

Module 5:Emission Control for SI Engines

Lecture21:Engine Exhaust Aftertreatment

The Lecture Contains:

- INTRODUCTION TO EXHAUST AFTERTREATMENT
- THERMAL REACTORS
- Catalytic Reactors
- Catalyst
- Catalyst Substrate
- Palletized Catalysts
- Metal Monoliths
- Washcoat
- Converter Housing
- Space Velocity and Converter Size

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INTRODUCTION TO EXHAUST AFTERTREATMENT

Improvements in engine design and adjustment of engine parameters carried to control engine emissions were inadequate to meet the first set of stringent emission regulations introduced in the USA from 1975. Devices were developed to treat exhaust gas for conversion of engine emissions to harmless gases. Conversion of pollutants present in the exhaust gas is termed as 'exhaust aftertreatment'. Two basic types of exhaust treatment systems were considered;

- Thermal reactors
- Catalytic reactors or converters

Initially, thermal reactors for oxidation of HC and CO to CO_2 and H_2O were developed. However, as high conversion rates of pollutants could not be obtained in the thermal reactors these did not find widespread application and very soon the catalytic converters became a standard exhaust aftertreatment device for the spark ignited engine vehicles.

THERMAL REACTORS

If high exhaust gas temperatures are maintained and sufficient free oxygen is present in the exhaust gases, CO and HC can be oxidized in the engine exhaust system. Oxidation rate of HC can be estimated by an expression given in Module 2. Thermal conversion efficiency for HC and CO as a function of temperature is presented in Fig 5.9.

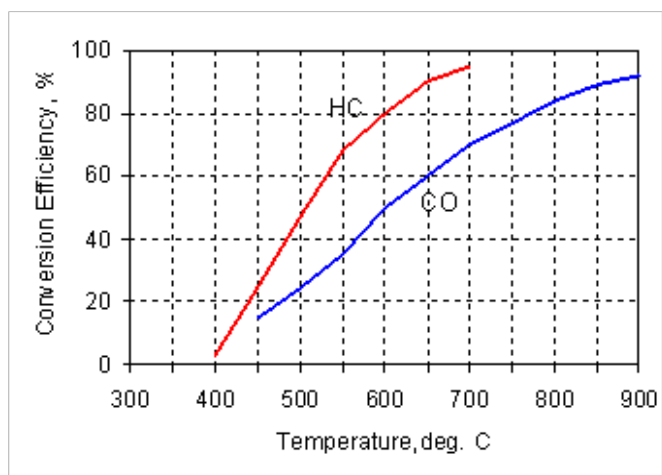


Figure 5.9

Conversion efficiency versus temperature for thermal oxidation of HC and CO

- For 50% oxidation of CO and HC temperatures in excess of 500 and 600 C, respectively are required.
- For conversion of 80 percent, temperatures required are about 600 and 750° C for HC and CO, respectively.
- Residence time in reactor is another is another important variable. At 750° C, conversion of HC up to 90 percent may be obtained in 100 ms while at 850° C only 50 ms are required. Similarly, for 90 percent oxidation of CO 250 ms and 70 ms would be necessary at 750° C and 850° C, respectively.

The thermal reactors are to be located in the exhaust manifold.

In the conventional spark ignition engines, the gas temperature near the exhaust port may vary from about 300° C at idle to 900° C at full load. Exhaust gas temperature are higher for rich mixtures and increase with retard of spark timing. When the exhaust gas flows down the exhaust pipe, it cools at a rate of about 50° C to 100° C/meter. The design of the thermal reactors has the following features to ensure adequately high gas temperatures;

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- The thermal reactor has to be located as close to the exhaust port as possible. In fact, the exhaust manifold is modified to act as thermal reactor.
- Exhaust manifold is made as a two wall design with an air gap in between to reduce cooling of the exhaust gases. Volume of the manifold is increased to increase residence time for the gases to undergo oxidation reactions.
- Engine is operated rich to obtain high exhaust gas temperature and secondary air amounting to 10 to 20% of air flow to the engine is injected at the port by an engine driven or electrical air pump. The rate of secondary air injection is controlled so that excessive cooling of the exhaust gas does not result which otherwise may chill out the oxidation reactions.

