Severe Safety Problems during Ammonia Converter Optimization

One of the most favorite options to increase energy efficiency or plant capacity is the optimization of the synthesis converter internals. After implementing a new converter basket and catalyst in Ammonia plant 2 in 2005, the performance of the converter hardly improved and several severe process safety incidents occurred. In 2010 the plant was shut down to open the ammonia converter. The underlying reason for all the problems was insufficient sealing between the casing of the cold gas line and the bottom of the catalyst bed. This lack of sealing led to a catalyst loss from the first bed into the heat exchanger and gas compartment of the second bed, allowing the fluidized catalyst particles to damage the mesh of the second catalyst bed by abrasion.

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Introduction

In many parts of the world the most important factor to be considered when it comes to ammonia production costs is energy efficiency. As old installations from the 1970s and 1980s are still in operation there is a high interest in achieving improvements in energy efficiency and/or plant capacity. Furthermore, European energy and CO$_2$ emission policy drives plant revamps forward. According to BAT (Best Available Technology) energy consumption of 27.6 – 31.8 GJ/T (low heat value) must be achievable through plant revamps [1].

Optimization of converter internals and plant revamp

The most challenging fact about revamps is to obtain the best possible improvement on plant performance at minimum cost. As the syngas compressor and the high pressure equipment of the synthesis are very expensive to debottleneck, the optimization of the converter internals is one of the methods of choice to improve the performance of the synthesis section.

The converter basket operates in a very aggressive environment. Hydrogen attack and nitriding are severe problems in the synthesis loop, which especially occur on converter internals (basket) due to high temperature, high ammonia concentration and thin wall thickness [2]. Furthermore, to ensure an economical
optimum in the operation of the synthesis loop, the synthesis catalyst has to be replaced every 10 – 20 years because of activity loss. When the catalyst, and in many cases the basket, have to be renewed it opens a good opportunity for plant optimization at relatively low cost. Many licensors, like Ammonia Casale, Haldor Topsoe, KBR and Uhde, support these revamps and offer different designs to improve the efficiency of the converter. A state of the art converter design should optimize the following parameters: low operating pressure of the synthesis loop, high conversion rate and low pressure drop across the converter.

Experiences of Borealis Agrolinz Melamine

Synthesis Improvement Concept 2005

The Borealis Agrolinz Melamine (BAM) Ammonia plant 2 completed a revamp in 2005. This plant is a mixture of various technologies. The reforming section is 1968 vintage Humphreys & Glasgow. The CO₂ removal section was originally built 1941 and was revamped in 1988 by Uhde. The synthesis section was built in 1991 by Uhde.

Besides the installation of a new DCS, shut down system and the implementation of a process condensate stripper in the reforming section a part of the revamp scope was further improvement of the energy efficiency. As the synthesis catalyst had to be replaced after 14 years of service and the condition of the converter basket was not exactly known, it was decided to replace the existing 3 bed (1 radial bed and 2 axial beds) Uhde designed basket as well. As Ammonia plant 2 is operated with two electrically driven reciprocating compressors, equipped with valve float (Hydrocom), a decreased synthesis pressure would result in saving of electrical energy. The cooperation with Uhde was very good in previous projects and it was decided to go for the 3 bed radial Uhde design. The next important decision concerned the choice of the catalyst vendor. Sud-Chemie offered a new type of catalyst. Instead of iron oxide magnetite (Fe₃O₄), it uses Wustite Fe₁₋ₓOₓ (where x = 0.03 – 0.15) as the main catalyst component. As there were limited references BAM performed several tests such as crush strength and analysis of dust content. The results of the tests were encouraging, because compared with two magnetite based products the Wustite granules were harder and showed less dust content. Furthermore the guaranteed performance of the catalyst was very good, so it was decided to try AmoMax® 10 in all 3 beds.

Plant Performance after revamp

After replacing the converter basket and the catalyst the reduction process was started. The reduction lasted for more than one week because of several shut downs of the start-up heater. After these problems the synthesis of the plant could be operated at approximately 100 % of the previous design capacity. Nevertheless the expectations for the improved converter internals and the new catalyst were not met. About one year later the first of several problems occurred.

