology.

The TWC has been the primary emission control technology on light-duty gasoline stoichiometric vehicles since the early 1980s. The use of TWCs, in conjunction with oxygen sensor-based, closed-loop fuel delivery systems, allows for simultaneous conversion of the three criteria pollutants, hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO<sub>x</sub>), produced during the stoichiometrically calibrated air/fuel combustion process of an internal combustion, spark-ignited engine. The active catalytic materials are present as a thin coating of precious metals (e.g., Pt, Pd, Rh), and oxide-based inorganic promoters and support materials on the internal walls of a honeycomb substrate. The substrate typically provides a large number of parallel flow channels to allow for sufficient contacting area between the exhaust gas and the active catalytic materials without creating excess backpressure on the engine.

The honeycomb-based substrates are typically either ceramic or metal foil-based. Cordierite, a magnesium aluminosilicate compound, is the preferred ceramic substrate material due to its low coefficient of thermal expansion, good mechanical strength characteristics, and good coating adhesion properties. The ceramic substrate is typically formed as a single body using an extrusion process followed by high temperature firing. Metal-foil based substrates are made from thin ferritic-based specialty stainless steel foils brazed together to form the parallel flow passages. The ferritic foil alloy provides good oxidation resistance in the exhaust environment, good mechanical strength, and an oxidized surface that promotes good adhesion of the catalytic coating to the foil. In the case of ceramic substrates, a special oxide fiber-based mounting material (typically referred to as a "mat") is used between the substrate and the metal outer shell to hold the substrate in place, provide thermal insulation, and cushion the ceramic body against the shell. The outer metal shell or mantle is an integral part of the metal substrate production scheme and no additional mounting materials are generally required. In some cases the converter housing or "can" can be surrounded by a second metal shell with an annular gap between these two metal shells. This type of arrangement provides additional heat insulation to the converter. The annular region between the two shells may be left as an air gap or filled with an insulating material such as an inorganic fiber-based material.

Although the primary components and function of a three-way catalytic converter have remained relatively constant during its more than thirty years of use on light-duty gasoline vehicles, each of the primary converter components (catalytic coating, substrate, mounting materials) has gone through a continuous evolution and redesign process aimed at improving the overall performance of the converter while maintaining a competitive cost effectiveness of the complete assembly. The performance-based catalytic converter re-engineering effort has had three main focuses: (1) wide application of close-coupled converters mounted near the exhaust manifold of engines for improved performance following a cold engine start; (2) the development of thin-wall, high cell density substrates for improved contacting efficiency between the exhaust gas and the active catalyst, and lowering the thermal mass of the converter; and (3) the design of advanced, high performance TWCs for both close-coupled and underfloor converter applications that emphasize excellent thermal durability and efficient use of the precious metals platinum (Pt), palladium (Pd), and rhodium (Rh).

Advanced TWC formulations often utilize multi-layer architectures and/or axial placement of different catalyst materials along the length of the substrate that allow for the optimization of specific catalytic functions (e.g., improved light-off characteristics or improved overall efficiency for reducing hydrocarbons, CO, and/or NO<sub>x</sub>). These advanced catalysts also utilize a variety of advanced materials (in addition to the active precious metals) that promote the oxidation and reduction reactions associated with three-way catalysts and allow these catalysts to maintain activity in severe thermal exhaust environments. Catalyst substrate channel or cell densities as high as 1200 cells/in<sup>2</sup> have been used on production catalytic converters with 600 cells/in<sup>2</sup> substrates used in many late model vehicle applications. A similar re-engineering effort has occurred with other exhaust system components such as exhaust manifolds and exhaust pipes that complement improvements in catalytic converter technology. The focus of these manifold and other exhaust component improvements has been exhaust system thermal management and heat conservation through the use of low thermal mass, air gap insulated components or other heat insulation strategies.

High cell density ceramic and metallic substrates provide significant increases in substrate geometric surface area versus standard designs used in U.S. Tier 1 and earlier model light-duty vehicles. Larger substrate geometric surface area translates into more efficient contact between the exhaust gas constituents and active catalyst components displayed on the substrate channel walls. The result is more emission conversion efficiency per unit volume of substrate as cell densities are increased. Increasing the substrate channel density also results in smaller channel flow dimensions, which in turn improves mass transfer between the flowing exhaust gas and active catalyst sites on the walls of the substrate. High cell density substrate designs that utilize thinner ceramic or metallic walls separating flow channels further reduce the thermal mass of the substrate and facilitate heat-up. In this way, the overall mass of a given sized substrate is reduced relative to older designs with lower cell density and thicker wall dimensions. The resulting lower thermal mass is able to heat-up more quickly during critical start-up operations and contribute to improved performance during cold and warm-start driving modes, making these advanced high cell density substrates ideal for close-coupled converter applications.

Through the use of advanced, thermally stable support and promoter materials, improved precious metal impregnation strategies, and sophisticated catalyst coating architectures, the

performance of today's advanced three-way catalysts are far beyond performance levels exhibited by U.S. Tier 1 light-duty vehicles. These advanced three-way catalysts offer improved light-off properties, wider air/fuel windows of operation, higher NO<sub>x</sub> conversion efficiencies, and improved long term durability in higher temperature operating environments. These improvements have been extended to catalysts that utilize one or more of the preferred catalytically active precious metals used in automotive catalysts (i.e., Pt, Pd, Rh). Additional system performance benefits have been achieved by combining advanced three-way catalysts with advanced engine controls that, for example, closely control the air/fuel ratio at the catalyst inlet.

## **Gasoline Quality**

Lead removal efforts from gasoline in the U.S. began with the introduction of catalytic converters in late 1974. The gasoline lead specification in the U.S. reached today's diminutive level beginning on January 1, 1996. The United Nation Partnership for Clean Fuels and Vehicles (PCFV) has been working to globally phase-out lead in gasoline since 2002. More than 185 countries have stopped adding lead to gasoline, with only six (Afghanistan, Algeria, Iraq, North Korea, Myanmar and Yemen) still using small amounts. These last remaining countries with leaded gasoline are expected to remove lead from their gasoline pools by 2014 or 2015.

The gasoline fuel sulfur specification has also tightened with each tightening of emission standards for light- and heavy-duty vehicles. Reducing the level of sulfur in gasoline is important because gasoline sulfur, upon combustion, results primarily in sulfur dioxide (SO<sub>2</sub>) in the exhaust gas, with small amounts of sulfur trioxide (SO<sub>3</sub>). SO<sub>2</sub> and SO<sub>3</sub> are known to inhibit the catalytic function of catalytic converters. In fact, SO<sub>2</sub> is known to inhibit most gaseous heterogeneous catalytic reactions. Ultra-low gasoline sulfur levels are critical to achieving the very low emission levels required for future U.S. emission standards, such as EPA's Tier 3 and California's LEV III vehicle emission limits. A move to ultra-low sulfur gasoline fuel across the U.S. will also result in improved performance of three-way catalysts already installed on the nearly 250 million cars and trucks that are part of the existing U.S. vehicle fleet.

Sulfur inhibition of precious metal-based catalyst emission performance depends on a variety of catalyst- and vehicle-related parameters, including: precious metal type/precious metal catalyst concentration; oxygen storage composition/concentration; catalyst design (e.g., placement of precious metals and/or oxygen storage components); catalyst location/converter volume/operating temperature; catalyst aging history; inlet exhaust gas composition (e.g., engine calibration); and fuel sulfur level.

Numerous vehicle studies have been completed that consistently show lower exhaust emissions result from a wide range of vehicle technologies operating with lower gasoline sulfur levels. A recent published study shows sulfur inhibition for a late model, aged vehicle's three-way catalysts operating at very low emission levels (SULEV exhaust emission levels) and at very low fuel sulfur levels (33 ppm vs. 3 ppm sulfur fuel comparison). The vehicle emission system included close-coupled and underfloor catalytic converters utilizing advanced three-way catalysts. The performance of the vehicle's cooler-running, underfloor converter was most impacted by operation on higher fuel sulfur levels (see page 16 for more details).

## **Emission Certification Fuel vs. Commercially Available Fuel**

It is well known that vehicle in-use emissions do not correspond to those achieved in the certification process used to prove that vehicles comply with U.S. EPA vehicle emission standards. This difference between certification emission levels and in-use vehicle emissions stems, in part, from differences between the indolene-grade gasoline used for vehicle certification work and fuel properties of commercial-grade gasolines sold in the U.S. Indolene fuel used in vehicle certification work typically has a very low sulfur content (the current indolene specification calls for sulfur levels below 80 ppm). In comparison, U.S. commercial gasoline sulfur content ranges between 20 and about 100 ppm, with a national average of about 30 ppm. Indolene gasoline results in reproducible tailpipe emissions from a test vehicle. Emission results with commercial gasoline grades will vary widely based largely on variations in fuel sulfur content. Both EPA and California are now moving toward the use of certification fuel specifications that are more representative of the average gasoline properties available within California or across the U.S.

Federal Phase II reformulated gasoline (RFG) has resulted in lower sulfur levels in gasoline, but the rule applies only in selected urban areas in the United States. Reformulated gasoline is gasoline blended to burn more cleanly than conventional gasoline and to reduce ozone and toxic air pollutants. The first phase of the RFG program began in 1995 and the second phase (current) began in 2000. RFG is required in cities with high smog levels and is optional elsewhere. RFG is currently used in 17 states and the District of Columbia, and makes up about 30% of gasoline sold in the U.S. As a result of the National Fuel Policy Act of 1992 and other initiatives, clean fuels have become increasingly available. However, gasoline remains the major fuel product.

On May 1, 2007, EPA finalized the Renewable Fuel Standard (RFS), establishing a comprehensive RFS program for 2007 through 2012 and beyond. In February 2008, EPA amended the RFS to reflect amendment to the Energy Independence and Security Act (EISA) of 2007. EISA increases the overall volume of renewable fuels that must be blended each year, reaching 36 billion gallons in 2022. On March 26, 2010, EPA finalized its RFS-2 regulation for 2010 and beyond. This regulation establishes new specific volume standards for cellulosic biofuel, biomass-based diesel, advanced biofuel, and total renewable fuel that must be used in transportation fuel each year.

Currently, more than 95% of the U.S. gasoline contains up to 10% ethanol to boost octane, meet air quality requirements, or satisfy the RFS. E10 gasoline is sold in every state in the U.S. Recent increases in ethanol usage in gasoline have made E0 and MTBE rare in the U.S. California has moved to require E10 as its LEV III certification fuel, and EPA is considering moving its certification E0 gasoline to E10 or E15, as a part of its Tier 3 proposal. ARB has included both regular and premium certification fuels in their LEV III program, and EPA has indicated that it is planning to do the same as a part of Tier 3.

## Regulations and Fuel Standards

Currently, EPA's Tier 2 light-duty emissions regulation, finalized in December 1999, requires U.S. gasoline suppliers to meet a 30 ppm average sulfur level with a maximum refinery gate cap of 80 ppm and a 95 ppm retail sulfur cap. This requirement took effect in 2006. California's gasoline sulfur cap, as required by ARB's Low Emission Vehicle II (LEV II) program, reduced the gasoline sulfur cap from 60 ppm to 30 ppm in 2006 and that sulfur cap was further reduced to 20 ppm in 2012 for gasoline sold in California.

