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**SELECTIVE CATALYTIC REDUCTION (SCR) PERFORMANCE IN
STEAM-METHANE REFORMER SERVICE:
THE CHROMIUM PROBLEM**

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Selective Catalytic Reduction (SCR) Performance in Steam-Methane Reformer Service: The Chromium Problem

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ABSTRACT

SCR performance has been seen to deteriorate with catalyst age at a greater than expected rate in steam-methane reformers (SMRs) and ethylene plants. Loss of catalyst activity has been attributed to deposition of chromium-oxide species from alloy furnace tubes and coils on the catalyst surface, thereby masking active catalyst sites. This deposit is visible to the naked eye as a brown or iridescent black discoloration along the passages of a flow-through honeycomb catalyst, darkest at the entrance face and gradually becoming lighter as one proceeds downstream. The color becomes more intense with increased exposure to flue gas.

It is important for proper design and catalyst-replacement strategy to understand the governing phenomena at a fundamental level, especially at a time when SCR is increasingly being turned to as BACT to comply with the more stringent nitrogen oxides (NO_x) regulations. This paper describes a correlation of previously unpublished experimental data from catalyst test-sections (logs) exposed in the field over a period of several years at multiple SMR plant locations.

Consistent with the observed color change, chromium pickup increases with time and varies with operating conditions from plant to plant. Any given log, at any given time, shows an exponential, or semi-logarithmic, decrease in chromium concentration over its length. Activity decay of the catalyst has been correlated with the chromium concentration. This single correlation holds true for all of the different plants investigated and can be used to predict remaining catalyst life and optimize future catalyst designs. Scanning electron microscope (SEM) results and surface analyses from the SCR catalyst and SMR reformer tubes are also discussed, along with suggested countermeasures to mitigate the effects of chromium oxide deposition.

INTRODUCTION

SCR catalyst performance has been observed first-hand to deteriorate in SMR hydrogen plants at a faster than expected rate,^{1,2} and such accelerated deterioration has been reported for ethylene plants as well.^{3,4} It is important, therefore, to account for this loss of activity when sizing the initial charge of catalyst and to make an accurate prediction of the useful life of that catalyst before replacement is necessary. To do so, one really must understand the governing phenomena on a fundamental level.

A basic understanding will include:

- Where the chromium comes from.
- How it reaches the SCR catalyst.
- What it does to the catalyst.
- How NO_x removal is affected.
- How the effect can be mitigated.
- When the catalyst must ultimately be replaced.

This paper presents the results of a systematic experimental investigation as outlined in Table 1. It is designed to extend the knowledge gained from our own observations and experience and that of others, as reported in the literature. Those results are discussed following some necessary background information.

H₂ PROCESS DESCRIPTION

The steam-methane reforming (SMR) process reacts a hydrocarbon with steam (H₂O) to produce a mixture of hydrogen (H₂) and carbon monoxide (CO), generically known as *synthesis gas* (*syngas*). Major process steps consist of sulfur removal, reforming, water-gas shift in high temperature shift (HTS) and low temperature shift (LTS) converters, and H₂ product purification. A typical process flow sheet is available elsewhere.⁵

The hydrogen is separated from the syngas in a pressure-swing-adsorption (PSA) unit capable of producing a hydrogen purity of 99.9 % to 99.999 %.^{6,7} The other components in the PSA feed plus some hydrogen end up in the so-called *PSA purge gas*, a low-Btu gas which is recycled as the bulk of the fuel to the reformer-furnace burners. Combustible components in the PSA purge gas include hydrogen, carbon monoxide, and methane. This is supplemented typically by natural gas or refinery fuel gas as auxiliary, or trim, fuel. Oxides of nitrogen (NO_x) are generated in the combustion process.

NO_x from a hydrogen plant reformer furnace burning PSA purge gas with natural gas as trim fuel and without air preheat can be as low as 0.03 lb NO_x/MM Btu, based on the higher heating value (HHV) of the fuel.^{8,9} This is equivalent to about 25 ppmv (dry) at 3 % O₂ (dry). However, in some regulatory jurisdictions, such as California and the Gulf Coast area of Texas, selective catalytic reduction (SCR) must be applied to reduce NO_x emissions still further.

Performance of SCR has been demonstrated on SMR hydrogen plants. A sampling of Air Products hydrogen plant projects using SCR for NO_x control is shown in Table 2; one of these installations, the Martinez I plant, is pictured in Figure 1. Air Products is the No. 1 Supplier in hydrogen sales to third parties.

Locations in the table represent a joint accumulated operating experience for Air Products and Cormetech of over 30 years. Cormetech has supplied SCR catalyst for other hydrogen-plant clients as well. As explained below, direct experience with hydrogen-plant flue gas is important for initial catalyst sizing and prediction of run length.

THE SCR PROCESS

In this process (Figure 2), the oxides of nitrogen NO and NO₂, commonly known as NO_x, are reacted with ammonia (NH₃) in the presence of a flow-through honeycomb catalyst to give nitrogen (N₂) and water vapor (H₂O).^{1,2} Reaction stoichiometry with ammonia, injected upstream, depends on the relative amount of each oxide and whether or not oxygen (O₂) is present. For combustion applications containing excess oxygen and parts-per-million (ppm) concentrations of NO_x with the typical 95 % NO and 5 % NO₂ split, the equations given in Figure 2 apply. In the absence of competing side reactions, the theoretical molar ratio of NH₃ reacted to NO_x destroyed is 1.0.

Not all of the ammonia added, however, will have enough time to react with the NO_x, and this unreacted NH₃ at the SCR outlet is termed the *ammonia slip*. Ammonia slip normally starts out at a very low level for new catalyst. It gradually increases at a given outlet NO_x when more ammonia must be fed to compensate for the loss of catalyst activity as time goes by.

The activity of SCR catalyst is often expressed by the value of a factor known as *K* in an equation relating inlet and outlet NO_x, ammonia, and residence time within the catalyst as expressed by area or space velocity. One such simple model has been discussed previously.^{1,2} The *K* so determined is a lumped parameter that includes the effects of catalyst composition, temperature, the combination of kinetic reaction-rate and mass transfer at that temperature, and the loss of catalyst activity with age/exposure to flue gas. A typical temperature range for base-metal catalysts composed of TiO₂, V₂O₅, and other ingredients is 600-750 °F (316-399 °C).^{1,2}

In turn, the kinetic reaction-rate depends on flue-gas oxygen and moisture, and the mass transfer on catalyst geometry, surface properties, and flue-gas velocity. A decline in catalyst activity is reflected by a decrease in the ratio *K/K_o*, where *K_o* is determined for fresh catalyst of the same geometry and composition under the same operating conditions. For brand-new catalyst, *K/K_o* is identically equal to 1.0.

THE PROBLEM

Some small loss of catalyst activity over time is to be expected, even when firing a clean gaseous fuel. However, we have found that the presence of chromium-oxide species in the flue gas of a hydrogen reformer furnace causes loss of SCR catalyst activity over time at a rate greater than

normally expected for a clean-gas application. The loss of catalyst activity has been attributed to a masking of active catalyst surface by an ongoing deposition of some form of chromium,² with the potential for evaporation at parts-per-billion (ppb) to parts-per million (ppm) concentrations from the alloy metals in contact with hot flue gas.¹⁰ This same loss of activity and chromium deposition have also been reported for ethylene plants,^{3,4} where pyrolysis-coil temperatures in the cracking furnace are similar and the same family of chromium/nickel alloys are used.¹⁰

This masking layer manifests itself as a discoloration of the SCR catalyst surface, heavy at the inlet and becoming gradually lighter approaching the outlet. The color deepens and spreads farther downstream with greater exposure time. The color varies from brownish to an iridescent black, possibly depending on the temperature of chromium oxide condensation on the catalyst.

