LEV III and Tier 3
Exhaust Emission Control Technologies
for Light-Duty Gasoline Vehicles

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Executive Summary

In response to continued public health concerns associated with ground level ozone and toxic hydrocarbon components of vehicle exhaust, the U.S. Environmental Protection Agency and California Air Resources Board established the Tier 2 and LEV II emission regulations, respectively, for light-duty vehicles in the late 1990s that began implementation starting with the 2004 model year. The Tier 2 and LEV II programs remain as the toughest light-duty vehicle standards in the world with the LEV II program being followed by LEV III in 2015. The U.S. EPA has finalized the next round of light-duty standards known as Tier 3 that will tighten light-duty tailpipe standards beyond Tier 2 starting in 2017. California's LEV III and EPA's Tier 3 standards are largely harmonized, forming essentially a single national program for reducing criteria emissions from light-duty vehicles in the U.S. The Tier 2/LEV II regulatory programs established a single set of fuel neutral, vehicle emission certification categories that auto manufacturers can select from for the broad weight range of light-duty cars and trucks that make-up the light-duty vehicle segment (up to 8500 lbs. GVW for all light-duty cars and trucks, and up to 10,000 lbs. GVW for passenger carrying vehicles). The Tier 2 and LEV II requirement established significantly lower levels of hydrocarbon and NOx emission levels with extended durability requirements (e.g., 120,000 miles) compared to the previous emission regulations (Tier 1/LEV I) for light-duty cars and trucks. Manufacturers must comply with not only the selected certification category emission limits but also meet fleet average emission limits: an oxides of nitrogen (NOx) emission fleet average in the case of Tier 2 and a non-methane organic gas (NMOG) emission fleet average in the case of LEV II. As part of these light-duty rulemaking efforts, both California and the EPA also established limits on gasoline fuel sulfur levels, a known catalyst deactivation agent. California's 15 ppm average gasoline sulfur level requirement began in 2004 and EPA's 30 ppm average gasoline sulfur level phase-in began in 2005. California currently requires a gasoline sulfur cap of 20 ppm (started in 2012) and EPA included a 10 ppm average gasoline sulfur requirement in its Tier 3 package that begins its phase-in in 2017.

In January 2012, California adopted their Advanced Clean Cars program that included tighter criteria pollutant standards for light-duty vehicles as part of their LEV III regulations, greenhouse gas (GHG) standards for model years 2017-2025, and revised zero emission vehicle (ZEV) requirements. The LEV III requirements impact passenger cars and light-trucks up to 8,500 lbs GVWR, medium-duty passenger vehicles up to 10,000 lbs and medium-duty trucks up to 14,000 lbs GVWR. The standards phase in from 2015 to 2025 and require that a manufacturer's light-duty fleet average meets a combined NMOG + NOx emissions limit of 30 mg/mile (or SULEV) by 2025 with a 150,000 mile durability requirement. The LEV III standards set tighter PM FTP emissions limits for both diesel and gasoline vehicles of 3 mg/mile by 2017 and 1 mg/mile starting in 2025. The U.S. EPA Tier 3 light-duty and medium-duty programs, finalized in March 2014, mirror California's LEV III standards with implementation set to begin with model years 2017 for lighter vehicles and model year 2018 for heavier vehicles. The Tier 3 proposal does not tighten FTP PM emission limits beyond the 3 mg/mile level.

To achieve the emission requirements of the Tier 2/LEV II and subsequently LEV III/Tier 3 programs, a systems engineering and optimization effort is required combining advanced engines, advanced engine control strategies, with advanced emission control technologies. Interest in high performance emission systems, along with the interest in lowering future light-duty vehicle emission standards, drove the development of advanced emission controls during the late 1980s and 1990s. The results of these developments are a number of key emission control technologies that manufacturers have implemented into their fleet for Tier 2/LEV II compliance on gasoline vehicles. Included in these key technologies are close-coupled converters, high cell density substrates, and advanced three-way catalysts. The maximum performance benefits for each of these advanced emission technologies result from combining these technologies with optimized engine operating strategies and high quality fuels and lubricants that are compatible with these high emission conversion efficiency components. The most advanced technologies have already been deployed on millions of vehicles in the fleet to achieve California SULEV and PZEV emission limits. LEV III and Tier 3 will build on this experience and extend the application of these advanced exhaust and evaporative emission control strategies across the entire fleet of light-duty vehicles to comply with a SULEV fleet average by the 2025 model year.

A significant challenge to achieving SULEV emission limits on the larger vehicles involves reducing cold-start emissions to the lowest possible levels. Close-coupled converters facilitate the fast converter heat-up necessary to significantly reduce emissions within seconds after the engine is started. Engine cold-start strategies aimed at accelerating converter heat-up, including spark retard during engine start and lean air/fuel engine start strategies, are used to complement and enhance the performance of close-coupled converters during the first few critical seconds following engine start. In the future, vehicle manufacturers will need to consider the impacts of GHG reduction strategies together with their efforts to reduce criteria pollutants when complying with California's Advanced Clean Cars program or the federal Tier 3 and GHG standards. One such strategy may involve engine calibration to maximize combustion efficiency while relying on exhaust controls to minimize NOx and other criteria pollutants.

High cell density ceramic and metallic substrates provide significant increases in substrate geometric surface area versus standard designs used in 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. Manufacturers have also developed high cell density substrate designs that utilize thinner ceramic or metallic walls separating flow channels. 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 quicker 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 and durability of today's advanced three-way catalysts are far beyond performance levels used with Tier 1 light-duty vehicles. These advanced three-way catalysts offer improved light-off properties, wider air/fuel windows of operation, higher NOx 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 input air/fuel ratio at the catalyst inlet.

Numerous published studies have reported on the characteristics and performance benefits of these new generations of advanced emission control technologies and the synergies realized by combining these technologies with advanced engine operating strategies. MECA completed a study in 2006 that demonstrated advanced emission control technologies on two large light-duty trucks. In this program, these SUV-class light-duty trucks achieved exhaust emissions significantly below LEV II ULEV standards with engine-aged emission systems. In its final Tier 3 regulatory package, EPA reported on a Tier 3 emissions demonstration program that was completed with MECA's assistance that achieved Tier 3, Bin 30 (LEV III SULEV30) emission levels on a V8-powered, full sized pick-up truck equipped with engine-aged, advanced three-way catalyst-based emission control systems. Because LEV III/Tier 3 standards demand lower PM emissions from all engine types, MECA completed a test program in 2012 that demonstrated the performance of a gasoline particulate filter on a late model gasoline direct injection (GDI) vehicle. An uncatalyzed filter, based on the wall flow technology derived from diesel particulate filters achieved an 80% reduction in PM from this vehicle over the FTP and high speed US06 test cycles. The current large volume demand for high performance emission technologies and the future forecasts for growth, around the globe, for these technologies are clear indications that the emission performance benefits they deliver are an integral part of the systems approach required to bring even the largest light-duty vehicles in to compliance with extremely low emission standards like the California LEV III and EPA Tier 3 programs.

1.0 Introduction

One of the most important technology bases that have emerged from the automotive industry in the past fifty years is the development, introduction, and continued evolution of automotive emission control technology. The centerpiece of this technology base is the three-way catalyst used on gasoline, stoichiometric, spark-ignited vehicles in all major world markets today. The name three-way catalyst was applied to catalytic controls that were capable of reducing all three criteria pollutants: carbon monoxide (CO), oxides of nitrogen (NOx), and volatile organic compounds (VOCs) within a narrow range of inlet exhaust gas compositions that corresponded to approximately the stoichiometric air/fuel ratio of the engine. Today, more than 95% of the new gasoline automobiles sold around the world are equipped with catalytic converters that utilize three-way catalysts, adding to the more than 800 million vehicles worldwide that have been equipped with catalysts since their first introduction in the U.S. in 1975.

Automotive catalytic emission controls were pioneered in the United States in response to public health concerns associated with elevated ambient ozone levels stemming, in part, from automotive tailpipe emissions of hydrocarbons and oxides of nitrogen. These public health concerns were translated into emission control regulatory programs by both the United States federal government and the state of California. On the federal level, the Clean Air Act Amendments of 1970 mandated significant reductions in automobile tailpipe emissions of CO, NOx, and volatile organic compounds starting in 1975. These federal standards led to the introduction of oxidation catalysts on automobiles starting with the 1975 model year to control CO and VOCs, and the use of three-way catalysts to control CO, NOx, and VOC tailpipe emissions starting in 1981. California, with severe smog problems in its large metropolitan areas, was provided with its own authority to set automobile emission standards and has typically led the U.S. federal government and the world with the tightest standards requiring the best available emission control technology for automobiles.

State-of-the-art stoichiometric gasoline exhaust emission systems are defined by light-duty vehicles certified to near-zero exhaust emission levels associated with California’s Partial Zero Emission Vehicle (PZEV) designation or Super Ultra-low Emission Vehicle (SULEV) designation. In these advanced stoichiometric emission control systems, advanced three-way catalysts are displayed on high cell density, ceramic or metallic substrates in combinations of close-coupled and underfloor converter locations. These advanced three-way catalysts utilize layered architectures and thermally stable oxygen storage materials, in combination with advanced engine controls, to reduce exhaust pollutants by more than 95% in both emission test cycle and real world driving conditions.

Light-duty motor vehicle tailpipe emission regulations have been pushed to lower levels in many world markets since the late 1990s in response to public health concerns. Included in these regulatory programs aimed at significantly reducing emissions from light-duty vehicles are the U.S. Environmental Protection Agency’s (EPA) Tier 2 and the California Air Resource

Board's (ARB) Low Emission Vehicle II (LEV II) programs. California acted first, adopting their LEV II program in late 1998, followed by EPA finalizing the Tier 2 regulations in December 1999. Now as we look toward the 2020 timeframe, EPA and ARB are moving forward with additional emissions tightening for light-duty vehicles with their Tier 3 and LEV III exhaust and evaporative emissions standards. California adopted their Advanced Clean Cars (ACC) program in January 2012 and EPA granted California's Clean Air Act waiver to enforce these regulations in December 2012. The LEV III criteria pollutant emission regulation applies to model year 2015 vehicles and beyond and is part of the broader ACC regulatory package that also included amendments to the states zero emission vehicle (ZEV) requirements and light-duty vehicle greenhouse gas (GHG) regulations over the 2017-2025 timeframe.[1,2] The U.S. EPA finalized their Tier 3 standards in March 2014. The largely harmonized LEV III and Tier 3 regulations form one national set of criteria pollutant standards for 2017 to 2025 model year light-duty vehicles. This latest wave of U.S. light-duty vehicle emission standards will provide further reductions in ambient ozone and particulate emissions that will translate into further substantial public health benefits.

The ARB LEV III light-duty emission program and EPA Tier 3 regulations, when fully implemented, will require all light-duty vehicles sold in the U.S. to be on average, emissions equivalent to the cleanest gasoline vehicles sold today – a Super Ultra-Low Emissions Vehicle (SULEV) fleet average. Today's SULEV and PZEV (equivalent to EPA's Tier 2, Bin 2 exhaust emissions certification level) vehicles have near-zero exhaust and fuel system evaporative emissions. SULEV and PZEV (Partial Zero Emission Vehicles) certified vehicles first appeared in the U.S. market in the 2001 timeframe in response to ARB's LEV II and ZEV program requirements. They feature state-of-the-art engine and emission controls technologies that are capable of maintaining ultra-high conversion efficiencies for criteria pollutants for up to 150,000 miles of vehicle operation.

This paper briefly reviews important aspects of the LEV III and Tier 3 programs, and highlights exhaust emission control technologies that will be an integral part of the overall engineered systems approach necessary for the wide weight-range of light-duty vehicles to comply with Tier 3/LEV III tailpipe emission levels. In particular the discussion will focus on advanced three-way catalysts (TWCs) and advanced substrates designed to achieve the high conversion efficiencies of regulated pollutants over extended vehicle mileage associated with meeting these regulations. Information on evaporative emissions technologies that will be used to achieve Tier 3/LEV III near-zero fuel system-related evaporative emission are described in the MECA white-paper, "Evaporative Emission Control Technologies for Gasoline Powered Vehicles" that is available at www.meca.org.

2.0 Technology Forcing Exhaust Emission Regulations

Since the mid-1970s, U.S. federal and California light-duty motor vehicle tailpipe emission regulations have been continually pushed to lower levels in response to air quality concerns. At the forefront of these new waves of regulatory programs aimed at significantly reducing emissions from light-duty vehicles are the U.S. Environmental Protection Agency's (EPA) Tier 2 and the California Air Resource Board's (ARB) Low Emission Vehicle II (LEV II) programs. Both the ARB LEV II regulations and the EPA Tier 2 regulations began their phase-in with the 2004 model year. In a parallel or slightly delayed timeframe relative to these U.S. initiatives, Europe (Euro 3 and Euro 4 regulations), Japan (Japan Low Emission Vehicle regulations), and Korea (Korea Low Emission Vehicle regulations) also established new, more severe light-duty emission regulations during the 1990s, and established even more stringent light-duty vehicle emission standards in the 2000-2011 timeframe (e.g., Euro 5 and Euro 6 regulations). Euro 5 standards were fully implemented in 2011 and Euro 6 will go into effect for all models in 2015. The Euro 6 standards tightened the limits by 68% for CO to 96% for PM below those established by Euro 1 in 1992. NOx limits on diesel cars decreased by 64% between Euro 3 (2000) and Euro 5 (2009).

Emission regulations for new vehicles based on the use of three-way catalyst technologies are now being implemented in almost every world market including large emerging markets in Brazil, India and China. The introduction of catalytic converters in the U.S. and other world markets also required these countries to introduce unleaded gasoline since vehicle operation on leaded fuel results in dramatic deactivation of the active precious-metal-based catalytic materials (e.g., Pt, Pd, Rh) present in three-way catalytic converters.

All of these current U.S. light-duty vehicle emission programs require significant reductions in hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxide (NOx) emissions relative to vehicle emission requirements associated with the regulations that precede each of these emission programs (e.g., EPA's Tier 1 or California LEV I regulations). The LEV II regulation, for example, maintains tight hydrocarbon emission levels established in the LEV I program (adopted in 1990; implementation began with the 1994 model year), but significantly reduce NOx emission requirements compared to LEV I requirements. The Tier 2 program draws from both the California LEV I and LEV II programs in significantly tightening both HC and NOx tailpipe emissions relative to Tier 1 regulations that were first implemented with the 1994 model year. An important input into each of these regulatory processes was the ability of emission control technologies to meet these increasingly tighter tailpipe emission standards in a cost effective manner. The Manufacturers of Emission Controls Association (MECA) provided important technical inputs into the EPA Tier 2 and California LEV II rulemaking process by completing a successful test program in the late 1990s that demonstrated that advanced three-way catalysts were capable of significantly reducing exhaust emissions from four different Tier 1-compliant passenger cars and trucks. Details of this test program were reported in a Society of Automotive Engineers (SAE) technical paper published in 1999 (Webb et al. 1999). Compared to pre-controlled vehicles sold in the U.S. prior to 1975, today's Tier 2 and LEV II cars and trucks are meeting emission standards that require reductions of up to 98+% with respect to VOCs, 96% for CO and 98% for NOx. The tightening of emission limits, as part of the LEV I and LEV II programs, for the two primary ozone forming pollutants is shown in Figure 1. MECA completed a second light-duty gasoline vehicle test program in 2006 that demonstrated that advanced three-way catalytic converter systems allow even the heaviest light-duty gasoline trucks (e.g. SUVs and larger pick-up trucks) to achieve very low exhaust emissions of hydrocarbons and NOx. Results of this test program are available in Kubsh and Anthony (2007).

