

SAFETY ASPECTS OF AMMONIA CATALYST REDUCTION AND CATALYST DISPOSAL

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There are a number of more or less independent safety aspects of ammonia catalyst reduction and disposal of spent catalyst. For discussion purposes these aspects will be split up into three parts, one on reduction, one on disposal of spent catalyst, and one on handling of active catalyst on occasions of repair work, for instance on the basket.

Ammonia catalyst reduction

It can be agreed that it is a safety aspect to prepare properly for the reduction. This involves the setting up of a program. Many of the questions which would otherwise present themselves during the operation can thus be dealt with in advance. One of the things which should be known is the maximum temperature versus pressure relationships for the high pressure shell and the converter outlet line. The latter is particularly important to know for a converter with an outside fired heater or an outside electric heater, and in this case one should also have a curve or table giving the maximum allowable coil outlet temperature at different pressures. When speaking of the maximum coil outlet temperatures one will have to consider the coil itself, the line to the converter, and the hot gas inlet to the converter.

When using prerduced catalyst it should be kept in mind that this catalyst is only stable up to a temperature of about 200°F. Therefore, one should not use a cutting torch when opening the drums, as the catalyst could start to oxidize and heat up upon opening. If catalyst loading takes place on a hot day, the catalyst drums should not be exposed to strong sun radiation.

Pressure testing

Before reduction can be started, the loop must be purged and pressure tested for tightness. It is assumed that any pressure testing for strength has been carried out previously.

With a new loop, particularly, it is advisable to test for tightness first at some lower pressure and ending up with a test at working pressure. Upon inspection at working pressure it is a good procedure to watch for pressure drop over a period of one hour with stopped circulator. Let us say, for instance, that we accept the situation if the pressure drop does not exceed 100 lb./sq. in. in one hour. One can then calculate the maximum size of a leak and compare it with the design

purge rate. One should be warned against the use of Freon in this connection. This warning concerns the safety of the catalyst; Freon is a bad catalyst poison. However, it has been used as a tracer in tightness testing with unreduced catalyst without, apparently, any bad effect. Very effective purging is recommended in such a case before start of the reduction. Freon should not be used in connection with prerduced catalyst.

The question of not exceeding the allowable temperature on the coil of a gas fired or oil fired heater has already been mentioned. The temperature is normally indicated by a thermocouple located a little downstream of the heater; normally the stack temperature is also measured. There is a point in connection with such a heater which it is appropriate to discuss. If circulation stops, the furnace is in a critical position. If there is no flow through the coil, the furnace outlet temperature may not even show this situation to exist.

Gas flow through the furnace

It is advisable in units equipped with an outside fired heater to have a good amount of make-up gas introduced downstream of the circulator and a fairly good purge taken for instance from the primary separator, which will normally be upstream of the circulator. In this way there should be a flow of gas through the furnace even if the circulator goes down. While this would not be enough to protect the coil, it would give a true reading of the furnace outlet temperature and thereby alarm the operator. The procedure is less effective if there is an open by-pass around the circulator.

When heating up with an outside heater the hot gas is normally sent directly into the basket, for instance via the normal cold shot line. It is advisable to have from the very beginning a small flow of gas along the high pressure shell, passing through the lower heat exchanger. In this way one avoids having to give the shell a small shock, when it becomes necessary to admit cooling gas to keep the shell temperature down, and it also serves to protect the converter outlet line. If the heater is not very large, one will most likely, at some time during the reduction, find oneself in the position of having to play with the amount of shell cooling gas to find a flow which leaves about the same leeway on the converter outlet line and on the heater outlet line. When the heater has been taken out of service one should be very careful not to introduce cold shot gas through the same converter piping before this piping and converter entrance have had a chance to cool down. Otherwise, there is every possibility of a severe thermal shock.

