Unfortunate start-up 2010

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Abstract

Decreasing the production rate of ammonia plant after annual shutdown due to deactivation of the ammonia synthesis catalyst and increase the ammonia percentage in the recycle gas inlet ammonia converter.

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Decreasing the production rate of ammonia plant after annual shutdown due to deactivation of the ammonia synthesis catalyst and increase the ammonia percentage in the recycle gas inlet ammonia converter.

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Ammonia plant, Egypt,was established on 1991 ,UHDE design 1000 Mton/Day ,with three beds ammonia converter radial flow indirect cooling ,Catalyst type[**S6-10** red pre-reduced for upper bed ,**S6-10**oxidic for other beds] catalyst was replaced after 10 years on 2001 ,the basket was repaired due to some weld defect.

On 22/11/2010 plant was stopped for annual shutdown , loop was put under nitrogen blanket for checking the waste heat boiler (08E001) downstream ammonia converter ,also cleaning and plugging of the defected tubes in the loop water coolers (07E004 – 08E003).SYN loop in ammonia plant II contains waste heat boiler , gas-gas exchanger , gas cooler ,cold exchanger ,loop chillers , ammonia separator fig(5) .

During shut down the ammonia separator (08F001) was cleaned, some deposits were removed from the bottom of the separator which had been collected every overhaul due to weld defect in the converter basket. The deposits are mainly organic matter .and contain the following components:

Analyte	Result (%w/w)
Na_2O	0.77
MgO	0.01
CaO	0.08
Cr_2O	0.02
MnO	0.18
NiO	0.13
Fe_2O_3	41.5
ZnO	0.04
Al_2O_3	0.06

Table (1)

Fig (1) deposits from ammonia separator

Also the control valves of the converter were sent to check in work shop, blind was erected to prevent air to escape to the catalyst which is under nitrogen blanket , temperature of the catalyst has not been effected it was under observation.

On 10/12/2010

While loading up to normal load and ammonia level start to appear in ammonia separator (25%) , catalyst beds temperatures starts to increase by heat of reaction and start up heater was put out of operation suddenly these phenomena was appeared :-

- Decrease in converter bed temperatures.
- Increase in recycle pressure.
- Increase in recycle flow.
- Decrease in make-up flow.
- Decrease in hydrogen percentage in recycle.
- Decrease in suction temperature of recycle stage.

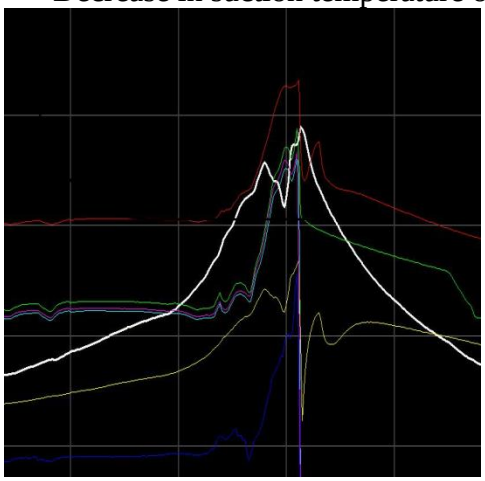

Fig (2) behavior of the syn loop pressure

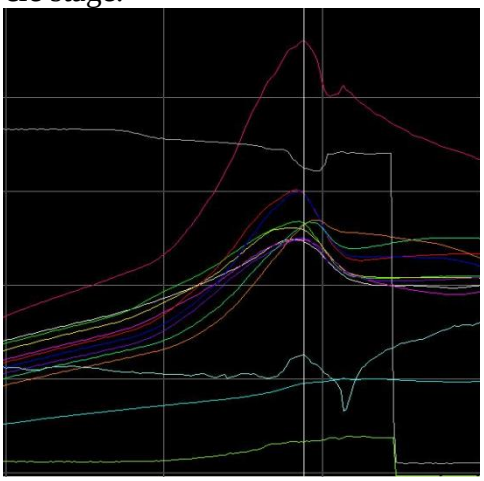

Fig (3) behavior of the converter temp

The syn-gas compressor was stopped after the anti-surge valves opened ,then the plant was restarted again and the phenomena was repeated, but the loop was controlled by decreasing the converter control valves opening ,the converter temperature start to stabilize on pressure of 155 bar (load 60%) ,the problem occur when increasing the recycle pressure.

