

IFA Technical Conference

**Beijing, China
20-23 April 2004**

CONSERVING ENERGY WHILE PROTECTING THE ENVIRONMENT

Jahangir Waheed and Aneeza Qazi
Engro Chemicals, Pakistan

1. ABSTRACT

Hydrolyzer and stripper are employed at various ammonia-urea complexes to treat contaminated condensates consisting of seal tank water, seal and flushing water of carbamate and ammonia pumps, and ammonia unit waste stream from CO₂ regenerator overhead condenser system. Steam is used for hydrolyzing as well as stripping off NH₃ from the hydrolyzed condensate. The use of this steam on urea unit is not uncommon but utilizing it on ammonia unit, especially as process steam, has been a skeptical speculation based on the fact that ammonia unit houses catalytic systems, very sensitive to contaminated streams. In addition to contaminants like chlorides and sulphates, presence of ammonia in this steam is also undesirable for the downstream system.

However, the incentive for this utilization is large, based on tremendous amount of energy saving. Such an incentive was taken back in 1998 when this steam was taken as process steam. However, due to unavailability of any sensitive detection equipment, Low Temperature Shift converter catalyst was de-activated before its predicted life and the steam was then off-lined. This highlighted the fact that if hydrolyzer stripper steam is to be utilized as part of ammonia unit process steam, careful monitoring and checks of sensitive nature will have to be conducted because although the incentive is high, the risks involved are also tremendous.

Availability of Ion chromatography, capable of detecting presence of ions in parts per billion, and careful periodic monitoring of reactor profiles has resulted in utilization of hydrolyzer/ stripper steam as process steam on ammonia unit again, minimizing hazard to the downstream catalysts and resulting in saving \$ 0.55 million/year.

2. HISTORY OF ENGRO CHEMICALS:

Engro's ammonia /urea site was established in 1968 as Esso Pakistan Fertilizer Company Limited with an annual urea production capacity of 173,000 tons and a local market share of 80 %. The company was later re-named Exxon Chemical Pakistan Limited (ECPL). By 1988, Exxon Chemical had attained an annual urea production capacity of

Received 10 January 2004 for presentation at the 2004 IFA Technical Conference, 20-23 April, Beijing, China

E-mail: jwaheed@engro.com

268,000 tons through a series of de-bottlenecking steps over the years. However, the continuous addition of large capacity plants by competitors had eroded company's market share to only 15%.

In this context, ECPL carried out an unprecedented relocation of mothballed ammonia and urea plants in 1992. The ammonia unit was relocated from Pascagoula, Mississippi, USA, while the urea unit was relocated from Billingham, UK. The relocation occurred after, as part of their global strategy, Exxon divested from Exxon Chemical Pakistan Limited and the company under the employee-led buy out was renamed as Engro Chemical Pakistan Limited. As a result of the commissioning of relocated plants in 1993, the site annual urea capacity increased to 600,000 tons per annum.

In 1998, the company undertook yet another debottlenecking step "ECES-850 (Engro Conservation & Expansion Step) to improve energy efficiency and increase plant capacity to 850 KT per annum urea. Further steps for service and capacity factor improvement, enabled to produce 950 KT in year 2003.

3. INTRODUCTION

Cost of steam generation on an ammonia plant is a typical area of concern, more so lately because of increased gas prices. Steam saving is, therefore, an area much concentrated upon and any step in this direction is of importance.

Utilization of hydrolyzer and stripper steam as ammonia process steam has had major impact on overall steam saving at the ammonia plant in Engro Chemical Pakistan Ltd.

Engro Chemical Pakistan Ltd operates 2700 MTPD urea plants. The waste water generation from these plants is treated in hydrolyzer and stripper unit where urea is hydrolyzed to give CO₂ and H₂O. In addition to the wastewater from urea units, the hydrolyzer stripper also treats waste stream from CO₂ regenerator overhead condenser system. The hydrolyzed stream is then taken to the stripper where NH₃ is stripped off using 6100 kN/m₂ (gauge) steam and the ammonia free condensate is sent to the lime-softening unit. The steam used for hydrolyzing comes from the stripper after stripping. This steam is usually vented or utilized at urea plants. However, at ECPL this has been used at ammonia unit as process steam.

The hydrolyzer treats two streams, seal water from urea unit and CO₂ condensate from ammonia unit. Total is 30 m³/hr of condensate containing 1.2% ammonia and 0.8% urea. About 9 MeT/hr of steam containing 5-6% ammonia was being vented in the atmosphere at a height of 30.5 m.

