



Fuel sulfur effects on diesel catalyst performance

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ABSTRACT

Many improvements have been achieved in the design of modern diesel engines (Khair, Gill^{1,2}). These design improvements enabled the diesel engine to meet strict limitations imposed by emissions regulations adopted by many governments in the industrialized world. In spite of the success achieved in controlling diesel emissions while maintaining good performance characteristics, particulate emissions still remain a challenge to researchers.

Attempts to control diesel particulate emissions led scientists to investigate diesel exhaust aftertreatment. Two methods of aftertreatment emerged as likely candidates for this task. The first method involved trapping and incinerating particulates at certain intervals. This method used a diesel particulate trap (Garner³) with a regeneration system, and was quite effective in reducing the insoluble components of particulates. Users of this device soon realized its durability limitations as well as the complexity of its regeneration system. A second aftertreatment method relying on catalytic oxidation of the soluble organic fraction gained popularity (Ball⁴). However, researchers also realized the negative impact of the fuel sulfur content on the effectiveness of this method.

INTRODUCTION

Several studies considered the effect of fuel sulfur on diesel particulate emissions (Knuth, Baranescu^{5,6}). Figure 1 shows the result of a test on two direct injection diesel engines. For every 0.1 percent by weight of fuel sulfur reduction, total particulate emissions were reduced by 0.02 to 0.025 g/bhp-hr. (Khair¹) Reducing fuel sulfur was also found to be favorable for applying catalytic aftertreatment to diesel exhaust.

Catalytic aftertreatment of diesel exhaust leads to the continuous oxidation of the volatile organic fraction (VOF) as long as conditions are conducive for the oxidation process. VOF oxidation is a function of many

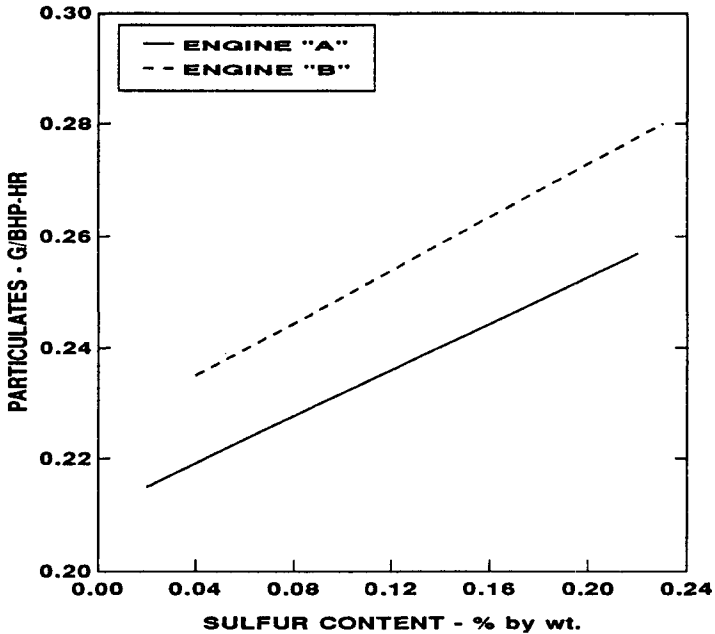


Figure 1. Effect of Sulfur on Diesel Particulates

variables such as the washcoat type, noble metal and its loading, space velocity, exhaust gas composition and temperature, type of substrate, and catalyst location in the exhaust system. These factors were found to impact the overall effectiveness of diesel catalytic converters. Some of these factors are quite independent from the catalyst formulation, and may only have a secondary impact on catalytic performance. Careful selection of the catalyst washcoat and noble metal type and loading will lead to the successful aftertreatment of diesel exhaust.