Reduction operation

As the converter temperatures come up, one starts to make water. This is what must go on in the reduction. The water cooler should be operating from the very start of heating up. The refrigeration cooler, if such a cooler is found, should not be used until a later time. Reduction water will collect in the primary ammonia separator. If possible, one will, in many cases, keep the level controller out of service, valve off and isolate the control valve, and have some temporary provisions to collect and measure the aqua-ammonia through other valves. If this is done, one must be careful not to fill too high a level in the separator or to blow down the pressure on the loop when taking out the aqua, particularly, one should bear in mind that liquid backed up by high pressure gas is quite dangerous. One should not handle or sample ammonia at such times without wearing rubber gloves and goggles. If the aqua drained is stored in a drum it should be an open drum because the aqua might heat up to ambient temperature. Tank cars for aqua may be required if the converter is a large one. At the proper time, of course, the product from the primary separator should be let down as in normal operation.

Water vapor being a catalyst poison, it is important that it is reduced to as low a concentration as possible at converter inlet. It is therefore important that the gas be cooled down in the refrigeration cooler as soon as this can be done, without any risk of freezing water anywhere in the refrigeration system. This depends on the aqua strength, which should be followed by checking the ammonia concentration of the product from the primary separator. The refrigeration cooler should be put into service when the aqua collected in the primary separator consistently has an ammonia concentration high enough to ensure against freezing, even if the cooler temperature should drop lower than intended. When the ammonia-water has a strength of about 190 g. of ammonia/l. of solution its freezing point is below the temperature of pure liquid ammonia boiling at a suction pressure of about 14.7 lb./sq. in. abs., and normally it may be advisable to wait until the aqua attains a strength of about 25% ammonia.

Plugged refrigeration cooler

Partial plugging of a refrigeration cooler with ice was observed on one occasion. In that particular case the refrigeration cooler was commissioned at an early time and operated so that the gas temperature out of it was always at least 32°F. Apparently the water condensed out was frozen because the cooling coils were slightly colder than the gas. If one wants to take advantage of the refrigeration cooler at an early time, one should inject ammonia; this is easy to do in a plant with more than one loop.

Some plants have air coolers. They can conceivably freeze water if the temperature is low enough.

It is impossible to anticipate how an emergency shutdown of a synthesis loop could best be carried out, especially when speaking in general terms. This is, however, something that should be given a little thought, and there is a certain sequence of events that may be kept in mind:

1. Block off make-up gas.
2. Close fuel gas valve to starting furnace, alternatively switch off electric heater.
3. Stop circulator (if multiple service compressors are used this may call for special procedure).

4. Block off around leak.
5. Depressure.
6. Never close an open valve hurriedly except in extreme emergency.

Disposal of spent catalyst

There are several possible ways of dumping a charge of spent catalyst. The most practical way in a given case depends a lot on local conditions. When one refers to local conditions, one is thinking particularly of basket design, provisions for removing the basket from the converter shell, the converter area, and the availability of large amounts of pure nitrogen. While the size of the converter enters these considerations, it is not of prime importance.

There is a clear distinction between cases where the catalyst is stabilized before opening of the converter and cases where it is not.

The question of catalyst dumping was discussed at the Tulsa meeting, and the discussion is on record in "Safety in air and ammonia plants," Volume 3 (1960). With it are practical experiences reported by J. Conklin and T. Kryzer. There is, therefore, no reason to repeat this information here. Reference should also be made to the industrial experience at the TVA described in Industrial Engineering and Chemistry (1953) by Burnett, Allgood, and Hall.

Stabilizing ammonia catalyst

General comments on stabilization of ammonia catalyst should be mentioned. One of these comments concerns the stabilizing agent that may be used: oxygen in low concentrations in a nitrogen stream. The question has been raised, from time to time, whether some other agent which might be easier to control could be used instead. An experiment was recently carried out in the laboratory investigating whether carbon dioxide could be used to stabilize the catalyst. Upon a normal reduction and routine testing of a catalyst sample in one of the laboratory converters the catalyst was cooled down in pure synthesis gas. A sensitive thermocouple was placed in the middle of the catalyst mass and hooked up to a recorder. When the catalyst was cold the flow of synthesis gas was replaced by a flow of pure carbon dioxide, and the recorder watched an exothermic reaction. Nothing appeared during a period of two hours; a flow of air was then substituted for the flow of carbon dioxide. This resulted in an immediate temperature increase. After a couple of minutes the temperature reached 600°F, at which time the flow again switched over to carbon dioxide in order to protect the small catalyst basket. As soon as the air had been purged, the temperature increase stopped immediately. This showed that stabilization cannot be carried out with carbon dioxide.