A photograph of an exposed SCR catalyst sample removed from an Air Products hydrogen plant is shown in Figure 3, along with a fresh, unexposed sample for comparison. The discoloration of the exposed sample (on the left) is dark brown at the inlet face and somewhat lighter brown at the outlet (not pictured). The fresh catalyst sample shown on the right in Figure 3 is a light tan, with a nominal pitch in the range of 2-4 mm, typical of clean-gas service.¹¹

Published plots of catalyst activity (K/Ko) vs. time for hydrogen and ethylene plants are depicted in Figure 4.¹⁰ As the SCR catalyst continues to age from chromium deposition during operation, K/Ko will eventually reach a point at which environmental permit requirements for outlet NOx and ammonia slip cannot be met simultaneously, and the plant must be shut down to replace the catalyst.

To conduct this process in an orderly manner during a planned shutdown with replacement catalyst on hand, one must be able to predict catalyst life accurately, a consideration leading to the present investigation.

INVESTIGATION OF THE CHROMIUM PHENOMENON

OVERVIEW

Various theories have been advanced concerning the origin of the chromium. Suggested sources include the trim fuel, the chromium content of the HTS catalyst, the alloys in contact with the flue gas (i.e., reformer tubes in the radiant section of the furnace and cooling fins/coils in the convection section), and even the combustion air.

It is possible to reject some of these almost immediately. With respect to the trim fuel, the chromium phenomenon occurs in SMR-furnace flue gas equally with natural gas or refinery fuel gas. Cormetech has supplied SCR catalyst in numerous other natural-gas-fired applications for which chromium poisoning is not an issue. Likewise, regarding combustion air.

The contention that chromium contained in HTS catalyst is somehow working its way from the process side through the PSA to the flue gas can also be ruled out; chromium deposition is observed on SCR catalyst in ethylene-plant pyrolysis furnaces,^{3,4} where no process catalyst of any kind is employed.

That leaves the furnace metallurgy, which is a focal point of this investigation. This assumes vaporization and vapor deposition to be the underlying mechanism, as opposed to particulate transport and capture. Experimental data, applicable thermodynamics, and a proposed mechanism are explored in greater detail in the Results and Discussion Section.

TEST PROCEDURES AND EQUIPMENT

A series of separate, though related, experimental procedures outlined in Table 1 was conducted. Metallurgical samples were analyzed using energy dispersive X-ray spectrometry (EDS). Fresh and exposed catalyst samples were examined using a scanning electron microscope (SEM). Details are provided in the Results and Discussion Section.

Periodically over many years, catalyst test-sections (commonly known as *logs* or *test logs*) were removed from the Air Products H₂ plants and were analyzed for chromium by Air Products using inductively coupled plasma-optical emissions spectroscopy (ICP-OES) and for catalytic activity by Cormetech. Test details are given below; data are considered in the Results and Discussion Section.

Chromium Analyses. These were obtained by first sectioning the test log into four equal segments, whose length depends on the overall length of the original sample (Figure 5). One-inch (2.54-cm) cubes were removed from the inlet face of each segment as well as from the outlet face of the last segment. The 1-inch cubes were then ground up and placed in a mixed acid solution, sealed, and heated in a microwave oven to dissolve the catalyst sample. ICP-OES was employed, as indicated, to measure the bulk percent chromium in each sample. This technique can be used to obtain a more complete elemental analysis as well.

Activity Testing. Catalyst activity was evaluated in a *pilot* reactor in Cormetech's laboratory. The quarter-segments cut from some of the original sample logs were tested in a *micro* reactor following the pilot test on the entire log.

The pilot reactor is a large-scale test apparatus used to evaluate the performance of SCR catalyst at actual operating conditions (Figure 6). It consists of a water-cooled combustion chamber and electric heater to achieve the desired test velocity and temperature. Excess air is introduced to obtain the desired flue-gas O₂ concentration, and levels of NO_x and SO₂ (if necessary) can also be adjusted to simulate field conditions. Ammonia is injected to produce the desired NH₃/NO_x ratio. Gases are blended by means of a static mixer, and a honeycomb flow straightener produces a uniform flow distribution. As many as four full-size logs, each measuring up to 1.1 meters, can be accommodated in a series arrangement. Sampling ports are located at the inlet and outlet of the reactor and between each sample layer. Additional information is provided elsewhere.¹²

The micro reactor is a small-scale glass tubular vessel that fulfills the same function as the pilot reactor, but for smaller samples of SCR catalyst.

SOURCE OF THE CHROMIUM

From the very beginning, it was believed that the chromium seen to be poisoning the SCR catalyst is coming from either the reformer tubes or the fins on the coils in the convection section. Literature searches were completed to understand the volatility characteristics of various chromium species. Initial work focused on chromium trioxide, CrO₃, a chromium oxide species

thought to have a sufficiently high vapor pressure to allow vaporization to occur at operating temperatures. However, this work suggested that the reformer-tube temperature had to be above 1900 °F (1038 °C) to volatilize the amount of chromium observed on the SCR catalyst. Generally, the tubes operate between 1600 and 1700 °F (871 and 927 °C), and the convection coils at a lower temperature. And so, this did not seem consistent.

A literature search then uncovered a 1996 paper¹³ that calculated the different vapor-phase chromium species in equilibrium with solid Cr₂O₃ as a function of temperature, O₂ concentration, and moisture. The authors found that the predominant species in the presence of water vapor and at the temperatures in question is a chromium oxyhydroxide species, CrO₂(OH)₂. The volatility of this species is several orders of magnitude higher than that of CrO₃ and easily within the range of our operation, both for the reformer tubes as well as for the fins on the convection coils. CrO₃ is the predominant species under oxidizing conditions when water vapor is absent from the equilibrium mixture, a situation not representative of flue-gas conditions. Other papers in the literature provide additional information on the vaporization behavior of Cr₂O₃.¹⁴⁻²¹

These calculations¹³ supported the possibility for chromium to be volatile at process conditions. However, we still wanted to know whether the reformer tubes or fins were truly losing chromium or whether the chromium were bound so tightly that it would not be released. To help answer this question, samples from an HP-50 reformer tube that had been in service for three years were sectioned and analyzed for chromium concentration. A section of stainless steel convection-coil fin was also removed and analyzed. The samples were analyzed using EDS, as indicated.

The EDS analysis produces impressive colored pictures based on the individual elements that make up the metals. These photographs show the relative concentration of those elements for the first several hundred micrometers (microns, μ) of the surface. The chromium pictures clearly depict the layer of chromium oxide that builds up on all surfaces. There is also a significant chromium-depletion zone. Figure 7 shows the chromium profile for the fin sample; Figure 8 the profile for the outside of the reformer tube at a point ~ 15 ft (4.6 meters) down the reformer tube in the “hot” part of the furnace.

EDS is able to measure the chromium concentration at various depths. For the fin sample (Figure 7), the chromium-depletion zone is relatively small: The chromium oxide film contains 47 % chromium, the chromium-depletion zone 12 % chromium, and the bulk chromium level 19 % chromium. A chromium balance was attempted in order to determine whether there is a net loss of chromium, based on the concentrations and depths. It appears that the surface layer contains more chromium than was depleted, suggesting minimal loss to the flue gas, at least within the accuracy of the pictures and measurements.

For the reformer tube (Figure 8), it is clear that there is a substantial chromium-depletion zone (~160-180 μ), as one might expect, based on previous work.²³ The measured chromium concentration in the chromium-depletion zone was found to be 18 %; the bulk chrome is 26 %. Unfortunately, a chromium concentration was not obtained for the chromium-rich surface layer. Assuming, however, the same chromium concentration as measured for the surface of the fin, the chromium balance indicates a significant loss of chromium to the flue gas. This loss is on the order of 100 lbs (45.4 kg) total over three years when all the tubes in the reformer furnace are considered. This is not a concern for the integrity of the tubes,²² but the loss is consistent with the 15-20 lbs/yr (6.8-9.1 kg/yr) of chromium buildup seen on the SCR catalyst.

All these numbers are rough, but they do suggest that the chromium which ends up on the SCR catalyst is coming predominantly from the reformer tubes and, at least for stainless steel fins, that the fins are not the major source of chromium on catalyst.

