Maintenance of Rotating Equipment:

Improved
Ammonia Plant
Catalysts

There have been recent advances
in the techniques for loading catalysts, but unloading operations
can stand considerable improvement.

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For the last year or so, there has been a trend toward greater use of ceramic base catalysts in ammonia plant primary reformers to achieve greater physical strength, especially in the reduced state. Ceramic catalysts are composed primarily of alumina base with nickel contents ranging from 4 to 20 wt.%, and contain low levels of chemical impurities such as sulfur, silica, sodium, potassium, and zinc. At low temperatures they activate when properly calcined.

In high pressure plants, some of these catalysts have performed well at 8,000 theoretical hydrogen space velocities and above. In some plants, average heat transfer rates above 30,000 B.t.u./hr. sq. ft., based on the inside area of the tube in the fired zone, have been achieved in long runs without excessive tube skin temperatures.

The greatly reduced crush strength has allowed the production and utilization of smaller particles size rings. Rings of nominal 5/8 × 3/8 × 5/16 in. and 5/8 × 1/4 × 1/4 in. (outside diameter × height × hole diameter) have been used successfully.

With the ceramic base reforming catalysts, the increase in pressure drop in a two year run in some plants has been found to be as little as 2 to 4 lb./sq. in. Most high pressure plants have continued to use two or more particle sizes of catalyst to achieve optimum catalyst loading.

Since most ceramic catalysts have been heat treated after they were formed, the actual physical dimensions have generally been less than the nominal sizes. It has been necessary to take this characteristic into account in estimating pressure drops. Operators have become more selective in specifying particle sizes to meet specific requirements. The activity and pressure drop for four common particle sizes are shown in Table 1. The nominal dimensions of several types of catalysts are given in Table 2.

The life demonstrated by a few charges of the ceramic catalysts has not been satisfactory. Catalyst life in a high pressure, high production plant should be a minimum of

two years to be satisfactory in our judgment. With additional work and experience, it is anticipated that an even longer catalyst life will be achieved.

Catalyst tube inspection procedures have been markedly improved during the last year. TV cameras, suitable for use in small diameter tubes, have gained wide spread acceptance. And, the use of X-ray equipment to check tubes, pig tails, and headers has increased and been integrated into plant shutdowns on a more practical basis.

Techniques for loading catalysts have been improved, and the quality of loading jobs have been upgraded. Test pressure drops of ± 5% have been achieved on many jobs. The coordination of loading in overall shutdown plans has been substantially improved and coordination between operations and maintenance to meet emergency situations and planned turn-arounds has also improved markedly. More specific time schedules have been estimated and met. Catalyst unloading has also been upgraded, but it is an area where there is much more room for improvement.

Problems still occur during start up

Catalyst start-up procedures remain a significant problem. Some plants have been subjecting new catalysts to excessive thermal and chemical shock before achieving normal operating conditions. Some operators have been placing catalysts in service with poor activation procedures. Each catalyst requires its own special reduction condition to achieve optimum performance.

Some catalysts offered for sale have been unsuitable for use in most high-pressure plants.

Improvement has been made in control of furnace firing. Tube skin temperatures have been more carefully followed and, in most cases, effectively controlled. Individual burners are being better maintained. Draft control has been improved. Computer-controlled firing has been successful on a practical day-to-day basis.

The quality of primary reformer process feed gas has become more of a problem. The industry has been experiencing more variations in feed composition, and it has become necessary to rely on more sources for the feeds. Further, it has become necessary to use oil firing in more plants as gas supplies have been curtailed.

Further improvement in primary and secondary reformer catalyst performance requires continued study and evaluation. The practical commercial improvements in catalysts and in reforming technology are being implemented at an accelerated pace.

The life of low temperature shift catalyst has been extended in many plants through better utilization of higher activity catalysts. Run lengths in excess of three years—and a few over four—have been achieved in several plants with low poison levels in the process feed; the average being about two years. Some charges of catalyst have been damaged during the reduction to activate. Other charges have been operated in environments that inevitably led to short run lengths.