Passivating with water

The catalyst can be passivated by wetting it with water and, as discussed at Tulsa, advantage is sometimes taken of this effect. The water itself does not stabilize the catalyst. As the water evaporates and the catalyst dries, it will oxidize in the atmosphere and heat up again. One may have to put water on it at intervals so as to never allow it to get too hot. After some time it will have oxidized to such an extent that it will have become stabilized.

There is one thing which should be repeated here, before starting the stabilization with nitrogen containing a few hundred parts per million of oxygen, or maybe up to 1,000 ppm, the converter has to be cooled down completely and purged for hydrogen and ammonia. The best stabilization temperature is probably 100 to 150° F, and the temperature should not be allowed to exceed 200° F. The amount of oxygen taken up during a correct stabilization is 1 to 2%, as compared with a content of about 25% of reducible oxygen in an unreduced catalyst. One will not gain time by taking higher oxygen concentrations and allowing temperatures to go higher. If a zone of the catalyst becomes too warm, all the oxygen may be taken up in that zone and the following catalyst may not become stabilized at all. Therefore, if temperatures tend to become too high, maybe at some later stage of the stabilization when the oxygen concentration is higher, the oxygen concentration should be decreased again. To stop a reaction that tends to be too wild it may be necessary to stop the gas flow and pressure down the system. The preferred stabilization pressure is generally 50 to 100 lb./sq. in. gauge.

Catalyst removal

When the catalyst has been stabilized, there are different ways of removing it from the basket. Sometimes the basket is tipped or the catalyst can be removed from the basket by suction. (In one case this is done by means of a 350 cu. ft./min. blower, and a blower of this size can probably operate with four 1 to 2 in. diameter vertical suction tubes at the same time.)

Without stabilization in the converter, passivation will eventually follow by oxidation in the atmosphere, which if not slowed down will lead to high temperatures. To slow down oxidation, wetting of the catalyst with water has proved a good procedure. In such cases the catalyst will have to be under a nitrogen blanket until it can be emptied out. As an example, the completely cooled down and purged basket may be pulled out of the pressure shell, the catalyst still in an atmosphere of nitrogen from purging. Conditions differ, but in most cases it would be advisable to hook up a small nitrogen flow on the basket while it is being pulled out of the pressure shell and placed outside and opened.

Some converter cartridges are very easy to empty. One can, in some cases, let the catalyst fall out of the bottom into a steel container or a steel wagon.

In most cases the catalyst has to come out through the top. A procedure used in one case is as follows: The catalyst and converter have been cooled down and purged. Purge nitrogen is added through the converter outlet while the shell is opened and heater and thermocouples removed. A flexible hose to supply nitrogen is put on the outlet pipe from the basket while the basket is lifted out. Nitrogen addition is continued while the basket is put on a sledge and transported to the proper place for emptying. Measures have to be taken to ensure that the nitrogen admitted into the basket really gets to the catalyst and not out some other opening. The basket is opened, the bottom of the basket is lifted to an angle of maybe 15 to 20°, and a water hose is directed into the basket while the catalyst is removed.

Repair work on a basket

Quite a lot of repair work can be carried out on a basket filled with pyrophoric catalyst provided that the catalyst is properly protected with a blanket of nitrogen. In many cases this procedure is much preferred to a procedure based on stabilization which requires a subsequent reactivation of the catalyst. It is, of course, easy to do this in a plant which has air fractionation, so that the question of supply of pure nitrogen is no problem.

The procedure has been followed in many cases with success. Sometimes the active catalyst has been removed from the basket under nitrogen and recharged, but the result of this has generally not been satisfactory, probably due to the mixing of catalyst from different zones of the converter. In one case the whole cross-sectional surface of catalyst in a basket, opened for inspection, has been observed, which caused no trouble. One is not in a position to state the nitrogen flow through the catalyst required for this, but it is believed that a velocity based on the empty basket of about 4 in./sec. (corresponding to 8 in./sec. in the bed) should be satisfactory. For a 300 ton/day converter this would amount to a nitrogen consumption in the order of 800 lb./hr.