It was suspected that the ammonia catalyst activity was decreased

Poisons.[2]

Temporary poisoning

Loss of activity from exposure to oxygen compounds is normally reversible provided that the partial pressure of the oxygenate is low and the period of exposure has been restricted to a few days. Under these circumstances the catalyst can normally be reactivated by following a reduction procedure.

Permanent poisoning

Exposure to oxygenates for several weeks normally results in permanent deactivation of the ammonia synthesis catalyst. Activity does not completely recover when pure synthesis gas is re-introduced or the catalyst is re-reduced. When the reduced catalyst is exposed to moderate partial pressures of water vapor, partial and reversible surface oxidation takes place.

Other compounds will affect the catalyst irreversibly. These poisons include sulphur, chlorine, arsenic and phosphorous. Sulphur remains on the catalyst surface as bulk iron sulphide. Catalysts in operating plants that have lost activity as a result of poisoning have been found to contain less than 0.1% sulphur.

Chlorine compounds are also severe poisons because the metal chlorides are relatively volatile and their transient formation can lead to irreversible sintering and hence loss of activity.

In addition to chemical poisoning of the iron surface, ammonia synthesis catalysts are also susceptible to loss of activity due to the physical covering of the active sites by an otherwise inert material. Compressor lubrication oil leaking into the process will

result in cracking of the hydrocarbons to form carbon, which will act as a physical barrier. This poisoning can be partly reversible provided that the problem is recognized quickly, however permanent damage sometimes occurs.

Several assumptions were made:

1. Life time of catalyst.
2. Contaminated oxygen in nitrogen.
3. Contaminated carbon monoxide or carbon dioxide.
4. Trouble in nitrogen battery because some nitrogen liquid enters the loop.
5. Nitrogen blanket affect the catalyst while cooling down.

Sample was taken from the make-up gas and the CO and CO_2 was in range also water contamination in ammonia product was found in range.

We suggest that due to the catalyst cooling down with nitrogen the shrinkage rate was fast that the nitrogen molecules were catch inside the catalyst particles.

So the catalyst bed temperature was adjusted by using:

1- Quench valves opening decreased.
2- Hydrogen percentage was kept high up to 70% (H_2:N_2 = 3.1).
3- Startup heater was used to left the inlet temperature up to 450 ^oC
4- Decrease the flow of purge (we found the purge flow decrease the H2 % increase)

On 14/12/2010

The recycle analysis shows an increase in ammonia percentage inlet to converter (4.5 %).

To decrease the ammonia content in recycle we improve the separation temperature from -9 ^oC to -14 ^oC, that improve the load to 65% but the ammonia in recycle stream remain unstable (3.5% - 6 %).

Plant was tripped again and loop was purged with syn-gas then restarted, the same result was found.

Increase Inlet ammonia concentration decrease conversion since the reaction rate decrease and adiabatic equilibrium conversion decrease.[1]

Ammonia in feed decrease the capability of produced ammonia to release from the catalyst surface so it lead to stoppage the ammonia formation reaction .

Assumptions were made:

1- Defect in separator (fig 4).
   - Partial blockage in the demister increases the space velocity of the recycle gas which leads to carry over of ammonia.
   - Down comer blockage will accumulate the collected ammonia in the demister which lead to increase ammonia in the recycle stream.

- Down comer partial blockage: the ammonia collected in the down comer will be affected by the separator level and the loop pressure ,so as we increase the pressure loop at constant level ammonia concentration increase in recycle stream.
- Defect in the inlet baffle plate will increase the ammonia concentration the recycle stream.

