

Operational Experience of De-hydrogen Reactor at CFCL

Chambal Fertilizers and Chemicals Limited is committed towards maintaining high standards for Environment, Health and Safety protection of employees, customers and community while conducting all its business and operations. It is in this endeavour steps have been taken for abatement of process safety hazards by adopting latest technology.

The phase-II urea plant safety hazard mitigation due to potential of explosive mixture formation has been made possible by installation of De-hydrogen Reactors. This paper describes the scenario of explosive gas mixture, potential fire and explosion risk, its mitigation with operation practices, installation of De-hydrogen Reactor and its operational experience and troubleshooting.

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CHAMBAL FERTILISERS & CHEMICALS Ltd (CFCL), the flagship company of Zuari-Chambal group is a leading nitrogenous fertiliser producer in the private sector. The CFCL complex at Gadepan, Kota has two independent Ammonia and Urea Plants with common offsite facilities. Phase-I plants based on Haldor Topsoe Steam Reforming Ammonia Technology and Snamprogetti Urea Technology were commissioned in Jan'94. Phase-II plants based on Kellogg Conventional Ammonia Technology and Toyo Engineering Corporation's ACES Urea Technology were commissioned in October 1999.

Post Bhopal tragedy period generated high safety awareness in community and the Government started responding by enacting newer statutory provisions for higher safety standards in industries. It is in this period significant improvements took place in plant safety with up-gradation and advancement of technology. CFCL right from inception adopted green technologies and took further initiatives to get certified for both ISO 14001 and OHSAS 18001 systems. The safety management systems in line with guidelines set by British Safety Council were adopted subsequently.

PHASE-II UREA PLANT

UREA-II PLANT IS THE ONLY PLANT IN THE country based on Toyo's state-of-the-art ACES process. ACES process is well known for its heat recovery and overall process efficiency. The plant has been running quite satisfactory since

commissioning. It has two parallel identical streams called Train-A and Train-B with ammonia receiving, prilling and Process Condensate Treatment section as common facility.

Synthesis section operating at 175 kg/cm²g consists of reactor, stripper (CO₂ stripping), 2 nos of carbamate condensers and a scrubber. The solution outlet from synthesis section goes to lower pressures for subsequent decompositions and recovery in MP section and LP section operating at 17 kg/cm²g and 2.5 kg/cm²g respectively. The outlet solution from LP section is concentrated in vacuum evaporators to achieve 99.7% urea solution for prilling.

THE EXPLOSION HAZARD IN UREA PROCESS

ADDING OXYGEN TO THE UREA PROCESS has proven to be an effective and reliable method to minimise corrosion of the stainless steel piping and equipments. In ACES process 0.5 V% oxygen is added with CO₂ feed. This oxygen is utilised for passivation of synthesis piping and equipments by forming protective layer. CO₂ containing 0.76% hydrogen is fed to synthesis section through the stripper. The oxygen, hydrogen and inerts, mixed together along with ammonia and CO₂ exits HP scrubber top and enter HP section. Finally the gaseous mixture of O₂, H₂ and inerts almost devoid of ammonia and CO₂ leaves washing column and goes to atmosphere via vent stack. Simplified process flow is shown in **Figure 1**.

It is established and proven that the gaseous mixture of O₂, H₂ and inert forms explosive mixture at certain range of composition. The risk associated with the possibility of explosion and subsequent large release of hazardous ammonia gas into the atmosphere calls for special attention in design and operation for safe production. The risk of explosion can be eliminated when mixed with large quantity of other gaseous components such as ammonia. In ACES process, gaseous mixture of O₂, H₂ and inert pose threat primarily at two locations. These are HP scrubber vapour space and washing column vapour exit up to vent stack.

