

TECHNICAL SUBMISSION  
AUTOMOTIVE SULFATE EMISSIONS

Submitted to:  
ENVIRONMENTAL PROTECTION AGENCY  
HEARINGS ON DELAY OF THE 1977 CO  
AND HC AUTOMOTIVE EMISSION STANDARDS

January 29, 1975

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SUMMARY

This document presents data generated by Exxon Research and Engineering Company on factors affecting the emission of sulfates from vehicles equipped with oxidation catalysts. Much of the data reported herein was developed as parts of two EPA contracts: Contract 68-03-0497, "An Assessment of Sulfate Emission Control Technology," and Contract 68-02-1297, "The Characterization of Particulate Emissions from Prototype Catalyst Vehicles."

Our major findings are as follows:

- Under FTP conditions monolithic catalysts emit about 10-15% of the sulfur in gasoline as sulfate. This is lower than the 25-35% emission rate previously reported by Exxon Research based on preliminary measurements on prototype catalysts.
- Under FTP conditions pelleted catalysts emit about 5-10% of the sulfur in gasoline as sulfate. This value is in agreement with earlier findings.
- Under high speed (60-70 mph) cruise conditions both types of catalyst emit about 25-35% of the sulfur in gasoline as sulfate, again in agreement with earlier findings.
- Storage of  $\text{SO}_2$ ,  $\text{SO}_4^{\equiv}$ , or both on catalyst surfaces occurs with both types of catalyst and accounts for many of the differences in  $\text{SO}_4^{\equiv}$  emission rates observed.
- Significant differences exist between the amount of  $\text{SO}_4^{\equiv}$  emitted from nominally similar monolithic catalysts. Catalysts from one manufacturer emitted less  $\text{SO}_4^{\equiv}$  under certain conditions and also stored less sulfur oxide than did

nominally similar catalysts manufactured by another. The reasons for these differences are unknown.

- Reducing the amount of excess air used over a catalyst significantly lowers  $\text{SO}_4^{\equiv}$  emissions. Removing air pumps could lower  $\text{SO}_4^{\equiv}$  emissions by 50-75% in pelleted catalyst systems. We have yet to test this approach in vehicles using monolithic catalysts, but laboratory data indicate that air pump removal would also lower  $\text{SO}_4^{\equiv}$  emissions in these systems. This fact should be considered in the delay decision because the higher the CO and HC emissions allowed, the less the need for air pumps.
- CaO was demonstrated to be effective in removing  $\text{SO}_4^{\equiv}$  from exhaust, but trapping  $\text{SO}_2$  and  $\text{SO}_4^{\equiv}$  causes the sorbent to swell and unacceptable back pressure buildup occurs. Work is continuing to find better sorbents and to overcome this problem.

We have made no estimates of  $\text{SO}_4^{\equiv}$  emission factors for production 1975 vehicles because all of our work has been done with cars modified to meet emission levels of 3.4 g/mi CO and 0.41 g/mi HC. Similarly we have not commented on the impact of automotive sulfate emissions on either atmospheric  $\text{SO}_4^{\equiv}$  levels or human health because we have no data of our own in either of these two areas.

## I. Introduction

To meet the 1975 interim emission standards for carbon monoxide (CO) and hydrocarbons (HC), most cars sold in the U. S. use emission control systems containing oxidation catalyts. In addition to meeting the statutory requirements for CO and HC control, these systems provide the additional benefits of lowering the reactivity, or smog-forming potential, of the hydrocarbons emitted (1)\*, and substantially reducing emissions of aldehydes (2), and polynuclear aromatics (3) . Oxidation catalyst systems do, however, create their own special concerns. They require the use of unleaded, phosphorus-free gasoline, which places a burden on the petroleum industry. They also convert some of the sulfur naturally present in gasoline to sulfate particulate.

The purpose of this document is to present, in detail, the data generated by Exxon Research and Engineering Company on the factors affecting automotive sulfate emissions. Where relevant, we will also quote data developed by others. Much of the data which will be reported has been generated as parts of two EPA Contracts: Contract 68-03-0497, "An Assessment of Sulfate Emission Control Technology", and Contract 68-02-1279, "The Characterization of Particulate Emissions from Prototype Catalyst Vehicles". Both of these contracts are currently in progress at Exxon Research and Engineering Company.

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\* Numbers in parentheses refer to references listed at the end of this paper.

The following topics will be discussed in this presentation:

- formation of sulfate in oxidation catalyst systems,
- measurement techniques used to study sulfate emissions,
- sulfate emission rates from oxidation catalyst-equipped vehicles, and
- methods which could potentially lessen automotive sulfate emissions.

## II. Formation of Sulfate in Oxidation Catalyst Systems

Sulfur is present in gasoline in trace quantities, usually less than 0.1 wt. %. The amount of sulfur in any given gasoline sample is a function of the sulfur content of the crude from which the gasoline was made, and the refining processes used in making the gasoline. National average gasoline sulfur is about 0.03 wt. %. The only area of the country having a significantly different gasoline sulfur content is Southern California, where the average is 0.06 - 0.07 wt. %.

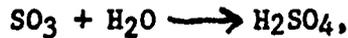
When gasoline is combusted in an internal combustion engine, sulfur is oxidized to sulfur dioxide (SO<sub>2</sub>):



In vehicles without an oxidation catalyst, sulfur is emitted in that form. When an oxidation catalyst is present, some of the SO<sub>2</sub> formed in the engine is oxidized to sulfur trioxide (SO<sub>3</sub>):



The fraction of SO<sub>2</sub> converted to SO<sub>3</sub> is a function of the type of oxidation catalyst used, its operating temperature, the amount of excess oxygen present, and the residence time during which the SO<sub>2</sub> is in contact with the catalyst. Each of these subjects will be discussed in detail later in the presentation. In the exhaust system, SO<sub>3</sub> combines with the water present in the exhaust to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>):



and is emitted as such. Since the analytical techniques used to measure the amount of H<sub>2</sub>SO<sub>4</sub> in automotive exhaust are incapable of distinguishing between SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and any products of reaction between H<sub>2</sub>SO<sub>4</sub> and cations present in the exhaust, it is customary to refer to all of these materials as sulfate (SO<sub>4</sub><sup>≡</sup>) emissions.

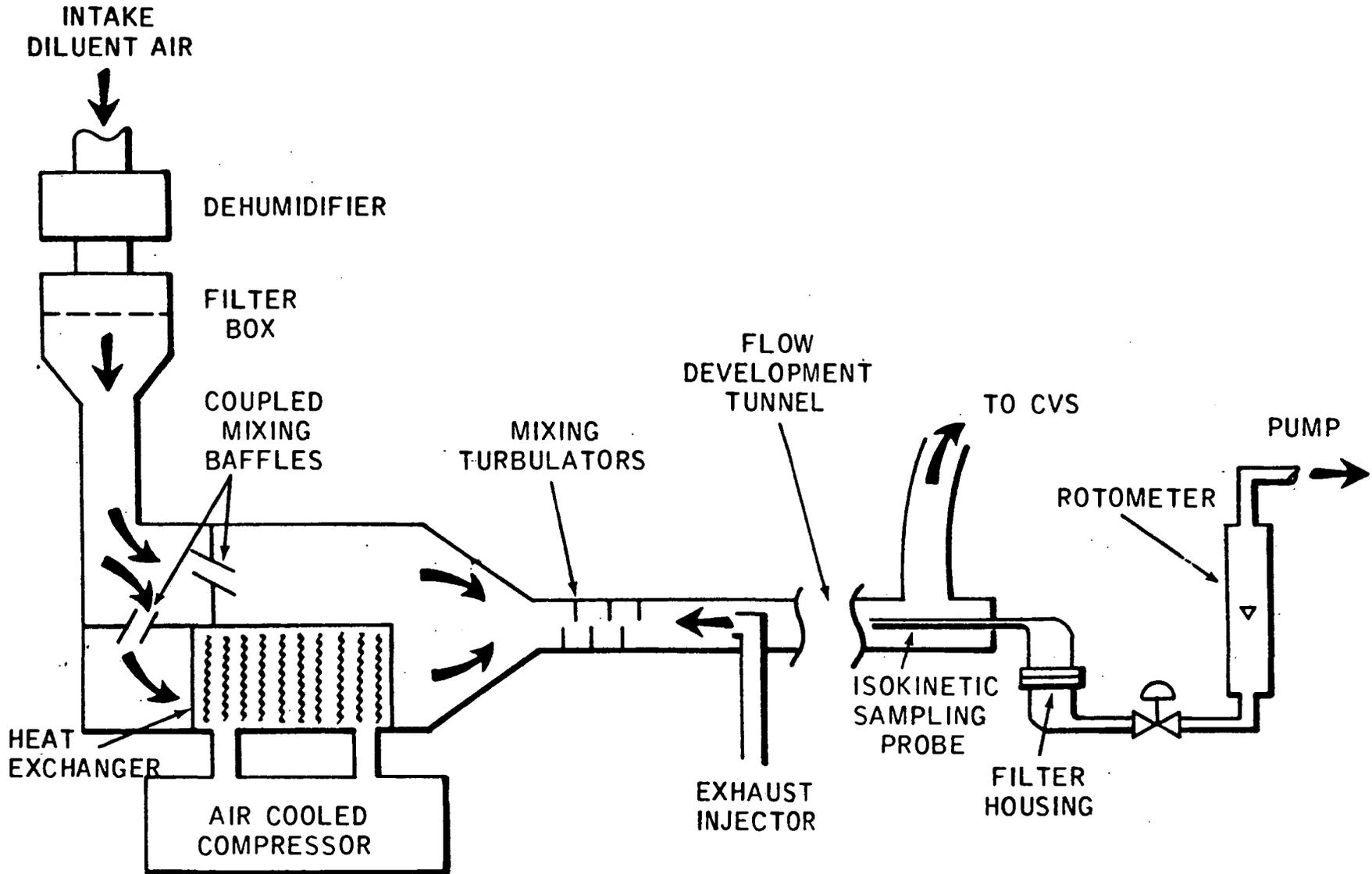
### III. Measurement Techniques Used to Study Sulfate Emissions

#### A. Collection of Sulfate Particulate

Sulfate is present in automotive exhaust as fine particulate. To correctly measure the amount of SO<sub>4</sub><sup>≡</sup> emitted, it is necessary first to filter it from the exhaust. Exxon Research accomplishes this task with a device we call the Exhaust Particulate Sampler, shown schematically in Figure 1. This device was designed to meet three basic criteria:

1. The equipment must be compatible with constant volume sampling (CVS) procedures for gaseous automotive emissions and must allow operation of the Federal Test Procedure (FTP) mandated for the measurement of these emissions.

Figure 1  
EXHAUST PARTICULATE SAMPLER



2. The sampling must be made under conditions in which a true proportional sample of the exhaust gas is taken for measurement, i.e., isokinetic sampling must be obtained.
3. The temperature at the point of sampling must be less than 90°F., to ensure the collection of all material that would be in particulate form in the atmosphere.

The major features of this sampler include a 7.5 ft. flow development tunnel, which is shorter than other devices developed for these measurements, and an advanced diluent air system. This latter point is important in that it allows low temperature (≤90°F.) sampling without excessive dilution and/or long flow development tunnels.

Diluent air is drawn into the particulate sampler in a manner analogous to that for a conventional CVS unit. This air is dehumidified, and filtered through a charcoal filter assembly. A portion of the dehumidified, filtered air is passed through an air-cooled heat exchanger which lowers its temperature to about 40°F. This chilled air is then blended with the remainder of the diluent air prior to being mixed with the exhaust gas. The amount of air passed through the heat exchanger is controlled by a signal from a thermocouple adjacent to the isokinetic sampling probe. When the probe temperature increases, the position of the mixing baffles is changed to divert more air through the heat exchanger. This increase in chilled air assures the maintenance of probe temperatures less than 90°F during the FTP.

Data demonstrating the ability of this system to maintain 90°F filter temperature without condensation of water on the filter, and to prevent significant loss of particulate material in the flow development tunnel or probes have been presented by Beltzer, et al. in SAE Paper 740286, "Measurement of Vehicle Particulate Emissions". A copy of this paper appears as Attachment I.

Exxon Research's dilution tunnel (10.9 cm diameter, 2.3 meters long) is smaller than those used by EPA (45.7 cm diameter, 4.5 meters long). However, in their soon to be published SAE Paper, "Sulfate Emissions from Catalyst Cars: A Review", Bradow and Moran of EPA, conclude that the two systems are equally effective. They state:

"A comparison of the two systems has been conducted at EPA in Research Triangle Park where an Exxon-type tunnel had been fabricated and installed on an engine dynamometer test stand. Sulfate determinations with the GM catalyst have been found to be comparable with both systems. Further, experimental determinations of wall losses indicated comparable performance. Thus, non-catalyst organic aerosol wall losses were about 3% of the aerosol handled and sulfate losses about 1% with the Exxon tunnel. Thus, both the Exxon and EPA dilution systems appear to be effective sulfate aerosol samplers."

B. Analysis of SO<sub>4</sub><sup>2-</sup> on Filters

The sulfate collected by the filter in the exhaust particulate sampler is leached from the filter with dilute nitric acid. The

leach solution is heated to boiling to drive off excess nitric acid, filtered to remove insoluble material, passed through an ion-exchange column to remove interfering cations, and then buffered with methenamine to a pH of 3-4. The resulting solution is titrated with barium perchlorate using Sulfanazo (III) as an indicator. This method has been found to be sensitive to levels of  $2 \mu\text{g SO}_4^{2-}/\text{cm}^2$  of filter, a level equivalent to about 0.0005 g/ml.  $\text{SO}_4^{2-}$  on the 1975 FTP. In their above mentioned paper, Bradow and Moran indicate that this method is one of several which, when correctly practiced, give comparable results.

### C. Measurement of $\text{SO}_2$

The measurement of  $\text{SO}_2$  is necessary to close the sulfur balance around a car, i.e., to account for all of the sulfur consumed with the fuel. Exxon Research uses a Thermo Electron Corporation (TECO Model #40)  $\text{SO}_2$  Analyzer which operates on a pulsed-fluorescence UV absorption principle. This instrument operates by exciting  $\text{SO}_2$  molecules with ultraviolet light, and measuring the fluorescent light emitted as the  $\text{SO}_2$  returns to ground state. The intensity of the fluorescence is directly proportional to the  $\text{SO}_2$  concentration.

This instrument is supposed to be specific for  $\text{SO}_2$  and not affected by the other molecules typically found in auto exhaust. This, however, is not the case. Water vapor interferes with the operation of the system, and it is necessary to completely dry the gas sample prior to its introduction into the unit. We have also found that  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  strongly quench the fluorescence. The instrument is therefore sensitive to the composition of the background gas. To obtain accurate  $\text{SO}_2$

concentrations it is necessary to calibrate the instrument with a background representative of the sample to be analyzed. For use with CVS system diluted exhaust, these problems can be circumvented by calibrating with dilute  $\text{SO}_2$  in air. However, if the instrument is to be used to analyze raw exhaust or a synthetic exhaust blend, recalibration is necessary. Further development of instruments for measuring  $\text{SO}_2$  would be helpful.

We also use the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) bubbler technique to determine average  $\text{SO}_2$  concentrations in exhaust. In this technique, dilute or raw exhaust gas is filtered to remove  $\text{SO}_4^{=}$  particulate and passed through a bubbler containing 80 ml. of 3%  $\text{H}_2\text{O}_2$  in high purity water. The  $\text{SO}_2$  present in the exhaust is quantitatively oxidized to  $\text{SO}_4^{=}$  in this solution. Tests with bubblers run in series have shown that collection efficiency, at flows up to about 5 liters/minute, is greater than 95%. After increasing solution volume to 100 ml., the collected  $\text{SO}_4^{=}$  is analyzed using the same method as is used to analyze for  $\text{SO}_4^{=}$  leached off the particulate filters, except that the step involving ion exchange to remove cations which might interfere with the analysis is not necessary.

#### IV. $\text{SO}_4^{=}$ Emission Rates

##### A. $\text{SO}_4^{=}$ Emissions from Non-Catalyst Cars

Sufficient data have now been accumulated to demonstrate conclusively that non-catalyst cars emit very low levels of  $\text{SO}_4^{=}$ . Table 1 contains a summary of the  $\text{SO}_4^{=}$  emission rates measured on non-catalyst cars tested at Exxon Research. These data show conversions of gasoline sulfur to  $\text{SO}_4^{=}$  of less than 1%, and are in general agreement with results published by GM<sup>(4)</sup> and Ford<sup>(5)</sup>.

