Mathematical Modeling of Catalytic Converter Lightoff

Part III: Prediction of Vehicle Exhaust Emissions and Parametric Analysis

The converter warmup model developed previously (Oh and Cavendish, 1985) has been used to simulate the performance of a packed-bed converter during the cold-start portion of vehicle emission tests. Despite the highly transient converter inlet conditions, the model successfully predicts tailpipe mass emissions as a function of time.

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SCOPE

It has been widely recognized that a large fraction of CO and hydrocarbon emissions occurs during the cold-start portion of the Federal Test Procedure (FTP) driving schedule (Pozniak, 1980; Kummer, 1980). In our previous paper (Oh and Cavendish, 1985), a mathematical model was developed which describes the warmup performance of a packed-bed catalytic converter. The converter model was then verified by comparing model predictions with the results of engine-dynamometer warmup tests.

In view of the importance of converter warmup performance to overall CO and hydrocarbon emissions on the FTP, it is of practical interest to further evaluate the capability of the model to predict the performance of a packed-bed converter during the warmup portion of actual vehicle emission tests. This problem presents a considerable challenge because, as will be shown, a catalytic converter is subject to highly transient inlet conditions with respect to exhaust gas flow rate, exhaust composition, and exhaust temperature. This paper, the third part of our converter modeling studies, describes the results of computer simulations for the first two cycles (333 s of warmup period) of the FTP and their comparisons with vehicle test data. We also analyze, using the model, how the exhaust emissions during cycles 1 and 2 of the FTP are influenced by catalyst/converter design parameters. Finally, the results of design calculations will be presented which illustrate how to determine an optimum converter volume for a given amount of Pt per converter.

CONCLUSIONS AND SIGNIFICANCE

The converter warmup model developed previously (Oh and Cavendish, 1985) has been used to simulate the performance of a packed-bed catalytic converter during the first two cycles of the FTP. The simulation results agree well with the test data for all of the three widely different Pt/Al_2O_3 catalysts considered, indicating that the model provides a computational tool for quantitative predictions of tailpipe mass emissions generated during the warmup portion of the government-prescribed emission test procedure.

The model was also used to examine how tailpipe emissions during cycles 1 and 2 of the FTP are affected by variations in the design parameters, such as catalyst properties and converter dimensions. Results of the parametric calculations revealed that converter performance at early times (cycle 1 and the early portion of cycle 2) is favored by high Pt loading of the catalyst pellet, while a sufficiently large converter volume is crucial in maintaining adequate performance in the late portion of cycle 2. For a given Pt content per converter, therefore, there exists an optimum converter size which yields minimum exhaust emissions for cycles 1 and 2 of the FTP. The optimum converter volume for a given vehicle system can be determined from the results of design calculations such as those shown in Figure 12.

Although oxidizing catalytic converters are considered in this study, our model is also applicable to dual-bed converters because the latter converters normally operate in the oxidizing mode during warmup.

The first paper in this series was published in *AIChE J.* in 1980; see the Literature Cited section for complete information.

CONVERTER WARMUP MODEL

Description of the Model

A detailed description of the converter warmup model and the numerical technique used to solve the equations is given in our earlier papers (Oh et al., 1980; Oh and Cavendish, 1985). The single-pellet equations represent a steady-state two point boundary value problem (diffusion-reaction within the catalyst pellet) coupled with a transient initial value problem (energy balance for the catalyst pellet). The numerical technique involved the use of Galerkin's method for the spatial discretization and the GEARIB Fortran subroutine code (Hindmarsh, 1976) for the time integration. The performance of the entire converter was then calculated by approximating the reactor by four axial mixing cells.

The model considers the Pt-catalyzed oxidation reactions of CO, hydrocarbon (propylene and methane), and H_2. Here propylene is assumed to be representative of "fast-oxidizing" hydrocarbons in automobile exhaust and methane of "slow-oxidizing" hydrocarbons (Kuo et al., 1971). It is further assumed that the fast-oxidizing hydrocarbons constitute 90% (by volume) and the slow-oxidizing hydrocarbons 10% (by volume) of the total hydrocarbon concentration. Additionally, the concentration of H_2 in the exhaust gas is assumed to be $\frac{1}{3}$ of the CO concentration. The same reaction rate expressions as those given in Oh and Cavendish (1985) were used in the computations.