CHROMIUM ON THE SCR CATALYST

To understand better the mechanism of catalyst deactivation, samples of exposed catalyst were examined using the scanning electron microscope (SEM), with a fresh catalyst sample for comparison. Several samples were prepared from the inlets and outlets of catalyst logs obtained from two different plants. Both plants had been on line for a good number of years, one twice as long as the other.

It was found that the chromium deposits in the pores on the first 25 microns of the catalyst surface. There was no chromium peak observed beyond this point. The thickness of the chromium layer appears to be dependent on the exposure time to the flue gas and to the total amount of chromium amount that has been laid down. The chromium layer is thicker for the plant that was on line for the longer period, and the thickness of the chromium layer decreases from the inlet to the outlet of the log consistent with the drop off of chromium concentration that therefore occurs in the flue gas.

Based on these results, the chromium fills less than 15 % of the pore volume, even for the worst case to date. This reduces the number of active sites and the diffusion through the catalyst structure, resulting in a significant decrease in catalyst activity compared to that of fresh catalyst. Nevertheless, it is theorized that the flue gas can still migrate through the porous catalyst structure and find active catalyst sites even amidst substantial concentrations of chromium. It continues to appear that the catalyst surface is partially “masked” rather than completely “blinded”. Blinding would result in very low activity.

Catalyst scans are shown in Figures 9 and 10. The chromium deposit in the first 10 microns of the catalyst layer can be observed in both of these pictures. These observations are consistent with the 20-30 microns for the chromium compound reported on SCR catalyst in ethylene-plant service.³

HOW IT GETS THERE

Oxidation resistance of stainless steels and many high-temperature nickel-based alloys containing chromium is provided by a protective Cr₂O₃ surface layer; the Cr₂O₃ normally forms spontaneously upon exposure to oxidizing conditions at high temperatures.²⁴ For an HP Cr/Ni alloy, this oxide is not pure Cr₂O₃ but consists of a relatively thick layer of Cr₂O₃ closest to the metal, topped by a thin external layer consisting of a mixed manganese-iron chromate (Mn,Fe)Cr₂O₄ spinel.²³

An oxide such as Cr₂O₃ undergoes what is termed an *oxidative vaporization*^{15,16} at high temperature and reverts to its original form upon condensation,^{18,21} a behavior apparently quite common.²¹ The Cr₂O₃ disproportionates into products like Cr, CrO, CrO₂, and molecular and atomic oxygen in the vapor phase in the absence of oxygen from an outside source.¹⁹ When external oxygen is present, as in a flue gas containing excess air, CrO₃ is also produced,^{18,19} and the equilibrium is shifted among the various oxide species.¹³⁻¹⁵ With accompanying flue-gas

water vapor in addition to the oxygen, gaseous hydroxides and oxyhydroxides such as $\text{CrO}_2(\text{OH})_2$, CrO_2OH , and $\text{CrO}(\text{OH})_2$ are formed as well.^{13,14,16}

Each of the resultant species exerts its own partial pressure, the sum of which might be loosely termed the *vapor pressure* of Cr_2O_3 . This so-called vapor pressure depends on gas composition as well as on temperature, and the temperature dependence of the partial pressure for each of the constituent species in the vapor phase is different. “Vapor pressure” increases by several orders of magnitude with increasing gas-phase O_2 and H_2O but shows a much more moderate increase with temperature.^{13-16,24}

Identification of these intermediate chromium species by direct measurement has proven difficult.²⁴ Instead, calculations requiring thermochemical data for all participating species are typically performed to predict the distribution of products at such low partial pressures.²⁵ For example, thermodynamic calculations at 1200 °K (927 °C, 1700 °F) for a combustion effluent containing 0 % excess O_2 and 20 % moisture lead to a “vapor pressure” for Cr_2O_3 of about 10^{-9} atmospheres and therefore a concentration of about 1 part per billion (ppb) by volume in a flue gas at atmospheric pressure.¹⁴ For flue gas containing 10 % each of O_2 and H_2O at this temperature, the resulting effective vapor pressure for Cr_2O_3 is several orders of magnitude higher, 2×10^{-6} , or a concentration of 2 parts per million (ppm).¹⁴

Therefore, the chromic oxide (Cr_2O_3) film that forms on the outside surface of the chromium/nickel alloy tubes in the reformer furnace most likely undergoes this oxidative disproportionation into various chromium hydroxides, oxyhydroxides, and other oxides upon evaporation, the predominant species being the chromium oxyhydroxide, $\text{CrO}_2(\text{OH})_2$. These resulting compounds, it is theorized, then reassemble downstream into Cr_2O_3 when they condense on (and mask) the SCR catalyst at its relatively cooler temperature. Additional information is contained in a previous presentation.¹⁰

CHROMIUM ON CATALYST AND ACTIVITY LOSS

Chromium Concentration vs. Exposure Time. The results from the ICP-OES data obtained for bulk chromium concentration are plotted in Figure 11 versus exposure time, with the axial distance of the sampling position downstream as parameter. Several curves are shown, one for each measurement location in the sample log, plus a curve reflecting the average computed for the entire log. (Refer again to Figure 5 for sample locations and the calculation of the average.) Typically the calculated average falls within the second quarter.

Measured chromium increases proportionally with exposure time until the catalyst surface and pores begin to show some degree of saturation, first at the entrance face and then to a lesser extent at the second measurement position. This causes the curvature observed with increasing exposure time. Over the range of exposure times encountered, the downstream data are still approximately linear.

The data for all the curves in Figure 11 have been fitted by a least-squares technique using a single, well-behaved mathematical function and a factor varying regularly with the distance downstream from the entrance face. In addition, the asymptote representing saturation was determined statistically by allowing the asymptote to vary in a systematic manner and minimizing the sum of the squares of the deviations between calculated and measured values for the inlet data. This asymptote was then assumed to be a fundamental property of the catalyst and applicable to all the curves.

The correlation coefficient (R^2) for the curve fits ranges from 90 % to 95 % or more, strongly suggesting applicability of the model to the chromium adsorption phenomenon that it describes. The mathematical function also behaves correctly at limiting conditions; for example, the chromium concentration at any time approaches zero (the x-axis) with increasing catalyst length.

Chromium vs. Distance from Entrance Face. The curves from Figure 11 are cross-plotted in Figure 12 to show the chromium profile along the length of the catalyst sample, parametric in exposure time. These curves approximate an exponential decay function, whose initial value increases with increasing exposure to flue gas. Longer exposure times are characterized by the upper curves in the figure; in the extreme, the model predicts a horizontal line parallel to the x-axis and coincident with the same asymptotic value obtained from the data set in Figure 11.

Catalyst Activity (K/Ko) vs. Chromium. Figure 13 relates catalyst activity (K/Ko) to chromium pickup, regardless of how long it took to attain the observed chromium level. K/Ko data determined for whole catalyst logs in the pilot-test reactor and for cut-up segments run in the micro reactor are plotted in the figure against their average chromium content, along with a single correlating curve. Despite the scatter in the data, this curve of best fit has a correlation coefficient (R^2) of 83 %. It starts out at K/Ko = 1.0 for fresh catalyst and traces the activity loss as more chromium is deposited. The x-axis in the figure does not necessarily correspond to K/Ko = 0.

Chromium content for the individual segments is calculated as the arithmetic average from the segment's inlet and outlet values; average chromium content for the whole logs is calculated according to the trapezoidal rule for areas, as outlined in Figure 5. This method gives an average that compares within measurement error to the average computed from a semi-logarithmic fit of the data for a given log and is much simpler to calculate. Use of the results from the micro reactor allows more data to be considered and also extends the range to higher chromium values.

K/Ko vs. Time. The average chromium determined from Figure 11 as a function of time combined with the relationship plotted in Figure 13 gives the curve shown in Figure 14. Data points from pilot testing are shown in the figure for comparison. Because of the inherent scatter of such data, the composite curve fits as well as a direct empirical fit for data from each plant. Once again, the curve starts out from K/Ko = 1.0 at zero chromium, but the x-axis in the figure does not necessarily correspond to K/Ko = 0.

