

CARRYOVER POTASSIUM AMIDE IN CRACKER AT HWP HAZIRA**A CASE STUDY****OPERATIONS GROUP, HWP HAZIRA**

The heavy water plant at Hazira is based on the monothermal hydrogen ammonia exchange process. The raw material for the process is synthesis gas (mixture of H₂:N₂ in the ratio of 3:1) available from the ammonia plants of KRIBHCO. Broadly various stages in the process are :

- (a) Boosting of synthesis gas
- (b) Drying and purification
- (c) Isotopic exchange and primary enrichment
- (d) Ammonia synthesis
- (e) Potassium amide catalyst recovery
- (f) Secondary enrichment
- (g) Heavy water production
- (h) Ammonia cracking

The main purpose of cracking unit is to convert the ammonia, rich in deuterium from the isotopic exchange towers into gas mixture of N₂, H₂, D₂, which is returned to main plant as reflux for isotopic exchange. The cracking of NH₃ is achieved in catalytic tubular furnace containing ceramic based iron catalyst. The cracking unit also consists of heat exchanger for heating of feed NH₃ by recovering the heat from process gas and for cooling the effluent. The liquid ammonia fed to cracker is made available from potassium amide catalyst recovery unit, where catalyst potassium amide is separated by distillation. Extreme care is taken to ensure that ammonia is totally free from potassium. Also the gas used for catalyst heating during start up, should be free of any possible amide contamination and should be pure & dry as moisture is a poison for the catalyst.

Main plant 'A' which was running normal on full load tripped at 0829 hrs. (29.3.1991) due to power failure. On power restoration, the plant was being restarted & the main cracker catalyst bed heating was on, with start up synthesis gas, preparatory to liquid feed. At 1755 hrs. there was again a partial power failure leading to tripping of 11KV machines (booster compressors K4102 A/B, refrigeration compressor K4101, 27K1A & the recycle compressors 20K41A/B), due to local electrical fault.

Main cracker 'A' catalyst bed heating was continued with 5 MT/hr flow of start up synthesis gas with venting at (cracker outlet) 12PCV61 'A' (vent control valve at 12T2 outlet) downstream of 12T2A (due to the stoppage of 20K41A). In the HP loop 11HCV38 remained closed (as its actuator had

become defective & was not functional) and so 12HCV01 (gas inlet valve to isotopic unit) remained open (There is an interlock that HCV1 will close only when HCV38 (isotopic bypass valve) is fully open, as closing of both valves is not permissible to avoid differential pressure build up across 11E1 & 12E1) gas/gas exchangers.

At 1800 hrs a sudden decrease in bed temperature of main cracker 'A' was observed. Gas flow was stopped at 1816 hrs. to arrest the downward trend of bed temperatures. At 1825 hrs. when gas flow was started the bed temperatures started falling again. At 1825 hrs. 12V4 'A' (buffer vessel) level was observed to rise rather sharply. The gas flow to main cracker 'A' was cut off at 1838 hrs as liquid carryover from 12V4 was doubted.

12V4 level continued to increase and got flooded by 1855 hrs. Start up gas line, on checking at drain points indicated amide and so it was inferred that KNH₂ liquid transfer occurred in to 12V4 and same had carried over to startup gas line.

Source of amide to 12V4 (Buffer vessel) :

Three possibilities existed for entry of amide into 12V4.

i) Back flow of amide from purifier 12A11/12 if check valve 12CP2 downstream of 12HCV1, not holding.

ii) Leakage of 12E4 or E5 (Gas/liquid double pipe exchangers in HP loop).

iii) Back flow from purifier to 12V4 by the normal liquid feed line if check valve was not holding.

Leakage of 12E4 or 12E5 was eliminated in the following way :

20K4 discharge circuit was isolated from 12A11/12 and T1 loop by closing 12HC01, 12LC30(12V4 level control valve), its isolation and bypass valves, and 12RS44. 12V4 level was brought down to minimum and pressure was brought down to 155 kg/cm²g. 12LCV33.1 & 33.2(bypass valves of 12E5) and its isolation valves were closed first and 12LCV54(level control valve) & 12HCV253(T1 liquid outlet shutdown valve) opened to 12T2, subjecting 12E4 only to full pressure of 195 kg/cm²g. No liquid build up confirmed that E4 was not leaking. 12LC33.1 & 33.2 were opened out after closing LCV54, 12HC253 & its isolation valves subjecting 12E4, E5 to full pressure. No rise in 12V4 level confirmed that 12E4/E5 were leak proof.