Treatment of Model Inputs

The input information required for model calculations can be divided into three groups: catalyst properties, converter dimensions, and inlet exhaust gas conditions. The first two groups of model parameters will be discussed in the next section. The third group, inlet exhaust gas conditions, deserves some comments here.

The Federal Test Procedure (FTP) driving schedule is composed of various driving modes (idle, cruise, acceleration, and deceleration), as illustrated in Figure 1 for the first two cycles of the FTP. Vehicle speed varies from idle to nearly 100 km/h and this causes a multitude of highly transient converter inlet conditions with respect to exhaust gas flow rate, exhaust composition, and exhaust temperature. In this work the converter inlet conditions are treated by dividing the test period of interest (i.e., cycles 1 and 2) into an appropriate number of small time intervals called calculation modes. Over each calculation mode, the reactant concentrations, exhaust flow rate and temperature are averaged and assumed to be constant at their average values. The error involved in this approximation scheme would generally depend on how the total time interval is divided and the number of calculation modes. For our calculations, the first two cycles of the FTP were broken down to 22 calculation modes based on the modes of driving, as shown in Figure 1. As we will see, this approximation is adequate to simulate the transient behavior of catalytic converters during the warmup period.

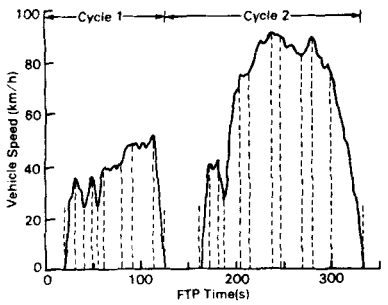

Figure 1. Vehicle speed during cycles 1 and 2 of FTP driving schedule.

VEHICLE EMISSION TESTS

Apparatus and Instrumentation

In order to test the applicability of our converter model to the warmup portion of the FTP, cold-start emission tests were conducted using a 1982 Buick LeSabre equipped with a 4.1 L V-6 engine and a Computer Command Control (C-3) system. Prior to testing on the FTP, the vehicle was driven for approximately 8,000 km in an attempt to stabilize the engine-out emission characteristics. The production exhaust aftertreatment system included a 4.1 L (250 $in.^3$) pellet-type dual-bed catalytic converter with an air plenum between the front and rear beds. For the tests reported here, this production converter was replaced by a 2.62 L (type 160) pellet-type single-bed catalytic converter (frontal area = 516.1 cm^2, depth = 5.1 cm) and supplemental air was injected to the exhaust upstream of the converter using the production air pump. It should be noted that the location of the air injection point was chosen to be downstream of the exhaust oxygen sensor in order to ensure that the operation of the closed-loop engine control system was unaffected. Four thermocouples were installed to measure the gas temperatures at the entrance to the converter, in the inlet plenum, in the catalyst bed, and at the exit of the converter. (See Figure 5 of Oh and Cavendish, 1985, for a cutaway view of a GM packed-bed converter.) The thermocouple probe for measuring the inlet-plenum gas temperature was located approximately at the center of the converter longitudinally (fore-to-aft) as well as transversely (side-to-side). The gas temperature in the bed was measured using a thermocouple which was housed in a thin, perforated tube. The thermocouple was located approximately 4 cm below the top of the catalyst bed. Also, sample lines for emission measurements were installed both at the inlet and outlet of the converter.

Catalysts

Three aged alumina-supported platinum catalysts were used in the tests: two surface-impregnated catalysts of different Pt loadings (0.09 wt. % and 0.056 wt. % Pt) and one subsurface-impregnated catalyst. These are the same catalysts that were used for engine-dynamometer experiments in our earlier study (Oh and Cavendish, 1985). All the catalysts were prepared by impregnating Grace θ-alumina beads (pellet radius = 0.1620 cm, BET surface area = 113 m^2/g, pellet density = 0.776 g/cm^3) using a nonaqueous method developed by D'Aniello (1983). Both the 0.09 wt. % surface-impregnated ("Surface-Hi") and subsurface-impregnated ("Subsurface") catalysts were poisoned for 40 h in exhaust generated from an engine operating on P-doped fuel. The 0.056 wt. % surface-impregnated catalyst ("Surface-Lo") was thermally aged in air at 780°C for 18 h. A detailed description of the catalyst aging conditions and the techniques used to prepare and characterize the catalysts can be found elsewhere (Oh and Cavendish, 1985). The properties of the three aged catalysts tested are listed in Table 2 of Oh and Cavendish (1985).

