

PRIMARY REFORMING CATALYST

Here's a discussion on the advantages, disadvantages, desirable characteristics, and process variables affecting the operation of primary reformer catalysts.

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Operators of large tonnage ammonia plants have made tremendous progress in overcoming the initial problems of getting these plants into production (1). They are now in a position to critically review the causes of their problems, which are to be found in categories such as catalysts, new materials, chemicals, equipment, and operating techniques.

The primary reforming catalyst deserves careful review due to its significance in the successful production of ammonia. A look through the port hole of many primary reformers readily reveals that hot spots, hot bands, and/or hot tubes are a common problem to many operators. Where these problems exist, they usually become progressively worse with time, or may suddenly become worse after a plant upset or repeated shutdowns.

A hot zone is caused by a condition in that area of the tube which prevents sufficient heat removal by the endothermic reaction to maintain a normal temperature, or by an internal condition which allows more heat transfer to the tube wall than normally can be absorbed. Inadequate heat removal may result from a catalyst void, a plugged tube, channeling due to fines or crushed catalyst, coke formation, or an inactive catalyst. Excessive heat in an area may result from flame impingement, poor burner or draft adjustment, or high heat flux. The characteristics of the catalyst used in the primary reformer tubes and the operating conditions imposed upon the catalyst may eliminate or greatly minimize the hot areas, or they may be the direct cause of the main contributor to the problem.

The purpose of this article is to pin-point the types of commercial catalysts being used today, the advantages and disadvantages, the desirable characteristics, the process variables affecting the operation of the catalyst and the procedures required to obtain good performance.

Catalysts available

There are four catalyst vendors actively offering to sell primary reforming catalysts: Catalyst and Chemicals, Inc., Girdler Catalyst, Division of Chemetron Corp., Haldor-

Topsoe, and Katalco. Each has his own proprietary recipes and "know-how" and offers one or more types.

Over the last 25 years, the active catalytic agent, nickel, has remained the same, but the base has undergone several changes. During this period there have been three general types of primary reforming catalysts sold. They are 1) calcium-aluminate-silicate base (2), 2) calcium aluminate base (3), 3) a low surface area refractory base similar to those offered for sale by Norton and Carborundum Companies (4, 5).

The calcium aluminate silicate base catalyst was manufactured from about 1945 to 1965 when it was largely replaced by the calcium aluminate base catalyst, because the ammonia industry insisted upon a low silica catalyst. The original calcium aluminate silicate base catalyst contained from 0.2- to 0.3 wt. % sulfur as sold, and had to be desulfurized or activated in the primary reformer furnace before use. The silicate base catalyst was sold later in a desulfurized, preshrunk, and reduced form that didn't require much activation. During the last few years this catalyst was sold in the oxidized form with a low sulfur content requiring no activation. The advantages of the silicate base catalyst are:

1. Low temperature activity
2. Low temperature activity
3. Inorganic nickel compounds formed reduce readily

The disadvantages of the silicate base catalyst are:

1. Shrinkage with use
2. Sintering temperature of 1800- to 2000°F
3. Loss in activity with shrinkage and/or sintering
4. Strength of unshrunk rings marginal
5. Loss of porosity with time
6. High silica

The calcium aluminate base catalyst rapidly replaced the silicate base material with the advent of the 500 lb./sq. in. gauge primary reformer because of the problems of silica migration. This replacement of high silica catalyst started

about 1964. The advantages of the calcium aluminate base catalyst are:

1. No shrinkage with use
2. Low temperature activity
3. High crush strength in oxidized state
4. Fewer weak rings - more uniformity of crush
5. Low silica

The disadvantages of the calcium aluminate base catalyst are:

1. Lower crush strength after reduction
2. Continued loss of crush strength with use
3. Higher temperatures cause even more loss of crush strength
4. Loss in activity due to formation of nickel aluminate (6)
5. Loss of surface area weakens physical strength of base