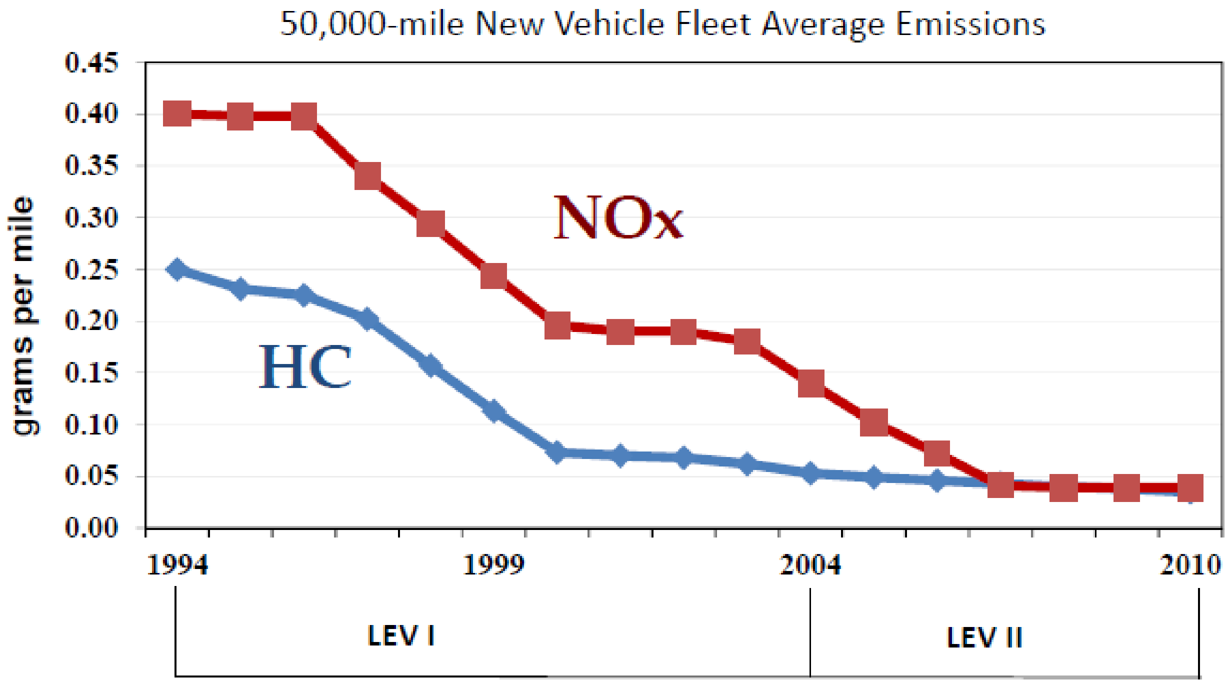


Figure 1. The gradual tightening of fleet average emission limits of the LEV programs for NMOG and NOx.

Although this whitepaper focuses on emission control technologies that will be required by LEV III and Tier 3 to meet the equivalent SULEV/Tier 2 Bin 2 standards across the entire light-duty fleet by 2025, some additional details concerning the EPA Tier 2 and California LEV 2 emission regulations are provided here since each program includes the tightest light-duty emission certification categories currently in place in the world today. The types of emission control technologies that will be implemented across the light-duty fleet to meet LEV III/Tier 3 requirements are already available and being used on dozens of PZEV/SULEV/Tier 2 Bin 2 vehicle models under the current LEV II and Tier 2 programs.

Full useful life tailpipe emission standards for the fully phased-in U.S. EPA Tier 2 and California LEV II programs are summarized in Tables 1 and 2, respectively. Each of these programs provides auto manufacturers with several different certification categories to choose from for their light-duty vehicle fleet. In the case of EPA's Tier 2 program, auto manufactures may select appropriate vehicle emission certification categories that allow their fleet of new vehicles to achieve a fleet average NOx emission limit of 0.07 g/mi (equivalent to a Tier 2, Bin 5 NOx fleet average). To comply with California's LEV II requirements, auto manufacturers must select appropriate vehicle emission certification categories that allow them to meet a declining annual fleet average NMOG standard that reached 0.035 g/mi for passenger cars and 0.043 g/mi for heavier, light-duty trucks in 2010.

Tailpipe emissions are measured on a chassis dynamometer using the U.S. Federal Test Procedure (FTP, a vehicle speed vs. time driving cycle). The concept of multiple certification categories was first introduced with California's LEV I program. The EPA Tier 1 light-duty emission regulations also had weight class specific emission regulations but only one set of emission standards for each gasoline vehicle weight class. The Tier 2/LEV II programs have several common features that are also significant changes from either Tier 1 or LEV I requirements: 1) fuel neutral requirements (emission standards are equivalent for gasoline and diesel-fueled vehicles); 2) 120,000 mile full useful life durability; and 3) a single set of standards that does not vary with light-duty vehicle weight class (up to 8500 lb. gross vehicle weight for all passenger cars and light-duty trucks; up to 10,000 lb. for medium-duty passenger vehicles [MDPVs]). Treating passenger cars and light-duty trucks on an equivalent emissions basis is an important focus for both the Tier 2 and LEV II programs. Both of these programs place a premium on cold-start emission performance and high emission system efficiencies with respect to NOx emissions.

Reaching the tailpipe emission levels associated with today's Tier 2 and LEV II emission regulations, or future Tier 3 and LEV III emission limits on stoichiometric gasoline vehicles, requires a concerted systems approach that includes the use of advanced spark-ignited engines, advanced engine control strategies, clean fuels, clean lubricants, and advanced emission control technologies. Both ARB and EPA have included the clean fuel component in their LEV II and Tier 2 regulatory programs with respect to gasoline sulfur levels. ARB established a 30 ppm sulfur average for gasoline as a part of their California Phase II reformulated gasoline requirements. This sulfur level was further reduced to an average of 15 ppm sulfur starting in 2004 with the introduction of California Phase III reformulated gasoline regulations, and was capped at 20 ppm starting in 2012. Similarly, the EPA included gasoline sulfur level regulations as an integral part of their Tier 2 regulatory package with the phase-in of 30 ppm average and 80 ppm cap S levels started in 2005. EPA has included a 10 ppm gasoline sulfur average in conjunction with its final Tier 3 light-duty vehicle emissions program that begins its phase-in in 2017.

Table 1. California LEV II 120,000 mile FTP tailpipe emission limits

Certification Level	*NMOG (g/mi)*	*CO (g/mi)*	*NOx (g/mi)*
LEV-2	0.090	4.2	0.07
LEV-2/LDT2*	0.090	4.2	0.10
ULEV-2	0.055	2.1	0.07
SULEV	0.010	1.0	0.02

* The LEV-2/LDT2 certification category is limited to no more than 4% of the LDT2 light-duty truck production for a given manufacturer.

Table 2. U.S. EPA Tier 2 120,000 mile FTP tailpipe emission limits

Certification Level	*NMOG (g/mi)*	*CO (g/mi)*	*NOx (g/mi)*
Bin 1	0.0	0.0	0.0
Bin 2	0.010	2.1	0.02
Bin 3	0.055	2.1	0.03
Bin 4	0.070	2.1	0.04
Bin 5	0.090	4.2	0.07
Bin 6	0.090	4.2	0.10
Bin 7	0.090	4.2	0.15
Bin 8	0.125	4.2	0.20

2.1 California's LEV III and EPA's Tier 3 Emission Standards

California finalized their next round of light-duty vehicle emission standards in 2012. LEV III will further reduce U.S. vehicle emission limits to a fleet average level consistent with California's current SULEV exhaust emission limit and EPA's Tier 2, Bin 2 exhaust emission limit by 2025. LEV III implementation will begin with the 2015 model year. The LEV III criteria pollutant regulation was rolled out as part of the state's Advanced Clean Cars Program that also includes greenhouse gas (GHG) standards for the 2017-2025 model years, as well as, revised zero-emission vehicle (ZEV) requirements.

EPA finalized a similar set of criteria emission regulations in 2014 as part of a Tier 3 regulatory package that is largely harmonized with California's LEV III standards, with slightly delayed implementation that starts in the 2017 and 2018 model years (4). In addition to tighter emission standards for hydrocarbons, CO, and NOx, LEV III and the Tier 3 regulations tighten emission standards for particulates and evaporative emissions from future light-duty vehicles. The Tier 3 emissions program is also aligned with and implemented over the same time frame as U.S. EPA's GHG emission standards for light-duty vehicles starting in the 2017 model year. The harmonization of the federal and California regulations will, for the first time, allow automobile manufacturers to comply with one set of standards across all 50 states.

The primary strategy employed to reduce emissions from future light-duty vehicles under the LEV III regulation is to phase in SULEV type technologies across the entire light-duty and medium-duty fleet by 2025. The individual NMOG and NOx limits were combined under LEV III to provide vehicle manufacturers additional flexibility in employing strategies to meet the combined limit values rather than individual limits under LEV II. By 2025, when it is fully implemented, LEV III will result in a 75% reduction in NMOG plus NOx emissions across the California fleet whereas the federal fleet achieves an 80% reduction in NMOG + NOx and 70% reduction in PM with Tier 3. The phase-in for the requirements is slightly different for passenger cars and smaller light-duty trucks (LDT1) versus larger LDT2 SUVs and pick-up trucks. The phase-in schedule for the combined fleet average emission limits is shown in Figure 2 with both curves converging on a SULEV limit of 0.030 g/mi NMOG+NOx in 2025. A more detailed picture of all of the emission limits for the certification classifications that manufacturers must meet as a part of this rule is laid out in Table 3 (note that Table 3 does not include LEV III PM limits). The federal Tier 3 standards for LDVs, LDTs and MDPVs up to 10,000 lbs GVWR are classified into seven Bins designated from Bin 0 to Bin 160 where the numberical value corresponds to the NMOG+NOx milligram limit. The fleet average required from the Tier 3 standards would match the two curves in Figure 2 starting in the 2017 model year.

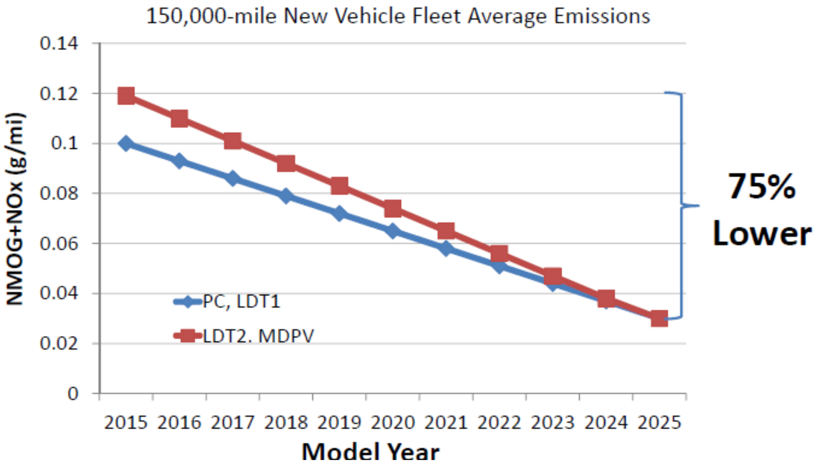
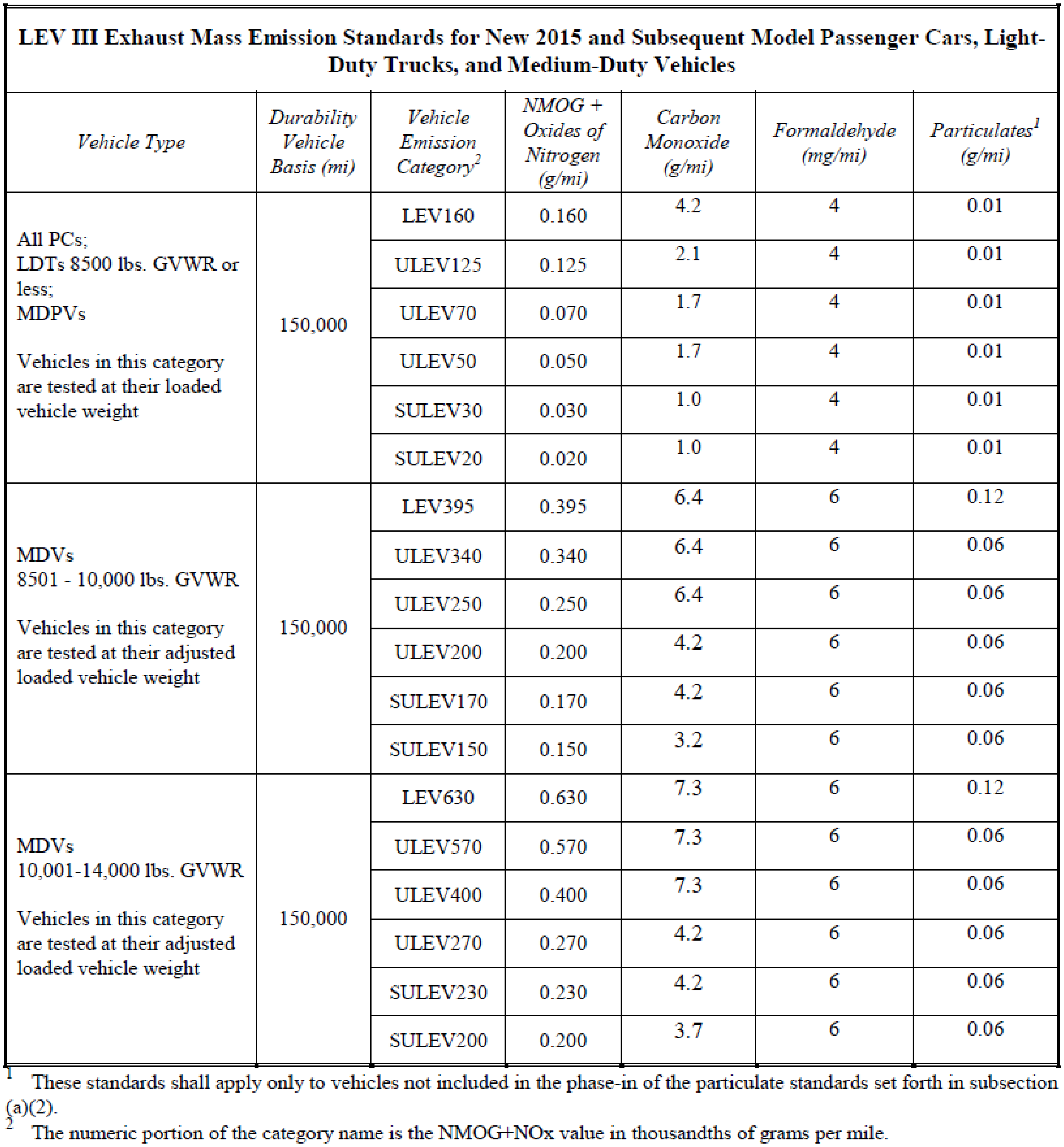


Figure 2. Fleet average NMOG + NOx emission limits under LEV III and Tier 3 (Ref. 1).

As a way to force new emission control technologies and provide manufacturers with greater flexibilities in meeting the average emission limits in Figure 1, ARB added three new emission categories including one below SULEV (SULEV20) and two between SULEV and ULEV (ULEV50 and ULEV70). The numerical designations refer to the combined NMOG+NOx emission limit, in mg/mile, associated with each vehicle certification category. Table 3 shows that LEV III has specific formaldehyde requirements listed as a criteria pollutant. Eliminated under LEV III is the intermediate, 50,000 mile, emission standards and an increase of the full useful life (FUL) durability requirements from 120,000 to 150,000 miles for all vehicle classifications under the program. The Tier 3 program includes 120,000 mile FUL certification for the lighter vehicles (< 6,000 lbs GVWR), however the emission limits are lowered by a corresponding 15% (a manufacturer may also choose to certify this lighter vehicles to the 150,000 mile standards). The federal Tier 3 mandatory emissions warranty remains at 8 years or 80,000 miles which is the same as under Tier 2 (7 years or 70,000 miles for California LEV II and LEV III). Under both programs, a manufacturer can receive a 5 mg/mile NMOG+NOx credit for offering a full 150,000 mile warranty.

Table 3. LEV III Category Exhaust Emission Limits (Ref. 1)



LEV III Exhaust Mass Emission Standards for New 2015 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles

Vehicle Type	*Durability Vehicle Basis (mi)*	*Vehicle Emission Category*[2]	*NMOG + Oxides of Nitrogen (g/mi)*	*Carbon Monoxide (g/mi)*	*Formaldehyde (mg/mi)*	*Particulates*[1] *(g/mi)*
All PCs; LDTs 8500 lbs. GVWR or less; MDPVs Vehicles in this category are tested at their loaded vehicle weight	150,000	LEV160	0.160	4.2	4	0.01
		ULEV125	0.125	2.1	4	0.01
		ULEV70	0.070	1.7	4	0.01
		ULEV50	0.050	1.7	4	0.01
		SULEV30	0.030	1.0	4	0.01
		SULEV20	0.020	1.0	4	0.01
MDVs 8501 - 10,000 lbs. GVWR Vehicles in this category are tested at their adjusted loaded vehicle weight	150,000	LEV395	0.395	6.4	6	0.12
		ULEV340	0.340	6.4	6	0.06
		ULEV250	0.250	6.4	6	0.06
		ULEV200	0.200	4.2	6	0.06
		SULEV170	0.170	4.2	6	0.06
		SULEV150	0.150	3.2	6	0.06
MDVs 10,001-14,000 lbs. GVWR Vehicles in this category are tested at their adjusted loaded vehicle weight	150,000	LEV630	0.630	7.3	6	0.12
		ULEV570	0.570	7.3	6	0.06
		ULEV400	0.400	7.3	6	0.06
		ULEV270	0.270	4.2	6	0.06
		SULEV230	0.230	4.2	6	0.06
		SULEV200	0.200	3.7	6	0.06

[1] These standards shall apply only to vehicles not included in the phase-in of the particulate standards set forth in subsection (a)(2).