Table 1

SO<sub>2</sub> and SO<sub>4</sub><sup>==</sup> Emission data from Non-Catalyst Cars

<u>Vehicle</u>	<u>Fuel Sulfur, %</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions g/mi.</u>	<u>Emissions % of Gasoline S</u>	<u>SO<sub>4</sub><sup>==</sup> Emissions g/mi.</u>	<u>Emissions % of Gasoline S</u>	<u>% Sulfur Balance</u>
1973 Chev.	0.040	1972 FTP	*	*	<0.007	<2.0	*
" "	0.067	40 mph	*	*	0.004	0.1	*
" "	"	"	*	*	0.004	0.1	*
" "	"	"	*	*	0.009	0.2	*
" "	"	"	*	*	0.0015	0.5	*
1969 Ply.	0.140	1972 FTP	0.647	107	0.018	2.0	109
" "	"	"	0.660	103	0.012	1.3	104
" "	0.056	"	0.268	115	0.007	2.1	117
" "	"	"	0.262	110	0.007	1.7	112
" "	0.032	"	0.178	135	*	*	*
" "	"	"	0.166	120	0.006	2.9	123
1974 Chev.	0.019	1975 FTP	0.100	115	0.0014	1.07	116
" "	"	40 mph	0.040	71.4	0.0003	0.36	71.8
" "	"	70 mph	0.056	93.3	0.0018	2.00	95.3
" "	0.091	1975 FTP	0.498	112	0.0024	0.36	113
" "	"	40 mph	0.257	89.9	0.0006	0.14	90.0
" "	"	70 mph	0.219	82.3	0.0027	0.66	83.0
" "	0.110	1975 FTP	0.466	117	0.0024	0.40	117
" "	"	40 mph	0.325	79.3	0.0008	0.13	79.4
" "	"	70 mph	0.269	83.5	0.0027	0.55	84.1
1974 Chev.	0.065	1975 FTP	*	*	0.002	0.4	*
" "	"	60 mph	*	*	0.002	0.6	*
" "	0.032	1975 FTP	*	*	0.003	1.1	*
" "	"	60 mph	*	*	0.001	0.7	*
1974 Mazda	0.065	1975 FTP	0.40	126	0.002	0.4	126
" "	"	60 mph	0.22	116	0.000	0.0	116
" "	0.032	1975 FTP	0.20	122	0.004	1.6	124
" "	"	60 mph	*	*	0.000	0.0	*
1974 Honda	0.065	1975 FTP	0.12	75	0.001	0.4	75
" "	"	60 mph	0.13	108	0.000	0.0	108
" "	0.032	1975 FTP	0.06	120	0.000	0.0	120
" "	"	60 mph	0.06	70	0.000	0.0	70

\* Not measured

## B. SO<sub>4</sub><sup>m</sup> Emissions from Cars Equipped with Oxidation Catalysts

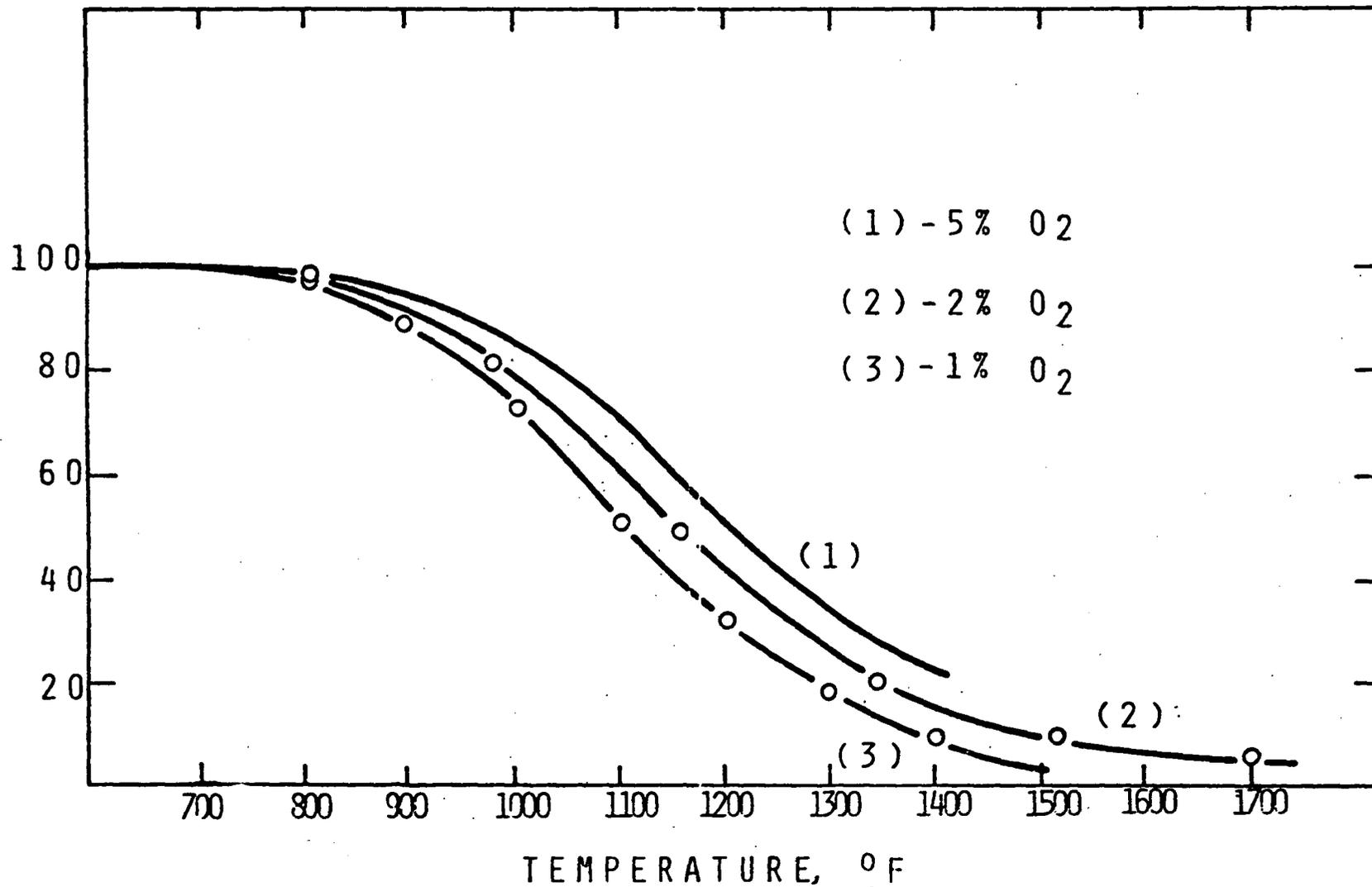
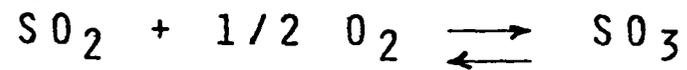
Data obtained by Exxon Research and others show wide variations in the amount of SO<sub>4</sub><sup>m</sup> emitted by cars equipped with oxidation catalysts, and adjusted to control emissions to 3.4 g/mi. CO and 0.41 g/mi. HC. For example, under FTP conditions, vehicles equipped with pelleted oxidation catalysts emit about 5% of the sulfur in gasoline as SO<sub>4</sub><sup>m</sup>, while vehicles equipped with monolithic oxidation catalysts emit as much as 10-15% of the sulfur in gasoline as SO<sub>4</sub><sup>m</sup>. At high speed cruise conditions, SO<sub>4</sub><sup>m</sup> emissions from the two types of systems are comparable, at 25-35% conversion of the sulfur in gasoline.

Before trying to explain these differences and comment on their meaning, the data obtained in laboratory studies of the factors affecting SO<sub>4</sub><sup>m</sup> formation, and vehicle tests demonstrating storage of SO<sub>4</sub><sup>m</sup> on catalyst surfaces, will be presented. These two subjects provide the background necessary to resolve some of the differences observed in vehicle SO<sub>4</sub><sup>m</sup> emission rates. It should be pointed out, however, that a complete explanation of these differences is not available, and many questions still remain.

### 1. Factors Affecting SO<sub>4</sub><sup>m</sup> Formation - Laboratory Studies

Thermodynamic equilibrium calculations for mixtures containing less than 100 ppm SO<sub>2</sub> and 1-5% O<sub>2</sub> show that at temperatures above about 1500°F, equilibrium conversion to SO<sub>3</sub> is very low, while at temperatures below about 800°F, equilibrium conversion to SO<sub>3</sub> is essentially 100%. The results of these calculations are shown in Figure 2. The conditions under which SO<sub>3</sub> concentration is a function of both temperature and oxygen content are exactly the conditions under which automotive oxidation catalysts operate.

EQUILIBRIUM CONVERSION



To learn more about the effect of operating variables on  $\text{SO}_4^{\equiv}$  formation, a laboratory program to study the effects of catalyst type,  $\text{O}_2$  concentration, temperature, and residence time on  $\text{SO}_4^{\equiv}$  formation was carried out. The equipment used in this study is shown schematically in Figure 3. The procedure used was as follows: A synthetic exhaust containing the components shown in the figure was blended and passed over a sample of commercial oxidation catalyst contained in the reactor tube. Temperature of the catalyst sample could be varied between room temperature and  $1500^\circ\text{F}$ . Conversions of  $\text{SO}_2$ ,  $\text{CO}$ , and  $\text{HC}$  were measured using the TECO  $\text{SO}_2$  analyzer described earlier, and conventional exhaust gas analytical instrumentation. The use of the Goksøyr-Ross technique (6) for  $\text{SO}_4^{\equiv}$  determination was attempted, but because of the low flow rates of sample available at that time, accurate values for  $\text{SO}_4^{\equiv}$  could not be obtained. This problem has now been solved, but the unit is being used for the  $\text{SO}_4^{\equiv}$  trap studies reported at the end of this paper.

The results of this study show significant differences between the behavior of monolithic and pelleted oxidation catalysts. Many of these differences appear to be related to the different tendencies of these catalysts to store  $\text{SO}_2$  and  $\text{SO}_4^{\equiv}$ . The results for monoliths are presented first, followed by the results for pellets, followed by a discussion of what conclusions can be drawn from this study. Since the measurement made was  $\text{SO}_2$  in and out of the reactor, the results are reported in terms of  $\text{SO}_2$  disappearance, which is the sum of  $\text{SO}_2$  converted to  $\text{SO}_4^{\equiv}$  and net  $\text{SO}_2$  stored, if any, on the catalyst.

a. Results for Monolithic Catalysts

Figure 4 shows  $\text{SO}_2$  disappearance as a function of temperature over a monolithic oxidation catalyst operated at a space velocity of

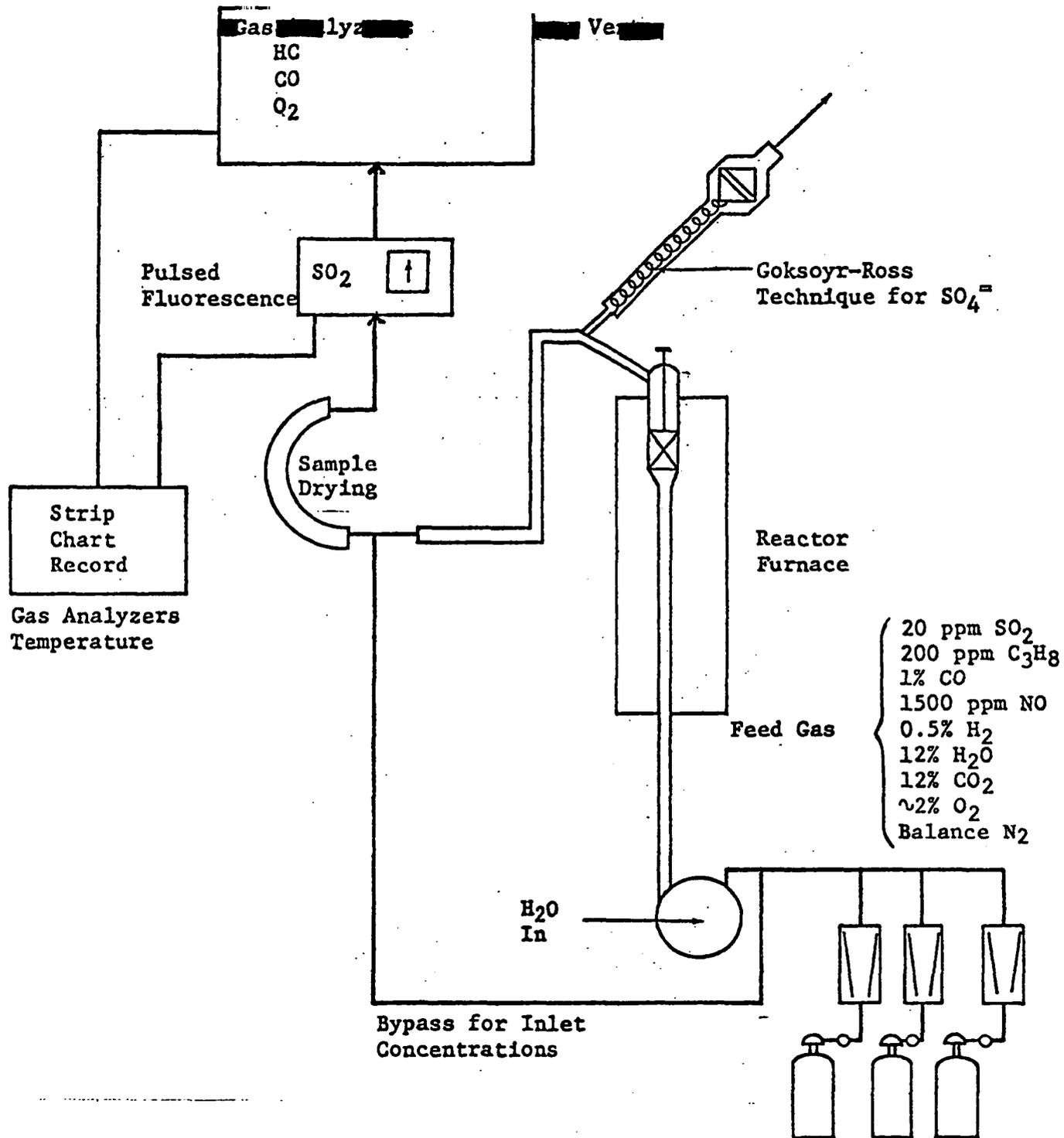


FIGURE 3 - LABORATORY REACTOR

62,500 v/v/hr. Data were obtained by changing catalyst temperature in 50-100°F. increments and maintaining that temperature until outlet SO<sub>2</sub> concentration stabilized. At temperatures below 600°F, essentially no SO<sub>2</sub> disappearance was found. Between 600 and 800°F, SO<sub>2</sub> disappearance rose rapidly towards the value for equilibrium conversion to SO<sub>4</sub><sup>m</sup>. Above 800°F, SO<sub>2</sub> disappearance rate was maintained at 75% or more of the equilibrium conversion to SO<sub>4</sub><sup>m</sup>.

Figure 5 shows SO<sub>2</sub> disappearance as a function of reactor exit oxygen concentration at 1000°F and a space velocity of 100,000 v/v/hr. for a monolithic catalyst. Reactor exit oxygen concentration is roughly equivalent to excess oxygen since it represents what remains after reaction with CO, H<sub>2</sub>, and HC. SO<sub>2</sub> disappearance is relatively independent of O<sub>2</sub> concentration about 1% excess O<sub>2</sub>, but drops sharply below 1% excess O<sub>2</sub>. CO conversion, also shown in Figure 5, drops off much less than does SO<sub>2</sub> disappearance. The same is true of HC conversion, though these data are not shown.

Figure 6 shows the effect of space velocity on SO<sub>2</sub> disappearance over a monolithic catalyst at temperatures between 800 and 1100°F. Between 800 and 1000°F, the results show the expected decreases in disappearance with increased temperature and increased space velocity. The data obtained at 1100°F shows disappearance to be relatively independent of space velocity, which can be explained by the fact that at this temperature, the oxidation of SO<sub>2</sub> to SO<sub>3</sub> is limited by thermodynamic equilibrium. At 1100°F, storage of SO<sub>2</sub> or SO<sub>4</sub><sup>m</sup> does not appear to be significant.

FIGURE 4

SO<sub>2</sub> DISAPPEARANCE VS. CATALYST TEMPERATURE  
OVER A MONOLITHIC CATALYST

OXYGEN CONCENTRATION: 2% EXCESS  
SPACE VELOCITY = 62,500 V/V/HR.