REVIEW OF THE NOBLE METAL AND WASHCOAT EFFECTS

THE NOBLE METAL EFFECT - Figure 2, published in the *Platinum Metals Review* in 1989, compares the ability of various noble metals to convert sulfur dioxide (SO_2), into sulfur trioxide (SO_3) as a function of the exhaust temperature. Because the formation of sulfate is dependent on the amount of sulfur trioxide, using platinum as a diesel exhaust catalyst is expected to produce relatively high amounts of sulfate. By contrast, palladium would produce moderate amounts of sulfate emissions, even at higher exhaust temperatures compared to its platinum counterpart.(Khair¹)

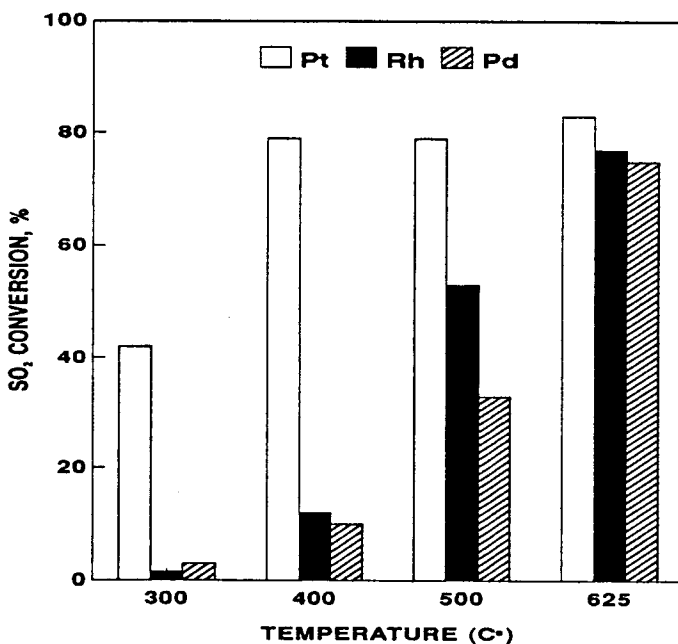


Figure 2. Effect of Noble Metals on SO₂ Conversion as a Function of Temperature

Rhodium is considered a stoichiometric NO_x reduction catalyst; and therefore, is not considered the noble metal of choice for diesel exhaust aftertreatment. However, rhodium has been used to curb the ability of platinum to produce SO₃, as shown in Figure 3. Choosing the noble metal and its loading for a given application depends to a large extent on the composition of the exhaust and the specific objective desired. One objective may be the reduction of polynuclear aromatics (PNA) as opposed to reducing total particulates. In this case, platinum may be considered a prime choice, especially with a relatively small fraction of rhodium (Pt/Rh=10-20:1). However, if total particulate reduction is the objective, then palladium may be the preferred noble metal due to its low SO₂ to SO₃ conversion characteristics.

THE WASHCOAT EFFECT - The most important criterion for the selection of the washcoat is its capability to store and release sulfur compounds. Alumina, in various forms, is a very popular washcoat system for gasoline exhaust aftertreatment. However, its use in the diesel exhaust environment may not be optimal because it has shown undesirable sulfate storage and release characteristics. Silica, on the other hand, has shown less sulfate storage and release capability. Therefore, it is gaining acceptance as