This paper covers the experience of introducing hydrolyzer stripper exit steam as process steam at ammonia unit that helped to improve the environment and site energy index. Initially, the activity failed due to fast deactivation and loss of Pre-reformer and LTS

catalyst life. Miscellaneous problem and the subsequent remedial actions taken to save the catalyst and Cu/Ni exchangers have been discussed in detail with actual data.

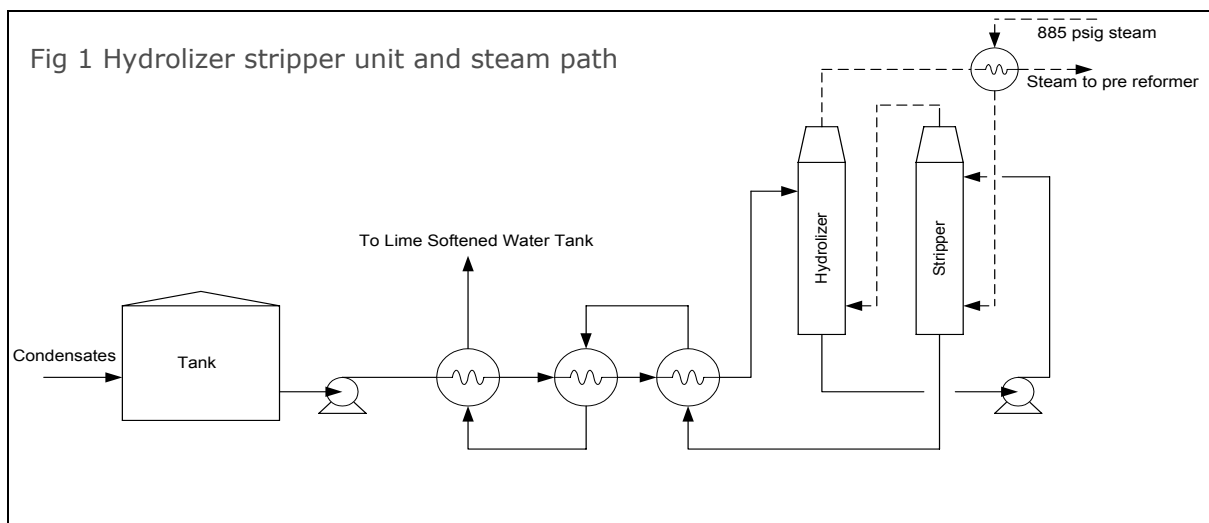


Fig.1 is the process flow diagram of hydrolyzer stripper unit and its steam path. The dotted lines show steam.

4. BENEFITS

Following benefits were gained after the implementation of this project.

- ➔ Utilization of hydrolyzer stripper steam as ammonia unit process steam improved the energy index of the site. Energy saving of 209 Joules per MeT of urea was realized.
- ➔ Localized pollution in the area due to venting of NH₃ rich steam at lower height was addressed after the project.
- ➔ Previously, when hydrolyzer stripper steam was being vented, cooling tower pH was observed to increase. After this project, this issue has been taken care of.

5. VULNERABILITIES ASSOCIATED WITH USE OF HYDROLYZER/ STRIPPER STEAM AS PROCESS STEAM

Use of hydrolyzer and stripper steam as process steam has several vulnerabilities associated with it that are explained in the following.

Presence of sulphates and chlorides

Hydrolyzer/ stripper steam has the possibility of containing chlorides and sulphates in it. Several cooling water exchangers are installed both on urea units and ammonia unit, in the process, for cooling the streams before knocking off condensate from them. These condensates are then treated in the hydrolyzer stripper unit. If the exchangers happen to

have any leakages, chlorides and sulphates escape into the system condensates. These ions can be detrimental to the process in the following ways:

- High sulphate level in the process steam reduces pre reformer catalyst life although to a lesser extent than hydrogen sulphide or organic sulphur compounds that may slip from the desulphurizer.
- Low temperature shift converter catalyst is sensitive to chloride poisoning. Unchecked exposure of the catalyst to chlorides can result in permanent loss of catalyst activity.

High Ammonia Levels in Process Condensate

Steam from hydrolyzer stripper has the potential of increasing ammonia level in the condensate from carbon dioxide stream as well as other process streams.

6. PREVIOUS EXPERIENCE WITH HYDROLYZER STRIPPER STEAM AS PROCESS STEAM

Hydrolyzer stripper steam was lined up with the process in 1998 for the first time. However, following problems arose due to which the steam was backed off and vented.