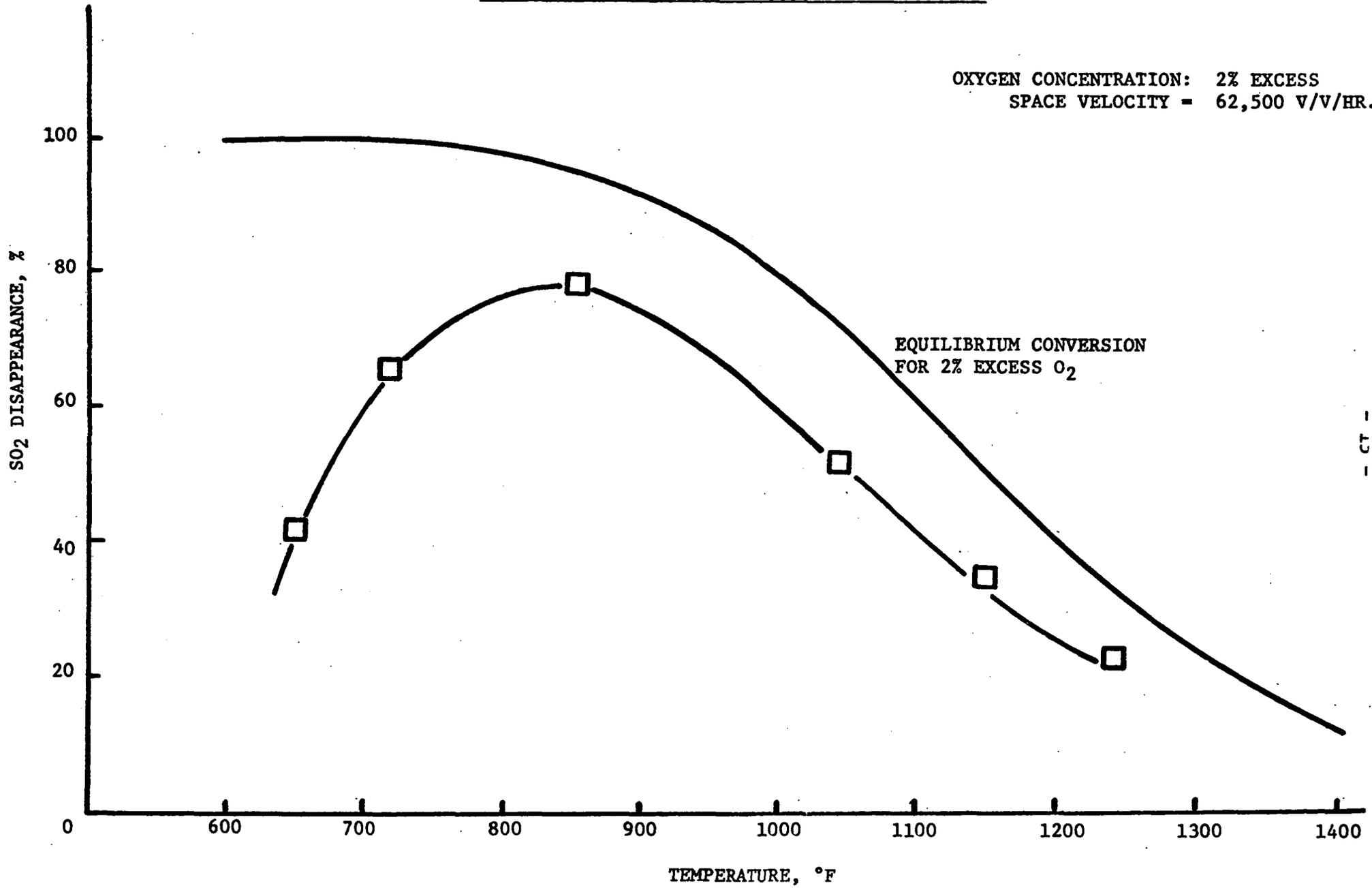
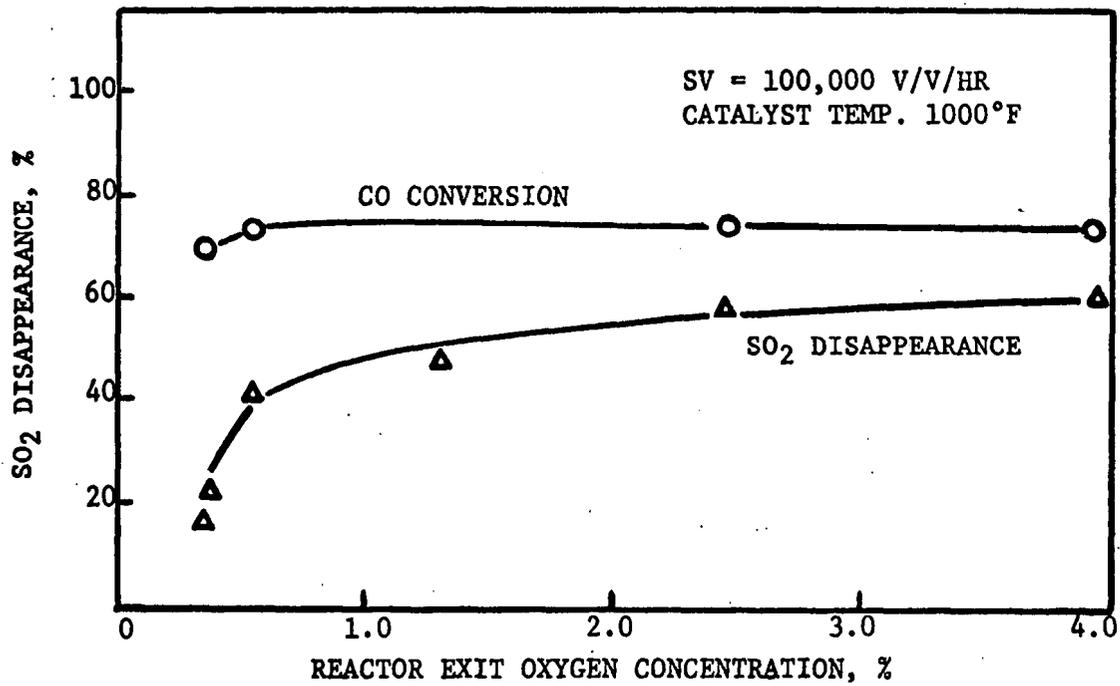


FIGURE 5

SO<sub>2</sub> DISAPPEARANCE VS. EXIT OXYGEN CONCENTRATION  
FOR A MONOLITHIC CATALYST



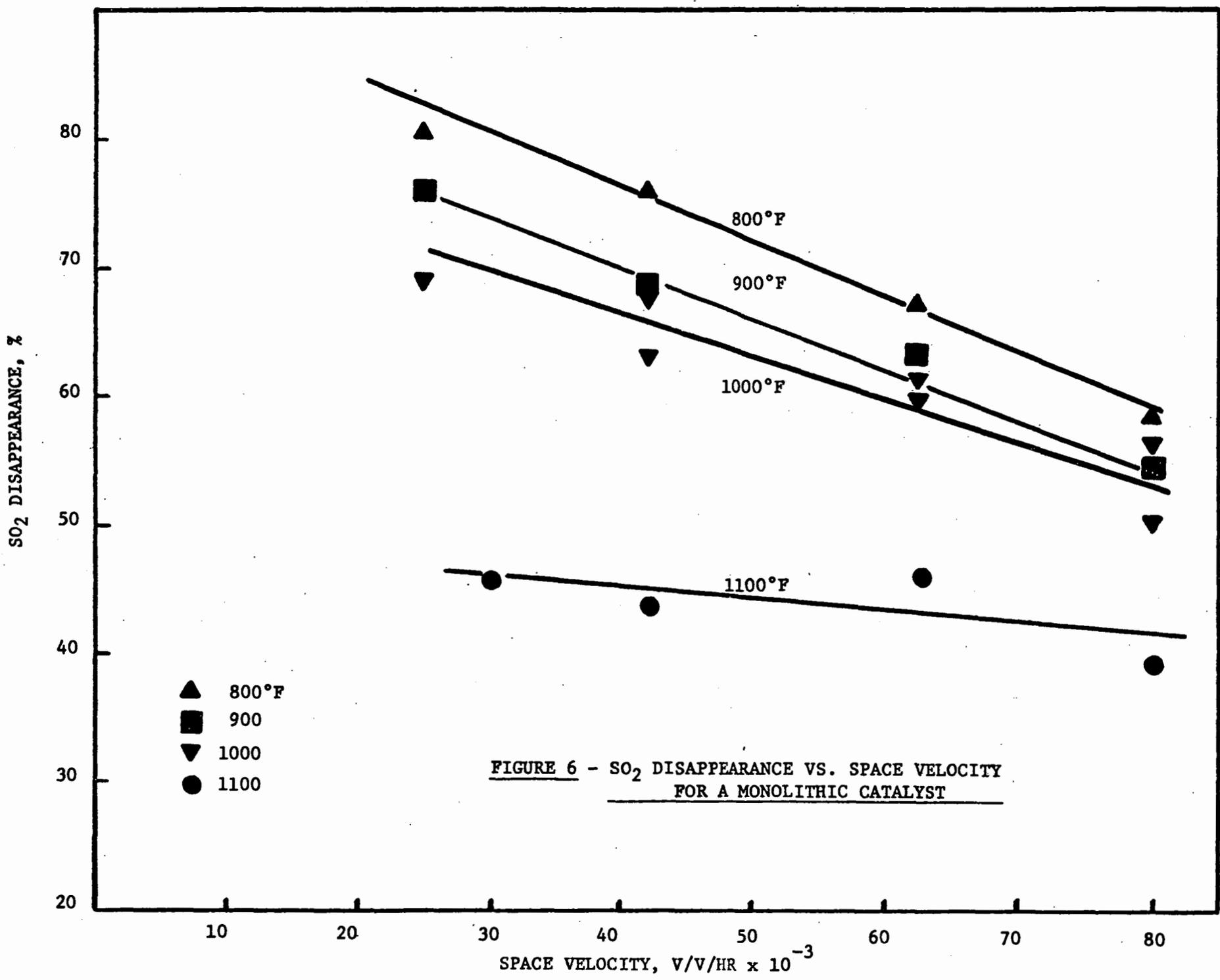


FIGURE 6 - SO<sub>2</sub> DISAPPEARANCE VS. SPACE VELOCITY FOR A MONOLITHIC CATALYST

b. Results for Pelleted Catalysts

All of the data obtained in this study with pelleted catalysts show lower  $\text{SO}_2$  disappearance rates than were observed with monolithic catalysts. Figure 7 shows  $\text{SO}_2$  disappearance as a function of temperature at a space velocity of 28,500 v/v/hr. This is a lower space velocity than was used with the monolithic catalyst, but typical of that encountered in pelleted catalyst systems.  $\text{SO}_2$  disappearance rates in this system do not approach the equilibrium for conversion to  $\text{SO}_4^=$  as closely as they did for the monolith.

Figure 8 shows  $\text{SO}_2$  disappearance as a function of reactor exit oxygen concentration for a pelleted oxidation catalyst at a space velocity of 28,500 v/v/hr. These results are similar to those observed for monolithic catalysts except that instead of dropping sharply at  $\text{O}_2$  concentration below 1%, as was the case with the monolith, with pellets,  $\text{SO}_2$  disappearance decreases with decreasing  $\text{O}_2$  concentration over the whole range of  $\text{O}_2$  concentrations studied.

Figure 9 shows  $\text{SO}_2$  disappearance as a function of space velocity and temperature for pelleted catalysts. Up to 1000°F, this relationship is as expected with  $\text{SO}_2$  disappearance decreasing with increasing space velocity and temperature. As in the case of monoliths, the  $\text{SO}_2$  disappearance data at 1100°F shows no space velocity effect, because at this temperature, the reaction is limited by thermodynamic equilibrium.

