Safety and Reliability in Ammonia Synthesis Converters

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Ammonia synthesis converters are key items in ammonia plants. Their reliability is essential, as a plant cannot run if the converter is down. Since their performance has a significant impact on the overall plant energy consumption, they also have to operate efficiently. In addition, the ammonia synthesis converter is the reactor with the longest run between catalyst changes, and therefore, they must run for 10-15 years without the eventuality of repairs or inspections. These units have also an impact on the safety of plants, as they are subject to different metallurgical deterioration phenomena, and, as they have a quite complicated mechanical design with multiple catalyst beds. The catalyst replacements and inspections are difficult tasks also from a safety point of view. This paper presents these various aspects in detail, and the experience and solutions to problems achieved so far by Ammonia Casale S.A.

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Introduction

Ammonia synthesis converters are key items in ammonia plants. Their reliability is essential, as a plant cannot run if the converter is down. In addition, the ammonia synthesis converter is the reactor with the longest run between catalyst changes, since they must run for 10-15 years. Ammonia catalyst, once reduced, should not come in contact with oxygen since is highly pyrophoric. Therefore converters should operate between Catalyst changes without repairs or inspections. To achieve this result without any impact on the safety and reliability of plants, several aspects have to be considered as converters are subject to different metallurgical deterioration phenomena, and, as they have a complicated mechanical design with multiple catalyst beds. From a safety point of view, the catalyst replacements and inspections are critical as well.

1. Ammonia Synthesis Environment and Metallurgy

Due to the aggressive environment created by the combination of high pressure, high temperature and peculiar gas composition in which the converter operates, the first aspect to be considered in the design of the Ammonia synthesis converters, to ensure a high reliability, is the materials selection. This has to consider the conditions and the composition of the gas. The concurrence of Hydrogen related damages and Nitriding is typical of the Ammonia synthesis loop, particularly of the ammonia converter, where the highest temperatures and pressures are combined with high content of hydrogen and ammonia.

1.1. Hydrogen Influence

1.1.1. 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 (Fig. 1). 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 pressurised component.

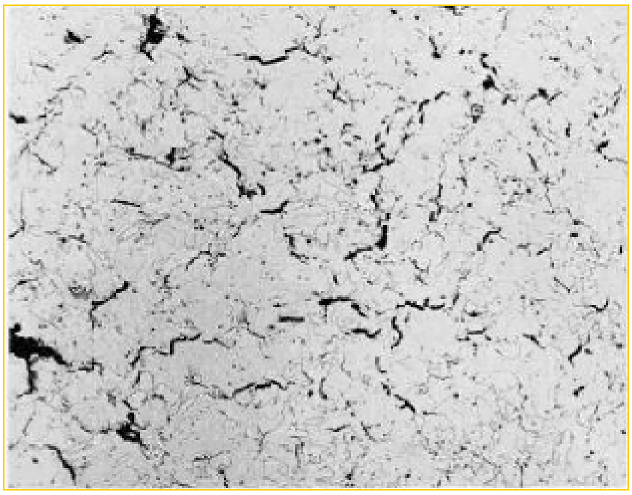

Fig. 1 - High Temperature Hydrogen Attack

1.1.2. Hydrogen Debonding

Equipment involving moderate to high temperatures and moderate to high hydrogen pressures, are commonly manufactured from low alloy (Cr-Mo) steels with an internal surface overlay of an austenitic material such as a 300 series stainless steel or Inconel 600.

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.

1.2. Nitrogen Influence

1.2.1. 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 (Fig. 2).

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.