The state of California recognized the benefit of reducing sulfur in gasoline on the emission control of existing vehicles and the need for low sulfur fuel to optimize the performance of new vehicles designed to meet their stringent LEV II vehicle standards. As a result, California, in establishing its Phase II reformulated gasoline requirements, set an average sulfur level of 30 ppm, with a cap of 80 ppm sulfur in gasoline. In 2006, ARB further reduced the sulfur level to a cap of 20 ppm. Current gasoline sulfur levels in California average a bit below 10 ppm. For similar reasons, the European Union (EU) agreed to establish a two phase reduction in gasoline sulfur to <150 ppm in 2000 and <50 ppm in 2005. The EU further reduced its fuel sulfur levels to maximum of 10 ppm starting in 2009. Similarly, starting in April 2005, Japan reduced its fuel sulfur level to a maximum of 10 ppm for gasoline and diesel fuels, and South Korea has also reduced its gasoline sulfur limit to 10 ppm starting in 2009. China has recently committed to reducing its gasoline sulfur level to 10 ppm maximum by December 31, 2017.

In March 2013, EPA proposed its Tier 3 Motor Vehicle Emission and Fuel Standards, which includes creation of a national set of criteria pollutant standards largely harmonized with California's LEV III emission standards, and proposed reduction in gasoline sulfur levels from the current 30 ppm average to a 10 ppm average across the nation starting in 2017. According to EPA, the feasibility of the proposed Tier 3 30 mg/mi NMOG+NO<sub>x</sub> 2025 fleet average exhaust emission standard depends on a degree of emissions control from exhaust catalyst systems that will require gasoline at 10 ppm sulfur or lower. The most likely control strategies would involve using exhaust catalyst technologies and powertrain calibration primarily focused on reducing cold-start emissions of NMOG and on reducing both cold-start and warmed-up emissions of NO<sub>x</sub>.

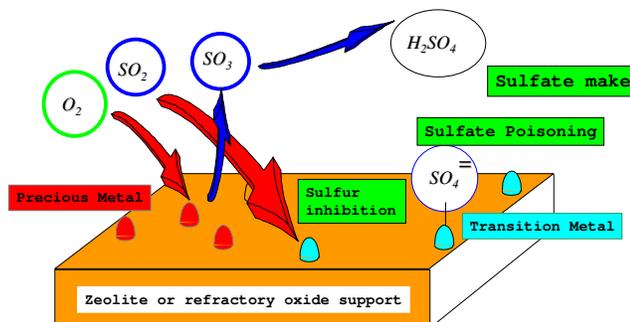
EPA notes that the impact of gasoline sulfur poisoning on exhaust catalyst performance and the relative stringency of the Tier 3 standards, particularly for larger vehicles and trucks, when considered together, make a compelling argument for the virtual elimination of sulfur from gasoline. While lowering gasoline sulfur to levels below 10 ppm would further help ensure in-use vehicle compliance with Tier 3 standards, EPA believes that a gasoline sulfur standard of 10 ppm would allow compliance by gasoline-fueled engines with a 2025 national fleet average of 30 mg/mi NMOG+NO<sub>x</sub>.

### III. EFFECTS OF FUEL SULFUR ON EMISSION CONTROL PERFORMANCE

#### A. Background

Sulfur is not a catalyst poison like lead which completely and permanently destroys catalyst activity. Rather, sulfur is an inhibitor which strongly competes with the exhaust pollutants for “space” on the active catalyst surface sites. The issue of sulfur compounds inhibition on emission control systems performance is quite complex. Upon combustion, fuel sulfur is oxidized to sulfur oxides, primarily sulfur dioxide ( $\text{SO}_2$ ) with small amounts of sulfur trioxide ( $\text{SO}_3$ ).  $\text{SO}_2$  and  $\text{SO}_3$  are known to inhibit the catalytic function of automobile exhaust catalysts. Sulfur inhibition varies in degree according to the gasoline sulfur level, the catalyst formulation, catalytic function, combustion products from various air/fuel mixtures, and exhaust temperature range.

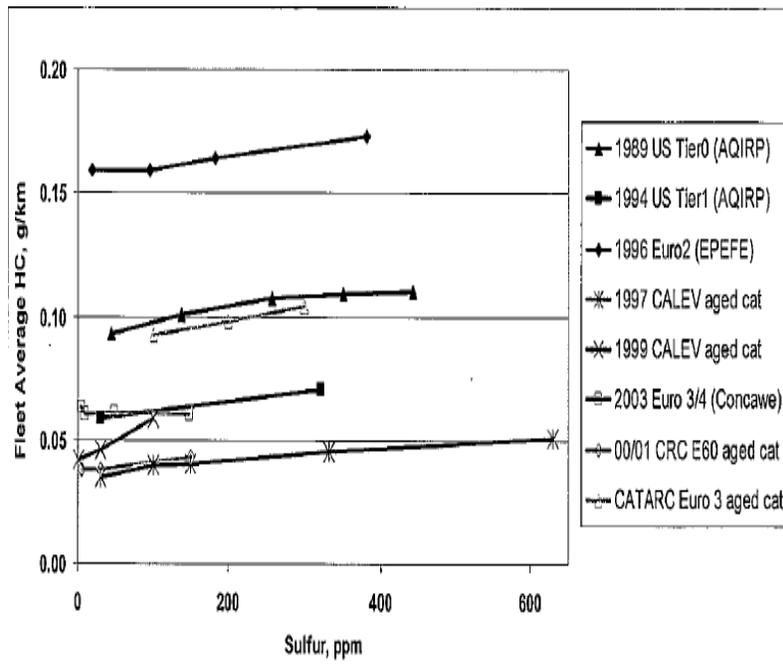
Catalyst sulfur inhibition is caused by chemisorption of a sulfur species on an active catalyst site (1,2,3,4,5,6,7). The presence of sulfur as an oxide or sulfide (e.g. hydrogen sulfide ( $\text{H}_2\text{S}$ ) which can also be present in the exhaust) invariably has a negative, and typically immediate, effect on the performance of heterogeneous catalysts. The sulfur species adsorbs on the catalyst site which is then not available for the preferred catalytic reactions resulting in less overall activity - this is the case with  $\text{SO}_2$  and with  $\text{H}_2\text{S}$ . Another undesirable effect of sulfur in gasoline is that the catalyst oxidizes  $\text{SO}_2$  to  $\text{SO}_3$  which forms sulfates easily with base metal oxides in the washcoat layer or forms sulfuric acid in reaction with water. Precious metals have an advantage over base metal oxides as they are much more resistant to  $\text{SO}_2$  and  $\text{SO}_3$ . Base metal catalysts and oxygen storage materials more easily form sulfates which are also more difficult to regenerate (3).



**Figure 1. Diagram of the adverse impact of fuel sulfur on emission control technology – sulfur species react with catalyst materials resulting in degraded catalyst performance.**

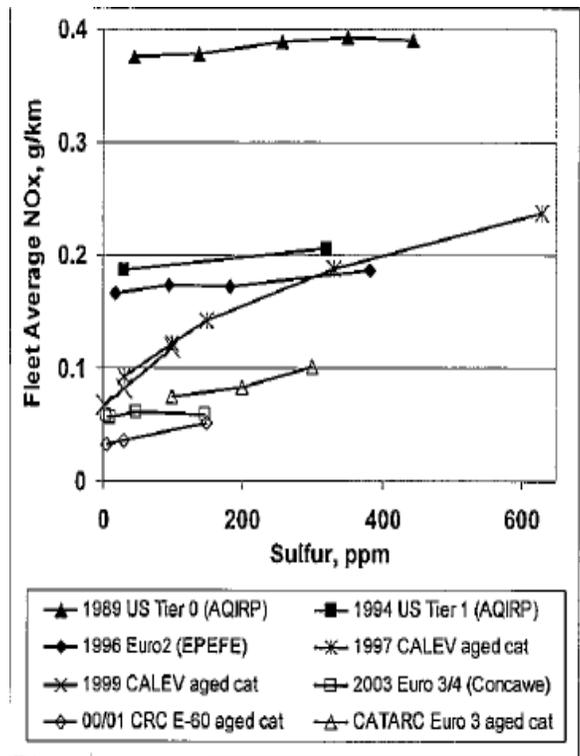
## B. Vehicle Studies

According to a Coordinating Research Council (CRC) report reviewing prior studies of fuel effects on vehicle emissions, from an exhaust emissions perspective, sulfur level is probably the most important gasoline property because it impacts the operation of the TWC and other components of modern emission control systems (8). Prior to the Auto/Oil Air Quality Improvement Research Program (AQIRP), initiated in 1989, there was little published research on the impact of sulfur. Studies conducted since have shown that reducing fuel sulfur levels lowers vehicle emissions of HC, CO, and NO<sub>x</sub>. Although there is some conflicting data, the effects appear to be linear, especially at levels of sulfur below about 150 ppm (see Figures 2 and 3 below). In 1989 model year vehicles, the sulfur effect was shown to be completely reversible under mild driving conditions. More recent testing has concluded that, in the short-term, some level of reversibility is possible only under extreme driving conditions, which is likely the result of tight control of engine conditions and temperatures in newer vehicles, and possibly changes in catalyst formulations (8).



**Figure 2: Sulfur Effect on Emissions from Older Vehicles**

*Source: CRC Project E-84*



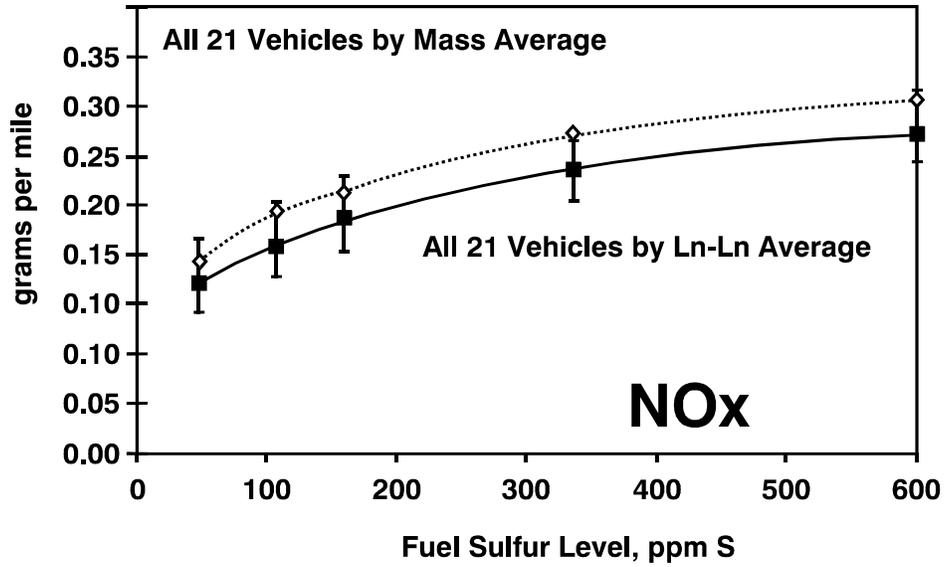
**Figure 3: Sulfur Effect on Emissions from Older Vehicles**