FIGURE 7

SO<sub>2</sub> DISAPPEARANCE VS. TEMPERATURE FOR A PELLETTED CATALYST

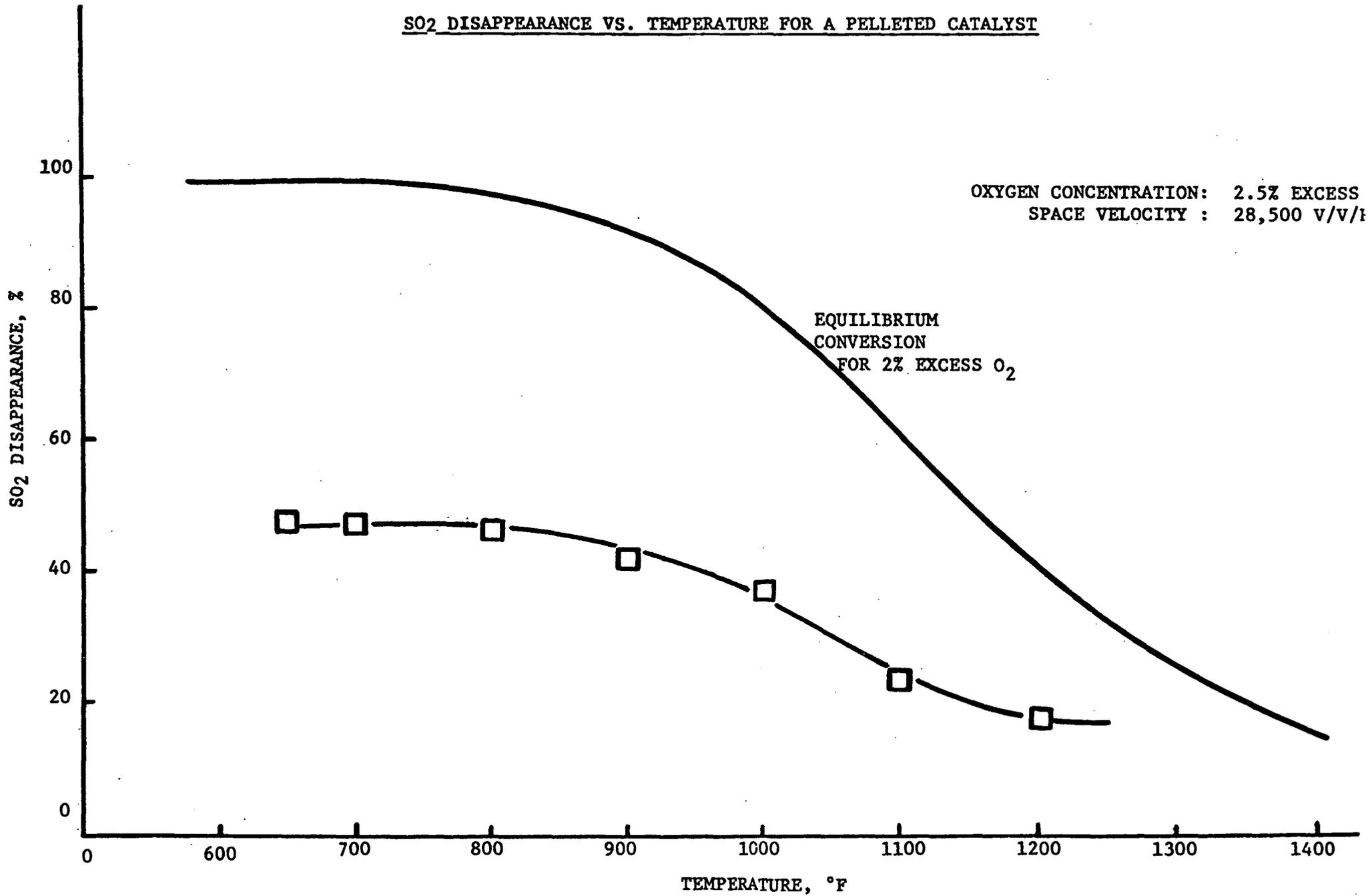


FIGURE 8

SO<sub>2</sub> DISAPPEARANCE VS. EXIT O<sub>2</sub> CONCENTRATION FOR A PELLETTED CATALYST

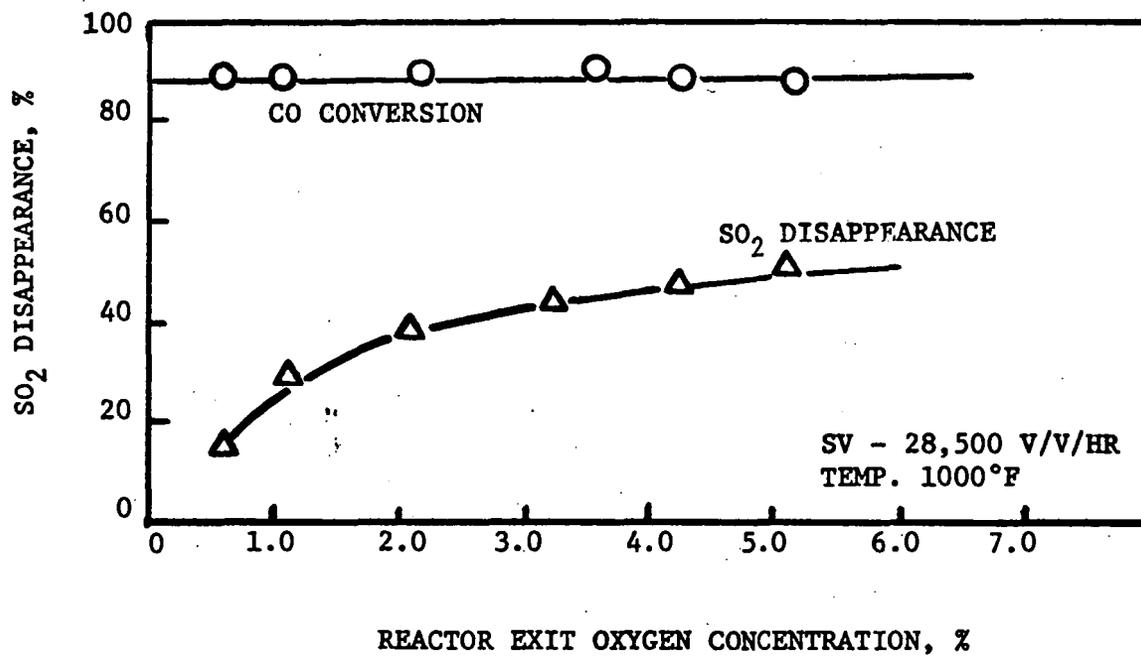
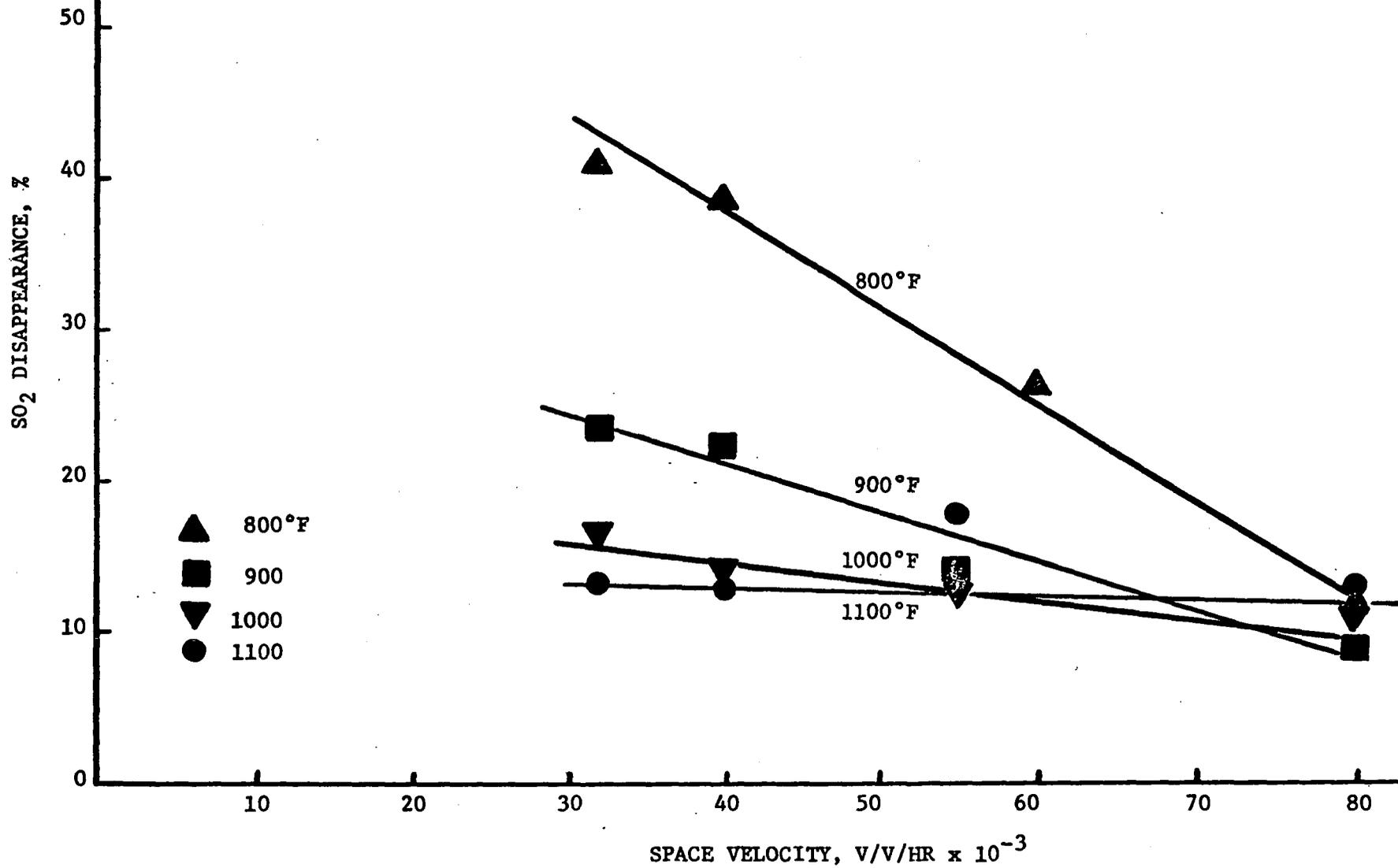


FIGURE 9

SO<sub>2</sub> DISAPPEARANCE VS. SPACE VELOCITY FOR A PELLETTED CATALYST



c. Discussion of the Laboratory Data

The results obtained by varying O<sub>2</sub> concentration, space velocity, and temperature are what would be predicted from simple equilibrium and kinetic considerations. The drop-off in SO<sub>2</sub> disappearance with decreasing O<sub>2</sub> concentration is of particular interest because it suggests a method of minimizing SO<sub>4</sub><sup>□</sup> formation without significantly decreasing CO and HC conversion. More will be said on this subject in Section V on Control of SO<sub>4</sub><sup>□</sup> Emissions. Space velocity effects probably do not offer a practical method of controlling SO<sub>4</sub><sup>□</sup> emissions. It must be assumed that the auto manufacturers sized their catalyst systems to provide the degree of CO and HC control required. Decreasing catalyst volume, the only practical way of increasing space velocity on a vehicle, would probably result in unacceptable CO and HC emissions.

The temperature effect data for pelleted catalysts could be interpreted as meaning that these catalysts are less active for SO<sub>2</sub> oxidation than are monoliths. This explanation seems unlikely, however, because both catalyst types show equivalent performance for CO and HC oxidation. The laboratory data are not in agreement with vehicle SO<sub>4</sub><sup>□</sup> emission data, which will be presented later in this paper. At high speed cruise conditions, where vehicle results should compare most directly with laboratory results, vehicle tests show the emission of SO<sub>4</sub><sup>□</sup> to be similar for both types of catalysts. Until the sulfur balance can be closed for both vehicle and laboratory tests, and sulfur oxide storage phenomena understood, the reasons for the differences between laboratory and vehicle test results will remain unexplained.

## 2. Storage Phenomena

Both monolithic and pelleted catalysts have a coating of high surface area alumina. It is well known that alumina can sorb both  $\text{SO}_2$  and  $\text{SO}_4^{\equiv}$ , the amounts being determined by temperature, and the structure of the alumina present. Alumina tends to store  $\text{SO}_2$  or  $\text{SO}_4^{\equiv}$  at lower temperatures, corresponding to lower operating speeds, and release them at higher temperatures corresponding to higher speeds.  $\text{SO}_4^{\equiv}$  storage has been studied in some detail, though  $\text{SO}_2$  storage has not received much attention. It is known, however, that alumina and other sorbents sorb  $\text{SO}_4^{\equiv}$  more readily than  $\text{SO}_2$ .

In early 1974, two sets of experiments were conducted to demonstrate  $\text{SO}_4^{\equiv}$  storage on pelleted catalysts, one in which the catalyst was conditioned with 0.14 wt. % sulfur fuel, the other in which it was conditioned with 0.004 wt. % sulfur fuel. The conditioning procedure used involved 500 miles of operation on the Federal Durability Driving Schedule (AMA Cycle) followed by a cold start 1975 FTP. After this conditioning procedure, the vehicle was operated for two hours at 60 mph cruise. The particulate filter was changed every 20 minutes to allow an evaluation of  $\text{SO}_4^{\equiv}$  emissions as a function of time. Data from these runs is summarized in Figures 10 and 11.

Figure 10 shows the results of tests with 0.14 wt. % S fuel on a pelleted catalyst conditioned with 0.14 and 0.004 wt. % S fuel. Initial  $\text{SO}_4^{\equiv}$  emissions from the run in which the catalyst was conditioned with 0.14 wt. % S fuel are much higher than initial  $\text{SO}_4^{\equiv}$  emissions from the run in which the catalyst was conditioned with 0.004 wt. % S fuel. After ~60 minutes both runs show the same  $\text{SO}_4^{\equiv}$  emission rate. This is strong evidence of storage. After the catalyst was conditioned with 0.14 wt. % S fuel, its surface contained an excess of  $\text{SO}_4^{\equiv}$ , which was released at the start of the run. Conversely, after conditioning with 0.004 wt. % fuel, the catalyst sorbed  $\text{SO}_4^{\equiv}$  at the start of the run.

Figure 11 shows the results of tests with 0.004 wt. % S fuel. The effect of conditioning is even more dramatic in this case. In the test with a catalyst conditioned with 0.14 wt. % S fuel, almost seven times as much  $\text{SO}_4^{\equiv}$  was emitted during the first 20 minute period as at steady state after 60 minutes of operation.

After  $\text{SO}_4^{\equiv}$  storage on pelleted catalysts was verified, we conducted a similar set of experiments to determine whether  $\text{SO}_4^{\equiv}$  was stored on monolithic catalysts. The major change in the experiments on monoliths was that 175 miles of Federal Durability Driving Cycle mileage accumulation was used in conditioning the catalyst. For the pelleted catalyst, 500 miles of conditioning had been used. Results of these experiments appear in Figures 12 and 13. These tests show some of the same type of behavior as was seen with the pellets, but the storage effect is not as large.

Figure 10

Sulfate Emissions at 60 mph Cruise  
Pelleted Catalyst, 0.14% Sulfur Fuel

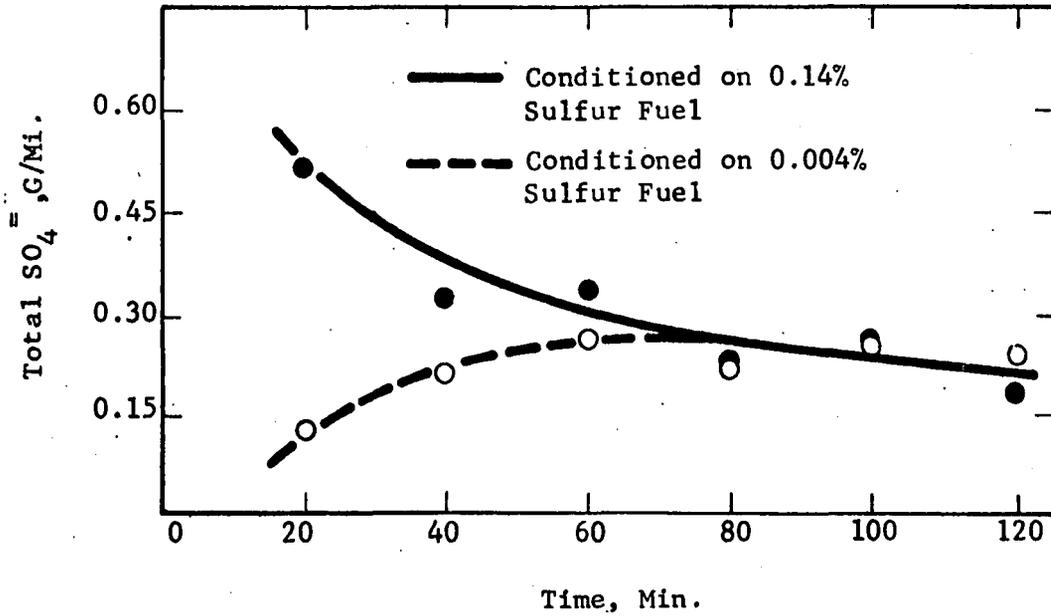


Figure 11

Sulfate Emissions at 60 mph Cruise  
Pelleted Catalyst, 0.004% Sulfur Fuel

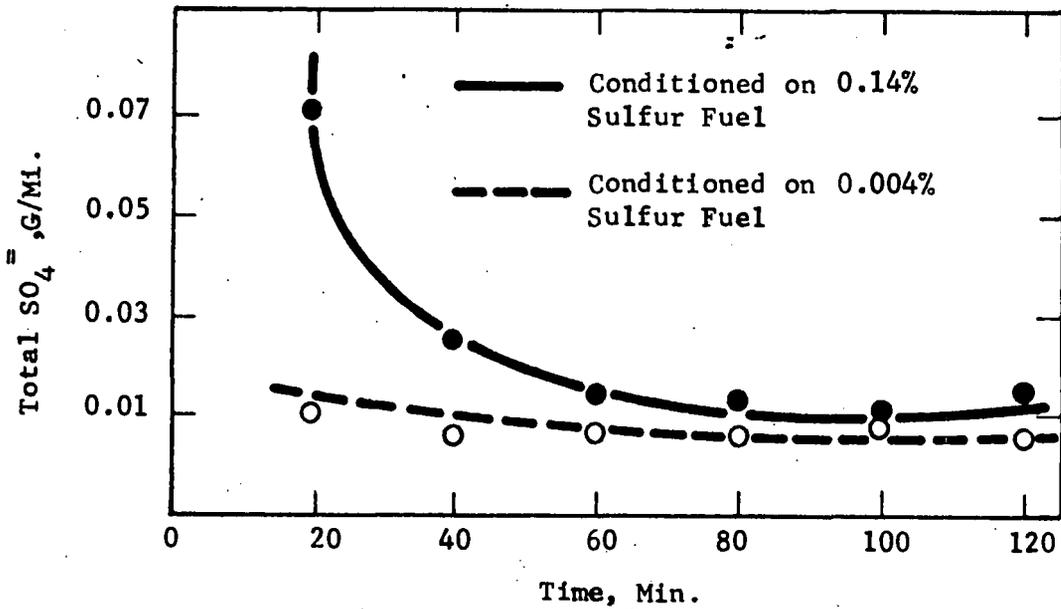


Figure 12

Sulfate Emissions at 60 MPH Cruise  
Monolith Catalyst, 0.14% Sulfur Fuel

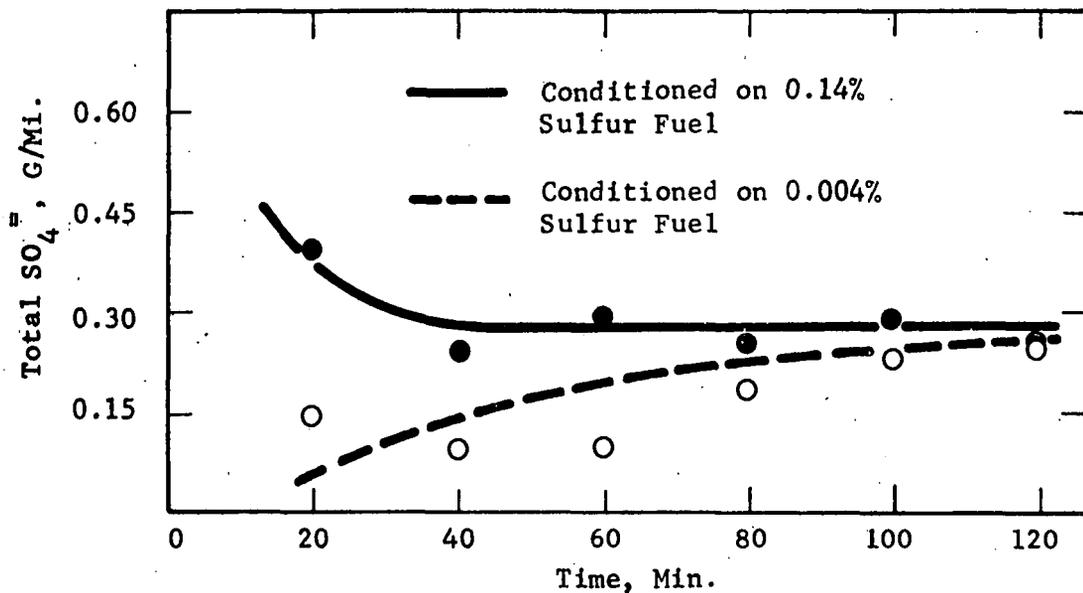
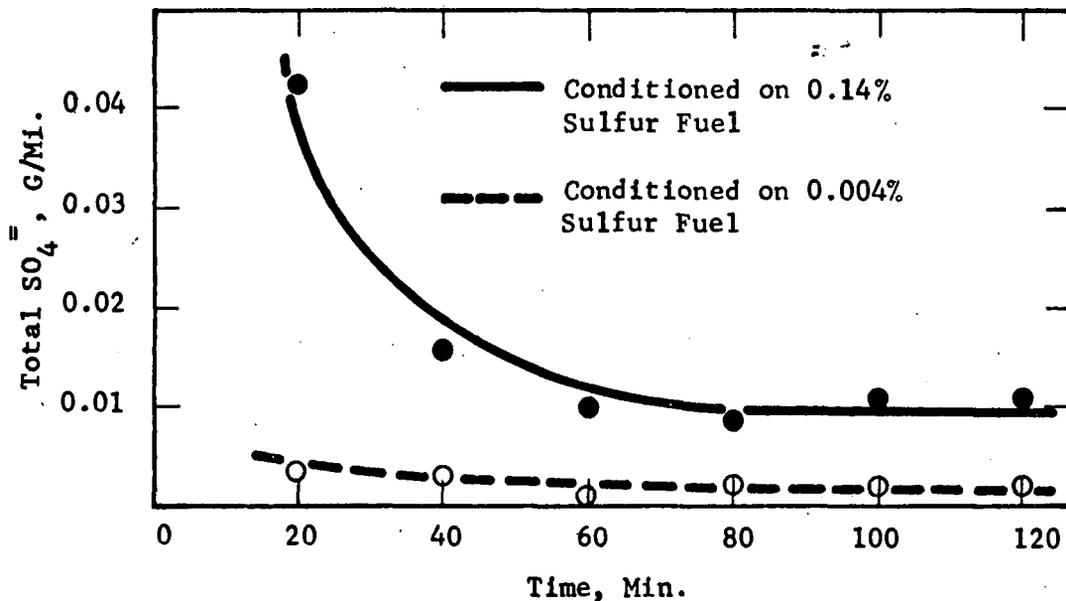


Figure 13

Sulfate Emissions at 60 MPH Cruise  
Monolith Catalyst, 0.004% Sulfur Fuel



Since this initial set of experiments was conducted, we have confirmed these storage effects in other tests. These tests all show very strong storage effects with pelleted catalysts, and lesser, but definite, storage effects with monoliths.

