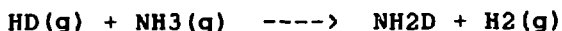


## EFFECT OF OPERATION OF AMMONIA PLANTS ON THE PERFORMANCE OF HEAVY WATER PLANTS

Heavy Water Plant, Hazira is based on monothermal ammonia-hydrogen exchange process. The process involves isotopic exchange of deuterium between gaseous hydrogen and liquid ammonia.



The source of H<sub>2</sub> is synthesis gas generated by two ammonia plants of KRIBHCO. Each ammonia plant is designed to produce 158265 NM<sup>3</sup>/hr (61.3 Mt/hr) of synthesis gas of following composition.

- (1) H<sub>2</sub> - 74.12%
- (2) N<sub>2</sub> - 24.74%
- (3) CH<sub>4</sub> - 0.83%
- (4) Ar - 0.32%
- (5) CO/CO<sub>2</sub> - less than 1 ppm. AV Mol. weight of gas is 8.68.

Heavy Water Plant, Hazira has two streams and each stream is designed to process 48 MT/hr of synthesis gas to produce the rated quantity of heavy water. However in actual practice, it is observed that actual gas composition is different from the above due to various reasons. This article relates effects of various parameters of ammonia plant on the functioning of Heavy Water Plants.

Various factors that affect the heavy water plant capacity are listed below.

- (A) Concentration of D/D+H in synthesis gas
- (B) Concentration of hydrogen in synthesis gas
- (C) Concentration of inerts in synthesis gas
- (D) Pressure of synthesis gas
- (E) On stream days of ammonia plant
- (F) Concentration of impurities like CO/CO<sub>2</sub> in synthesis gas

- (A) Concentration of D/D+H in inlet synthesis gas :

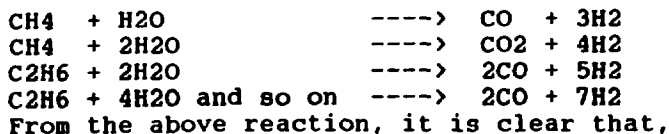
Heavy Water Plant, Hazira is designed for inlet concentration D/D+H of 115 ppm in synthesis gas. Deuterium being the basic raw material for production of heavy water, change in deuterium concentration in synthesis gas will directly affect heavy water production.

Various factors that can change the inlet deuterium concentration are as follows.

1) Effect of natural gas (quality of feed gas to ammonia plant) :

KRIBHCO is the second fertilizer complex utilising the Bombay High Natural Gas. The quality of natural gas supplied by ONGC has a direct effect on the deuterium concentration in synthesis gas which is explained below.

Hydrogen required for production of ammonia is produced by reforming reaction between hydrocarbon and steam.



(a) Produced hydrogen is the sum of hydrogen of hydrocarbon and that of steam. (Water)

(b) Hydrogen produced by reforming of higher hydrocarbon has more hydrogen, fixed from steam than that in the case of lower hydrocarbons (CH<sub>4</sub>). It is a fact that steam (Water) contains higher concentrations of deuterium of about 155 ppm than natural gas which is around 125 ppm. Hence increase in lower hydrocarbons or decrease of higher hydrocarbons from feed stock of ammonia plant (natural gas) will result in reduction of deuterium in synthesis gas.

When KRIBHCO commissioned its ammonia plants, ONGC supplied rich gas (containing higher hydrocarbons) and at that time the concentration of D/D+H in synthesis gas at methanator outlet was around 126 ppm. After ONGC commissioned its dew point depression units (to knock off higher hydrocarbons to prevent condensation enroute HBJ piping) & gas sweetening units (to remove sulfur down to 10 ppm) the composition of deuterium dropped to 121 ppm. On commissioning of LPG units, the concentration of deuterium has further dropped to 118 ppm. The composition of natural gas at different periods are as below.