The commercial catalysts have been offered with 20 to 43 wt.% copper oxide. Most catalysts in service contain 31 to 43 wt.% copper oxide. Bulk density has usually been in the range of 54 to 83 lb./cu. ft. Impurities have been maintained at very low levels during the past two years, even though there have been wide swings in the prices of copper and zinc oxide. Excellent control has been attained of the sulfur and chloride levels in the catalysts.

The principal form and particle sizes being supplied to industry continue to be the 5.4 × 3.6 mm. and 1/4 × 1/8 in. tablets. The catalysts have been noted to shrink 5 to 17% during reduction, depending upon the method of manufacture. Average side crush strength in the reduced state has generally been better than 10 lb. dead weight load.

Better load estimates improve performance

Estimates on the volumes of catalyst required for a given requirement are becoming more conservative.

Plant operators have increased their catalyst loadings where possible and improved their overall performance and life. Typical 1,000 ton/day ammonia units have been charged with 1,800 to 2,900 cu. ft. of low temperature shift catalyst, depending upon their design. Units originally designed to achieve end-of-run dry gas CO contents of 0.5 mol % have been achieving 0.16 to 0.30 mol % during long runs. Plants designed for CO leakages of 0.25 to 0.35 mol % have been achieving long runs with the exit CO in the range of 0.10 to 0.15 mol %. Some second stage units have been achieving CO leakages on the order of 0.04 to 0.08 mol %.

In many cases, ammonia plant operators have been operating their units at 8 to 20% above name plate capacity. The excellent CO conversion achieved has been one of the vital factors allowing for the greater production. The purchase of high activity catalyst, the use of good loading procedures, the careful control of reduction and activation procedures, and the operation of the catalyst in an environment low in poisons are all essential in achieving peak performance.

Plant shutdown procedures have been better defined. The precautions needed to protect the reduced low temperature shift catalyst from damaging conditions has been practiced in most plants. Some plants, however, are still experiencing problems related to reduction, sulfur poisoning, chloride poisoning, carbonates in the catalysts, water carry-over into the catalyst, and/or inadequate volume of catalyst for the desired conversion of carbon monoxide. Progress is being made in overcoming these problems.

In general, the performance of methanation catalysts has been excellent. Methanation is a simple catalytic process to operate compared to the older copper liquor and

Table 1. Primary reforming catalyst particle size effects.

Particle Size, in.	Relative Activity	Relative Pressure Drop
3/4 × 3/4 × 1/4	0.80	0.87
5/8 × 5/8 × 1/4	1.00	1.00
5/8 × 3/8 × 1/4	1.18	1.25
5/8 × 1/4 × 1/4	1.39	1.59

caustic systems. Since the Chevron plant at Ft. Madison, Iowa, was constructed during the 1950's, essentially all new ammonia unit designs have utilized methanation.

During the past two years a great deal of attention has been given to methanation catalysts due to low concentrations of carbon oxides entering the ammonia synthesis loop and causing problems with loop circulation, synthesis gas compressors, and the ammonia synthesis catalyst.

There is a general trend toward tighter specifications on methanator performance. Plants formerly satisfied with 5 to 10 parts/million of $CO + CO_2$ concentration in the methanator effluent have recently been achieving 1 to 2 parts/million by vol. levels at rates 105 to 115% of name plate capacity.

Plants with feed effluent exchangers have established more rigid procedures for checking the exchangers for leaks. Most plants have been using more than one analytical method to cross-check the methanation catalyst performance.

The quality of synthesis gas produced the past two years with respect to CO and CO_2 content has been superior to that of previous years. The long run lengths, 7 to 9 years of ammonia synthesis catalysts, attest to the excellent performance of the methanation catalysts.