### 3. Vehicle SO<sub>4</sub><sup>m</sup> Emission Data

In its May 30, 1974 submission to EPA of data on automotive sulfate emissions, in response to a request which appeared in the March 8, 1974 issue of the Federal Register, Exxon Research summarized its data on SO<sub>4</sub><sup>m</sup> emissions as follows:

- Over both pelleted and monolithic catalysts actual conversion of gasoline sulfur to SO<sub>4</sub><sup>m</sup>, and SO<sub>4</sub><sup>m</sup> emission rate, can differ. Under FTP or low speed cruise conditions, some of the SO<sub>4</sub><sup>m</sup> formed is stored on the catalyst, or possibly in the exhaust system. Stored SO<sub>4</sub><sup>m</sup> can be emitted at high speed conditions.
- In vehicles using monolithic oxidation catalysts, 25-35% of the sulfur in gasoline is emitted as SO<sub>4</sub><sup>m</sup> under FTP, 40 mph, and 60 mph cruise conditions.
- In vehicles using pelleted oxidation catalysts, only 5-10% of the sulfur in gasoline is emitted as SO<sub>4</sub><sup>m</sup> under FTP and 40 mph cruise conditions. With these catalysts, storage of SO<sub>4</sub><sup>m</sup> is a major factor. At 60 mph cruise conditions, at least part of the SO<sub>4</sub><sup>m</sup> stored

at lower speeds is released, and  $\text{SO}_4^{\text{m}}$  emissions are similar to those observed with monolithic oxidation catalysts.

Recent data, obtained in the program described in Section III.B.3.a., suggest that over monolithic catalysts, no more than 10-15% of the sulfur in gasoline is emitted as  $\text{SO}_4^{\text{m}}$  during the FTP. Furthermore, substantial differences in  $\text{SO}_4^{\text{m}}$  emission rate may exist depending on which monolithic catalyst is used. Our earlier results were obtained on prototype catalysts using less controlled aging and conditioning techniques than were used in later programs. The 25-35% emission of gasoline sulfur as  $\text{SO}_4^{\text{m}}$  for monoliths at 40 and 60 mph cruise is also found in our later data, but again substantial differences are found depending on which catalyst is used.

Our recent data on pelleted catalysts supports the estimate of no more than 10% emission of gasoline sulfur as  $\text{SO}_4^{\text{m}}$  under FTP conditions. However, at 40 mph cruise conditions,  $\text{SO}_4^{\text{m}}$  emission rates as high as 25% of gasoline sulfur were measured. At 60-70 mph cruise 25-35% of gasoline sulfur was emitted as  $\text{SO}_4^{\text{m}}$ . Details of the program in which these data were generated are given below.

a. Effect of Catalyst Type

Under EPA Contract 68-02-1279, "The Characterization of Particulate Emissions from Prototype Catalyst Vehicles", Exxon Research has measured  $\text{SO}_4^{\text{m}}$  emissions from seven different oxidation catalysts, four monolithic and three pelleted catalysts. The following procedure was used.

- 1) Each catalyst was aged by operating for 2000 miles of AMA cycle on a fuel containing 0.004% sulfur.
- 2) The catalyst was removed from the car used for aging and mounted on a 1974 350 CID Chevrolet V-8, equipped with an air pump, and calibrated to control CO and HC to 3.4 g/mi. and 0.41 g/mi., respectively.
- 3) The vehicle was then operated through the following series of tests on each of three fuels.
  - a. 200 miles of conditioning on the AMA cycle followed by a 16 hour cold soak.
  - b. 1975 FTP
  - c. 1 hour idle
  - d. 1 hour, 40 mph cruise
  - e. 2 hour, 60 or 70 mph cruise
  - f. overnight soak
  - g. 1975 FTP

SO<sub>4</sub><sup>≡</sup> emissions were measured for both 1975 FTP's, the idle, 40 mph, and 60-70 mph cruise modes. The three fuels used were:

- 1) the EPA reference fuel, which contains 0.019 wt. % sulfur,
- 2) the EPA reference fuel doped with a 50% thiophene-50% t-butyl disulfide mixture to a sulfur content of 0.110%, and
- 3) a high aromatic content fuel doped with the thiophene-t-butyl disulfide mixture to a sulfur content of 0.091%.

The fuels were always tested in the order listed above.

SO<sub>2</sub> and SO<sub>4</sub><sup>≡</sup> measurements for all catalyst/fuel combinations are given in Table 2. In this table SO<sub>2</sub> and SO<sub>4</sub><sup>≡</sup> emissions in g/mi. and percent of gasoline sulfur are reported for the average of the two FTP's, and for the 40 mph, and the 60-70 mph cruise. The fraction of gasoline sulfur accounted for by the sum of the SO<sub>2</sub> and SO<sub>4</sub><sup>≡</sup> emitted is also reported. These data are also presented graphically in Figures 14-19. Figure 14 shows SO<sub>2</sub> and SO<sub>4</sub><sup>≡</sup> emissions for the monolithic catalysts for FTP conditions; Figure 15, for 40 mph cruise; and Figure 16, for 60-70 mph cruise. Figure 17 shows SO<sub>2</sub> and SO<sub>4</sub><sup>≡</sup> emissions for the pelleted catalysts for FTP conditions; Figure 18, for 40 mph cruise; and Figure 19 for 60-70 mph cruise.

In interpreting the data presented in Table 2, and in Figures 14-19, it should be remembered that, with the exception of Mono (III) monolith, only one sample of each catalyst was tested. Replicate testing should be carried out before any action is taken based on these data. With that caution in mind, the following observations can be made.

- Under FTP conditions, no more than 10-15% of the sulfur in gasoline is emitted as SO<sub>4</sub><sup>≡</sup> when monolithic oxidation catalysts are used. This is lower than the 25-35% reported earlier.
- The Mono II catalyst showed lower SO<sub>4</sub><sup>≡</sup> emission rates at 40 mph than did the other two brands of monoliths tested. For the FTP and at 60-70 mph the SO<sub>4</sub><sup>≡</sup> emissions from this catalyst were comparable to SO<sub>4</sub><sup>≡</sup> emission rates from the other two brands of monoliths. The lower SO<sub>4</sub><sup>≡</sup> emission rates from

TABLE 2

SO<sub>2</sub> AND SO<sub>4</sub><sup>=</sup> EMISSION DATA FROM EPA  
 CONTRACT NO. 68-02-1279

Catalyst	Fuel Sulfur, %	Mode	SO <sub>2</sub> Emissions		SO <sub>4</sub> <sup>=</sup> Emissions		% Sulfur Balance
			g/mi	% of Gasoline S	g/mi	% of Gasoline S	
MONOLITHIC CATALYSTS							
Mono (I)	0.019	FTP	0.00	0.00	0.005	2.1	2.1
		40 mph	0.00	0.00	0.019	12.8	12.8
		60-70 mph	0.00	0.00	0.016	13.2	13.2
	0.110	FTP	0.220	37.3	0.091	10.5	47.8
		40 mph	0.092	25.9	0.163	30.4	56.3
		60-70 mph	0.014	2.9	0.088	12.2	15.1
	0.091	FTP	0.143	29.1	0.110	14.8	43.1
		40 mph	0.080	25.8	0.122	25.7	51.5
		60-70 mph	*	*	0.092	15.7	*
Mono (II)	0.019	FTP	0.043	39.8	0.005	3.1	42.9
		40 mph	0.060	85.7	0.010	9.4	95.1
		60-70 mph	0.035	23.8	0.016	7.2	31.0
	0.110	FTP	0.422	71.6	0.077	7.5	79.1
		40 mph	0.317	83.9	0.088	15.3	99.2
		60-70 mph	0.343	79.6	0.109	16.7	96.3
	0.091	FTP	0.422	85.1	0.087	4.4	89.5
		40 mph	0.257	74.8	0.069	13.1	87.9
		60-70 mph	0.312	79.6	0.093	15.8	95.4
Mono (III)-1	0.019	FTP	0.072	67.9	0.003	1.9	69.8
		40 mph	0.000	0.0	0.021	20.3	20.3
		60-70 mph	0.050	30.9	0.018	7.4	38.3
	0.110	FTP	0.302	50.0	0.040	4.3	54.3
		40 mph	0.050	12.5	0.294	47.7	60.2
		60-70 mph	0.188	21.8	0.105	8.1	29.9
	0.091	FTP	0.063	21.9	0.032	4.2	26.1
		40 mph	0.069	21.2	0.265	52.9	74.1
		60-70 mph	0.172	20.3	0.098	7.8	28.1

TABLE 2 (CONT.)

Catalyst	Fuel Sulfur, %	Mode	SO <sub>2</sub> Emissions		SO <sub>4</sub> <sup>=</sup> Emissions		% Sulfur Balance
			g/mi	% of Gasoline S	g/mi	% of Gasoline S	
Mono (III)-2	0.019	FTP	0.021	18.4	0.011	6.5	24.9
		40 mph	0.000	0.0	0.024	26.5	26.5
		60-70 mph	0.029	36.7	0.039	32.9	69.6
	0.110	FTP	0.154	26.6	0.098	11.0	37.6
		40 mph	0.072	18.3	0.282	46.0	64.3
		60-70 mph	0.177	44.9	0.182	31.0	75.9
	0.091	FTP	0.226	47.0	0.108	14.6	61.6
		40 mph	0.098	29.8	0.257	51.0	80.8
		60-70 mph	0.008	2.4	0.177	35.7	38.1
PELLETED CATALYSTS							
Pellet (I)	0.019	FTP	0.087	87.0	0.004	2.6	89.6
		40 mph	0.000	0.0	0.002	1.5	1.5
		60-70 mph	*	*	0.043	36.0	*
	0.110	FTP	0.121	12.6	0.030	2.9	15.5
		40 mph	0.000	0.0	0.167	27.2	27.2
		60-70 mph	0.000	0.0	0.166	25.3	25.3
	0.091	FTP	0.102	19.5	0.018	2.5	22.0
		40 mph	0.035	9.5	0.126	22.4	31.9
		60-70 mph	0.208	50.5	0.074	12.0	62.5
Pellet (II)	0.019	FTP	0.034	32.7	0.007	4.5	37.2
		40 mph	0.010	14.7	0.010	9.8	24.5
		60-70 mph	0.035	46.1	0.031	27.1	73.2
	0.110	FTP	0.161	27.1	0.037	3.8	30.9
		40 mph	0.122	32.8	0.142	25.1	57.9
		60-70 mph	0.211	49.5	0.230	36.1	85.6
	0.091	FTP	0.123	25.7	0.031	4.6	30.3
		40 mph	0.088	28.8	0.108	22.8	51.6
		60-70 mph	0.008	2.1	0.154	27.2	29.3

TABLE 2 (CONT.)

<u>Catalyst</u>	<u>Fuel Sulfur, %</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions</u>		<u>SO<sub>4</sub><sup>=</sup> Emissions</u>		<u>% Sulfur Balance</u>
			<u>g/mi</u>	<u>% of Gasoline S</u>	<u>g/mi</u>	<u>% of Gasoline S</u>	
ellet (III)	0.019	FTP	0.023	14.7	0.023	9.8	24.5
		40 mph	0.003	4.2	0.019	17.4	21.6
		60-70 mph	0.026	35.5	0.027	24.6	70.1
	0.110	FTP	0.066	12.1	0.080	10.3	22.4
		40 mph	0.048	11.3	0.156	24.0	35.3
		60-70 mph	0.129	39.3	0.145	29.2	68.5
	0.091	FTP	0.127	26.6	0.077	10.7	37.3
		40 mph	0.071	21.8	0.159	32.7	54.5
		60-70 mph	0.154	42.5	0.166	30.4	72.9

FIGURE 14

SO<sub>2</sub> and SO<sub>4</sub><sup>m</sup> Emissions For Monolithic Catalysts For The 1975 FTP

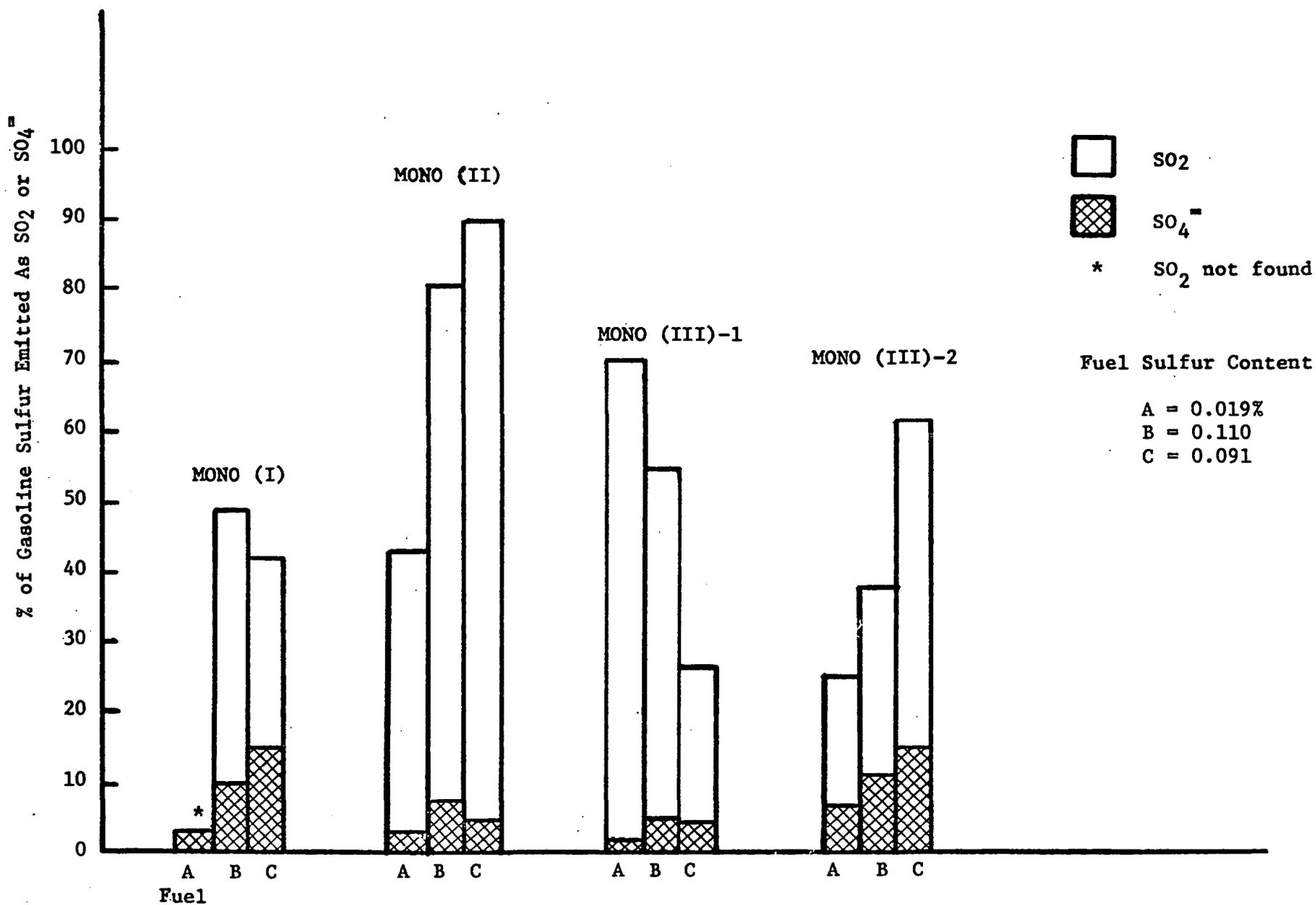


FIGURE 15

SO<sub>2</sub> and SO<sub>4</sub><sup>m</sup> Emissions For Monolithic Catalysts At 40 Mph Cruise