The low surface area base catalyst is in its infancy for use in primary reformers. Both Norton and Carborundum have sold low surface area base catalyst carriers for years. The Carborundum Co. gives this description of catalyst carriers for steam reforming (4), "Carborundum SAHT-99 is a high purity (99.5%) alumina carrier that remains stable to temperature above 2,700°F. It has proven outstandingly successful in both primary and secondary gas reforming. An exclusive bond system makes these hollow cylinder shapes resistant to steam and hydrogen. SAHT-99 will not shrink, powder, or fuse during upset conditions, as do calcium aluminate-based carriers." Each catalyst vendor is offering, or will be offering, their version of a low surface area primary reforming catalyst based upon their proprietary information and "know-how." A few commercial charges of this type of catalyst were sold about 1967. As commercial experience accumulated, additional charges were sold. The advantages of the low surface area base catalyst are:

1. Physically strong
2. No loss of crush strength after reduction
3. Minimum loss of crush strength during use
4. Withstand carbon formation better than other types
5. No shrinking or sintering in primary reformer
6. Low temperature activity
7. Less tendency to form nickel aluminate

The disadvantages of the low surface area base catalyst are:

1. Higher cost
2. Lower nickel
3. More susceptible to sulfur poisoning
4. Lack of commercial operating experience under all types of process conditions
5. Limited experience

Primary Reforming Catalyst

What is it? The reforming catalyst is composed of inorganic materials, usually in the oxide state and may contain an organic lubricant. The active catalytic agent is nickel, with a base composed of calcium oxide, magnesia, silica, titania, zirconia and/or alumina. The form is a ring or cylinder ranging in diameter and length from 1 in. down to 1/4 in. with the hole diameter varying from 1/4 to 3/8 in. The rings or cylinders may look like rocks, but they are as different from rocks as day is from night. Rocks are

impervious, and have a varied composition and physical characteristics, and large crystals, whereas these characteristics in a reforming catalyst are closely controlled according to each vendor's proprietary recipes and "know-how." A catalyst is very porous with small crystals resembling a honeycomb if the pores are magnified thousands of times. These pores may be destroyed by overheating causing crystal growth and the formation of new compounds. If the temperature is high enough, a rock is formed. A rock is difficult to crush. A reforming catalyst in an operating tube may be crushed rather easily.

A reforming catalyst may be compared to, and is similar to, a living organism, and must be handled and treated accordingly. A catalyst ages, grows old, and may be poisoned just as you and I. The environment of the reforming catalyst must be closely controlled within specified limits to keep it in an active state, to prevent rapid aging or poisoning, to keep it physically strong, and to maintain its porosity and crystalline characteristics.

The operating temperatures for primary reforming catalysts are usually in the range of 800- to 1,600°F (7). Many operators introduce the mixed feed gas to the reformer tubes in the range of 900- to 1,000°F (8), and maintain the temperature at the exit of the catalyst in the range of 1400- to 1,500°F. With these temperatures and a high activity reforming catalyst, the reforming reaction starts near the inlet of the tube, and essentially all of the catalyst is utilized to promote reforming. Usually, about 65- to 80% of the hydrocarbon process feed is reacted with the process steam at these temperatures (9).

The operating pressures for the primary reforming catalyst have gradually been raised through the years from near atmospheric pressure to about 38 atm (10). Many plants are presently operating the primary reforming catalyst with exit operating pressures near 450 lb./sq. in. gauge. Higher operating pressures have the effect of increasing contact time of the reactants with the catalyst, and allow operation at higher through puts with a lower pressure drop. At higher operating pressures, a greater hydrocarbon conversion is realized per unit volume of catalyst, though the equilibrium is less favorable for the reforming reaction.

The steam to gas ratio, or more specifically, the steam to carbon molar ratio varies considerably in commercial primary reformers. Usually, it is in the range of 3.5 to 7.0 at the inlet to the primary reformer. From the viewpoint of preventing carbon formation, a steam to carbon ratio of not less than 2 is considered necessary with natural gas process feed for most reforming catalysts. From the viewpoint of obtaining low methane leakage from the secondary reformer, usually 3.5 or higher ratio is utilized to establish favorable equilibrium conditions at secondary reformer exit temperatures on the order of 1,750- to 1,850°F.