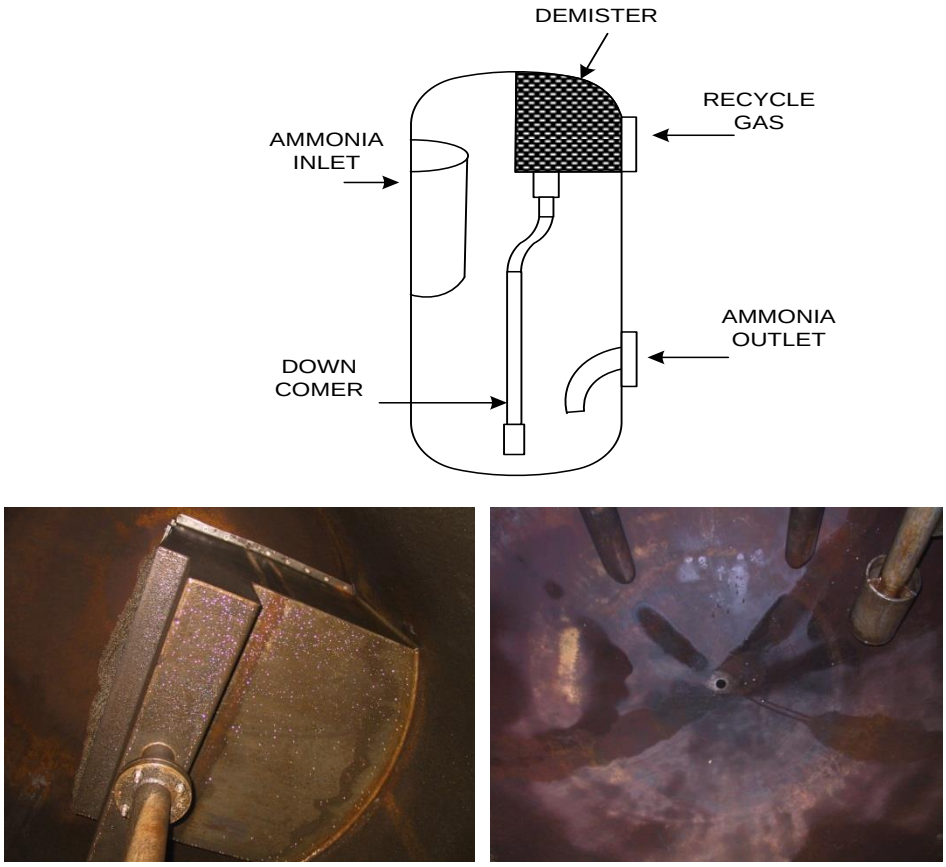

Fig (4) Ammonia Separator

2- Cold exchanger (08E004).

- The rich ammonia stream outlet converter exchange with the lean ammonia recycle stream outlet separator in the cold exchanger.
- The cold exchanger was avoided due to oscillation in ammonia percentage in recycle gas also its design specification that it has small pressure deference.