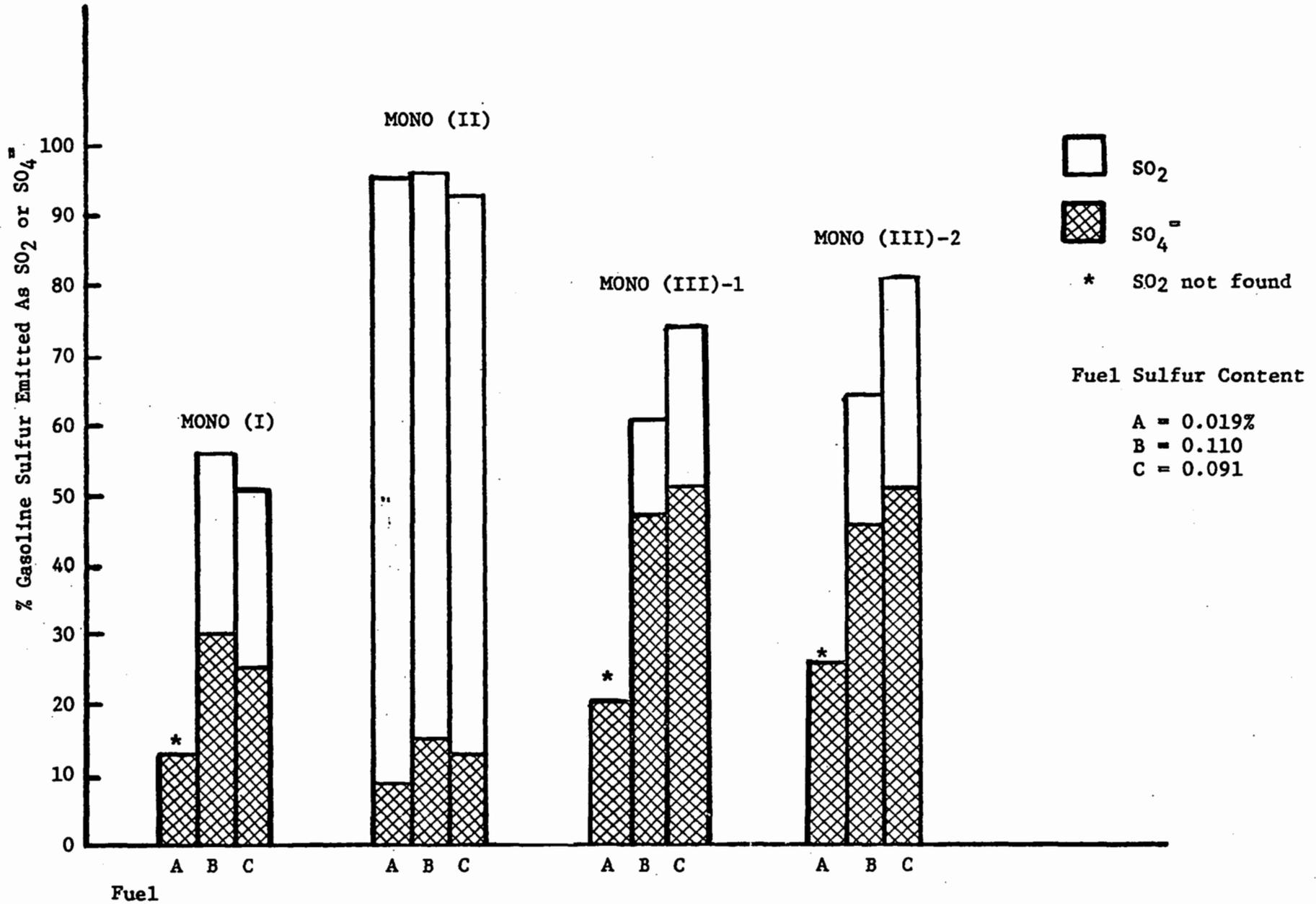


FIGURE 16

SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> Emissions For Monolithic Catalysts At 60-70 Mph Cruise

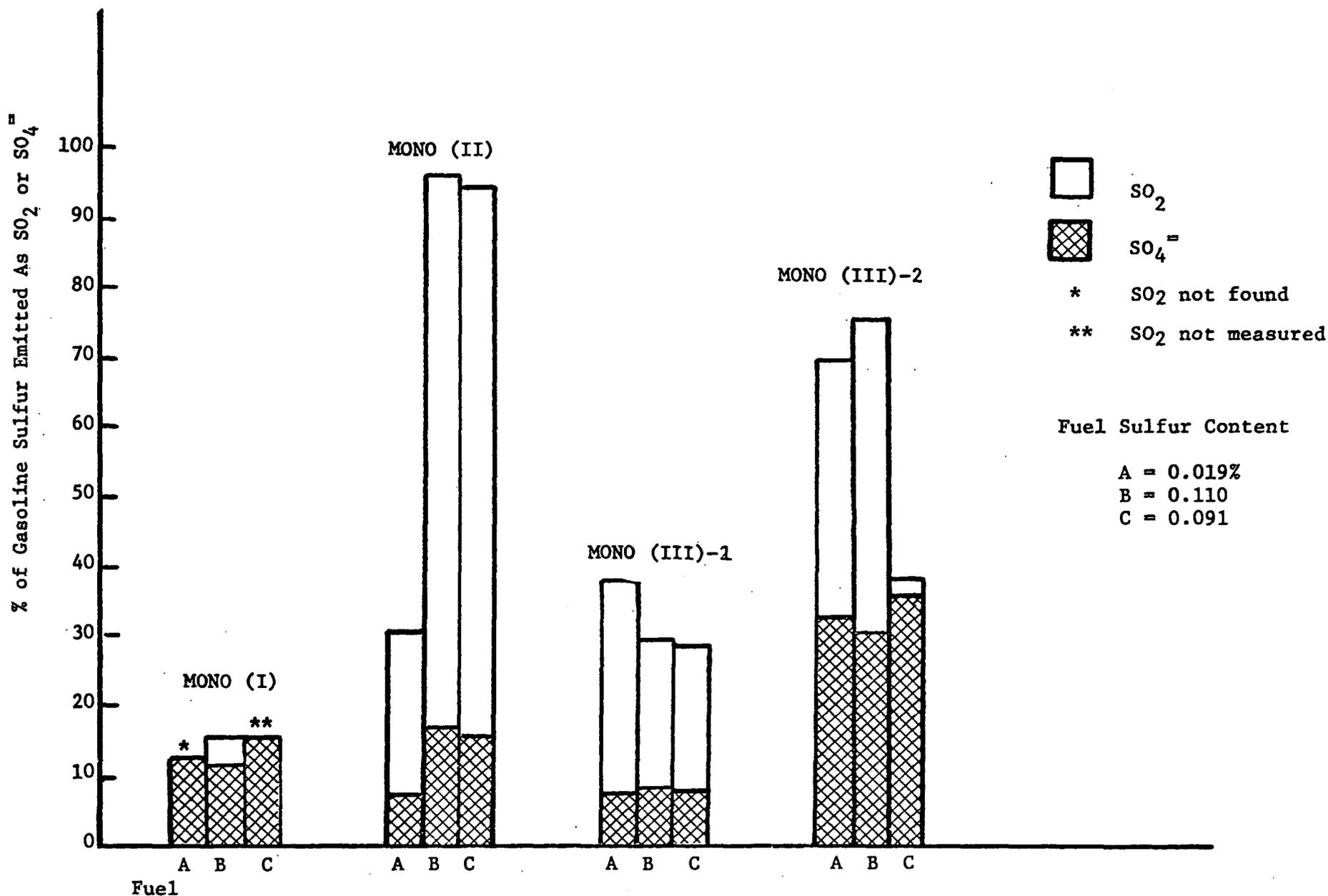


FIGURE 17

SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> Emissions For Pelleted Catalysts For The 1975 FTP

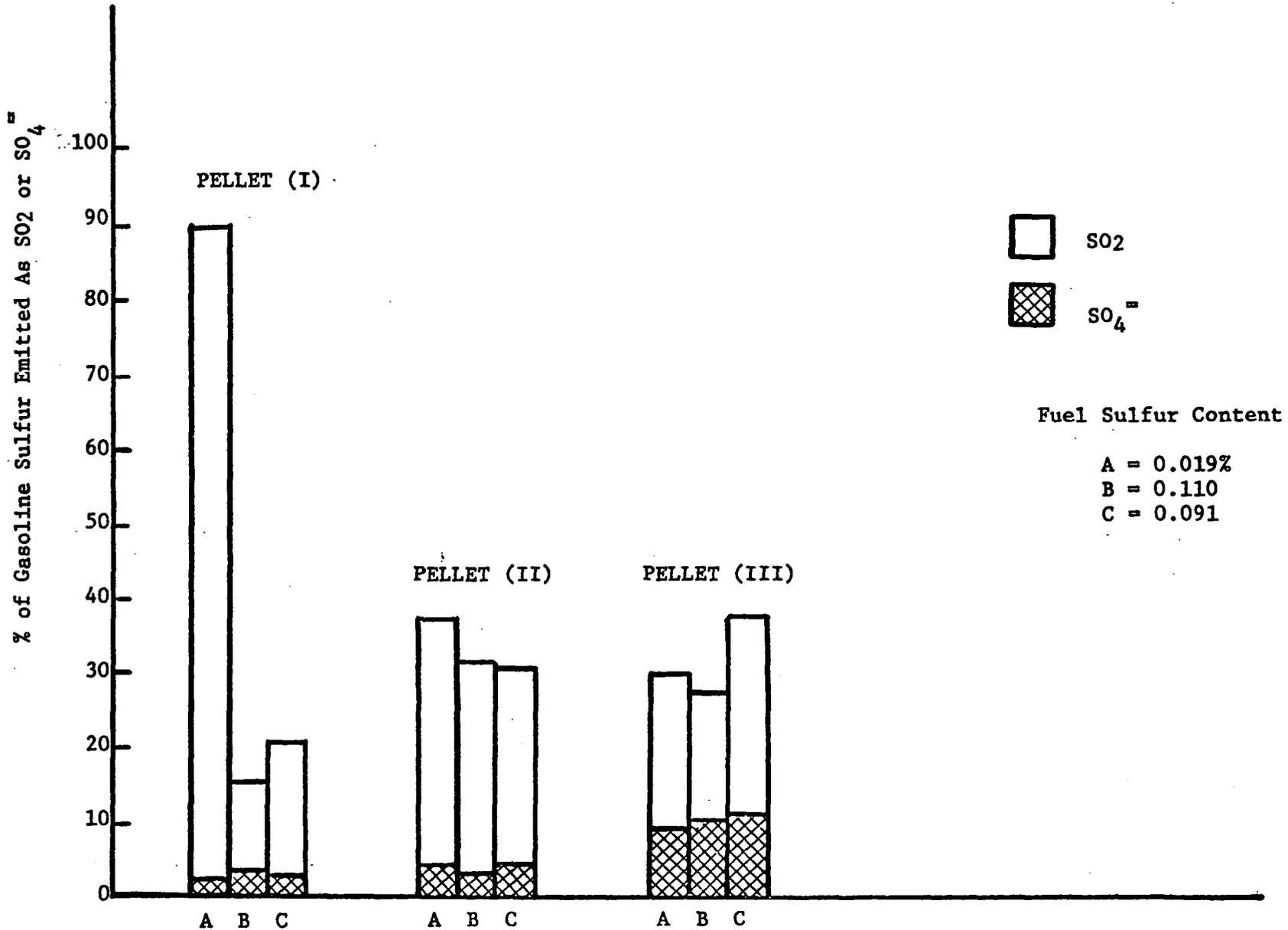


FIGURE 18

SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> Emissions For Pelleted Catalysts At 40 Mph Cruise

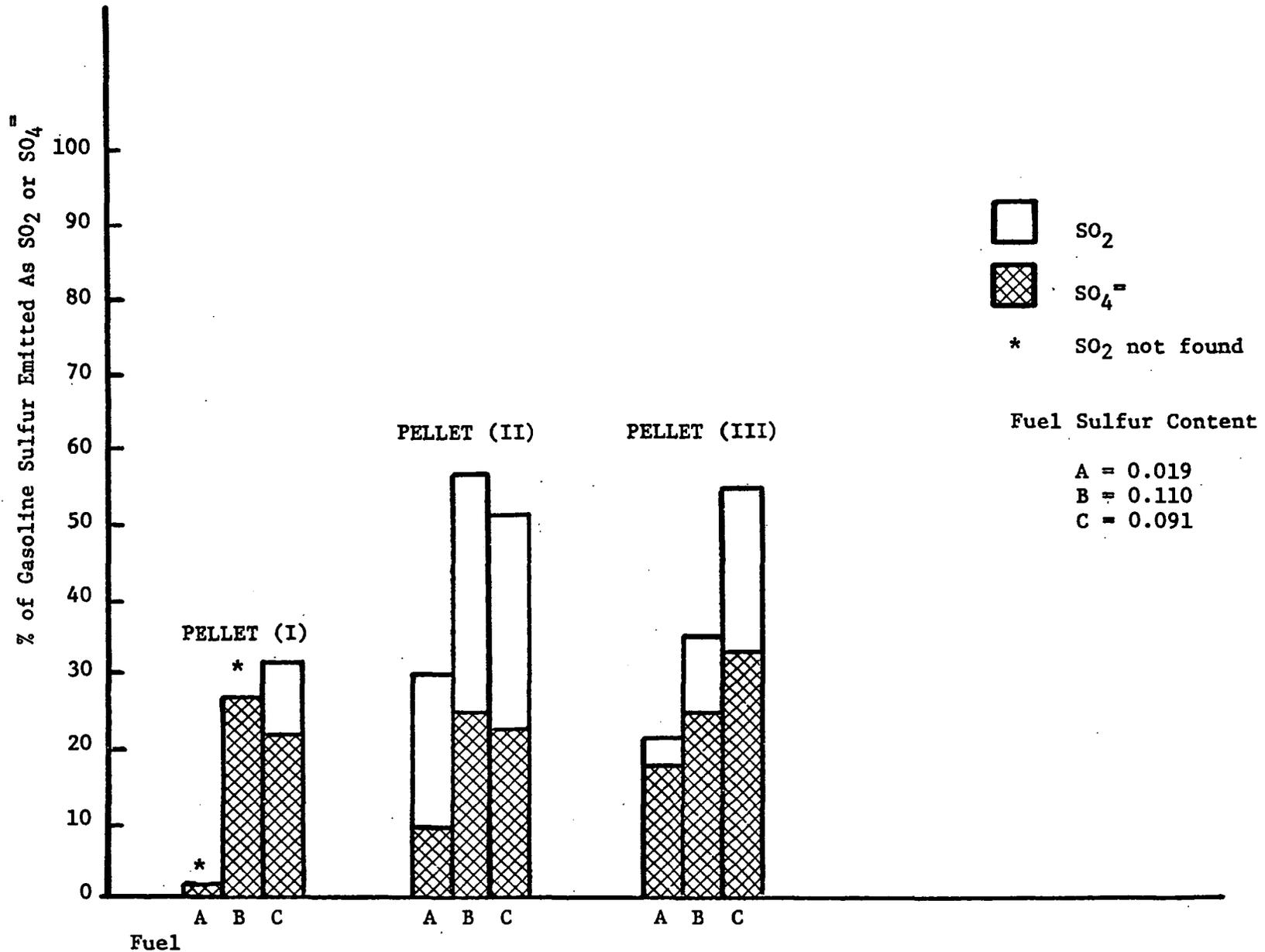
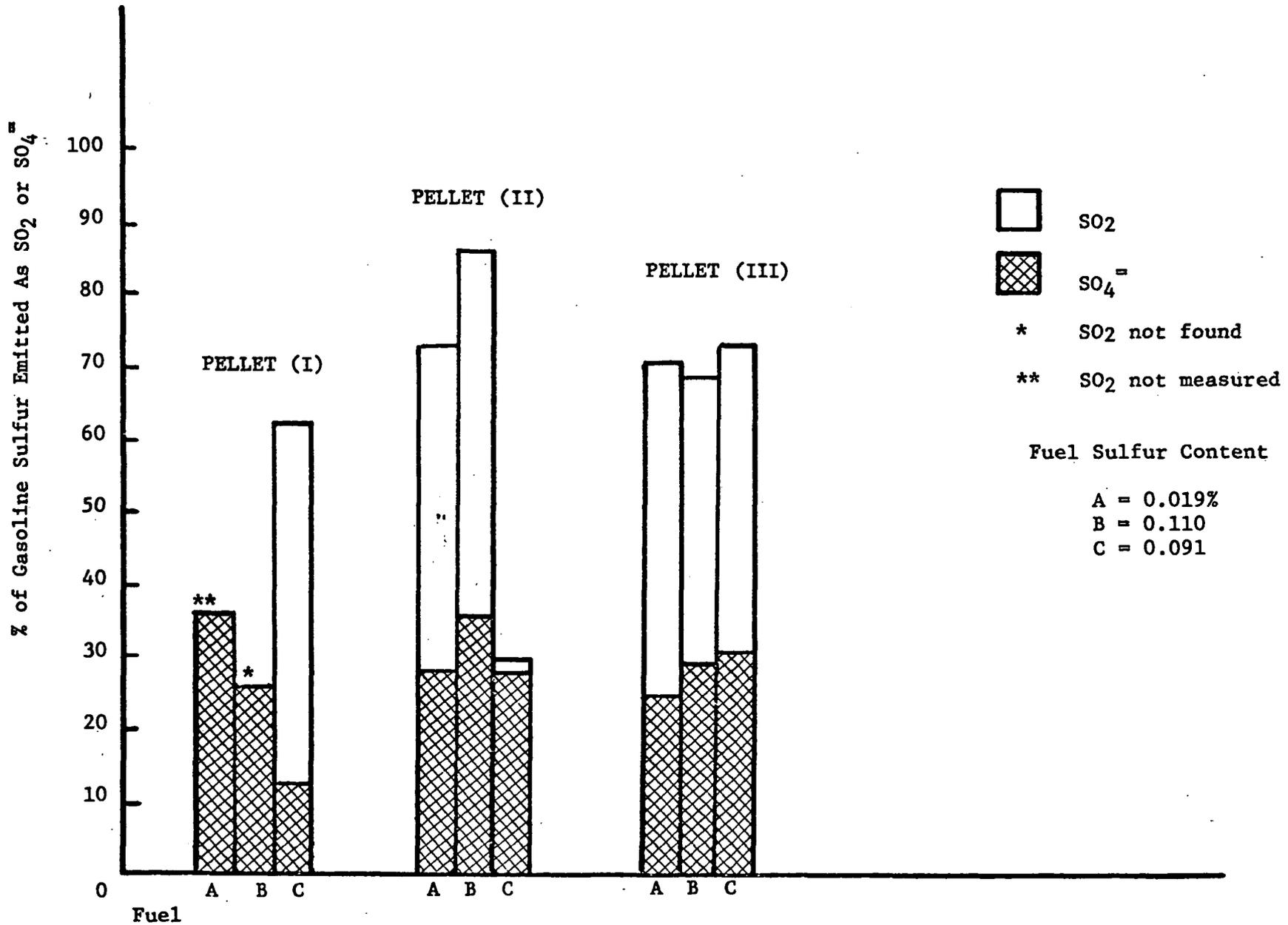