Additional Conclusions to Be Drawn from the Chromium Data. The chromium levels depicted in Figures 11 and 12 are common to the many plants studied. They represent worst-case observations for the range of tube temperatures noted above and at typical concentrations of O₂ and H₂O in the flue gas. The flue-gas chromium concentration estimated from pickup by the catalyst is consistent from plant to plant and in approximate agreement with the evaporation loss of chromium estimated from the examination of the reformer-tube section. This concentration is in the ppb range and apparently less than the equilibrium value.

As indicated by the thermodynamic calculations,^{13,14} chromium concentration in the flue gas is not too sensitive to temperature but is more affected by flue-gas oxygen and water vapor. We have also found a strong effect of flow on measured chromium. This is consistent with an evaporation model in which the actual chromium being lost from the tubes is less than the maximum possible equilibrium concentration. Other investigators have seen metal loss to vary directly with gas flow below some critical velocity.²⁶

Chromium species entering the gas phase must also diffuse through a fluid-flow boundary layer surrounding the external surface of the tubes¹⁵ and may cause the rate of chromium generation to decrease. Although the curves of Figure 11 predict a gradual lessening in the rate (slope) of chromium deposition on the catalyst with exposure time, there is no evidence so far to conclude that the rate of chromium being emitted from the tube metal is affected by the service-age of the metal. Such a decrease in chromium production could be caused by a larger chromium-depletion zone. In that case, there would be less chromium to react and a longer path through which the bulk chromium must diffuse to reach and react with flue-gas oxygen. These effects would not be felt if the rate-limiting step were the mass transfer from the reformer tubes to the flue gas at less than equilibrium conditions.

COUNTERMEASURES

Short of an unlikely change in tube-metal alloys, countermeasures at the present time all involve some way to design around the chromium problem by increasing catalyst volume. Options include installation of a single larger catalyst bed, two (or more) independent stages of catalyst in series, or a short sacrificial guard-bed. A larger catalyst volume allows operation for a longer time before having to shut down for catalyst replacement.

Multiple stages allow the lead bed to become more completely exhausted before replacement while still remaining in compliance with one's air quality permit. As many as five stages of SCR catalyst have been reported in ethylene plant service.³ For a two-stage system, the initial first stage (lead bed) is discarded when spent; the second (lag bed) is promoted to the lead position, and fresh catalyst is installed in the lag position.

Experience has shown SCR catalyst itself to be a good guard-bed material, and some work has been done to optimize the properties of the guard-bed catalyst to enhance chromium removal. We have found a catalyst guard-bed to remove over half the reformer flue-gas chromium before it reaches the main bed downstream. This approach works best when the plant is willing/able to take somewhat more frequent shutdowns to allow the necessary replacement of spent guard-bed catalyst. Every so often, the main bed must also be replaced.

SUMMARY AND CONCLUSIONS

- SCR performance has been observed to deteriorate with catalyst age at a greater than expected rate in steam-methane reformers and ethylene plants.
- Loss of catalyst activity has been attributed to deposition of chromium oxide species on the SCR catalyst surface and in the pores of the catalyst.
- Based on the evidence gathered here, the chromium species appear to originate from the alloy tubes in contact with the hot flue gas in the reformer furnace.

- Suggested mechanism is spontaneous formation of Cr_2O_3 on the tubes at high temperature followed by oxidative vaporization into a host of decomposition products.
- The vaporization equilibrium is more affected by O_2 and water vapor in the flue gas than by the reformer-tube temperature.
- Actual mass transfer from the furnace tubes to the flue gas is sensitive to other factors as well, including flue gas velocity/flow rate and results in less than calculated equilibrium concentrations.
- According to this theory, the constituent chromium species reassemble into Cr_2O_3 upon condensation on the “cooler” surface of the SCR catalyst downstream.
- Adsorption of chromium on the catalyst is proportional to exposure time and is heaviest at the catalyst inlet; the chromium profile at a fixed point in time approximates an exponential decay function.
- Chromium adsorption partially masks rather than completely blinds active catalyst sites, resulting in a gradual (and predictable) decrease in catalyst activity.
- With an understanding of the chromium issue on a fundamental level, it is possible to design around the problem, institute catalyst management procedures, and achieve long runs before replacement is necessary.

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Robert G. Kunz joined Cormetech, Inc. in April 2001 as Technical Project Manager. He supports sales and marketing efforts in the petroleum refining and petrochemical industries by advising on business development strategy, development of training materials, technical report writing, and evaluation of laboratory and field data.

Dr. Kunz has had extensive experience in the petroleum and chemical industries, much of which has been focused on environmental control and testing of operating plants for a wide variety of atmospheric emissions and aqueous discharges. Prior to joining Cormetech, Inc., he was an environmental engineering manager at Air Products and Chemicals, Inc., Allentown, PA, and previously held engineering positions at Esso Research and Engineering Company, Florham Park, NJ and The M.W. Kellogg Company, New York, NY.

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He is a member of the American Institute of Chemical Engineers (AIChE), the American Chemical Society (ACS), and the Air & Waste Management Association (A&WMA) and is a licensed professional engineer in Alabama, Louisiana, New Jersey, Pennsylvania, and Texas.

T. Robert von Alten is Manager of Projects at Cormetech, Inc. in Durham, North Carolina. Cormetech engineers and manufactures SCR catalyst for fossil fuel plants and stationary combustion systems. Mr. von Alten’s SCR project experience ranges from large utility boiler retrofits to small demonstration units.

Before joining Cormetech, Mr. von Alten was a Research Engineer with Energy and Environmental Research Corporation, where his work focused on air pollution projects, supporting the USEPA in developing Clean Air Act regulations. Previously, he served as a Process Engineer with Exxon Chemical Corporation.

Mr. von Alten received his BS degree in Mechanical Engineering from the University of Texas.

Table 1

Summary of Investigation

Literature Searches

Examination of Metallurgical Samples (EDS)

- Reformer Tube
- Convection Coil Fin

Examination of SCR Catalyst Surface (SEM)

- Exposed Samples
- Fresh Sample

Analysis of Chromium on SCR Catalyst (ICP-OES)

Catalyst Activity Testing

- Pilot Reactor
- Micro Reactor

Correlation of Results

Table 2
Air Products and Chemicals
Hydrogen Plant Locations
Employing Cormetech SCR Catalyst

Plant Location	H2 Production (MMSCFD)	Commissioning Date	Source of Further Information
Martinez, CA (I) ¹	25, expanded to 35	1993	Refs. 1, 2, 26, 28, 29
Martinez, CA (II) ²	90	1995	Refs. 28-30
Wilmington, CA	83	1996	Refs. 29, 31, 32
Pasadena, TX	90	1996	Refs. 29, 33
Carson, CA	96	1999	Refs. 28, 29, 31, 32
Port Arthur, TX	100	2000	Ref. 34

Notes:

1. Located at the Ultramar Diamond Shamrock refinery (formerly the Tosco Refining Co. Avon refinery).
2. Located at the Equilon (formerly Shell) refinery in Martinez, CA.