Test Procedure

In accordance with the FTP (Federal Register, 1972), cold-start tests were conducted after the vehicle was soaked a minimum of 12 h at room temperature. All tests were carried out on a chassis dynamometer at an inertia weight of 1,814 kg using 91 Research Octane Number lead-free fuel. Fuel consumption was measured using a positive displacement fuel meter with 1 mL resolution. The gas temperatures (inlet, plenum, bed, and outlet) and concentra-

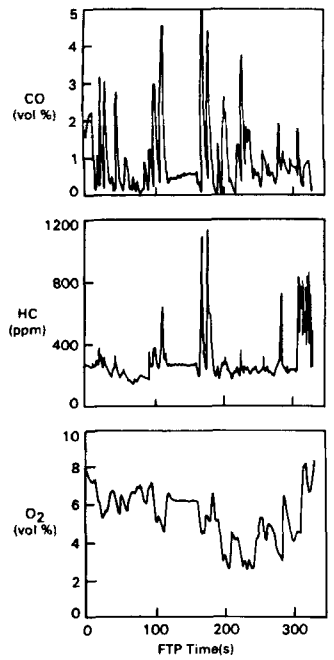

Figure 2. Exhaust concentrations of CO, HC(C_6), and O_2 entering converter during cycles 1 and 2 of FTP driving schedule.

tions (inlet and outlet) were recorded at half-second intervals by a multichannel data acquisition system. Mass emissions of the individual pollutants were determined using the fuel-based mass emission measurement technique described by Stivender (1971). Also, all the concentration measurements were corrected for the analyzer dynamics and transportation lag in a manner similar to that described in the Appendix of Oh and Cavendish (1985).

Inlet Exhaust Gas Conditions

One important factor in analyzing the behavior of an automotive catalytic converter during the FTP is that it is subject to highly dynamic inlet conditions with respect to reactant concentrations, exhaust temperature, and exhaust flow rate. Figure 2 shows the time variations of the concentrations of CO, HC (as C_6), and O_2 in the exhaust gas measured during the first two cycles of the FTP using the 1982 LeSabre. The exhaust gas temperatures measured at the converter inlet (solid line) as well as in the inlet plenum (dotted line) over the same period of time are depicted in Figure 3. Notice that the plenum-gas temperature is considerably lower (by over 100°C at early times) than the exhaust gas temperature

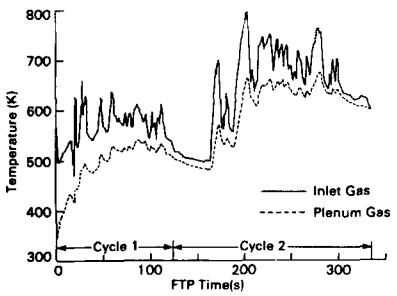

Figure 3. Exhaust gas temperatures at converter inlet and in inlet plenum during cycles 1 and 2 of FTP driving schedule.

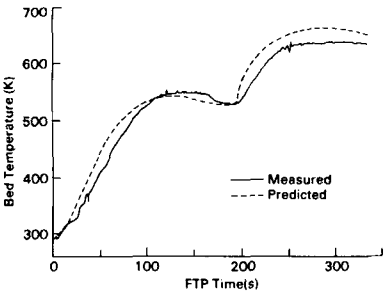

Figure 4. Comparison of measured and predicted bed temperatures for a converter packed with inert alumina beads.

measured at the converter inlet. The difference between the inlet-gas and plenum-gas temperatures is not surprising, because a significant amount of heat is transferred from the exhaust gas to the inlet header and retaining grid during the early phases of the FTP. The relatively rapid temperature rises during the 165–205 s interval (which are associated with a sequence of accelerations; see Figure 1) lead to high-temperature (~400°C) converter operation in the late portions of cycle 2.