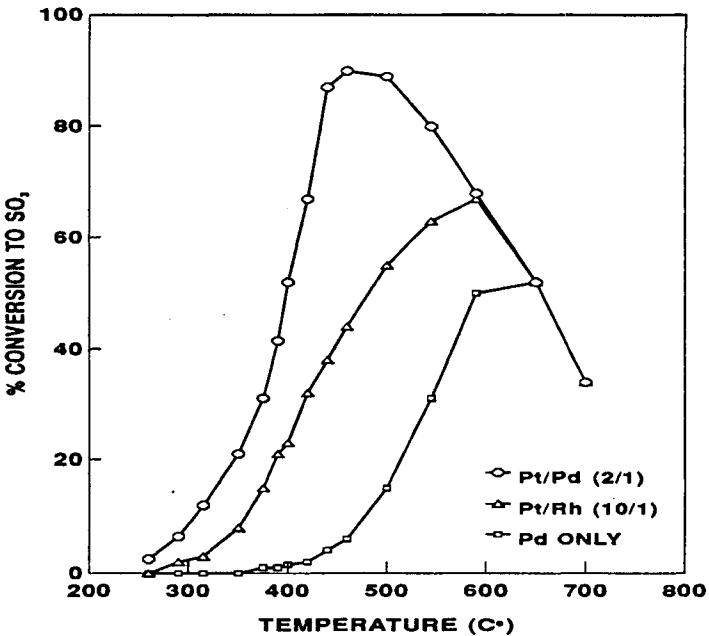


Figure 3. Performance of Three Catalysts - Conversion to SO₃ Relative to Exhaust Temperature

a favored diesel catalyst washcoat system. Figure 4 shows the effect of increasing the amount of an inorganic oxide in the catalyst washcoat on the total particulate reduction. The mere substitution of alumina by silica should not be viewed as the total answer for the washcoat effect. Inclusion of a variety of base metals such as cerium and zirconium is being investigated by several catalyst companies, due to the base metal contribution in promoting and stabilizing catalyst reactions.(Khair¹)

SULFATE FORMATION ASSESSMENT TEST

GENERAL - The main purpose for the sulfate formation assessment test was to evaluate the impact of sulfur in diesel fuel on exhaust emissions of an engine equipped with catalytic aftertreatment. This test utilized a Caterpillar 3176 heavy-duty diesel engine calibrated to meet the 1991 emission standards. Details of that engine appear in Table 1.

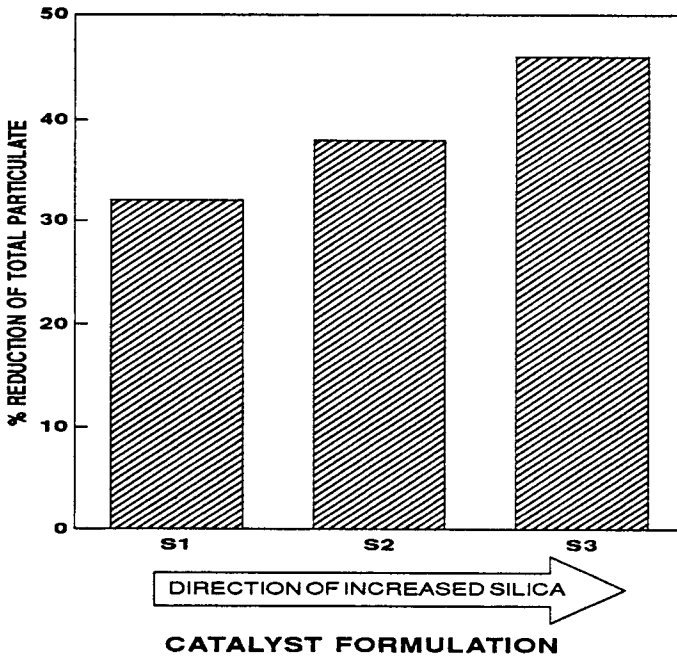


Figure 4. Effect of Washcoat on Particulate Reduction

TABLE 1 - CATERPILLAR 3176 S/N 1A9453 ENGINE

Rated engine speed	1900 rpm
Rated engine horsepower	325 hp
Fuel rate at rated speed and load	102.4 lb/hr
Peak torque speed	1200 rpm
Peak torque	1225 lb-ft
Fuel rate at peak torque speed	87.6 lb/hr
Injection timing	variable
High idle (governed)	1920 ± 5 rpm
Low idle (curb idle)	600-750 rpm
Cranking speed	150 rpm
Pressure drop across intercooler	54.4 in. H ₂ O
Air temperature after intercooler	110 °F

CATALYSTS AND CATALYTIC CONVERTERS - Six catalyst formulations were included in this program. These formulations varied not only in the noble metal type and loading, but also in their washcoat type and total surface area. Four catalyst suppliers provided the samples for this test program. They were given total freedom in designing their catalyst formulations as well as the catalytic converter volume. Table 2 gives a generalized description of the catalytic converters involved in this study. The variety provided by these different formulations, volumes, substrates, and manufacturing processes was considered an asset for the study of sulfate formation, storage, and release.

