



Leak Detection Systems in Urea Plants

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Summary

To assure the safe operation of the High Pressure synthesis vessels in a urea plant the sound condition of the loose liners is very important. The soundness of these liners should be inspected during maintenance turnarounds. And its integrity should be continuously checked during operation of the plant via a proper leak detection system. Best practice is to appoint one person to be responsible for the system plus shift responsibility for frequent checking.

A leak detection system with a short response time is important to avoid the formation of solids behind the liner. To wait until one sees fumes from the leak detection tubes is in my view not a proper leak detection system.

Assure yourself that all leak detection holes communicate, be aware that multi layer carbon steel vessels have weep (ventilation) holes which are not to be confused with the leak detection holes.

Regarding the use of steam in a leak detection system different views exist in the industry. Be aware that the use of steam in a leak detection system can lead to unacceptable risks; namely stress corrosion cracking of the carbon steel pressure wall from the inside or in the liner, thus in an area which is impossible to inspect.

In case of doubt contact your Licensor or equipment manufacturer. For example Stamicarbon has developed a state of the art leak detection system. Please refer to their website for more information.

1. Introduction

It is common knowledge that the process to produce urea from the raw materials ammonia and carbon dioxide required elevated pressures and temperatures. Depending on the process technology the pressure typically varies between 140 and 210 bars and the temperature between 170 and 200 °C.

The formation of urea proceeds in two steps:

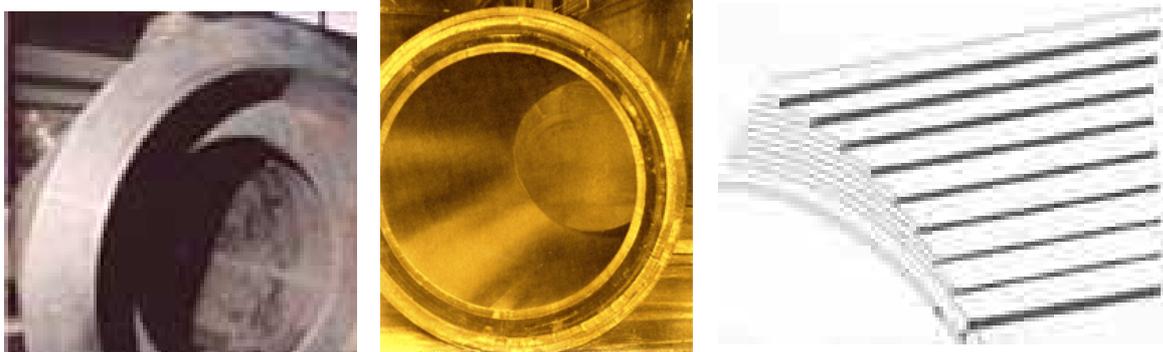
Step 1: $2 \text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{Carbamate}$

Step 2: $\text{Carbamate} \rightleftharpoons \text{Urea} + \text{H}_2\text{O}$

The first reaction is fast while second is slow. This is the reason that every urea plant has a urea synthesis reactor with a relatively large volume which contains a mixture of ammonia, carbon dioxide, carbamate, urea and water. Carbamate is here the only but at the same time a very corrosive product. Also the presence of NH_3 and CO_2 under condensing conditions (thus forming carbamate) are considered as a potential risk for severe corrosion.

High pressure synthesis reactors, same as the other high pressure equipment items in a urea plant, consist of a carbon steel wall with a protective layer.

The function of carbon steel part is to resist the high pressure at which the process operates. The carbon steel wall can be typically a solid wall type, multi wall or a multi layer type.



Pictures: mono wall (left), multi wall (middle) and multi layer (right)



In these pressure vessel walls leak detection holes are drilled to be able to detect a possible leak. Be aware of the fact that in a multi layer also weep holes are drilled; that might lead to confusion.

These weep holes are blind holes drilled in the multilayer and serve during the fabrication and allow the pressure vessel to breath during operation.

The total thickness of the carbon steel wall depends on many factors such as the type of pressure vessel applied, design pressure, the diameter, type of carbon steel and the used design code but to have an indication it will be some 100-300 mm. As the corrosion speed of carbon steel caused by carbamate is high (about 1000 mm/year), a protective layer is needed to protect the carbon steel. The protective layer can be a liner or an overlay welding and of course a combination of both. The material of construction can be 316L Urea Grade, 25-22-2 stainless steel, titanium or duplex. The thickness of the liner typically varies between 4 and 10 mm and depends on the Licensor.

The protective layer (liner or overlay weld) has a limited lifetime. The ongoing carbamate corrosion can vary between 0.03 – 0.2 mm/year in case a proper passivation is present. However there are circumstances that a proper passivation is not assured and then corrosion speeds are higher.