EXPLOSION RISK IN HP SCRUBBER VAPOUR SPACE

IN NORMAL OPERATING CONDITION, THE gaseous mixture remains outside explosive range and does not pose any risk. This is represented by the triangular diagram, **Figure 2**. However there are certain deviations which can shift gaseous mixture composition into the explosive range. This situation arises when ammonia content of scrubber off gases are low as shown in the triangular diagram, **Figure 3**. These situations are described below :

- Excess condensation and absorption in scrubber: Condensation and absorption rate in scrubber depends on top temperature. If temperature is low, NH₃ gas absorption into recycle carbamate is greatly promoted and gaseous mixture composition may approach flammable limit. It is represented by the triangular diagram.
- During plant start-ups the composition

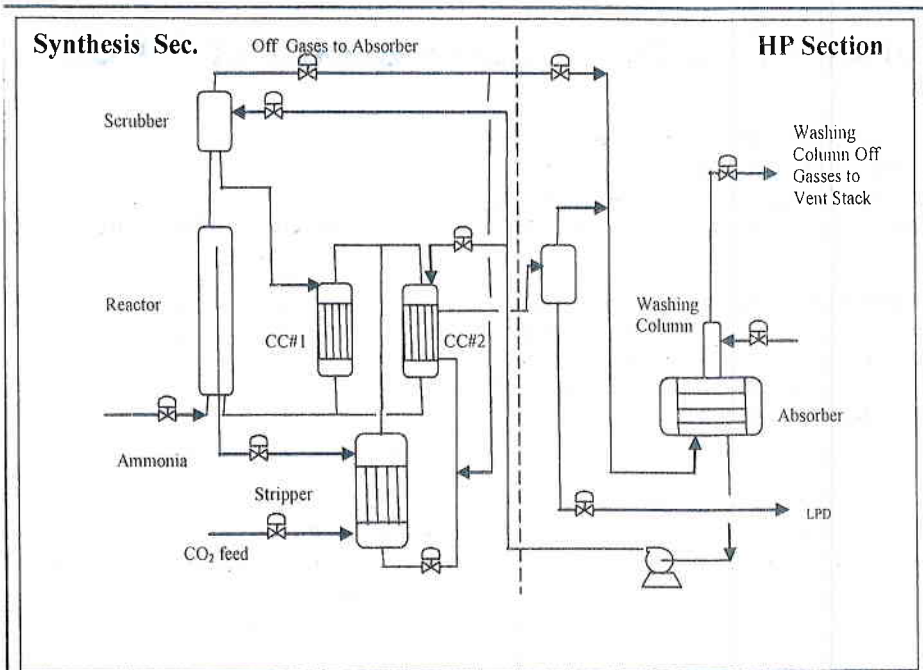


Figure 1 – Process flow diagram of ACES urea plant showing inerts flow route

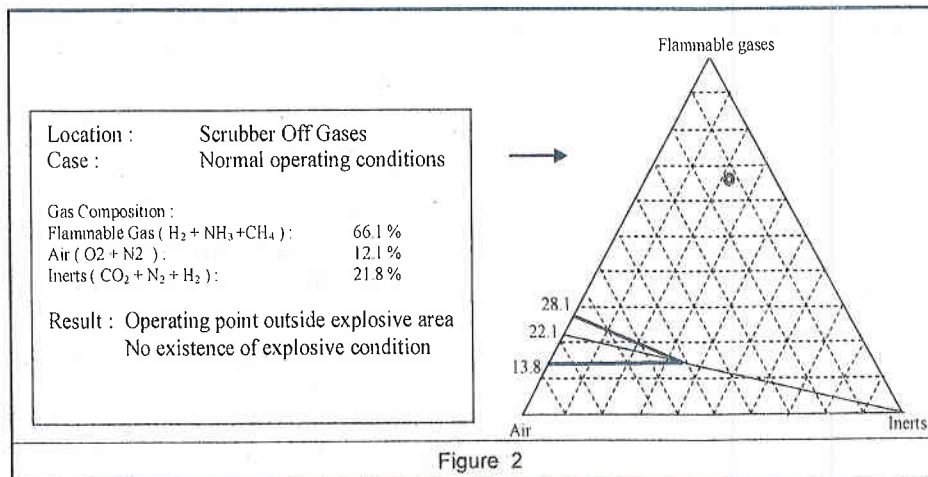


Figure 2

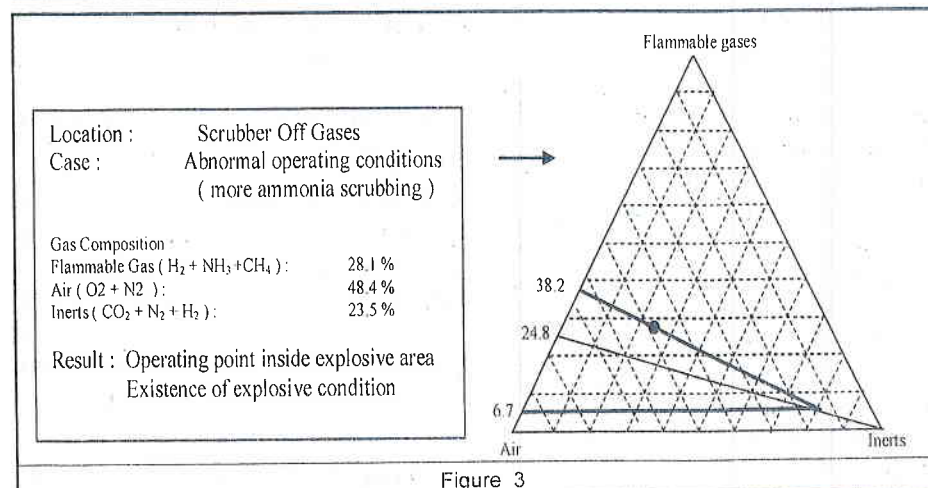


Figure 3

of gaseous mixture varies at every moment till the operation parameters are normal.

c. During plant shutdown and reactor hold up condition the gaseous mixture of O₂, H₂ and inert gets accumulated in the scrubber top. When synthesis section is flushed with water, ammonia gas is absorbed and this gaseous mixture approaches flammable range.

Recommended counter measures by the designer Toyo Engg. Corporation are :

- i. Maintain scrubber top temperature more than 145°C (design temperature is 170°C).
- ii. To eliminate the possibility of local condensation of the gas, it is required to keep scrubber top steam jacked charged.
- iii. Keep sufficient gas flow from reactor to scrubber which is achieved by maintaining reactor top temperature between 186°C to 190°C.
- iv. Maintain sufficient opening of scrubber pressure control valve, PV 1101 (>30%) to have sufficient gas flow so that continuously gasses are purged out in large quantity.