The theoretical hydrogen space velocities currently achieved with industrial primary reforming catalysts vary over the range of 4,000 to 8,000 depending on the specific design and type of catalyst. Both higher temperatures and higher pressures favor the use of high space velocities over primary reforming catalysts with higher activities allowing the use of higher space velocities.

The composition of the feed to the primary reforming catalyst vitally affects the performance of the catalyst. Coking of the primary reforming catalyst may occur either from heavy hydrocarbons in the feed or from low steam to gas ratio. Plant operators, who have experienced the coking of

a charge of reforming catalyst at sometime in their career, usually install the necessary equipment and controls to avoid this problem. However, this is like each generation reinventing the wheel. More care, operator education, and plant design could go a long way toward reduction of lost production due to damaged catalyst.

The presence of sulfur in the feed stream is a common poison occurring in plants. Since various forms of sulfur are difficult to sample and measure in low but significant concentrations, (200- to 300 ppm by volume) the effect on reforming catalyst is often underestimated. Reforming catalysts will operate with low concentrations of sulfur present, however, the effect of sulfur on the through put of a reformer is so great that removal of measurable sulfur is justified. Arsenic is also a poison for reforming catalyst, however, it is only rarely encountered in the feed streams of reforming plants.

Since about 1959, primary reformers have been operating commercially with heat fluxes in the range of 20,000- to 30,000 b.t.u./sq. ft. inside tube area/hr. Many large tonnage plants operate with heat fluxes in the range of 20,000- to 26,000 depending on the throughput. A heat flux in these ranges requires a high activity reforming catalyst to maintain the tube skin temperature within reasonable limits.

The pressure drop across the primary reforming catalyst is usually in the range of 35- to 70 lb./sq. in. in a modern tonnage ammonia unit. The use of relatively long reformer tubes has necessitated the use of the ring form of catalyst to minimize pressure drop.

Abnormal conditions imposed on catalysts

Abnormal process operating conditions are frequently imposed on catalysts during start-up and shutdown of a reformer. The inability to control furnace temperatures during emergency shutdowns may subject the catalyst to temperatures up to 2,100°F. The newer types of reforming catalysts withstand these temperatures with a minimum of deactivation, while some of the older types of catalyst suffered shrinkage and deactivation at these temperatures.

During shutdown of a reformer, it is necessary to stop the flow of process hydrocarbon feed to the reformer, and this results in the reduced catalyst being oxidized with steam. In the presence of steam at elevated temperatures, components of the catalyst may react to yield a relatively inactive form of catalyst, nickel aluminate (6).

During operation of the catalyst at reduced rates, or at other than design pressure, the flow meters may be relatively inaccurate and result in the catalyst being subject to low steam to gas ratio. Also, poor mixing of the steam to gas at low rates may subject the catalyst to low steam to gas ratios and cause the deposition of carbon on the catalyst.

When the flow of steam is started to a reformer, water may be slugged into the catalyst. At elevated temperatures when water comes into contact with hot catalyst, the generation of steam within the pores of the catalyst and thermal gradients in the pellet impose destructive forces on the physical structure of the catalyst. Modern catalyst are more resistant to these processes, but when a boiler carries over due to loss of level control, catalyst damage may result.

Wet steam from boiler carry-over or condensation and entrainment usually contain considerable amounts of solids.

Over a period of time, the water vaporizing in the lines to the catalyst and in the top of the catalyst tube will leave solids deposited on the catalyst. Usually these materials contain fluxing agents which lower the fusion temperature of the catalyst. When a salt coated catalyst is cooled in the presence of water vapor, hydrates are formed which may permanently damage its physical strength and activity.

An abnormal condition one encounters in operating the reforming catalyst is the breakthrough of poisons into the feed. Carbon drums require regeneration to be an effective sulfur guard. Zinc oxide drums require changing when they are spent. Failure to take these precautionary actions frequently result in reforming catalysts being poisoned. Carbon drums do not usually offer as much protection against sulfur as zinc oxide drums because of the adverse effect of heavy hydrocarbons on activated carbon and the inability of activated carbon to completely remove slugs of sulfur, especially hydrogen sulfide.