Also possibility of back flow of amide from liquid feed line to 12V4 was eliminated due to confirmation of tightness of valves in the line. So it was concluded that carryover was due to reverse flow from purifier (due to 12CP2 check valve not holding) with delta P existing, as HCV38 remained close. This was confirmed by a metallic piece lodged at the seat of check valve, when opened out for inspection.

The carried over amide both in the pipings and in the exchangers and the contaminated portion of the catalyst had to be thoroughly removed because the amide contaminated catalyst would disintegrate leading to higher resistance in flow through those tubes. That would in turn lead to overheating of those catalyst tubes and would seriously restrict the cracker load & therefore the plant load. Also amide acts as foulant for heat transfer by depositing on exchanger and tube surfaces leading to drastic reduction and improper heat transfer.

As long as liquid NH₃ is present in amide solution, its behaviour will be similar to liquid NH₃. However, after drying of NH₃, the residue is explosible at ambient and higher temperatures, especially in the presence of synthesis gas. Dry KNH₂ will react with oxygen leading to explosion as under.



Washing with copious amounts of water is the only way to remove the amide and eliminate the hazard.



Amide removal operation required three independent actions.

1. Removal of amide from the pipings.
2. Removal of amide from the feed/effluent heat exchanger E5101.
3. Removal of amide contaminated catalyst and charging of fresh catalyst in the catalyst tubes.

1. Removal of amide from pipings :

The check valve at the downstream of 12E3 (gas/liquid heat exchanger), in the cracked gas circuit, was removed and a fire hydrant nozzle was connected. With fire hydrant connection we could ensure a flow of 50 M³/hr of water and thereby could destroy the amide in the system very fast.

(a) Back flushing was done at 6" cut open pipe of E5101 (feed/effluent heat exchanger) outlet, feeding water at 12E3 outlet till all potassium was washed out. The cut pipe was blinded with a plate and then forward flushing was done through 12E2, keeping N2 atmosphere in 12V2.

(b) Flushing was done at liquid feed 4" line to E5101 filling 12V2, taking flow through FCV91 (liquid feed to cracker control valve).

(c) A temporary piping of BFW, was connected at 12FCV42 (startup synthesis gas flow control valve) and start up gas line was flushed from FCV42 to E5101 (feed effluent heat exchanger) inlet.

(d) Also the line from 20A1 (20K4 discharge activated carbon filter) to 12V4 was flushed with DM water.

(e) Superheater was washed by filling water from the nipple (welded with a valve) provided at the outlet of E5101 (earlier cracker tubes - inlet manifold end cover was cut out). Great care had to be exercised while filling to prevent entry of water into catalyst tubes, as water would have washed off the promoters from catalyst apart from oxidising it.

2. E5101 inlet/outlet (on the cracked gas path) showed amide deposits. Both shell & tube sides were thoroughly washed with copious amounts of water. In view of the intricate nature of fabrication and proneness to problems during maintenance, the exchanger was sent to L&T Works, Powai, who were the original manufacturer for inspection and rectification. The exchanger was overhauled and fitted back.

3. Cracker tubes :

All top covers were opened out. While pressure drop was observed to be marginally high 0.52 to 0.58 kg/cm² (as against 0.48 measured during the initial catalyst loading) in most of the tubes, tubes 35, 69 & 70 (farthest from superheater end) showed of more than 1.0 kg/cm². As a specimen to have idea of physical choking, tube No.35 which had maximum (hairpin as well as pigtail) was cut out, and were found to be fairly clean.

Layer of amide was seen on all the tubes over the alumina balls and tube No.35 & 69 had a very hard & thick layer.

To establish a criteria for the amount of catalyst to be removed from each tube, catalyst sample was collected from all the tubes at 0M, 1M, 2 Metre - depth and analysed

for K+. The fresh catalyst sample was analysed to have a K+ of 4.8 g/kg. Initial strategy adopted was to remove the catalyst till the catalyst analysis revealed K+ equivalent to fresh catalyst. However, it was observed that, while the top layer of catalyst were sticky and getting heated up when exposed to air, layers below 2 metres were dry, freely flowing, not getting heated up & yet K+ results were inconsistent. So the strategy was changed in that, catalyst removal was stopped as soon as catalyst tended to flow freely. Except tube No.35 where the entire tube was emptied out. Catalyst removal varied between 2&3 metres in all other tubes. The catalyst removal was done under inert atmosphere. Fresh catalyst & alumina balls were charged in all the tubes and the average was measured to be 0.52 kg/cm².