TABLE 2. GENERAL CATALYST DESCRIPTION

Catalyst ID	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6
Substrate	Cordierite Honeycomb	Metallic Tortuous	Metallic Tortuous	Metallic Tortuous	Metallic Monolith	Cordierite Honeycomb
Cell Density	300 cpi	225 cpi	225 cpi	225 cpi	400 cpi	400 cpi
Volume	781 cu.in.	600 cu.in.	600 cu.in.	600 cu.in.	769 cu.in.	572 cu.in.
Washcoat	Alumina+Zr	Silica	Silica	Silica	Al+Metal Oxides	Al+ Other Oxides
Catalyst	Pd/Rh	Pd	Pd/Rh	Pd	Pt	Pt/Rh
Noble Metal Loading	40 g/ft ³ (1.41 g/L)	50 g/ft ³ (1.77 g/L)	50 g/ft ³ (1.77 g/L)	100 g/ft ³ (3.53 g/L)	50 g/ft ³ (1.77 g/L)	50 g/ft ³ (1.77 g/L)

TEST PLAN - Testing consisted of three separate segments:

1. Pre-aging evaluation and documentation - where three sets of EPA cold transient test cycles each followed by three EPA hot transient test cycles were run on all six catalysts. Sulfur content of the diesel fuel used was 0.05 percent by weight. This segment was run in order to carefully document the emissions characteristics of each catalyst prior to aging. The number of tests carried out provided good information on the repeatability and the consistency of data.
2. Aging - this segment consisted of transient engine operation running repetitive portions of the EPA transient test. These portions were the New York Non-Freeway (NYNF) and Los Angeles Non-Freeway (LANF). By selecting this aging cycle, it was felt that any sulfate formed would be stored but not released, since the exhaust temperature would remain low (<300°C). Since the interest was in accelerating the effect of sulfur on the catalysts, diesel fuel with one percent sulfur by weight was used during this segment. The duration of the aging process was arbitrarily selected at forty-eight hours.

3. Post-aging evaluation - immediately following the aging process and without any additional conditioning, all six catalysts were evaluated. This evaluation was a duplicate of the testing performed during the pre-aging segment.

A graphic illustration of the above test sequence appears in Figure 5.