FIGURE 19

SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> Emissions For Pelleted Catalysts At 60-70 Mph Cruise



SO<sub>4</sub><sup>≡</sup> emission rates from the Mono (II) catalyst are not the result of increased SO<sub>4</sub><sup>≡</sup> storage, since this catalyst showed the lowest tendency to store sulfur oxides of any of the catalysts tested.

- The previously reported low (about 5-10%) SO<sub>4</sub><sup>≡</sup> emission rates for pelleted catalysts under FTP conditions were again observed. However, higher (no more than 25-35%) than previously reported SO<sub>4</sub><sup>≡</sup> emission rates were observed at 40 mph cruise when using pelleted catalysts. This may be due to release of stored SO<sub>4</sub><sup>≡</sup>, since the 40 mph cruise mode was the first run after the FTP.
- SO<sub>4</sub><sup>≡</sup> emission rates at 60 or 70 mph cruise were similar for both monoliths and pellets and ranged up to 35%.

The low SO<sub>4</sub><sup>≡</sup> emission rates combined with low storage of sulfur oxides found with the Mono (II) catalyst is worthy of further study. This catalyst sample was supposedly representative of those manufactured for commercial use, and therefore should have been capable of good control of CO and HC. Data for the FTP runs with this catalyst, presented in Table 3, show that it did, in fact, control CO and HC near or below our targets of 3.4 and 0.41 g/mi., respectively.

Table 3 - FTP Emissions From Monolithic Catalysts

<u>Catalyst</u>	<u>CO</u>	<u>HC</u>
Mono (I)	3.00	0.74
Mono (II)	2.45	0.40
Mono (III)-1	3.21	0.35
Mono (III)-2	1.49	0.22

b. Effect of Gasoline Sulfur Level

In our previous submission to EPA on automotive sulfate emissions, Exxon Research reported that, in catalyst vehicles, these emissions in g/mi. were proportional to gasoline sulfur level. No further studies to investigate this question have been carried out. The data used to reach this conclusion in our earlier report are reproduced in Tables 4 and 5.

c. Effect of Catalyst Age and Noble Metal Loading

Exxon Research has obtained limited data in these two areas under EPA Contract 68-03-0497. Since this contract is discussed in detail in Section V, presentation of these data will be delayed until Section V.C.

V. Potential Methods for Controlling SO<sub>4</sub><sup>≡</sup> Emissions

In Figures 5 and 8, laboratory data indicating that SO<sub>4</sub><sup>≡</sup> emissions can be limited by limiting excess air were presented. In this section, vehicle tests of this concept, as well as data obtained in a study of the feasibility of trapping SO<sub>4</sub><sup>≡</sup> in the exhaust system on a suitable sorbent, will be presented. Both of these studies were conducted as parts of EPA Contract 68-03-0497, "An Assessment of Sulfate Emission Control Technology". Work under this contract is still in progress at Exxon Research, and the data reported herein are limited to those available as of December 19, 1974, the last monthly reporting period for which data have been submitted.

A. Vehicle Tests of Limited Excess Air

1. Vehicle Preparation and Baseline Testing

The vehicle tests of the effect of limited excess air on SO<sub>4</sub><sup>≡</sup> emission rate were conducted on a production model 1975 350 CID Chevrolet

Table 4

Sulfate Emissions From Monolithic Oxidation Catalysts

<u>Catalyst</u>	<u>No. of Tests</u>	<u>Fuel Sulfur, %</u>	<u>SO<sub>4</sub><sup>≡</sup> Emissions, g/mi.</u>	<u>Conversion S → SO<sub>4</sub><sup>≡</sup>, %</u>
<u>1972 FTP</u>				
Monolith A	5	0.067	0.119	21
	4	0.032	0.064	24
	3	0.004	0.010	29
Monolith B	2	0.067	0.145	25
	2	0.032	0.061	23
	2	0.004	0.014	41
<u>40 mph cruise</u>				
Monolith A	2	0.067	0.158	28
	2	0.032	0.055	20
	2	0.004	0.008	35
Monolith B	5	0.067	0.090	16
	4	0.032	0.048	17
	3	0.004	0.005	18
<u>60 mph cruise</u>				
Monolith A	2	0.140	0.253	32
	2	0.004	0.007	29

Table 5

Sulfate Emissions From A Pelleted Oxidation Catalyst

<u>Catalyst</u>	<u>No. of Tests</u>	<u>Fuel Sulfur, %</u>	<u>SO<sub>4</sub><sup>≡</sup> Emissions, g/mi.</u>	<u>Conversion S → SO<sub>4</sub><sup>≡</sup>, %</u>
<u>1975 FTP</u>				
Pelleted	3	0.140	0.111	10.6
	2	0.065	0.036	5.8
	3	0.056	0.015	3.2
	2	0.034	0.011	4.2
	3	0.004	0.003	7.7
<u>40 mph cruise</u>				
Pelleted	2	0.065	0.049	12.8
	2	0.034	0.009	4.7
<u>60 mph cruise</u>				
Pelleted	6	0.140	0.313	35.6
	5	0.056	0.113	31.4
	6	0.032	0.063	27.7
	5	0.004	0.007	26.0

V-8 modified to control CO and HC emissions to 3.4 and 0.41 g/mi. respectively. This modification consisted of adding an air pump to inject secondary air ahead of the oxidation catalyst. The catalyst used was the pelleted catalyst received with the vehicle.

The unmodified test vehicle was first broken in with 2,000 miles of AMA cycle operation on an unleaded, low sulfur fuel. It's 1975 FTP emissions were then measured and found to be 8.3 g/mi. CO and 0.48 g/mi. HC, well below the standard of 15 g/mi. CO and 1.5 g/mi. HC for which the vehicle was designed, but above the 3.4 g/mi. CO, 0.41 g/mi. HC level at which the tests were to be conducted. Adding an air pump lowered these emissions to 3.5 g/mi. CO and 0.27 g/mi. HC. A series of baseline tests were then conducted using two fuels (0.032 and 0.012 wt. % sulfur) and two different modes of conditioning (500 miles of simulated turnpike driving and 500 miles of simulated city driving). Each test consisted of the following series of operating modes:

1. 500 miles of conditioning followed by an overnight cold soak
2. 1975 FTP
3. 20 minute idle
4. 2 hours at 60 mph during which time  $SO_4^{\square}$  was measured for each 30 minute interval
5. Overnight cold soak
6. 1975 FTP

$SO_4^{\square}$  emission results for the baseline runs are reported in Table 6.

The data in Table 6 show an average  $\text{SO}_4^{\text{m}}$  emissions equivalent to about 4% of the sulfur in the gasoline used under FTP condition. This is in good agreement with the FTP results for pelleted catalysts presented earlier in Tables 2 and 5. The 60 mph cruise runs were two hours in duration with separate  $\text{SO}_4^{\text{m}}$  samples taken for each half hour interval.  $\text{SO}_4^{\text{m}}$  emissions were highest during the first half hour of operation and gradually decreased with time. By the final half hour,  $\text{SO}_4^{\text{m}}$  emissions were down to the 25-35% of gasoline sulfur reported above. This initial high rate of  $\text{SO}_4^{\text{m}}$  emission is due to the release of stored sulfate.

A similar pattern was observed with  $\text{SO}_2$  emissions. At the beginning of the 60 mph run, high levels of  $\text{SO}_2$  emission were recorded as the result of stored  $\text{SO}_2$ . As the test proceeded,  $\text{SO}_2$  emission rates dropped to a steady state level comparable to the levels reported in Table 2.

## 2. Tests of Limited Air

The effect of limited air was tested using the 0.032 wt. % sulfur fuel and both turnpike and city driving preconditioning. The operating sequence outlined above was followed with air injection used only for the first two minutes of each FTP and not at all under cruise conditions. This limited use of air injection raised FTP CO emissions to an average of 5.4 g/mi. and HC emissions to an average of 0.31 g/mi., both well below the 1975 California standards. The effect of  $\text{SO}_4^{\text{m}}$  emissions was dramatic, about a 75% reduction in  $\text{SO}_4^{\text{m}}$  emissions under FTP conditions, and about 60% reduction in  $\text{SO}_4^{\text{m}}$  emissions at 60 mph

Table 6

SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> Emissions from a 1975 Chevrolet with Air Pump During Baseline Testing

<u>Fuel Sulfur, %</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions</u>		<u>SO<sub>4</sub><sup>=</sup> Emissions</u>		<u>% Sulfur Balance</u>
		<u>g/mi.</u>	<u>% of Gasoline S</u>	<u>g/mi.</u>	<u>% of Gasoline S</u>	
TURNPIKE DRIVING PRECONDITIONING						
0.032	FTP *	0.044	24	0.010	4.2	28
	60 mph-1 **	0.19	144	0.168	84	228
	2	0.13	94	0.099	47	141
	3	0.11	80	0.076	37	117
	4	0.08	60	0.061	30	90
0.012	FTP *	0.020	30	0.0025	3.6	34
	60 mph-1**	0.066	122	0.084	103	225
	2	0.059	107	0.054	65	172
	3	0.059	105	0.050	59	164
	4	0.083	145	0.052	61	206
CITY DRIVING PRECONDITIONING						
0.032	FTP *	0.055	33	0.0088	3.6	37
	60 mph-1 **	0.15	106	0.15	72	178
	2	0.09	64	0.080	38	102
	3	0.10	70	0.081	38	108
	4	0.08	55	0.075	34	89
0.012	FTP *	0.055	82	0.0048	4.6	87
	60 mph-1 **	0.09	164	0.081	96	260
	2	0.04	78	0.034	41	119
	3	0.04	78	0.037	46	124
	4	0.04	78	0.033	41	119

\* Average of the initial and final FTP tests.

\*\* Numbers after the 60 mph indicates 1st, 2nd, etc. 30 minutes of operation at 60 mph cruise.

cruise. Data for these tests is presented in Table 7. Similar tests on a monolithic catalyst system are expected to be completed within the next month.

These vehicle tests, together with the laboratory data presented earlier, offer strong evidence that limiting excess air will reduce  $SO_4$  emissions appreciably. This point should be considered by EPA in deciding whether to grant a delay in enforcement of the 1977 CO and HC standards for the following reason. The higher the CO and HC standards, the less need for air pumps. An appreciable fraction of the catalyst-equipped vehicles meeting 1975 Federal emission standards do not use air pumps. Many of these vehicles also meet 1975 California CO and HC emissions standards. If not required to meet CO and HC standards, the \$27-33/car cost<sup>(7)</sup> of the air pump and its associated plumbing would likely be sufficient incentive for their removal. If 1975 Federal standards were extended through 1977, it is likely that an even greater number of cars which used catalysts would not use air pumps. If 1975 California CO and HC standards were imposed for the 1977 model year nationwide, it is still likely that a significant number of cars could be designed without air pumps. However, maintaining the statutory 3.4 g/mi. CO, 0.41 g/mi. HC standards in 1977 would make it very unlikely that air pumps could be eliminated.

B. Use of SO<sub>4</sub><sup>m</sup> Traps

1. Background

On November 6, 1973, Exxon Research testified before the Committee on Public Works of the U. S. Senate on the subjects of gasoline desulfurization and automotive sulfate emissions. At that time we indicated that it might be possible to trap SO<sub>4</sub><sup>m</sup> on a solid sorbent in the exhaust system. This position, which was based on work done at Exxon Research in the mid-1960's, was amplified in a November 16, 1973 letter to Senator Jennings Randolph, Chairman of the Committee on Public Works. This letter appears as Attachment II.

A program to study the feasibility of SO<sub>4</sub><sup>m</sup> traps was included as part of EPA Contract 68-03-0497, "An Assessment of Sulfate Emission Control Technology". This program included both vehicle durability tests and a laboratory screening program to find new sorbents. The first vehicle durability test was carried out using 1/8" pellets of 85% CaO/10% SiO<sub>2</sub>/5% Na<sub>2</sub>O as the sorbent. Results of this test are presented below.

2. Vehicle Test of 85% CaO/10% SiO<sub>2</sub>/5% Na<sub>2</sub>O as an SO<sub>4</sub><sup>m</sup> Sorbent

The test was conducted using a 1973 351 CID Ford V-8 equipped with an air pump and two Engelhard PTX-IIB oxidation catalysts in the post manifold position. Prior to testing the SO<sub>4</sub><sup>m</sup> trap, the vehicle, without trap, was operated for 2,000 miles of AMA cycle on a fuel containing 0.048 wt. % sulfur. SO<sub>4</sub><sup>m</sup> emissions were then measured at 40 mph cruise conditions, were 0.066 g/mi., equivalent to about 37% of the sulfur in the gasoline.

Table 7

SO<sub>2</sub> and SO<sub>4</sub><sup>m</sup> Emissions in Vehicle Test of Limited Excess Air

<u>Preconditioning</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions</u>		<u>SO<sub>4</sub><sup>m</sup> Emissions</u>		<u>% Sulfur Balance</u>
		<u>g/mi.</u>	<u>% of Gasoline S</u>	<u>g/mi.</u>	<u>% of Gasoline S</u>	
All Tests with 0.032 wt.% S Fuel						
Turnpike	FTP *	0.14	130	0.0020	0.8	131
	60 mph-1 **	0.34	244	0.093	44	288
	2	0.26	179	0.034	16	195
	3	0.16	109	0.026	11	120
	4	0.16	105	0.026	11	116
City	FTP *	0.19	121	0.0032	1.2	122
	60 mph-1 **	0.24	213	0.053	32	245
	2	0.23	212	0.010	5.8	218
	3	0.34	312	0.0016	1.0	313
	4	0.11	99	0.0018	1.0	100

\* Average of the initial and final FTP tests.