Independent measurements of the gas temperature at various longitudinal locations in the inlet plenum of a GM packed-bed converter revealed significant fore-to-aft variations (approximately a linear decrease with distance) in the plenum-gas temperature during converter warmup. Since a one-dimensional converter model is employed here, such longitudinal variations in the inlet plenum temperature were accounted for by calculating the average inlet-plenum gas temperature under the assumption that both the mass flow rate and the temperature of the exhaust gas in the inlet plenum decrease linearly from the front to the rear of the plenum. A linear decrease in the mass flow rate would occur if the flow through the packed bed is uniform. These assumptions lead to the following formula for calculating the average inlet-plenum gas temperature:

$$T_{av} = \frac{1}{3} T_{in} + \frac{2}{3} T_{pl}$$

where T_{in} is the gas temperature measured at the converter inlet (i.e., the front of the inlet plenum) and T_{pl} represents the gas temperature measured midway between the front and rear of the inlet plenum. The calculated average inlet-plenum gas temperature was then used as temperature inputs for our converter model.

The mass flow rate of the exhaust gas was not directly measured during the test; it was determined from the measured fuel consumption rate and the air-fuel ratio calculated from concentration measurements. The time variations of the converter inlet conditions are approximated by piecewise constant functions; that is, the concentrations, temperature, and flow rate of the exhaust gas at the converter inlet are assumed to be constant within each of small time intervals called calculation modes, but these constants are allowed to vary from one calculation mode to another.

COMPARISON OF MODEL PREDICTIONS WITH TEST DATA

Thermal Response of Inert Bed

Comparison is made in Figure 4 of the measured and predicted bed temperatures during cycles 1 and 2 of the FTP for a type-160 catalytic converter packed with inert alumina beads. The thermocouple was located approximately 4 cm below the top of the catalyst bed; this corresponds to cell 4 in our model. Reasonably

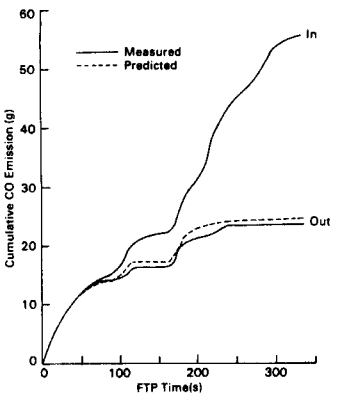

Figure 5. Cumulative CO emissions into and out of converter for "Subsurface" catalyst.

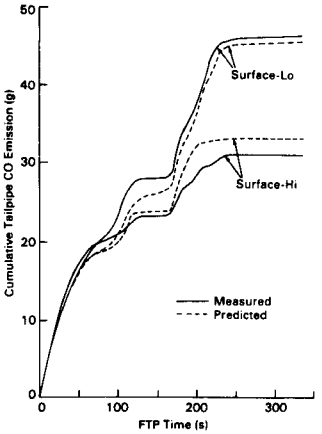

Figure 7. Comparisons of measured and predicted cumulative CO emissions leaving converter for "Surface-HI" and "Surface-Lo" catalysts.

good agreement was obtained in Figure 4 between the measured and predicted thermal responses for the inert bed, indicating that the model adequately describes the heat transfer process occurring in GM packed-bed converters during the warmup portion of the FTP.

Performance and Thermal Response of Active Bed

A further evaluation of the model was made by comparing measured and predicted cumulative emissions of CO leaving the converter during the first two cycles of the FTP. (Comparison of hydrocarbon emissions yields essentially the same results because of the kinetic coupling between the two species.) Such a comparison is made in Figure 5 for the "Subsurface" catalyst. The agreement between the model prediction and experimental data is very good throughout the warmup period considered. Also included in Figure 5 for reference purposes is the measured cumulative CO emission entering the converter as a function of time. Comparison of the measured converter-in and converter-out CO emissions shows that significant reaction begins to occur at approximately 70 s into the FTP. The plateau in the measured converter-out CO emission curve for $t > 240$ s is the consequence of high conversion efficiencies obtained during the high-temperature converter operation over that period (see Figure 3).