The overall corrosion of titanium is almost zero but titanium is a very sensitive material for welding and for erosion, so also here the lifetime of the protective layer is limited.

Heating up and cooling downs causes stresses on the protective layer as the thermal expansion coefficients of the carbon steel wall and the protective layer are in most of the cases quite different. For example when a reactor is shut down, opened and sprayed with water to cool more quick the following situation can occur. The thick carbon steel wall is still at 180 °C while the liner which is relatively thin might be only 80 °C. The thermal expansion coefficient of carbon steel is about 1.2 mm/m/100°C and of stainless steel is about 1.8 mm/m/100°C. Assuming that the distance between two fixed liner welds can be 6 m, in this situation the austenite stainless steel wants to be $1.2 \times 6 = 7.2$ mm shorter than the welds allow. One can imagine under these conditions cracks can occur, most likely in the weakest spots such as the heat affected zones of the welds. It is advisable therefore to follow the instructions of the licensor or manufacturer regarding maximum heating up and cooling down rates.

To conclude the protective layer of a High Pressure equipment in a urea plants has a limited lifetime and thus requires regular inspection. In case the protective layer is an overlay welding this inspection can take place only during a maintenance turnaround. But in case the protective layer is a loose liner, which is most often the case, a continuous inspection during operation or with other words a leak detection system is very important to assure a safe operation of the high pressure synthesis section of a urea plant.

2. Failure mechanism of loose liner vessels

Several different failure mechanism can cause a loss of integrity of a loose liner, depending on the type of process, material of construction of the liner, type of carbon steel and even the way the leak detection system is designed and operated. Most common are welding faults in the liner welds and corrosion in the Heat Affected Zone (HAZ) of the welds.

Let me give you an overview of the possible failure mechanism:

i. Weld defects

The first most obvious failure mechanism in loose liners are weld defects. Any weld can contain fusion defects and/or wormholes due to moisture or fouling during the welding process, especially when the welding has been made in the field under difficult circumstances.

These weld defects can cause corrosion problems as indicated in paragraph ii, but weld defects like fusion defects can also cause reduction or loss of the mechanical strength as a result of forces on the liner during heating and cooling down cycles.

ii. Crevice corrosion at stainless steel and duplex liners*

Crevice corrosion typically occurs in liner welds or in welds of the clips of internals to the liner. For example clips of trays in a reactor or gas/liquid dividers in heat exchangers. Many times the wormhole is a sub surface defect and is not detected during the fabrication process. However after a certain period of operation and after some passive corrosion the worm hole opens and carbamate can enter the worm hole (crevice). In the crevice no refreshment of oxygen is secured, the oxygen gets depleted and active corrosion with higher corrosion speeds starts. Another area for crevice corrosion risks are in cracks which can be a result of heating up and cooling down cycles.

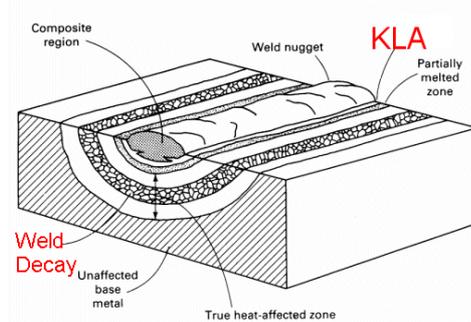


*Stamicarbon states that the duplex Safurex® does not experience active corrosion

iii. Corrosion in the HAZ of the liner welds

Due to the temperatures during the welding process, the area adjacent to the welds, the so called Heat Affected Zones, are more sensitive to corrosion problems. Several times one see Weld Decay or Knife-Line Attack phenomena in this area.

Knife-Line Attack is a form of intergranular corrosion, razor sharp and present between the weld and the liner. The attack appears razor-sharp and hence the name of "knife-line" attack.



iv. Condensation corrosion at stainless steel and duplex liners*

In the urea process urea itself is not corrosive. It is the intermediate product ammonium carbamate, which is highly corrosive. The applied special stainless steels which are used as a liner should remain in a passive state. The corrosion rate of passive corrosion of austenitic stainless steels is some 0.1 mm/year while active corrosion is some hundred times faster. Addition continuously air (oxygen) or hydrogen peroxide to the process is therefore of utmost importance. Further one should realize that the (electrochemical) corrosion can take place only in the liquid phase; in a gas phase corrosion cannot take place.



Pictures: Bad insulation of a nozzle (left) can cause condensation corrosion (right)

However when condensation of gasses occurs in the gas phase a carbamate liquid will form in which no oxygen or hydrogen peroxide is present. Due to the lack of oxygen the passive layer on the liner will not be maintained and active corrosion of the liner starts.