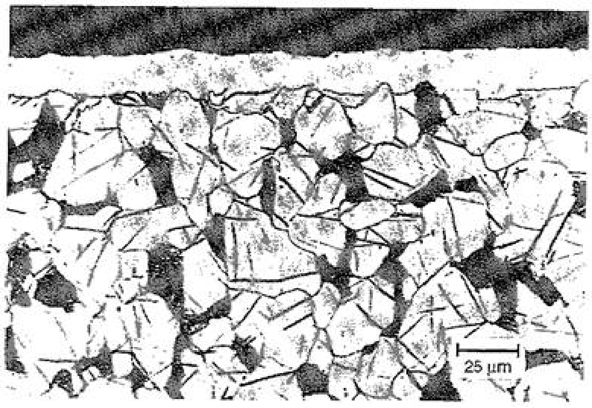

Fig. 2 - Example of Nitriding

2. Safety - Casale Design for Ammonia Synthesis Environment

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 the latter needs to be kept as low as possible. Casale philosophy consists in a suitable material selection and generally keeping the materials at a lower temperature through a suitable thermal insulation and/or gas flush. This concept allows intrinsically increasing the safety of high-pressure parts and is a fundamental starting point for the revamp of existing equipment.

2.1. Hydrogen Influence

2.1.1. High pressure parts

The pressure vessel usually has a much lower operating temperature than the internals, and, for economical reasons, ferritic materials such Carbon steel or Chrome-Moly steels are generally used, selected according to the API 941 standard.
Since the ferritic components of hot pressure parts (typically outlet nozzle and start-up nozzle) suffer from nitriding, a designer can consider to weld overlay the parts with austenitic materials or high nickel alloys.
However this solution does not protect against Hydrogen debonding. For this reason, Casale design considers to thermally insulate the hot vessel regions rather than cladding them.
The insulation consists of an Inconel liner filled with insulating materials (e.g. ceramic fiber).
The insulation is easily accessible, easy to inspect and simply replaceable.
In case of revamp, this kind of insulation can be fitted in existing pressure vessels without major modifications. This situation is the most critical, since the base material sometimes is not suitable to the new conditions or the experience has demonstrated that it is not totally free from Hydrogen attack at the operating condition: this is the case of ½ Mo steel operating above the present respective alloy steel 'Nelson' curve.
It is also important to avoid any weld on the existing pressure vessel in order not to additional affect the base material that may be damaged by Hydrogen or nitriding and to avoid the need of a new post weld heat treatment.
High-pressure heterogeneous welds of hot parts which are critical due to thermal stresses combined to hydrogen debonding are avoided, replacing them with special flanged connections

2.1.3. Case History –Bottom Fitting

Casale has experience of converters, designed by others, whose bottom fitting (outlet nozzle), in Low alloy steel with Inconel 600 weld overlay, suffered from cracks due to hydrogen debonding. In one case, during the revamp of the converter, Casale removed the cracks and installed insulation according to the above-mentioned design, solving permanently the problem (in service with since 1995). The resistance of the bottom fitting after the cracks removal by grinding had been checked by means of finite elements calculations (Fig. 3).