Trend is to higher nickel content

The cost of the catalyst per cubic foot has been high the past few years. Its cost is relatively low, however, in relation to the costly problems that poor catalyst performance can cause. There has been a trend to the use of higher nickel content methanation catalysts. Most new charges of the catalyst have contained nickel contents in the range of 18 to 35 wt. %. Catalyst bulk densities have varied from 50 to 80 lb./cu. ft. The three forms most widely used have been tablets, spheres, and extrusions. These vary in sizes

Table 2. Catalyst types vs. actual dimensions, in.

	Diameter	Height	Hole
Dimensions	5/8	5/8	1/4
Nominal	0.625	0.625	0.25
Ceramic	0.61	0.61	0.24
Calcium Aluminate Cement	0.63	0.62	0.25
Calcium Silicate Cement	0.58	0.58	0.23

from 3/8 × 1/4 in. tablets to 1/8 to 1/4 in. spheres. Most plants use particle sizes that average from 3/16 to 1/4 in. The trend has been to use the minimum particle size allowable by pressure drop.

The trend towards using a higher activity methanation catalyst results from the requirement to maintain the CO_2 content of the synthesis gas at the 1 to 2 parts/million level during an upset in the CO_2 removal system.

All accepted methanation catalysts reduce the CO content of the synthesis gas to the required level; however, a high activity methanation catalyst is required to maintain the CO_2 in the synthesis gas at the 1 to 2 parts/million level when there is an upset in the CO_2 removal system. If the use of a high activity methanation catalyst prevents a plant shutdown only once in five years, it has been well worth the extra cost.

The sulfur contents of recent shipments have usually been less than 0.05 wt. %. The sodium oxide contents have usually been less than 0.20 wt. %. Average side crush strengths have been greater than 20 lb. dead weight load. Some methanation catalysts have an average crush strength as high as 100 lb. dead weight load.

The methanators in large tonnage ammonia units usually contain 600 to 1,600 cu. ft. of catalyst. Dry inlet hourly gas space velocities on the order of 3,000 to 7,500 have been satisfactory. Most units have operated with inlet temperatures in the range of 500 to 600°F, with pressures in the range of 320 to 390 lb./sq. in. gauge.

Several large tonnage ammonia plants have achieved run lengths of six to eight years with their methanation catalyst.

Although considerable progress has been made in design and operation of methanators, much remains to be done. Further improvement in analytical instruments, and especially their application to routine plant operation, is needed.

Sulfur analyses not practical yet

Sulfur concentrations in methanation process feed streams required for good methanator catalyst life cannot presently be analyzed on a practical basis. Catalyst charges have been poisoned before the problem became known. The sulfur concentrations leaving the low temperature shift catalyst usually have been relatively low, on the order of 10 parts/billion or less. However, during start-up and shutdown when the low temperature shift catalyst is bypassed or, when new high temperature shift catalyst has been placed in service, the sulfur level may be much higher.

During periods when heat exchangers are leaking, sulfur may be present in the feed. Sulfur may be introduced into the system ahead of the methanator when natural gas is used to pressure a CO_2 absorption system. Often during natural gas shortages, potassium carbonate has been calcined in fuel oil fired equipment. These carbonates may introduce sulfur into the promoted carbonate systems. The carryover of sulfur containing solvents sometimes reaches the methanator. One is interested in knowing sulfur levels in the range of 5 to 20 ppb. Few units have analytical equipment suitable for day-to-day service in this range.

The design of knockout pots ahead of methanators and methanator preheat exchangers warrants substantial improvement. The stability of catalyst with regard to high temperature excursions can be improved. The resistance of most methanation catalysts to sulfur poisoning is low, with as little as 0.08 to 0.15 wt. % sulfur deposited on the catalyst, reducing the activity level of the catalyst to near end-of-run. The effect of the shift activity of poisoned methanation catalyst warrants further study with relation to the performance of methanation catalyst. The shift of CO to CO_2 results in a more difficult methanation job.