Thus the areas in High Pressure equipment vessels where a gas phase is present during normal operation are critical for this type of corrosion. These parts of the vessels should be traced and well insulated.

Condensation corrosion will occur in the gas phase at locations where a cold sink is presents (nozzles, man way covers, lifting lugs, stud bolts) and/or where the tracing and insulation of the vessel is not in good condition.

*Stamicarbon states that the duplex Safurex[®] does not experience active corrosion

v. Stress corrosion cracking of carbon steel

In general carbon steel is sensitive for stress corrosion cracking by several ions such as nitrates, but also carbonates. In case for example the insulation of a High Pressure



equipment vessel is not in a good condition and nitric acid or ammonium nitrate plants are in the neighborhood, with rain or cooling water towers mist nitrates can get into contact with the carbon steel. This leads to cracks from the outside of the carbon steel vessel leading to a degradation of the integrity of the vessel. Best practice is to have a good insulation in combination with a coating and in the worst case construct a shelter against rain above the High Pressure vessel.

Several times however also cracks from the inside in the carbon steel wall have been experienced, so on the site were the loose liner is connected. Cracks in this area can hardly been found during normal inspections and many times lead to a sudden catastrophe. These kind of cracks can occur when leak detection systems are flushed with steam or condensate. On one side one may believe that steam be the most obvious and best medium to flush away carbamate and urea in the leak detection system behind the liner. However with steam many times also ions are introduced which can cause stress corrosion cracking of the carbon steel vessel. It appears that in the industry quite different views are present regarding the use of steam in leak detection systems. The challenge here might be to find an alternative for steam to open a clogged leak detection system.

vi. Pitting corrosion

Impurities in the feed streams to the urea plant like sulphur and chlorides can cause pitting corrosion in the liner, so very locally higher corrosion speeds occur.

vii. Fatigue crevices

As indicated earlier the thermal expansion coefficient of carbon steel is about 1.2 mm/m/100°C, while of stainless steel it is about 1.8 mm/m/100°C. Further please realize the liner is relatively thin while the carbon steel wall is relatively thick. While heating up the reactor the liner is pushed against the carbon steel when the distance between the liner and carbon steel wall is minimum hardly any expansion will occur. Except when the liner is a loose liner, so hardly connected to the carbon steel, then some buckling can occur for example at locations where the liner is bended sharply.

Furthermore in cooling down conditions the thin liner is cooled down more quick than the thick carbon steel wall and the liner will face strong forces causing crevices after a certain number of heating up / cooling down cycles.



viii. Erosion of titanium liners

Titanium has the disadvantage that this material is relative soft at elevated temperatures and thus sensitive for erosion, so wherever high velocities are present erosion can take place and the liner will become thinner.

To conclude the integrity of the loose liner can be at risk due to many different reasons, even from the design and operation of the leak detection system itself.

Lets discuss the leak detection system more in detail.

3. Leak Detection Systems

There are many different leak detection systems available in the industry. First of all the design philosophy of a leak detection system of the different licensors and manufacturers differs. A leak detection system in general is designed to detect leaks in the liner. A liner consists of plates, which are welded together and it are these welds which are to be considered the most critical areas. These liner connections can be divided in loose liner welds (two liner plates welded together without any fixation to the carbon steel) and fixed liner welds (two liner plates welded together while at the same time fixed to the carbon steel). The loose liner welds can be inspected by Non Destructive Testing (NDT) and when done correctly, these welds can be considered as sound as the liner plates itself. However the fixed liner welds cannot be inspected by radiography and are thus a potential risk for leaks. This means that basically leak detection systems are designed in such a way that leakages in these welds will be detected earliest.

Second the visible part of the leak detection system differs also from one plant to the other: some plants flush with air, others with carbon dioxide, again others with steam and some even wait until fumes exit the leak detection tubes, some use as an indicator of a leak a bottle with phenolphthalein, others an ammonia detector and again other measure the conductivity.

It is not important what kind of system one is using but it is important that one is using a system. Best practice is to appoint one person to be responsible for the system plus shift responsibility for frequent checking.



Pictures: Different Leak detection systems



When operating a leak detection system some points of attention are important.

i. Maximum operating pressure

As the liner is rather thin and has a relatively big area, the maximum pressure difference a liner can withstand is limited: This means that typically the pressure of the leak detection system should not be higher than 0.3 bars higher than the pressure inside the vessel.

ii. Short response time

Leaks can occur in the gas phase or in the liquid phase.