Composition of natural gas supplied by ONGC

	June, 1987	September, 1988	Present
CH <sub>4</sub>	82.57	87.88	86.97
C <sub>2</sub> H <sub>6</sub>	7.78	7.59	7.96
C <sub>3</sub> H <sub>8</sub>	3.87	2.14	1.33
C <sub>4</sub> H <sub>10</sub>	0.95	0.09	0.04
C <sub>4</sub> H <sub>10</sub>	1.47	0.07	0.02
C <sub>5</sub> H <sub>12</sub>	0.35		
C <sub>5</sub> H <sub>12</sub>	0.25		
C <sub>6</sub> H <sub>14</sub>	0.03		

	June, 1987	September, 1988	Present
CO2	2.50	2.02	3.48
N2	0.23	0.21	0.20
S			
NCVK cal/s/m3	9511.00	8718.40	8501.60
CGV cal/s/m3	10503.10	9653.60	9416.80
Supply	NG before	NG after	NG after
	Dew point	Dew point	LPG plant
	Depression unit/ sweetching unit	Depression unit/ sweetching unit	Commission -ing
	Commissioning	Commissioning	
D2 in syn. gas	126 ppm	121 ppm	118 ppm

**2) Commissioning of hydrogen recovery from purge gas and its effect on D/D+H :**

As indicated earlier synthesis gas at methanator outlet contains 0.83% CH<sub>4</sub> and 0.32% Ar. During NH<sub>3</sub> production, while H<sub>2</sub> and N<sub>2</sub> are consumed as per the following reaction.



CH<sub>4</sub> and Ar remain in synthesis gas and so their concentration in ammonia synthesis loop keeps on increasing. To maintain inerts at optimum levels, a continuous purge at convertor outlet is to be maintained.

Purge gas recovery unit is an energy savings scheme to recover 90% H<sub>2</sub> from such purged synthesis gas (The depleted gas from heavy water plant mixes with the circulating gas and goes to synthesis convertor after cooling and NH<sub>3</sub> separation for ammonia production and so convertor outlet gas is lean in deuterium (28 ppm). The recovered hydrogen is hence lean in deuterium and mixes with fresh synthesis gas in the compressor as shown in the Figure-1. This results in dilution of D/D+H by 3 ppm.

**(3) Concentration of deuterium in make up water :**

Make up water for ammonia plant is DM water and it normally contains 156 ppm. With heavy water plant on stream, the NH<sub>3</sub> supplied to urea plant is lean in deuterium. If the process condensate is fully recovered as a scheme for pollution control and savings of DM water, there is a net surplus of condensate which when diverted to ammonia plant as make up will result in reduction of concentration of D<sub>2</sub> in make up water. This will ultimately result in reduction of D<sub>2</sub> concentration in synthesis gas.

**(4) Process condensate management :**

As part of process, the steam in the process gas after LT shift, converter is condensed and separated before the gas is sent to CO<sub>2</sub> absorber. The process condensate becomes rich in deuterium (210 ppm D/D+H) due to shift in deuterium from hydrogen to steam in primary reformer and down the line upto LT shift converter, where both these components coexist. So it is absolutely essential from heavy water plant point of view to conserve the condensate fully in ammonia plant so that the synthesis gas produced has the maximum possible D/D+H.

In KRIBHCO there is a dedicated condensate recovery system in which, the process condensate is stripped with LP steam and then polished in ION exchanger unit and returned to the boiler fully for make up. There is loss of about 7 MT of water vapour at stripper top and this if recovered will contribute towards improvement of D/D+H in synthesis gas. Refer Figure-2.

**(5) Leakage through seals/balance line of synthesis gas compressor :**

In all ammonia plants, final stage compression of synthesis make up gas and converter recirculation stage is incorporated in a single barrel and in such a configuration a small flow of gas from recirculating stage to the make up gas compression stage is inevitable. This small flow of gas (is provided in every centrifugal compressor) from high pressure side to low pressure for balancing the thrust forces generated by the differential pressure developed across the impellers. This results in mixing of converter inlet gas of composition of about H<sub>2</sub> - 63.3%, N<sub>2</sub> - 21.1%, CH<sub>4</sub> - 9.5%, Ar - 3.9%, NH<sub>3</sub> - 2.2% which is also lean in deuterium with the fresh gas. This is resulting in the dilution of D/D+H by 3-4 ppm apart from rising the inerts component in synthesis gas.

The deuterium concentration in synthesis gas at methanator outlet is 112 ppm and at heavy water plant inlet is 105 ppm in view of the above mentioned dilution effects.

**(B) Hydrogen concentration : Ammonia :**

Converter operation is quite stable as long as H<sub>2</sub> to N<sub>2</sub> ratio is in the ratio of 3.1 to 2.7. However with higher ratio, H<sub>2</sub> availability being high heavy water plant D<sub>2</sub> extraction will also be high.