[2] The numeric portion of the category name is the NMOG+NOx value in thousandths of grams per mile.

The LEV III regulation also establishes more stringent limits on medium-duty vehicles (MDVs) up to 14,000 lbs GVWR starting with the 2016 model year under LEV III and 2018 for Tier 3. Tier 3 classifies vehicles in the 8,501 to 14,000 lb. GVWR range as heavy-duty and offers voluntary standards starting in 2016 that are available for early credits. By 2022, manufacturers are required to certify 90% of these respective weight class vehicles to SULEV170 or SULEV230 and 10% to ULEV250 and ULEV400, respectively. Federal Tier 3 standards retain analogous Bin classification for the heavier vehicles with corresponding milligram per mile designations. Furthermore all MDVs in the 8501-10,000 lbs GVWR weight class must certify on a chassis dynamometer starting with the 2020 model year, which will facilitate the ability to perform in-use compliance on these heavier vehicles.

With the expectation that direct injection technology will be rolled out over a larger portion of the gasoline light-duty fleet, ARB established more stringent particulate matter (PM) limits for light and medium-duty vehicles. For light-duty vehicles, a 3 mg/mi FTP PM standard begins in 2017 for both LEV III and Tier 3, and is fully phased-in by 2021 for LEV III and by 2022 for Tier 3. The LEV III regulations continue to tighten to a 1 mg/mi FTP PM limit that begins in 2025 with a four year phase-in across the fleet. MDVs (8500-10,000 lb.) will need to meet an 8 mg/mi FTP PM standard and the heavier MDVs (10,000-14,000 lb.) a 10 mg/mi standard starting in 2017 (fully phased-in by 2021). Due to manufacturer concerns over the ability to meet a 1 mg/mile PM limit or to accurately measure at those PM levels, ARB agreed to convene a formal technical review in the 2015-2017 timeframe. The review will address measurement issues, the state of PM reduction technologies, the potential of a future particle number standard as a compliance option to the more difficult to measure mass-based limit, and the implementation dates for the 1 mg/mile PM limit.

For the first time, LEV III established full useful life standards for the supplemental federal test procedure (SFTP) including extending these standards to MDVs. LEV II has a 4,000 mile SFTP requirement for light-duty vehicles. The gaseous criteria pollutants are tested over the SC03 and US06 test cycles that reflect more aggressive driving (US06) and air conditioner operation (SC03). Both programs include SFTP PM standards of 6 mg/mile over the US06 test cycle for passenger cars and LDT1 vehicles (this SFTP PM limit is set at 10 mg/mile for 2017 and 2018), and 20 mg/mi for LDT2s and MDVs up to 14,000 lbs GVWR.

LEV III extended PZEV type, near zero evaporative emission requirements to all light-duty vehicles by 2022. Manufacturers have two compliance options that include a zero evap based fuel system test and a 2-day and 3-day + hot soak whole vehicle test in a Sealed Housing for Evaporative Determination (SHED) apparatus. OEMs have the option to certify to a running loss standard (50 mg/test limit), a whole vehicle standard, and use the existing fuel system rig test to show that their fuel system emissions are at near zero grams (0.054 g/test) per test and meet a 2-day + hot soak & 3-day + hot soak SHED whole vehicle limits of 350 mg/test for passenger cars, 500 mg/test for LDT1s, 750 mg/test for LDT2s, MDPVs, MDVs, and HDVs (over 14,000 lbs. GVWR). The other option allows OEMs to certify to a running loss standard of 50 mg/test, a tighter fleet average whole vehicle standard based on the 2-day + hot soak & 3-day

+ hot soak SHED test. Under this option the whole vehicle fleet average limits are 300 mg/test for passenger cars and LDT1s, 400 mg/test for LDT2s up to 6000 lbs. GVWR, 500 mg/test for heavier LDT2s and medium-duty passenger vehicles (MDPVs), 600 mg/test for MDVs and HDVs. Rather than performing a complete fuel system rig test, under this option, manufactures are allowed to meet canister emission limits using a simplified, canister bleed emission test protocol. Canister bleed emission limits are set at 20 mg/test for smaller vehicles up to 10,000 lbs GVWR and 30 mg/test for MDVs and HDVs. For more on ARB's LEV III evaporative standards and test methods please see MECA's white paper on Evaporative Emission Control Technology for Gasoline Powered Vehicles at www.meca.org.

The U.S. EPA has included a similar set of evaporative standards as part of their Tier 3 program with only a few minor differences (4). The standards represent a 50% reduction from Tier 2 levels. The federal standards are identical to the Option 2 requirements under LEV III however; manufacturers may use the LEV III Option 1 standards for vehicles certified prior to 2017. The FUL is extended to 150,000 miles. As under LEV III, an identical canister bleed emission standard and test method is included in Tier 3. EPA and ARB have also added a leak test and emission standard to insure that the cumulative equivalent diameter of any leak does not exceed 0.02 inches anywhere in the fuel and evaporative control system. This leak test is also being included in the In-Use Verification Program, establishing in-use requirements for evaporative emissions for the first time.

Both California and EPA will migrate to an E10 certification fuel for LEV III and Tier 3 to better represent the fuels that will be available across the country. EPA has included a new E85 test fuel for flex fuel vehicles (FFVs). As with other recent federal emission regulations such as Tier 2 and the 2007/2010 on-road heavy-duty diesel standards, the Tier 3 standards include new sulfur limits on gasoline with a 10 ppm average value beginning in 2017. The federal gasoline sulfur cap will remain at the current cap of 80 ppm sulfur. To achieve the average value of 10 ppm will require that most of the gasoline produced must remain very close to the average value. The tighter gasoline sulfur standard is expected to reduce NOx emissions in the existing fleet of vehicles by 20-30% due to a reduction in sulfur poisoning of the catalyst while making it easier for new vehicles to meet the tighter NOx + NMOG limits under the Tier 3 regulations. The impact of gasoline sulfur on catalyst systems is discussed in Section 3.3.1. Both LEV III and Tier 3 tailpipe and evaporative emission regulations include a number of phase-in flexibilities, credit and allowance programs, hardship provisions and more lead time for small volume manufacturers that produce less than 5,000 vehicles per year. The 10 ppm fuel sulfur standard for gasoline under Tier 3 also includes an averaging, banking and trading program for refiners to spread out their capital investments.

3.0 Gasoline Emission Control Technology

The three-way catalytic converter (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 system, allows for simultaneous conversion of the three criteria pollutants, hydrocarbons, CO, and NOx, produced during the stoichiometricly calibrated air/fuel combustion process of an internal combustion, spark ignited engine. Figures 3 and 4 depict a cut-away drawing and a cut-away photo of typical three-way catalytic converters, one using a ceramic substrate and one using a metallic substrate. 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 the 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 losses due to back pressure.

Catalytic materials are typically applied by contacting the substrate with a water-based slurry containing the active inorganic catalyst materials. The coated substrate is contained within an outer metal-based shell that facilitates connection of the converter to the vehicle's exhaust system through flanges or welds. The honeycomb-based substrates are typically either ceramic or metal foil-based. Cordierite, a magnesium alumino-silicate 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 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. As shown in Figures 3 and 4, 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.

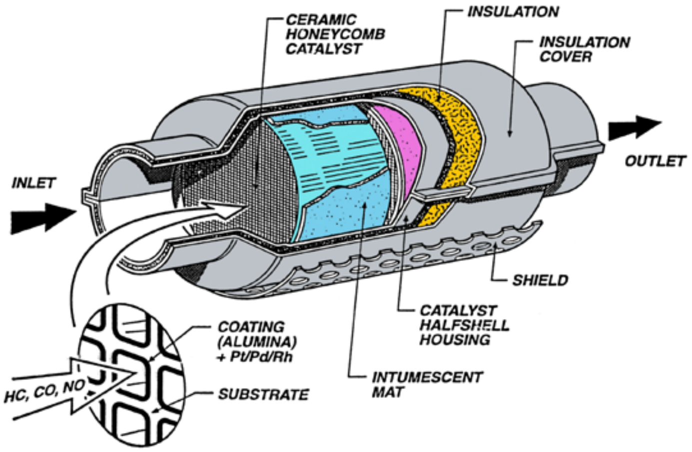


Figure 3. Three-way catalytic converter with ceramic substrates.

Although the primary components and function of a three-way catalytic converter has 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, palladium, and rhodium. Each of these three emission control technology platforms are discussed in more detailed in subsequent sections of this chapter.

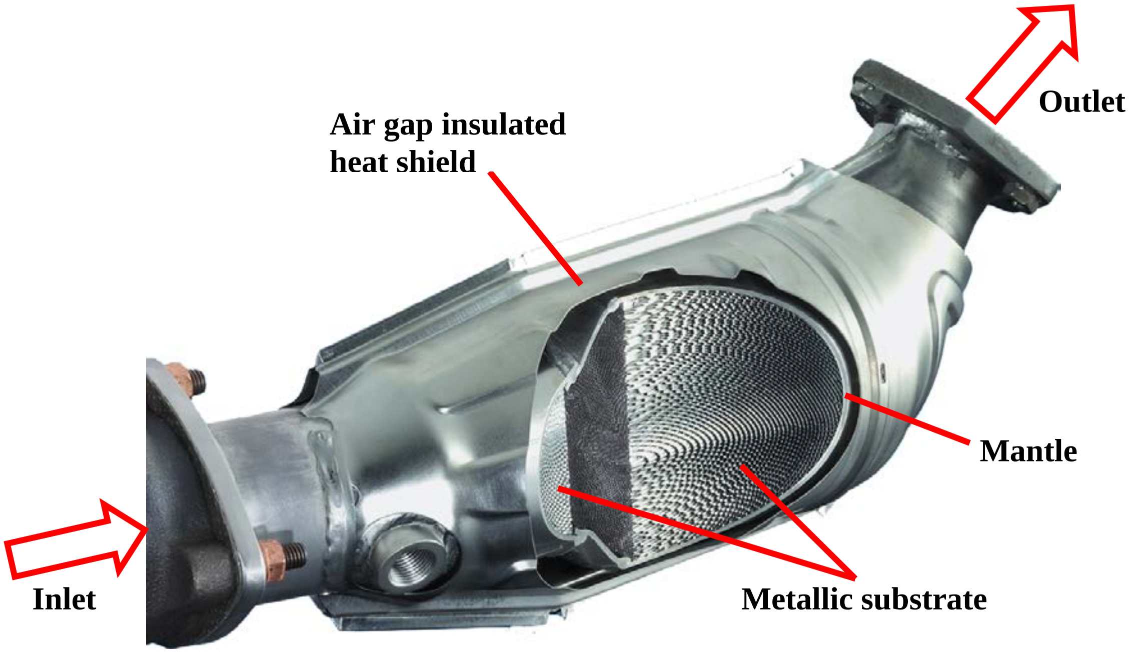


Figure 4. Three-way catalytic converter with metallic substrates.

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 NOx). 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^2 have been used on production catalytic converters with 600 cells/in^2 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.

Current state-of-the-art, stoichiometric gasoline emission control systems are defined by SULEV (Super Ultra-low Emission Vehicle) or PZEV (Partial Zero Emission Vehicle) compliant light-duty vehicle sold in the U.S. market. There are a number of recent references (Ball and Moser 2012; Inoue and Mitsuishi 2009; Matsuzono et al. 2008; Laurell, Dahlgren, and Vaisanen

2007; Kidokoro et al. 2003; Oguma et al. 2003) that describe these systems that typically include combinations of close-coupled and underfloor converters systems that utilize high performance three-way catalysts displayed on high cell density substrates. These SULEV/PZEV systems utilize advanced cold-start calibration schemes including cold-start engine spark retard, higher cold-start idle speeds, and/or secondary air injection during the initial engine cold-start to accelerate the warm-up of the close-coupled converter within a few seconds after a cold engine start.

3.1 Close-Coupled Converters

Achieving high conversion efficiencies for both HC and NOx emissions during normal vehicle operation represented by the FTP driving cycle, for example, has focused attention on cold-start performance of catalytic converters for both U.S. Tier 2 and LEV II light-duty applications. LEV I hydrocarbon emission requirements introduced by California in 1994 provided the first regulatory driver that placed importance on cold-start emissions. Numerous studies published in the late 1980s and 1990s have discussed the high percentage of FTP driving cycle emissions associated with the early stages of vehicle operation following a cold engine start situation (Hughes and Witte 2002; Pfalzgraf et al. 2001; Nishizawa et al. 2001; Brueck et al. 2001; Domesle et al. 2001; Williamson et al. 2000; Lafyatis et al. 2000; Holy et al. 2000; Moore et al. 1999; Webb et. al 1999; Ehmann et al. 1999; Takahashi et al. 1998; Kishi et al. 1998). This is especially true for 1990s vintage vehicles sold in the U.S. designed to comply with less severe Tier 1 emissions standards. Hydrocarbon tailpipe emission profiles during FTP testing of Tier 1 vehicles are generally dominated by emissions emitted during the first one to two minutes of operation after the cold-start. This large fraction of cold-start emissions in Tier 1 vehicles stemmed from significant fuel enrichment used by auto manufacturers to facilitate engine start under cold conditions and significant delays in converter warm-up to catalyst operating temperatures required for high conversion efficiencies (e.g., 350°C or higher). Heat-up delays were usually associated with relatively long distances and the associated poor heat transfer between the converter location and the engine exhaust ports. NOx emission profiles also have a component related to cold-start operation but are generally distributed more uniformly through the FTP driving cycle on Tier 1 certified vehicles due to NOx emission events associated with vehicle accelerations and decelerations.

To more effectively deal with cold-start emissions, converter volumes have been moved closer to the engine exhaust ports to minimize exhaust system heat losses and accelerate the heat-up of catalysts during the critical time following engine start. Converters located near the engine exhaust valves (e.g., at the exit of the exhaust manifold) are referred to as close-coupled converters (or sometimes light-off converters or pre-converters). LEV I and ULEV I compliant light-duty vehicles introduced in the mid-1990s were the first significant applications of exhaust systems featuring close-coupled catalytic converters. In some applications (typically smaller displacement engines), a vehicle may have all or a large fraction of the required catalyst volume located close to the engine exhaust manifold. In other applications (typically larger displacement engines), the exhaust system will include smaller volume converters located close to the engine followed by a larger converter volume located further downstream in the exhaust in an underfloor location. In these multiple converter exhaust schemes, the size of the close-coupled converter is balanced between thermal mass (minimal catalyzed substrate mass for faster heat-up), diagnostic (adequate oxygen storage capacity), and durability considerations (sufficient volume to maintain required performance over extended mileage).

In larger engines, dual exhaust system configurations are often used with parallel systems for each cylinder bank (in the case of V-type engine designs) or groups of cylinders (in the case of in-line engine designs). These parallel systems may each incorporate close-coupled and underfloor converters or parallel close-coupled converters that lead into a y-pipe and a single underfloor converter. A schematic of an exhaust system layout featuring dual close-coupled converters flowing into a single underfloor converter is shown in Figure 5. Due to their close orientation to the engine, the close-coupled converter(s) can reach temperatures required for high conversion efficiencies of hydrocarbons, CO, and NOx in 30 seconds or less following engine start, compared to heat-up times of 60 seconds or more associated with underfloor-only converter systems.

Fast dynamic converter heat-up, a requirement for low cold-start emissions, is also facilitated by advanced cold-start engine calibration strategies. These strategies include retardation of the engine spark, reduced idle speed, use of secondary air injection, and/or lean start strategies. Numerous examples of these cold-start strategies have been described in the literature (Ball and Moser 2012; Inoue and Mitsuishi 2009; Laurell, Dahlgren, and Vaisanen 2007; Kidokoro et al. 2003; Oguma et al. 2003; Matsuzono et al. 2003; Brueck et al. 2002) and are a key part of the systems approach required to achieve high conversion efficiencies for HC and NOx at the early stages following engine start. Each of these engine start-up strategies seeks to maximize conditions at the close-coupled converter that accelerate its heat-up following engine start (e.g., additional unburned fuel to combust over the catalyst, minimized total exhaust flow during initial engine idle, slight excess of oxygen to combustibles in the exhaust to promote full oxidation at the catalyst).