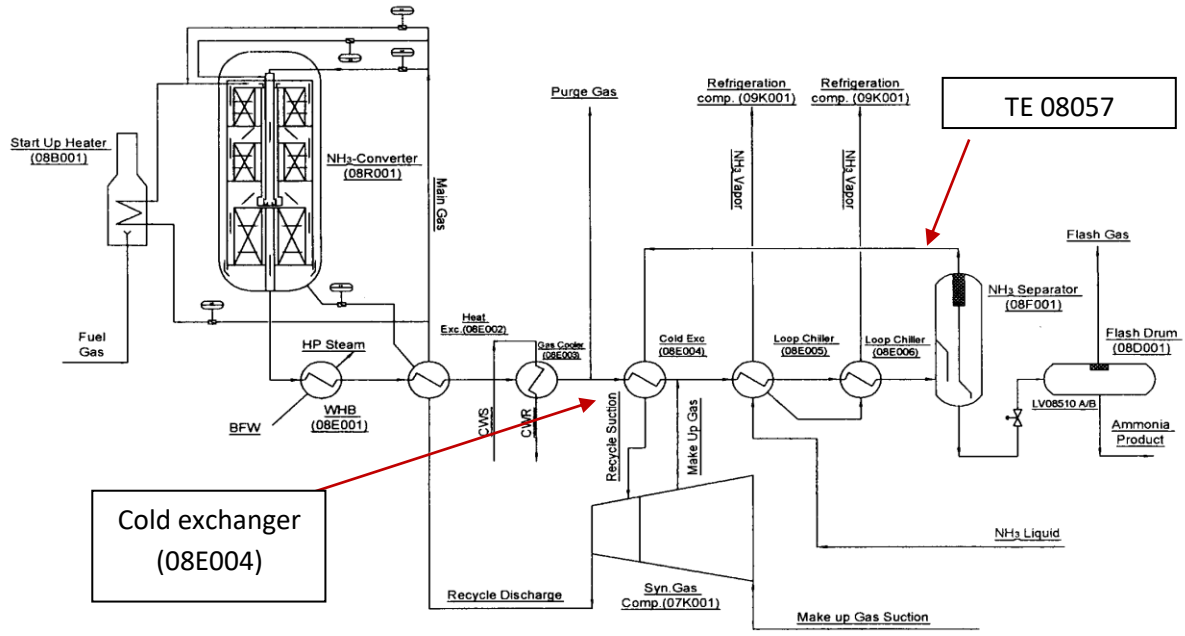

Fig (5) Ammonia syntheses loop

Suspicion was directed toward the ammonia separator, the separator level is indicated by two level indicator and they shows the same level.

Separator level was decreased from 45% to 34% then 26 % then 22% then 14% (through 10 days) that shows improvement in ammonia contamination in recycle, the load was increased to 90 % (fig 6)

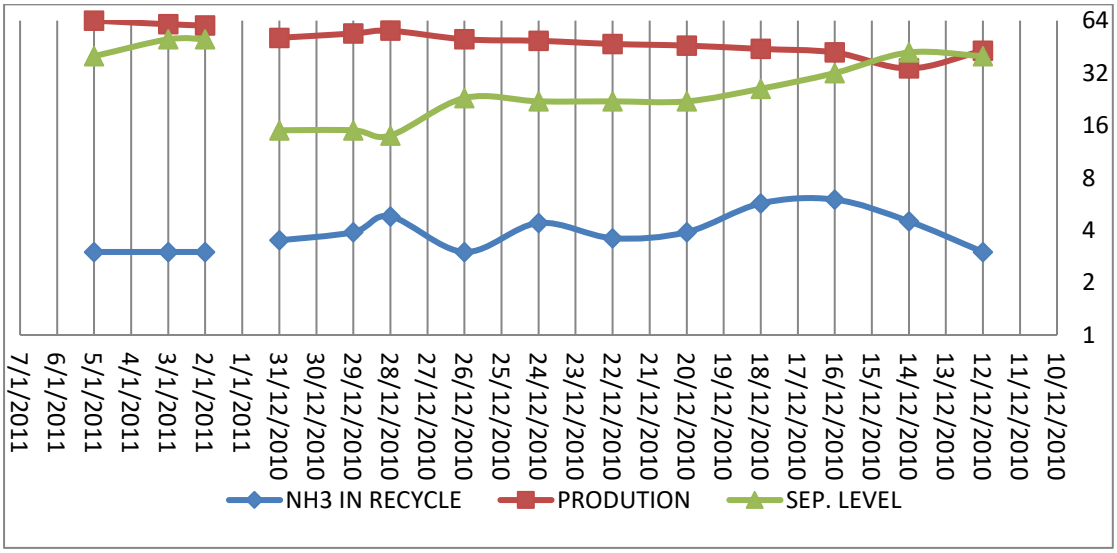

Fig (6) ammonia production versus ammonia % in recycle & separator level.

As decreasing the separator level:-

3- The pressure of the recycle stream decrease and the bed temperatures increase that allow opening the control valves and increasing flow enter the converter, also the anti-surge valves opening decrease.
4- The ammonia flash drum vessel pressure increased.
5- Flow of flash gas increased.

On 1/1/2011

Due to the slow improvement in the production rate and working under these abnormal circumstances, a decision was made to stop the back end and open the separator for inspection.

Procedure:

1- Depressurizing the loop was done followed by nitrogen purge.
2- The purge was take place for 12 hours.
3- The separator manhole was dismantled at 3% ammonia.
4- Nitrogen blanket was covered the converter catalyst.
5- The thermo element TE 08057 was replaced with nitrogen hose for purge.
6- Drain of the separator was dismantled.
7- Cleaning of the down comer and demister with demineralized water, dried with hot nitrogen then with rages.
8- Inspection and cleaning was done for the two level indicator and they were found ok.