Ammonia plant normally operates with a H<sub>2</sub>/N<sub>2</sub> ratio of 3.0.

(C) Increase of inerts in synthesis gas :

In primary reformer NG and steam mixture in the mole ratio of 1:3.5 is reformed in presence of nickel catalysts at around 800 degree C. When the catalyst activity is reduced either due to end run conditions or due to poisoning of catalysts, furnace temperature may have to be increased to maintain the same methane slip exit primary reformer and in case there is limitation on further rising of the tube skin temperature, then methane slip exit primary reformer increases if the same reformer load is maintained. This will lead to higher CH<sub>4</sub> content in synthesis gas.

Similarly CH<sub>4</sub> in synthesis gas will increase if there is improper combustion or loss of activity of secondary reformer catalyst, HT, LT catalysts. Also if there is problem in CO<sub>2</sub> removal system, like limitation of solution circulation rates, improper regeneration of solutions, improper efficiency of absorber or foaming conditions in towers can all lead to higher CO<sub>2</sub> slip exit absorber and all these will lead to higher CH<sub>4</sub> in synthesis gas after methanation. If there is leak in methanator feed heat exchanger (which is exchanging heat with CO/CO<sub>2</sub> rich gas exit HT shift conveter) there will be flow of CO/CO<sub>2</sub> into the methanator leading to higher CH<sub>4</sub> in synthesis gas.

As explained earlier, flow through balance line of synthesis gas compressor results in the by passing of inerts rich recycle gas into the make up synthesis gas line. This contributes to the increase of CH<sub>4</sub>, Ar and NH<sub>3</sub> in the synthesis gas. To the extent there is increase in CH<sub>4</sub>, Ar and NH<sub>3</sub> there is corresponding decrease of H<sub>2</sub>. This reduces the capacity of the plant. The increase in inerts increases the mol. weight of the gas. This results in not only higher power consumption in booster compressor in HWP for processing the synthesis gas but also reduces effective plant capacity corresponding to reduction in available hydrogen in synthesis gas stream.

Increase of CH<sub>4</sub> in synthesis gas means increase of purge in synthesis loop. This will lead to overall high energy consumption in ammonia plant. So every effort is made in ammonia plant to maintain inerts as low as possible. With planning of catalyst replacements at the right time and better management of CO<sub>2</sub> removal system, a trade off is done between extending the catalyst life and the increased operation cost.

The presence of NH<sub>3</sub> in synthesis gas (0.2%) while contributing negatively towards reduction of H<sub>2</sub>, helps the dryers to be operated at -5 degree C (as against +5 degree C design) there by knocking off most of the moisture at dryer

bottom and improving the dryer performance and also remove most of CO<sub>2</sub> by dissolving in condensed ammonia. This reduces load on purifiers installed further downstream for removal of CO, CO<sub>2</sub> and residual moisture.

(D) Pressure of synthesis gas :

The pressure of synthesis gas available at heavy water plant inlet is a function of over all ammonia plant load, activity of synthesis catalyst and the inerts content in the synthesis loop. There can be constraints on the plant load due to any of the following reasons.

- (1) Primary reformer limitations
- (2) Excessive pressure drop across any catalyst vessel or heat exchangers
- (3) Limitation on any of the moving equipments, boiler or exchangers
- (4) Highly fouled condition of cooling water exchangers
- (5) Feed stock limitation

Heavy water plant booster compressor is designed for inlet pressures of 180 - 210 kg/cm<sup>2</sup>. If ammonia plant synthesis loop operating pressure is lower than 175 kg/cm<sup>2</sup>g either due to incorporation of energy efficient design or due to constraints in plant load heavy water plant processing capacity will be correspondingly reduced.

(E) On stream days of ammonia plant :

Higher the on stream factor and reliability of ammonia plant, higher is the possibility of on stream run of heavy water plant. If the ammonia plant is self sufficient in steam requirements and least dependant on power there is tremendous scope for better on stream factor. Apart from natural gas, KRIBHCO's power requirement from outside is very small, being about 18 KW/tonne of NH<sub>3</sub>, which is easily met by DG set during power disturbances and hence has established excellent on stream factor.