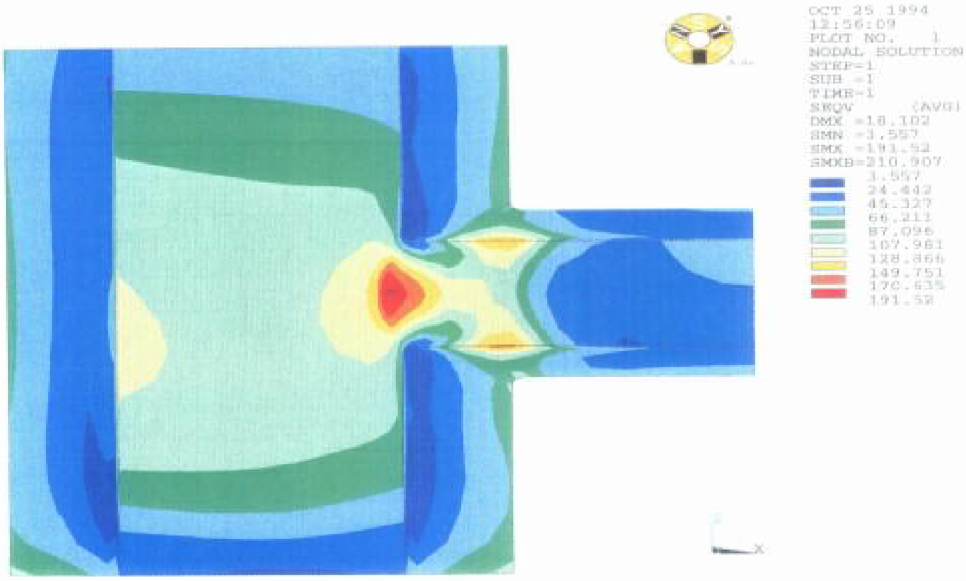

Fig. 3 - Bottom Fitting Thermal Stress Analysis Fig. 10

2.1.4. Case History – Hot Wall Pressure Vessel

Hot wall vessels have no cold gas flushing, so that they operate at the temperature and gas composition prevalent at the inlet of each bed. This design, adopted for example by C.F. Braun, has proven to be susceptible to damage, as demonstrated in many plants, since, after some years of operation the vessels show extensive damages due to the combined effect of hydrogen attack and nitriding. Casale has revamped or replaced some of these converters. The revamp introduced a fresh gas flush and a thermal barrier.

3. Internals Maintenance

While safe operation depends on the integrity of the high-pressure parts, entering the reactor during shutdowns to perform work or inspections presents a different set of hazard considerations. In fact the presence of ammonia or nitrogen purge to avoid catalyst oxidation represents poisonous conditions for the humans and the presence of hydrogen may involve risk of explosions while working inside the converter.

For this reason internals should be designed to be essentially maintenance free in between catalyst replacement.

Moreover, these potentially dangerous conditions can be overcome or minimized through an apposite design of the internals.

3.1. Safety - New Converters

To limit the potentially dangerous access to the converter during catalyst replacement and maintenance, Casale has developed specific design features, which therefore increase the safety of the converter.

3.1.1. Removable Baskets – Catalyst Drop Out

The advantage of the well-known full opening pressure vessel is easy access to the internals and the possibility to lift complete beds. These features should however be improved, so that installation or dismantling could be carried out without performing any welding or bolting inside the reactor. For this purpose Casale developed in the late 70s a basket design allowing installation and removal from a full opening pressure vessel without any mechanical work inside the reactor.
This is possible thanks to patented design features such as the reverse bottom basket (Fig. 4) where the edge of the basket bottom seals the inlet of the bed against the support ring on the cartridge through a special gasket.
The advantages of this design, apart from the higher catalyst volume available and the easier and faster catalyst replacement are evident in terms of safety.
In fact, it is possible to perform catalyst loading outside the pressure vessel, without any life support system, even in case the first bed is loaded with pre-reduced catalyst. After catalyst loading, the baskets can be lifted full of catalyst and inserted in the cartridge without entering the reactor.

3.1.2. Catalyst Drop Out

For an easy catalyst unloading, the bottom of each basket is provided with drop out nozzles: in this way it is possible to remove the basket from the cartridge and dump the spent catalyst in the proper area. Usually the third bed is integral with the cartridge, which is also provided with drop-out nozzles.

3.1.3. Other Features

There are other features that are particularly positive in case of partial opening pressure vessel.