Figure 1

Photograph of Air Products Martinez I Hydrogen Plant



Figure 2

SCR Reaction Chemistry

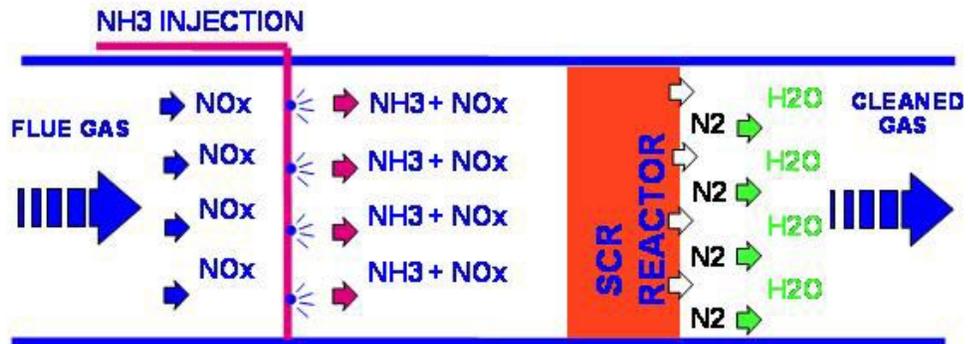


Figure 3

Photograph of SCR Catalyst Samples

Left: Exposed Sample from SMR Service

Right: Fresh Sample



Figure 4

Decline in SCR Catalyst Activity