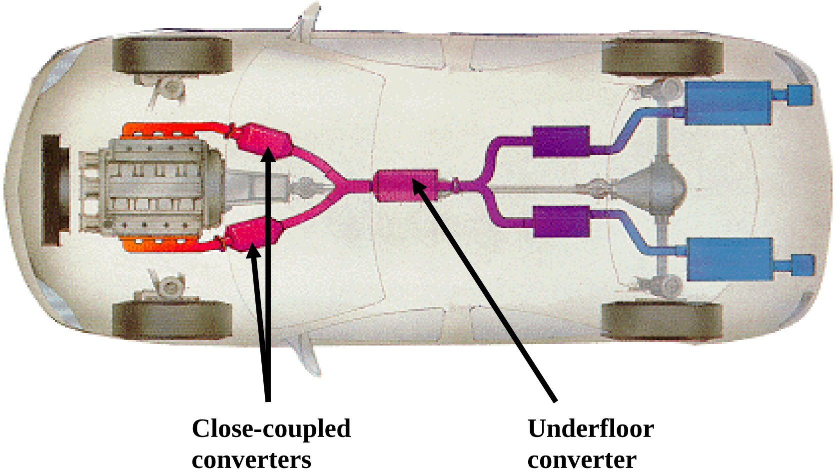


Figure 5. Exhaust system with close-coupled converters.

Rapid converter heat-up has also placed greater emphasis on exhaust system thermal management. Efficient transfer of heat generated during the combustion process to the catalytic converter with minimal heat losses to the surrounding environment is facilitated by insulated exhaust manifolds and insulated exhaust pipes (Kidokoro et al. 2003; Oguma et al. 2003; Pfalzgraf et al. 2001; Webb et al. 1999). The preferred method of insulation is through the use of low thermal mass, air gap components. Insulated manifolds and pipes featuring dual wall construction separated by air gaps have been developed to improve light-duty vehicle cold-start and warm-start emission performance (see Figure 6). These air gap components generally make use of a thin, low thermal mass, durable inner wall to facilitate fast heat-up characteristics. An air gap between the thin inner wall and a thicker outer wall provides insulation to minimize heat losses between the engine and the converter(s). These air gap exhaust components provide significant reductions in converter heat-up during the FTP test protocol, which in turn provides significant reductions in cold-start and warm-start vehicle emissions.

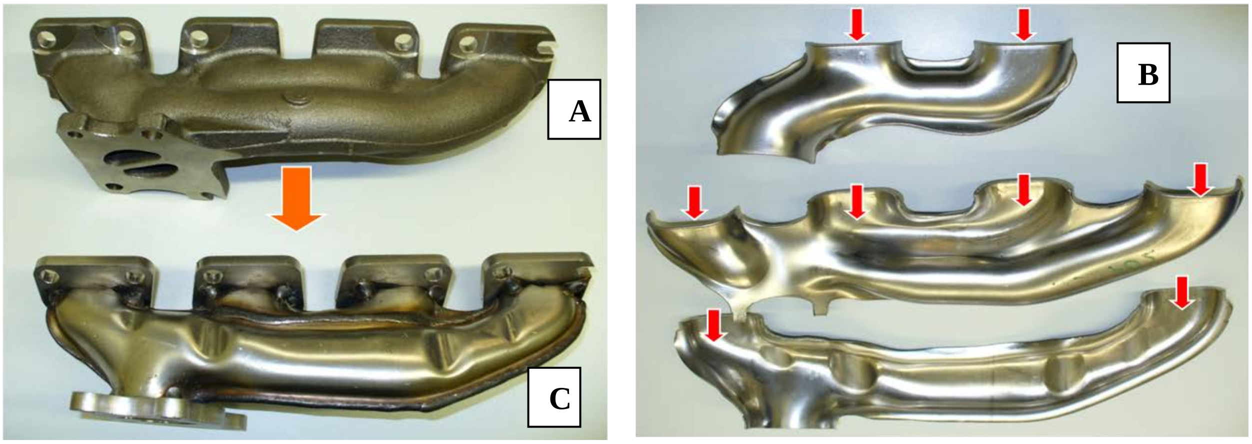


Figure 6. A traditional cast iron exhaust manifold (A) is re-engineered using thin walled stainless steel stampings (B) into a dual walled manifold (C).

Placement of catalytic converters closer to the engine results in dramatic reductions in cold-start emissions of all criteria pollutants (especially hydrocarbon and CO emissions that are most associated with cold engine start conditions). The close-coupled converter environment also raises converter maximum operating temperatures relative to underfloor environments. This, in turn, has placed added demands on the thermal durability of catalysts and other converter components used in these more severe close-coupled converter applications. In particular, fiber-based mounting materials and packaging assemblies used with ceramic substrates have been re-engineered and optimized to meet these more severe thermo-mechanical environments, as well as the longer durability requirements associated with the Tier 2/Tier 3 and LEV II/LEV III emission regulations. The support mat has many functions but fundamentally it is to lock-in and protect the ceramic substrate from moving or being damaged under ever changing thermal and mechanical forces. Support mat suppliers have worked with exhaust system designers and canners in understanding the changes in conditions of LEV III emission systems to further develop the support mat. System conditions and needs such as; lower overall temperatures, longer substrates, ultra thin wall substrates, close coupled converters, higher gas velocity, heavier mass, thermal spikes, and the need for greater durability have led to the development of new support mats. The most notable new support mat is the development and use of non-intumescent support mats made of polycrystalline ceramic fibers. The non-intumescent mats do not rely on thermal expansion to protect the substrate but the fibers act as mechanical springs to provide holding forces that remain constant from room temperature to 1000 ^{o}C. Similarly, metal substrate construction methods and brazing schemes have been optimized for the high mechanical loads and high temperatures encountered in close-coupled applications. For a discussion of high temperature TWC catalyst designs, please go to Section 3.3.

3.2 High Cell Density Substrates

Tier 1 compliant vehicles generally relied on substrate designs that utilize straight flow channeled monoliths with square cross-sectional channel openings. Channel sizes that equate to 400 channels or cells per square inch of frontal area (designated as 400 cpsi) became an industry standard for many applications in the late 1980s and 1990s. In Tier 1 applications of ceramic substrate designs with 400 cpsi, ceramic substrate wall thickness was typically 0.0065 in or 6.5 mils, with some limited usage of 400 cpsi substrates with 8 mil walls. Limited applications of ceramic monoliths with triangular shaped cells have also been used for Tier 1 applications with cell densities of 236 cpsi or 300 cpsi (wall thickness of 6.5-11.5 mils). Metal substrates were also introduced with channel densities of up to 400 cpsi but with thinner metal foil walls that were typically 50 microns (approximately 2 mils) in thickness. These standard metal substrate designs typically utilize sinusoidally corrugated metal foils layered between flat foils to produce parallel flow channels.

Interest in automotive emission systems with high conversion efficiencies and improved cold-start performance to meet more severe emission requirements, such as Tier 2/3 and LEV I/II/III standards, encouraged the development of a new generation of both ceramic and metallic substrate designs that offer significantly higher cell densities (more flow channels per cross-sectional area) and thinner walls separating flow channels. These two key substrate characteristics provide increased geometric surface area (GSA) per unit volume of monolith for efficient distribution of the active catalytic coating, relatively small flow channels (or more precisely, relatively small values for the channel hydraulic diameter) for good heat and mass transfer characteristics, and reduced substrate thermal mass for faster heat-up during emission critical cold-start events. Figure 7 provides a comparison of relative specific geometric areas and bulk densities of ceramic substrates with progressively higher cell densities and thinner wall thickness.

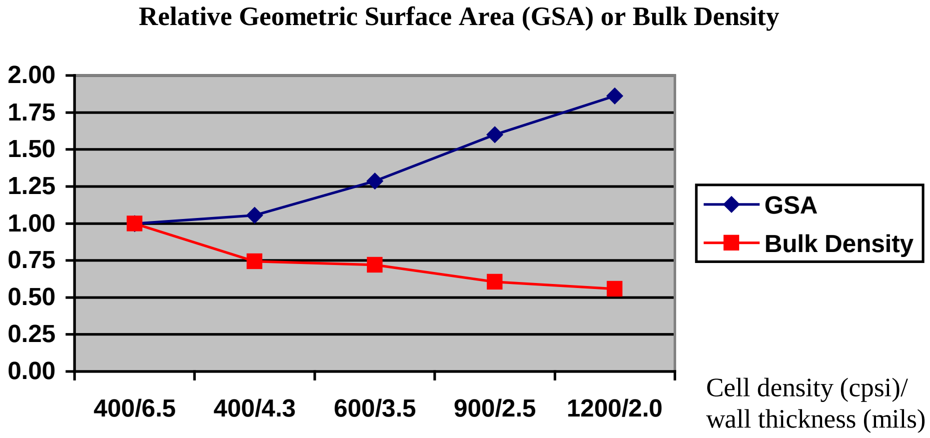


Figure 7. Relative geometric surface area and bulk density of ceramic substrates.

As discussed in the many references associated with these high cell density substrates, substrate geometric surface area is an important physical property in heterogeneous catalysis associated with the effective mass transfer of reactants present in the exhaust stream of an engine (e.g., HCs, CO, NOx, H_2O, and O_2) to the solid surfaces that contain the active catalytic sites (references include: Mueller-Haas et al. 2003; Hughes et. al 2003, Hughes and Witte 2002; Leonhard et al. 2002; Brueck et al. 2002). Increasing this specific geometric area provides for more efficient contact between the reactants and the active catalyst sites and, in turn, a higher overall conversion efficiency of these reactants in a given volume of catalyzed monolith. Increasing cell density at a constant monolith wall thickness provides increased geometric surface area but results in higher bulk density or thermal mass due to the resulting higher fraction of walls per given cross-sectional area (or, stated in another way, higher cell density at a constant wall thickness lowers the fraction of the frontal area open to the flow of exhaust gas). To compensate for this bulk density effect, substrate manufacturers have successfully developed high cell density products with significantly thinner walls than the “standard products” used primarily in Tier 1 applications. For example, ceramic substrates with 6.5 mil walls offered in “standard products” have been reduced to wall thickness in the range of 1.5-3.5 mils in high cell density substrates. Similarly, metal substrates utilize 50 micron foils in “standard products” with high cell density products typically constructed with foil thickness ranging from 20-40 microns (approximately 0.8-1.6 mils). Thinning the monolith walls provides significant reductions in the thermal mass/bulk density of high cell density products. This low thermal mass characteristic enables catalyst-coated substrates to heat-up more quickly than heavier, “standard” wall thickness substrates. Fast dynamic heat-up of converters is key to achieving low tailpipe emissions during the critical cold-start and warm-start periods associated with normal driving operations, and required to comply with Tier 2 and LEV II emission regulations. To further illustrate the properties and benefits associated with thin wall, high cell density substrates, results from three technical papers are briefly discussed below.

Hughes and Witte (2002) completed a comprehensive study of the impacts of high cell density substrates on light-duty vehicle emission performance in both the FTP and US06 test cycles. Their study made use of ceramic substrates covering a range of cell densities, including the “standard” ceramic substrate product with 400 cpsi/6.5 mil wall thickness, used in many Tier 1 applications, and high cell density, thin wall ceramic substrates such as 600 cpsi substrates with 3.5 and 4.5 mil wall thickness, and 900 cpsi substrates with 2.5 mil wall thickness. Table 4 summarizes ceramic substrates used in this study along with their accompanying properties including specific geometric surface area (GSA) and bulk density.

Table 4. Ceramic substrate properties for standard and high cell density products [from Hughes and Witte (2002)]

Cell Density (cpsi)	**400**	**400**	**600**	**600**	**900**
Wall Thickness (mils)	**6.5**	**4.5**	**4.5**	**3.5**	**2.5**
Open Frontal Area (%)	75.7	82.8	80.0	83.6	85.6
Geometric Surface Area (m^2/liter)	2.74	2.87	3.45	3.53	4.37
Bulk Density (g/liter)	401	279	324	267	267

The performance of these substrates was investigated by catalyzing each substrate with an identical advanced Pd/Rh TWC (100 g/ft^3 total precious metal loading with Pd/Rh = 14/1; all substrates coated with a total coating weight of 140 g/liter of substrate), aging the converters containing these catalyzed substrates using a Ford accelerated aging protocol, and performing triplicate FTP and US06 drive cycle tests on each aged converter. The Ford accelerated aging protocol was performed on an engine dynamometer and simulated approximately 50,000 miles of actual service life. FTP and US06 chassis dynamometer tests were run using a 2.0 liter, 4 cylinder, 4 valve test vehicle with a single aged converter mounted at the exit of the exhaust manifold in a close-coupled location on the test vehicle. Catalyzed monolith volumes of both 1.0 liter (50% of engine swept volume) and 0.5 liters (25% of engine swept volume) were evaluated on the test vehicle using both drive cycles.

Figures 8 and 9 summarize NMHC and NOx average emission performance, respectively, of aged converters evaluated on the test vehicle during FTP evaluations as a function of substrate type (cell density and wall thickness) (Hughes and Witte, 2002). Emissions data are included in these figures for both the 1.0 liter catalyzed volume and 0.5 liter catalyzed volume converters, appropriately weighted for each of the three phases of the FTP driving cycle (cold-start (Bag 1), hot transient (Bag 2), and hot-start (Bag 3)). These data clearly show the significant decrease in both NMHC and NOx emissions that result from the use of high cell density/thin wall substrates relative to the base case 400 cpsi/6.5 mil wall standard. Lower emissions of NMHC and NOx emissions are evident in each phase (or "bag") of the FTP drive cycle: cold-start phase (phase 1 or "bag" 1), warmed-up transient phase (phase 2 or "bag" 2), and warm-start phase (phase 3 or "bag" 3). These reduced tailpipe emissions stem from the higher geometric surface area of these advanced substrates, the smaller hydraulic diameter of each coated channel, and the lower thermal mass of the higher cell density substrates. Thermal mass is proportional to the substrate bulk density values shown in Table 4 (thermal mass = [substrate bulk density] x [substrate volume] x [substrate mass specific heat capacity]).

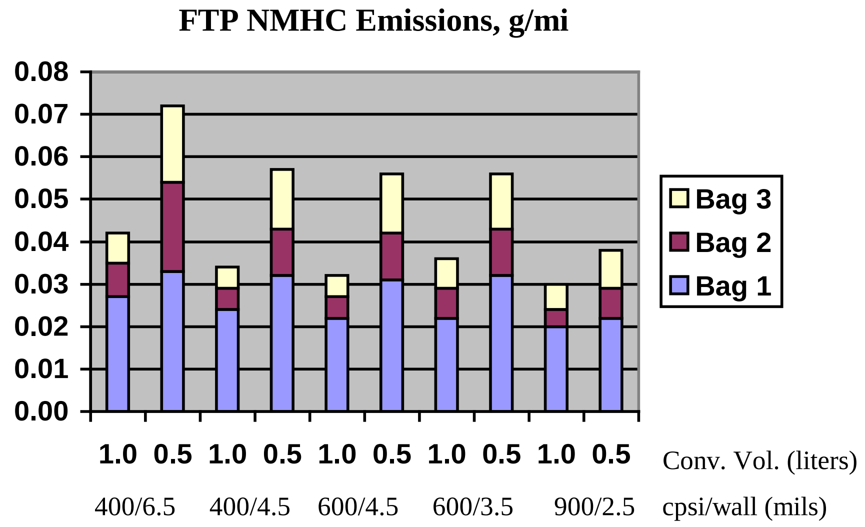


Figure 8. NMHC FTP emissions as a function of cell density and wall thickness of substrates.

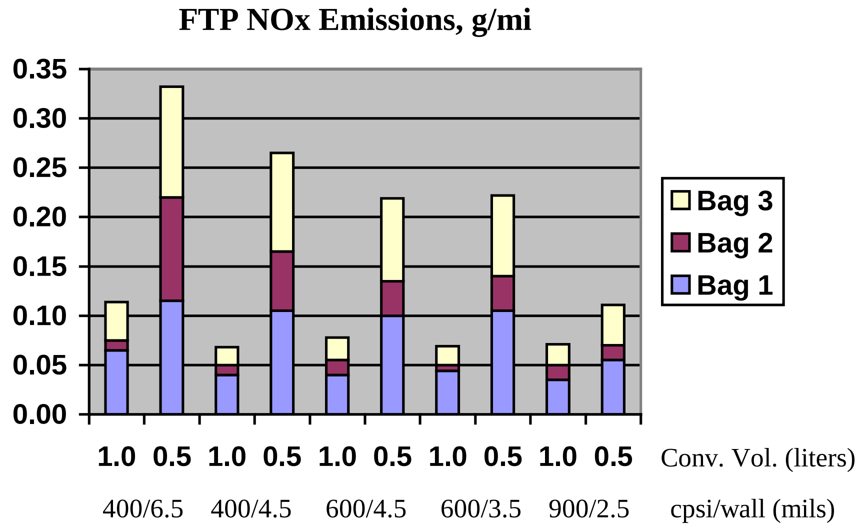


Figure 9. NOx FTP emissions for substrates with varying cell density and wall thickness.