Source: CRC Project E-84

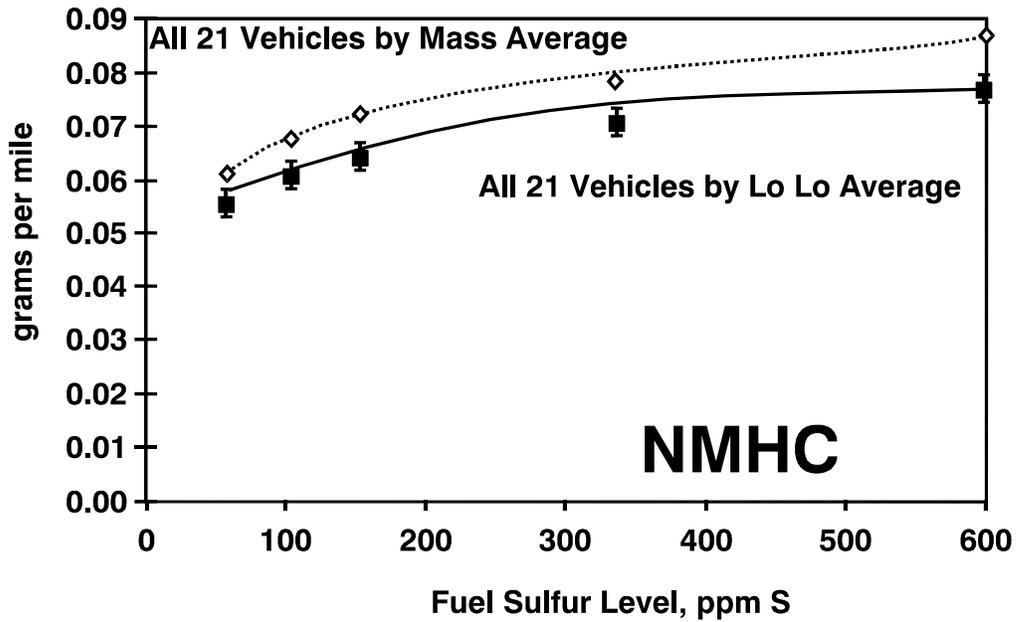
It has been reported that sulfur inhibition is worse with vehicle systems calibrated to meet the California LEV standards (8, 9, 10). Gorse (8) reported data showing that sulfur inhibition increases the emission levels of a LEV vehicle to that of a Tier 0 vehicle. Benson (10) reported data showing a 60% increase in HC, 65% increase in CO, and 180% increase in NOx when going from 40 to 1000 ppm sulfur fuel.

The Alliance of Automobile Manufacturers (formerly American Automobile Manufacturers Association (AAMA)) and the Association of Global Automakers (formerly Association of International Automobile Manufacturers (AIAM)) (11), as well as the CRC (12), conducted independent studies examining the effect of fuel sulfur on LEV I-type vehicles. In the first study, twenty-one vehicles from ten automobile manufacturers were each tested with fuels containing various levels of sulfur from 40 to 600 ppm. The catalysts were aged to simulate 50,000 or 100,000 miles of on-road driving. The combined results of all vehicles are shown in Figures 4 and 5 for NOx and NMHC exhaust emissions, respectively. The results of the AAMA/AIAM Fuel Sulfur Study (11) showed that LEV I-type systems experience greater increases in emissions due to sulfur for HC and NOx than do older U.S. Tier 0 or Tier 1 vehicles. In the second study by CRC, twelve vehicles from six automobile manufacturers were each similarly tested with fuels containing various levels of sulfur in the same range as the AAMA/AIAM study and with a catalyst with 10,000 mile vehicle accumulation and, again with 100,000 mile aged catalysts. The results of the CRC study for NOx are shown in Figure 6. The NOx results from this CRC vehicle study show larger sulfur impacts for vehicles equipped with 100,000 mile aged catalysts compared to catalysts with 10,000 miles of service (especially in the 40-150 ppm fuel sulfur range). Both of these vehicle studies show similar sulfur effect results

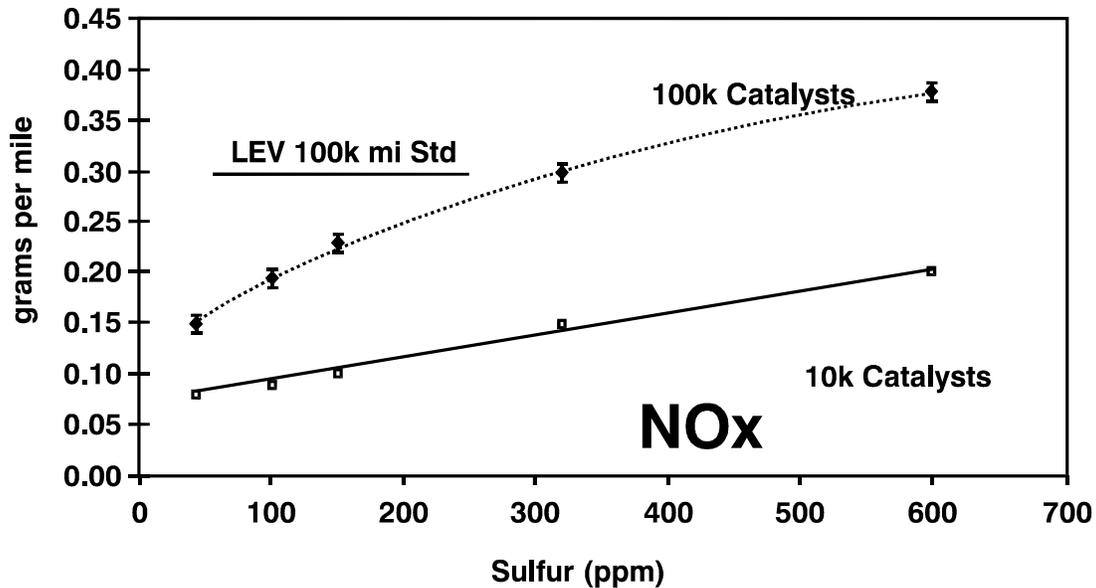
with significant increases in all emissions as the sulfur level was increased. Conversely, stepwise lowering of the gasoline fuel sulfur resulted in reduced emissions.



**Figure 4: Effect of Fuel Sulfur on LEV Type Vehicles**  
*Source: AAMA/AIAM Fuel Sulfur Study*



**Figure 5: Effect of Fuel Sulfur on LEV Type Vehicles**  
*Source: AAMA/AIAM Fuel Sulfur Study*

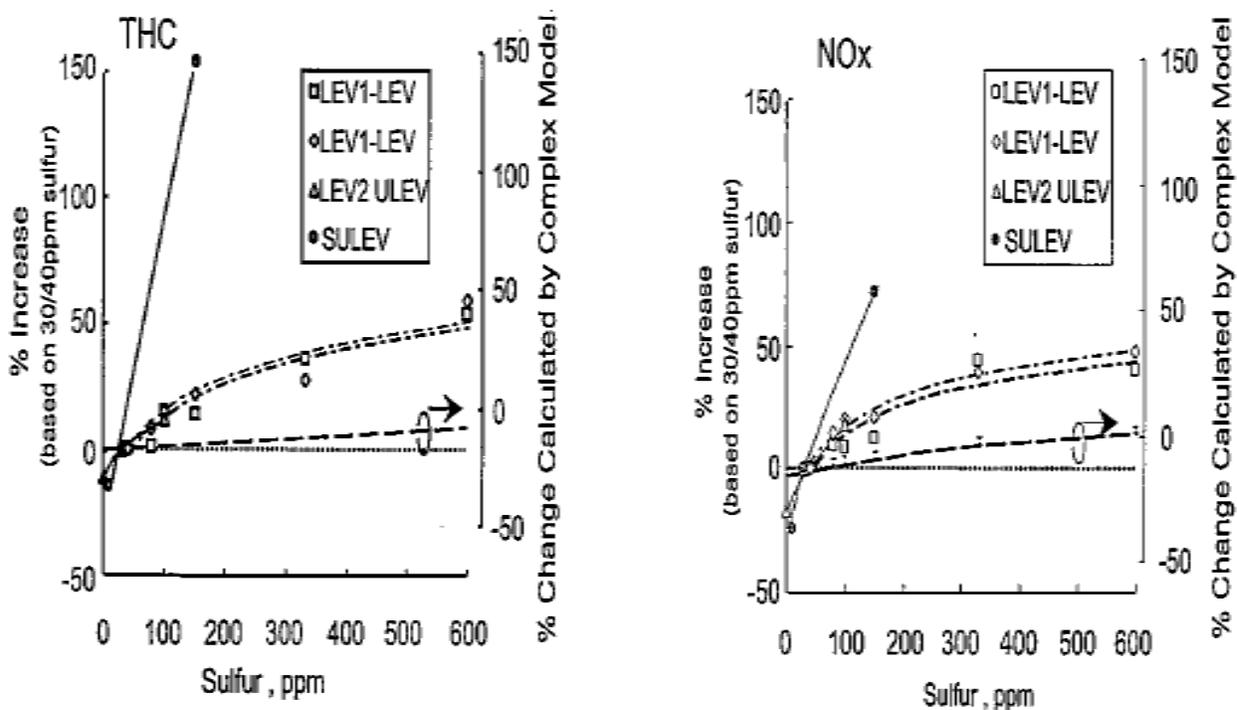


**Figure 6: CRC Study on the Effects of Fuel Sulfur on LEV Type Vehicles**

*Source: AAMA/AIMA Fuel Sulfur Study*

In a study reported by Toyota in a 2000 Society of Automotive Engineering (SAE) paper, the effects of gasoline fuel properties on exhaust emissions were evaluated using a variety of gasoline vehicles including port injected LEVs, a ULEV II vehicle, a prototype SULEV vehicle with TWCs and two vehicles with direct injection spark ignition (DISI) engines equipped with NOx storage reduction (NSR) catalysts (13). The researchers note that although emission control technology has been vastly improved, near-zero emissions levels are not possible without significant fuel quality improvement.

In this study by Toyota, four vehicles were equipped with a TWC and were prepared for evaluating sulfur effect on exhaust emissions. Sulfur levels in the test fuels were varied from <1 ppm to 60 ppm. Emission tests were conducted in accordance with FTP-75 or LA-4 driving cycles and each test was repeated from two to six times (13). The emissions testing found that reducing gasoline sulfur lowers the exhaust emissions in all TWC systems. It also found that the prototype SULEV vehicle was the most sensitive to sulfur. Figure 7 below summarizes the effects of gasoline fuel sulfur on exhaust HC and NOx for four different stoichiometric gasoline vehicles.



**Figure 7: Effects of Fuel Sulfur on Exhaust HC and NOx**

*Source: SAE Paper 2000-01-2019*

In addition, two vehicles equipped with lean burn, DISI engines were used to test gasoline sulfur effects on the performance of NOx NSR catalysts. Fuels with sulfur levels that varied from 8 ppm to 500 ppm were used. Emissions were evaluated with the Japanese 10-15 mode test cycle. The results from the testing showed that as the sulfur content increased in the fuel, the NOx conversion efficiency deteriorated significantly. The NOx conversion efficiency at 32,000 km using 8 ppm and 30 ppm sulfur fuel was 93% and 82%, respectively. This difference means 2.5 times higher tailpipe NOx emissions for the 30 ppm sulfur fuel (13). The gasoline sulfur impacts on NOx NSR catalysts reported in this work is consistent with the strong sulfur sensitivity observed for NOx storage catalysts evaluated on a variety of light-duty and heavy-duty diesel vehicles.