In the large tonnage, 600 to 1,500 ton/day, ammonia

units, utilizing centrifugal compression and loop pressures in the range of 2,000 to 3,500 lb./sq. in. gauge, some of the charges of catalyst have been in service for seven to nine years, attesting to the conservatism of the original designs. In general, the ammonia synthesis catalysts in these plants have been operated to yield 105 to 120% of name plate capacity. Conversions per pass have been exceeding the design values at over design space velocities.

Proper evaluation procedure needed

Several plants have had to change catalyst for the first time. This type of decision requires an evaluation of the performance of the existing charge of catalyst, and an estimate of the benefits to be gained by the change. As part of this study it has been the practice to examine the particle size of the catalyst in relationship to the loop characteristics and then to select the optimum loading. Also it has been found advisable to consider the alternates: 1) loading all oxidized catalyst; 2) using a mixed loading of pre-reduced catalyst and oxidized catalyst; or 3) loading all pre-reduced catalyst. This of necessity has been a plant-by-plant decision. Economics varied greatly.

When planning to change the catalyst, it is advantageous to plan for inexpensive loop changes that can be made to enhance production.

Good coordination between operations and maintenance aids in reducing turn-around time. Planning is invaluable in preparation and minimizing the time required. Safety in handling the catalyst requires many extra precautions.

The cooled, purged, reduced catalyst as expected has been found highly pyrophoric. As an example, catalysts in large commercial converters that have been cooled, purged, and stabilized by skin oxidation have been found to be highly pyrophoric in sections of a bed.

This means that pure air flowing at about 80 lb./sq.in. gauge, 160°F and about 500 hourly space velocity for several hours had failed to reach all parts of the catalyst bed. The flow was stopped and restarted in one case with no evidence of temperature increase or oxygen disappearance.

Apparently significant portions of a large bed may be sealed off so that gas does not flow into the sealed zone. However, once the catalyst has been moved, the sealed catalyst becomes exposed and immediately reacts with oxygen producing glow level heat.

Safety in handling the reduced ammonia synthesis catalyst has been achieved when the proper precautions were taken. Basically, this consisted of controlling the contact of the reduced catalyst with air.   #

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DISCUSSION

Q. You state that with additional working experience, this is with regard to ceramic reforming catalysts, you state that the additional work and experience that is anticipated, that run lengths longer than two years will be achieved. How will this be achieved? Through better catalyst production techniques, through higher nickel contents? How will these longer run lengths be achieved?

CROMEANS: One of the problem areas with the primary reforming catalysts is that the nickel crystallite grows in size, and industry has not yet found a good way to stabilize the nickel crystallite. You may start an operation with a catalyst with 50 to 80 angstrom crystallite size and then finish with 200 angstroms. If one looks at some of these reformers and plots the tube skin temperatures versus time, one would observe approximately 30-35 degrees fahrenheit temperature increase per year. With a good clean feedstream and no sulfur poisons, to speak of, one would still have this aging effect of the catalyst.

One usually goes onstream with a 1600 to 1630 degree F. tube skin temperature. The normal end of run limit is about 1700° F. I think we will eventually find a way to stabilize these crystals, but right now we don't really have the answer. We have found the higher nickel catalysts to aid in sustaining life, but we still have a lot to learn in this particular area.

Q. I don't want to detract from your catalyst discussion, but I'd like to know one thing if you can tell me. You indicated earlier that there was some people, one company that had not changed reformer catalysts since 1960. Can you tell me what design reformer and what alloy tubes are used?

CROMEANS: This was actually a hydrogen furnace in Hawaii, and it was not being pushed. In the hydrogen reformer designs there is more catalyst per unit of gas being processed. The tube alloys were the same as presently used.

Q. You indicated about some people who were operating at 30,000 fluxes. Can you elaborate on how long they operated there, what their skin points are, and how they are maintaining their control in their furnace?

CROMEANS: These fluxes are with down fired furnaces, where all of the tube surfaces are seeing the fires all around. These furnaces run for two years with that type of heat transfer.

Q. Peak transfer, that's highest maximum fluxes, not average fluxes?

CROMEANS: No, this is average flux.