Plants designed to extract heavy hydrocarbons from natural gas are usually oil absorption or refrigeration type plants. These require periodic shutdown for maintenance, and it is not unusual for these extraction plants to trip out six to eight times a year for a period of one to a few hours. During such times, the reformer may be slugged with heavy hydrocarbons depending on the number of fields supplying a natural gas line.

During shutdown of a reformer, process natural gas frequently leaks into the reformer in the absence of steam even though the process natural gas control valve is closed. Usually for many hours, the furnace walls retain sufficient heat to coke the catalyst if gas is allowed to leak into the reformer. The catalyst can recover from the deposition of ½- to 1% carbon on the surface, but higher carbon concentrations begin to attack the physical structure of the catalyst and cause it to lose strength.

The sudden pressuring or depressuring of a reforming catalyst can cause serious damage to the catalyst. In some high pressure reformers if the back pressure on the system is raised before the reformer tubes are hot, the steam condenses and fills the tubes with water. Then when the furnace temperature is brought up very slowly, the water may damage the catalyst as it is vaporized. In some furnaces, the bottom of a reforming tube may be cold and full of carbonated water during normal operation. A sudden depressuring of the reformer can result in water being blown up into the hot catalyst and physically weakening the catalyst. When a line or manifold inlet or exit the catalyst tube ruptures, tremendous velocities may develop through the catalyst as a unit depressures, which may cause damage by lifting or compressing the bed. The primary concern in such instances is the possible physical breakdown of the catalyst.

Other variables

Primary reforming catalysts are usually loaded in tubes with lengths of 10- to 45 ft. with diameters of 2- to 9 in. and with wall thickness of ¼- to 1 in. (11) For each type of tube and service, there is an optimum catalyst loading.

The technique of loading the catalyst in the tube, and the checks on uniformity of tube loading are vital to insure uniform flow through the catalyst. The catalyst loading companies have made great strides in developing economical and uniform loading of primary reformers.

A primary reforming catalyst may be charged in one of several types of furnaces, and the optimum conditions for each furnace are somewhat different. In the ammonia industry in the U.S., the following types of primary reforming furnaces are being operated at this time: Alcorne, C & I Girdler, Chemical Construction, Foster Wheeler, Hercules, Kellogg, Lummus, Selas, and Struthers-Wells.

Each furnace manufacturer imposes certain mechanical restrictions which must be taken into account in preparing an operating procedure for starting up and shutting down primary reforming catalysts. The location and sizing of vents also imposes restrictions on methods of starting up and shutting down reforming catalysts. The location and sizing of vents also imposes restrictions on methods of starting up and shutting down reforming catalysts. Adequate venting of product gases during brief periods when the ammonia loop is down is essential to the optimum performance of primary reformers. The capability of pumping boiler feed water and supplying steam on a reliable basis are essential to achieving a good life with primary reforming catalysts. Starting up and shutting down a primary reformer twenty times in six months may be accurately described as a method of rapidly aging reforming catalysts.

The philosophy of the plant operator has more to do with the success of operating reforming catalysts than is generally recognized. We believe this is a very significant factor in achieving successful operation. Having reviewed some of the circumstances that can seriously damage reforming catalyst, it must be stressed over and over that good operating practices are essential. These include making changes slowly, proper maintenance of instruments, attention to operating conditions, reliance on analytical results and scrupulous attention to the quality of the feed streams, hydrocarbon, steam and air.

Operating problems

Hot spots develop during the operation of the primary reforming catalyst, and may cause a tube failure. The development of a single or a few hot spots in a furnace is usually the result of starting up and shutting down a furnace. The catalyst tube contracts during shutdown and conditions are favorable for forming a catalyst bridge. Starting the reformer causes tube expansion, and the catalyst bridge allows a void to form below or along the side of the bridge. These hot spots are usually 4- to 12 in. in length and may disappear during operation.

Hot spots develop also from both coking and breakage of catalyst. Slugging a reformer with water will develop hot spots due to breakage of the catalyst. Operating with low steam to carbon ratio will first show up by a development of hot spots in the reformer. With this type of operation, usually several hot spots show up in a brief period of operation, and some change in pressure drop may be noted. However, pressure drop changes are more difficult to note on the high pressure reformers than in the older low pressure reformers. If coking is occurring, it will soon develop further into the appearance of hot bands.