Shown in Figure 6 is a comparison of the time variations of the measured and calculated bed temperatures during cycles 1 and 2 for the same "Subsurface" catalyst. During the first 225 s of the test, the predicted and measured thermal responses agree reasonably well. For $t > 225$ s, however, the model overpredicts the bed

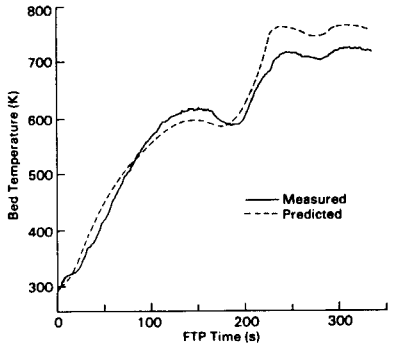

Figure 6. Comparison of measured and predicted bed temperatures for "Subsurface" catalyst.

temperature by approximately 40°C. At least part of this discrepancy can be attributed to the fact that our adiabatic converter model does not account for the heat loss from the converter to the surroundings, which becomes significant during the late portion of cycle 2 as a result of the high converter temperature. As can be seen from Figure 5, however, this does not significantly affect the predictions of converter-out emissions, because converter performance becomes relatively insensitive to temperature at high temperatures.

Additional comparisons between measured and predicted cumulative tailpipe (i.e., converter-out) emissions of CO are made in Figure 7 for the two surface-impregnated catalysts ("Surface-Hi" and "Surface-Lo"). Here again the model provides reasonably good predictions of the cumulative emissions of CO during the first two cycles of the FTP. It should be noted that the predicted curve for the "Surface-Hi" catalyst was generated by assigning $1/20$ of the fresh activity to the poisoned Pt layer as in our earlier study (Oh and Cavendish, 1985). In accordance with our anticipation, the total CO emission during cycles 1 and 2 for the "Surface-Hi" catalyst is considerably lower (by ~15 g) than that for the "Surface-Lo" catalyst. (This difference in cold-start CO emission translates into about 0.9 g/mi in the overall FTP emission of CO, compared to the current emission standard of 3.4 g/mi.) This demonstrates that converter warmup performance is generally sensitive to the amount of active noble metals in the catalyst pellet. (Recall that the "Surface-Hi" catalyst contains approximately four times more active Pt than the "Surface-Lo" catalyst.) Notice, however, that in the late portion of cycle 2 ($t > 240$ s) this Pt loading effect disappears and both catalysts gave nearly complete conversion of CO, due to the high exhaust gas temperature entering the catalyst bed (see Figure 3).

PARAMETRIC SENSITIVITY ANALYSIS

The comparisons made in Figures 4 and 7 between the model predictions and experimental data reveal that the model provides a computational tool for quantitative predictions of the thermal response and conversion performance of GM packed-bed catalytic converters during the warmup period of the FTP. Consequently, the model can be used with confidence to investigate the effects of converter design and operating parameters on cold-start exhaust emissions.

This section describes some of the results of parametric calculations obtained using our converter model. Of particular interest

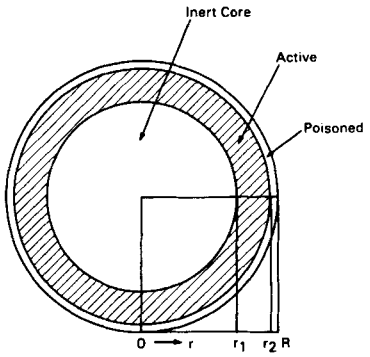

Figure 8. Schematic diagram of the cross section of a typical vehicle-aged catalyst pellet.

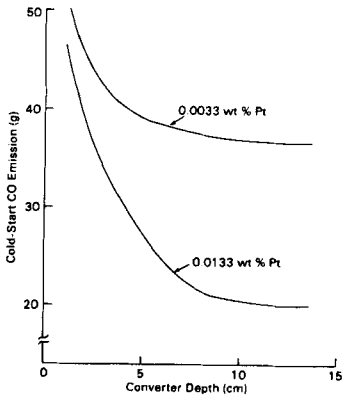

Figure 9. Effects of converter volume (frontal area fixed at 516.1 cm^2) on cold-start CO emissions for two different active Pt loadings of catalyst pellets.

here is the dependence of the total tailpipe CO emissions during cycles 1 and 2 of the FTP (hereafter referred to as "cold-start CO emissions") on converter dimensions and catalyst properties. In this section we will focus on the effects of changing one variable at a time. Such parametric sensitvity analysis is useful because it identifies important design parameters and quantifies the sensitivity of converter performance to changes in each of those variables.