- v. During plant start-up add nitrogen with CO₂ feed for dilution of scrubber off gases. Also try to follow above steps i to iv to the extent possible.
- vi. During reactor hold up condition, always vent gases during flushing of scrubber top and keep steam jacket charged with a steam pressure of 10 kg/cm².

RISK OF FLAME IN WASHING COLUMN VENT LINE

THE GASEOUS MIXTURE LEAVING washing column and travelling up to vent stack exit at prilling tower top is always in the explosive range even under the normal operating conditions. This is represented by the triangular diagram, **Figure 4**. Following measures are taken to avoid fire:

- i. Downstream of washing column pressure control valves are provided with steam flushing connection for dilution of gaseous mixture.

ii. A flame arrestor is provided near to the exit point of vent stack to stop back travel of fire in case it happens.

iii. Later on nitrogen purging connection also provided in vent stack for addition dilution during lightening.

NEED FOR DE-HYDROGEN REACTOR

THOUGH STRICT OPERATION CONTROL practices are adopted to avoid explosive condition, some risk of forming explosive mixture cannot be ruled out as modern urea plants are designed to give maximum efficiency of ammonia/tonne urea. In line with its commitment for high standards of safety and continual improvement, CFCL management took a conscious decision to install De-hydrogen Reactor in both the streams of urea plant – II in the year 2004.

De-hydrogen reactor requires oxygen for burning of H_2 , which is supplied by additional air supply into CO_2 . Many options were considered to locate De-hydrogen Reactor and CO_2 Compressor 2nd stage discharge was opted to be the most optimum location as shown in **Figure 6**. The De-hydrogen reactor was designed, erected and commissioned by Toyo (India) on LSTK basis. The reactor was fabricated by M/s Phils Engineering and catalyst was procured from M/s Engelhard. Total project cost was Rs. 216 lakhs.