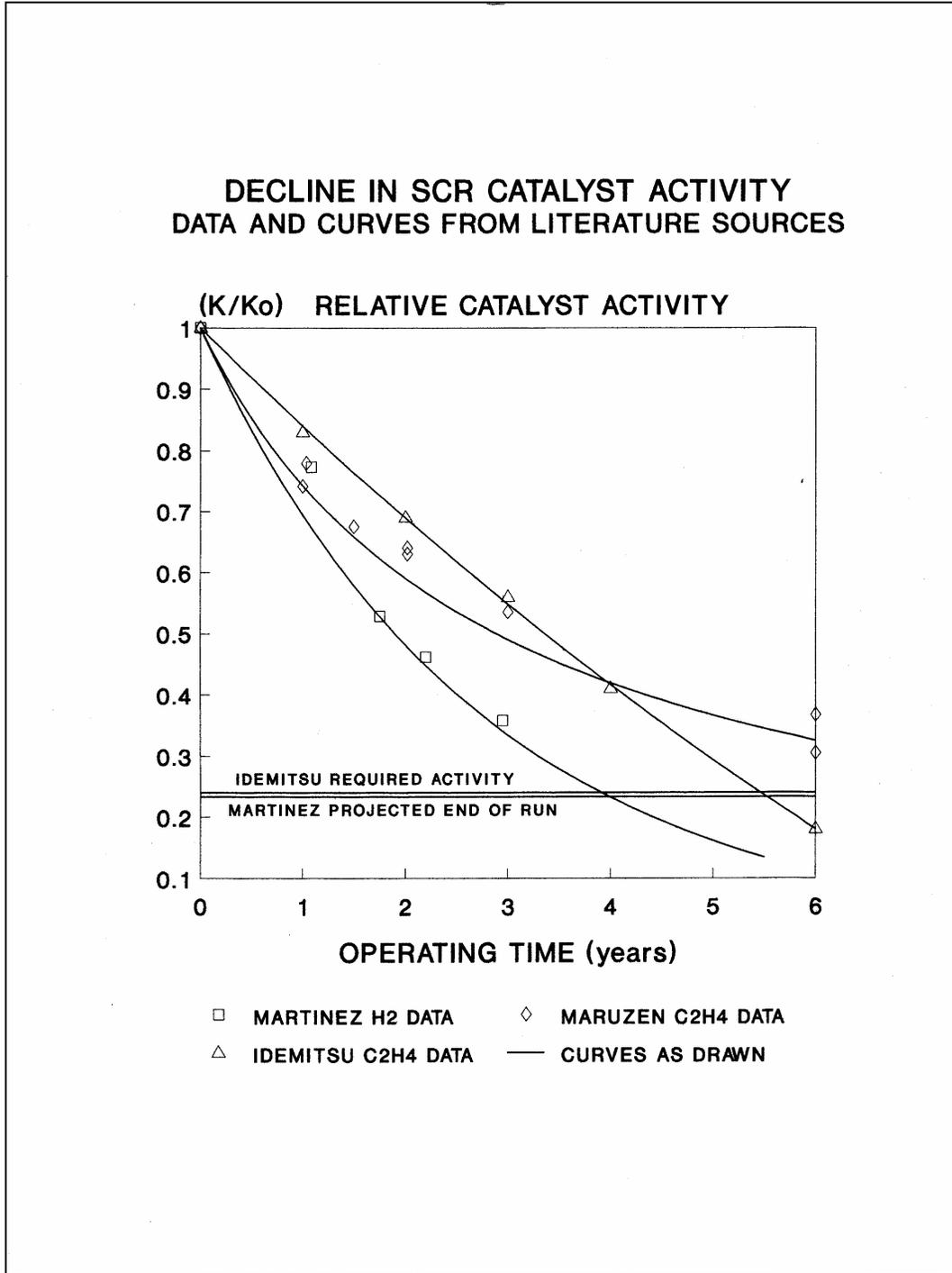


Figure 6
Pilot Reactor



Figure 7

EDS Chromium Profile for Fin Sample

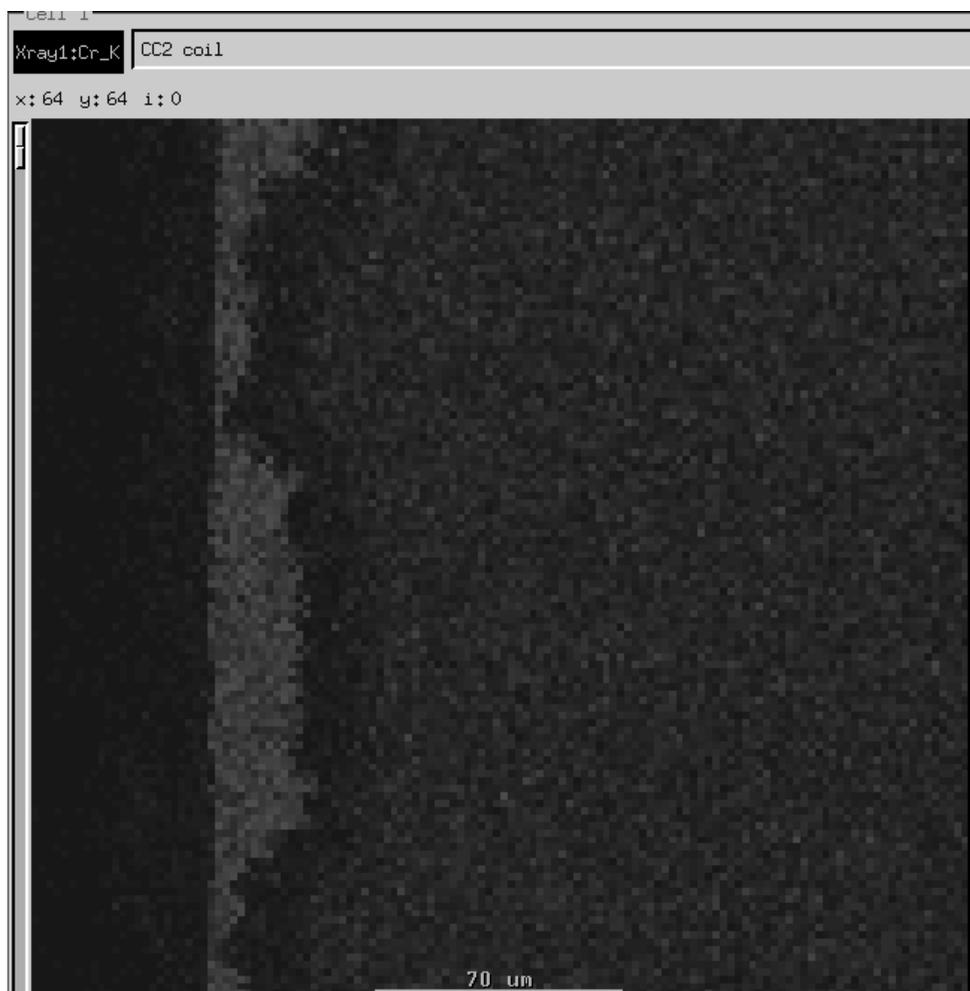


Figure 8

EDS Chromium Profile for Reformer-Tube Sample

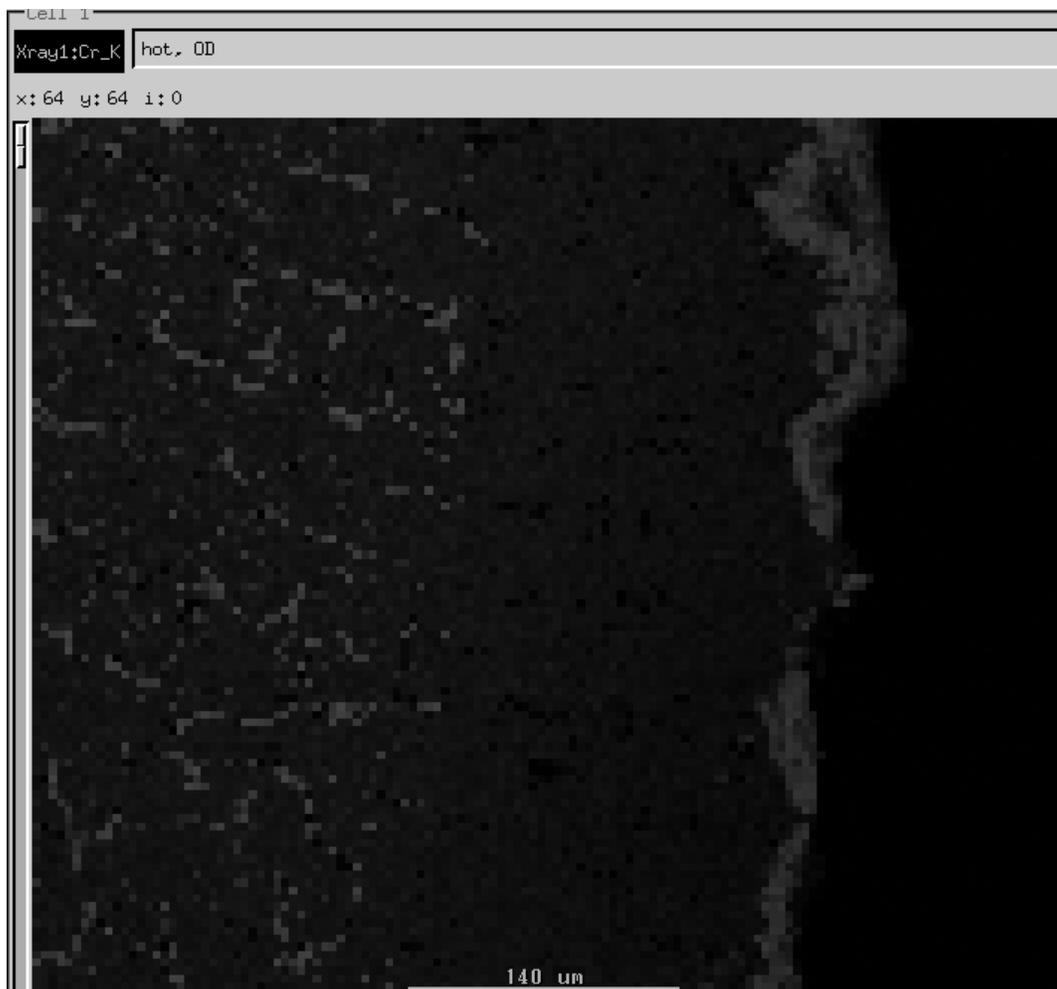


Figure 9

SEM Scan of Exposed Catalyst Sample No. 1