6.1 Poisoning of LTSC Catalyst

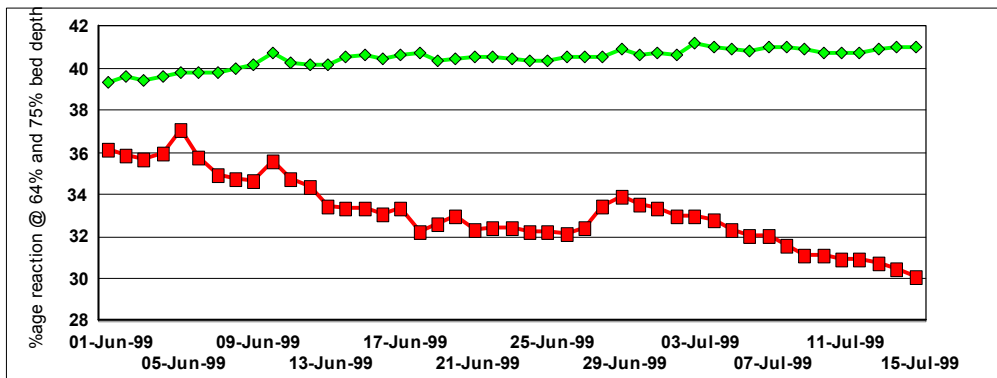
A cooling water exchanger for carbon dioxide was leaking due to which chlorides were creeping into the process condensate. This condensate was lined up to hydrolyzer stripper and hence chlorides were entering the process via hydrolyzer/ stripper steam. LTSC catalyst was exhausted before its due time.

LTSC reaction profile curves at various bed depths during the period of rapid deactivation are illustrated in Fig. 2. As illustrated in the figure reaction at 64% bed depth reduced by 7% during a period of less than a month when chlorides were entering with the system along with hydrolyzer stripper steam. At the same time reaction at 75% bed depth showed an increase indicating that reaction had shifted lower into the bed. The lower curve is percentage reaction at 64% bed depth while the upper curve is reaction at 75% bed depth.

6.2 Deactivation of Pre Reformer Catalyst

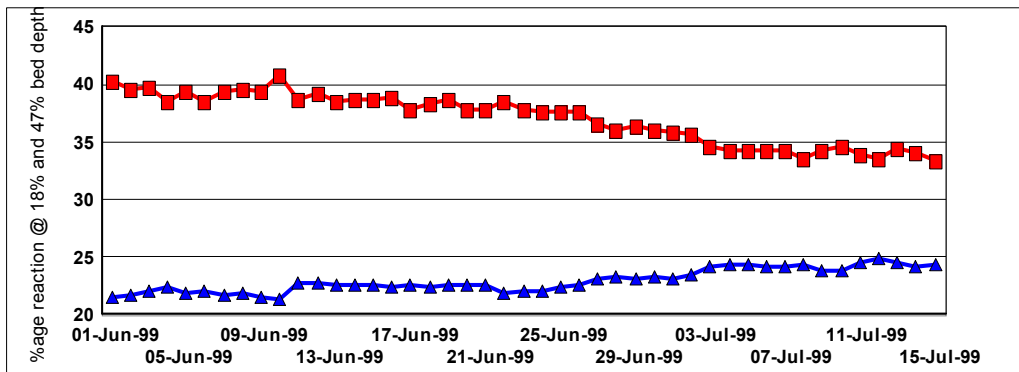
Faster deactivation of pre-reformer catalyst was also experienced during the time hydrolyzer stripper steam was lined up with the process. Although the catalyst did not exhaust at that time and was changed several months later, however, the rate of deactivation was more pronounced than the normal deactivation rate.

Fig 2



Reaction profiles of pre reformer at 18% and 47% bed depths during the time hydrolyzer stripper steam was lined up and sulphates were in the system due to exchanger leakage are shown in Fig 3.

Fig 3



As can be seen from the curves, reaction has dropped lower into the bed rapidly indicating fast deactivation during a period of about one month. Upper curve indicates reaction at 18% bed depth while lower curve indicates reaction at 47% bed depth.

6.3 Ammonia in CO₂ and Enhanced Corrosion of Cu-Ni Exchangers

Before carrying out this venture, it was generally believed that due to high temperature any ammonia present in the process is broken down into hydrogen and nitrogen in the secondary reformer. However, this did not happen in actual experience where increased ammonia levels were experienced in process condensates indicating high ammonia level in the process.

Increased ammonia level in process resulted in presence of ammonia in CO₂ stream going to the urea units. Urea units had Cu-Ni exchangers as inter stage coolers of the CO₂ compressor and increased ammonia caused corrosion of these exchangers. Corrosion was detected by observed leakage in these exchangers.

