EFFECT OF DESIGN AND OPERATION OF MODERN AMMONIA PLANTS 
ON THE PERFORMANCE OF INTEGRATED 
HEAVY WATER PLANTS

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1. Introduction:

One of the processes adopted for the production of 
heavy water in India is ammonia-hydrogen exchange process. 
Raw material for this process is synthesis gas (3H2 + N2) 
produced by the ammonia plant. The modern ammonia plants 
are based on steam reforming of natural gas and are rated 
for the production of 1350 tonnes ammonia per stream per 
day. Block diagram of typical ammonia plant - using natural 
gas as feed stock - showing various steps involved in the 
production of synthesis gas is shown in figure-1. In some 
cases the fertilizer plants consist of two identical streams 
(1350 tonnes/day/stream) of ammonia plant.

The synthesis gas produced in the fertilizer plant, 
before converting into ammonia, is routed through the heavy 
water plant for extraction of deuterium. The extraction of 
deuterium is effected by the following exchange reaction 
between synthesis gas and ammonia in an exchange tower and 
in presence of potassium amide catalyst.

\[
\text{HD}(g) + \text{NH}_3(1) \xrightarrow{\text{NH}_2\text{D}(1) + \text{H}_2(g)}
\]

The synthesis gas, depleted in deuterium, is thereafter 
returned to the ammonia plant. Block diagram showing the 
extraction section of a typical heavy water plant is shown 
in figure-2.

The heavy water plant being parasitic in nature, its 
design, operation and performance is affected to a great 
extent by the design, performance and operation of the 
ammonia plant. Some of the factors which affect the per-
formance of heavy water plant are enumerated below:-

i) Onstream hours and capacity utilisation of the ammonia 
plant.

ii) Deuterium concentration (D/D+H) in feed synthesis g.

iii) Operating pressure of synthesis loop of ammonia plant.

iv) Composition of feed synthesis gas.

v) Level of oxygenated impurities in feed synthesis gas.
2. Effect of on-stream hours and capacity utilisation of ammonia plant:

i) Availability of feed synthesis gas from ammonia plant:

In heavy water plants which are connected to single stream ammonia plants like the one at Tuticorin, availability of synthesis gas and the on-stream hours of the ammonia plant affect the capacity utilisation of the heavy water plant.

It has been observed that annual average capacity utilisation of modern fertilizer plants is of the order of approximately 110% of the rated capacity, and the on-stream hours achieved is around 8000 hours per annum. Thus, availability of feed synthesis gas is not a constraint for the operation of heavy water plant at the desired load.

In case the heavy water plant is coupled to a multi stream ammonia plant, the availability of synthesis gas as well as on-stream hours are likely to improve further due to phasing of planned/unplanned shutdowns of both streams of ammonia plant. This is because the heavy water plant can still be kept in operation even when one stream of ammonia plant is under shutdown.

ii) No. of trips/stoppage of ammonia plant:

No. of trips/stoppage of ammonia plant plays an important role in the performance of heavy water plant. Any stoppage of ammonia plant, even for a short duration, causes loss of production of approximately 2 days in addition to the period of stoppage of ammonia plant. With the improvement in reliability of modern fertilizer plants, no. of trips are also less. This enables heavy water plant to achieve higher on-stream hours.

3. Effect of operating condition of ammonia plant on deuterium concentration in feed synthesis gas:

The capacity of heavy water plant is directly proportional to the deuterium concentration in feed synthesis gas. The deuterium concentration in feed synthesis gas depends on factors like

i) source of hydrogen.

ii) condensate management.

iii) dilution of fresh synthesis gas due to bypassing/mixing of synthesis gas depleted in deuterium.

iv) method of reuse of water produced in urea hydrolyzer.
i) Source of hydrogen:

In the modern ammonia plants synthesis gas is produced by steam reforming of natural gas. In this process around 45% of hydrogen comes from the steam while the balance 55% comes from the natural gas. Since the deuterium content of the natural gas is only of the order of 120 to 125 ppm compared to water (145 to 150 ppm), synthesis gas produced by this process is expected to contain maximum 130 ppm of deuterium (considering no loss of deuterium from the process).

