

SAFETY PROBLEMS AND PRACTICES FOR CATALYTIC UNITS

In the new large ammonia plants, suitable precautions should be taken each time the catalysts are handled or their operations changed.

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Safety in the new large ammonia plants not only is concerned with the protection of personnel, but should also be directed toward the protection of the physical plant to insure the maximum use and life of these facilities. The catalysts used represent only 2-3% of the total plant investment. Improper use of them, however, can result in an appreciable loss—not only in the value of the catalyst itself but, more important, in terms of lost production.

The value of installed catalysts in a typical 1,000 ton/day ammonia plant is about \$400,000. However, the service life of catalysts is relatively short when compared to equipment so that the total value of those used over the life of the plant may amount to \$1.5 million to \$2 million over a 10-yr. period. When viewed in this light the value of catalysts is comparable to compressors and other large items of equipment. As such, they should be given as much consideration in their treatment and maintenance as these items.

It should be appreciated that the designs of the new large ammonia plants impose much more severe operating conditions on the catalysts than do the older low pressure plants. Higher pressures and temperatures, greater throughput resulting in higher pressure drops across the catalysts, and greater expansion and contraction forces on the catalysts all contribute to this more severe service. In order to realize the maximum utilization of the catalysts, it is essential that the plant operators have a thorough working knowledge of the catalytic units and the operating procedures to be used with the catalysts to insure the safe and efficient performance of the catalysts.

General handling procedures

This discussion will concern itself with the handling procedures to be used with all catalysts. It will outline potential safety hazards not only to the catalysts, but also the personnel hazards associated with the use or handling of the catalysts.

There are a number of general rules for handling and operating any catalyst. These include:

1. Most catalysts used in modern ammonia plant are quite rugged, but they can be damaged by rough handling. Care must be used during charging of the catalysts to avoid damaging them.

2. All catalysts are screened before shipment; however, there will be some dusting and possible breakage in transit and handling. It is recommended that all catalysts be screened before charging to the reactor. In some cases it is not necessary to screen it all, but certainly the bottom portion of each drum should be screened.

3. In charging catalysts to a reactor, care must be taken not

to drop them from too great a height. The catalysts should not be loaded into the reactor in a pile. Raking of catalysts loaded in this fashion will not insure even packing or distribution throughout the reactor. The proper procedure is to evenly distribute the material when loading. This can be done by pouring the catalysts directly from the drum around the reactor, or by charging them through a funnel or flexible chute which is moved around the reactor to direct the catalyst to all parts of the bed. In some cases, it may be necessary to have personnel inside the reactor, in which case the workmen should stand on boards to distribute their weight over a large area and prevent damage to the catalysts.

4. The state of the catalysts as delivered should be known, i.e., is it pyrophoric or hygroscopic, and suitable precautions observed if required.

5. Many catalysts used in an ammonia plant are pyrophoric in the reduced condition. Generally speaking, these should be reoxidized before removing them from a reactor or before opening a reactor for maintenance work or catalyst examination.

6. If personnel are to enter a reactor, the catalyst should first be oxidized if required. The vessel should then be thoroughly purged and the personnel should be provided with sufficient and adequate safety equipment before entering the vessel.

7. The vendor's recommendations should be followed in the handling, loading, startup operation, and shutdown of the catalyst.

Critical operating experiences

In the modern ammonia plant, these general rules apply to each of the catalytic units. Time will not be taken to discuss in detail the complete handling, startup, operating, and shutdown procedure for each unit. However, the critical considerations which have caused some difficulties in a few plants were selected and some of these experiences will be reviewed.

Carbon drums

In plants using natural gas as a feedstock, the most usual and effective method used for removing sulfur compounds from the gas is by adsorption over chemically-treated activated carbon. The principal function of these units is to remove the sulfur from the feedstream, since sulfur is a temporary poison to the reformer catalysts. In order to afford maximum protection to the catalysts, the carbon drums should

be regenerated periodically to insure proper removal of sulfur from the feedgas.

The only hazards to personnel associated with these units is in the loading and unloading of the catalyst and then only if the personnel are to enter the vessels. In the case of loading, the men should be provided with dust masks to guard against the inhalation of carbon dust. They should also be provided with an adequate supply of fresh air, either from forcing air through the vessel or from air masks. When unloading a reactor, the carbon should be thoroughly steamed and the vessel purged before unloading the catalyst. If the vessel is to be entered before unloading, the personnel should be provided with air masks.