Emission results presented by Aoki et al. (2002) also detail the performance of advanced high cell density ceramic substrates with respect to FTP NMHC emissions on a late model, 4 cylinder test vehicle. This study evaluated engine-aged converters with equivalent volume (substrate dimensions of 106 mm dia. X 114 mm long) and equivalent precious metal loading (150 g/ft^3 advanced trimetal [Pt/Pd/Rh] catalyst) on a vehicle with a 2.3 liter engine (vehicle calibrated for ULEV I performance with lean start strategy; converter inlet approximately 1.1 m downstream of the engine's exhaust valves). Converters were aged for 50 h using an accelerated engine aging protocol with a maximum catalyst temperature of 850^{o}C. Aged converters with substrate cell densities from 300 to 1200 cpsi and varying wall thickness were evaluated on the test vehicle using the FTP drive cycle. Figure 10 compares the NMHC FTP emissions measured on the test vehicle for the various aged converters versus the specific geometric surface area of the substrates evaluated by this program. In this figure each ceramic substrate design is denoted by its cell density (cpsi) and wall thickness in mils (e.g., 600/3.5). The results show a strong relationship between NMHC emissions and substrate geometric surface area with higher substrate geometric surface area contributing to lower NMHC emissions in the FTP test cycle, a result consistent with the results shown in Figures 8 and 9. The results from Aoki et al. also show a relatively large benefit in emission performance for 600 cpsi substrates relative to 300 and 400 cpsi substrate designs. Smaller relative emission benefits were achieved in this study for additional increases in cell density beyond 600 cpsi (e.g., 900 cpsi and 1200 cpsi substrate designs). The relative magnitudes of the emission benefits shown in Figures 7-9 for different substrate cell density and wall thickness options will be impacted by the vehicle application environment including the number and location of catalysts in the exhaust system and the engine calibration strategy employed on the test vehicle. These optimization parameters again emphasize the overall systems design philosophy that needs to be employed to achieve the required emission performance with the most cost effective system design.

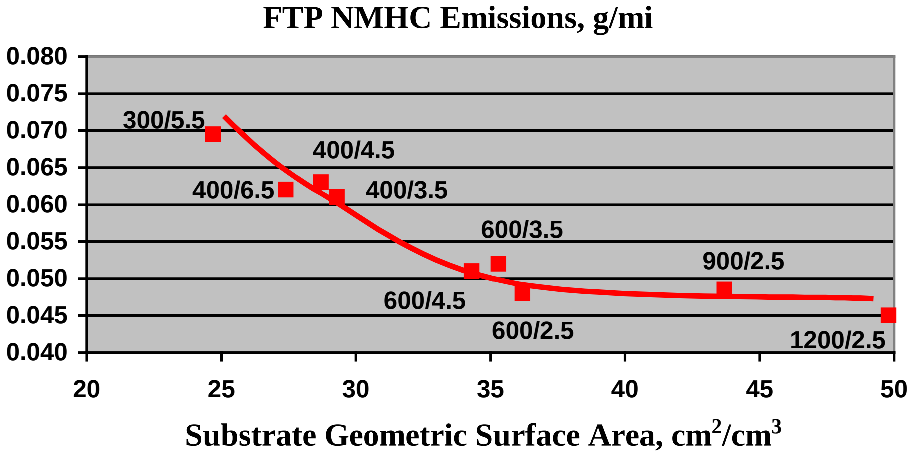


Figure 10. NMHC FTP emissions vs. substrate geometric surface area [see Aoki et al. (2002) for details].

Results presented by Marsh et al. (2001) show similar trends in reducing HC and NOx emissions with advanced high cell density metal substrates during FTP emission tests utilizing a 2.4 liter, 5 cylinder test vehicle. In this study cell densities as high as 1600 cpsi were evaluated for their impacts on emissions performance. Physical properties for the metallic substrates evaluated in this study are summarized in Table 5 below, including values of the flow channel hydraulic diameter. As in the study by Hughes and Witte 2002, converters were evaluated on the test vehicle using the same volumetric precious metal and total catalyst loading of an advanced TWC on each metallic substrate. Converters were located near the exit of the exhaust manifold on the 5 cylinder engine. FTP HC and NOx emissions reported by Marsh et al. (2001) for these various high cell density metallic substrate-based catalysts are detailed in Figures 11 and 12, respectively. Similar to the results reported by Hughes and Witte (2002), FTP HC and NOx emissions were reduced in this study by utilizing higher cell density, thinner wall metal substrates. Improvements in HC emissions were most strongly impacted by the combined increase in cell density with thinner walls between channels since this substrate design strategy lowers thermal mass and increases geometric area (e.g., moving from 600 cpsi/30 micron wall to 1000 cpsi/20 micron wall), critical properties for maximizing converter heat-up and mass transfer characteristics during the HC intensive cold-start period. Further increases in cell density at constant wall thickness (e.g., 1000, 1200, 1600 cpsi with 20 micron wall thickness) equates to higher thermal mass substrates with poorer heat-up characteristics during the cold-start phase of the FTP test cycle. The additional geometric area of these highest cell density designs helped to compensate for the higher thermal mass but no net benefit in cold-start HC performance was realized. NOx benefits were shown in each case as cell densities increased, largely due to more effective contacting efficiency between the exhaust gas constituents and the active catalyst coating present on the walls of the substrate. Somewhat higher pressure drop of these substrates with increasing cell density may also have contributed to some reductions in engine-out NOx levels in certain driving modes due to increased levels of internal exhaust gas recirculation within the engine's combustion chambers.

Table 5. Metallic substrate properties for high cell density products [from Marsh et al. (2001)]

Cell Density (cpsi)	**600**	**800**	**1000**	**1200**	**1600**
Wall Thickness (mils)	**30**	**25**	**20**	**20**	**20**
Hydraulic Diameter (mm)	0.85	0.75	0.66	0.60	0.52
Geometric Surface Area (m^2/liter)	3.77	4.32	4.88	5.36	6.08
Thermal Mass (J/K)	689	681	641	680	750

Results like those shown in Figures 8 through 12 and the many other studies aimed at understanding the impacts of advanced substrate properties such as cell density, hydraulic diameter, and thermal mass have allowed researchers and design engineers to develop sophisticated mathematical models that accurately predict the performance of catalytic converters during vehicle operation including performance during the FTP test protocol (Leonhard et al. 2002; Aoki et al. 2002; Becker et al. 2001; Marsh et al. 2001; Lafyatis et al. 2000; Umehara et al. 2000). These models generally include mathematical descriptions of the heat and mass transfer processes that occur within catalytic converters. Becker et al. (2001) used a modeling approach to predict the emission performance of a variety of substrate types and designs. In their work they report that the catalytic performance of these substrates could be strongly correlated with key substrate physical properties: higher catalytic efficiency was proportional to substrate geometric surface area, and inversely proportional to bulk density and substrate channel hydraulic diameter.

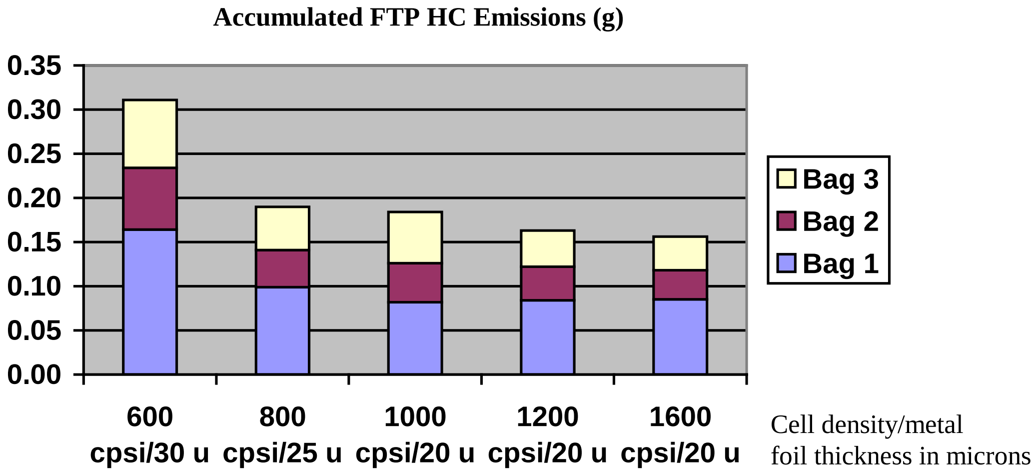


Figure 11. Accumulated FTP HC emissions for a three-way catalyst coated on high cell density metal substrates [see Marsh et al. (2001) for details].

Large geometric surface area in combination with small channel diameters provide good heat and mass transfer characteristics, while low substrate bulk density results in fast dynamic converter heat-up properties. In addition to cell density and wall thickness modifications, metal substrates have been developed and put into production that incorporate structural elements that help to promote turbulence and mixing within and/or between flow channels that promotes enhanced contacting efficiencies between the gas phase reactants and the active catalyst components that are coated on the substrate channel surfaces. The use of perforated metal foils in metal substrates also provides additional opportunities for reducing the thermal mass of the substrate.

The production of high cell density ceramic and metallic substrates is subject to the many quality system requirements of the auto industry. These advanced substrates are manufactured with precise specifications on all key fabrication parameters, resulting in only small variations in the key performance-related physical properties such as bulk density, cell density, and wall thickness. For example, ceramic monolith wall thickness typically varies by +/- 0.5 mils or less for nominal wall thickness in the 2-4 mil range. Similarly metal foil thickness in metal substrates varies by +/- 0.2 to 0.3 microns for foils in the 20-50 micron range.

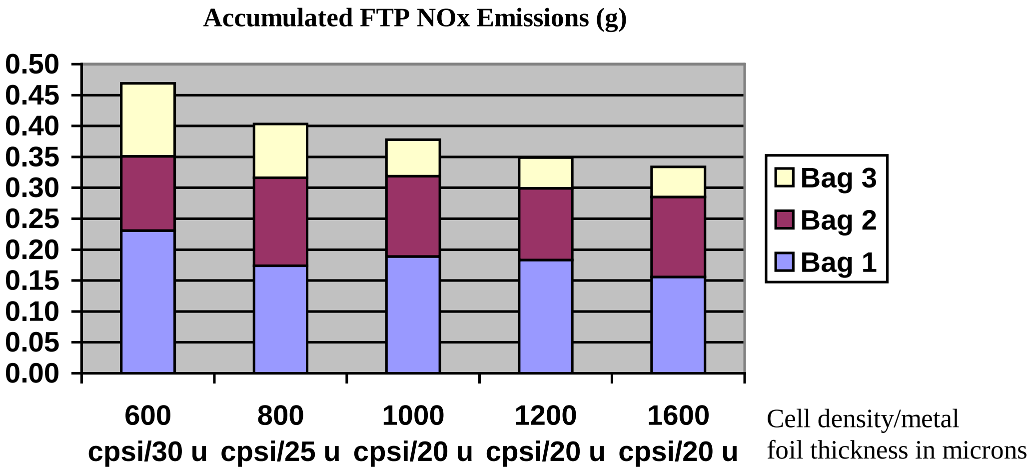


Figure 12. Accumulated FTP NOx emissions for a three-way catalyst coated on high cell density metal substrates [see Marsh et al. (2001) for details].

Cell densities in ceramic substrates are controlled by the precision die used in the extrusion process and process controls associated with the extrusion and firing operations. Cell densities in metal substrates are controlled by tight specifications on the process used to produce corrugated foils, as well as process controls on other key production operations. As an example, cell densities in metal substrates vary by +/- 5% for high cell density substrates ranging from 600 cpsi to 1600 cpsi. Modifications to traditional canning operations and mounting materials have also been developed for high cell density, thin wall ceramic substrates to ensure a mechanically robust, durable converter package. Similarly, the use of high cell density, thin wall metal substrates have re-engineered brazing strategies and matrix/mantle connection methods to maintain required mechanical durability for all light-duty vehicle applications. The methods of securing the catalyst honeycomb in the stainless steel housing with the support mat have undergone similar design evolution to minimize gap tolerances.

High cell density ceramic and metallic substrates are already seeing significant applications on gasoline vehicles that comply with the world's tougher emission standards like Tier 2, LEV II, Euro 4, and Euro 5. In major vehicle markets in the U.S., Europe, Japan, South Korea, and China substrates with cell densities of 600 cpsi and higher had market penetration rates of 50-70% in 2013. Tier 3, LEV III, and Euro 6 vehicle emission regulations will further drive applications of high cell density substrates with penetration rates forecast to reach 70-80% by 2020 in the major vehicle markets of the U.S., Europe, Japan, South Korea, and China.

3.3 Advanced Three-Way Catalysts

Three-way catalysts have traditionally relied on highly dispersed precious metals (Pt, Pd, Rh) supported on high surface area aluminum oxide with the addition of a variety of base metal oxide promoters and oxygen storage materials to provide the simultaneous HC and CO oxidation and NOx reduction behavior required in automotive emission control applications. Oxygen storage and release behavior of TWCs is an important functionality required to maintain acceptable performance during air/fuel perturbations that occur as a result of the closed loop air/fuel feedback control algorithm associated with oxygen sensors. Cerium oxide-based materials contained in TWC formulations have been the primary source of this oxygen storage behavior. Catalyst performance criteria associated with meeting the low emission requirements of Tier 2/3 or LEV II/III applications include maintaining high conversion efficiencies for all three criteria pollutants during all phases of vehicle operation (e.g., start phases, accelerations, decelerations, cruise conditions) for extended operational lifetimes (i.e., 150,000 mile durability). These demands for high conversion efficiencies and extended durability have evolved TWC formulations and design strategies significantly in the last fifteen years.

The interest in cold-start performance discussed with close-coupled converters previously puts emphasis on TWC light-off characteristics, especially with respect to HCs (light-off generally refers to the catalyst temperature required to achieve (>50%) significant conversion activity with respect to the pollutants of interest.). Pd-based TWCs (e.g., Pd-only, Pd/Rh, or Pt/Pd/Rh trimetallic catalyst formulations) became the preferred choice for close-coupled applications due to the inherent good HC light-off performance of Pd relative to Pt or Rh (Ohmoto et al. 2002; Truex et al. 2002; Williamson et al. 2001; Nagashima et al. 2000; Williamson et al. 2000; Waltner et. al. 1998). Close-coupled applications, also place a premium on catalyst thermal stability/durability since these close-coupled converters expose catalyst materials to significantly higher operating temperatures than temperatures associated with converters located in cooler, underfloor locations. This thermal durability requirement also placed attention on Pd-based close-coupled TWCs due to Pd's superior thermal stability compared to other precious metals. The thermal stability of other catalytic materials used in TWC formulations was equally important in meeting the demands of close-coupled catalysts. This need resulted in the concerted development of new catalyst materials such as stabilized aluminas (a support material for precious metals), stabilized cerias and zirconias (both are catalytic promoters and oxygen storage materials), and the development of more stable precious metal impregnation strategies that helped to push maximum catalyst operating temperatures from 800^{o}C to over 1000^{o}C over the last fifteen years. The longer durability requirements of Tier 2 and LEV II emission regulations, as well as the inclusion of heavier light-duty trucks with their relatively higher exhaust temperatures compared to passenger cars, contributed to this focus on improving TWC thermal stability.

TWCs with high conversion efficiencies and extended durability with respect to NOx (hydrocarbons and CO, as well) are additional important criteria of Tier 2 and LEV II emission systems. The need for high performance and extended durability catalysts influenced all aspects of catalyst design and the selection of materials used as supports, promoters, and oxygen storage materials. Enhancements in oxygen storage materials, in particular, have been a key element in pushing catalyst performance in advanced TWC formulations. New families of ceria-zirconia materials have been developed that provide higher capacities of thermally stable oxygen storage and release functionalities to TWCs (references include: Hirasawa et al. 2009; Rohart et al. 2007;

Kanazawa et al. 2003; Truex et al. 2002; Schmidt et al. 2001; Williamson et al. 2001; Williamson et al. 2000). Synergies between these new ceria-zirconia materials and the catalytically active precious metals have led to improvements in intrinsic catalyst light-off characteristics, broader three-way operating windows with respect to the simultaneous oxidation and reduction reactions as a function of inlet air/fuel ratio, and more highly dispersed and thermally stable precious metal activity. Figure 13 provides an example of TWC performance improvements with respect to NOx emissions stemming from the use of new materials like advanced ceria-zirconia-based oxygen storage materials (Williamson et al. 2001).