The heavier the feed stock like naphtha, fuel oil, coal etc. the more is the hydrogen percent from the water and thus the deuterium content of the synthesis gas will be higher (e.g. 145 ppm in a coal based plant).

ii) Condensate management:

In the CO-shift converter of the ammonia plant, deuterium content of synthesis gas gets depleted due to following exchange reaction.

\[
\text{H}_2\text{O} \text{(steam)} + \text{HD} \text{(gas)} \rightarrow \text{HDO} \text{(steam)} + \text{H}_2 \text{(gas)}
\]

The exchange reaction is catalysed by the CO-shift converter catalyst. The depletion factor \( \frac{(D/H) \text{ in } \text{HDO} \text{(steam)}}{(D/H) \text{ in } \text{HD} \text{(synthesis gas)}} \) decreases with increase in operating temperature of CO-shift converter. That is, the lower the operating temperature, the higher will be the transfer of deuterium to steam. At the operating temperature of 190 deg.C of the modern ammonia plants the depletion factor is 1.9. Therefore, it is essential to recycle this deuterium rich condensate back to the process to improve deuterium concentration in the synthesis gas. It has been calculated that with total recycle of condensate, it is possible to get a deuterium concentration of 130 ppm (with natural gas as feed stock).

The design of modern natural gas based ammonia plants envisage efficient recycling of condensate to the extent of 92% (loss of 8%, due to leakage, boiler blow down and loss in polishing of condensate). However, our experience in the ammonia plants presently under operation shows loss of rich condensate to a much higher level. By adopting an efficient condensate management system this loss can be restricted to around 20%.

Deuterium concentration in the synthesis gas (methanator outlet) at various levels of rich condensate loss is shown in Table-I.
In the ammonia plants, presently under operation, deuterium concentration of the synthesis gas is observed to be varying between 118 ppm to 124 ppm at the methanator outlet.

Where two streams of heavy water plant (design module handling 48 tonnes per hour feed gas) is integrated to 2-stream ammonia plant having 1350 Tonnes per day per stream capacity, it is possible to further improve the deuterium concentration of feed gas to heavy water plant by using deuterium-rich process condensate of both the ammonia plants in one of the ammonia plants and processing the total synthesis gas produced in this stream while the balance being taken from the other stream of ammonia plant. Under this condition, assuming 20% loss of rich condensate deuterium concentration in feed synthesis gas to heavy water plant is calculated to be 130 ppm (methanator outlet).

iii) Dilution of fresh synthesis gas due to bypassing/mixing of synthesis gas depleted in deuterium:

a) Leakage in synthesis gas compressor:

In almost all the ammonia plants the final stage of synthesis gas compressor and the recirculating stage are housed in a common casing. Due to leakage in the sealing and balancing system, mixing of depleted synthesis gas from the recirculator stage to the fresh synthesis gas - to the extent of 5 to 10% - has been observed. The reduction in deuterium concentration in the feed synthesis gas due to this leakage is calculated to be 4 to 7 ppm. This can be avoided if the final stage of synthesis gas compressor and the recirculating stage are housed in separate casings. However, this can be taken care of only during the design stage of the ammonia plant. Though this may marginally increase the overall cost of synthesis gas compressor this will be offset by extra heavy water production.

b) Mixing of purge gas:

In order to keep the level of inerts (Argon, methane etc.) low in the synthesis gas of recirculating loop of ammonia plant, about 5 tonnes/hour of recirculating gas is withdrawn and is either burnt as fuel in the reformer or passed through a purge gas recovery unit where the inerts are removed and the remaining gas is fed to the suction of second stage of synthesis gas compressor. Since the recirculating gas is depleted in deuterium, any mixing of this gas with the feed synthesis gas will reduce the deuterium concentration of feed gas. This reduction is calculated to be 4 to 6 ppm. This problem can, however, be avoided if a separate compressor is used for compressing the inert free
purge gas and the gas is fed directly to the recirculating loop. This may marginally increase the capital and operating cost of fertilizer plant.

The expected deuterium concentration in the feed synthesis gas at the battery limit of heavy water plant under various conditions of operations of ammonia plant is given in Table-II.

iv) Method of reuse of water produced in Urea hydrolyzer:

In some of the new ammonia plants the water produced in the hydrolyzer of urea plants is being used as make up to process boiler. Since this water is produced from ammonia containing lower deuterium concentration, the water and consequently the process steam used in the reformers will have low deuterium concentration. This will reduce the deuterium concentration of feed synthesis gas by 5 to 7 ppm. Therefore, it will be advisable to use this water either as make up to cooling tower or in other auxiliary boilers.

4. Effect of operating pressure of ammonia synthesis loop

The operating pressure of ammonia synthesis loop of fertilizer plant depends on the design of ammonia converter and activity/type of catalyst used. The operating pressure of synthesis loop of modern ammonia plants varies between 175 to 190 kg/sq.cm at the rated capacity.