Primary and secondary reforming

The greatest single hazard to guard against in the operation of primary reformers is the loss of steam in the feed to the reformer. Loss of steam will result in carbon formation in the tube, which can result in physical breakup of the catalyst and plugging of the tube. In extreme cases, this will result in a rapid overheating of the tube with subsequent rupture and a potential fire hazard. The usual procedure for guarding against steam failures is by interlocking the gas and steam flow controllers, which will divert the natural gas feed to vent in case of a steam failure.

When putting a reformer back in service after a steam failure, the tubes should be observed for hot spots, which will indicate whether catalyst breakup or tube pluggage has occurred. If carbon has been formed in the tubes, it can usually be removed by steaming for a period of time. In severe cases the carbon can be removed by the addition of air to the steam.

Severe cases of carbon formation are hazards not only to the reformer furnace but to virtually every catalytic unit in the system. If the carbon formation is severe enough to cause rupturing of a tube, the rapid depressuring of the system subjects all the other catalysts to abnormal pressure stresses. This may result in physical breakup of the catalyst in these units as well.

Another problem sometimes encountered in primary reformers is breakup of the catalyst due to carry-over of liquid water to the reformer tube. Since the reformer catalyst is essentially a ceramic-type material, it will not withstand excessive thermal stresses such as those caused by dumping cold water on hot catalysts.

Operation of secondary reformers in the new large ammonia plants has been relatively trouble-free. In several instances there have been mechanical failures in air and synthesis gas distribution nozzles which have resulted in the direction of a high velocity stream onto the catalyst with resulting overheating and fusion of the catalyst.

A potential hazard of secondary reforming is stoppage of synthesis gas flow to the reactor, which might occur from an upset in the primary reformer. Provisions must be made for diverting the air from the secondary reformer in such instances. Another potential problem is putting too much air into the secondary, which would result in overheating and possible damage to the catalyst. Air flow is normally controlled by a ratio controller which controls the amount of air addition as related to the methane content of the primary reformer exit gas. Since this catalyst also operates at a high temperature, care must be taken to prevent any water carry-over to the catalyst.

Shift converter operations

The performance of high temperature shift catalyst has been

relatively trouble-free. The principal problems encountered have been pluggage of the catalyst bed, due to solids deposition on the top of the catalyst, and catalyst breakup due to water carry-over.

In the case of solids carry-over to the reactor, this is usually evidenced by a gradual buildup in pressure drop across the bed. In some cases if the solids deposition is not too severe, the problem can be simply handled by periodically shutting down and vacuuming off the top layer of catalyst. When doing this it is necessary that the catalyst be either reoxidized or the catalyst first be cooled and then maintained under an inert atmosphere such as nitrogen or CO₂. If the catalyst has not been reoxidized, it is necessary to insure that no air is allowed to contact the catalyst. A large flow of air will oxidize the catalyst too rapidly, resulting in overheating and possible fusion of the catalyst.

Numerous problems have occurred with the low temperature shift catalyst in the new plants, most of which involve poisoning of one kind or another. This catalyst is extremely sensitive to sulfur and chloride poisoning, and great care must be taken to assure that these elements are not introduced. A number of plants have installed a zinc oxide guard which offers some protection against sulfur poisoning, but which will not guard against chlorides. The source of chlorides is normally the boiler feedwater treating system, or in some cases, the lubricants used in the air compressors.

Sulfur contamination is normally the result of an upset condition in the front end of the plant where sulfur is allowed to break through the carbon drum. The sulfur is normally taken up by the reformer catalyst but it will gradually strip off with continued operation. Eventually it will migrate downstream to the low temperature shift catalyst where it reacts with the copper in the catalyst to form a permanent poison. Another potential source of sulfur poisoning is in the air to the secondary reformer. This is especially true in plants located adjacent to or near a sulfuric acid plant.

The low temperature shift catalyst is also sensitive to high temperatures; those in excess of 700° will permanently damage the catalyst. Several cases of catalyst overheating have resulted in plants which use a direct quench system between the high and low temperature shift. A failure in the quench system will allow high temperature gas from the primary shift converter to contact the low temperature shift catalyst.

The temperature sensitivity of this catalyst must also be considered when it is being reduced prior to startup. Since the reduction of the catalyst is highly exothermic, the reduction must be carefully controlled to prevent excessive temperatures from occurring. This was a major problem in many of the earlier plants. As the reduction techniques became more familiar and better established, however, the loss or damage of low temperature shift charges from this source has been virtually eliminated.