Since converter performance after 80,000 km driving (rather than fresh performance) is of primary interest for automobile emission control applications, our model calculations assume a catalyst configuration characteristic of vehicle-aged commercial automotive catalysts; they typically have a catalytically active band sandwiched between an unimpregnated inert core and a relatively shallow poisoned layer, as illustrated in Figure 8. For the results of parametric calculations reported here, the poisoned layer was assumed to be completely deactivated. (Assigning small residual activity to the poisoned layer generally changes predicted emissions only slightly.)

Effects of Converter Dimensions

Table 1 shows how the tailpipe CO emissions during cycles 1 and 2 are affected by variations in the ratio of the converter frontal area to its depth (while keeping the converter volume constant). For the calculations, it was assumed that the catalyst pellets contain a 25 μm outer poisoned layer surrounding a 75 μm catalytically active band (0.003 wt % active Pt). All other catalyst properties were taken to be the same as those used for the model verification studies described in our earlier paper (Oh and Cavendish, 1985). Also, the calculations were made based on the inlet exhaust gas conditions measured during the FTP tests using the 1982 Buick LeSabre. It can be seen from Table 1 that cold-start CO emissions are predicted

TABLE 1. EFFECTS OF FRONTAL AREA-TO-DEPTH RATIO ON COLD-START CO EMISSIONS

Case	Frontal Area cm^2	Depth cm	Cold-Start CO Emissions g
1	1,032.2	2.54	41.3
2*	516.1	5.08	39.1
3	258.1	10.16	38.3

*GM type-160 converter.

to be favored by small frontal area, but the effect is rather small.

Illustrated in Figure 9 are the effects of variation in converter volume on the tailpipe CO emissions during cycles 1 and 2 for two different active Pt loadings of the catalyst pellet (i.e., the amount of Pt remaining in the unpoisoned Pt band of the pellet). The other catalyst properties and inlet exhaust gas conditions were taken to be the same as those used for Table 1. Here the converter volume was perturbed by varying the depth of the catalyst bed while keeping its frontal area constant at 516.1 cm^2. (The choice of the frontal area is not crucial because, as Table 1 shows, exhaust emissions during the warmup portion of the FTP are rather insensitive to variations in the frontal area-to-depth ratio within the practical limits considered.) As expected, for each of the two Pt loadings considered, CO emissions at the converter outlet generally decrease with increasing converter volume. Notice, however, that increasing the catalyst volume (while holding its properties constant) beyond a certain value gives only a small reduction in exhaust emissions during converter warmup. This can be explained based on the finding of our earlier study (Oh and Cavendish, 1985) that the catalyst pellets in the upstream portion of a converter are primarily responsible for converter lightoff; the additional catalyst in the rear portion of the bed does not warm up fast enough to contribute significantly during the early portions of the FTP. The difference in the asymptotic emission levels of the two catalysts predicted in Figure 9 reflects the sensitivity of cold-start emissions (primarily the emissions for $t < 240$ s; see Figure 7) to the noble metal loading of catalyst pellets. The results of Figure 9 demonstrate the importance of a proper choice of catalyst noble metal loading in converter design; it determines an upper limit on converter warmup performance that cannot be overcome simply by increasing the converter volume.

Effects of Catalyst Properties

The parameters associated with catalyst design include pellet size, pore structure (and thus pellet density and effective diffusivities), and noble metal loading and its impregnation pattern. Here we will examine only the effects of variations in the last two parameters using the inlet exhaust gas conditions of the Buick LeSabre measured during the FTP.

Figure 10 shows how tailpipe CO emissions during cycles 1 and 2 change with the catalyst's active Pt loading for four different converter volumes (frontal area fixed at 516.1 cm^2). Here again, it was assumed that the catalyst pellet consists of a 75 μm active band surrounded by a 25 μm poisoned layer. The simulations

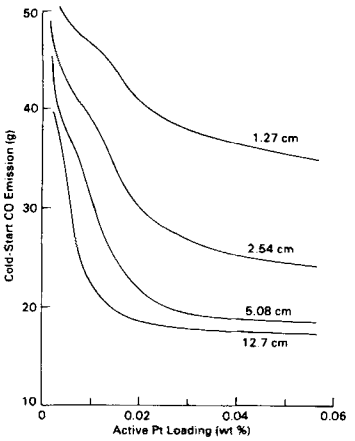

Figure 10. Effects of active Pt loading on cold-start CO emissions for four different converter volumes (frontal area fixed at 516.1 cm^2).

