

result, the sulfate make rate for the C1 cycle and the SET cycle would be

expected to be similar. The data can be used to estimate the PM emissions from

diesel engines operated on fuels with average fuel sulfur levels in this range.

TABLE III. F-1—ESTIMATED PM EMISSIONS FROM A DIESEL ENGINE AT THE INDICATED FUEL SULFUR LEVELS

Fuel sulfur [ppm]	Steady state emissions performance	
	Tailpipe PM ^b [g/bhp-hr]	PM increase relative to 3 ppm sulfur
3	0.003	
7 ^a	0.006	100%
15 ^a	0.009	200%
30	0.017	470%
150	0.071	2300%

Notes:

^a The PM emissions at these sulfur levels are based on a straight-line fit to the DECSE data; PM emissions at other sulfur levels are actual DECSE data. (Diesel Emission Control Sulfur Effects (DECSE) Program—Phase II Interim Data Report No. 4, Diesel Particulate Filters-Final Report, January 2000. Table C1.) Although DECSE tested diesel particulate filters at these fuel sulfur levels, they do not conclude that the technology is feasible at all levels, but they do note that testing at 150 ppm is a moot point as the emission levels exceed the engine's baseline emission level.

^b Total exhaust PM (soot, SOF, sulfate).

Table III.F-1 makes it clear that there are significant PM emission reductions possible with the application of catalyzed diesel particulate filters and low sulfur diesel fuel. At the observed sulfate PM conversion rates, the DECSE program results show that the 0.01 g/bhp-hr total PM standard is feasible for CDPF equipped engines operated on fuel with a sulfur level at or below 15 ppm. The results also show that diesel particulate filter control effectiveness is rapidly degraded at higher diesel fuel sulfur levels due to the high sulfate PM make observed with this technology. It is clear that PM reduction efficiencies are limited by sulfur in diesel fuel and that, in order to realize the PM emissions benefits sought in this rule, diesel fuel sulfur levels must be at or below 15 ppm.

c. Increased Maintenance Cost for Diesel Particulate Filters Due to Sulfur

In addition to the direct performance and durability concerns caused by sulfur in diesel fuel, it is also known that sulfur can lead to increased maintenance costs, shortened maintenance intervals, and poorer fuel economy for CDPFs. CDPFs are highly effective at capturing the inorganic ash produced from metallic additives in engine oil. This ash is accumulated in the filter and is not removed through oxidation, unlike the trapped soot PM. Periodically the ash must be removed by mechanical cleaning of the filter with compressed air or water. This maintenance step is anticipated to occur on intervals of well over 1,500 hours (depending on engine size). However, sulfur in diesel fuel increases this ash accumulation rate through the formation of metallic sulfates in the filter, which increases both the size and mass of the trapped ash. By increasing the ash

accumulation rate, the sulfur shortens the time interval between the required maintenance of the filter and negatively impacts fuel economy.

2. Diesel NO_x Catalysts and the Need for Low Sulfur Fuel

NO_x adsorbers are damaged by sulfur in diesel fuel because the adsorption function itself is poisoned by the presence of sulfur. The resulting need to remove the stored sulfur (desulfate) leads to a need for extended high temperature operation which can deteriorate the NO_x adsorber. These limitations due to sulfur in the fuel affect the overall performance and feasibility of the NO_x adsorber technology.

a. Sulfur Poisoning (Sulfate Storage) on NO_x Adsorbers

The NO_x adsorber technology relies on the ability of the catalyst to store NO_x as a metallic nitrate (MNO₃) on the surface of the catalyst, or adsorber (storage) bed, during lean operation. Because of the similarities in chemical properties of SO_x and NO_x, the SO₃ present in the exhaust is also stored by the catalyst surface as a sulfate (MSO₄). The sulfate compound that is formed is significantly more stable than the nitrate compound and is not released and reduced during the NO_x release and reduction step (NO_x regeneration step). Since the NO_x adsorber is essentially 100 percent effective at capturing SO₂ in the adsorber bed, the sulfur build up on the adsorber bed occurs rapidly. As a result, sulfate compounds quickly occupy all of the NO_x storage sites on the catalyst thereby rendering the catalyst ineffective for NO_x storage and subsequent NO_x reduction (poisoning the catalyst).

The stored sulfur compounds can be removed by exposing the catalyst to hot (over 650 °C) and rich (air-fuel ratio below the stoichiometric ratio of 14.5 to 1) conditions for a brief period.²²⁴ Under these conditions, the stored sulfate is released and reduced in the catalyst.²²⁵ While research to date on this procedure has been very favorable with regards to sulfur removal from the catalyst, it has revealed a related vulnerability of the NO_x adsorber catalyst. Under the high temperatures used for desulfation, the metals that make up the storage bed can change in physical structure. This leads to lower precious metal dispersion, or "metal sintering," (a less even distribution of the catalyst sites) reducing the effectiveness of the catalyst.²²⁶ This degradation of catalyst efficiency due to high temperatures is often referred to as thermal degradation. Thermal degradation is known to be a cumulative effect. That is, with each excursion to high temperature operation, some additional degradation of the catalyst occurs.

One of the best ways to limit thermal degradation is by limiting the accumulated number of desulfation events over the life of the vehicle. Since

²²⁴ Dou, Danan and Bailey, Owen, "Investigation of NO_x Adsorber Catalyst Deactivation," SAE 982594.

²²⁵ Guyon, M. et al, "Impact of Sulfur on NO_x Trap Catalyst Activity—Study of the Regeneration Conditions", SAE 982607.

²²⁶ Though it was favorable to decompose sulfate at 800 °C, performance of the NSR (NO_x Storage Reduction catalyst, *i.e.* NO_x Adsorber) catalyst decreased due to sintering of precious metal.—Asanuma, T. et al, "Influence of Sulfur Concentration in Gasoline on NO_x Storage—Reduction Catalyst", SAE 1999-01-3501.