Oxidation of 1.0 percent CO in the gases increases gas temperature by about 145° C. Hence, with rich engine operation and secondary air injection sustained oxidation reactions of HC and CO occur giving higher conversion compared to lean engine operation when the starting temperatures are lower by about 100 C. Rich mixture operation and use of retarded ignition timing result in deterioration of fuel economy. Overall, the thermal reactors provide rather low conversion rates as during city driving conditions engine operates at part load and exhaust gas temperature are quite low. The thermal reactors have no effect on NO_x emissions.

Catalytic Reactors

Catalytic converters are now a standard fitment to SI engine powered vehicles. The exhaust gas flows over a bed of catalyst where pollutants are converted to harmless gases. The catalyst lowers the reaction temperature and hence high conversion rates are obtained compared to thermal reactors. A catalytic converter consists of the following main elements besides housing;

- (i) Catalyst
- (ii) Catalyst substrate or support, and
- (iii) Intermediate coat or washcoat

Catalyst

The active catalyst material is required to possess the following main characteristics

- High specific reaction activity for pollutants
- High resistance to thermal degradation
- Good cold start performance, and
- Low deactivation caused by fuel contaminants and sulphur Other desirable requirements are low cost.

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The oxides of base metals such as copper, chromium, nickel, cobalt etc. have been studied. The base metal oxides are effective only at higher temperatures. In addition, they sinter and deactivate when subjected to high exhaust gas temperatures experienced at high engine loads. Their conversion efficiency is severely reduced by sulphur dioxide produced by sulphur in fuel. The noble metals platinum (Pt), palladium (Pd) and rhodium (Rh) were found to meet the above mentioned performance requirements. In practice, only the noble metals are used although these are expensive.

Mixtures of noble metals are used to provide higher reactivity and selectivity of conversion. Following are typical formulations;

- Pt : Pd in 2:1 ratio for oxidation catalysts
- (Pt + Pd): Rh in ratio of 5 :1 to 10: 1 for simultaneous oxidation and reduction such as in 3-way catalysts

Palladium has higher specific activity than Pt for oxidation of CO, olefins and methane. For the oxidation of paraffin hydrocarbons Pt is more active than Pd. Platinum has a higher thermal resistance to deactivation. Rhodium is used as a NO_x reduction catalyst when simultaneous conversion of CO, HC and NO_x is desired as in the 3-way catalytic converters.

The amount of noble metal used typically varies from about 0.8 to 1.8 g/l (25 to 50 g/ft³) of catalytic converter volume. For a passenger car the total amount of noble metal in the converter is typically in the range 0.8 g to 2 g.

The active metal is in a highly dispersed state when impregnated on the surface of the catalyst support. The size of the noble metal particles on the fresh converter is about 50 nm. However, when used the noble metal particles sinter and may grow to a size of around 100 nm.

Catalyst Substrate

The active catalyst material is impregnated on the surface of catalyst substrate or support. The function of catalyst substrate is to provide maximum possible contact of catalyst with reactants. Following are the main requirements of catalyst substrate:

- High surface area per unit volume to keep a small size of the converter
- Support should be compatible with coating of a suitable material (washcoat) to provide high surface area and right size of pores on its surface for good dispersion and high activity of the catalyst.
- Low thermal capacity and efficient heat transfer properties for quick heat-up to working temperatures.
- Ability to withstand high operating temperatures up to around to 1000° C.
- High resistance to thermal shocks that could be caused by sudden heat release when HC from engine misfire get oxidized in the converter.
- Low pressure drop
- Ability to withstand mechanical shocks and vibrations at the operating temperatures under road conditions for long life and durability of 160,000 km and longer

The following types of catalysts supports are used;

- Pellets
- Monolithic supports

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- Ceramic monoliths
 - o Metal monoliths

Palletized Catalysts

The first catalytic converters introduced in 1970s and used until early 1980s employed spherical ceramic pellets, which were packed in a catalyst bed. The pellets of 3 to 6 mm dia were made of γ - alumina (Al_2O_3). The porous surface of alumina pellets provides a large surface area on which the noble metal salts are impregnated to a depth of about 250 μm . The pellet catalysts are loaded with approximately 0.05% by weight of noble metals. A typical pellet type catalytic converter is shown in Fig 5.10.

