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Solving The Problem Of Hot Walled Ammonia Synthesis Converter

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In the ammonia industry there are a certain number of synthesis converters that are characterized by the absence of cooling of their pressure vessel. These converters therefore have their high pressure vessel operating at the reaction temperature, normally the inlet beds temperature. Some of these converters are known for having developed problems in the pressure vessel due to the high operating temperature in presence of hydrogen and ammonia, where the combined action of these three critical factors has led to the development of cracks. In some cases the situation was so serious that the vessel had to be replaced. Now AMMONIA CASALE has developed and applied a system to transform these hot walled converters to cold wall. The system consist in building "in situ" an insulated cartridge wall, that separates the pressure vessel from the catalyst beds environment, allowing the creation of an annulus that is utilized for flushing the vessel inner wall with colder gas. This system is an alternative to the expensive replacement of the vessel, and ensures a long and safe life of the unit.

1. INTRODUCTION

Ammonia synthesis converters are key items in ammonia plants. Their reliability is essential, as a plant cannot run if the converter is down and risk involved in its failure are significant because of the high pressure and flammable gas contained. This equipment is usually built from low alloy material.

The operating condition of the ammonia converter is characterized by an aggressive environment created by the combination of high pressure, high temperature and a gas composition including high content of hydrogen with ammonia, which implies the concurrence of Hydrogen related damages and Nitriding, in addition to the typical problems of thick low alloy materials.

All this potential problems can be reduced by enclosing the catalytic bed where the ammonia is generated at high temperature in a protective shell inside the pressure retaining vessel. This shell usually called "cartridge" permits to cold flush the external vessel with the inlet gas, which is at lower temperature and lower ammonia content. This design is called cold wall design.

In the past a so called hot wall design was also used. This design with the aim of reduce capital cost avoided the cartridge by inserting the catalytic bed directly in the pressure vessel. The same design is sometimes still used when an additional converter is added downstream to the main converter.

Several of this vessel faced problems during their operating life.

Casale recently developed a scheme to change these converters from hot wall design to cold wall design, reducing the potential problems or keeping under control the existing ones.

This scheme is described in this paper.

2. METALLURGICAL PHENOMENA IN AMMONIA CONVERTERS

A brief introduction to the metallurgical phenomena that affect the Ammonia converter is required to understand the different choice in the design of ammonia converters, the problems related to these choices and the solution proposed.

The operating condition of the ammonia converter is characterized by an aggressive environment created by the combination of high pressure, high temperature and peculiar gas composition.

The combination of a high content of hydrogen with ammonia implies the concurrence of Hydrogen related damages and Nitriding.

The use of low alloy imposed by hydrogen attack in combination with medium to high temperatures could trigger over time the phenomenon of temper embrittlement.

Moreover it should be considered that low alloy construction are critical, especially when high thickness is involved, and several damages could arise along the equipment life due to construction problems not readily detected.

All these aspects are summarized in the next paragraphs.

Hydrogen Influence

High Temperature Hydrogen Attack

In hydrogen rich service environments, under certain conditions of temperature and pressure, carbon and low alloy steels can suffer irreversible damage due to hydrogen attack. Its mechanism, detailed treated in International recognized standards such as API 941, has two detrimental effects, namely loss of mechanical strength due to loss of carbon and the formation of a network of fissures and cracks throughout the microstructure. With on-going exposure, these micro fissures continue to grow and consolidate into macro-cracks and, if not detected, will eventually grow sufficiently to result in failure of the pressure vessel.

Hydrogen Debonding

Equipment involving moderate to high temperatures and moderate to high hydrogen pressures, are commonly manufactured from low alloy (Cr-Mo) steels. For some component where temperature are high (e.g. the outlet section of an ammonia converter), an internal surface overlay of an austenitic material such as a 300 series stainless steel or Inconel 600 is sometimes provided.

The intent of the overlay is believed to provide protection against such degradation mechanisms as high temperature hydrogen attack and nitriding.