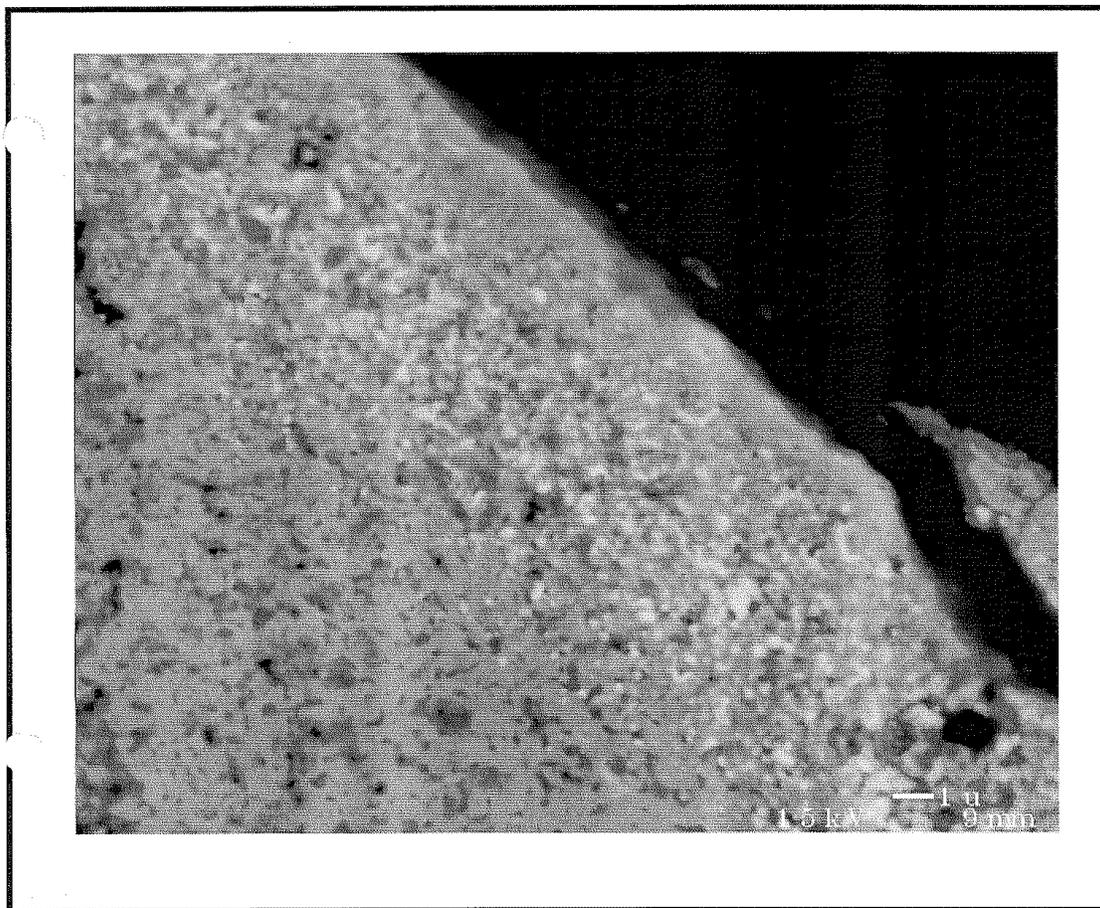


Figure 10

SEM Scan of Exposed Catalyst Sample No. 2

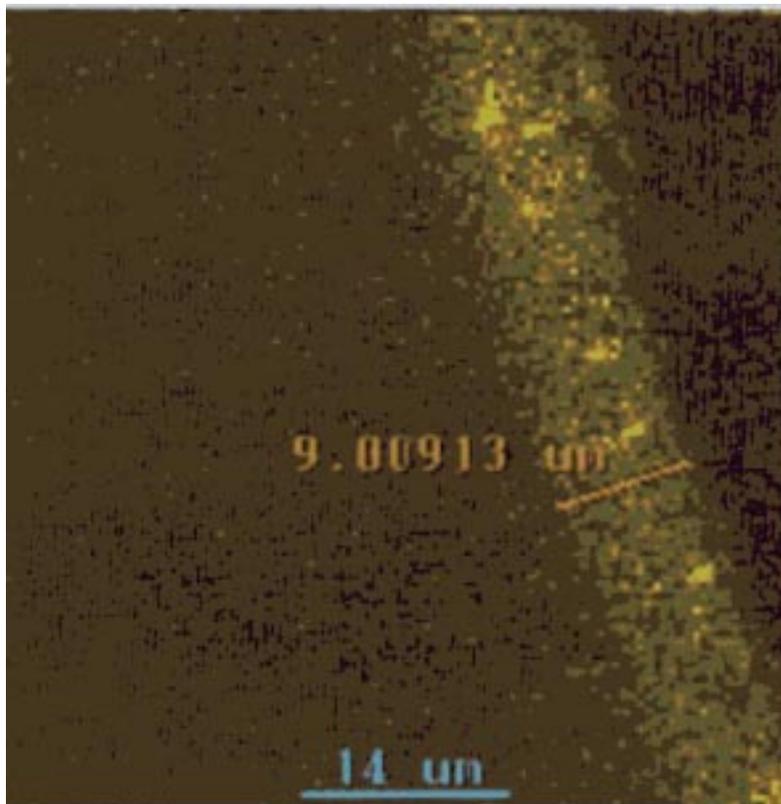


Figure 11

Chromium on Catalyst vs. Exposure Time

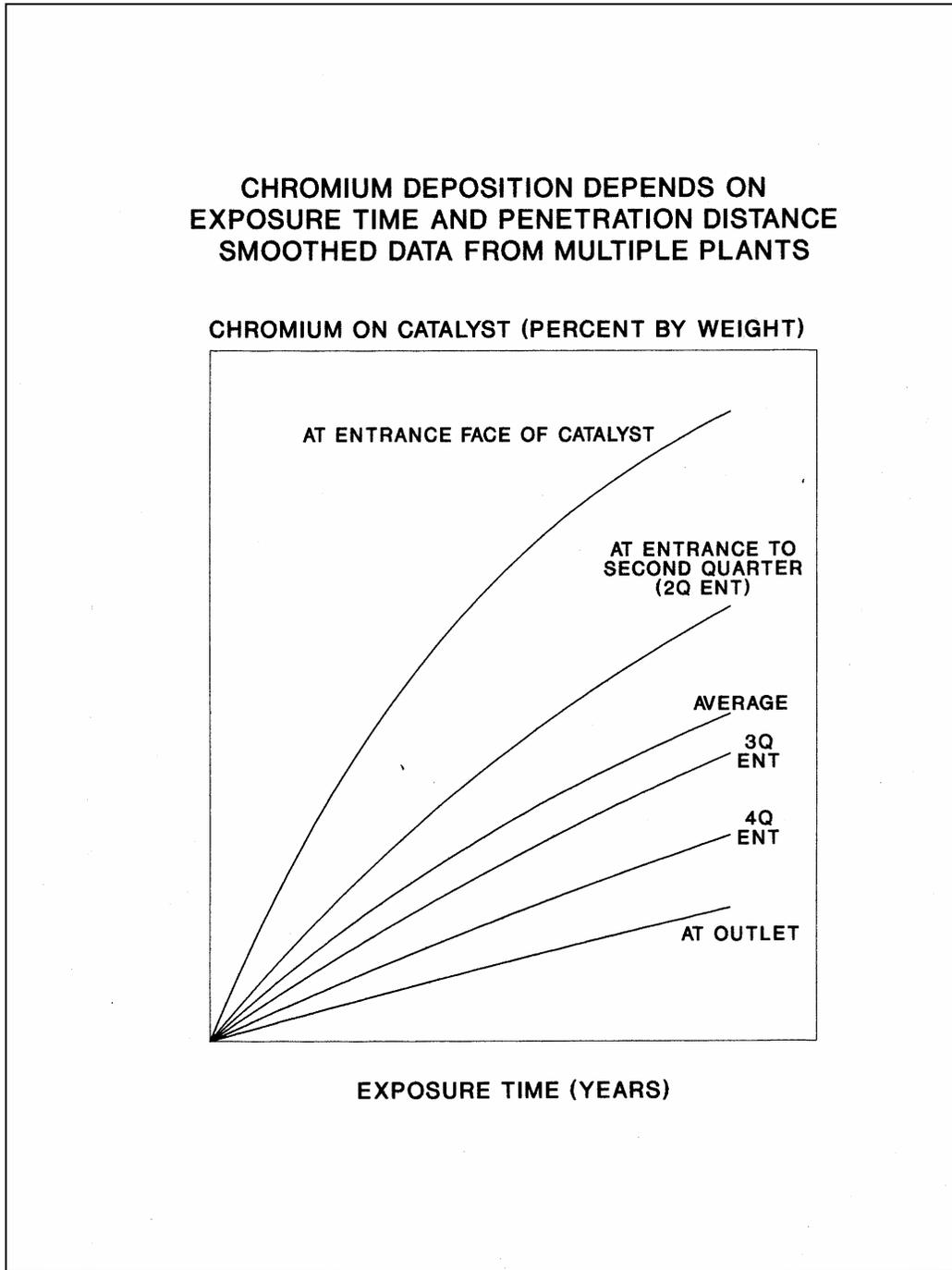


Figure 12

Chromium vs. Distance from Entrance Face