FEATURES OF DE-HYDROGEN REACTOR

DE-HYDROGEN REACTOR INSTALLED AT 2nd discharge of CO_2 compressor is designed to reduce H_2 from 0.76% to 100 ppm (max) in CO_2 .

The process of de-hydrogenation is carried out over a catalyst packed bed as per details given in **Table 1**. The packed bed top and bottom layer contain alumina balls of different size as shown in **Figure 7**. The flow of process gas is from top to bottom and design pressure drop across the reactor is 0.5 kg/cm². Outlet temperature depends upon H_2 concentration at the inlet because removal of hydrogen results in temperature rise due to exothermic reaction of H_2 burning. The allowable design temperature of reactor outlet is 250 °C.

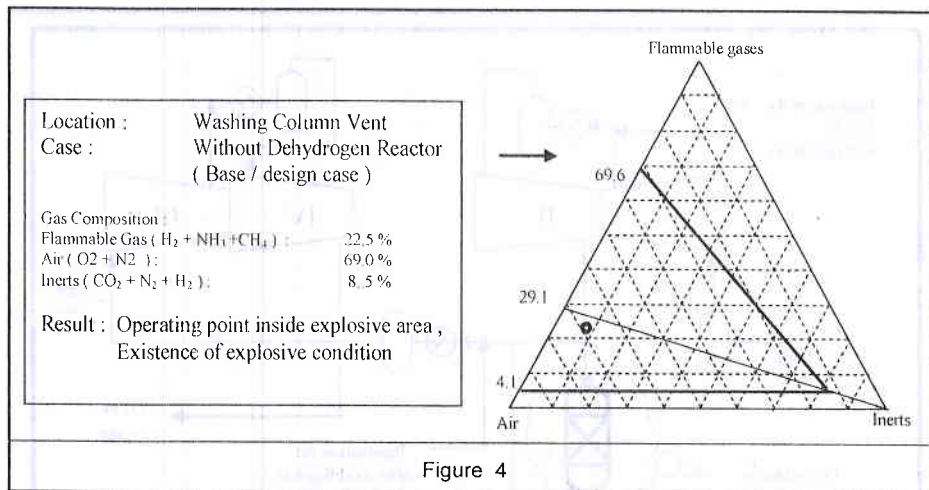


Figure 4

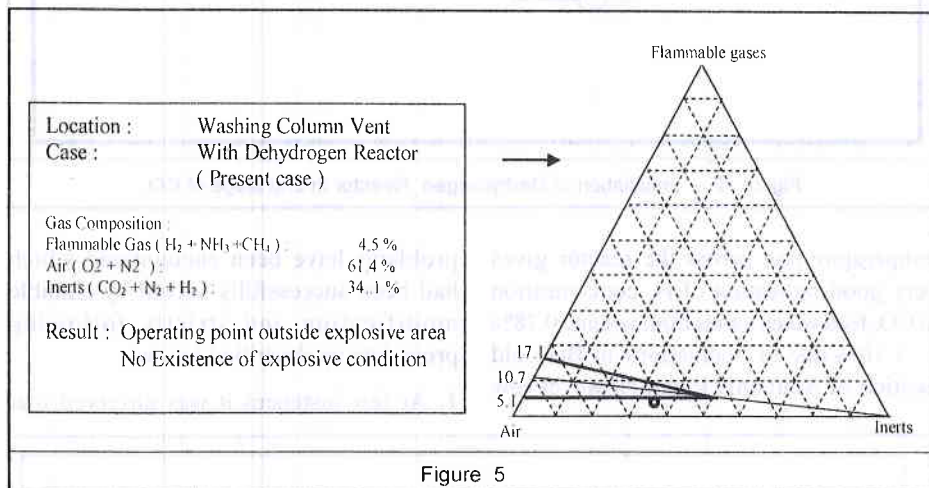


Figure 5

OPERATING EXPERIENCE

THE DE-HYDROGEN REACTORS WERE commissioned in both the trains of urea plant - II in May 2004. The operating experience of last two years plus is satisfactory. CO_2 received from ammonia plant containing about 0.8 % H_2 is getting removed quite effectively and H_2 content

at outlet of De-hydrogen Reactor is less than 100 ppm. The triangular diagram of gaseous mixture analysis of scrubber off gases and washing column vent gases are plotted on weekly basis. These diagrams give good indication of no explosive conditions and gaseous mixture at both locations has been found out of flammable range (**Figure 5**). The