The gas flow through the packed bed pellet reactors is a mix of axial and radial flow so as to provide large flow area and reduce flow resistance. The gas flow through pellet bed is turbulent resulting in high mass-transfer rates. The packed bed catalysts suffer from the following disadvantages:

- High pressure drop
- Are heavy, have high thermal inertia and hence slow to warm-up.
- Loss of catalyst from abrasion due to rubbing of pellets against each other.

Therefore during 1980s the ceramic honeycomb or metallic matrix monolith converters replaced the pellet type converters.

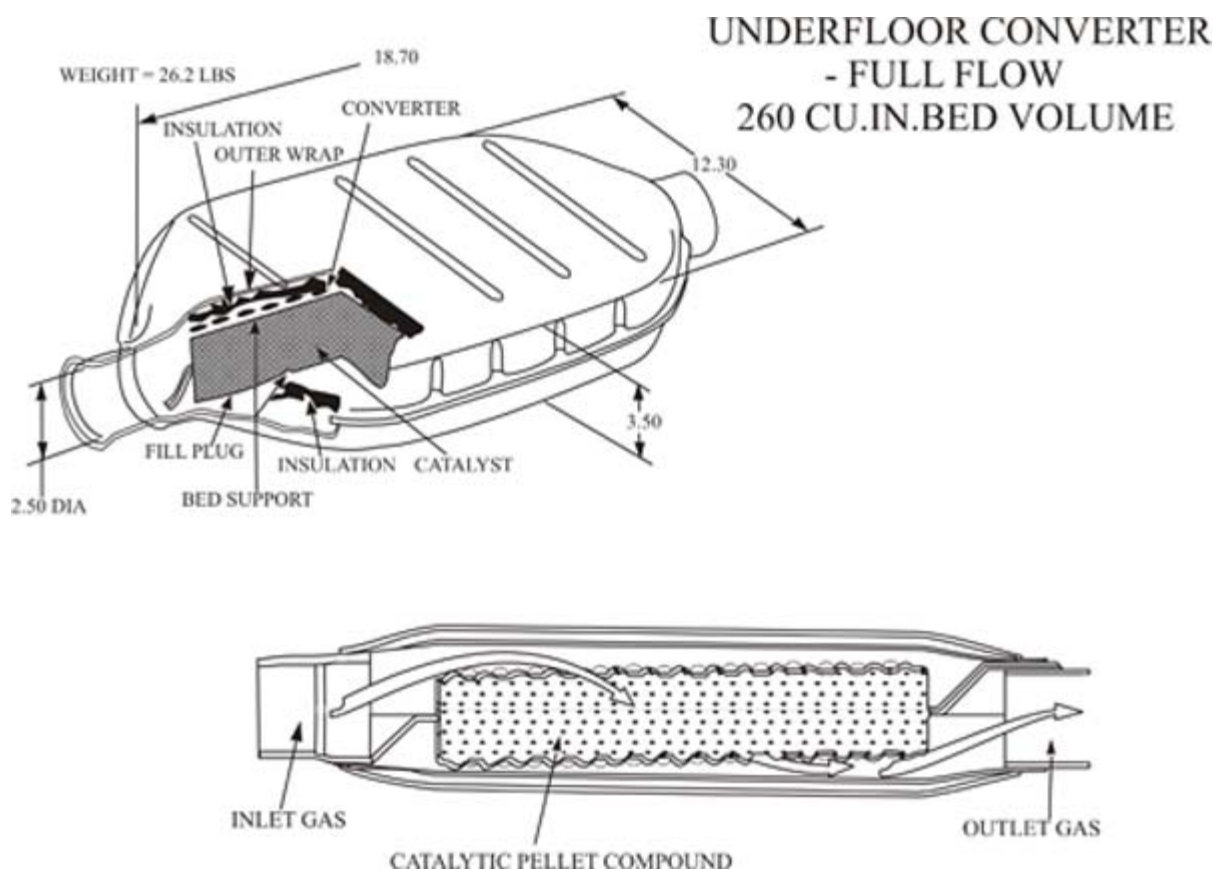


Figure 5.10

Pellet type catalytic converter.