Inlet hairpins were individually blown with N₂ and across each of the hairpins was checked to confirm that there was no partial choke. The measured and average was 0.08 kg/cm². Also inspection with boroscope was done on each of the hairpin tubes to confirm that there was no choking of hairpins.

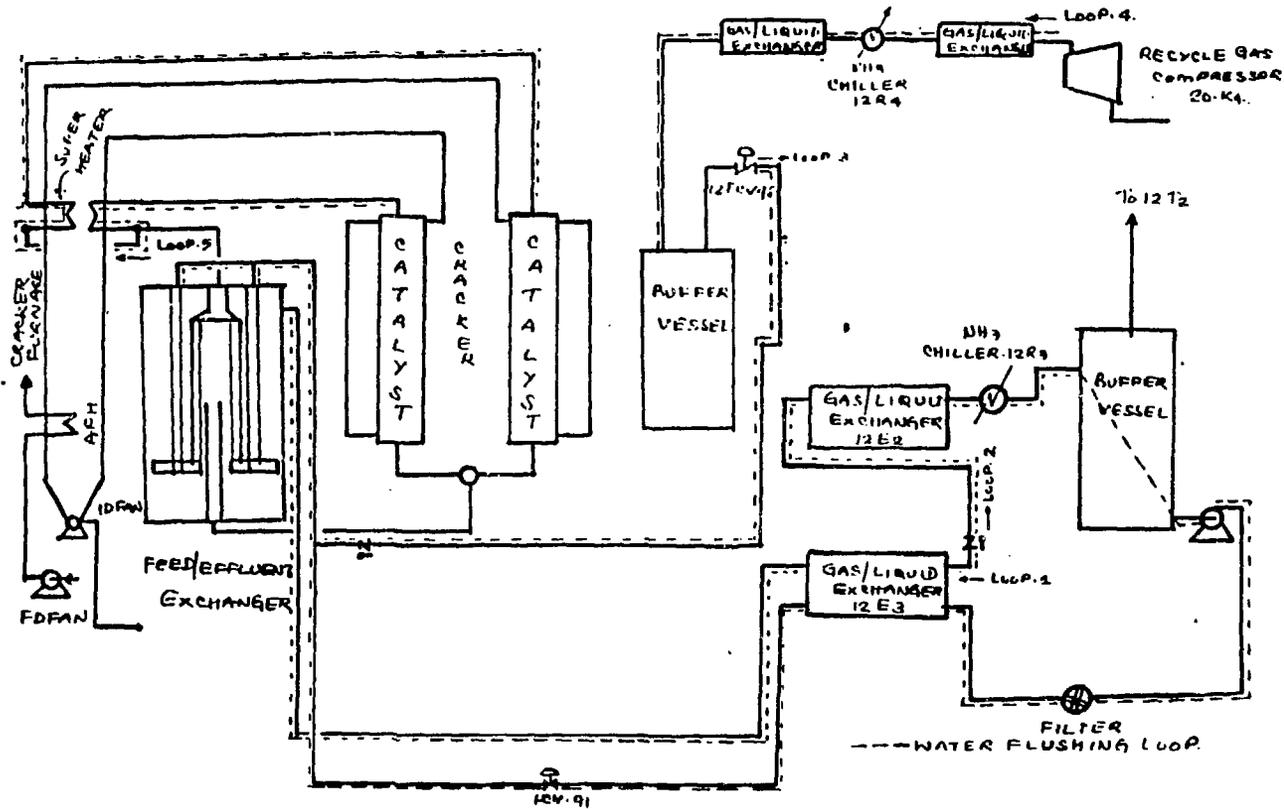
Catalyst tubes - outlet collector also had deposit of amide and so, were also washed with DM water.

After boxing up of the whole system, thorough purging with N₂ was done to remove the moisture. The top layer of catalyst was reduced in seven days and then put into normal operation. Cracker is now functioning well.

In order to prevent the recurrence of amide carryover to cracker tubes from start up gas line the following modifications have been done.

(a) The startup gas line tapping has been changed from 12V4 top to outlet of isotopic exchange units, ensuring flow of 'amide free gas' always in the positive direction so that malfunctioning of motorised valves and or not holding of check valves does not cause recurrence of amide carryover to cracker.

(b) 11HCV38 (isotopic unit bypass valve) has been rectified and the shutdown logic of 11HCV1 closing after the opening of 11HCV38 has been made functional. Logic has further been changed to keep 12HCV35 (outlet valve 12T1) open in the event of trips. With 12HCV35 remaining open, tower T1 top and bottom pressures equalises and the chances of back flow of ammonia/amide solution through 11HCV38 is totally ruled out.



FLUSHING ARRANGEMENT