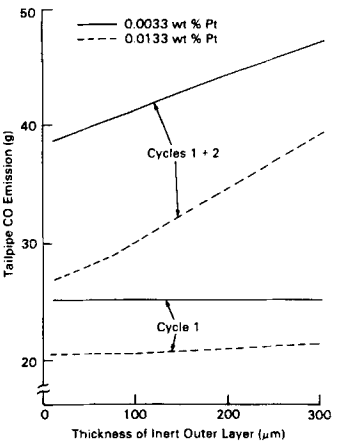

Figure 11. Effects of location of Pt band (75 μm thick) on cold-start CO emissions for two different active Pt loadings.

yielded the expected results that for each of the converter volumes considered, cold-start CO emissions decrease as the amount of active Pt in the catalyst pellet (and thus the Pt content in the converter) increases. More interesting is the prediction that in the regime of high Pt loadings, CO emissions during converter warmup are relatively insensitive to a variation in the Pt loading. The decreasing sensitivity at high Pt loadings places a practical limit on the maximum converter warmup performance that can be achieved by increasing the Pt loading of the catalyst for a given converter size. The different asymptotic emission levels predicted for various converter sizes at high Pt loadings are largely related to the dependence of cycle 2 emissions on converter volume, as demonstrated in Table 2 where the cycle-by-cycle emissions are shown for an active Pt loading of 0.053 wt. % (the same data as shown in Figure 10). It is interesting to note in Table 2 that the tenfold variation in converter volume (1.27 cm vs. 12.7 cm) is predicted to change cycle 1 CO emissions only by 3.2 g.

The performance of automobile exhaust catalytic converters can be significantly influenced by diffusion resistances within the catalyst pellets. One convenient way of examining the degree of intrapellet diffusion-reaction interactions is to place a Pt band of fixed thickness and loading subsurface to various depths away from the pellet's outer edge. Figure 11 shows the results of such simulations for two different active Pt loadings (75 μm Pt band, GM type-160 converter). Cycle 1 CO emissions are dependent on the amount of active Pt in the catalyst pellet but are virtually unaffected by the location of the Pt band, indicating that converter performance during cycle 1 of the FTP is kinetically controlled. Converter performance during cycle 2, on the other hand, is adversely affected by intrapellet diffusion resistances, due primarily to the high-temperature (~400°C) converter operation encountered for $t > 200$ s (see Figure 3). As a result, the total tailpipe CO emissions during cycles 1 and 2 increase with increasing thickness of the inert outer layer (i.e., as the Pt band is buried deeper), as illustrated in the top portion of Figure 11. In addition to elucidatng the nature of converter operation during warmup, the results of Figure 11 provide guidance in the design of subsurface-impregnated catalysts.

In general, poison accumulation in automotive catalysts deactivates the catalyst as a result of the combined effect of the removal of catalytic sites by the poison and decreased accessibility of the rectants to the active (unpoisoned) sites caused by diffusion resistances through the poisoned outer shell. The results of Figure 11 show that for typical posion penetration depths encountered in exhaust emission control (< 40 μm), the latter effect contributes little to the deterioration of converter warmup performance. (About 1 g increase in cold-start CO emissions is predicted over this range of poison penetration depths, which translates into only 0.05 g/mi increase in the overall FTP emission of CO.) This indicates that the warmup performance of a partially poisoned automotive catalyst depends primarily on the amount of noble metal remaining in the unpoisoned portion of the impregnated band (and is little affected by the poison penetration depth itself).

TABLE 2. BREAKDOWNS OF COLD-START EMISSIONS FOR VARIOUS CONVERTER VOLUMES*

Converter Depth cm	Tailpipe CO Emissions Cycle 1 g	Cycle 2 g	Total g
1.27	20.4	14.7	35.1
2.54	18.4	5.8	24.2
12.7	17.2	0.1	17.3

* Frontal area = 516.1 cm^2.

OPTIMUM CONVERTER DESIGN

In this section we will address the following two design questions of practical interest:

(1) Maximizing converter warmup performance with a given amount of Pt.

(2) Minimizing Pt usage for a given performance requirement.