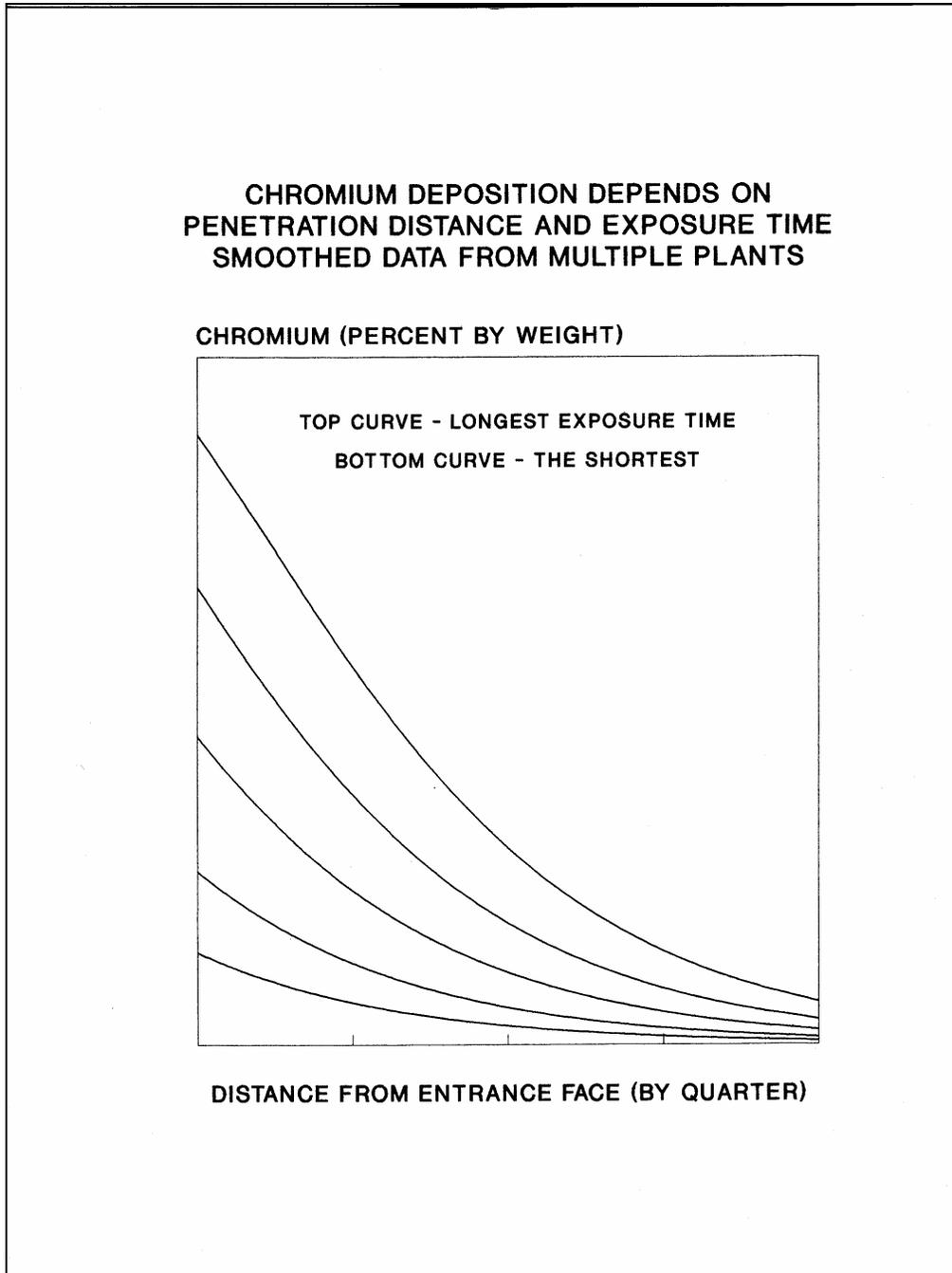


Figure 13

Relative Catalyst Activity (K/K_0) vs. Average Chromium

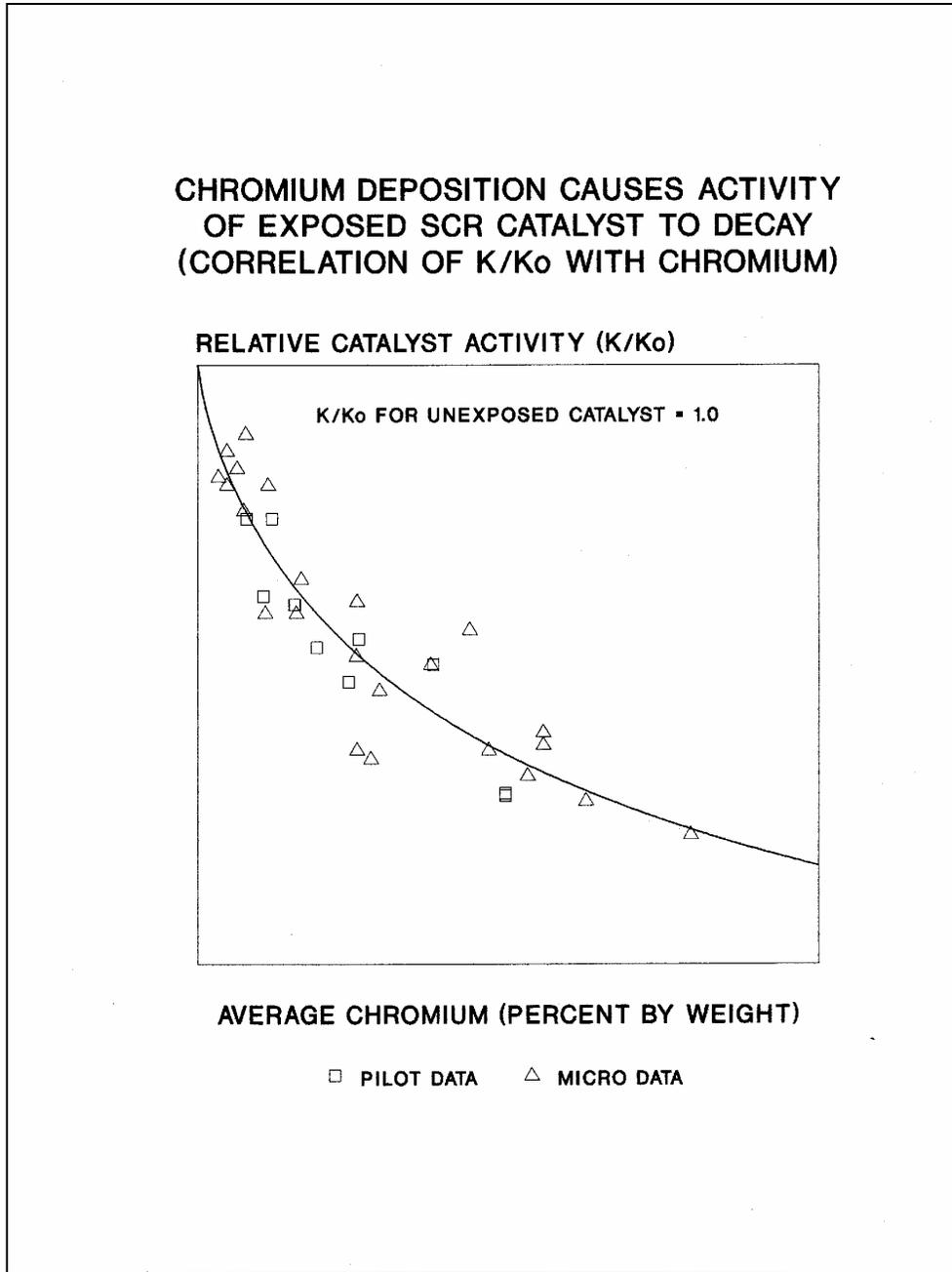
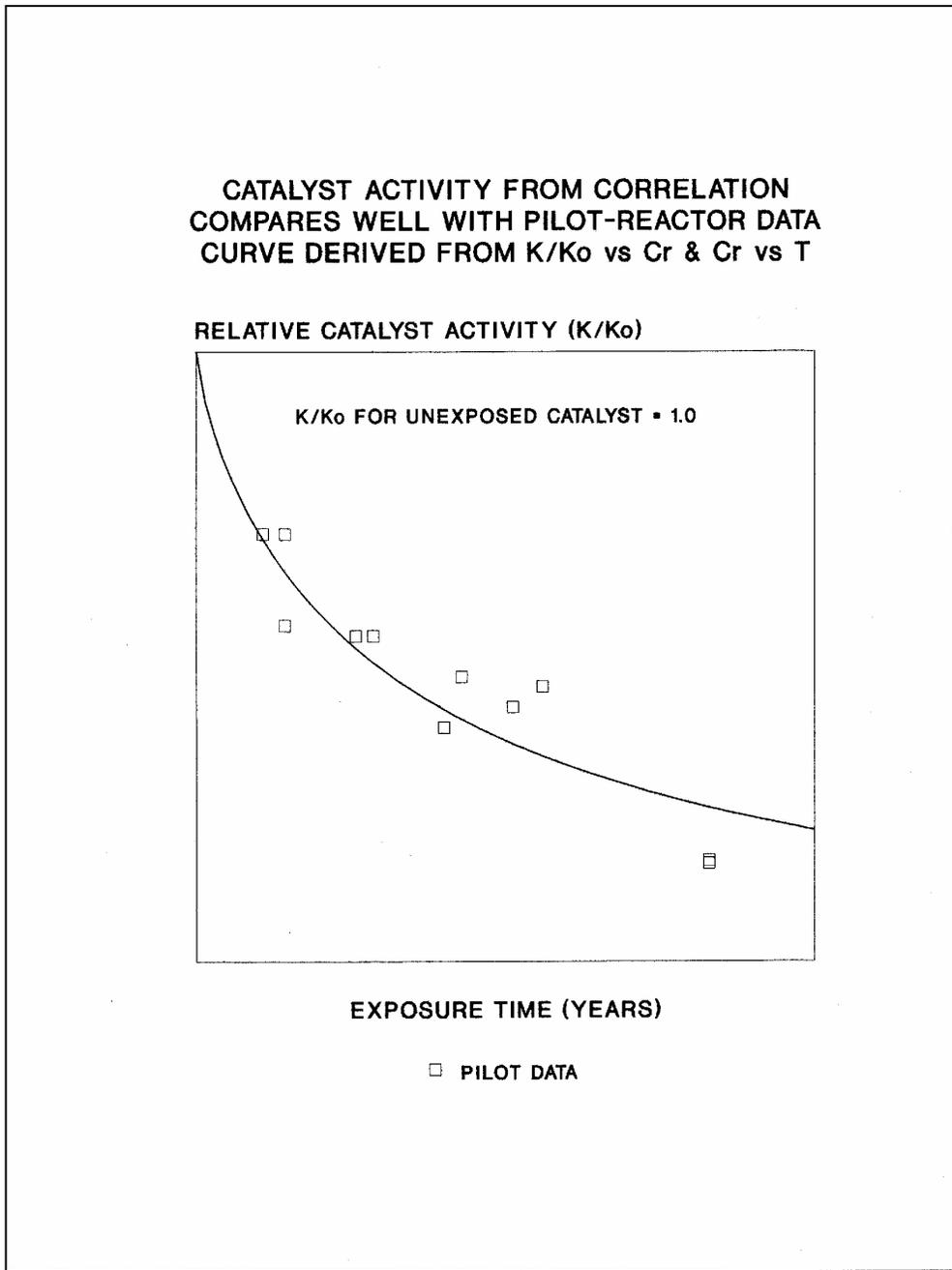


Figure 14

Relative Catalyst Activity (K/Ko) vs. Exposure Time



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