Proper planning is an important step in such an operation, both for success and from a safety point of view. One must consider where best to add the nitrogen, maybe at different locations at different times of the operation, and which openings from the basket must be closed off by some temporary provision. The object is to keep the catalyst in nitrogen and to prevent air from getting into any part of the basket. Also in this case, of course, the converter should be cooled down and purged with nitrogen before starting the operation. Sometimes it is most practical to purge the whole loop with nitrogen before starting the work on the converter. In other cases it may be satisfactory to isolate the converter from the loop by means of valves and flanges.

Introducing nitrogen

The exact location or locations for introducing nitrogen into the basket must be decided upon on the basis of its design. Frequently, the cold by-pass tube or a quench line would be an appropriate location for introducing nitrogen. If the cold shot line is used, one may attach to it a flexible hose long enough to reach from the bottom up to the top of the pressure shell. The shell should be purged with nitrogen via the outlet while the basket is being lifted out and again when it is put down into the shell. Sometimes the best thing may be to drill a hole in the basket lid in order to introduce nitrogen that way, sometimes two nitrogen inlets may be necessary.

In cases where the basket is severely damaged, one should give some thought to the emergency situation that could arise if the basket should break while being taken out. In cases where the nitrogen comes from a nitrogen plant on the site, it may still be a good idea to have some bottled nitrogen for an emergency situation, should the supply stop.

For the case where there is no nitrogen plant on the site, it is estimated that the amount of nitrogen required be between 800 lb. and 8 ton, depending on the size of the converter and the amount of work that is to be done on it.

DISCUSSION

LAWRENCE—Central Nitrogen: Dr. Nielsen, you didn't go into great detail about the purity of the nitrogen. From a safety point of view, I don't know whether you would say a couple of thousand parts per million would cause any hazard but it would have a tendency to make the catalyst very difficult to light, wouldn't it? Do you worry about that in the nitrogen you use?

NIELSEN: The nitrogen from a combustion generator would contain a lot of other things, like carbon dioxide. If the catalyst is to be dumped, this would be all right, from a safety point of view, provided the oxygen concentration is low enough. I think 2,000 ppm of oxygen is somewhere close to the limit from a safety point of view. In some cases you might find this too high a concentration and see catalyst temperatures start to rise, while in other cases one might get through with 2,000 ppm of oxygen in the nitrogen to start off with. We have carried out more than a hundred stabilizations in our catalyst reduction plant, where we stabilize 8 tons of catalyst at a time. We start off with a few hundred parts per million, and even this gives us a temperature increase, which we follow, in the catalyst. Then when temperatures have gone up and start to drop again we increase the oxygen concentration, and the same will repeat itself. Later we go to 2,000 ppm and higher before we open the converter. I did not go into

this because it is discussed in Volume 3 of "Safety in Air and Ammonia Plants" covering the Tulsa meeting.

LAWRENCE: I was wondering not so much of the stabilization but on catalyst damage where you're burning—you either get carbon monoxide on the one hand or maybe a 1,000 parts of oxygen on the other. You can't avoid both of them. Now if you're going to work on the basket which one would you take?

NIELSEN: We have succeeded in stabilizing with carbon monoxide at conditions, the details of which, I do not know. We would advise against this except for cases where it is part of a dumping procedure.

If you are going to reuse the catalyst, I think the impurity which you can tolerate is oxygen. For blanketing I think there is no problem in having 2,000 ppm of oxygen as long as there is no large flow of nitrogen, but I do not think you should have a large amount of carbon dioxide or carbon monoxide from the point of view of not hurting the catalyst.

As an afterthought I should like to add to this last case that 2,000 ppm of oxygen may be too high. I think that at some conditions 2,000 ppm might lead to excessive temperature increase in the catalyst, while with 500 to 1,000 ppm this might not be the case.