There have been numerous documented instances where process equipment incorporating this 'clad design' has suffered from cracking after being in service for a period of time. This cracking, often referred to as debonding, commonly occurs at the interface of the austenitic weld overlay and the base metal.

The mode of cracking / debonding is believed to be hydrogen-induced with the hydrogen entering the wall of the pressure equipment during normal operation and possibly also during original weld fabrication. During a cooling down cycle (plant shutdown) hydrogen can become entrapped at the overlay-base metal interface of pressure equipment, reaching saturation levels at ambient conditions. The faster the rate of cooling of the pressure equipment, the higher the likelihood of entrapped hydrogen causing debonding.

Nitrogen Influence

Nitriding

Above a certain temperature, depending on the type of steel, ammonia reacts with iron to form a hard and brittle Fe-N inter-metallic compound. This phenomenon is called Nitriding.

The nitriding rate depends on temperature and on ammonia partial pressure. Nitriding develops on low alloy steels and on stainless steels, however the latter at a much reduced rate compared with low alloy steels.

For this reason, in ammonia atmosphere, usually above 370-380°C, carbon steel and low alloy steels are not used in contact with fluid and replaced with austenitic stainless steel or even non-ferrous alloy.

In regions where sufficiently high stresses are applied, crack of the nitrided layer can start; after that, the apex of the crack nitrides, allowing the crack growing faster and faster.

Temperature and Time Influence

Temper Embrittlement

Temper embrittlement is a phenomenon which occurs to Low alloy steel reducing is resilience at mild temperature. It occurs after years of operation.

Temper embrittlement usually occurs when low alloy steels are operated in the temperature range between 370 and 580 °C for a sufficient period of time, typically several years. Its effects are a reduction of the steel resilience at temperatures around or slightly above ambient temperature. When pressurized at these temperatures, the equipment may develop brittle fractures, which could cause failure of the equipment, but also go undetected and later induce delayed failures.

Whereas not completely understood the phenomenon is related to the presence of "tramp" elements like P, Sn, Sb and As in the steel.

In actual steel production specific chemical composition limitations have been developed to avoid this problem and specific test, such as step cooling, are performed to evaluate the resistance of new products.

Anyway also for modern steels with very low contents of "tramp" elements, which should be resistant to such phenomenon, some failure case shows no obvious correlation between chemical composition and embrittlement .

Material and Construction

Low alloy steels

Low alloy steels are difficult to fabricate because of their strong tendency to form brittle structures during welding or heat treatment, especially in case of high thicknesses, when temperature control is more difficult and residual stresses higher.

Problems may arise during material production or during manufacturing. The latter are more difficult to detect since tests are less effective and production activities more complex and difficult to control.

Most of the potential problems typically relate to Welding.

Some of the possible causes are:

- Delayed HIC (Hydrogen Induced Cold Cracking)
- HAZ (Heat Affected Zone) hardness
- Reheat Cracking/Cracking during fabrication
- Low toughness in the weld

These problems may not be immediately detected and their consequences can become manifest only after years of operation.

3. AMMONIA CONVERTERS – COLD VS. HOT WALL CONVERTERS

The solutions to the metallurgical problems described above are a suitable choice of materials and design of the equipment.

Since the detrimental effects of the environment on the materials increases by increasing the temperature, one possibility is to keep the latter as low as possible.

This concept has been developed in the so called cold wall design of ammonia converters, where inside the pressure shell is provided a cartridge externally insulated containing the catalytic beds where the ammonia synthesis develops, which is outside fluxed by a cold gas that keep low the temperature of the vessel.

The cartridge is a vessel inside the vessel. While the pressure acting on the cartridge is low, this design is anyway expensive considering the double construction and the increase in dimensions of the pressure vessel.

Moreover if the cartridge should be removable, the pressure vessel shall be provided with a full diameter opening, involving a big flange and relevant cover. As an alternative the cartridge can be inserted in the vessel during fabrication before the final closure welding, but in this case vessel inspection, hydro-testing or repair and also catalyst replacement are more difficult.

An alternative to cold wall design is hot wall design.

In this case the catalytic beds are directly installed inside the converter.