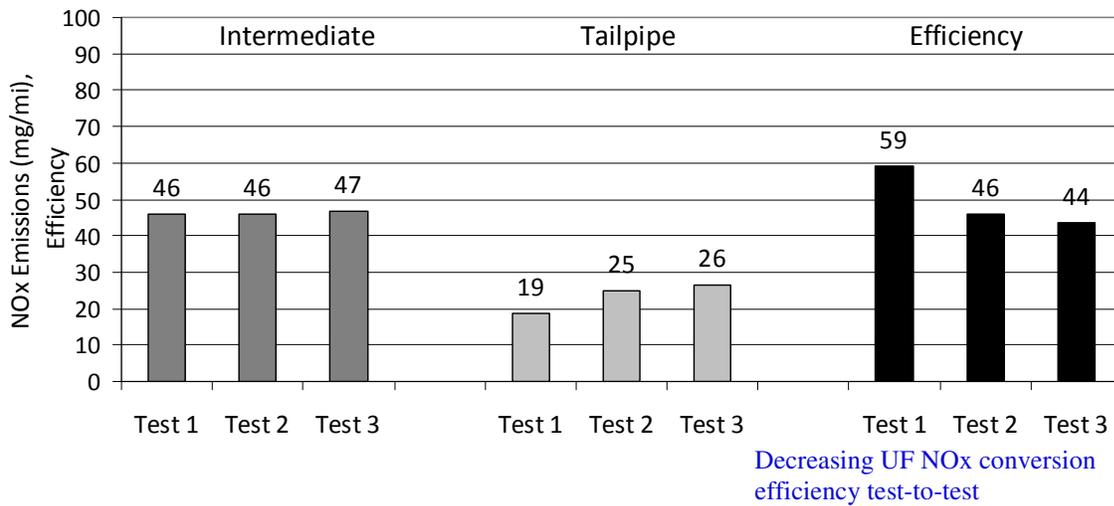
In the same Toyota study, the reversibility of NOx conversion efficiency of NSR catalysts was investigated. Four catalysts that were aged up to 16,000 km with 8 ppm, 30 ppm, 90ppm and 500 ppm sulfur fuels were prepared. NOx conversion efficiency of each catalyst was measured on an engine dynamometer before and after regeneration of sulfur poisoning. The condition of sulfur regeneration was at 620°C catalyst bed temperature and at an air fuel ratio of 14.0 (rich of stoichiometric). The study showed that the NSR catalyst that was aged with higher sulfur fuel shows lower reversibility. The NOx conversion level of the catalyst aged with 8 ppm sulfur fuel recovered nearly to the fresh condition level after a short regeneration period. However, the NOx conversion efficiency of the NSR catalyst aged with 30 ppm sulfur fuel could not be regenerated to the fresh level after 25 minutes of regeneration.

In another study that looked at the effects of fuel sulfur on FTP NO<sub>x</sub> emissions from a PZEV 4 cylinder vehicle, the authors measured FTP emissions from a 2009 model year, 4 cylinder, 2.4L Malibu PZEV vehicle with 3 ppm and 33 ppm sulfur fuels (14). The system consisted of two catalytic converters, positioned in a series configuration within a single channel exhaust. The close-coupled converter (1.3L, 4.5/0.165 g/L Pd/Rd) was located at the outlet of the exhaust manifold. The under-floor converter (1.5L, 0.6/0.16 g/L Pd/Rh) was located approximately 76 cm from the close-coupled converter. Three test combinations were evaluated with 33 ppm fuel, utilizing two unique preparation driving cycles leading into the first FTP. Three FTPs were run in each of the three test combinations.

Test combination one was performed with a “hot clean” cycle, followed by two LA-4 cycles, all run consecutively. This served as the vehicle “prep”, and was followed by three FTPs with a 24 hour soak time between each FTP. The “hot clean” cycle is a drive cycle which involves a steady state warm-up portion, followed by 5 back-to-back, wide-open throttle accelerations to 125 kph. The hot clean vehicle preparation exposes the catalysts to a hot and rich exhaust condition, thereby acting to reduce the oxidative state of the catalyst. The second test combination was performed with the same hot clean cycle + 2 LA-4 preps before the first FTP, as was used in test combination one. However, a high speed, US06 test cycle was run at the end of each of the 3 FTPs. The third test combination used a different vehicle preparation before the first FTP: 2 LA-4 cycles followed by a US06 cycle. The third test combination also used the US06 test cycle at the end of each of the FTP emission tests.

The result for test combination one (see Figure 8) shows individual test FTP NO<sub>x</sub> emission totals in the intermediate exhaust position (after the close-coupled converter, before the underfloor converter), the tailpipe position and associated underfloor converter NO<sub>x</sub> efficiency. For this particular data set, the run-to-run performance in the intermediate position was very consistent, allowing an easy judgment of the trend in run-to-run underfloor converter conversion efficiency. The test result shows that the performance of the underfloor converter degrades from run-to-run with this particular test combination. Even with consistent intermediate emissions entering the underfloor converter, the tailpipe NO<sub>x</sub> emissions are increasing from run-to-run, indicating that the efficiency for the underfloor converter is decreasing.

Test Combination One - NOx  
Intermediate and TP Total FTP Emissions, UF Efficiency

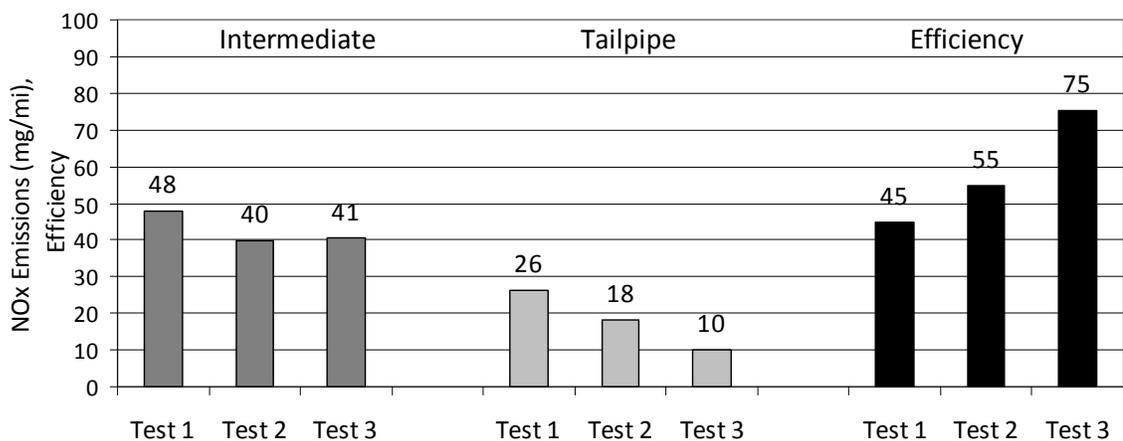


**Figure 8: NOx Emissions with 33 ppm S: “Hot clean” + 2 LA4s/FTP/FTP/FTP**

Source: SAE Paper 2011-01-0300

Test combination two resulted in an opposite drifting affect compared to test combination one. Emissions are reduced for each subsequent test, after adding the high temperature US06 in between FTP test cycles. By the time the 3<sup>rd</sup> FTP test is conducted, the US06 preps have resulted in an increase in NOx underfloor catalyst efficiency from 45% to 75% (see Figure 9). Tailpipe NOx emissions were reduced from 26 to 10 weighted mg/mile.

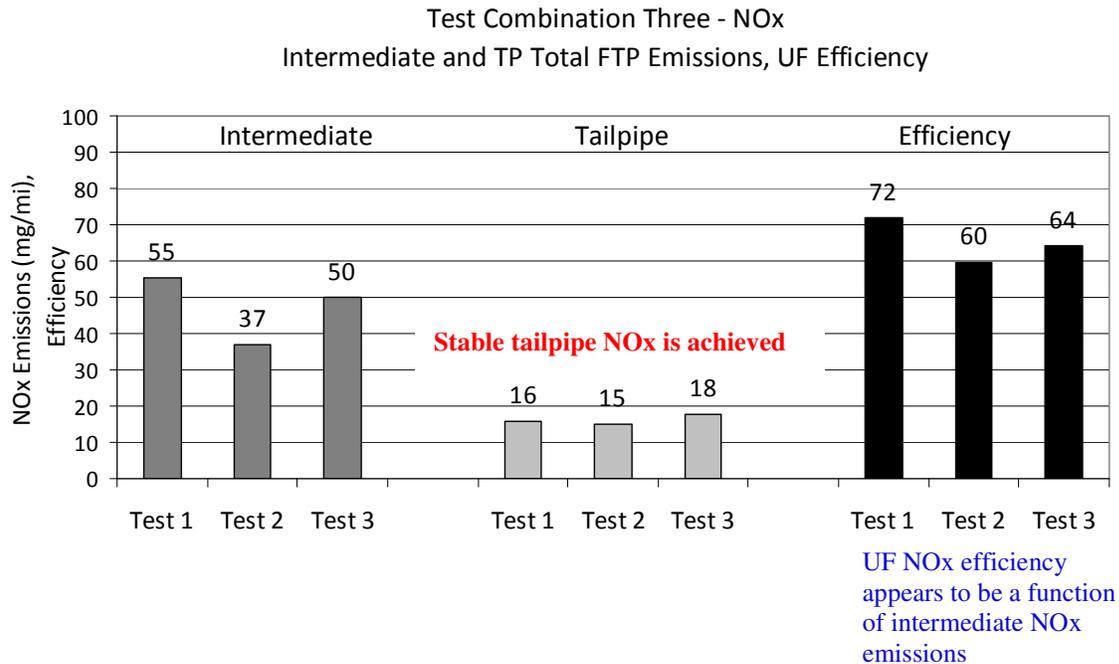
Test Combination Two - NOx  
Intermediate and TP Total FTP Emissions, UF Efficiency



**Figure 9: NOx Emissions with 33 ppm S: “Hot clean” + 2 LA4s/FTP+US06/FTP+US06/FTP**

Source: SAE Paper 2011-01-0300

Figure 10 indicates that the vehicle preparation sequence used in the third case (two LA-4s + a US06 test cycle before the first FTP; with a US06 test cycle run following the first and second FTP) resulted in stabilization of tailpipe NOx performance from run-to-run. Although intermediate emissions varied by as much as 18 mg/mi between runs, there was no NOx drift trend.