Ceramic Monoliths

A ceramic monolith is shown schematically in Fig 5.11. It has parallel flow channels or cells of square or triangular cross section. The flow through these channels is laminar. The ceramic material commonly

used is porous *cordierite* ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$). The monoliths are characterized by cell density (cells /in² or cells/cm² of monolith cross section area) and wall thickness of the cells. A typical substrates used during 1980s and 1990s had 400 cpsi (cells /in²) and a wall thickness of 6×10^{-3} inch (0.15 mm), and it is designated as 400/6. The unit cpsi used is cells /in² of cross section area of monolith (1 cpsi = 6.45 cells /cm²) . In the current vehicles, the ceramic substrates of 600/4 configurations are quite common. The 900/2.5 and 1200/2 substrates are also being used for special catalytic converters such as closed-coupled catalysts for cold start and warm-up emission control. With increase in cell density, geometric surface area (GSA) increases providing more catalyst activity for the same volume of substrate. However, at higher cell density the cell dimensions get smaller and flow resistance (R_f) increases. Open front area of the substrate is expressed as percent of cross sectional area perpendicular to the flow direction and represents actual flow area for gases. Some important characteristics of ceramic monoliths of different structures are given in Table 5.1. Due to high surface area, the high cell density substrates provide overall higher emission .reductions.

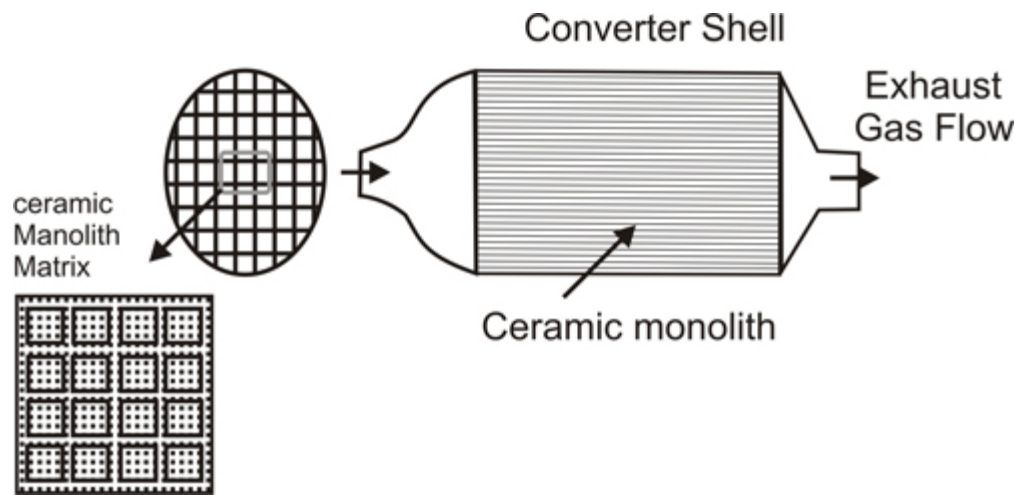


Figure 5.11	Ceramic monolith catalyst substrate having square cells.
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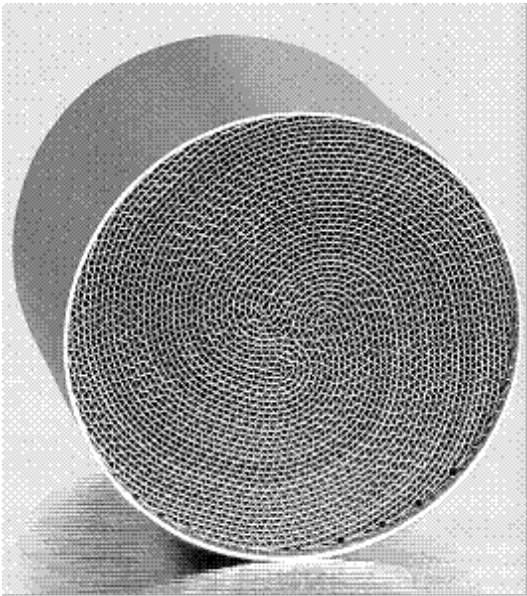
Table 5.1
Key characteristics of Ceramic Monoliths, Square Cells

Parameter	Ceramic Cell Density , cells per in ² / wall thickness,10 ⁻³ in (cells per cm ² / wall thickness , mm)		
	400/6.5 (62/0.17)	600/4 (93/0.10)	900/2.5 (140/0.064)
Substrate diameter, mm	105.7	105.7	105.7
Substrate length, mm	98	76	76
Substrate volume, l	0.86	0.67	0.67
GSA, m ² /l	2.74	3.48	4.37
OFA, %	75.7	81.4	85.6
Rf , litres/cm ²	3074	3990	5412
Substrate mass, g	339	202	156