New high performance TWCs have also required the development of new precision substrate coating processes and equipment capable of producing and placing complex coating formulations on the interior walls of ceramic and metallic substrates (both standard and advanced high cell density substrates) in high volume production. These advanced catalyst formulations have also been tailored to be compatible with advanced high cell density substrates (Hughes et al. 2003; Schmidt et al. 2002; Domesle et al. 2001; Williamson et al. 2001; Williamson et al. 2000; Lafyatis et al. 2000). For example, the volume-based catalyst loading on a high cell density substrate must be balanced to provide required performance and durability characteristics without adversely affecting the overall thermal mass (and the resulting dynamic heat-up) and pressure drop characteristics of the coated substrate. Like substrate manufacturing processes, catalyst manufacturing processes must also be operated within the rigorous automotive industry quality control requirements. Catalyst formulation and coating specifications on all materials (precious metals, support materials, oxygen storage materials, etc.) minimizes physical and chemical variations between production parts and production lots of a given catalyst type.

New catalyst design strategies have also been developed to better tailor precious metal performance in advanced catalysts. A primary example of these tailored design strategies is the development of multi-layer catalyst coating architectures in which preferred precious metal functionalities and oxygen storage performance can be segregated to maximize performance and minimize unwanted negative interactions that may result by co-mingling certain catalyst materials (Aoki et al. 2011; Aoki et al. 2009; Ball et al. 2005, Schmidt et al. 2002; Ohmoto et al. 2002; Schmidt et al. 2001; Williamson et al. 2001; Nagashima et al. 2000; Lindner et al. 1996; Punke et al. 1995). For example, undesirable alloying of precious metals due to high temperature sintering phenomenon can be minimized by segregating precious metals in unique chemical layers in a multi-layer coating format. The process known as zone coating allows catalyst metals to be segregated within layers of coating, top or bottom, as well as within front and back portions of the same catalyst brick (Aoki et al. 2011).

An example of the performance improvements achieved by new multi-layer catalyst architectures is shown in Figure 14 (Lindner et al. 1996). These advanced catalyst materials and catalyst design strategies have cascaded through all TWC formulations (precious metal types including: Pd-only, Pd/Rh, Pt/Rh, and trimetal) and applications (close-coupled and underfloor converters) to deliver cost-effective high performance and durable catalysts required to meet the needs of Tier 2/3 and LEV II/III light-duty applications.

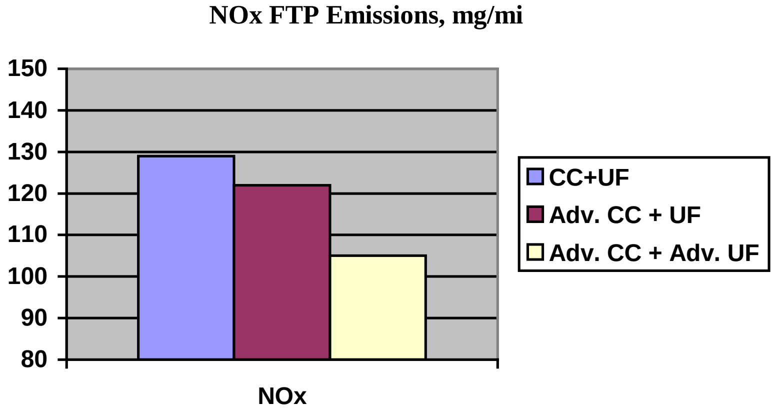


Figure 13. Impact of advanced catalyst formulations on NOx FTP emissions from a 5.3 liter, V8 test vehicle equipped with close-coupled (50 g/ft^3 Pd-only) + underfloor converters (30 g/ft^3 Pt/Rh=3/1) [see Williamson et al. (2001) for details].

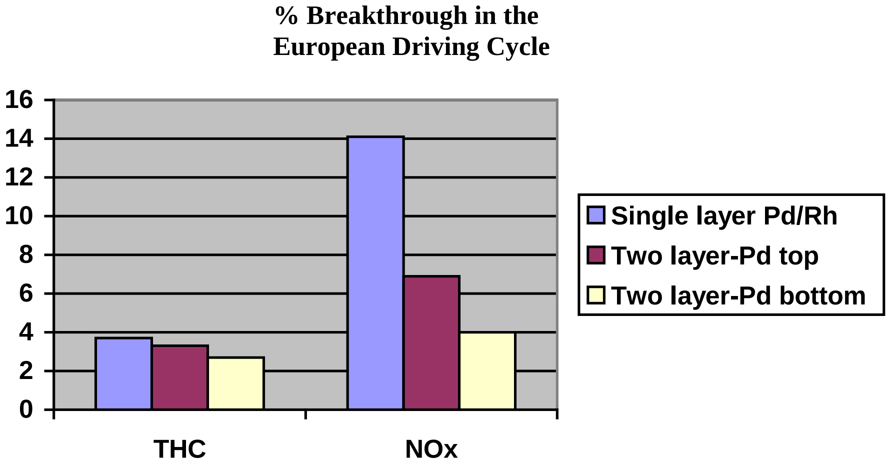


Figure 14. Impact of catalyst coating architecture (single layer vs. double layer) on total hydrocarbon (THC) and NOx performance of a Pd/Rh three-way catalyst (100 g/ft^3 total precious metal loading with Pd/Rh=5/1; 100 h aged catalyst on a 1.8 liter, 4 cylinder test vehicle; (see Lindner et al. (1996) for details).

The need to reduce cold-start hydrocarbon emissions for Tier 2/LEV II and future Tier 3/LEV III applications has also resulted in the development of hydrocarbon adsorber functions that can be added to three-way catalyst formulations or stand alone hydrocarbon adsorbers that are integrated into the exhaust system of light-duty vehicles that utilize three-way catalysts. Hydrocarbon adsorbers have seen only limited commercial applications on a few selected models of SULEV or PZEV-compliant vehicles thus far. In these applications, materials that can adsorb typical exhaust hydrocarbons at ambient temperatures and then desorb the hydrocarbons at elevated temperatures are used to capture hydrocarbon emissions during the cold-start phase of the emissions test cycle. When the hydrocarbons are desorbed later in the cycle, as the adsorber materials reaches its hydrocarbon desorption temperature(s), the desorbed hydrocarbons can be oxidized by available three-way catalysts (assuming that the catalyst has reached a temperature that facilitates hydrocarbon oxidation). Synthetic zeolites have been the hydrocarbon adsorber material of choice for automotive applications. In some cases the adsorber can utilize a mixture of zeolites in order to broaden the hydrocarbon capturing efficiency of the adsorber relative to the range of hydrocarbons that are associated with automotive exhaust gas. Zeolite properties such as silica/alumina ratio, crystal structure, the presence and composition of exchanged cations, and zeolite pore size have been shown to impact the specific adsorption capacity and desorption properties of a zeolite relative to the hydrocarbon species present in the exhaust (Mukai et al. 2004; Kanazawa and Sakurai 2001; Goralski et al. 2000). A precious metal catalyst can be incorporated into the zeolite to facilitate HC oxidation during desorption. A key design property for maximizing the impact of a hydrocarbon adsorber on cold-start hydrocarbon emissions is the overlap of the desorption temperature with the onset of catalyst hydrocarbon oxidation activity over the whole regulated durability timeframe of the emissions system (e.g., 120,000 or 150,000 miles). Recent work using novel zeolites together with dual coating technology has revealed that short chain hydrocarbons can oligomerize within an acidic zeolite to heavier hydrocarbons and be retained in the trap to higher temperatures for effective oxidation over a TWC over layer (Nunan et al. 2013).

A zeolite adsorber layer has been added to commercial three-way catalyst formulations that are displayed in underfloor converters to reduce cold-start hydrocarbon emissions (Inoue and Mitsuishi 2009; Lupescu et al. 2009; Oguma et al. 2003; Ballinger and Andersen 2002). In this configuration the ceramic or metallic monolith is coated with successive layers of the zeolite-based adsorber material and the three-way catalyst formulation to form an integrated, multi-functional converter. In another commercial application (Inoue et al. 2000), the underfloor hydrocarbon adsorber material is physically separated from the underfloor three-way catalyst and an exhaust valving arrangement is used to first direct the bulk of the cold exhaust through the adsorber-containing monolith. Once the close-coupled three-way converter has reached catalyst light-off temperatures, the exhaust valve is opened to allow flow through the underfloor three-way converter. As this converter warms-up, heat is transferred to the adsorber function (located in an outer annulus of the underfloor converter) and hydrocarbons are desorbed and directed into the underfloor converter for conversion via a catalyzed hydrocarbon oxidation reaction.

To achieve the full performance benefits of these advanced catalyst/advanced substrate combinations for Tier 2 and LEV II applications, it has also been necessary to develop improved engine operating algorithms that more closely match inlet catalyst conditions with the optimal operating window of the catalyst in order to maximize catalyst efficiency for all three criteria pollutants. The discussion on close-coupled converters included the development of cold-start engine operating strategies that accelerate converter heat-up during the crucial cold-start process. Similarly with respect to NOx emissions, tighter air/fuel control strategies during all modes of vehicle operation (especially high NOx emission modes associated with vehicle accelerations and decelerations) have been developed to achieve the low NOx emission requirements of the Tier 2 and LEV II programs. Precise air/fuel control strategies balance the relative concentration of oxidants and reductants in the exhaust stream within the catalyst's preferred operating window under highly dynamic vehicle operations. Similarly, vehicle calibrators can make use of exhaust gas recirculation (EGR) strategies to minimize engine-out NOx levels during some vehicle operating modes and maximize emission system performance. These EGR calibration strategies may involve either internal EGR calibrations through changes in exhaust valve lift or timing characteristics or external EGR calibrations through changes in the duty cycle of an external EGR valve during certain portions of a given driving cycle.

Cold-start performance of catalysts and thermal management strategies are even more critical in mild and full hybrid powertrains employing start-stop technology and parallel hybrid systems. Balancing engine and electric motor operation and periodic shut-down strategies employed by hybrid powertrains provides additional opportunities for catalysts to cool down below their light-off temperatures. Therefore retaining heat within the catalyst during brief engine shut-down and rapid warm-up calibrations are approaches that vehicle manufactures and catalyst developers must consider when incorporating hybrid technology into their fleet. The interaction and optimization of engine controls and emission control technology is a necessary part of the overall systems approach and integration required in meeting Tier 2/LEV II low NOx emission goals on light-duty vehicles. These same approaches will be important for achieving LEV III/Tier 3 emission goals across the entire range of vehicle classes.

Starting in 2017 and beyond, under the next round of criteria pollutant tailpipe standards, vehicle manufacturers will have to also consider the greenhouse gas emissions of the vehicle and CO_2 limits established by U.S. EPA, NHTSA and ARB as part of the 2017-2025 light-duty GHG standards. Implicit in EPA and ARB greenhouse gas emission analyses is the ability of advanced powertrain options to meet the applicable criteria pollutant emission standards. Vehicle manufacturers must combine advanced, light-duty powertrains with the appropriately designed and optimized emission control technologies to meet LEV III and future Tier 3 criteria emission requirements. The use of advanced emission controls for criteria pollutants enable advanced powertrains to also achieve lower greenhouse gas emissions. The range of powertrain technologies include; engine turbochargers, exhaust gas recirculation systems, advanced fuel systems, variable valve actuation technology, advanced transmissions, hybrid powertrain components, and powertrain control modules and can be applied to both light-duty gasoline and diesel powertrains to help improve overall vehicle efficiencies, and lower CO_2 exhaust emissions. In many cases, the application and optimization of advanced emission control technologies on advanced powertrains can be achieved with minimal impacts on overall fuel consumption. Auto manufacturers will also take advantage of synergies between advanced emission control technologies and advanced powertrains to assist in their efforts to optimize their performance with respect to both greenhouse gas and criteria pollutant exhaust emissions.

Vehicle manufacturers will utilize a portfolio of powertrain designs in meeting their fleet average GHG standards. Light-duty diesel powertrains will continue to use emission control technologies like diesel particulate filters, NOx adsorber catalysts, and selective catalytic reduction catalysts to meet EPA's light-duty exhaust emission standards. Advanced diesel emission control technologies like particulate filters, with lower backpressure characteristics, SCR catalysts with improved performance at lower exhaust temperatures, passive NOx adsorbers that trap NOx prior to light-off of the SCR and SCR catalyst coated directly on particulate filter substrates are examples of emerging diesel emission control technologies that will be an important component of the overall fleet mix to allow manufacturers to meet fleet average SULEV tailpipe standards while delivering improved fuel consumption characteristics and lower greenhouse gas emissions. Several demonstrations of SULEV emission limits from diesel engines utilizing advanced diesel emission controls have been reported (Henry, 2012 and Cooper, 2009).

For gasoline vehicles, direct injection technology enables spark-ignited (SI) engines to achieve greater fuel efficiency and is becoming a dominant pathway to meeting future light-duty greenhouse gas emission standards. Under stoichiometric conditions, three-way catalysts are used to achieve ultra-low emissions of NOx, HC and CO. GDI engines can emit higher levels of PM than conventional port fuel injected engines especially during higher speed-load operation. Gasoline particulate filters (GPFs), based on the wall flow filter technology employed in diesel particulate filters (DPFs), are one of the approaches to meet stringent LEV III/Tier 3 PM limits. The performance of GPFs on GDI vehicles is discussed in greater detail in Section 3.4.

Under lean combustion conditions, similar emission control technologies used on diesel vehicles can be used to reduce emissions from lean, gasoline direct injection powertrains. These include particulate filters to reduce PM emissions, and SCR and/or lean NOx adsorber catalysts to reduce NOx emissions. Lean NOx adsorber catalyst performance has a high degree of sensitivity to fuel sulfur levels (see Section 3.3.1). Some vehicle manufacturers have reported on novel approaches to achieving low NOx emissions from lean-burn SI engines that utilize a TWC to reduce NOx and generate ammonia during periodic stoichiometric to rich excursions in combination with a downstream SCR that stores ammonia for the reduction of NOx during lean operating modes (Kim, 2011).

3.3.1 Impacts of Gasoline Fuel Sulfur on TWC Performance

Sulfur in gasoline or diesel fuel inhibits the emission control performance of various emission control technologies. Sulfur adsorbs to the surface of the catalysts and competes for catalytically active sites with exhaust pollutants. A summary of sulfur impacts on emission control technologies can be found on the MECA website (http://www.meca.org/galleries/default-file/fuelsfact%200811%20FINAL.pdf) and a more detailed discussion is included in MECA's gasoline sulfur white paper titled: "The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems" (http://www.meca.org/galleries/default-file/sulfur.pdf). 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 (e.g., see Hochhauser, CRC E-84 report, 2008 and Thoss, 1997).

Lubricant constituents such as phosphorus and inorganic elements such as Zn and Ca have also been shown to act as catalyst poisons or catalyst masking agents driving lubricant producers to optimize lubricant formulations to insure adequate engine lubrication characteristics with minimal impacts on catalyst performance and driving engine designers to minimize engine oil consumption characteristics of advanced engines (Darr et al., 2000). Clean fuels and clean lubricants are a necessary pre-requisite for maintaining the high performance levels of the advanced engine and emission systems required for Tier 2/LEV II compliance, as well as future compliance with Tier 3/LEV III emission limits.

A recently published study (Ball, Clark, and Moser 2011) shows sulfur inhibition for a 2009 model year Chevrolet Malibu certified to the PZEV emissions level or SULEV tailpipe limits. The vehicle's three-way catalysts were aged on a dynamometer to a full useful life of 150,000 miles and tested over the FTP test cycle using very low fuel sulfur gasoline levels of 33 ppm and 3 ppm sulfur. NOx FTP emissions were measured following various driving cycle pretreatments including the low exhaust temperature (<600 °C) LA4 and higher exhaust temperature (700-750 °C) US06 test cycles. 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. The emissions impact of the 33 ppm sulfur fuel included higher overall NOx FTP levels and greater test-to-test variability (i.e., increasing NOx emissions with each subsequent FTP test cycle). Most of the negative impact of the higher sulfur fuel could be recovered by exposing the catalysts to higher exhaust temperatures experienced during higher speed driving over the US06 test cycle. The use of the 3 ppm sulfur fuel eliminated the negative effect of sulfur on the NOx emissions from this vehicle (see Figure 15 below).