The pressure vessel for economic reasons is made from ferritic materials such Carbon steel or Chrome-Moly steels, selected according to the API 941 standard.

Since the ferritic components suffer from nitriding above 370/400°C, usually the design includes weld overlay of the parts above this temperature with austenitic materials or high nickel alloys.

C.F. Braun introduced hot wall design for ammonia converter in modern plants since the second half of last century. This design is featured by multi-bed converters in separate vessel, where there is no internal cartridge cold gas flushing and the vessel operates at the temperature and gas composition of the inlet to each bed.

In existing plants, a revamping option to increase ammonia conversion is to provide an additional catalytic bed downstream the existing ones.

The new bed requires a significant volume of catalyst and operates at colder temperature than the existing ones, because of the high content of Ammonia. A new, big pressure vessel shall be installed.

To reduce costs, recently, other Companies selected the hot wall design for the additional bed in revamping and new plants.

4. PROBLEMS IN HOT WALL CONVERTERS

The experience on Braun designed plants is important because it is sufficiently long to permit an evaluation of the entire life cycle of this equipment and because many papers have been published on the subject.

This experience shows that the use of hot wall pressure vessels for ammonia converters is very risky. In many plants, after some years, the vessels showed damages due to the combined effect of hydrogen attack, nitriding, temper embrittlement and possible manufacturing problems.

Ammonia Casale has had direct exposure to these problems because was involved in revamping, or replacing, few of these converters. Some examples are as follows.

In an ammonia plant in Augusta - USA the converter was subject to extensive cracking in the bottom nozzles and in the circumferential weld between the top hemispherical head and the cylindrical body. This last crack was almost passing through the entire thick of the metal, and was extending over about 48". The vessel has been repaired twice. At least one paper on the subject had been presented at the Aiche in 1991, and 1997 Casale revamped this two beds.

The converter of an ammonia plant in Ludwigshafen - Germany suffered from cracks to circumferential welding extending through the whole thickness of the metal. A paper was presented by Basf at the Aiche in 1991 and 1994.

In an ammonia plant in Tolouse - France the first converter had to be replaced completely due to the damages. Casale supplied the internals for a flush cooled new converter. A paper on this subject was published at Aiche in 1994.

From the literature we can mention a significant case, related to newly designed hot wall converters.

Tata Chemicals Limited experienced a failure on an additional converter bed, designed according to the hot wall design in 1995.

A fire was detected in the proximity of the first circumferential weld of the second converter, which was then bypassed to resume production. Failure occurred in one of the two circumferential weld joints carried out at the site, the nearest to the vessel bottom. Failure was due to crack propagated through the entire thickness of the weld.

A paper was presented by Tata Chemicals Limited on this matter at Aiche in 1999.

Another occurrence of problems to additional hot wall converters is the case where the Casale technology described in this paper has been applied and it is described in the following paragraph.

As a general consideration, it is to be noted that often the nitriding effect is important for the development of the damage, because it is adding to hydrogen embrittlement, favouring the propagation of the cracks. Moreover the effects of improper operations during manufacturing are magnified by embrittlement, which could occur for low alloy at elevated temperature enhanced by the presence of hydrogen.

The reason to adopt an hot wall design for ammonia synthesis converters can be only to reduce its cost, as the traditional cold gas flushing has never shown any drawbacks. The question is if the saving is real in view of the considerable risks inherent in this solution, which may lead to the necessity of complete converter replacement, or worse to the vessel catastrophic failure.

5. FROM HOT WALL TO COLD WALL

Concept

Casale philosophy has always favoured the cold wall design.

Apart from new converters, wherever possible the same philosophy has been applied to revamping, often as a preventive measure, sometimes to solve actual problems of converter pressure vessel.

These solutions are generally tailored on the specific equipment and problems, but recently Casale developed a new process scheme to provide cold flushing to additional bed converter designed as hot wall. This solution could be used to save already damaged Hot Wall additional bed pressure vessels or as a preventive measure to increase safety and reliability.