Incident 1: Vibration of Steelwork and Rupture of High Pressure Pipe Weldments

On October 30th 2006, the first incident in the synthesis section occurred. The plant was operating at half capacity and the second syngas compressor was started to increase the plant load to 100 %. At 66 % capacity the whole steel work of the synthesis section began to tremble. The outside operator in the compressor hall shifted a part of the recycle gas flow from one machine to the other. Immediately the vibrations vanished. After several minutes the noise of escaping gas was recognized by the operator. He stopped the synthesis section at once with the emergency stop.

At the top of the product flash vessel a mixture of ammonia and tail gas (nominally 50 vol%
hydrogen, 20 vol% nitrogen, 17 vol% ammonia, 9 vol% methane and 4 vol% argon) was released to the atmosphere. Luckily the gas did not ignite. Within two minutes the site fire brigade arrived and washed down the released ammonia clouds with hydro shields and water guns.

After the shutdown of the plant all weldments in the affected section were checked. Two cracks in the product line from the product cooler to the product flash vessel (see Figure 1, 3) and a crack in the tail gas line (see Figure 2, 3) were detected. The release of ammonia was approximately 250 kg (550 lbs).

**Figure 1** - Crack in weldment of the product line

**Figure 2** - Crack in the weldment of the tail gas line

**Figure 3** – synthesis loop:

1 converter, 2 steam generator, 3 refrigeration unit, 4 product separator, 5 product flash vessel, 6 syngas compressor, 7 recycle stage, 8 separator & pulsation dampener (pressure side) recycle stage

Clogged drain
**Incident Investigation**

During the incident investigation it was discovered that the drain valves of the separator and the pulsation dampener of the recycle gas line of syngas compressor B were blocked with oil degradation product. About 30% of the pulsation dampener on the pressure side (volume 680 l) and 25% of the separator (volume 142 l) were filled with oil. The separator was equipped with a level indicator and a level high sensor, but they did not indicate the level. The level indicator was glued with sludge, and the geometry of the high level sensor tap favoured the formation of a gas boulder, which inhibited contact with the oil (see Figure 4). Because of the filled separator and pulsation damper, the impulses from the reciprocating compressor were not absorbed but transferred to the recycle gas line and steelwork. At the same time several scaffolds for insulation work connected to the steelwork and changed the resonance frequency resulting in strong oscillations of the steelwork.

**Corrective Measures**

The following measures have been implemented and should avoid a reoccurrence of this incident: The time controlled drain of the oil separator was replaced with a manual procedure to drain the separator with a local push bottom. Additionally, the operator must observe the pressure increase and drop on a local manometer during the draining process to detect blocked drain pipes. The steelwork was equipped with a vibration pick up unit. The sensor was mounted in the section, where the highest oscillations were observed. The switch values were set at 20 mm/s (compressor bypass valve opens) and 25 mm/s (machine trip).

After cleaning of the separator, the damper and the drain, the plant was restarted.

**Incident 2: Fire in the Compressor House**

On October 29th 2008, (two days before incident 2) the syngas compressor V-1.601A was shut down for the following work:

A leaking shaft seal was repaired, the piston rings were replaced and an additional temperature indicator for the sealing was installed. No work on the pulsation damper was done, but the steam tracing on the bottom of the vessel was shut off. In the night shift of October 30th blockages of the on/off valve (PV 645) and the bypass-valve were recorded (see Figure 4).

*Figure 4 – Sketch of draining system*
On the morning of October 31st it was decided to remove the blockages at the drain line. A work permit for replacing the two valves (the on/off valve and the bypass valve) was issued for the instrument technician. The work permit indicated that the system was isolated and depressurised. The operator closed the hand valve on the bottom of the pulsation dampener. This valve is normally fully open and is used for process isolation only. The union of draining line at orifice upstream was then opened (see Figures 4, 5 and 6).

No noise of depressurising was recognized while opening the piping. The system remained tight for several minutes while the operator was waiting for the instrument technician. The operator recognized the heavy clogging so he started cleaning the line. Suddenly syngas was released out of the open drain line. The operator tried to close the valve even tighter by using the hand wheel, which loosened and fell off. At the same moment the released synthesis gas ignited and a huge flash fire (radius > 6m / 20ft.) occurred in the basement of the compressor hall. Luckily the operator could leave through an escape door in his vicinity with only minor burns on his back.