GEORGE BRIDGER, ICI: I was very interested to hear this paper because it does make many points that as a research man I've been involved with. I will be talking about the nickel content of reforming catalysts and of methanation catalysts in my paper in a minute or two. The activity of catalysts can be increased by increasing the nickel content, but only up to a certain point. If you raise the nickel content of the catalyst obviously there is less of the stabilizing material, such as alumina, and therefore you can come to a nickel content where, in fact, you lose stability on the catalyst. And another point too is that at the higher nickel contents, on reduction the catalyst's strength can decrease. As regards activity, an important factor is the total weight of nickel in a methanator and you have to take into consideration the density of the catalyst. A lower nickel content in a higher density catalyst will obviously put the same weight of nickel into a methanator as a lower density catalyst with a higher nickel content.

I was also interested in the reference in the reforming catalyst section of this paper to the question of getting uniform charging of the tubes. Uniform tubes are very necessary in order to obtain the same performance from every tube, and it is most important to get the same weight of catalyst into every tube. And it's worth extra shutdown time to make sure you get this. We find with our catalysts in our plants, that we can get well within the plus or minus 5 percent constancy of pressure drop from tube to tube. The important thing here obviously is to use the same charging method for every tube, to vibrate the tube and to be consistent with handling and tipping etc.

CROMEANS: It should be mentioned that those who have larger tubes do not have a difficult loading problem, but as time has passed, we've gone to smaller tubes. It's in these small tubes that are about 2.8 to 3.3 inch ID where one must use extreme care and special techniques, to be sure that one gets uniform loading. And we do generally run pressure drops on the individual tubes to verify that we do have a good loading.

Q. I would like your comments on the relative catalyst activity versus the relative pressure drop, the table that you have given in your paper. Is there, do you think that there is a premium on high relative activity in the case of higher relative pressure drop?

CROMEANS: I understand your comment on the pressure drop versus the size, but I don't understand the rest of what you were saying.

Q. As the relative activity increases, the particular size decreases, and that increases the relative pressure drop.

CROMEANS: That's a good question. I understand you now. The values that I gave on activity are related to throughput. With the tube skin constant, one could operate with relative throughputs shown in the table. The pressure drop values are based on constant throughput. The particle size varies the pressure drop. One would, if one operated at a higher rate, have a compounded effect on the pressure drop.

JOHN LIVINGSTON, ICI, Billingham: I would just like to ask John, if you'd like to comment on, in a little more detail, what you mean regarding a thousand ton-a-day plant, in terms of a long run of life on LT shift. Because in this day and age, when we seem to have gotten into a better stream for a quick change-out of catalyst, the downtime is becoming a very vital factor, as well as the approach to equilibrium in deciding when you change that LT catalyst. And we are finding, for instance at ICI, that our economics are such that a 3 year life is about optimum for LT shift catalyst, and it's still operating at equilibrium when we change out.

CROMEANS: The optimum time to change the catalyst will depend on the individual plant. In general terms, for a 1000 ton per day ammonia unit, a one tenth percent CO increase represents loss of 12 tons a day of ammonia on a

low pressure loop.

OSMAN: You mentioned that the relative activities of primary reforming catalysts were compared on a constant tube metal temperature basis, and these figures represented the relative flowrate increases possible at constant tube metal temperature. Is there a dependence upon furnace design, whether it's top-fired, side-fired, or bottom-fired, of the relative throughput credits achievable from the various particle sizes?

CROMEANS: It would to a certain extent. What I was doing there was taking a furnace with a single row arrangement that sees all the fires. Then, I changed the particle size and held the tube skin constant. If you do that with a computer program, these are the kind of numbers you'll develop.

OSMAN: But don't the relative credits for the different particle sizes depend on at what point on the tubes, the tube metal temperature hot spot occurs?

CROMEANS: These were where the peak temperature would be about a third of the way down the tube.

OSMAN: So that would be a top fired furnace?

CROMEANS: That's right.