The typical additional converter scheme is shown in figure 1. This scheme is basically similar to the Brown multi-vessel scheme, but the first converter is usually a cold wall multi-bed converter and only the additional converter is a hot wall design. Typically the additional converter has been added at a later stage to increase Ammonia conversion or to reduce consumption.

In the additional converter, featured by partial opening, the hot gas coming from the first converter rich in ammonia is in direct contact with the pressure vessel walls.

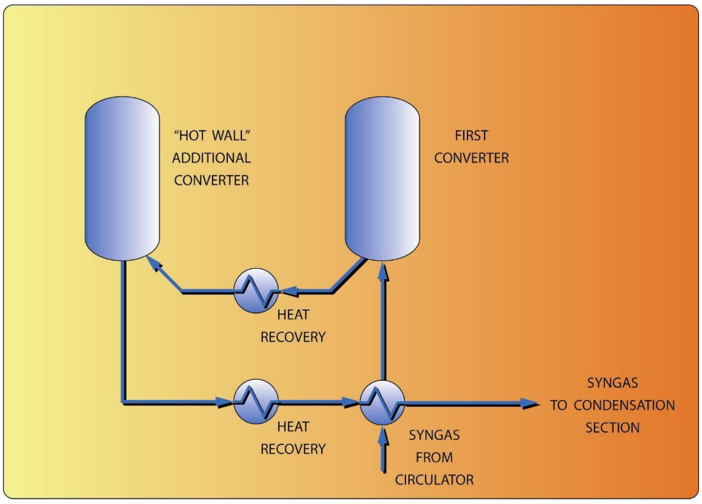


Fig. 1: traditional scheme for additional hot wall converter

CASALE Modification, which is shown in figure 2, utilize a small percentage of the cold feed gas going to the first converter as a flush gas for the additional converter vessel. After flushing this gas mixes with the hot gas coming from the first converter before entering the catalytic bed contained in a new cartridge built inside the additional converter.

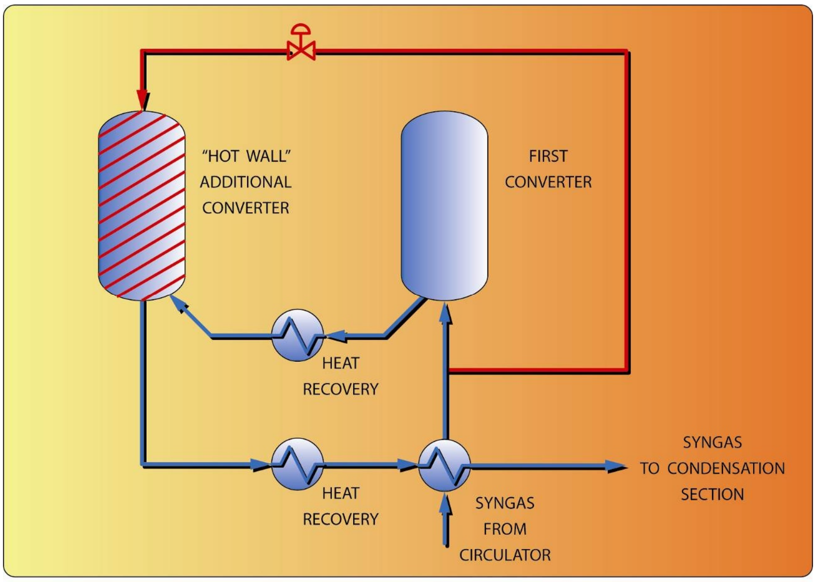


Fig. 2: Modifications to change from hot wall design to cold wall design the additional converter

The cold flushing gas is therefore taken from the hot gas-gas outlet, bypassing the first reactor and acting as a small quench for the additional converter.

The internal flushing is made possible thanks to the installation of a new cartridge and new internals. Since the vessel often is not a full open one, the cartridge and the internals should be mounted and welded directly on field, inserting them in pieces through the available manway/opening.

In addition to the new internals the intervention includes a new top cover with an additional nozzle for flushing gas inlet from the manway/opening and a new bypass line to feed the flushing gas to the converter, equipped with a regulating valve.