Table 1	
Catalyst/type	0.3% Pt on Alumina Pellets / Deoxor, Code 4755
Pellets, shape/size	Cylindrical / 3.2 mm X 3.2 mm
Bulk density/quantity	1000 kg/m ³ / 1200 kg
Catalyst packing ht/dia	900 mm / 1300mm
Feed flow rate :	23996 Nm ³ /h
Feed Composition :	$CO_2 = 93.99\%$, $N_2 = 3.51\%$, $O_2 = 0.89\%$, $H_2 = 0.76\%$, $H_2O = 1.47\%$
H_2 removal capability	Less than 100 ppm H_2 at outlet
Pressure, operating/design:	21.8 kg/cm ² g / 36 kg/cm ² g.
Pressure drop :	0.5 kg/cm ²
Temp. operating in/out :	181 °C / 222 °C
Design temperature :	250 °C

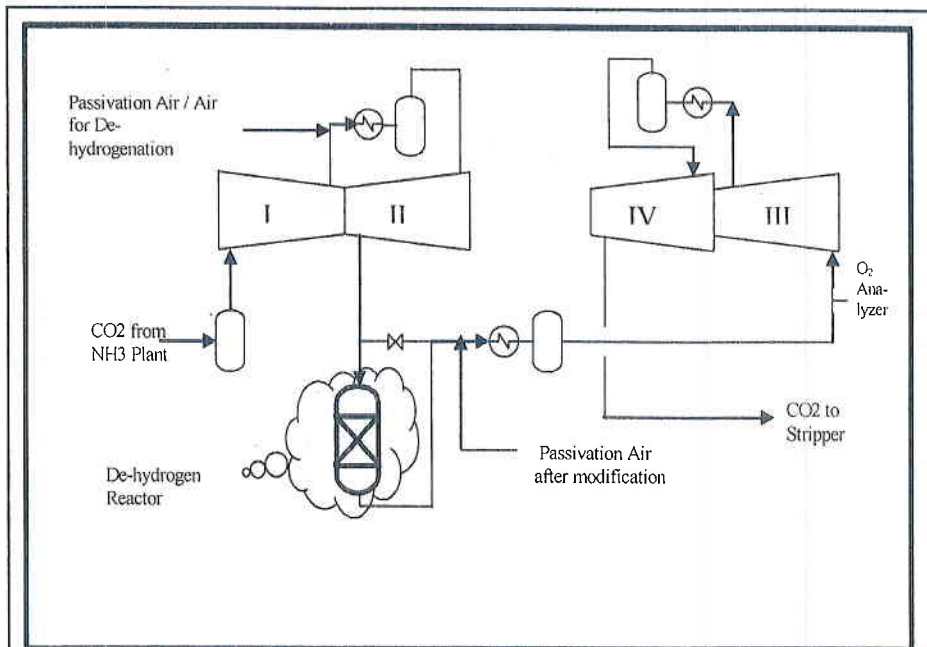


Figure 6 – Installation of De-hydrogen Reactor in 2nd stage of CO₂

temperature rise across the reactor gives very good indication of H₂ concentration in CO₂ feed which varies from volume 0.78% ~ 1.10% due to fluctuations in Benfield Section of Ammonia Plant. However few

problems have been encountered which had been successfully solved by suitable modification and strictly following procedure as described below:

1. At few instances it was observed that

high concentration of H₂ is received with CO₂ feed from ammonia plant. This high H₂ in inlet CO₂ stream of urea plant De-hydrogen unit results in run-away reaction on platinum catalyst as O₂ is already present in excess at the inlet of Reactors. The De-hydrogen Reactor is isolated manually from the field to avoid catalyst run-away reaction as well as compressor tripping from interlock at 250°C outlet temperature. In original design total O₂ required for passivation was fed at 2nd stage suction of compressor. A modification of split air supply to compressor was conceived and implemented in April 2006. Only stoichiometric air for burning about 0.8% H₂ is fed at 2nd stage suction, so that run-away reaction does not take place. The additional air required for passivation is fed at 3rd stage suction as shown in **Figure 6**. This high pressure air is supplied from final discharge from process air compressor of ammonia plant.