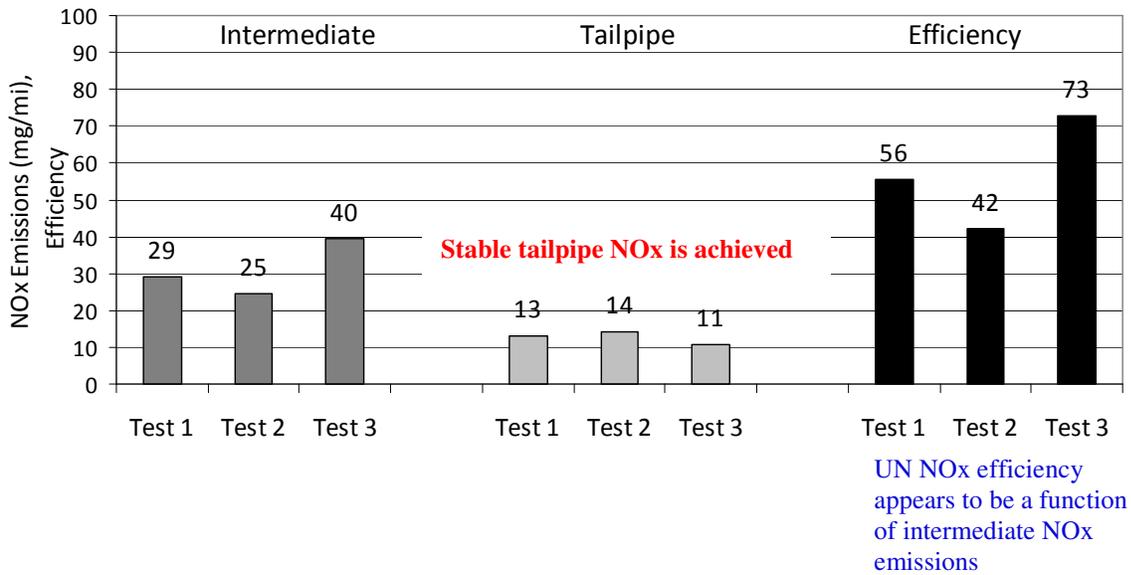


**Figure 10: NOx Emissions with 33 ppm S: 2 LA4s + US06/FTP+US06/FTP+US06/FTP**

Source: SAE Paper 2011-01-0300

To determine the cause of these trending tailpipe NOx emissions and changing underfloor converter efficiencies, it was thought that sulfur (33 ppm) from the CARB Phase II test fuel may be poisoning the underfloor catalyst's ability to reduce NOx emissions. Additional testing was conducted with an indolene-grade test fuel with a 3 ppm sulfur level. Figure 11 shows relatively stable test-to-test tailpipe NOx emissions with the 3 ppm sulfur fuel. The intermediate NOx emissions for this test sequence showed some variability.

Sulfur Free Confirmation Testing - NOx  
Intermediate and TP Total FTP Emissions, UF Efficiency

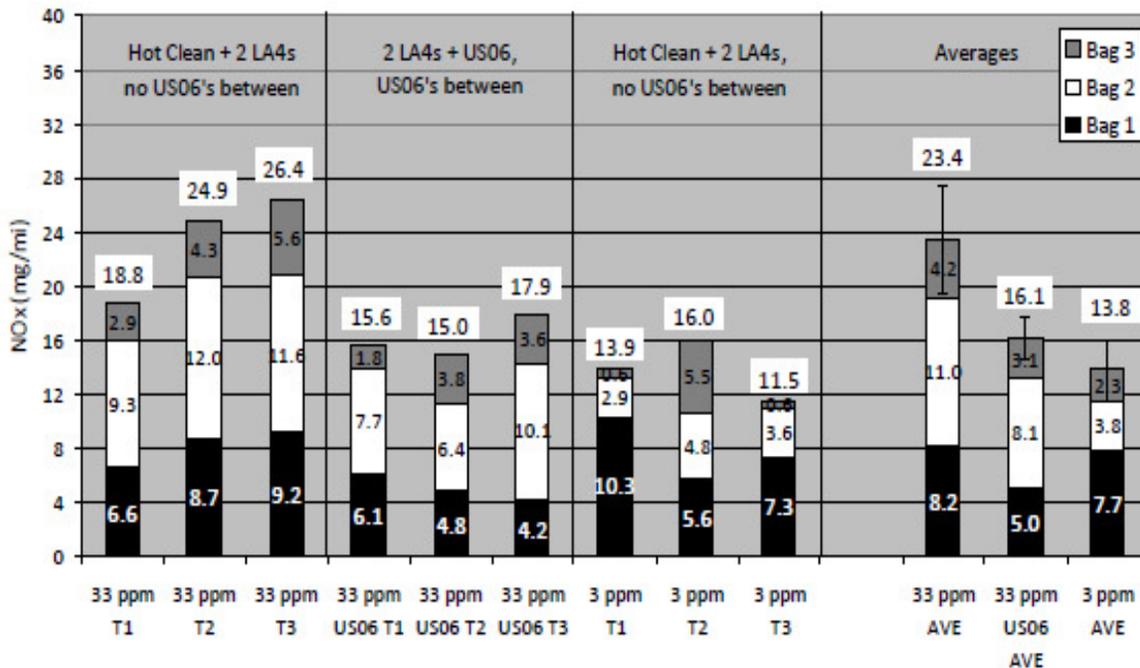


**Figure 11: NOx Emissions with 3 ppm S: Hot Clean + 2LA4/FTP/FTP/FTP**

Source: SAE Paper 2011-01-0300

Figure 12 summarizes the overall NOx FTP Bag emissions observed on this PZEV Malibu. The advantages of using the US06 cycle between the FTP test cycles or using 3 ppm sulfur fuel can be seen. Tailpipe NOx emissions were reduced from 23.4 to 16.1 weighted mg/mile by including a US06 test cycle between the FTP tests. Testing with the 3 ppm sulfur fuel provided stable and the lowest NOx emissions over the triplicate FTP test cycles.

Summary of NOx Tailpipe Emissions by Bag



UF never above 600°C with FTP; NOx “creep”

UF at 700-750°C during US06; NO NOx “creep”

NO NOx “creep” with 3 ppm S

Figure 12: Chevy Malibu PZEV FTP NOx Performance vs. Vehicle Prep & Fuel Sulfur Levels

Source: SAE Paper 2011-01-0300

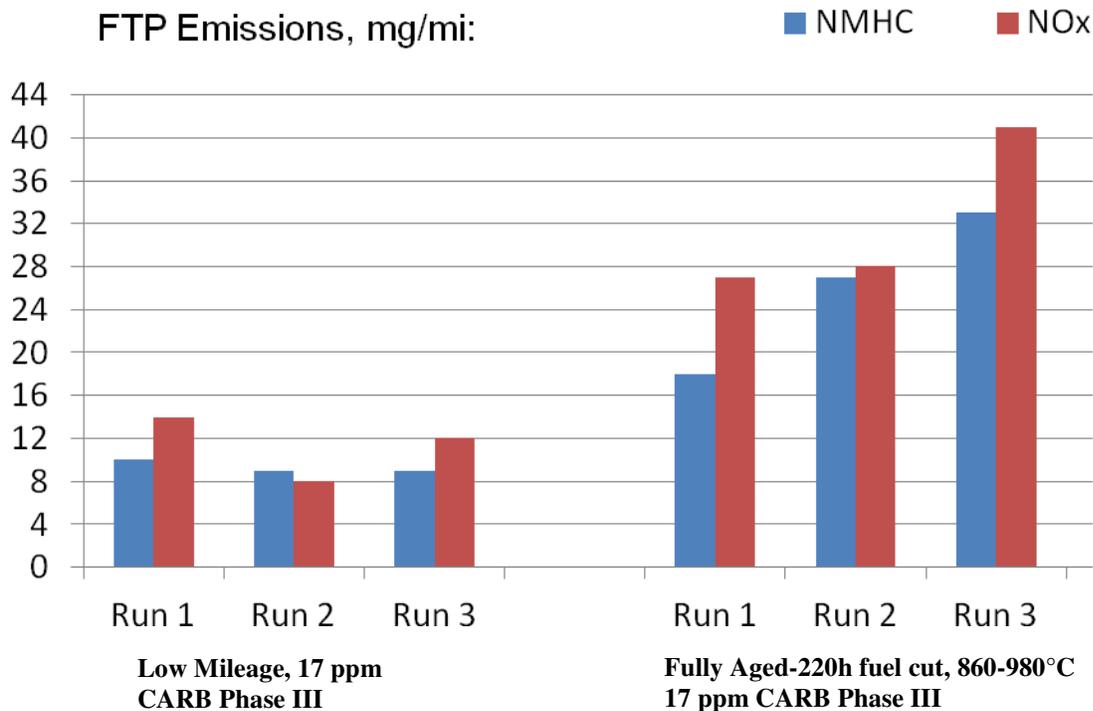
This study showed that at the very low level of exhaust emissions that were being measured on the PZEV vehicle, even a small amount of the sulfur in fuel, 33 ppm, has an effect on test-to-test NOx stability during FTP testing (14). Data from this study showed that underfloor catalyst temperatures of 600°C can still result in sulfur poisoning that inhibits NOx performance and consistency in tailpipe results. By using a high exhaust/high engine load driving cycle, such as the US06, between FTP test cycles, underfloor catalyst bed temperatures of 750°C were achieved and that reversed the sulfur poisoning effect that occurred on the underfloor TWC converter. One important aspect of this study was measuring the ability of different driving cycles to reverse the catalyst poisoning and the potential for “NOx creep”, the incremental permanent reduction in catalytic efficiency as a result of repeated sulfur exposure.

The study found that FTP evaluations with California Phase II certification fuel with 33 ppm sulfur exhibited increasing NOx emissions with subsequent FTP evaluations (NOx creep). Results from tests to minimize NOx creep using 3 ppm sulfur fuel indicate that using the US06 cycle in between FTP tests can mitigate NOx creep. FTP evaluations with 3 ppm sulfur fuel exhibited no NOx creep regardless of FTP preparation cycle and yielded overall lower NOx emissions. The study also concluded that reducing the fuel sulfur level further from 33 ppm to 3

ppm will have additional benefits with close-coupled + underfloor emission systems. The authors found that reducing fuel sulfur level from 33 to 3 ppm significantly reduced the tailpipe NO<sub>x</sub> emissions by 40% and could result in the overall achievement of lower emission regulations and/or the use of lower precious group metals concentrations (14).

In an another test program completed by the Manufacturers of Emission Controls Association (MECA) that studied the potential for achieving lower HC and NO<sub>x</sub> exhaust emissions from a large, heavy light-duty gasoline vehicle, an advanced TWC system showed significant sulfur sensitivity after full useful life accelerated aging compared to the same low mileage TWC system (15). This MECA test program employed California Phase III reformulated gasoline with a sulfur content of 17 ppm. Two large, heavy light-duty gasoline vehicles (2004 model year Ford F-150 with a 5.4 liter V8 and GMC Yukon Denali with a 6.0 liter V8) were baselined for emission performance over the FTP driving cycle in their stock configuration. Advanced emission systems were designed for both vehicles using advanced TWCs, high cell density ceramic substrates, and advanced exhaust system components. These advanced TWC systems were integrated on the test vehicles and characterized for low mileage emission performance on the FTP cycle using the vehicle's stock engine calibration and, in the case of the Denali, after modifying the vehicle's stock engine calibration for improved cold-start and hot-start performance. The TWC systems were aged for 220 hours using an accelerated, engine dynamometer aging schedule and then re-evaluated for FTP emissions on both vehicles.