The hot bands which have been discussed in connection with high throughput furnaces are due to carbon formation in some cases, and to a lack of activity in the reforming catalyst in others. The hot bands, or hot zones, are sufficiently hot in some plants to cause early tube failures. Hot bands are usually 3- to 10 ft. in length, and may represent 40- to 100% of the tubes.

Hot tubes (usually defined as tubes that are hot 3/4 or full length) develop during operation due to the blockage of flow through a tube. The cause of blockage of flow may be broken catalyst, coking, or a leaking inlet pigtail or inlet hose. In a case where essentially all of the tubes heat up, catalyst poisoning or firing may be the problem. If the furnace will not take the normal fuel gas, and yet the tubes are hot with normal flows, this is a good indication that a catalyst poison is present in the feed. When a poison is present in substantial concentration and the catalyst becomes inactivated, carbon formation and pressure drop build-up may develop in a short period of time.

Many charges of primary reforming catalysts are changed because of the development of excessive pressure drop during operation. The principal causes for developing excessive pressure drop are coking and physical breakdown of the catalyst. Coking may be caused by low steam to gas ratio, heavy hydrocarbons in the feed, a high concentration of poisons in the feed, or inactive catalyst. Physical breakdown of the catalyst may be caused by weak catalyst, too many start-ups and shutdowns, coking of the catalyst, and slugging hot catalyst with water.

In most of the new large tonnage plants, high methane leakage from the primary reformer has not been a problem. Operation of the equipment to produce steam in many plants has resulted in a tendency to overfire the primary reformer, and to leak less than design methane. The overfiring only marginally affects catalyst life but must be evaluated against down-time cost and tube replacement cost.

Waste heat boiler fouling, a problem in many plants, has been reduced by the use of cleaner feed streams, purer refractory, and catalysts containing lower contents of volatile impurities (12).

Characterization of the catalyst

In order to select a primary reforming catalyst best suited for a plant and to correlate the plant performance with the catalyst, one must know the chemical, physical and operational characteristics of the catalysts loaded in the reformer tubes.

Chemical - The chemical characteristics required are an analysis for all the elements present even in the ppm range. This knowledge is required to judge the long time effects of impurities upon the activity and the strength of the catalyst during operation, and the quantity of volatile elements that may vaporize under the operating conditions of the primary reformer which may result in fouling of the waste heat boiler, and/or an accumulation of fines on the high temperature shift catalyst. This knowledge will prevent the loading of a catalyst that has been inadvertently contaminated during manufacture.

Physical * The physical characteristics required are:

1. Size
 - a. The length, diameter, and hole with tolerances.
2. Crush strength
 - a. Oxidized
 - b. Reduced
 - c. Under plant process operating conditions for X hours
 - d. Actual plant conditions for X months
3. B E T surface area
4. Pore volume distribution

- a. 60,000lb. mercury porosimeter preferred
5. Thermal history - loss or ignition at:
 - a. 250°F
 - b. 1,000°F
 - c. 1,500°F
6. Bulk density, lb/cu. ft.
7. X-ray diffraction pattern
 - a. To determine compounds present in the catalyst and the size of the crystals
8. Electron microscope scan
 - a. To determine the distribution of the major elements throughout the catalyst particle.

Operating - The operating characteristics must be obtained on the catalyst of known chemical and physical characteristics. Judgment is made upon two areas of information, the operating performance of the catalyst in several plants, and the laboratory activity of the catalyst at several temperatures, both before and after aging. The information required for the operating performance is the type of plant, the operating process conditions, and the history of the key operating variables. The performance of the catalyst in the operating plants far outweighs any other considerations, but is only meaningful after the chemical and physical characteristics have been documented.

How to obtain the best operation

There are four functions that affect the performance of a primary reforming catalyst, and any one of them may cause hot spots, hot bands, and/or hot tubes. They are: catalyst, feed stream, furnace, and operations.

The ideal choice of each function is never available when a plant is purchased. The operators must run the plant with these four functions as they find them. However, ideals must be established and every effort made to come as close to the ideals as is practical.