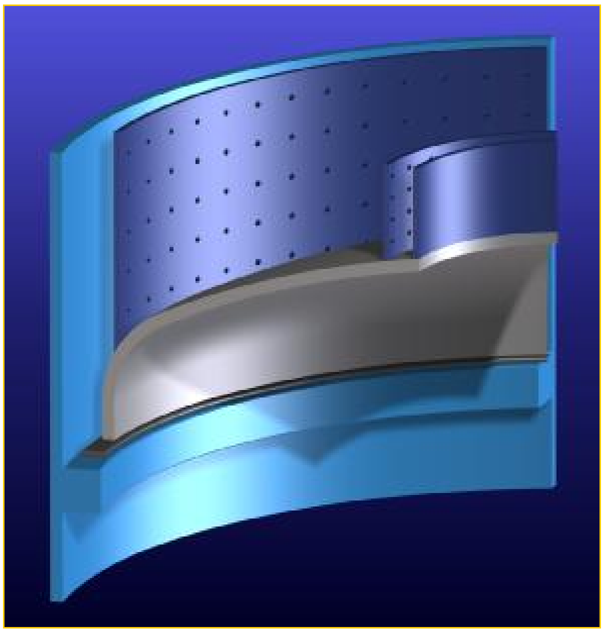

Fig. 4 - Reverse Bottom Basket

3.2. Revamping

The most critical condition concerning safety of personnel during turnaround of the converter occurs mainly for revamped equipment. For partial opening converters, additional safety steps are necessary during the catalyst replacement and revamp. Partial opening converters are provided
with a small manhole on the neck of the pressure vessel that allows access through the pressure vessel and the cartridge (Fig. 5). The access is further restricted during the work, as the manhole is partially engaged by hoses necessary for fresh air supply, electricity and or for introducing parts or loading the catalyst. Clearly in case of an emergency, a fast and easy access to / from the converter is necessary.

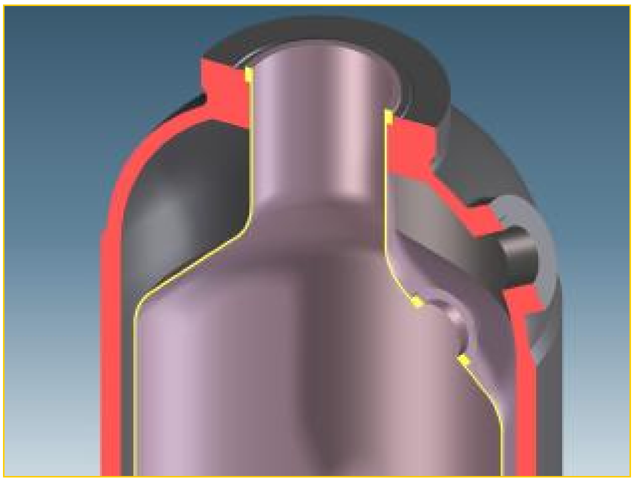

Fig. 5 - Manholes in Partial Opening Converters

3.2.1. Removable Exchangers / Interchangers

Welding in presence of catalyst requires a bulky life support system within the narrow space available inside the pressure vessel; grinding may be even worse due to difficult access to the parts and possibility of generating sparks in presence of hydrogen spots.
A Casale patented elastic ring seal (described in par. 4.2.1) allows to connect / disconnect the exchangers or interchangers from the outside, without performing any weld (nor bolting), or grinding during disassembly.
In the revamping of bottle shaped converters, this design applies for the upper gas in-gas out exchanger, in this way it is possible to use the exchanger shell as an easy and wide access to the converter. The lateral manhole can then be used only for auxiliaries and for the internal exchangers / interchangers, allowing the access through the relevant shell

3.2.2 Axial Radial Flow

The Axial Radial design allows simply bolted and light protection screens (Fig. 6) that can be easily handled by one person: this is fundamental for partial opening baskets, in order to facilitate the installation / dismantling works inside the converter during catalyst replacement. Entering the beds, maybe wearing the life support system, is easier and safer handling light segmental covers, compared to the heavier elements or even full top covers with narrow manhole typical of traditional radial beds.