The test program found that the GMC Denali equipped with an advanced TWC system that included both close-coupled and underfloor converters showed significant FTP emissions "creep" in three successive FTP tests after 220 hours of accelerated converter system aging compared to the same, low mileage advanced TWC system. Figure 13 below shows the results from the test program (15). The aged TWC system FTP emissions increased from a combined NMHC+NO<sub>x</sub> level of 45 mg/mile to over 70 mg/mile during the course of three back-to-back-to-back FTP emission tests with a 17 ppm sulfur test fuel. The low mileage converter system showed no evidence of emissions "creep" during triplicate FTP emissions testing.



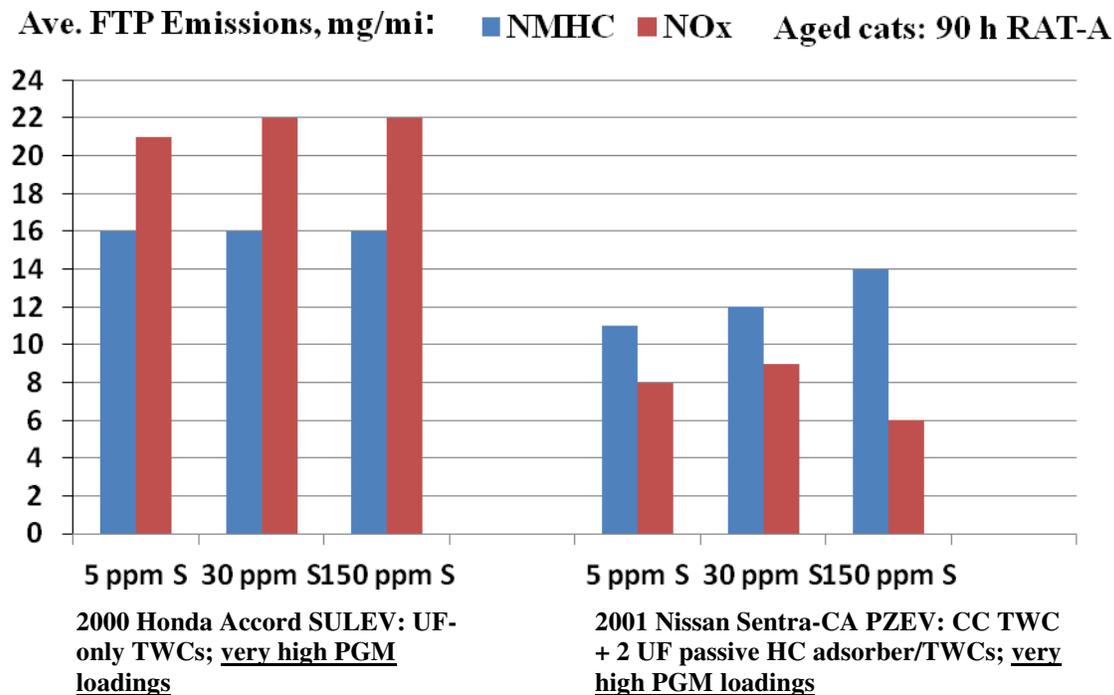
**Figure 13: GMC Denali With Advanced TWC System**

Source: SAE Paper 2007-01-1261

In a study conducted by the CRC, researchers studied the impact of fuel sulfur and catalyst age on 14 vehicles. The 14 vehicles included 12 California-certified LEV to SULEV vehicles and 2 European vehicles (16). Each vehicle was evaluated using 3 fuels (5, 30 and 150 ppm sulfur), using as-received and aged catalysts. The two European vehicles were tested over the NEDC European test cycle on each of the fuel/catalyst configurations.

The results from the study showed that for the FTP cycle, fleet average NOx emissions were higher at a statistically significant level for the 150 ppm sulfur fuel compared with both the 5 and 30 ppm sulfur fuels. Fleet average NMHC emissions were higher at statistically significant levels for the 150 ppm fuel compared with the 30 ppm sulfur fuel, although the magnitude of this fuel effect was small. The effects of fuel sulfur on both fleet average NMHC and NOx emissions were found to be statistically significant over the US06 cycle, although a statistically significant vehicle by fuel interaction was also found for NMHC. A pair-wise comparison showed that fuels with 5, 30 and 150 ppm sulfur were all different from one another at a statistically significant level for both fleet average NOx and NMHC emissions over the US06 cycle. The magnitude of the fuel sulfur effects over the US06 for NMHC and NOx was also found to be larger on a relative basis than those found for the FTP cycle (16). Included in this CRC study were two early SULEV and PZEV models from Honda (2000 Honda Accord SULEV) and Nissan (2001 Nissan Sentra-CA PZEV). FTP emission results from these two vehicles are summarized in Figure 14 for the three different gasoline sulfur levels used in this program. The Accord SULEV shows some degradation of NOx emission performance and the Sentra PZEV shows degradation in NMHC emission performance as fuel sulfur levels were

increased from 5 to 150 ppm. Sulfur deactivation was observed on these very low emission vehicles despite the very high precious metal content of the catalysts used on these first generation SULEV/PZEV vehicles.



**Figure 14: CRC E-60 Program SULEV/PZEV Sulfur Effects**

Source: CRC Project No. E-60

Following the successful implementation of the EPA Tier 2 sulfur standards, new research has focused on the emission reduction of lowering sulfur levels below 30 ppm, particularly on Tier 2-compliant vehicles. The hypothesis for this focus was that high efficiency catalytic converters used on Tier 2 vehicles will have a higher sensitivity to fuel sulfur content. A 2005 study by the EPA and several automakers found large decreases in NOx and HC emissions from vehicles meeting Tier 2, Bin 5 emission levels when operating on 6 ppm versus 32 ppm sulfur test fuel (17). To gain further understanding of how these emission reductions would translate into the in-use fleet, EPA conducted a study to evaluate the state of sulfur loading in typical in-use vehicles, as well as the effect of fuel sulfur level on these vehicles during subsequent mileage accumulation. The EPA study was designed to take into consideration what was known from prior studies on sulfur build-up in catalysts over time and the effect of periodic regeneration events that can occur during higher speed and load operation in day-to-day driving. The full EPA Tier 2 gasoline sulfur study is available at: <http://www.epa.gov/otaq/models/moves/t2sulfur.htm>. Highlights from this important gasoline sulfur effects study are included below.

The EPA Tier 2 study employed 81 cars and light trucks recruited from owners in southeast Michigan, covering model years 2007-2009 with approximately 20,000 to 40,000 odometer miles. The makes and models targeted for recruitment were chosen to be representative of high sales vehicles covering a range of types and sizes. Test fuels were two non-ethanol-containing gasolines with properties typical of certification fuel, one at a sulfur level of 5 ppm and the other at 28 ppm, the higher level chosen to be representative of retail fuel available to the public in the vehicle recruiting area.

Using the 28 ppm test fuel, emissions data were collected from vehicles in their as-received state, and then following a high-speed/load “clean-out” procedure consisting of two back-to-back US06 cycles intended to reduce sulfur loading in the catalyst. An analysis of the data showed highly significant reductions in several pollutants including NOx and HCs, suggesting that reversible sulfur loading exists in the in-use fleet and has a measurable effect on catalytic converter performance (see Table 1 below).

**Table 1: Average Clean-Out Effect on In-Use Emissions Using 28 ppm Test Fuel**

	<b>NOx (p-value)</b>	<b>THC (p-value)</b>	<b>CO (p-value)</b>	<b>NMHC (p-value)</b>	<b>CH<sub>4</sub> (p-value)</b>	<b>PM (p-value)</b>
<b>Bag 1</b>	--	--	4.7% (0.0737)	--	--	15.4% (<0.0001)
<b>Bag 2</b>	31.9% (0.0009)	16.5% (0.0024)	--	17.8% (0.0181)	15.3% (0.0015)	--
<b>Bag 3</b>	38.3% (<0.0001)	21.4% (<0.0001)	19.5% (0.0011)	27.8% (<0.0001)	12.0% (<0.0001)	24.5% (<0.0001)
<b>FTP Composite</b>	11.4% (<0.0001)	4.1% (0.0187)	7.6% (0.0008)	3.0% (0.0751)	6.9% (0.0003)	13.7% (<0.0001)
<b>Bag 1- Bag 3</b>	--	--	4.2% (0.0714)	--	--	--

*Source: Draft EPA-420-D-13-003, 2013*

In order to assess the impact of lower sulfur fuel on in-use emissions, a representative subset of vehicles was kept to conduct testing on 28 ppm and 5 ppm fuels with accumulated mileage. A first step in this portion of the study was to assess differences in the effectiveness of the clean-out procedure when done using different fuel sulfur levels. Table 2 shows a comparison of emissions immediately following (<50 miles) the clean-out procedures at the low vs. high sulfur level. These results show significant emission reductions for the 5 ppm fuel relative to the 28 ppm fuel immediately after this clean-out vs. following the clean-out on the 28 ppm fuel. This indicates that either the catalyst is not fully desulfurized after a clean-out procedure as long as there is sulfur in the fuel, or that there is an instantaneous effect of sulfur concentration in the exhaust gas on the catalysts’ activity.

**Table 2: Percent Reduction in Emissions from 28 ppm to 5 ppm for the First Three Repeat FTP Tests Immediately Following Clean-Out**

	<b>NOx (p-value)</b>	<b>THC (p-value)</b>	<b>CO (p-value)</b>	<b>NMHC (p-value)</b>	<b>CH<sub>4</sub> (p-value)</b>	<b>PM</b>
<b>Bag 1</b>	5.9% (0.0896)	5.4% (0.0118)	7.3% (0.0023)	4.6% (0.0465)	11.1% (<0.0001)	--
<b>Bag 2</b>	47.3% (0.0010)	40.2% (<0.0001)	--	34.4% (0.0041)	53.6% (<0.0001)	--

<b>Bag 3</b>	51.2% (<0.0001)	35.0% (<0.0001)	10.1% (0.0988)	45.0% (<0.001)	25.4% (<0.0001)	--
<b>FTP Composite</b>	17.7% (0.0001)	11.2% (<0.0001)	8.3% (0.0003)	8.8% (0.0003)	21.4% (<0.0001)	--
<b>Bag 1 – Bag 3</b>	--	--	5.8% (0.0412)	--	--	--

Source: Draft EPA-420-D-13-003, 2013

To assess the overall in-use reduction between high and low sulfur fuel, a mixed model analysis of all data as a function of fuel sulfur level and miles driven after clean-out was performed. This analysis found highly significant reductions for several pollutants (see Table 3). The reductions for FTP Bag 2 NO<sub>x</sub> were particularly high, estimated at 59% between 28 ppm and 5 ppm. For most pollutants, the data suggested the effect of sulfur level didn't depend on miles driven after the fuel change, and therefore the emission benefit of lower fuel sulfur occurred immediately and continued as miles were accumulated. Some results, such as Bag 1 HCs, did show a significant miles-by-sulfur interaction.