Catalyst - The catalyst is the heart of the primary reformer operation. Perfect operations from the other three functions cannot overcome a poor catalyst. Choose the best catalyst that money can buy. The ideal catalyst initiates the reforming reaction at the inlet temperature to the primary, gives design methane leakage at normal and up to design tube skin temperatures, and maintains this activity level for a period of at least two years. The physical strength of the catalyst is about the same after one year of operation as when loaded initially. These characteristics of a reforming catalyst are reasonable for normal operating conditions, but are not realistic for some upset conditions.

Feed stream, hydrocarbons, steam and air - The purity of the feed stream is of the utmost importance. Poisons in the feed stream will neutralize the best catalyst, sulfur is the most critical component, because it accumulates on the primary reforming catalyst in the temperature range of 900- to 1,200°F and builds up to a level which is in equilibrium with the concentration of sulfur in the feed stream. The equilibrium sulfur level on the catalyst may be 0.05- to 0.1 wt. % which is sufficient to cause deactivation at low temperatures.

How rapidly may sulfur accumulate on the catalyst to a level of 0.1 wt %? Just 125 days are required if we assume the reformer is loaded with 25,000 lb. of catalyst, the natural gas flow is 1 million std. cu. ft./hr. containing 0.1 ppm of sulfur and the catalyst absorbs all the sulfur. However,

only about 1/3 of the catalyst is in the temperature range of 900- to 1,200°F. If this portion of the bed adsorbs all the sulfur, the time to accumulate 0.1 wt. % is reduced to 42 days. If the steam to gas ratio is 4 and the steam contains 0.1 ppm of sulfur, the time to accumulate 0.1 wt. % sulfur on 1/3 of the catalyst is reduced to 11 days. Ideally, the sulfur in the feed stream should be reduced to about 1 ppb.

The composition of the natural gas is a variable. The most desirable natural gas has a consistent composition, and contains a minimum of C⁴⁺ hydrocarbons. The higher molecular hydrocarbons have a greater tendency to coke, especially during plant upsets and on inactive catalysts.

The solids in the process feed stream may cause a problem in the primary reformer, the waste heat boiler, or the high temperature shift. The solids usually accumulate first in the high temperature shift, but also accumulate in the upper part of the catalyst tube and foul the catalyst causing inactivation and poor flow distribution. In a clean system, the solids content of the mixed process feed stream to the primary reformer is well below 0.2 ppm by weight.

Furnace - There are many types of reforming furnaces. The same vendor's catalyst has operated in most of them. However, furnaces have different characteristics, and one may expect to obtain better operations from the reformer when the characteristics of the furnace and the catalyst are compatible. On the ideal furnace there will be adequate control of the burners and the draft fan to maintain the desired tube wall temperatures from the top to the bottom of the furnace as long as the catalyst retains its normal activity.

Operations - The ideal plant never shuts down. This is not practical, but every effort must be made to maintain the reformer above 1,000°F, and only cool it down when absolutely necessary. Plants are designed as steady state devices and to avoid undesirable swings in conditions, changes must be made slowly. The philosophy of the plant operators is a very significant factor in achieving successful performance with a reforming catalyst.

Acknowledgment

Our thanks to B. J. Mayland of C & I Girdler for his critical review and comments.

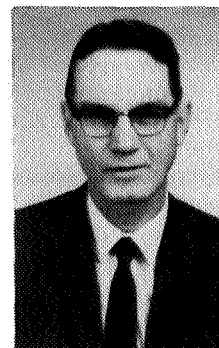
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DISCUSSION

Q. I have two; does the location of burners in the reformer furnace as related to tubes have an effect on the life of the catalyst, and is any thought being given to using several layers of various kinds of catalysts in the reformer tubes.

FLEMING: Well, now I think that you all know that a down fired reformer gives you more heat up towards the top than the side fired. Now, they don't necessarily need to do that, but if they try to heat up at the top with the side fired furnace, the convection section is over-heated. In general, the top fired reformer does get hotter closer to the top than the side fired reformers as operated.