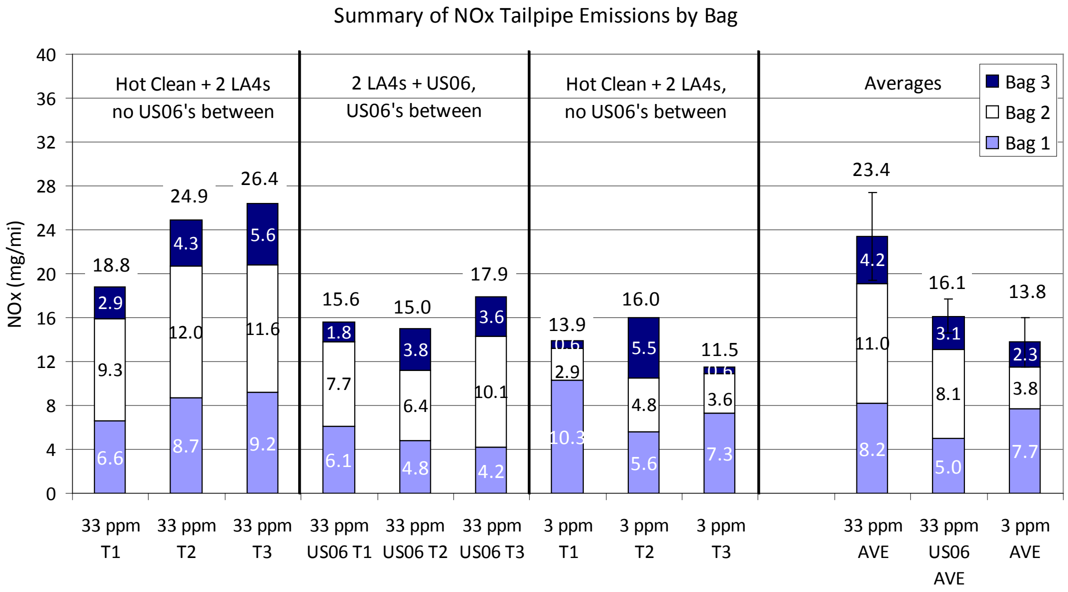


Figure 15. PZEV Chevy Malibu FTP-NOx performance using two different fuel sulfur levels and vehicle preparation test cycles (Ball et al., 2011).

Higher fuel sulfur levels can impact the performance of advanced gasoline emission control technologies such as NOx adsorber catalysts used on diesel and lean GDI applications. In these types of applications, the sulfur in the form of SO_3 is adsorbed to the same sites that capture NO_2. Because sulfur adsorbs more strongly to these sites, the temperatures typically used to regenerate the catalyst, by desorbing nitrates, are not sufficient to remove the sulfates and much higher temperatures are needed to desulfate the catalyst. Over time these high temperature desulfation events deteriorate the overall performance of the NOx trap leading to higher NOx emissions (Takei, 2001).

3.4 Gasoline Particulate Filters

The emerging interest and growing number of regulatory programs associated with reducing greenhouse gas emissions from motor vehicles (and improving vehicle fuel economy), has put significant attention on developing and commercializing gasoline direct injection (GDI) technology. This gasoline engine platform has combustion characteristics that parallel diesel engines that use direct fuel injection strategies, and provides lower fuel consumption compared to port injected gasoline engines that have been the dominant stoichiometric, gasoline engine technology on light-duty vehicles for more than a decade. Compared to port fuel injected gasoline engines, the initial wave of commercial GDI engines introduced in the 2005-2011 timeframe have been shown to produce higher levels of particulates under typical emission test cycle conditions (e.g., the U.S. EPA FTP cycle). Future U.S. and European light-duty emission standards (e.g., LEV III, Tier 3, Euro 6) are expected to lower PM emission requirements for some or all classes of gasoline vehicles. As a result of this interest in lower PM emission levels, emission control technology developers and auto manufacturers have begun to assess the feasibility of using gasoline particulate filters (GPFs) on future GDI engines. A number of recent references (Saito et al. 2011; Eakle, Zahn, and Weber 2010; Mikulic et al. 2010) are available that describe the development and performance of first generation GPFs on GDI vehicles. The filter technology base is drawn from the large experience base with diesel particulate filters (DPFs) based on wall-flow filter technology. In these recent references GPFs have been evaluated on GDI vehicles with and without a three-way catalyst coating present on the wall-flow ceramic filter. Like DPFs, the wall porosity of the GPFs can be adjusted to modify the press drop and catalyst coating capacity of the filter. Like DPFs, wall-flow GPFs are capable of large reductions (> 90%) of particulate emissions across a very broad range in particle size. Vehicle and engine manufacturers are also evaluating improved fuel injection strategies and other improvements to engine combustion parameters as a way of reducing particulate emissions from GDI engines. Some of these strategies may include; air/fuel ratio, injection timing, number of injections, injection pressure and combustion phasing. The topic of particulate emission from gasoline direct injection engines is expected to grow in interest in the coming decade as more work is done to understand the health impacts of ultrafine particulates.

4.0 MECA Large Light-Duty Truck Test Programs

In anticipation of future LEV III regulations that would tighten tailpipe emissions from the larger vehicles in the light-duty fleet, MECA conducted a test program in the 2005-2006 timeframe to test the potential for achieving ultra-low HC and NOx emissions from large light-duty gasoline vehicles such as SUVs and pick-up trucks (Anthony et al. 2007). The goal of the program was to select two, heavy light-duty LDT3/LDT4 vehicles, apply advanced emission control technologies, and integrate the emission control technologies with the engines to demonstrate the potential for achieving ultra-low hydrocarbon and NOx emission levels on large, heavier light-duty vehicles.

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 configurations. These advanced emission system designs incorporated three-way catalyst formulations, ceramic substrate designs, and exhaust components that are commercially available and are consistent with advanced emission system designs used to achieve ultra-low exhaust emissions on smaller, light-duty vehicles including four, five and six-cylinder passenger cars certified to California's SULEV emission standards.

Although some degradation in emission performance was observed for both advanced systems following the 220 hours of engine aging, it is important to note that in most cases these aged, advanced systems demonstrated high conversion efficiency for hydrocarbons and NOx. Aged catalyst efficiencies on the Denali were 99+ percent for NOx for all FTP phases, while hydrocarbon and CO aged catalyst efficiencies remained above 92 percent in the cold-start phase of the FTP (Bag 1), and greater than 96 percent efficiency in the stabilized (Bag 2) and hot-start (Bag 3) phases of the driving cycle. The engine-aged, advanced emission systems of both vehicles produced ultra-low hydrocarbon and NOx emissions at exhaust levels significantly below California's 120,000 mile LEV II ULEV emission standards.

In support of the EPA Tier 3 rulemaking activity, MECA participated in an EPA large light-duty truck demonstration program that utilized a 2011 Chevrolet Silverado full-sized pick-up equipped with a 5.3 liter V8. The engine included GM's cylinder deactivation technology for improved fuel economy. MECA supplied EPA with an advanced emission system designed for the Silverado that featured close-coupled converters that utilized 900 cpsi high cell density ceramic substrates coated with an advanced Pd/Rh catalyst technology. A single underfloor converter with an advanced Pd/Rh catalyst followed the close-coupled converters in this emissions systems. Following engine-aging of the advanced emission system to the equivalent of 150K miles of service, the test truck demonstrated FTP emissions of 18 mg/mile NMOG+NOx, emission performance consistent with meeting the Tier 3, Bin 30 standard (or SULEV30 standard) with a reasonable compliance margin. Some minor engine calibration modifications were also done to the test truck to improve cold-start emission performance (additional engine spark retard and increased engine idle during cold-start). Results from this EPA light-duty truck test program were included in the final Tier 3 regulatory documents (see Ref. 4).

Achieving ultra-low emissions on heavy, light-duty vehicles like the three used in these programs, are achievable using a systems approach that includes advanced engine controls and advanced emission system designs. These programs achieved these low exhaust emissions primarily through advanced emission system designs and relatively, straight-forward engine calibration strategies. Other system parameters not evaluated as a part of these programs, can also be further optimized on large, light-duty vehicles and provide additional opportunities for further emission reductions from such vehicles. These additional system options include more effective exhaust thermal management strategies such as lighter-weight exhaust manifolds, more sophisticated air-fuel control strategies, and more advanced fuel injection systems that help facilitate lean cold-start strategies. In some cases some engine-based system strategies may focus more on reducing engine-out emissions as part of an overall systems approach to achieving ultra-low exhaust emissions. Given the large engine-out emission profiles associated with large displacement engines, manufacturers are likely to employ combinations of optimized engine-based and emission system strategies to achieve future LEV III/Tier 3 standards.

5.0 MECA/Environment Canada GDI-GPF Test Program

Although the basic design of GPFs and DPFs may be similar, their performance may be different due to the differences between gasoline and diesel exhaust and PM characteristics. To better understand how PM characteristics might influence the particle filtration efficiency of a GPF, MECA partnered with researchers at Environment Canada to characterize the PM from a modern GDI (2011 Hyundai Sonata) and PFI (2010 Volvo S40) vehicle. The PM emissions from the stock vehicle were compared to the GDI vehicle fitted with an uncatalyzed GPF in the underfloor position just downstream of the OEM TWC (Chan et al., 2013). The GPF was a cordierite filter substrate with a cell density of 200 cpsi and a 12 mil wall thickness. The study characterized the gaseous criteria emissions, particle size distribution and particle number emission rates over the FTP-75 and US06 test cycles at ambient temperatures that ranged from -18 ^{o}C to 22 ^{o}C. The vehicles were tested using both E0 and E10 fuels.

A summary of the PM results from these two vehicles is shown in Figure 16 over the FTP-75 test cycle and Figure 17 for the higher speed US06 cycle under normal ambient testing temperatures. The PM measurements in the figures compare two different measurement techniques, the European PMP method and measurements using an Ultrafine Condensation Particle Counter (UCPC). The PMP technique only measures solid particles greater than 23 nm after a Volatile Particle Remover (VPR) is used to remove volatile species above 300 ^{o}C. The UCPC technique was also used in combination with the VPR to remove volatile species to allow a same basis comparison between the techniques. The UCPC instrument measured particles down to 5 nm to characterize the size distribution of particles in the ultrafine size range. A quick look at the data in the figures shows that the GDI vehicle emits many more particles per mile than the PFI vehicle for both fuel types and test cycles. Furthermore, a comparison of the PMP and UCPC results shows that both vehicles emit a significant number of solid, ultrafine particles that are less than 23 nm. The incorporation of the GPF into the exhaust system brought the PM number emissions from the GDI vehicle into the range of the PFI over the FTP cycle. The particle number emissions as measured by the PMP over the higher speed US06 cycle were lower for both the GDI and PFI with significant ultrafine particles shown by the UCPC method. Although the filtration efficiencies for this GPF were about 80% over both test cycles, they were slightly lower over the higher speed cycle. This was found to result from higher exhaust temperatures regenerating the soot filtration layer during the US06 test cycle. This was confirmed in further testing that showed the filtration efficiency gradually increasing in subsequent cold-start LA4 cycles as the soot filtration layer was allowed to build up without passive regeneration.

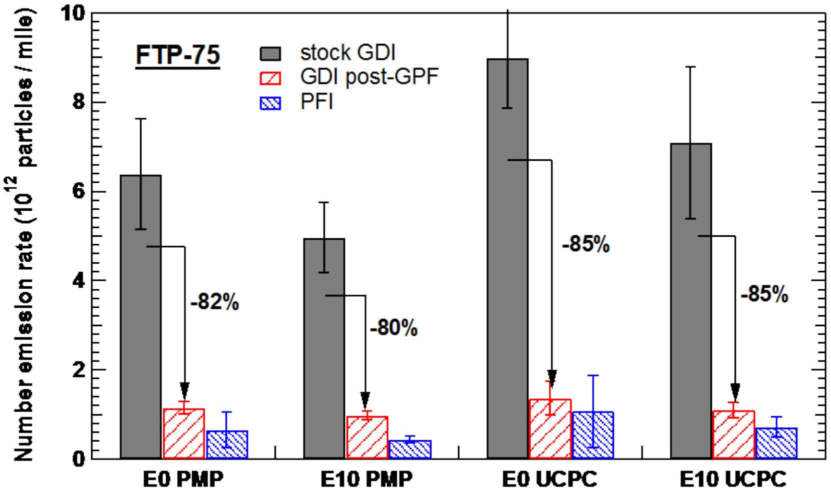


Figure 16. Particle number emissions from the GDI and PFI vehicles operated on gasoline and 10% ethanol over the FTP-75 test cycle. Arrows indicate the average filtration efficiency.

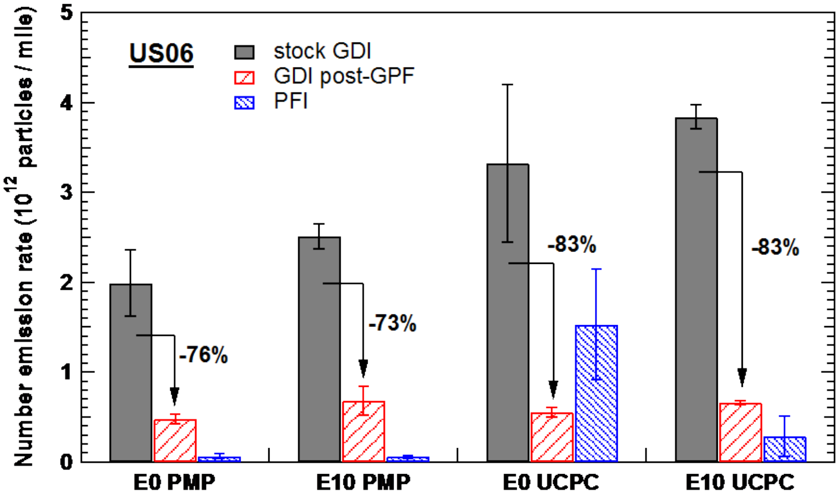


Figure 17. Particle number emissions from the GDI and PFI vehicles operated on gasoline and 10% ethanol over the US06 test cycle. Arrows indicate the average filtration efficiency.

The PM characterization also semi-quantitatively examined the composition of ash particles with and without a GPF. Metal oxide ash is typically made up of ultrafine particles in the 10-15 nm size range. Some studies have suggested that the combination of their small physical size and chemical nature of these metal oxide nanoparticles may make them more cytotoxic than diesel soot particles (Mayer et al., 2010 & 2012). Although the mass emissions of metal oxide particles was relatively low for both vehicles over the FTP cycle (< 5 µg/mile). It increased substantially over the higher speed US06 cycle. The GPF demonstrated a high capture efficiency for ultrafine metal oxide particles (80-95% capture efficiency observed).

6.0 Conclusions

The EPA Tier 2 and California LEV II light-duty programs established demanding emission compliance goals for the full range of light-duty cars and trucks sold across the United States starting with the 2004 model year. Included in these goals were super ultralow emission vehicle categories such as SULEV and Tier 2, Bin 2 with significantly lower hydrocarbon and NOx emission levels and PZEV with extended durability requirements within the light-duty segment. Advanced emission control technologies have been developed and used to achieve the emission limits established for these tightest emission categories. SULEV vehicles under LEV II employed heavy use of technologies such as; close-coupled converters, high cell density substrates, advanced three-way catalysts, and other advanced exhaust system components to achieve the fast converter light-off and high conversion efficiencies under all dynamic vehicle operating modes necessary for achieving extremely low emission levels. The performance of these advanced emission technologies depends strongly on integrating and optimizing their operation with other key engine combustion technologies in advanced engines, such as advanced engine operating strategies, clean fuels, and clean lubricants. This systems approach is the hallmark of bringing the entire fleet of light-duty vehicles into the age of super ultra-low emissions in 2025 as required by LEV III and Tier 3. The fact that motor vehicle and emission control manufacturers worldwide are pursuing the system strategies highlighted in this paper is compelling evidence that they represent the most cost effective, technically sound approach to meeting the very stringent LEV III and Tier 3 emission standards of the future.

References

The references included here provide a comprehensive list of SAE (Society of Automotive Engineers) technical papers published over the past twenty years that discuss the characteristics and performance of the key Tier 3/LEV III advanced emission control technologies highlighted in this paper (close-coupled converters, high cell density substrates, advanced three-way catalysts). The reference list is organized by year of publication, with 2003 papers listed first followed by successively later publication years. Details of the MECA light-duty truck test program discussed in Section 4.0 of this report can be found in SAE paper 2007-01-1261. Details of the MECA/Environment Canada gasoline particulate filter test program discussed in Section 5.0 of this report can be found in SAE paper 2013-01-0527.