**Table 3: Summary of Mixed Model Results for Emission Reductions from 28 ppm to 5 ppm Sulfur, Adjusted for In-Use Sulfur Loading**

	<b>NO<sub>x</sub></b> <b>(p-value)</b>	<b>THC</b> <b>(p-value)</b>	<b>CO</b> <b>(p-value)</b>	<b>NMHC</b> <b>(p-value)</b>	<b>CH<sub>4</sub></b> <b>(p-value)</b>	<b>NO<sub>x</sub>+NMOG</b> <b>(p-value)</b>	<b>PM</b>
<b>Bag 1</b>	10.7% (0.0033)	8.5% (0.0382)	7.5% (0.0552)	7.5% (<0.0001)	13.9% (<0.0001)	N/A	--
<b>Bag 2</b>	59.2% (<0.0001)	48.8% (<0.001)	20.1% (<0.0001)	49.9% (<0.0001)	29.2% (<0.0001)	17.3% (0.0140)	--
<b>Bag 3</b>	62.1% (<0.0001)	40.2% (0.0001)	20.1% (<0.0001)	49.9% (<0.0001)	29.2% (<0.0001)	N/A	--
<b>FTP Composite</b>	23.0%* (0.0180)	13.0%* (0.0027)	11.9%* (0.0378)	10.6%* (0.0032)	25.8%* (<0.0001)	17.3% (0.0140)	--
<b>Bag 1 – Bag 3</b>	--	5.2% (0.0063)	4.3% (0.0689)	5.1% (0.0107)	4.6% (0.0514)	N/A	--

\* Model with significant sulfur and mileage interaction term.

Source: Draft EPA-420-D-13-003, 2013

Some of the major findings from this study include:

- Reversible sulfur poisoning is occurring in the in-use fleet of Tier 2 vehicles and has a measureable effect on emissions of NO<sub>x</sub>, HCs, and other pollutants of interest.
- The effectiveness of high speed/load procedures in restoring catalyst efficiency is limited when operating on higher sulfur fuel.
- Reducing fuel sulfur levels from 28 ppm to 5 ppm produces significant reductions in emissions of NO<sub>x</sub>, HCs, and other pollutants of interest from a broad range of in-use Tier 2 vehicles.
- Bag 2 NO<sub>x</sub> effects, which are relatively large but based on low emission levels, were found to be robust to sensitivity analyses related to influential vehicles and measurement uncertainty at low emission levels.

## C. Catalyst Design Factors

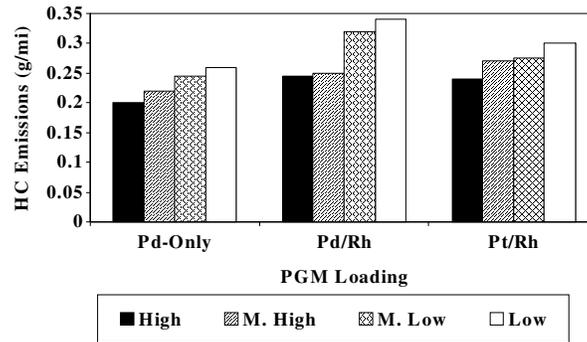
Table 4 summarizes some of the most significant factors that influence to what extent sulfur in the exhaust will influence the performance of the catalytic emission control system. In this section we will discuss each of these in more detail and point out some of the scientific evidence in the literature to explain the mechanisms and processes responsible for this performance deterioration. Furthermore we will discuss some of the approaches used by catalyst designers to reduce the extent of deterioration.

<b>Table 4</b>	
<b>FACTORS WHICH INFLUENCE SULFUR INHIBITION OF CATALYTIC EMISSION CONTROL SYSTEMS</b>	
1.	Catalyst Composition <ul style="list-style-type: none"><li>• Precious metals used - palladium (Pd), Pd and rhodium (Rh), platinum (Pt) and Rh, or Pt/PD/Rh</li><li>• Precious metal concentrations</li><li>• Base metal concentrations</li><li>• Catalyst volume</li><li>• Oxygen storage (i.e., cerium oxide or other compounds)</li></ul>
2.	Catalyst design
3.	Catalyst location
4.	Emission control system – type and control of fuel metering
5.	Engine calibration
6.	Vehicle use
7.	Fuel
8.	Regeneration/recovery conditions

**1. Catalyst Composition.** The precious metal compositions for three-way conversion catalysts have been Pd-only, Pt/Pd/Rh, Pt/Rh, and more recently, Pd/Rh. Each precious metal element is affected by sulfur differently. Thoss et. al. describe the inhibition of sulfur on three-way catalysts for three of these compositions, and each at several precious metal concentrations (7). This study examines the effects of 100 and 300 ppm sulfur gasoline respectively on the U.S. FTP performance of each catalyst after exposure to high and low exhaust gas temperatures. Sulfur deactivated all three catalysts for HC performance. The Pd-only three-way conversion catalysts gave superior overall HC performance whether exposed to low temperature/high sulfur or high temperature/low sulfur aging (see Figures 15 and 16). However, low temperature/high sulfur aging had a large negative effect on CO and NO<sub>x</sub> performance of the Pd-only three-way catalysts (see Figures 17 and 18). The conclusions present a rather compelling case supporting low sulfur gasoline fuel as a means of achieving best performance from any three-way conversion catalyst.

# Effect of PGM Type and Loading on HC Emissions

Low Temperature/High Sulfur Aging

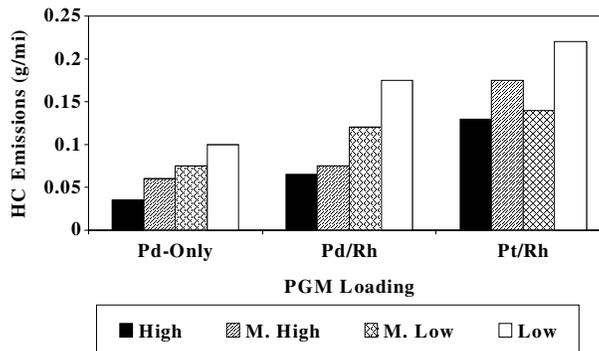


**Figure 15: Effect of Precious Gem Metal Type and Loading on HC Emissions—Low Temperature/High Sulfur Aging**

Source: SAE Paper 970737

# Effect of PGM Type and Loading on HC Emissions

High Temperature/Low Sulfur Aging

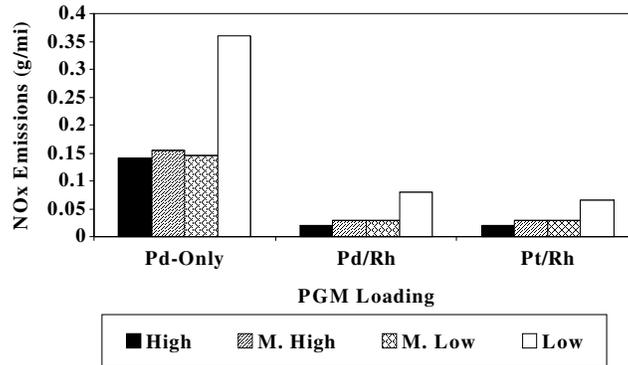


**Figure 16: Effect of PGM Type and Loading on HC Emissions—High Temperature/Low Sulfur Aging**

Source: SAE Paper 970737

# Effect of PGM Type and Loading on NO<sub>x</sub> Emissions

Low Temperature/High Sulfur Aging

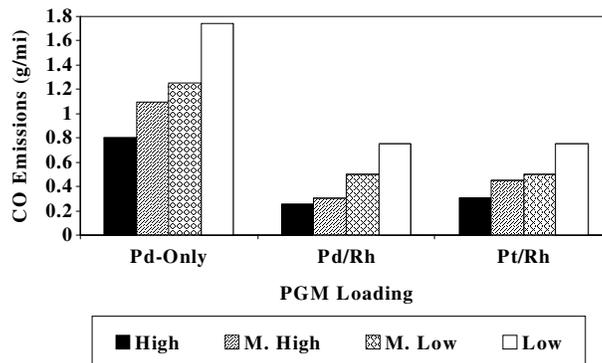


**Figure 17: Effect of PGM Type and Loading on NO<sub>x</sub> Emissions—Low Temperature/High Sulfur Aging**

Source: SAE Paper 970737

# Effect of PGM Type and Loading on CO Emissions

Low Temperature/High Sulfur Aging



**Figure 18: Effect of PGM Type and Loading on CO Emissions—Low Temperature/High Sulfur Aging**

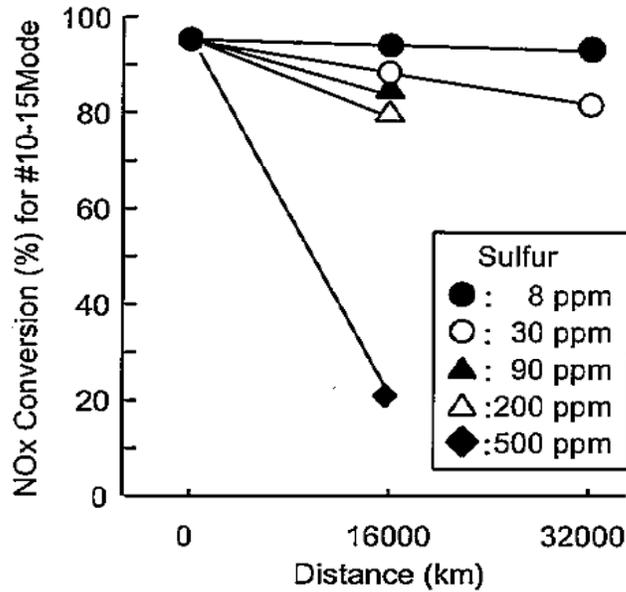
Source: SAE Paper 970737

Three-way catalyst oxygen storage is typically provided by rare earth oxide materials, including oxides of cerium. The air/fuel mixture in a closed loop system is constantly changing from slightly rich to slightly lean of stoichiometric and back again at a cycle rate between 0.25 to 1.0 seconds. The A/F mixture is only very briefly at the stoichiometric point. Thus, when the cycle is slightly lean there is excess oxygen which will pass through the catalyst and out the tailpipe. Rare earth oxide materials are incorporated within the catalyst to capture the excess oxygen and store it for use when the A/F mixture is rich and short of oxygen. Cerium oxide-based oxygen storage materials possess two oxidation states which change easily from one to the other with oxygen content in the exhaust. Thus, oxygen is captured when in excess and given up for oxidative reactions when it is in short supply. The result is a more efficient use of stored oxygen to oxidize CO and HC and more efficient reduction of NO by CO while oxygen storage takes place.

The quantity and form of rare earth oxides employed determines the oxygen storage capacity. Gasoline fuel sulfur has been found to reduce oxygen storage by absorbing to the oxygen sites as a sulfate. This blocks subsequent oxygen storage until the catalyst is cleaned through a high acceleration and high temperature exhaust event (9). Oxygen storage is an important factor for OBDII-compliant vehicle systems which rely on it as a catalyst monitoring technique.

**2. TWC Catalyst Design Factors.** Three-way catalyst designs are complex. Three-way catalysts are designed to provide separate functions - NO<sub>x</sub> reduction, and HC and CO oxidation. A Pd-only three-way catalyst designed for close coupled operation needs to have high temperature resistance, quick light-off performance, and maximum oxygen storage capacity. Pt/Rh and Pd/Rh three-way catalysts have to avoid unwanted alloy formation. Each has to be designed in combination with base metal promoters in such a way as to optimize all functions. The design has to be durable over the complete temperature range with a minimum of base metal and precious metal sintering and little loss of support surface area.