Now the second question is - it makes real good sense to talk about operating with more than one catalyst because the process feed stream enters a primary reformer at 900°F and exits in the range of 14- to 15 hundred °F. Now to ask the same catalyst to work satisfactorily over a range of five or six hundred degrees is asking really too much. It would be very desirable if a catalyst performed satisfactorily over this wide temperature range, but it's really not reasonable to expect to obtain this performance from a catalyst.

The catalysts we've described here are composed of very finely divided particles. They're made that way by the vendors due to the recipes they use and the know-how they accumulate. These very finely divided particles have a great driving force to grow larger due to the thermodynamics of the system. The hotter the temperature, the greater the driving force to grow larger. So you can not really make a catalyst that has the proper performance at 1500°F. and expect it to operate properly at 900° or 1000°F. I think you're going to see more of the two or three layer catalyst charged to primary reformers, and it makes good sense.

Q. You spoke of the sulfur poisoning problem. I wonder if you'd comment on the temporary poisoning. Suppose the catalyst is exposed to sulfur concentrations for two or three days, and the possibility of this catalyst recovering from such an exposure is what?

FLEMING: Well, again, the temperature range at which the catalyst is operating at is the important factor. Now at the higher temperatures the sulfur only temporarily affects it and the poisoning may not be too great. Small con-

centrations may not be noticed when the temperature is above 1200°F., because the sulfur adsorbs on the catalyst at these temperatures but moves on out rather readily. If the sulfur is removed from the gas stream at these higher temperatures, the sulfur usually leaves the catalyst fairly quickly.

Now the lower temperatures in the top part of your tube is where the problem is. This sulfur accumulates, in fact, it gets the first chance to accumulate, and at these lower temperatures it does not move out rapidly, so that if you have sulfur for two or three days and then you clear it up, the poisoning effect remains in the top part of the tube, even though you loaded the best catalyst possible, the most active catalyst, now you may have a dead catalyst. And it may stay dead for days because at 900 to 1000°F, the sulfur does not move off very readily.

Q. The primary and secondary reformer catalysts are the same or only slightly different. What is the sulfur tolerance in the secondary reformer where you're operating at much higher temperatures compared to the primary reformer, where I should say in two or three days you may deactivate the catalyst. Would the same phenomena take place if there happened to be sulfur somehow penetrating the secondary reformer due to sulfur in the air or the steam?

FLEMING: The temperature is all important here and of course, in your secondary reformers you are getting up to 1750, 1850°F. Now sulfur will have some effect here, but it is slight, and it will be very temporary. Within an hour after you have removed the source of the sulfur from the secondary reformer, the effect of the sulfur will disappear.

Q. I wonder if you might comment on the practicality or the techniques used to analyse sulfur in the feed stream in the low range that you were talking about in the one part per billion range.

FLEMING: I'm not sure that we have any on stream analyzers that will analyze down to a part per billion, but I see the Barton analyzer running on gas streams, and they are recording 20 to 50 Parts per billion against their standard. Their standard will show a lower level on their chart than the 20 or 50. Now the instrument manufacturer won't tell you necessarily that you can measure 20 parts per bil-

lion. However, the instrument is showing a difference between a standard with no sulfur and your process gas stream, indicating, at least, that there is a difference and that a very low concentration of sulfur is present.

So I think if you had a Barton instrument that you know was working satisfactory and it was showing nothing compared to the standard, you couldn't be absolutely certain you were at the one part per billion level, but you know you're way way down there.

DAVE WHITE, Borden Chemical: Last year at Portland we had some discussions of how to get rid of carbon and sulfur that had accumulated on the reformer catalyst. A

friend from Australia brought up the point that they had been oxidizing their catalyst while cooling down and heating up to oxidize these compounds. We have tried this based on their recommendation and find that it works very satisfactory. We were able to tell what was on the catalyst by analyzing the effluent from the secondary reformer during the oxidation. I don't have the details how we did it except that you have to be very careful about how much air you add. We called on Cromeans and Fleming to advise us on the procedure and it has worked out very satisfactory.

Where we originally had one of the worst temperature profiles I've seen in reformers, after this we ended up with an almost perfect profile.