[The present trend in the design of latest ammonia plants indicates reduction of ammonia synthesis loop pressure even further to approximately 130 to 135 kg/sq.cm].

The extraction tower of heavy water plant operates at a pressure of about 30 to 40 kg/sq.cm higher than the synthesis loop pressure. The operating pressure of extraction tower of heavy water plant when coupled to such ammonia plants will therefore be only 210 to 225 kg/sq.cm. The extraction tower of the existing module of heavy water plant is designed for a pressure of 249 kg/sq.cm. The feed gas handling capacity of heavy water plant at various pressures of ammonia plants are given in Table-III.

In case the operating pressure of the ammonia plant is lower, in order to process 48 tonnes per hour feed gas as envisaged in the design module, either the diameter of the extraction tower has to be increased or the operating pressure of extraction tower has to be increased by using a booster compressor with higher differential pressure. In case of extra boosting of pressure, the extra pressure has to be dropped either by providing a throttling valve on the return synthesis gas line to fertilizer plant or by using an expander to recover the energy.
Reduction in operating pressure will also have following adverse effects on the performance of heavy water plant.

1) Rate of exchange reaction between HD and NH3 will be less at a lower operating pressure and consequently reduce the exchange efficiency as well as effective separation factor. Graphs showing effect of pressure on the rate constant and effective separation factor are given in figure 3 and 4 respectively. For every 10 kg/sq.cm reduction in operating pressure, the overall effect in the reduction of percentage recovery of deuterium would be approximately 0.5%.

This reduction in recovery efficiency can be compensated by providing additional no. of exchange stages in the extraction tower.

ii) The conversion efficiency of ammonia converter of heavy water plant will reduce with a reduction in operating pressure and hence will call for a bigger ammonia converter.

iii) Lower operating pressure will increase the overall refrigeration load of the plant. The net effect of operation of the heavy water plant at lower pressure due to low operating pressure of ammonia plant is therefore reduction in the production capacity of heavy water plant and its higher energy consumption.

5. Effect of feed synthesis gas composition:

The production capacity of heavy water plant is directly proportional to the total moles of free hydrogen in the feed gas. This, in turn, depends on the molecular weight and mole percentage of hydrogen in feed synthesis gas. Molecular weight and mole fraction of hydrogen in feed synthesis gas depends on:

i) operating conditions of the reformer (e.g. temperature, pressure, steam to carbon ratio, catalyst conditions, etc.).

ii) Efficiency of CO2 removal section and

iii) Extent of leakage from recirculator stage to make up synthesis gas. Increase in molecular weight alone from the design value of 8.67 to the observed value to 8.85 in the modern ammonia plants will result in a reduction of heavy water production by approximately 1.5%.

Similarly reduction of hydrogen mole fraction from the design value of 0.75 to the observed value 0.73 in the modern ammonia plants will result in a reduction of heavy water production by another 2.5%.
This can be greatly minimised by housing the recirculating stage in separate barrel.

6. Effect of level of oxygenated impurities in the feed synthesis gas:

Oxygenated impurities in feed synthesis gas such as CO, CO2, H2O etc react with the catalyst potassium amide and forms insoluble impurities. In order to ensure trouble free operation of the exchange stages such impurities in the feed gas are removed in the purifier upstream of the extraction tower. The synthesis section of ammonia plant can tolerate upto approximately 10 ppm impurities like CO, CO2. The gas purification system in the ammonia plant (methanator) is designed keeping this requirement in view. Analysis of samples of synthesis gas collected from modern ammonia plants shows the level of these impurities (CO and CO2) to be 2 to 5 ppm.

The purifiers of the existing modules of heavy water plants are designed for a level of oxygenated impurities of less than 2 ppm. If the level of impurities exceeds 2 ppm, the design of purifiers needs extensive modifications. However, relatively simpler modifications in the ammonia plant (ultra methanator), in the design stage, can reduce the level of impurities below 2 ppm.

7. Conclusion:

The achievable production from a heavy water plant based on ammonia hydrogen exchange process depends on

i) quantity of feed synthesis gas processed in heavy water plant

ii) onstream hours

iii) operating pressure of the ammonia plant

iv) deuterium concentration of feed synthesis gas

v) composition (hydrogen concentration) of the feed synthesis gas.

In the modern ammonia plants having 1350 tonnes/day per stream capacity using natural gas as feed stock both onstream hours and the feed gas availability have been satisfactory.