In addition to sulfur poisoning of advanced TWCs, sulfur can impact advanced gasoline emission control technologies in other ways. As discussed previously, sulfur degrades the performance of NO<sub>x</sub> adsorber catalysts used in lean gasoline, direct injection applications (see Figure 19 below, taken from SAE paper 2000-01-2019). Fuel sulfur levels can also impact TWC emissions of NH<sub>3</sub> and N<sub>2</sub>O. A CRC study found that catalyst aging effects on NH<sub>3</sub> emissions were found to be statistically significant for the FTP and for the US06 test cycles, with higher emissions for the aged catalysts. Fleet average NH<sub>3</sub> emissions were 50% higher for the aged catalysts over the FTP and 17% higher for the aged catalysts over the US06 (16). These catalyst aging impacts include exposure to fuel sulfur.



**Figure 19: Sulfur Impacts on CC TWC + UF NOx Adsorber Catalyst on Lean GDI PC**

Source: SAE Paper 2000-01-2019

**3. Catalyst Location.** The position of a catalyst within the exhaust system is an important factor in the degree of sulfur inhibition. Pd-based TWC catalysts have more high temperature resistance and are often located very close to the exhaust manifold in order to function quickly after the engine is started. In this position, the Pd-based catalyst operates at higher exhaust temperatures. Sulfur inhibition is greatest at temperatures below 400-425°C and Pd-based catalysts located in the manifold position experience temperatures from 500°C to 1050°C, where inhibition is considerably lower. Pd-only catalysts located in positions where they are exposed to lower temperatures would be more greatly affected by sulfur. Pd is of increased importance for meeting future California LEV III or EPA Tier 3 vehicle standards due to its unique application in the close-coupled converter location required for vehicles certifying to very stringent emission standards. Pd is required in closed-coupled catalysts due to its resistance to high temperature thermal sintering. Sulfur removal from Pd requires rich operation at higher temperatures than required for sulfur removal from other PGM catalysts (18). A catalyst system with underfloor catalysts experience cooler temperatures and sulfur inhibition is greater. In addition, the underfloor position makes it more difficult to regenerate and recover lost performance due to sulfur.

**4. Vehicle Use.** Vehicles operate under a wide range of conditions of speed and load. Vehicles that operate at low speed and low load will have lower exhaust gas temperatures than those that operate at high speed and high load. As noted above, exhaust temperature is an important factor for sulfur inhibition. Sulfur inhibition is strongest at temperatures below 425°C and less strong at temperatures above 425°C. Therefore, vehicles which operate at low speed and load will experience greater sulfur inhibition and have fewer opportunities for regeneration. The type of vehicle, i.e. passenger car, sport/utility vehicle, or light/medium duty truck, will also be impacted differently for the same reasons detailed above.

**5. Regeneration.** Sulfur inhibition of automobile catalysts can be temporary and recovery to original performance has been achieved by return to low sulfur fuel under the appropriate operating condition. However, emissions data from tests on low-emitting vehicles indicated full recovery was not occurring. Ford reported test results on low sulfur fuel (60 ppm S base fuel), followed by exposure to high sulfur fuel (930 ppm S), and then again a return to low sulfur fuel (8). The tests were performed on a vehicle meeting the California ULEV standards. In this work, Ford showed that exposure to high sulfur fuel increased HC emissions from 0.04 g/mile to about 0.12 g/mile. A return to low sulfur fuel resulted in improved performance but only to about 0.07 g/mile, but a subsequent rich calibration hot cycle was required to return performance to the original performance level. Experiments conducted by Thoss et. al. did not show significant regeneration upon evaluation with low sulfur gasoline (87 ppm sulfur) or with treatments at 700°C under slightly lean conditions (7). A companion paper showed almost complete recovery of an improved Pd-only three-way catalyst when fuel was switched from 1000 ppm to 100 ppm sulfur (19). Benson noted that sulfur inhibition was reversible at high exhaust gas temperatures with low sulfur fuel for U.S. Tier 1 technology vehicles, but that sulfur effects are more critical with lower emission vehicles and may not be reversible (10).

In two studies on the effect of gasoline fuel sulfur on LEV and ULEV-type vehicles by AAMA/AIAM (11) and CRC (12), the issue of sulfur removal was addressed. Both studies used a sulfur purge cycle to remove previous accumulated sulfur from catalysts. The cycle employed a series of five vehicle wide-open-throttle (WOT) acceleration/cruise/deceleration excursions and a steady state drive to increase the catalyst temperature and provide a rich air-to-fuel operating condition to facilitate the release of the sulfur compounds that accumulate on the catalyst. This cycle was repeated to give a minimum of ten acceleration/cruise/deceleration excursions. In this LEV/ULEV test program, some manufacturers increased the stringency of the sulfur purge cycles to ensure adequate sulfur removal. To ensure adequate catalyst temperature (650°C or higher), the catalyst inlet temperature was monitored with a thermocouple. From these studies it appears that special cycle conditions have to exist in order to regenerate catalyst performance via sulfur purging.

Operating the catalyst at a sufficiently high temperature under net reducing conditions can effectively release the sulfur oxides from the catalyst components. However, it cannot completely eliminate the effects of sulfur poisoning. A study of Tier 2 vehicles in the in-use fleet recently completed by EPA shows that emission levels immediately following high speed/load operation is still a function of fuel sulfur levels, suggesting that lower fuel sulfur levels will bring emission benefits unachievable by a catalyst regeneration procedure alone (18). Additionally, regular operation at these temperatures and at rich air-to-fuel ratios is not desirable, due to several reasons. The temperatures necessary to release sulfur oxides are high enough to lead to thermal degradation of the catalyst over time via thermal sintering of active materials. Sintering reduces the surface area available to participate in reactions. It is also not always possible to maintain these catalyst temperatures (because of cold weather, idle conditions, light load operation) and the rich air-to-fuel ratios necessary can result in increased PM, NMOG and CO emissions.

In addition, higher engine efficiencies drive lower exhaust temperature, making sulfur poisoning more problematic. Similarly, hybrid electric vehicle's start/stop driving mode limits exhaust temperatures, leading to enhanced sulfur poisoning of the catalyst.

#### **IV. TECHNOLOGY TRENDS AND MECA RECOMMENDATIONS FOR SULFUR LEVEL IN GASOLINE**

The published vehicle studies and catalyst characterization studies provide a consistent result with respect to fuel sulfur effects: the exhaust emissions performance of precious metal-containing catalysts used in gasoline automotive applications is negatively impacted by fuel sulfur, even at relatively low fuel sulfur levels. The degree of catalyst performance loss depends on a variety of factors including catalyst composition, emission system design, catalyst temperature history, and vehicle operation.

Future stringent Tier 3 and LEV III emission standards will impact the full range of light-duty vehicles (and impose tighter emission standards on medium-duty vehicles). Furthermore, over the 2017-2025 timeframe, vehicle manufacturers will be required to reduce not only tailpipe criteria pollutant emissions but CO<sub>2</sub>/GHG emissions. To meet both of these challenges will require implementation of integrated emission control technologies with fuel efficient powertrains. As powertrain efficiencies are increased to meet future greenhouse gas emission standards, vehicle manufacturers are expected to employ more boosted engines and greater levels of hybridization. These more fuel efficient powertrains will tend to drive down exhaust temperatures compared to today's vehicles and this decline in exhaust temperatures will lead to higher coverage of sulfur poisons on catalysts and greater potential for catalyst performance inhibition. Strategies aimed at purging sulfur from these cooler exhaust systems will require fuel to generate exhaust heat and limit the fuel efficiency potential of the vehicle. These future constraints on criteria emissions and fuel efficiency make the deployment of ultra-low sulfur gasoline a must have for Tier 3 emissions compliance.

Direct gasoline engines are becoming more common with nearly every manufacturer offering a GDI engine option. In Europe and Japan, several manufacturers have commercialized lean burn GDI engines to help achieve lower CO<sub>2</sub> emissions and improve fuel economy. This is only possible because these regions already have a 10 ppm sulfur gasoline requirement. These lean GDI options offer a 5-15% fuel economy advantage over a comparable stoichiometric GDI engine (depending on what portion of the engine operating map is targeted for lean operation). In the U.S., major vehicle manufacturers are also developing lean GDI engine technology in anticipation of lower Tier 3 gasoline sulfur limits.

Exhaust catalyst manufacturers are working with their customers to address the NO<sub>x</sub> reduction challenges posed by this next generation of engine technology through the use of novel catalyst approaches. Lean GDI can come in different forms including various types of part-time lean operation all the way to full lean operation over the majority of the engine map. Most of these strategies require the use of NO<sub>x</sub> trap (LNT) or NO<sub>x</sub> storage (NSR) catalysts that hold on to NO<sub>x</sub> during lean operation and release it during periodic, rich excursions. The LNT has an

even larger affinity for storing sulfur that comes from the fuel or lubricant, resulting in deterioration of the NO<sub>x</sub> storage capacity.

Desulfation strategies can be employed to regenerate NO<sub>x</sub> storage capacity but the frequency of these high temperature desulfation steps eat into fuel efficiency and are limited by catalyst thermal stability. Ultra-low gasoline sulfur levels are a must have for lean GDI to maximize the fuel efficiency potential of this powertrain technology. A recent study examined a combined TWC/LNT in the close coupled position of a lean-burn GDI engine with a second, larger LNT catalyst in the underfloor location. Catalyst development/optimization work in this study focused on widening NO<sub>x</sub> conversion operating temperature windows and tailoring the desulfation temperatures of the LNT in each converter position to achieve NO<sub>x</sub> performance and fuel efficiency goals (22). At least one manufacturer is evaluating the use of a close coupled TWC to generate ammonia during rich operation that can be stored on a downstream SCR catalyst and used to reduce NO<sub>x</sub> during periodic lean cycles without the need for a second reductant (20). Fuel sulfur levels will likely have negative performance impacts on both the close-coupled TWCs and the under SCR catalyst in this approach.

MECA has consistently supported the introduction of the lowest possible fuel sulfur limits used with mobile sources to enable the use of best available exhaust emission controls and minimize the impacts of fuel sulfur on catalyst performance and durability. Adoption of a Tier 3, 10 ppm average gasoline sulfur limit by EPA will bring the U.S. in line with other major vehicle markets in Europe, Japan, South Korea, and China where 10 ppm gasoline and diesel fuel sulfur caps are already in place or will be in place by 2018. MECA is supportive of a 20 ppm gasoline sulfur cap for Tier 3 that would be aligned with California's current gasoline sulfur cap. However, MECA also appreciates the importance of providing some compliance flexibilities to the oil and refining industries (as EPA has done in past fuel sulfur regulations) to facilitate cost-effective compliance with the standards. MECA believes that a 10 ppm average gasoline sulfur standard with a gasoline sulfur cap of no higher than 50 ppm provides the U.S. refining industry with an adequate, cost-effective compliance pathway. MECA also supports defining fuel sulfur average limits or caps on any alternative transportation fuels (e.g., blends of alcohols with gasoline, natural gas) that are consistent with the proposed Tier 3, 10 ppm national average for gasoline or the existing 15 ppm U.S. sulfur cap on diesel fuel.

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