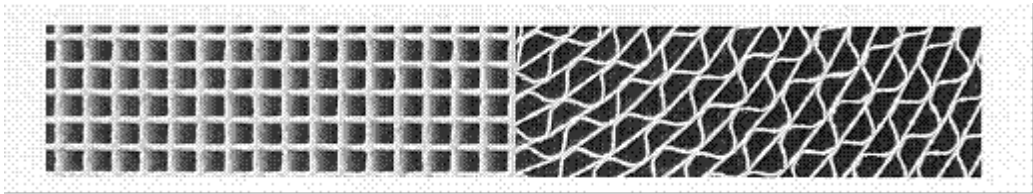
Metal Monoliths

Metallic monoliths as an alternative to ceramic were introduced to provide high mechanical strength.. In metallic monoliths, alternate flat and corrugated thin foils of made of high temperature and corrosion resistant steel containing aluminium, are wound in a spiral shape to form the honeycomb structure. The foils are about 0.05 mm thick and even thinner foils down to 0.02 mm thickness are now used. The honeycomb structure is fixed in an outer metal shell called as mantle.. Front view of a metallic monolith substrate is compared with ceramic monolith in Fig 5.11.

The size of corrugations in the corrugated foil is designed to obtain the required cell geometry and cell density. Various geometries of corrugations and hence the varying designs of cell structure are used to enhance turbulence. The coiled foils are coated with a special brazing material and brazing joins the coil with housing so that it functions as a single unit. The washcoat is applied to these monoliths mostly after their fabrication into final shape.



Frontal View of Metallic Monolith



Ceramic Monolith Cells

Metallic Monolith Cells

Figure 5.11	Frontal view of a metal monolith and comparison of cell formation in ceramic and metallic monoliths
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The foil thickness of a metallic monolith of 400-cpsi is typically 0. 0.04 to 0.05 mm compared to 0.15 to 0.20 mm for an early 400-cpsi ceramic monolith. A comparison of flow and physical characteristics of ceramic and metal monoliths is given in Table 5.2. The metallic monoliths in general, have 20 to 30% higher GSA and 10 to 20 % higher OFA. The mass of metallic monolith is however, about 2 times higher than the ceramic monolith of the same volume and cell density. The thermal capacity of metallic monoliths is 15 to 80% higher than the comparable ceramic monoliths. The metallic monoliths however, have 10 to 15% lower backpressure. A disadvantage with metal monoliths is that these cool down faster at lower loads and have to be fitted as close to the engine as possible taking into account the peak temperatures that might occur. The metallic support is non-porous and special techniques to obtain adherence of wash coat and hence catalyst on the surface have to be employed.

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Table 5.2

Comparison of Characteristics of Metallic and Ceramic Monolith Catalyst Substrates

Characteristics	Metallic Monolith	Ceramic Monolith
<u>Geometric Data</u>		
Wall thickness, mm	0.02 - 0.04	0.06 -0.20
Range of cell density , cells / cm ²	16 - 186	16 - 186
OFA (uncoated) for 62 cells / cm ² , % cross section	89- 91	67 -75.0
area	3.2	2.4-2.8
GSA (uncoated) for 62 cells / cm ² , m ² /l		
<u>Physical Data</u>		
Thermal conductivity, W/m.°K	14-22	0.1-0.8
Specific Heat capacity, kJ/kg.°K	0.4- 0.5	0.75-1.05
Density, g/cm ³	7.4	2.2-2.7
Coefficient of thermal expansion, 1/°K	15	1
Maximum short duration operating temperature, °C	1275-1375	1400
Maximum continuous operating temperature, °C	900-1150	1200
Mass (105.7 mm dia. x 98 mm length) 62 cells / cm ² , g	680	340

Metallic monoliths have the following advantages compared to the ceramic monoliths:

- Higher mechanical strength
- High thermal conductivity and faster warm-up
- Higher flow area and lower pressure drop
- Higher tolerance to high temperature spikes
- Higher conversion efficiency
- Smaller size
- No special housing is required.