An example will be given which illustrates how the model can be used to answer these converter design questions for specific engine-out emission characteristics (i.e., 1982 LeSabre with a 4.1 L engine).

The results of design calculations are summarized in Figure 12, where the tailpipe CO emissions during cycles 1 and 2 are plotted a a function of converter depth (its frontal area fixed at 516.1 cm^2) for three different amounts of *active* Pt in the converter. (In addition to poison penetration, sintering typically causes a 20-fold decrease in the amount of catalytically active noble metals in the converter during 80,000 km of vehicle use (Dalla Betta et al., 1976); so this factor was accounted for in choosing the Pt contents of

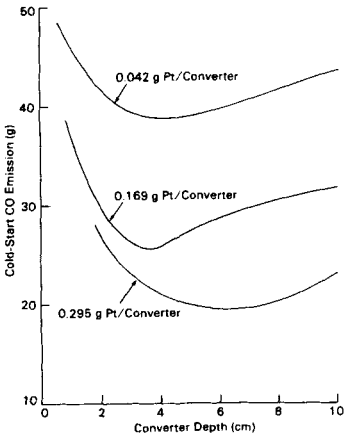

Figure 12. Dependence of cold-start CO emissions on converter volume (frontal area fixed at 516.1 cm^2) for three active Pt contents per converter.

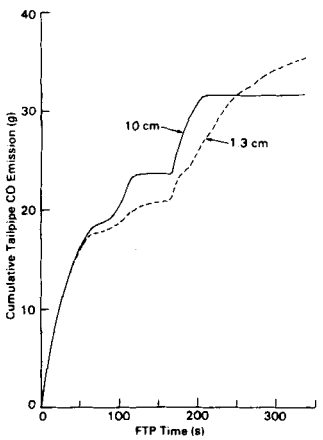

Figure 13. Comparison of cumulative tailpipe CO emissions for small and large converters.

Figure 12.) For the calculations, the partially poisoned surface-impregnated catalyst was considered which contains a 75 μm active band surrounded by a 25 μm poisoned shell. Notice that the total amount of Pt remaining unpoisoned in the converter is chosen as a parameter in Figure 12 because, as discussed earlier, this is the quantity governing cold-start exhaust emissions under poisoning conditions. Note also that since the total amount of Pt in the converter is fixed here, the Pt loading of the catalyst pellet is inversely proportional to converter volume.

Referring to Figure 12, minimum CO emissions are predicted to occur at an intermediate value of converter volume. If the converter volume is larger than the optimum value, the cold-start emissions increase as a result of the concomitant decrease in the Pt loading of the catalyst pellets. As shown in Figure 7, this decrease in the catalyst's Pt loading adversely affects the converter performance during cycle 1 and the early portion of cycle 2. If the converter volume is too small, on the other hand, the beneficial effect of the increased Pt loading on the early-time converter performance is dominated by the performance deterioration (caused by insufficient contact time) in the later portions of the warmup process, resulting in an increase in the total CO emissions during cycles 1 and 2. This difference in performance characteristics is clearly illustrated in Figure 13, which shows cumulative tailpipe CO emissions as a function of time for two different converter volumes (0.169 g active Pt/converter in both cases). The small converter (dotted line) outperforms the large converter (solid line) at early times because the former contains catalyst pellets of a higher Pt loading; however, the ability of the larger converter to convert CO nearly completely for $t > 205$s results in a lower cumulative emission level at the end of cycle 2.

It should be noted that Figure 12 can also be used to determine a minimum amount of Pt required to achieve a specified cold-start tailpipe emission level. It is clear from Figue 12 that for a given amount of Pt per converter there are, in general, two converter volumes giving the same emission level. A minimum amount of Pt required for a desired emission level can then be determined by ascertaining the Pt content for which the required converter volume collapse into one value. Once the optimum values of the Pt content and converter volume are established, the corresponding Pt loading of the catalyst pellet is automatically determined.

As discussed earlier, converter warmup performance under posioning conditions depends primarily on the amount of active Pt remaining in the catalyst (and not on the thickness of the poisoned shell itself). Therefore, the curves of Figure 12 are also applicable to catalyst pellets having poison penetration depths other than 25 μm but the same amounts of active Pt as those specified in the figure. The same generality applies to the results of parametric calculations presented in the previous section.

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