(F) Concentration of impurities like CO/CO<sub>2</sub> in synthesis gas:

The impurities in synthesis gas i.e. CO/CO<sub>2</sub>, can increase if there is loss of activity of methanation catalyst. This can be easily predicted and catalyst can be replaced with proper planning.

But one that cannot be predicated is the leakage of interchanger at the downstream of methanator as provided in most of the ammonia plants. Impurities in synthesis gas will drastically affect the purifier performance of heavy water plant and that will lead to operational difficulties.

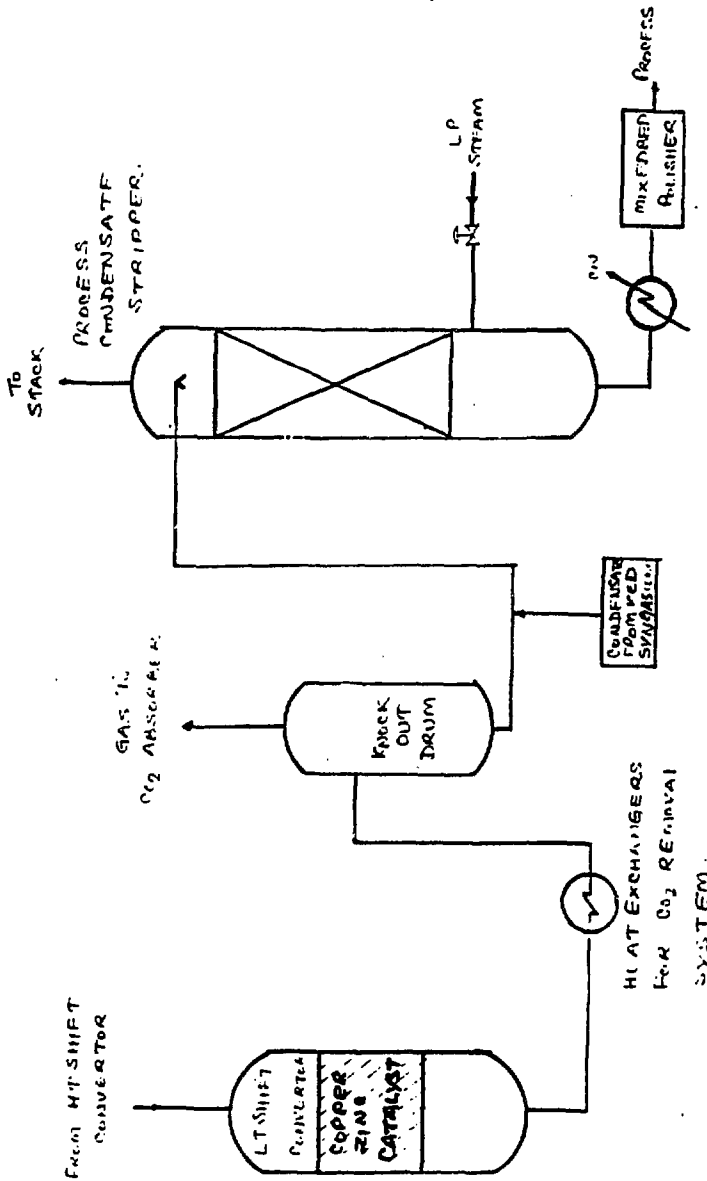
KRIBHCO's ammonia plant does not have an interchanger at methanator outlet and to that extent CO/CO<sub>2</sub> slip into synthesis gas is not possible.

In the light of the above, it can be said, that Hazira, Heavy Water Plant is favourably placed with respect to the factors B, C, D, E & F as these factors are already optimised in KRIBHCO ammonia plants. Regarding the concentration of D/D+H in synthesis gas there is excellent scope for improvement. The various schemes that are under consideration are :

- (1) Installation of a compressor to pump recovered hydrogen gas from PGR directly to synthesis convertor to prevent dilution.
- (2) Installation of an MP stripper to recover all the process condensate/water vapours (rich in deuterium) that are being drained out/vented out.
- (3) Interconnection of process condensate networks of ammonia plants and selective intake of synthesis gas for HWP by suitable regulation through provision of control valves.
- (4) Delinking of urea plants hydrolyser water from make up of ammonia plant.

The above schemes have the potential to improve the yield of Heavy Water by another 10-15%.