The typical process figure of this modification are:

- The flushing gas is taken from the hot gas-gas exit in the amount of about 10% of total circulating flow rate.
- The flushing gas is sufficient to provide a cold flushing on the vessel, keeping the wall temperature below 300°C.

- Ø The high efficiency of CASALE cartridge axial-radial design allows a negligible reduction in converter performances if compared with the "HOT WALL" design.
- Ø CASALE cartridge allows loading more than the 80% of the catalyst volume loaded before the intervention.
- Ø The flow path inside the modified additional converter is shown in figure 3.

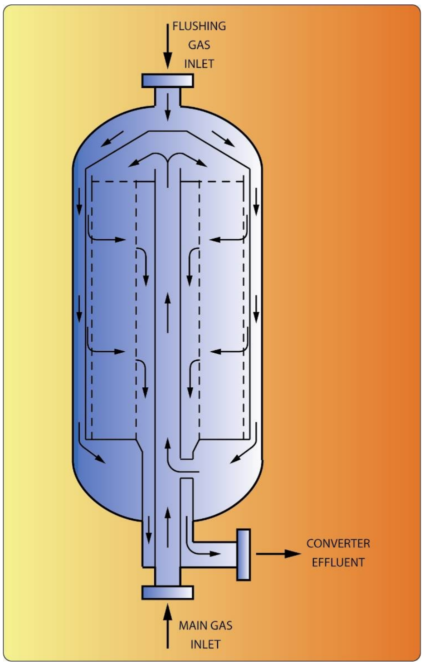


Fig. 3: Flow pattern in the modified converter

The flushing gas enters the converter from the new top cover nozzle and flushes the internal wall of the vessel by flowing downwards along the cylindrical annulus between the cartridge and the pressure shell. In this way, the pressure vessel is protected against high temperature and maintained at the same temperature of the feed gas. The cartridge is thermally insulated. The main gas enters from the existing inlet nozzle and mixes with the flushing gas on the bottom of the converter inside the new cartridge. Then the mixed gas goes up through the internal pipe and enters the axial-radial catalytic bed. The reacted gas is collected and goes out the converter through the existing outlet nozzle.

The main challenge from a mechanical point of view is the design of a cartridge that could be inserted through partial opening and then assembled inside the vessel.

Contrary to a catalytic bed, whose only scope is to retain catalyst, a cartridge shall be gas tight, resist the differential pressure between the two sides and provide insulation to the vessel, especially in case of shutdown, when cold flushing is no longer available.

For this reason a modular design was selected. Each module, which could be inserted through the opening, already incorporate the cartridge wall, its insulation and the catalytic bed outer wall. Each module is a full height independent sector of the cartridge, therefore once the new bottom is assembled the modules can be simply installed side by side to form the cartridge and the outer catalytic bed. After the modules are placed, the inner collector, is usually inserted in a single piece while the cartridge top cover is installed in sector.

Trial assembly in workshop are performed to assure final dimension and detect any possible problem.

Whereas often additional converters can be isolated and put off line while the plant is running, this design permits to perform the modification and the internal installation within the timeframe of a standard turnaround.

Casale patented this solution, whose distinctive solution, is the possibility to install a cartridge in an existing vessel not featuring a full opening during a normal catalyst change, permitted by the special design made by modules already incorporating all the components needed.

In principle, this design with a slightly modified scheme can be applied to any single bed hot wall converter, not only additional ones, but any case shall be studied specifically.

Application

This concept was successfully applied on a series of identical additional converter, where several problems occurred to the original pressure vessel.

In this case the hot gas feeding the additional converter contained a percentage of ammonia close to 20% in a temperature range up to 390°C.