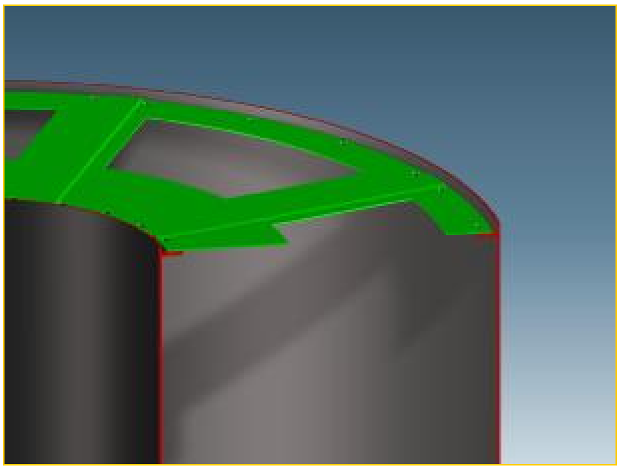

Fig. 6 - Axial Radial Flow Protection Screens

3.2.3 Drop out pipes from Bottom Bed in partial opening converters

For the bottom bed (usually 3rd bed), which has the highest catalyst volume, Casale design provides a catalyst drop-out. In this way discharging the main volume of catalyst becomes much quicker, and avoids the need of sucking the catalyst out with a crew of people inside the converter, working under nitrogen conditions.

4. Reliability

Ammonia synthesis converters are key items in ammonia plants. Their reliability is highly determined by the design of the converter internals.

4.1 Materials

Internals are the most exposed to the highest temperature and therefore the element where the combined effect of Hydrogen and ammonia is strongest.
The use of AISI 321 stainless steel for the internals of ammonia converters is preferable compared to other stainless steels since is stabilized with Titanium. In this way there is no risk of carbides precipitation (causing embrittlement of the materials in hydrogen service) that, on the contrary, is possible for grades 304 or 316.
For thin elements, where also the use of stainless steel is subject to failure since the thickness of the component is comparable to the nitrided layer, it is necessary to adopt inconel alloy 600 which is not susceptible to the problem. Also for the interchanger tubes working above a critical temperature (450 °C) selection of Inconel 600 is advised.
All the expansion joints bellows (also the 'cold' ones – in order to avoid possible mistakes) should be in Inconel alloy 600.

4.2 Design Features

4.2.1 Elastic Ring Seal

Another element facilitating installation / disassembly of the elements inside the reactor without entering it, is the elastic ring seal sliding joint (Fig. 7). This feature, patented by Casale, allows connections between internal elements of the converter (for instance replacing expansion joints) without welding or bolting.

Besides the already explained advantages in terms of safety, it also allows increasing the converter reliability.
In fact, the joint is sliding without any deformation or stress on the parts, hence the lifetime of the joint is practically unlimited. In stuffing boxes, a problem sometimes occurring is the erosion of the packing with consequent progressive increase of the leaks, while with the elastic ring seal the performance remains stable, even after years.
The first time this design was put in operation was in 1997, in two identical small ammonia converters in China.
After a couple of years, considering the satisfactory and constant performance of the sealing, we decided to use this design in all the ammonia converters manufactured by Casale. This sealing is normally used in all the locations of the converter where the seal is difficult to reach for installation / disassembly (e.g. removable baskets).
The seal, operating also at temperatures corresponding to the exit of the catalytic beds, requires a particular design, in order to keep the necessary elasticity of the sealing elements. The gaps and tolerances between sealing rings and relevant seatings are important as well.