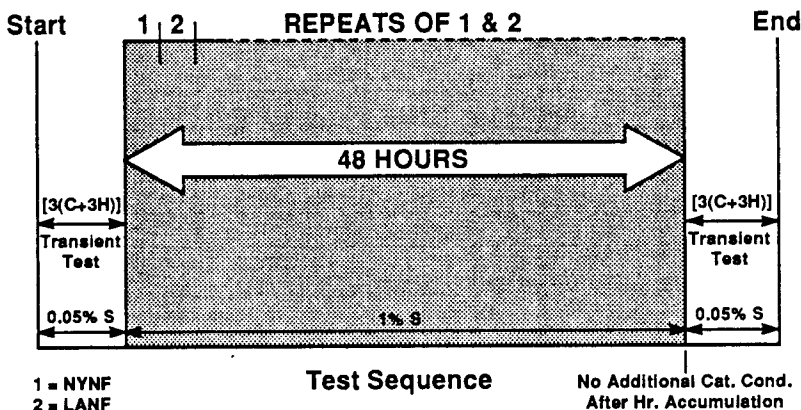


Figure 5. Expanded Sulfate Assessment Test Sequence

TEST RESULTS AND DISCUSSION

Total Particulate Emissions - Examination of the results disclosed that in all cases where a catalyst was used, an increase in the composite particulate emissions was recorded. Figure 6 illustrates the composite particulate (average of three sets of cold and hot transients) before and after the sulfate assessment test as well as the percent change which is represented by that increase. A cursory look at the data placed the catalysts in two categories. The first category included Catalysts SW-2, SW-3, and SW-4 and showed an increase of 30 to 35 percent in total particulates. The second category included SW-1, SW-5, and SW-6, showing an increase of 64 to 70 percent in total particulates. A possible explanation for this result lies in the washcoats of these catalysts, SW-2, SW-3, and SW-4 having silica based washcoats, while SW-1, SW-5 and SW-6 are known to contain alumina based washcoats.

VOF Emissions - The composite VOF emissions, after the 48-hour accumulation with one percent sulfur fuel, were found to be lower than before the start of the test for all six catalysts. This reduction is shown in Figure 7 together with the percent improvement in VOF emissions. Attempts to understand this phenomenon resulted in the following possible explanations:

Catalyst Volume - Residence Time - It was observed that some proportionality existed between the VOF emissions reduction and the catalyst

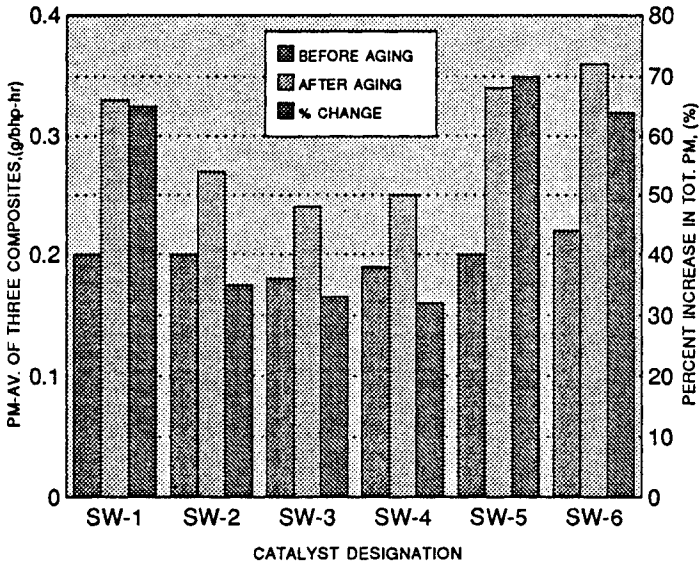


Figure 6. Expanded Sulfate Assessment Test-Effect of Catalyst Formulation on Particulate (48 Hours Aging with 1% Sulfur Fuel)

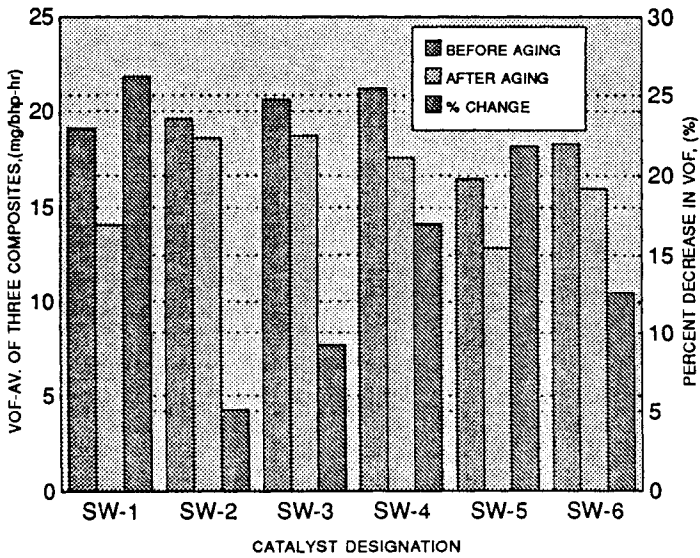


Figure 7. Expanded Sulfate Assessment Test-Effect of Catalyst Formulation on VOF (48 Hours Aging with 1% Sulfur Fuel)

volume. Figure 8 suggests that the higher the catalyst volume (i.e., the longer the residence time) the greater the VOF reduction. For instance, the two catalysts with the largest decreases in VOF emissions, SW-1 and SW-5 with 26 percent and 22 percent improvement in VOF emissions, respectively, had the two largest volumes (781 and 769 cu. in).