Washcoat

Monolithic substrates have a geometrical surface area of 2.0 - 4.0 m²/l of its volume. This is too low to provide high contact area between the catalyst and reacting gases for high conversion rates. A thin layer of γ -Al₂O₃ seeded with other oxides as 'washcoat' is

applied to the monolith cells to increase effective surface area for dispersion of catalyst material. About 20 percent of other oxides consisting of cerium oxide (CeO₂) and stabilizers such as zirconium oxide and barium oxide are added to alumina. The washcoat has pores of varying sizes ranging from 0.2 to 1 μ m. The ceramic monolith walls are porous and surface is rough so that good adhesion of washcoat is obtained.

High surface area created by Al₂O₃ washcoat and dispersion of active catalyst deposited by solution impregnation is shown schematically in Fig. 5.12. Adhesion of washcoat to metallic monoliths requires at first pre-treatment of surface to make it rough and improve its bonding characteristics with ceramic washcoat materials. For the prefabricated metallic monoliths then, a procedure similar that for the ceramic monoliths may be followed.

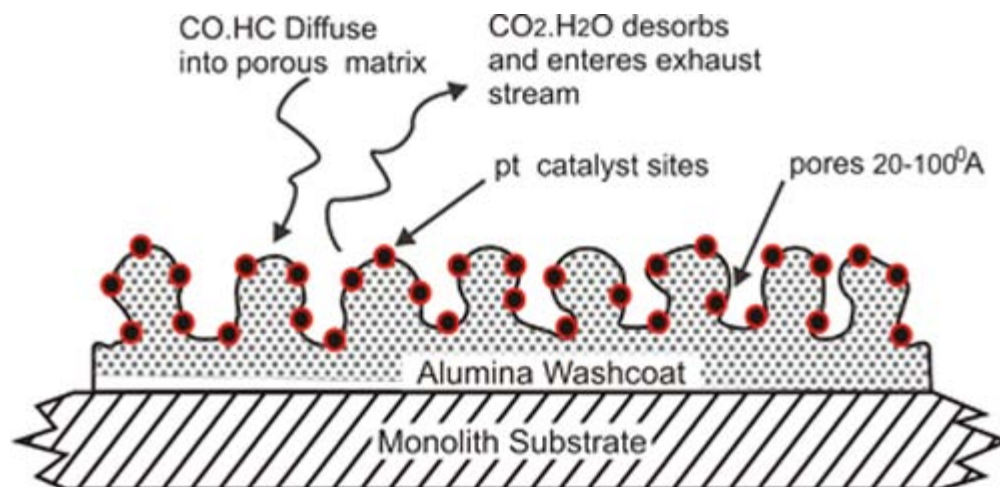


Figure 5.12

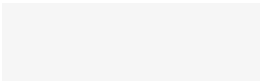
Conceptual model of catalytic sites dispersed on a high surface-area Al₂O₃ washcoat.

The washcoat constitutes 5 to 15 percent of the mass of ceramic monoliths. Its thickness typically varies in the range 10-30 μ m on the walls. The washcoat increases actual surface area of the catalyst substrate to 10000-40000 m²/l of monolith volume. are added.

Converter Housing

The ceramic monolith is mounted in a metal casing made of high quality corrosion resistant steel. A mat made of ceramic material around the ceramic monolith holds it tightly inside the casing. The mat protects the ceramic monolith against mechanical impact and vibrations, and also acts as heat insulation. The ceramic mat is made of aluminium silicate that expands as it is heated.

As the temperature of mat rises, gas bubbles are formed inside the mat and it ensures proper tightening of the ceramic monolith in the housing and sealing to prevent any bypass of the exhaust gases. The metallic monolith converters are easier to mount as the metal mantle that holds the metallic honeycomb structure is welded or brazed in the exhaust system of the engine.



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Space Velocity and Converter Size

The catalytic converter monolith volume is typically 0.5 to 1 times of the engine swept volume. Space velocity characterizes the residence time available to gases to undergo chemical reactions in the reactor bed. The space velocity is inversely proportional to the residence time and is defined as,

$$V_s = \frac{\text{Exhaust Flowrate, m}^3/\text{s}}{\text{Catalyst Volume, m}^3}, \text{ s}^{-1} \quad (5.2)$$

In the catalytic converters for SI engines, the space velocity typically reaches up to 50 s⁻¹. Higher the space velocity that can be used to achieve required conversion rates, smaller is the volume of the converter required. Higher usable space velocities have been achieved through improvements in the design of substrate, wash coat and catalyst dispersion technologies.

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