2. The De-hydrogen Reactor is designed for 0.5 kg/cm²g pressure drop. The pressure drop had increased from initial value of 0.2 kg/cm²g to 0.5 kg/cm²g after one year of operation in both the trains. This increase was because of potash deposition on catalyst bed which is carried along with CO₂ feed from Benfield section. This problem was also resolved in consultation with catalyst vendor. A procedure was developed for De-hydrogen Reactor washing with DM water of 7.0 pH and 1 micron conductivity and finally dried with CO₂. This is done by by-passing the Reactors during normal plant operation. The procedure was found to be effective and original pressure drop and H₂ removal performance was restored after each washing.

CONCLUSION

THE ELIMINATION OF H₂ FROM CO₂ GAS has enabled to mitigate the risk of such explosion hazard from urea plant from both the potential locations i.e. HP scrubber vapour space & washing column off gases up to vent stack top. This helps the operators to maintain very high recovery of ammonia thereby improving ammonia efficiency per ton urea and still maintaining absolute safe conditions in the plant. ■

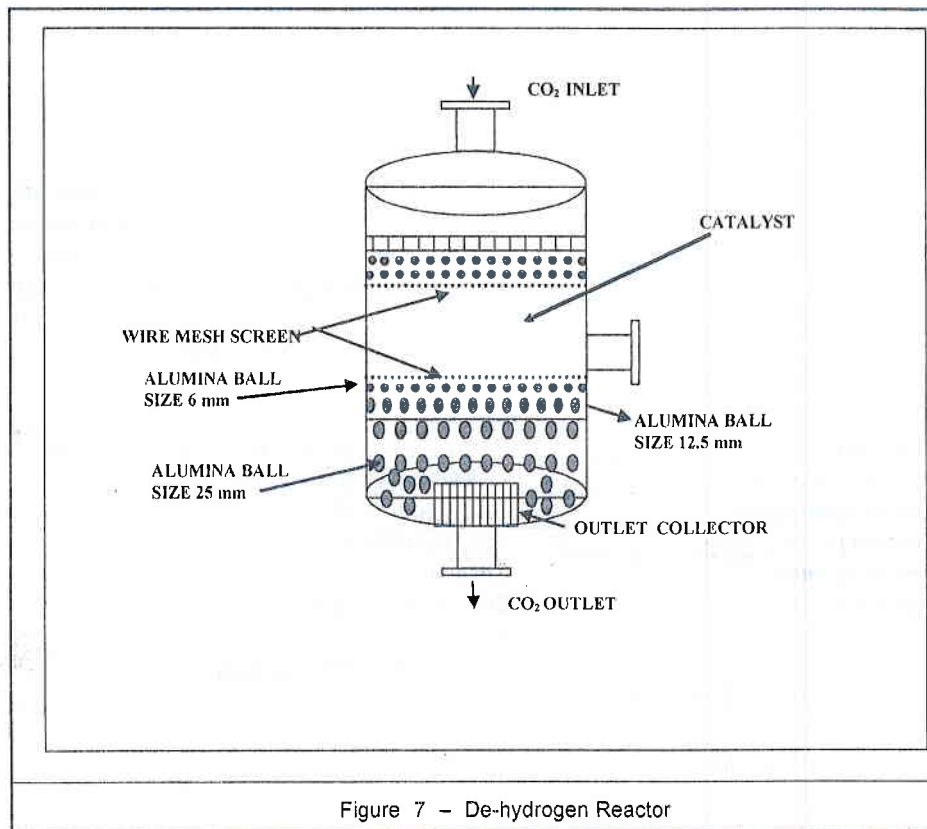


Figure 7 – De-hydrogen Reactor