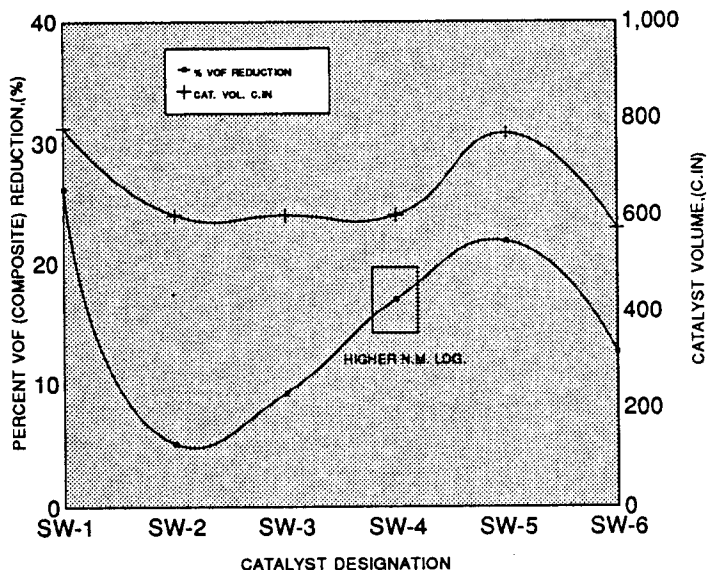


Figure 8. Effect of Catalyst Volume on VOF Emissions After Aging (48 Hours Aging with 1% Sulfur Fuel)

Noble Metal Activity - Catalysts SW-2, SW-3, and SW-4 had the same catalyst volume, but different improvement rates in VOF emissions. One possible explanation for this observation, especially applicable to catalyst SW-4, is the noble metal loading. With catalyst SW-4, the improvement in VOF reduction was about 16 percent, while SW-2 and SW-3 showed 5 and 9 percent, respectively. Examination of the catalyst descriptions showed that the noble metal loading for SW-4 was twice that of SW-2 and SW-3, with the higher noble metal loading responsible for the higher catalyst activity.

Mechanism for VOF Reduction - Reference 7 suggests that at typical analytical conditions, an increase in the extractable component of particulate with increasing sulfate was observed. This increase in sulfate was certainly experienced during the expanded sulfate assessment test. In addition, the reference stated that the sulfate particulate is generally composed of sulfuric acid, H_2SO_4 , with associated "bound" water. VOF reduction is believed to result from a scrubbing effect by the sulfuric acid. There is, however, no clear indication that elimination of VOF emissions through increased oxidation is taking place.

Sulfate Emissions - Relationship to VOF Emissions - Figure 9 shows the relationship between VOF and sulfate emissions for the six catalysts. Catalyst SW-6 had the highest composite sulfate emissions. By inference, SW-6 also had the highest formation of sulfuric acid; which in turn, reduced VOF more than the other catalysts, leading to the lowest VOF emissions. On the other end of the spectrum, Catalyst SW-1 had the lowest sulfate emissions and the highest VOF emissions.