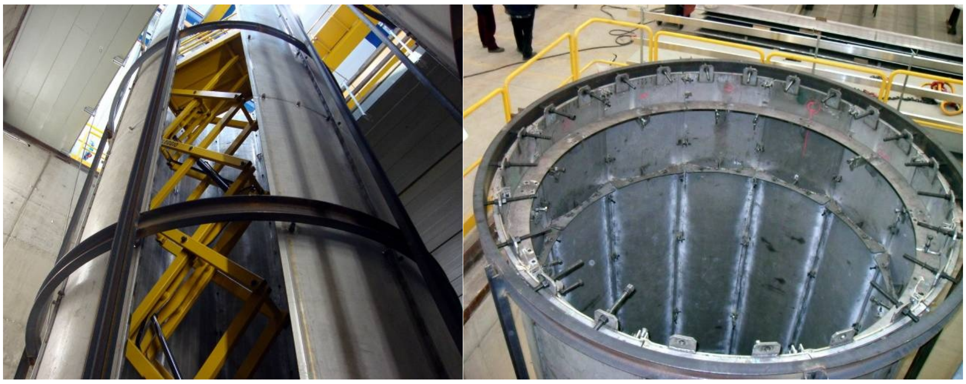
In this condition, nitriding and temper embrittlement could be a concern for the reliability of the pressure vessel.

To avoid any future problem, the modification have to guarantee a maximum metal temperature of the pressure vessel inner surface below 300°C in operation with a peak not over 400°C in case of shutdown without cold flushing.

The contract, which included the design of the modification and the supply of the new internals, had a tight schedule that required the supply of the material within 8 months from the contract award.

The timeframe was quite tight also considering that it was the first application of the concept.

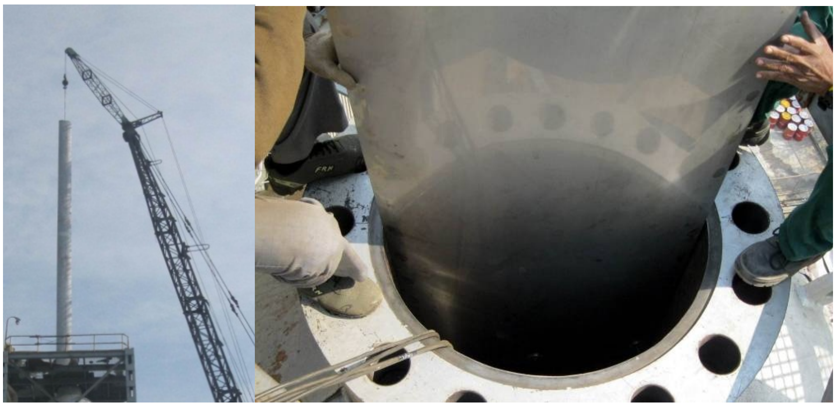
Anyway its experience in revamping works, where delivery and installation time is essential, helped Casale to meet such a close delivery. Some phase of the preassembly is shown in picture 1



Picture 1: Converter Internals assembly in workshop

Whereas the installation of the first set of internals took longer than foreseen, due to the need to fine tune the installation process and improve field organization, the subsequent identical set of internals was installed within 4 weeks.

Some picture of the modules insertion and installation is shown in picture 2 and 3.



Picture 2: Converter modules insertion in the vessel

After the additional converters were put in operation, the performed test run demonstrated that the new internals exceeded the expected and guaranteed performance from a process point of view.

The metal temperature were far lower than 300°C and the measure values ranged from 220°C to 260°C, having a flush gas temperature at about 220°C and an inlet gas at about 370°C.

Picture 3: Converter modules installation inside the vessel

6. CONCLUSION

In the ammonia industry there are a certain number of synthesis converters that are characterized by the absence of cooling of their pressure vessel. These converters therefore have their high pressure vessel operating at the reaction temperature, normally the inlet beds temperature.

Some of these converters are known for having developed problems in the pressure vessel due to the high operating temperature in presence of hydrogen and ammonia, where the combined action of these three critical factors has led to the development of cracks.

AMMONIA CASALE has developed, and applied, a system to transform hot walled partial opening converters into cold wall. The system consist in building "in situ" an insulated cartridge wall in modules, that separates the pressure vessel from the catalyst beds environment, allowing the creation of an annulus that is utilized for flushing the vessel inner wall with colder gas.

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