The nearby running purge gas line, still in operation, ruptured due to the heat of the flash fire and released approximately 1 m³ (260 gal US) of purge gas (nominally 58 vol% H₂, 21 vol% N₂, 9 vol% ammonia, 8 vol% methane, and 4 vol% argon). This release resulted in a deflagration (see Figure 7).

The fire escalated with the ignition of lubrication oil (approximately 3 m³ or 800 gal US) in the direct vicinity. Most of the oil was stored in steel tanks attached to an oil purification unit, which failed due to high temperature. The fire lasted for about two hours before it was finally extinguished. Due to the heat of the fire the roof construction of the compressor hall and the electrical installation were severely damaged (see Figure 8). Nevertheless after refurbishment of the less effected syngas compressor, the plant was restarted after six weeks.

**Incident Investigation**

The hand valve on the pulsation dampener is a Bolin needle valve (see Figure 9). These valves are considered to be very reliable at BAM, but it started leaking (synthesis gas) after the operator had opened the downstream tubing. The investigation of the dismantled valve showed, that the valve was not damaged but it was one turn open.
Figure 7 - Ruptured purge gas line

Figure 8 - Impact of the heat of the fire in the basement on the compressor hall
Heavy clogging was found inside the valve and the line. The analysis showed 96 % organic particles and 4 % iron.

Corrective Measures

The procedure for process isolation was reviewed and compared to Borealis Best Practise. The Borealis Best Practice is that if the double block and bleed cannot be applied in the field a mandatory risk assessment has to be done.

A technical study was started to investigate the source of the deposits and the consequential clogging problem on the drain of the pulsation damper.

A HAZOP study of the draining system was done. The study identified that the low pressure piping could be exposed to high pressure gas due to clogging downstream of the drain valve. To correct this hazard, the entire piping system was changed from low pressure to high pressure piping. At the same time as many bends and connections as possible were eliminated from the drain line to avoid possible deposits of machine oil degradation products. Drums with machine oil were removed out of the compressor halls.

Incident 3: Converter Performance Decrease

During the revamp of Ammonia plant 2 in 2005, the newly manufactured ammonia converter basket arrived just before the shut down. The inspection of the basket revealed, that a gap between cold gas line and bottom plate of the catalyst basket existed that made a loss of catalyst from the bed into the heat exchanger possible. An engineer of BAM decided to bridge the gap with a metal disk. The disk was not welded to the bottom plate of the heat exchanger but covered with catalyst mesh. To avoid a movement of the ring, the mesh was fixed with a tightening strap (see Figure 10). Because of severe time pressure Uhde was not informed about the problem to find another solution.

During reduction of the material the natural gas fired heater tripped seven times because of malfunctions of the start up heater furnace control. Therefore the reduction process took nearly 14 days. After one month a maximum capacity of approximately 540 MT/d (595 st/d) at a synthesis pressure of 180 bars (2610 psig) was reached, which was more or less comparable to the performance of the old basket and catalyst. During the remainder of 2005 the synthesis section of the plant experienced another 10 shut downs due to several reasons.
Although the increase of synthesis pressure was low in the beginning over the year 2007, 185 bars (2700 psig) were reached to maintain a capacity of 540 MT/d (595 st/d). In summer 2008 the plant load was decreased to approximately 520 MT/d (573 st/d) to limit the synthesis section pressure to a maximum of 187 bars (2710 psig).

As a result of the fire in November 2008 the plant had to be operated at half capacity until the end of March 2009. After the repair and the restart of the second syngas compressor, the plant could only be operated at 490 MT/d (540 st/d) at 187 bars (2710 psig). The reason for the worsening performance of the synthesis converter could not be explained.

An attempt to determine the temperature profile of the converter was made by analysing the shell with an infrared camera. No abnormal temperature differences could be detected. The data from the inter bed thermocouple suggested, that bed 1 was operating well (high delta T over the bed), whereas bed 3 showed no delta T over the bed.

To avoid further product loss it was decided to stop the plant in March 2010 for inspection of the converter internals. All facts suggested that there was a bypass in the converter internals and it was not a question of the catalyst. That was why AmoMax® 10 catalyst was ordered again, and the old Uhde basket (the one removed in 2005 revamp) was inspected and prepared for installation.