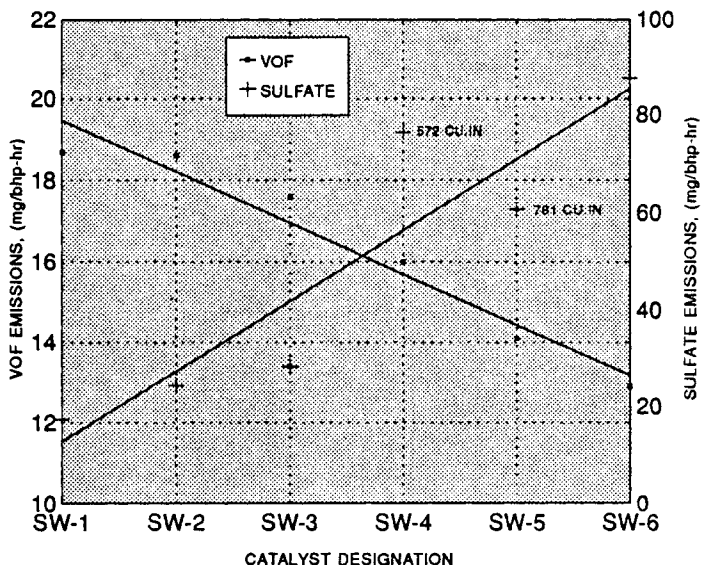


Figure 9. Expanded Sulfate Assessment Test-Relationship Between VOF and Sulfate (48 Hours Aging With 1% Sulfur Fuel)

Sulfate Emissions and Catalyst Recovery - Following the 48-hour accumulation, the catalysts underwent a series of transient cycles consisting of a cold and three hot tests repeated three times. No catalyst conditioning was performed prior to this transient test evaluation. The results of all twelve tests [3(C+3H)], are shown in Figure 10, from which the following observations can be made:

- Sulfate emissions were highest in the first test following service accumulation. This observation is generally true of all catalysts, but especially for SW-1, SW-5, and SW-6. These catalysts had alumina washcoats in their formulations.

As the transient testing proceeded, sulfate emissions gradually decreased, indicating a return of the catalyst to its condition prior to the service accumulation with high sulfur (1%) fuel. This decrease was more accentuated for the same catalysts (SW-1, SW-5, and SW-6).

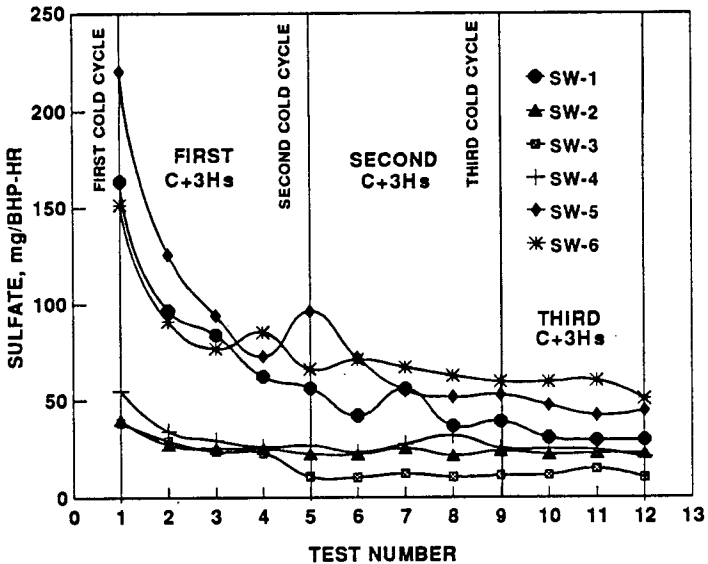


Figure 10. Expanded Sulfate Assessment Test-Sulfate Emission After Hour Accumulation (48 Hours Transient with 1% Sulfur Fuel)

- As anticipated, the catalysts with the lowest sulfate activity showed high VOF emissions. It did not seem, however, that the presence of sulfur in the catalyst had a detrimental effect on the net VOF emissions. This is believed to result from the scrubbing effect of the sulfuric acid.