Inspection:-

1- Partial blockage was found in the lower part of the down comer (with viscous green material which expected to be chemical compound escaped from the cleaning of the loop water coolers).
2- Slight blockage of the demister with catalyst dust.
3- There was no catalyst particles found in the separator.

Fig (6) viscous green material from the separator.

On 2/1/2011

Syn- loop was purged with syn-gas, then the back end start up goes on.

First we work on separator level at 50% and the production reached to 60M\hr after 2 days we decreased the separator level to 40% production reached to 65M\hr.

Temperatures of catalyst beds of the converter were increased by 10^{o}C due to end life of the catalyst.

Percentage of inert in loop decreased from 15.3 % to 14 % to increase the partial pressure of hydrogen to improve the synthesis reaction.

The following table contains the conditions of syntheses loop before and after the problem. (Table 2)

LOAD	%	100	60	87	100
PRODUCTION	Ton	1000	600	870	1000
MAKE-UP PRESSURE	Bar	170	160	166	173
RECYCLE PRESSURE	Bar	176	165	171	177
ΔP RECYCLE	Bar	9	7.9	8.5	10
MAKE-UP FLOW	Nm^3/hr	160 000			168000
RECYCLE FLOW	Nm^3/hr	435 000			435000
H_2 : N_2 RATIO	-	2.8	3.1	2.9	3
INERT	%	15	12	13	14
PURGE FLOW	Nm3/hr	6000	5500	6000	6000
ΔP CONVERTER	Bar	1.3			1.3
FIRST BED INLET TEMP	ºC	404	430	412	415
FIRST BED OUTLET TEMP	ºC	510	521	501	522
SECOND BED INLET TEMP	ºC	440	445	436	451
SECOND BED OUTLET TEMP	ºC	475	484	471	486
THIRD BED INLET TEMP	ºC	415	409	410	423
THIRD BED OUTLER TEMP	ºC	445	436	436	454
CONVERTER OUTLET TEMP	ºC	450	442	444	459
SEPARATION TEMP	ºC	-14	-10.6	-14	-14
SEPARATOR LEVEL	%	50	34	12	40
AMMONIA IN RECYCLE	%	3	3	3	3

Table (2) Ammonia plant conditions at different loads

Recommendation

- Cooling rate of the catalyst must be in normal range and thermal choke must be avoided.
- The catalyst beds temperatures profile must be monitored carefully during shut- down.
- After long shut down catalyst will be saturated with nitrogen it has to be purged with syn gas first before loading up.
- At the end of the catalyst life the temperature profile over the catalyst beds should be higher than normal operation also the inert percentage should be decreased in the recycle gas to increase the partial pressure of hydrogen to improve the reaction.
- Inspection and cleaning should be done for the mechanical parts of the ammonia separator every shutdown.
- The cracks in the converter basket must be maintained to prevent the catalyst from escaping to syntheses loop.

Conclusion

- The separation process which take place in the ammonia separator consider a major factor which affected on the performance of the synthesis loop since a small increase in ammonia percentage in recycle gas lead to stopped the synthesis reaction and decrease the conversion, production rate decrease also, these separation process affected by the loop pressure and separation temperature.
- Separation process in the ammonia separator affected by the ammonia level in the separator since high level lead to carry over for ammonia with the recycle gas and any mechanical damage for the separator internal parts.
- Blockage for the demister or the down comer lead to increase in ammonia percentage in recycles gas.
- At the end of catalyst life precautions must be taken especially during shut downs by keeping the catalyst under nitrogen blanket to prevent the catalyst from poisons so the temperature profile of the catalyst must be monitoring goodly during the shutdown.
- Loop boilers and steam preheaters normally run at a lower pressure than the loop so leaks lead to hydrogen/nitrogen in the steam rather than water on the synthesis catalyst. During shut-downs there is the potential for the driving force to be the other way resulting in deactivation/oxidation of the synthesis catalyst due to the ingress of water into the synthesis loop.

References

(1) Ammonia catalysis and manufacture by K.Aika, Nielsen.
(2) Ammonia synthesis theory and operation by Johnson matthey Group 2003 www.JmCatalysts.com