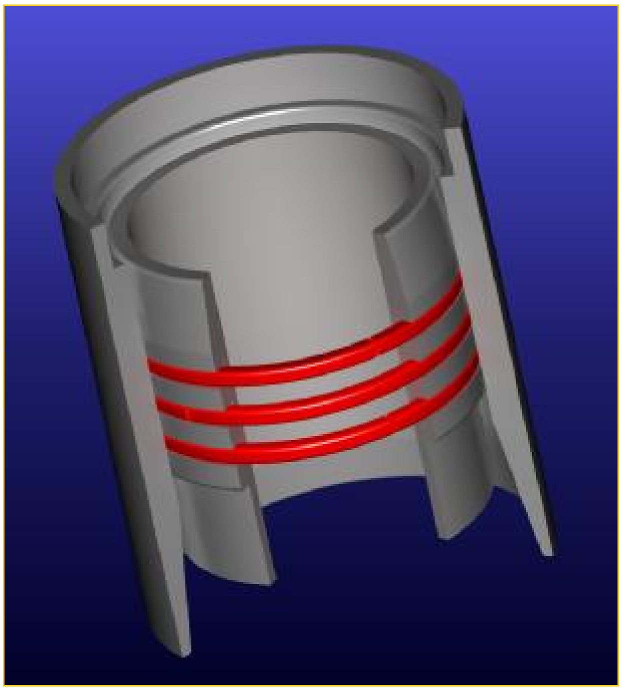

Fig. 7 - Elastic Ring Seal

4.2.2. Collectors – Slotted plates

Casale used for many years, for the collectors of ammonia converters, Inconel 600 wire mesh installed on embossed perforated plates.
In order to increase the reliability of our converter internals we started looking for alternatives to the wire mesh and it was also considered the possibility to adopt the commercial “V” wire screens design, which, however, as explained below, was not considered adequate.
For this reason, Casale developed the slotted plates walls (patented, Fig. 8). The slotted plates consist in stainless steel solid plates with cuts (slots) disposed in parallel rows. The geometry of the cuts allows an optimal flow of the gas although keeping the catalyst inside the bed.
The main advantages of slotted plates versus commercial screens are summarized below:

a. Slotted plates are solid, monolithic plates, while screens have lots of welds
b. Slotted plates panels can be easily welded each other or to solid plates in a reliable way, with homogeneous welding, while this is not the case of screens
c. Since slotted plates are monolithic, they have sufficient thickness to allow making them in the same material of the rest of the internals (AISI 321); therefore the welds to the rest of the internals are homogeneous. For most cases of inconel wire screens, the weld to the rest of the internals is dissimilar. This is a further factor reducing the reliability of the welds: thermal stresses + nitriding and hydrogen attack in dissimilar welds.

The easiness of welding makes the slotted plates particularly suitable for being welded inside the converter, as in case of refurbishment, during a normal turnaround for catalyst change, replacing the wire mesh with slotted plates, while the perforated plates remain in position.

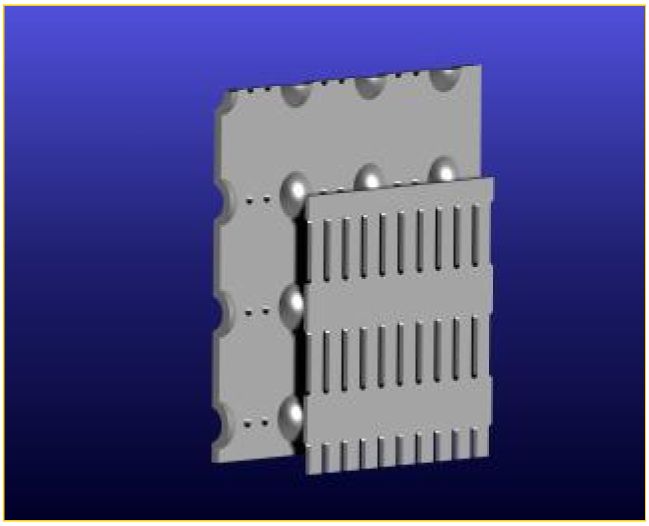

Fig. 8 - Slotted wall

4.2.3. Expansion joints

Vibration is a typical problem occurring in flexible hoses causing their failure.
A significant improvement on converter reliability can be achieved replacing flexible hoses connecting cartridge and pressure vessel in bottle shaped converters with expansion joints. Expansion joints are provided with internal sleeve: this feature allows reducing vibrations of the bellows also at high loads.

5.0 Conclusions

This paper has described how a proper design and materials selection can considerably increase the safety during turnaround and reliability during operation of the ammonia converter. The selection of this critical equipment has to consider not only the direct costs but also the possible unpredictable and sometimes huge costs caused by a lower reliability or safety. A key aspect in this selection is the consideration of the confidence in the proposed technical solutions confirmed by a decennial experience.
The described technical solutions are the fruit of Ammonia Casale's continuous investment aimed to improve the technology and reliability of its converters.