1. CARB Advanced Clean Car Regulations: http://www.arb.ca.gov/msprog/consumer_info/advanced_clean_cars/consumer_acc.htm
2. CARB LEV III Low Emission Vehicle Program: http://www.arb.ca.gov/msprog/levprog/leviii/leviii.htm
3. CARB Zero Emission Vehicle regulation: http://www.arb.ca.gov/msprog/zevprog/zevprog.htm
4. U.S. EPA Final Tier 3 Motor Vehicle Emission and Fuel Standards: http://www.epa.gov/otaq/tier3.htm
5. Anthony, J. and Kubsh, J. (2007) The potential for achieving low hydrocarbon and NOx exhaust emissions from large light-duty gasoline vehicles, SAE paper no. 2007-01-1261, 2007 SAE International Congress, Detroit.
6. Aoki, Y., Sakagami, S., Kawai, M., Takahashi, N., Tanabe, T., and Sunada, T. (2011) Development of advanced zone-coated three-way catalysts, SAE paper no. 2011-01-0296, SAE 2011 International Congress, Detroit.
7. Aoki, Y., Yoshida, T., Tanabe, T., Hatanaka, M., Nagai, Y., Sakagami, S., and Shimizu, M. (2009) Development of double-layered three-way catalysts, SAE paper no. 2009-01-1081, 2009 SAE International Congress, Detroit.
8. Aoki, Y., Miyairi, Y., Ichikawa, Y., and Abe, F. (2002) Product design and development of ultra-thin wall ceramic catalytic substrate, SAE paper no. 2002-01-0350, SAE 2002 International Congress, Detroit.
9. Ball, D. and Moser, D. (2012) Cold start calibration of current PZEV vehicles and the impact of LEV III emission regulations, SAE paper no. 2012-01-1245, SAE 2012 International Congress, Detroit.
10. Ball, D., Clark, D., and Moser, D. (2011) Effects of fuel sulfur on FTP NOx from a PZEV 4 cylinder application, SAE paper no. 2011-01-0300, SAE 2011 International Congress, Detroit.
11. Ball, D., Nunan, J., Blosser, P., Wilson, J., Mitchell, G., Davis, S., and Zammit, M. (2005) Flexmetal catalyst technologies, SAE paper no. 2005-01-1111, 2005 SAE International Congress, Detroit.
12. Ballinger, T. and Andersen, P. (2002) Vehicle comparison of advanced three-way catalysts and hydrocarbon trap catalysts, SAE paper no. 2002-01-0730, SAE 2002 International Congress, Detroit.
13. Becker, R., Wilson, R., Brayer, M., Vogt, C., and Makino, M. (2001) Prediction of catalytic performance during light-off phase with different wall thickness, cell density, and cell shape, SAE paper no. 2001-01-0930, SAE 2001 International Congress, Detroit.
14. Brueck, R., Mueller-Haas, K., Breuer, J., and Webb, C. (2002) Advanced performance of metallic converter systems demonstrated on a production V8 engine, SAE paper no. 2002-01-0347, SAE 2002 International Congress, Detroit.
15. Brueck, R., Kaiser, F., Konieczny, R., Webb, C., and Anderson, A. (2001) Study of modern application

strategies for catalytic aftertreatment demonstrated on a production V6 engine, SAE paper no. 2001-01-0925, SAE 2001 International Congress, Detroit.

16. Chan, T., Meloche, E., Kubsh, J., Brezny, R., Rosenblatt, D. and Rideout, G., (2013) Impact of ambient temperature on gaseous and particle emissions from a direct injection gasoline vehicle and its implication on particle filtration, SAE paper no. 2013-01-0527, SAE 2013 International Congress, Detroit.
17. Cooper, B., Diesel passenger car technology for low emissions and CO_2 compliance, Diesel Engine and Emissions Research Conference (DEER), 2009.
18. Darr, S., Chokso, R., Hubbard, C., Johnson, M., and McCabe, R. (2000) Effects of oil-derived contaminants on emissions from TWC-equipped vehicles, SAE Technical Paper 2000-01-1881, 2000.
19. Domesle, R., Lindner, D., Mueller, W., Mussmann, L., Votsmeier, M., Lox, E., Kreuzer, T., Makino, M., and Vogt, C. (2001) Application of advanced three-way catalyst technologies on high cell density ultra-thin wall ceramic substrates for future emission legislations, SAE paper no. 2001-01-0924, SAE 2001 International Congress, Detroit.
20. Eakle, S., Zahn, R., and Weber, P. (2010) Simultaneous reduction of PM, HC, CO, and NOx from a GDI engine, SAE paper no. 2010-01-0365, SAE 2010 International Congress, Detroit.
21. Ehmann, P., Rippert, N., Umehara, K., and Vogt, C. (1999) The development of a BMW catalyst concept for LEV/EU3 legislation for a 8 cylinder engine by using thin wall ceramic substrates, SAE paper no. 1999-01-0767, SAE 1999 International Congress, Detroit.
22. Henry, C., Advanced technology light-duty diesel aftertreatment system for meeting future emission requirements, Directions in Engine-Efficiency and Emissions Research Conference (DEER), 2012.
23. Hirasawa, Y., Katoh, K., Yamada, T., and Kohara, A. (2009) Study on new characteristic CeO_2-ZrO_2 based material for advanced TWC, SAE paper no. 2009-01-1078, 2009 SAE International Congress, Detroit.
24. Hochhauser, A.M., Review of prior studies of fuel effects on vehicle emissions, Coordinating Research Report, CRC-84, August 2008 (www.crcao.org).
25. Holy, G., Brueck, R., and Hirth, P. (2000) Improved catalyst systems for SULEV legislation: first practical experience, SAE paper no. 2000-01-0500, SAE 2000 International Congress, Detroit.
26. Hughes, K., Schmitz, K., Radke, D., Zerafa, K., and Light, B. (2003) Impact of ultra-thin wall catalyst substrates for Tier 2 emission standards, SAE paper no. 2003-01-0658, SAE 2003 International Congress, Detroit.
27. Hughes, K. and Witte, W. (2002) Ultra-thin wall substrates – trends for performance in FTP and US06 tests, SAE paper no. 2002-02-0356, SAE 2002 International Congress, Detroit.
28. Inoue, T., Kusada, M., Kanai, H., Hino, S., and Hyodo, Y. (2000) Improvement of a highly efficient hybrid vehicle and integrating super low emissions, SAE paper no. 2000-01-2930, SAE 2000 Fall Fuels & Lubricants Meeting, Baltimore.
29. Kanazawa, T., Suzuki, J., Takada, T., Suzuki, T., Morikawa, A., Suda, A., Sobukawa, H., and Sugiura, M. (2003) Development of three-way catalyst using composite alumina-ceria-zirconia, SAE paper no. 2003-01-0811, SAE 2003 International Congress, Detroit.
30. Kanazawa, T. and Sakurai, K. (2001) Development of the automotive exhaust hydrocarbon adsorbent, SAE paper no. 2001-01-0660, SAE 2001 International Congress, Detroit.
31. Kidokoro, T., Hoshi, K., Hiraku, K. Satoya, K., Watanabe, T., Fujiwara, T., and Suzuki, H. (2007) Development of PZEV exhaust emission control system, SAE paper no. 2003-01-0817, SAE 2003 International Congress, Detroit.
32. Kim, C.H., Perry, K., Viola, M., Li, W., and Narayanaswamy, K. (2011) Three-way catalyst design for urealess passive ammonia SCR: lean-burn SIDI aftertreatment, SAE Paper No. 2011-01-0306, SAE 2011 International Congress, Detroit.
33. Lafyatis, D., Will, N., Martin, A., Rieck, J., Cox, J., and Evans, J. (2000) Use of high cell density substrates and high technology catalysts to significantly reduce vehicle emissions, SAE paper no. 2000-01-

0502, SAE 2000 International Congress, Detroit.

34. Laurell, M., Dahlgren, J., and Vaisanen, J. (2007) The Volvo S40/V50 PZEV MY 2007 with an optimized 2.4l engine, SAE paper no. 2007-01-1260, 2007 SAE International Congress, Detroit.
35. Leonhard, T., Floerchinger, P., Degen, A., Held, W., Hinze, S., and Pott, E. (2002) Effect of cell geometry on emissions performance of ceramic catalytic converters, SAE paper no. 2002-01-0354, SAE 2002 International Congress, Detroit.
36. Lindner, D., Lox, E., van Yperen, R., Ostgathe, K., and Kreuzer, T. (1996) Reduction of exhaust gas emissions by using Pd-based three-way catalysts, SAE paper no. 960802, SAE 1996 International Congress, Detroit.
37. Lupescu, J., Chanko, T., Richert, J., and DeVries, J. (2009): Treatment of vehicle emissions from the combustion of E85 and gasoline with catalyzed hydrocarbon traps, SAE paper no. 2009-01-1080, 2009 SAE International Congress, Detroit.
38. Marsh, P., Acke, F., Konieczny, R., Brueck, R., and Hirth, P. (2001) Application guideline to define a catalyst layout for maximum catalytic efficiency, SAE paper no. 2001-01-0929, SAE 2001 International Congress, Detroit.
39. Matsuzono, Y., Iwamoto, T., Narishige, T., Hirota, T., Yamada, T., Tanikawa, K., Komori, M., Zhang, G., and Muraki, H. (2008) Advanced washcoat technology for PZEV application, SAE paper no. 2008-01-0812, 2008 SAE International Congress, Detroit.
40. Matsuzono, Y., Sakanushi, M., and Kitagawa, H. (2003) Development of a low precious-metal automotive perovskite catalytic system for LEV-II, SAE paper no. 2003-01-0814, SAE 2003 International Congress, Detroit.
41. Mayer, A., Czerwinski, J., Kasper, M., Ulrich, A., Mooney, J.J. (2012) Metal oxide particle emissions from diesel and petrol engines, SAE Paper number 2012-01-0841, SAE 2012 International Congress, Detroit.
42. Mayer, A.C., Ulrich, A., Czerwinski, J., Mooney, J.J. (2010) Metal oxide particles in combustion engine exhaust, SAE Paper number 2010-01-0792, SAE 2010 International Congress, Detroit.
43. Mikulic, I., Koelman, H., Majkowski, S., and Vosejpka, P. (2010) A study about particle filter application on a state-of-the-art homogeneous turbocharged 2L DI gasoline engine, 2010 FEV Aachen Colloquium, Aachen, Germany.
44. Moore, W., Richmond, R., Vaneman, G., and Dou, D. (1999) Evaluation of high cell density substrates for advanced catalytic converter emissions control, SAE paper no. 1999-01-3630, SAE 1999 Fall Fuels & Lubricants Meeting, Toronto, Canada.
45. Mueller-Haas, K., Brueck, R., Rieck, J., Webb, C., and Shaw, K. (2003) FTP and US06 performance of advanced high cell density metallic substrates as a function of varying air/fuel modulation, SAE paper no. 2003-01-0819, SAE 2003 International Congress, Detroit.
46. Mukai, K., Kanesaka, H., Akama, H., and Ikeda, T. (2004) Adsorption and desorption characteristics of the adsorber to control the HC emission from a gasoline engine, SAE paper no. 2004-01-2983, 2004 SAE Powertrain & Fluid Systems Conference, Tampa.
47. Nagashima, K., Zhang, G., Hirota, T., and Muraki, H. (2000) The effect of aging temperature on catalyst performance of Pt/Rh and Pd/Rh TWCs, SAE paper no. 2000-01-1954, SAE 2000 Spring Fuels & Lubricants Meeting, Paris, France.
48. Nunan, J., Lupescu, J., Denison, G., Ball, D., Moser D. (2013) HC traps for gasoline and ethanol applications, SAE Paper Number 2013-01-1297, SAE 2013 International Congress, Detroit.
49. Oguma, H., Inoue, K., and Mitsuishi, S. (2009) Development of atmospheric air-level emission vehicle technology for gasoline engines, SAE paper no. 2009-01-1076, 2009 SAE International Congress, Detroit.
50. Oguma, H., Koga, M., Momoshima, S., Nishizawa, K., and Yamamoto, S. (2003) Development of third generation gasoline PZEV technology, SAE paper no. 2003-01-0816, SAE 2003 International Congress, Detroit.

51. Ohmoto, H., Kobayashi, T., Ishikawa, K., and Yamada, T. (2002) Catalyst design for meeting stringent LEV-2 NOx regulation, SAE paper no. 2002-01-0348, SAE 2002 International Congress, Detroit.
52. Pfalzgraf, B., Fitzen, M., Siebler, J., and Erdmann, H. (2001) First ULEV turbo gasoline engine – the Audi 1.8 l, 125 kW 5-valve turbo, SAE paper no. 2001-01-1350, SAE 2001 International Congress, Detroit.
53. Punke, A., Dahle, U., Tauster, S., Rabinowitz, H., and Yamada, T. (1995) Trimetallic three-way catalysts, SAE paper no. 950255, SAE 1995 International Congress, Detroit.
54. Rohart, E., Verdier, S., Takemori, H., and Suda, E. (2007) High OSC CeO_2/ZrO_2 mixed oxides used as preferred metal carriers for advanced catalysts, SAE paper no. 2007-01-1057, 2007 SAE International Congress, Detroit.
55. Schmidt, J., Franz, J., Merdes, N., Brady, M., Mueller, W., Lindner, D., Bog, T., Clark, D., Buckel, T., Stoepler, W., Henninger, R., Ermer, H., Abe, F., Makino, M., Kunz, A., and Vogt, C. (2002) Utilization of advanced three-way catalyst formulations on ceramic ultra-thin wall substrates for future legislation, SAE paper no. 2002-01-0349, SAE 2002 International Congress, Detroit.
56. Saito, C., Nakatani, T., Miyairi, Y., Yuuki, K., Makino, M., Kurachi, H., Furuta, Y., Heuss, W., Kuki, T., Kattouah, P., and Vogt. C. (2011) New particulate filter concept to reduce particle number emissions, SAE paper no. 2011-01-0814, SAE 2011 International Congress, Detroit.
57. Schmidt, J., Busch, M., Waltner, A., Enderle, C., Heil, B., Lindner, D., Mueller, W., Mussmann, L, Lox, E., and Kreuzer, T. (2001) Utilization of advanced Pt/Rh TWC technologies for advanced gasoline applications with different cold start strategies, SAE paper no. 2001-01-0927, SAE 2001 International Congress, Detroit.
58. Takahashi, H., Y. Ishizuka, Tomita, M., Nishizawa, K. (1998) Engine-out and tailpipe emission reduction technologies of V-6 LEVs, SAE Technical Paper 980674: 1998 SAE International Congress, Detroit.
59. Takei, Y., Kinugasa, Y., Okada, M., Tanaka, T., Fujimoto, Y. (2000) Fuel property requirements for advanced technology engines, SAE Technical Paper 2000-01-2019, June 2000.
60. Thoss, J., Rieck, J., and Bennet, C. (1997) The impact of fuel sulfur level on FTP emissions - effect of PGM catalyst type, SAE Technical Paper 970737, 1997.
61. Truex, T., Golden, S., Polli, A., Hawthorne, R., Hatfield, R., and Cotton, M. (2002) Advanced low platinum group metal three-way catalyst for LEV-II and ULEV-II compliance, SAE paper no. 2002-01-0344, SAE 2002 International Congress, Detroit.
62. Umehara, K., Makino, M., Brayer, M., Becker, R., and Watson, R. (2000) Prediction of catalytic performance for ultra-thin wall and high cell density substrates, SAE paper no. 2000-01-0494, SAE 2000 International Congress, Detroit.
63. Waltner, A., Loose, G., Hirschmann, A., Mussmann, L., Lindner, D., and Mueller, W. (1998) Development of close-coupled catalyst systems for European driving conditions, SAE paper no. 980663, SAE 1998 International Congress, Detroit.
64. Webb, C., Bykowski, B., Weber, P., and McKinnon, D. (1999) Using advanced emission control systems to demonstrate LEV II ULEV on light-duty gasoline vehicles, SAE paper no. 1999-01-0774, SAE 1999 International Congress, Detroit.
65. Williamson, B., Richmond, R., Nunan, J., Bortun, A., and Robota, H. (2001) Palladium and platinum/rhodium dual-catalyst NLEV and Tier IIa close-coupled emission solutions, SAE paper no. 2001-01-0923, SAE 2001 International Congress, Detroit.
66. Williamson, B., Ball, D., Linden, D., Zammit, M., and Robota, H. (2000) Palladium and platinum/rhodium dual-catalyst emission solutions for close-coupled or underfloor applications, SAE paper no. 2000-01-0860, SAE 2000 International Congress, Detroit.