When a leak occurs in the gas phase ammonia and carbon dioxide vapors will leak with a temperature of some 170-200 °C and its pressure will reduce from 140-210 bars to nearly atmospheric in case the leak detection system is not clogged. The temperature in the leak detection system behind the liner is close to the process temperature while it will be ambient temperature in the leak detection lines in case these are not traced and insulated or installed under the insulation of the vessel.

At ambient temperatures these vapors can condense and form carbamate, crystallize and clog the leak detection lines. Once clogging occurs, the pressure in the leak detection system increases and then vapors might even condense in the leak detection system under the liner forming carbamate. The formed carbamate corrodes with the carbon steel pressure vessel with high speeds.

When a leak occurs in the liquid phase, carbamate liquid with possibly urea will leak. Two phenomena can occur: The carbamate can dissociate into ammonia and carbon dioxide vapors due to the lower pressure and/or the carbamate can convert into urea and further into biuret and triuret due to the high temperature. Biuret and triuret will crystallize and can clog the leak detection system under the liner. Which phenomena will occur depends on the size of the leak. But in case the leak detection lines are at ambient temperatures the ammonia and carbon dioxide vapors can condense, form carbamate, crystallize and clog in the cold leak detection lines. In that case the carbamate will not dissociate anymore and certainly corrosion of the carbon steel pressure vessel starts.

Typically after some 30 to 40 hours is it realistic that a blockage of the leak detection system may occur. Most critical in that situation is that the carbamate causes very high

corrosion speeds to the carbon steel, risking the integrity of the High Pressure equipment item.

Leaks are often very small and hardly any increase of pressure in the leak detection system is measurable. That means that there will be hardly any flow and that it will take a very long time before such a leak will be visible at the outside of the equipment. Thus a leak detector is needed to identify in an early stage a leak.

iii. Leak detection lines

It is important as indicated here above to avoid condensation of vapors in the leak detection lines. So it is advisable either trace (minimum temperature should be the crystallization temperature of carbamate 153 °C) and insulate the lines or install the lines below the insulation of the HP equipment. Both options have their disadvantages but the choice not to connect the leak detection tubes to a leak detector and rely on visual detection of leaks is in my view not acceptable.

The use of traced sample line bundles might be a good alternative, like shown in the picture below.



Picture: Traced sample lines

More information is available on internet:

http://www.kme.com/en/products_and_markets/special_semis/osnline_tube_bundles/



iv. Operate a leak detection system from the beginning

There is no discussion in the industry that a reliable leak detection system is a must, with aging equipment leak detection becomes more and more important and when one do not have a correct leak detection system from the beginning it appears almost impossible to obtain a reliable leak detection system; only with high efforts and against a high price one can establish again a proper leak detection system.

Many times operators find the leak detection system blocked. In most cases it will be only possible to realize a working leak detection system with modification to the HP equipment itself. Flushing the system with steam or condensate is a very doubtful measure to open a leak detection system as it can cause stress corrosion cracking in the carbon steel or/and in the Stainless Steel liner as described above.

4. Conclusions

To assure the safe operation of the High Pressure synthesis vessels in a urea plant the sound condition of the loose liners is very important. These liners should be inspected during maintenance turnarounds and its integrity should be continuously checked during operation of the plant via a proper leak detection system. Best practice is to appoint one person to be responsible plus shift responsibility for frequent checking.

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Mark Brouwer was born on July 6, 1966 in Groningen, The Netherlands. He graduated in 1988 at the Technical University of Eindhoven at the faculty of Chemical Engineering. His thesis was about the production of ethylene by partial oxidation of natural gas.

After University Mark joined Military Services, Dutch Royal Navy where he was working at the Prins Maurits Laboratory of TNO in Rijswijk. In this period he was involved in Process simulation studies on the absorption of poisonous gasses on active carbon.



In 1990 he joined DSM, working for the Ethylene Plant No.4 as a Process Engineer. In these seven years he was involved in the Basic Engineering of a debottlenecking project at Stone & Webster in London and in the implementation of the DSM Extraction Styrene project (from Conceptual Engineering up to the successful start up) .

In 1997 he joined Stamicarbon, the Licensing subsidiary of DSM as Licensing Manager Urea Revamps. Later he became Manager Stamicarbon Services responsible for all Stamicarbon's activities in existing urea plants, such as After Sales, Plant Inspections, Debottlenecking Projects, Reselling projects etc. In these nearly twelve years he did visit nearly one hundred urea plants worldwide and was involved in numerous revamp, relocation, debottlenecking and grass root projects.

End of 2008, Mark stopped working for Stamicarbon and started up a new initiative in the Urea industry: UreaKnowHow.com, where the urea industry meets.

UreaKnowHow.com is on line since early March 2009.

Please visit www.ureaknowhow.com.