\*\* Numbers after the 60 mph indicate 1st, 2nd, etc. 30 minutes of operation at 60 mph cruise.

The car was then equipped with an  $\text{SO}_4^=$  trap consisting of a GM toeboard catalyst reactor filled with 1/8" pellets of 85% CaO/10%  $\text{SiO}_2$ /5%  $\text{Na}_2\text{O}$ . With fresh sorbent,  $\text{SO}_4^=$  emissions at 40 mph were reduced to 0.003 g/mi., a reduction of 96%. The trap was tested for a total of 26,500 miles, during which time  $\text{SO}_4^=$  removal generally remained above 95%. Data on  $\text{SO}_4^=$  emissions during this test are presented in Table 8.

While CaO is a very active sorbent, it does possess one inherent liability, in that its volume increases significantly as it sulfates. Based on crystalline densities, the complete sulfation of CaO to  $\text{CaSO}_4$  would produce a three-fold increase in volume. While the pellets are somewhat porous, they cannot accommodate such an expansion internally and must expand into the void volume of the bed. This expansion will cause the pressure drop across the bed to increase as degree of sulfation increases. During the 26,500 miles described above, pressure drop across the sulfate trap increased from an initial value of 4" of  $\text{H}_2\text{O}$  to a final value of 115-140" of  $\text{H}_2\text{O}$  at 40 mph cruise conditions. Pressure drop data as a function of mileage for the trap are presented in Figure 20.

Despite the swelling and high pressure drop encountered with the CaO sorbent, attrition was not a problem. Calcium emission rates were measured periodically through the run. The maximum observed value was  $3.7 \times 10^{-4}$  g/mi., lower than the approximately  $6.5 \times 10^{-4}$  g/mi. observed on vehicles without traps. On vehicles without a CaO trap, calcium emissions occur as a result of the combustion of lube oil

Table 8

Summary of Results Obtained During Testing of 85% CaO/10% SiO<sub>2</sub>/5% Na<sub>2</sub>O  
As A Sulfate Sorbent

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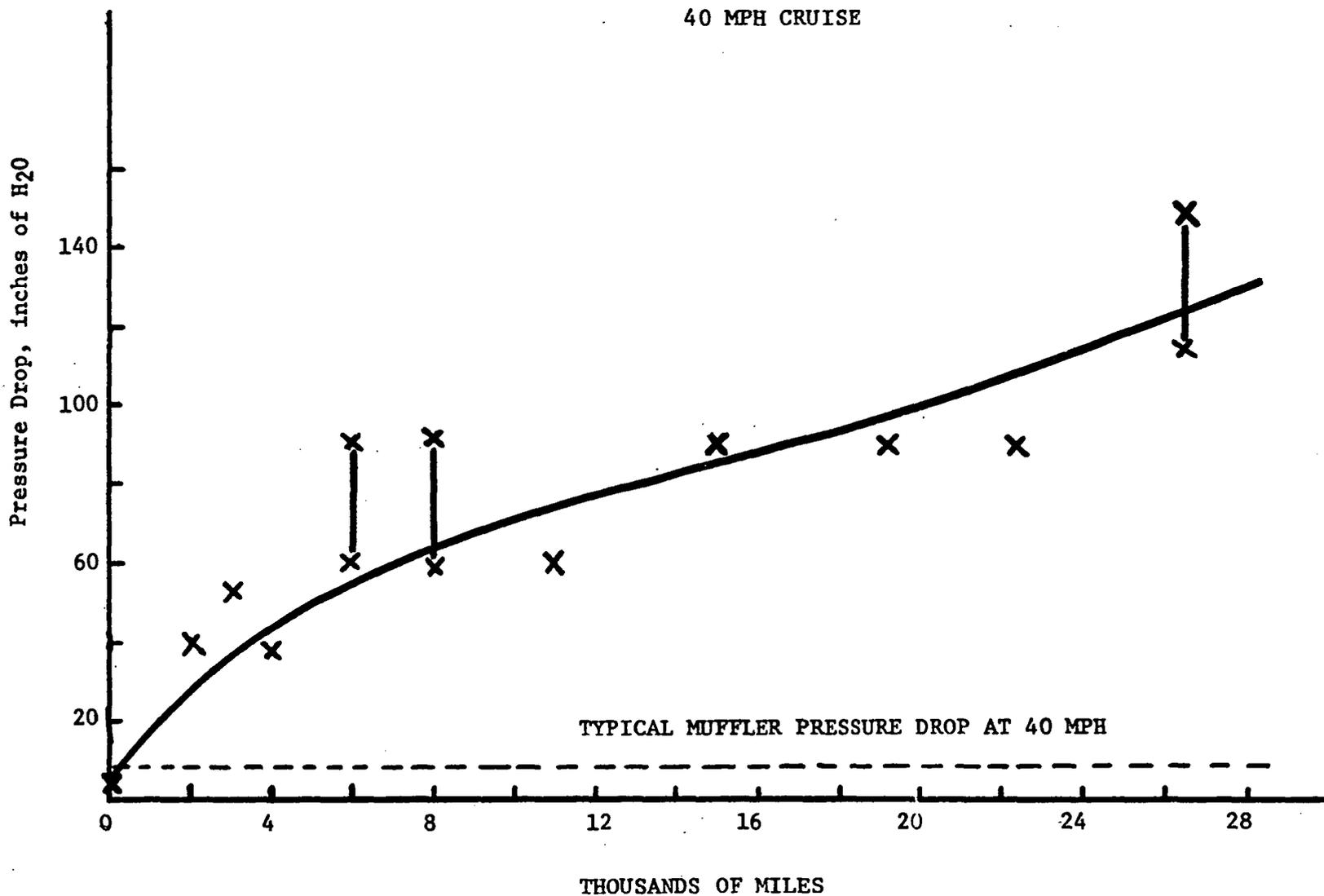
<u>Trap Mileage</u>	<u>Mode</u>	<u>SO<sub>4</sub><sup>=</sup> Emissions, g/mi.</u>	<u>% SO<sub>4</sub><sup>=</sup> Removed</u>	
Base Car *	40 mph	0.066	--	
	0	40	0.003	96
		40	0.005	92
		60	0.002	--
1,000	40	0.001	98	
1,100 **	40	0.002	97	
2,000	40	0.002	97	
3,000	40	0.002	97	
	40	0.004	94	
6,000	40	0.002	97	
8,000	40	0.002	97	
11,000	40	0.002	97	
	40	0.003	96	
15,000	1975 FTP	0.005	--	
	40 mph	0.001	98	
	40	0.001	98	
19,000	1975 FTP	0.005	--	
	40 mph	0.0005	99	
	40	0.0005	99	
22,000	1975 FTP	0.001	--	
	40 mph	0.001	98	
	40	0.001	98	
26,500	1975 FTP	0.003	--	
	40 mph	0.008	88	
	40	0.003	96	
	1975 FTP	0.003	--	

\* Fuel Sulfur Content = 0.048 wt.%

\*\* Fuel Sulfur Content changed to 0.032 wt.% for the remainder of the test

FIGURE 20

Pressure Drop Across the CaO/SiO<sub>2</sub>/Na<sub>2</sub>O SO<sub>4</sub> Trap Vs. Mileage



which typically includes calcium containing additives. Assuming the maximum calcium emission rate, slightly over 10 grams of calcium or 20 grams of sorbent was emitted during the entire durability test. This is less than 1% of the charge, and less calcium than would typically be emitted as lube ash in a non-trap car.

### 3. Work on Improved Sorbents

While the test of  $\text{CaO/SiO}_2/\text{Na}_2\text{O}$  as sorbent showed that it is possible to trap  $\text{SO}_4^{=}$  in the exhaust, the high pressure drop encountered with this material made its use in pelleted form unattractive. Three approaches to improved sorbents have been considered. These are:

- calcium compounds which swell less after sulfation,
- CaO in a high void volume shape, and
- materials which sorb less  $\text{SO}_2$ .

This last approach is being taken because the  $\text{CaO/SiO}_2/\text{Na}_2\text{O}$  material appeared to sorb about 50% of the  $\text{SO}_2$  passing through the trap. This reduces potential  $\text{SO}_4^{=}$  sorption capacity and increases further swelling, and is therefore undesirable. The results to date in each of these areas are discussed below.

#### a. Calcium Compounds Which Swell Less During Sulfation

One such material was tested,  $\text{CaCO}_3$ . Converting  $\text{CaCO}_3$  to  $\text{CaSO}_4$  increases volume 1.4 times, much less than the three-fold increase which occurs when CaO is converted to  $\text{CaSO}_4$ . A vehicle test was conducted on 4/17 mesh marble chips (marble is essentially pure  $\text{CaCO}_3$ ), but this material did not sorb  $\text{SO}_4^{=}$ . We speculate that this is because of the very low surface area of the marble chips, which did not allow good gas-solid contacting.  $\text{CaCO}_3$  will be reevaluated when pellets of compressed  $\text{CaCO}_3$  powder are available. Attempts to form

such pellets without binders were unsuccessful. Forming the pellets with binders will be attempted in the near future.

b. CaO In A High Void Volume Shape

Girdler Catalyst Company is currently fabricating CaO/SiO<sub>2</sub>/Na<sub>2</sub>O sorbent into 5/8"O.D X 3/8"I.D. X 1/4" high rings, a high void volume shape. We plan vehicle tests to determine whether this shape reduces pressure drop sufficiently, while maintaining SO<sub>4</sub><sup>2-</sup> sorption efficiency, to allow the use of this sorbent.

c. Material Which Sorb Less SO<sub>2</sub>

A laboratory program is now underway to screen new sorbent materials using the equipment shown in Figure 3. 15 ppm SO<sub>2</sub> is blended into a synthetic exhaust and 5 ppm SO<sub>3</sub> is added by controlled evaporation of dilute H<sub>2</sub>SO<sub>4</sub>. The first sorbent tested in the unit was 85% CaO/10% SiO<sub>2</sub>/5% Na<sub>2</sub>O, the material used in the vehicle durability test. It was tested to provide a base against which other material could be tested. In a three hour test at 900°F, 100,000 V/V/hr space velocity, a 13 ml sample of sorbent removed all SO<sub>3</sub> and >90% of SO<sub>2</sub>.

Of the new materials tested, a number can be eliminated from further consideration. Norton #4102 Al<sub>2</sub>O<sub>3</sub> collected only 55% of the SO<sub>3</sub>. We plan to test other forms of Al<sub>2</sub>O<sub>3</sub>. A test of BaO as a sorbent failed when the material hydrated to form Ba(OH)<sub>2</sub> and melted. A sample of commercially available MgO manufactured by Harshaw dropped from 100% SO<sub>4</sub><sup>2-</sup> removal to 17% SO<sub>4</sub><sup>2-</sup> removal in four hours. Marble chips dropped from 74% SO<sub>4</sub><sup>2-</sup> removal to 50% SO<sub>4</sub><sup>2-</sup> removal in four hours.

The following materials were identified as being potentially useful sorbents:

- zirconia
- 80% CaO/20%SiO<sub>2</sub>, and
- Micro-Cel, a commercially available calcium silicate.

A description of the tests of each of these materials is presented below.

Harshaw zirconia, in the form of very strong pellets, gave, in sequential tests, 100 and 84% sulfate trapping efficiencies. Since the test temperature is in the range of the zirconium sulfate decomposition temperature, these results suggest that the sorbent may be reacting with the acid to form the sulfate, which then decomposes to sulfur dioxide and oxygen. Unfortunately, the sulfur dioxide results were not sufficiently accurate to determine if the outlet sulfur dioxide concentration increased. Further testing will be done with this material.

An 80% CaO/20% SiO<sub>2</sub> composition was prepared in an attempt to produce a stronger calcium containing pellet. In addition, this composition allowed the assessment of the effect of sodium oxide on the trapping efficiency, by comparison with the benchmark material. The 80% CaO/20% SiO<sub>2</sub> removed all of the sulfuric acid, but only a small amount of the sulfur dioxide. Thus sodium oxide enhances trapping efficiency for the dioxide. However, sodium oxide acts as a binder, since its elimination decreased pellet strength. Development of a suitable binder material, which did not sorb SO<sub>2</sub>, would allow strong CaO pellets with increased SO<sub>4</sub><sup>=</sup> capacity to be made.

Micro-Cel, the commercial  $\text{CaSiO}_3$  sorbed 100% of the  $\text{SO}_4^{\equiv}$  in the first hour, and 97% in the second hour of testing.  $\text{SO}_2$  trapping efficiency was 15% in the first hour and 7% in the second hour. Forming this material into strong pellets is a problem.

Finally  $\text{MgO}$ , in certain forms also shows promise. One sample trapped 100% of the  $\text{SO}_4^{\equiv}$  in the feed but none of the  $\text{SO}_2$  in a 4.5 hour test. Further tests are planned on these and other materials.

C. Other Information from EPA Contract 68-03-0497

As parts of this contract, the effects of catalyst age and noble metal loading were also investigated. These results are reported below.

1. Effect of Catalyst Age

A pelleted oxidation catalyst which had operated for 25,000 miles of AMA cycle on lead sterile ( $<0.01$  gPb/gal) fuel, was mounted on the 350 CID Chevrolet used for the other work in this contract. Tests were conducted using the 0.032 wt.% sulfur fuel after preconditioning with 500 miles of city driving, and again after preconditioning with 500 miles of turnpike driving. Average CO and HC emissions for the four FTP tests involved in this sequence were 3.1 and 0.29g/mi respectively.  $\text{SO}_4^{\equiv}$  emissions data are presented in Table 9.

As might be expected, the aged catalyst gave lower  $\text{SO}_4^{\equiv}$  emissions than a fresh catalyst (Table 6), but the reduction was not as great as when reduced air was used. These data indicate that  $\text{SO}_4^{\equiv}$  emissions will not increase as catalysts age in customer use.

2. Effect of Noble Metal Loading

In this test, a standard 260 in<sup>3</sup> GM catalyst reactor was loaded with higher noble metal content catalyst normally used for the 160 in<sup>3</sup> GM catalyst reactor.

Table 9

SO<sub>2</sub> and SO<sub>4</sub><sup>==</sup> Emissions With An Aged Catalyst

Fuel Sulfur Content = 0.032 wt.%

<u>Preconditioning</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions</u>		<u>SO<sub>4</sub><sup>==</sup> Emissions</u>		<u>% Sulfur Balance</u>
		<u>g/mi</u>	<u>% of Gasoline S</u>	<u>g/mi.</u>	<u>% of Gasoline S</u>	
Turnpike	FTP *	0.027	17	0.0037	1.4	18
	60 mph-1 **	0.14	97	0.164	75	172
	2	0.11	79	0.063	29	108
	3	0.13	87	0.048	22	109
	4	0.08	61	0.035	16	77
City	FTP *	0.047	29	0.009	3.3	32
	60 mph-1**	***	***	0.14	61	***
	2	***	***	0.063	27	***
	3	***	***	0.061	27	***
	4	***	***	0.051	24	***

\* Average of the initial and final tests.

\*\* Number after the 60 mph indicates 1st, 2nd, etc. 30 minutes of operation at 60 mph cruise.

\*\*\* Accurate data not available due to air leak in SO<sub>2</sub> detector.

This resulted in about a 60% increase in the amount of Pt-Pd present in the catalyst bed. The high loading charge was tested with 0.032 wt.% of sulfur fuel after 500 miles preconditioning on turnpike operation. The  $\text{SO}_4^{\text{m}}$  measurements made (Table 10) showed no increase in  $\text{SO}_4^{\text{m}}$  emissions compared with normal catalyst loading (Table 6).

Table 10

SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> Emissions With A High Noble Metal Loading Catalyst

Fuel Sulfur Content = 0.032 wt.%

<u>Preconditioning</u>	<u>Mode</u>	<u>SO<sub>2</sub> Emissions</u>		<u>SO<sub>4</sub><sup>=</sup> Emissions</u>		<u>% Sulfur Balance</u>
		<u>g/mi.</u>	<u>% of Gasoline S</u>	<u>g/mi.</u>	<u>% of Gasoline S</u>	
Turnpike	FTP *	0.052	35	0.004	1.9	37
	60 mph-1**	0.14	114	0.16	88	202
	2	0.13	95	0.11	58	153
	3	0.10	75	0.076	38	113
	4	0.064	50	0.069	36	86

\* Average of the initial and final FTP tests.

\*\* Number after the 60 mph indicates 1st, 2nd, etc. 30 minutes of operation at 60 mph cruise.

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