Incident Investigation

After opening the converter the reason for its bad performance was detected. More than half a meter of catalyst was missing (see Figure 11) from a large portion of bed 1. The catalyst, which had passed through the heat exchanger, was found in the gas inlet chamber of the second bed.

Figure 11 - Missing Catalyst in bed 1

The disk used to bridge the gap between catalyst bed 1 bottom steel plate and the cold gas line (original configuration see Figure 10) had lifted approximately 3 cm (1 inch) from the bottom plate. The mesh covering and holding the plate in place was partly torn.

Gravity and the gas flow carried catalyst particles into the heat exchanger and further to the gas inlet chamber of the second bed. Catalyst was fluidised in the inlet gas chamber and lead to abrasion damage of the mesh. The location of the damage is marked on Figure 12. Parts of the mesh were completely destroyed (see Figure 13). The damaged mesh on bed 2 allowed about 10 cm (5 inches) of catalyst in bed 2 to flow into the gas chamber between beds 1 and 2.

Although not formerly proven, the most likely cause for the movement of the metal plate is the difference in thermal expansion of the cold gas line and catalyst bed bottom steel plate. Once the gap was open, catalyst particles kept the gap open.

Corrective Measures

The old catalyst basket was reinstalled and filled with AmoMax® 10 catalyst. After restart of the plant and reduction of the catalyst, the performance of the synthesis loop was quite surprising. The synthesis pressure dropped to 168 bars (2435 psig) at a plant capacity of more
than 550 MT/d (606 st/d). In order to increase production capacity further syngas from the methanator of Ammonia plant 1 has been transferred to the syngas compressors of plant 2.

The performance of the synthesis loop is now more than 600 MT/d (660 st/d) at a pressure of 173 bars (2510 psig). After 14 months of operations no signs of increasing synthesis pressure or decreasing performance (load, temperature profile and ammonia content) have been observed.

**Root cause analysis / Discussion**

The energy efficiency improvement using a 3 bed radial design converter basket failed in this case, because the seal between catalyst bed and cold gas line could not be designed efficiently by BAM to avoid the failure. As a consequence catalyst poured down into the heat exchanger and the gas chamber between bed 1 and 2, and the converter showed poor performance.

The fluidized catalyst particles led to abrasion of metal and created catalyst and metal dust. This dust was carried along with the recycle gas to the recycle stage, where catalyst and metal particles from the converter internals led to a high wear on the piston rings. The wear on the piston rings led to the formation of oil sludge, which blocked the drain of the compressor. As a consequence severe safety relevant incidents occurred in the plant.

After exchanging the converter internals back to the old design the plant has been able to be operated very smoothly at high capacity for more than 15 months. Neither vibrations nor blockage of the compressor’s recycle stage drain have been observed.

Several failures of converter internals are described in literature [3, 4], although the impacts to the plants were different. In the case
of BAM the oil lubricated recycle stages of the reciprocating compressors increased the safety relevance of the underlying problem in the converter.

The impact of the mechanical forces on the converter internals is described by Thomsen [5]. According to this publication rapid increase in temperature puts very large forces on the converter internals. During heating the outer diameter of the bed and the centre pipe are expanding. On the other hand the cold gas line, which is in operation during the reduction of the catalyst, remains cold and does not expand, resulting in sideward stress on the line. Furthermore the outer wall and the centre pipe of the converter expand vertically due to the temperature increase, whereas the temperature difference in the cold gas line does result in contraction. The result of the differences in expansion between the hot components and the cold components was the torn mesh and the lifted sealing disk. A better seal, such as a stuffing box, would have increased the reliability and is also part of the new design of Uhde.

**Conclusion**

This paper demonstrates the necessity to manage even very small technical details.

In an effort to increase the plant’s efficiency a small detail caused several years of trouble and two very serious safety incidents. In the end the previous configuration of the converter internals was installed again.

The project finally was a success as the synthesis section can be operated far above design capacity at a comparatively very low synthesis pressure just by catalyst optimization. In our case this results in savings of more than a million Euros per year.

Beside the technical lesson, our organization realized that, when you lack number and competence of experienced engineers, it is better to go for turn key projects with a contractor where ever possible. BAM decided to increase the number of technical specialists in the organisation, even though it takes many years to regain technical competence in a bigger organisation.

**References**