Heavy Water Plant can perform well if the plant gets clean synthesis gas at consistently higher pressures. The reliable operation of ammonia plants is of paramount importance for the steady operation of Heavy Water Plant. On both counts Hazira Heavy Water Plant is endowed with well running ammonia plants. This has helped HWP not only to stabilise quickly but also to aim at achieving higher production.



PROCESS CONDENSATE RECOVERY IN KRI-BHCO (FIG 1)



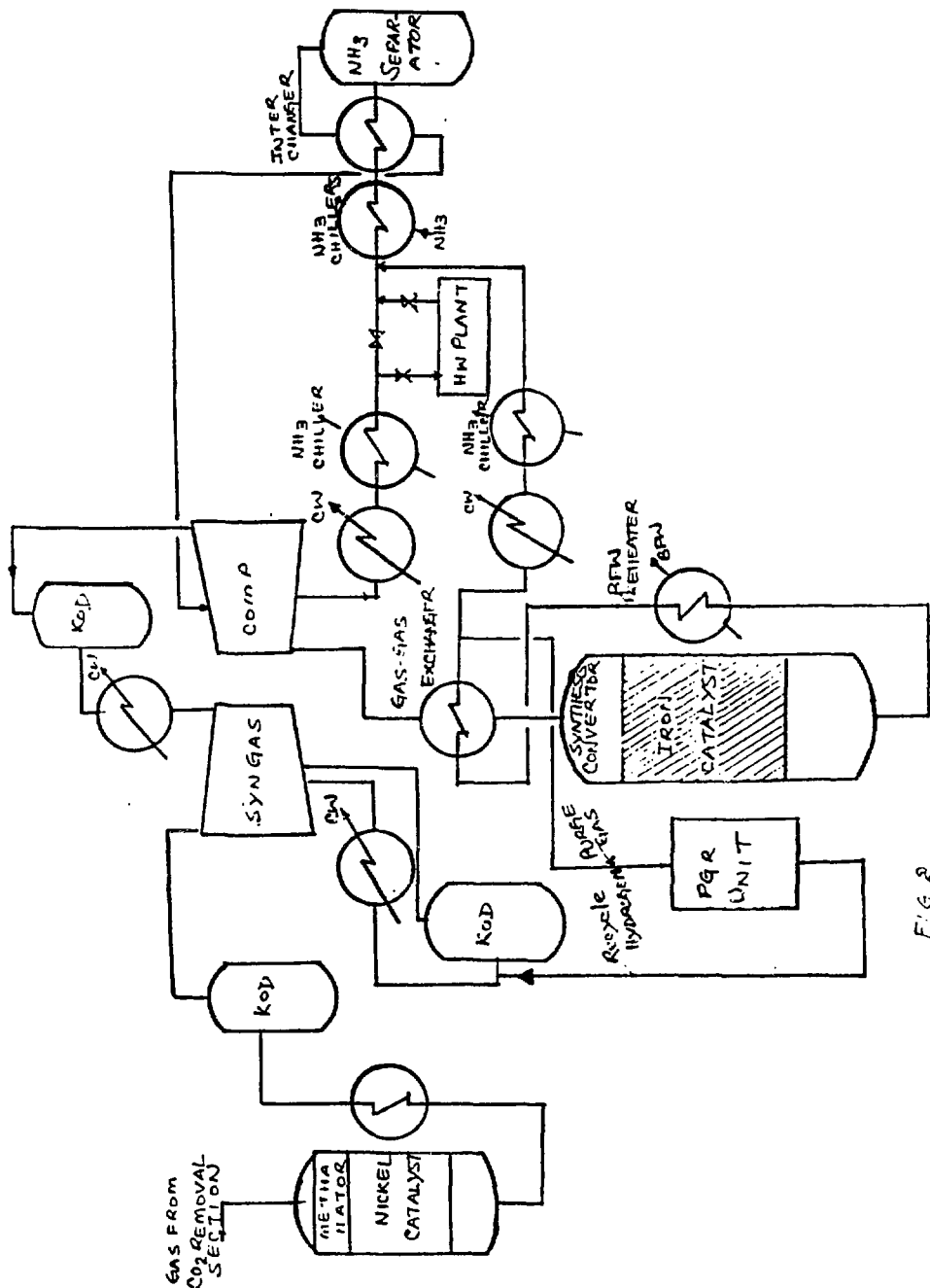


FIG 2

AMMONIA PLANT SYNTHESIS SECTION - KRIBHCO