Sulfate Emissions and Catalyst Washcoat - Another observation from Figure 10 is that the catalysts with alumina type washcoats showed a greater tendency to store, then release sulfate than silica type washcoats. This relationship was true throughout the transient testing that followed the service accumulation. However, the difference is quite dramatic during the first cold cycle, where the sulfate emitted from SW-1, SW-5, and SW-6 were three to four times greater than those emitted from SW-2, SW-3, and SW-4.

Sulfate Contribution to Total Particulate - Catalyst SW-6 was used to analyze the makeup of the particulates after the hour accumulation and to determine the sulfate contribution to the total particulate. The total particulate matter difference for SW-6 was 0.14 g/bhp-hr. The sulfate emissions increase was 0.0639 g/bhp-hr. This increase in sulfate emissions does not take into account the trapped water which is associated with sulfuric acid (the primary component of sulfate particulate) as reported in the reference.(Wall⁷) The mass increase in total particulate could be as high as 2.3 times the mass of



sulfate alone because of the associated water. In the case of SW-6, this ratio was 2.19 (or 0.14/ 0.0639). This finding was first published in Reference 8.

Total Sulfate and VOF Emissions - In analyzing the effectiveness of a catalyst, its capability in reducing VOF is considered the strongest attribute. This quality, however, may be tempered by the catalyst propensity to convert SO_2 to SO_3 and form sulfate. It is, therefore, desirable that a catalyst would maintain the summation of VOF and SO_4 at a minimum. Figure 11 shows that summation of VOF+ SO_4 was least for Catalyst SW-3, with SW-2 and SW-4 giving very close performance to that of SW-3. Examination of the catalyst description given in Table 2 shows that all three catalysts (SW-2, SW-3, and SW-4) have silica-based washcoats, and contain palladium as a main ingredient in their catalyst formulation.

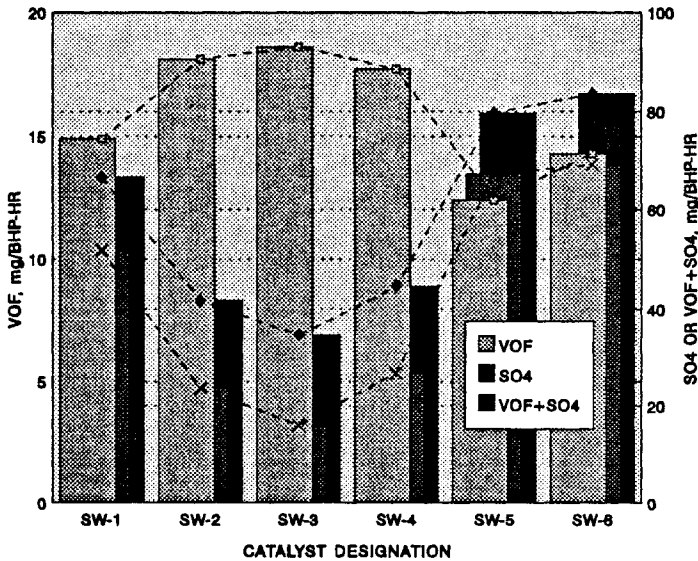


Figure 11. Evaluation of Catalyst Performance 0.04% Sulfur Afer Aging With 1% Sulfur (Composite Average)

SUMMARY AND CONCLUSIONS

- The presence of sulfur in diesel fuel is detrimental to catalyst performance. Therefore, fuel sulfur content should be minimized where catalytic aftertreatment is applied.
- Careful formulation of diesel catalyst can lead to good VOF reduction without excessive sulfate formation.



- Catalytic systems with alumina-based washcoats and platinum for noble metal gave good VOF control, but tended to convert more SO₂ to SO₃.
- Catalyst deactivation resulting from the presence of sulfur in the fuel appears to be reversible. This is achieved by exposing the catalyst to high exhaust temperature when operating an engine with low sulfur ($\leq 0.05\%$ by weight) fuel.
- Sulfate emissions and VOF exhibit an inversely proportional relationship.

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