The reduced catalyst is highly pyrophoric and should not be exposed to oxygen or air except under closely controlled conditions. When removing the catalyst for a changeout, it is normally cooled with steam and then wetted with water before removing from the vessel. If the catalyst is not wetted, the vessel is normally maintained under an inert atmosphere when removing the catalyst to prevent its rapid oxidation within the vessel.

Methanator precautions

In general, the methanation reactors have been relatively free from operating problems although two potentially dangerous situations are present.

Since the methanation reaction is highly exothermic, provisions should be made to prevent excessively high concentrations of carbon oxides from entering the vessel. This situation can occur from an upset in the CO₂ removal system wherein substantial quantities of CO₂ could be present in the synthesis gas to the methanator. The normal protection against upsets of this nature is a temperature control which will divert the gas from the methanator to vent in the case of an excessive temperature rise in the methanator.

Another potential hazard which can permanently damage the catalyst is the carry-over of scrubbing solution from some of the CO₂ removal systems. Some of these solutions contain sulfur and/or arsenic, both of which are permanent poisons to the methanation catalyst. The normal protection against upsets of this nature is to provide water scrubbing behind the CO₂ removal system and knockout drums for removing entrained liquid.

In the event personnel must enter a methanator vessel for inspection purposes, care must be exercised to guard against poisoning by nickel carbonyl. Reduced nickel is extremely active and will react with carbon monoxide under certain conditions to form the toxic nickel carbonyl. Generally speaking, nickel carbonyl will not be formed at temperatures above 300°F. Therefore, when shutting down the reactor, the usual practice is to stop the flow of process gas at temperatures above 300°F and complete the cooling of the catalyst with nitrogen or hydrogen. Even when following this procedure, it is advisable that inspectors entering the vessel be equipped with an air mask.

Reduced methanation catalyst is highly pyrophoric, and the catalyst should normally be wetted down with water prior to unloading.

Ammonia synthesis

No serious problems relating to the catalyst have been experienced in the ammonia synthesis converters in the new plants. Although the catalyst is subject to poisoning from oxygen, the normal purity of the synthesis gas entering the ammonia loop is such that virtually no hazard to the catalyst is presented from this source. In the older plants, oil from the synthesis gas compressors was a problem in some plants; the new plants with their centrifugal compressors have virtually eliminated this problem.

Since the ammonia synthesis reaction is also highly exothermic, care must be exercised during the initial reduction of the catalyst to control the temperature and rate of the reaction to prevent overheating and damage to the catalyst. The reduced catalyst is highly pyrophoric, and care must be used to oxidize the catalyst when removing for a changeout.

Conclusion

The handling, loading, starting up, and shutting down of the catalysts in the various process units is only one facet in the overall operation of the ammonia plant. However, an incorrect or inadequate procedure can be critical to the performance of the catalyst and can ultimately shut down the plant.

Since these various operations are normally carried out only infrequently in the ammonia plant, it is important that the vendor's recommended procedures are reviewed and suitable precautions taken each time it is necessary to handle or change the operation of the catalyst.

Discussion

LYN KRISCHKE, Rohm & Haas Co.; Concerning nickel carbonyl, I want to mention that we at Rohm and Haas have been making nickel carbonyl for about 15 years at our Houston plant, and we have spent quite a bit of time and money in developing techniques for insuring the safety of our employees in manufacturing this material.

There are simple methods available to detect a nickel carbonyl exposure in an individual without him having to develop some of the more drastic symptoms. There is a urinalysis technique for detecting nickel in the urine that will identify a significant exposure within 8 to 24 hours after the exposure has occurred. This is particularly useful in low level exposures where treatment is desirable but not obvious due to lack of immediate symptoms.

I hesitate to offer our company's services broadly, but if you ever become involved in a possible carbonyl exposure incident, we would be glad to help in whatever way we can from the knowledge we have gained through the years of experience in handling this material. I would suggest that

you contact our Chief Chemical Engineer at our Houston, Texas plant, Dr. George H. Cummings.

The second comment I want to make concerns working inside vessels with nitrogen atmospheres. We had an incident in our plant about a year ago that caused us to carefully review this situation. One of the things that concerned us was interference with the air supply to an individual working inside the vessel, as might result, for example, if equipment movement were to clip or crimp the air supply line. We subsequently have obtained from MSA several small 5-minute emergency air cylinders that are equipped with a check valve assembly. An individual can comfortably have this cylinder strapped to himself while he works inside the vessel and can provide himself with an immediate emergency air supply for tank exit in the event that his external air supply is interrupted. No switching of air lines or masks is required; only the opening of one valve on the check valve assembly.