The observed trend in the reduction of operating pressure of the ammonia plants, in order to minimise the energy consumption, will continue to adversely affect the performance of the heavy water plant.
The deuterium concentration in the feed gas to heavy water plant is lower than the calculated value mainly due to loss of deuterium rich condensate in the ammonia plant and dilution of fresh synthesis gas by the leakage gas from the recirculating stage and purge gas. In the ammonia plants, already in operation, scope for improvement, by way of modifications is limited. However, if all such modifications are incorporated in the new ammonia plants during the design stage itself, they can effectively improve the deuterium concentration of the feed synthesis gas to the heavy water plant which in turn improves the heavy water production.
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>% Loss of rich condensate</th>
<th>D-conc. Methanator outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 (Design)</td>
<td>127.00</td>
</tr>
<tr>
<td>2</td>
<td>20.00</td>
<td>124.00</td>
</tr>
<tr>
<td>3</td>
<td>30.00</td>
<td>121.00</td>
</tr>
<tr>
<td>4</td>
<td>40.00</td>
<td>118.00</td>
</tr>
</tbody>
</table>

Note: Feed stock: nature gas
### TABLE - II

**Deuterium Concentration in Feed Synthesis Gas to Heavy Water Plant**

**Under Various Operating Conditions of Ammonia Plants**

<table>
<thead>
<tr>
<th>S1. Feedstock No.</th>
<th>Type of condensate management in ammonia plant assuming 20% loss of rich condensate</th>
<th>Leakage in recirculator/final stage of compressor (percent of make-up gas)</th>
<th>Mixing of purge gas with feed synthesis gas (Tonnes/hr.)</th>
<th>Calculate D-content of feed gas (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Natural gas</td>
<td>Yes</td>
<td>No</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>Yes</td>
<td>No</td>
<td>5-10</td>
<td>0</td>
</tr>
<tr>
<td>3.</td>
<td>Yes</td>
<td>No</td>
<td>5-10</td>
<td>5</td>
</tr>
<tr>
<td>4.</td>
<td>No</td>
<td>Yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5.</td>
<td>No</td>
<td>Yes</td>
<td>5-10</td>
<td>0</td>
</tr>
<tr>
<td>6.</td>
<td>No</td>
<td>Yes</td>
<td>5-10</td>
<td>5</td>
</tr>
<tr>
<td>7. Naphtha</td>
<td>Yes</td>
<td>No</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8.</td>
<td>Yes</td>
<td>No</td>
<td>5-10</td>
<td>5</td>
</tr>
<tr>
<td>9. Coal</td>
<td>Yes</td>
<td>No</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10.</td>
<td>Yes</td>
<td>No</td>
<td>5-10</td>
<td>5</td>
</tr>
</tbody>
</table>
### TABLE III

**FEED GAS HANDLING CAPACITY OF HEAVY WATER PLANT AT VARIOUS PRESSURES OF AMMONIA PLANT**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Synthesis loop pressure of ammonia plant Kg/sq.cm</th>
<th>Inlet pressure at extraction tower of HWP Kg/sq.cm</th>
<th>Feed gas handling capacity Tonnes/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>175.00</td>
<td>210.00</td>
<td>42.00</td>
</tr>
<tr>
<td>2.</td>
<td>185.00</td>
<td>220.00</td>
<td>43.00</td>
</tr>
<tr>
<td>3.</td>
<td>195.00</td>
<td>230.00</td>
<td>44.50</td>
</tr>
<tr>
<td>4.</td>
<td>205.00</td>
<td>240.00</td>
<td>46.00</td>
</tr>
</tbody>
</table>

*Note: Liquid to gas ratio = 0.223*
FIG. 1

BLOCK DIAGRAM SHOWING THE STEPS INVOLVED IN THE PRODUCTION OF SYN GAS
BLOCK DIAGRAM SHOWING THE D-EXTRACTION SECTION OF HWP (PLANT)

SYNTHESIS GAS
TO FERTILIZER PLANT

NH3 SYNTHESIS
UNIT

EXTRACTION
TOWER

ENRICHMENT
& OTHER SECTIONS
OF HWP PLANT

PURIFICATION
UNIT

BOOSTER
COMPRESSOR

SYNTHESIS GAS
FROM FERTILIZER PLANT

Fig. 2
PRESSURE VS RATE CONSTANT FOR EXCHANGE REACTION BETWEEN H2 AND NH3 AT 25 GRAMS OF KNH2 PER KG OF AMMONIA

FIG 3
EFFECTIVE SEPARATION FACTOR FOR EXCHANGE REACTION BETWEEN H₂ AND NH₃ AT -25°C VS PRESSURE

FIG. 4