Based on these issues, hydrolyzer stripper steam was off-lined from the process.

Fig 4

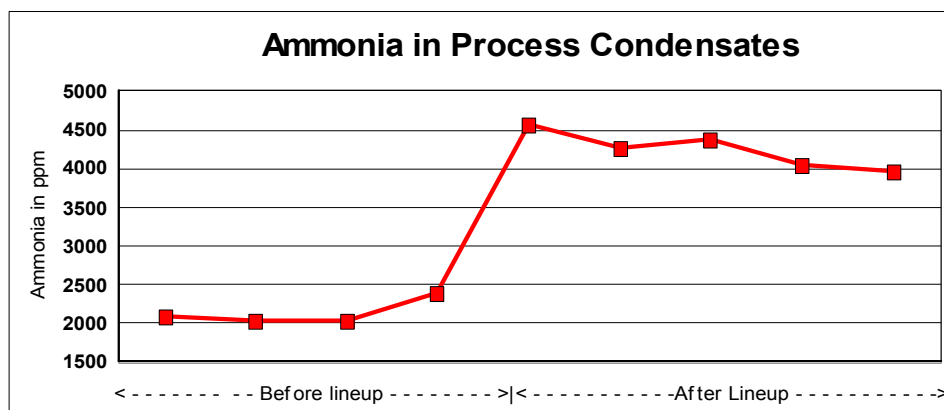


Fig 4 shows increase in ammonia in a process condensate knock out drum before and after lineup of hydrolyzer stripper steam to the process.

7. IMPROVEMENTS

The incentive for steam saving remained high and resulted in devising strategies to carry out the venture again but with improved monitoring techniques and controls.

On chromatographer

The availability of ion chromatographer solved the problem of deficiency in monitoring techniques. Ion chromatographer can detect presence of ions in levels as low as parts per billion. The chromatography is based on conductivity principle and provided with conductivity suppressor module. It can detect a number of ions in the form of conductivity peaks and can be used for the quantitative as well as qualitative measurement of various anions.

Previously, LTSC catalyst was poisoned due to unavailability of monitoring technique capable of measuring minuscule chloride and sulphate levels. Due to this blind spot, chlorides escaped unnoticed into the system and caused poisoning of LTSC. With the ion chromatographer and an efficient monitoring schedule in place, no unnoticed contaminants can enter the system. As soon as any contaminant beyond its acceptable level is detected, hydrolyzer stripper steam is off lined from the process and the problem is trouble-shooted and rectified. Steam is not lined up to the process again unless the contaminant levels return to their acceptable limits.

Replacement of Cu-Ni Exchangers

Replacement of Cu-Ni exchangers at urea plants with stainless steel ones has reduced the vulnerability associated with increase in ammonia levels.

8. MORE AREAS OF CONCERN

Possibility of Carbamate Formation

Introducing the hydrolyzer stripper steam into the system as process steam increases the overall ammonia level in the process condensates. Increased ammonia in the process stream, as discussed above, has the potential of being carried over with CO₂ to urea units. It has been experienced in two instances, specially during plant start up, that when waste water containing higher than normal operating concentration of ammonia has been lined up with hydrolyzer stripper, ammonia concentration has increased in hydrolyzer/ stripper steam with subsequent increase in ammonia concentration in CO₂. Presence of ammonia in CO₂ has resulted in carbamate formation in CO₂ compressor valves.

However, presence of ammonia alone cannot cause carbamate formation. Water should also be present in addition to favorable temperature and pressure. Following steps have been taken to check the formation of carbamate:

- Ensuring the absence of water in CO₂ stream. This means making sure no knock out drum after CO₂ compressor inter stage coolers is malfunctioning.
- Carrying out regular monitoring of process condensates at ammonia unit for presence of ammonia. Increased ammonia in process condensates is usually a harbinger of presence of ammonia in CO₂.
- Based on these close checks, increased ammonia in process streams is handled and hydrolyzer/ stripper steam off-lined from process in case of increase beyond acceptable levels.

9. CONCLUSION

Industrial units usually incur large expenses operating an environmental improvement project that are justified only by the improvement in environmental standards being practised by the industry. However, utilization of hydrolyzer stripper steam in the process has given a new dimension to this project as it has ended up causing savings worth millions of dollars in addition to being a necessity for effluent treatment. Another associated benefit has been elimination of localized air pollution. The essence of the whole project, however, lies in improved monitoring techniques and stringent monitoring standards without which it can cause damage to the process far exceeding its benefit. It is a perfect example of how good analysis and monitoring techniques can cause conservation of energy and improvement of energy indices