# DEUTERIUM CONCENTRATION BY CHEMICALLY-REFLUXED AMMONIA-HYDROGEN EXCHANGE

## FINAL REPORT

E.A. Mason, M. Benedict, E.R. Chow, J.S. Baron

June 1969

(MITNE-102)

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# 1.0 SUMMARY

A study has been carried out to design and evaluate the potential of a chemically-refluxed ammonia-hydrogen exchange process for the recovery and concentration of deuterium contained in ammonia synthesis gas. The work was supported during FY 1968 and 1969 under the U.S.-Canada Cooperative Agreement. The objective of the study was to compare the estimated cost of producing heavy water, a moderator for nuclear reactors, from the chemically-refluxed ammonia-hydrogen exchange process with the cost from the thermally refluxed water-hydrogen sulfide process now used for heavy water production in the U.S.A. and Canada.

The ammonia-hydrogen exchange reaction is
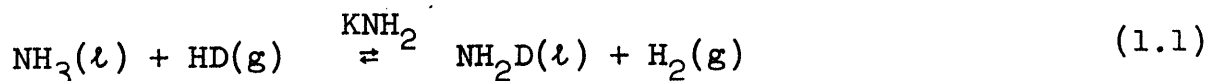
$$NH_3(\ell) + HD(g) \overset{KNH_2}{\underset{}{\rightleftarrows}} NH_2D(\ell) + H_2(g) \tag{1.1}$$

The reaction must be operated at high pressure because of the low solubility of hydrogen in liquid ammonia and requires catalysis by potassium amide, $KNH_2$. With the exception of the water electrolysis process, the separation factor for this process and its temperature coefficient are the highest of all hydrogen-deuterium separation processes considered to date. The separation factor, for concentration of deuterium in the liquid phase, ranges from 3.7 at $20^\circ C$ to 8.3 at $-70^\circ C$ (3).

In the ammonia-hydrogen $(NH_3-H_2)$ exchange process, hydrogen gas and liquid ammonia are brought into contact with each other to effect a net transfer of deuterium from the

gas phase into the liquid ammonia. There are two ways of accomplishing this net transfer. First, in the bithermal version the transfer is brought about by running two gas-liquid exchange towers at different temperatures in a fashion similar to the water-hydrogen sulfide ($H_2O$-$H_2S$) dual temperature process. Second, in the chemically refluxed (or monothermal) version, with which this study is concerned, one exchange tower is run at a constant temperature, but enriched ammonia liquid leaving the bottom of the tower is cracked into hydrogen and nitrogen which provide the gaseous reflux for the tower. A small fraction of the en-riched ammonia liquid leaving the bottom of the tower is withdrawn, prior to the ammonia cracker, as the deuterium-enriched product. The depleted hydrogen gas at the top of the exchange tower is reacted with nitrogen to form ammonia which provides the liquid reflux to the exchange tower. Thus the chemically-refluxed process consists of three systems: deuterium exchange, ammonia synthesis, and ammonia cracking.

For large heavy water production rates, the deuterium heavy water plant must be associated with a large source of hydrogen. At the present time, synthesis gas ($3H + N_2$) produced as feed for ammonia production represents the most readily available large-scale source of hydrogen. Consequently this study considered a plant employing the chemically-refluxed ammonia-hydrogen exchange process for the extraction

of deuterium from the gas feed to a synthetic ammonia plant.
At a deuterium concentration of 132 ppm in the hydrogen
of the synthesis gas feed to an ammonia plant, complete
recovery of the deuterium would result in a heavy water
production of 0.466 lb $D_2O$/ton $NH_3$ product. Thus, a 1000
ton/day ammonia plant could produce a maximum of 77 tons of
$D_2O$/yr.

To facilitate cost estimation, it has been assumed
that the deuterium extraction plant will be added to an
existing ammonia synthesis plant, without materially alter-
ing the amount of ammonia available for sale (919.6 tons
liquid ammonia/day). The rate of production of synthesis
gas is assumed to remain the same after the deuterium
extraction plant is added, so that the cost of producing
synthesis gas need not be estimated or charged against
deuterium extraction. The feed synthesis gas was considered
to have 132 ppm deuterium (atom basis) in the hydrogen.
The deuterium extraction plant is designed to recover 90%
of this deuterium, so that the gas leaving the exchange
section as feed for the ammonia synthesis plant would contain
13.2 ppm deuterium; this gas forms the feed for the synthesis
of 1401 tons/day deuterium-depleted ammonia in the combined
(original plus added) synthesis plants. 910.9 tons/ day
of this depleted liquid ammonia are sold, and the remainder
recycled to the exchange towers. The liquid ammonia reflux
leaves the bottom of the exchange tower containing 13,200

ppm deuterium, of which 8.7 tons/day provides the deuterium
enriched product of the plant; the remainder of the liquid
reflux is sent to the ammonia cracking section to provide
the gas reflux to the exchange towers. The 8.7 tons/day of
enriched ammonia product can be further concentrated and
oxidized to heavy water; the deuterium content of the
enriched ammonia is equivalent to 66.8 tons $D_2O$/yr.

The main units of the added deuterium extraction
plant are a deuterium exchange section, and ammonia cracking
section to provide the gas reflux, an added ammonia syn-
thesis section with capacity of 482 tons per day to provide
the liquid reflux, and a new recycle compressor. The deu-
terium exchange system contains four sets of exchange towers:
(1)  deuterium stripping tower (234 sieve plates); (2) deu-
terium enriching tower (300 sieve plates); (3)  catalyst
deuterium stripping tower (packed); and (4)  feed gas purifi-
cation and humidification tower (20 sieve plates).

The time available for this study before contract
close-out due to termination of funding of the U.S.-Canada
Cooperative Agreement did not permit plant and economic
optimization. However, in order to give a rough estimate
of the cost of recovering deuterium from ammonia synthesis
gas using chemically refluxed (monothermal operation)
ammonia-hydrogen exchange, a set of operating conditions
was arbitrarily selected, a process design developed, and
a cost estimate was prepared with the appreciated assistance of
Air Products and Chemicals, Inc., (a firm with experience with

low temperatures) using this design as a basis. The cost
estimates presented must therefore be regarded as preliminary
and in all probability are not representative of an optim-
ized design.

An estimate of the investment and operating costs
for the entire added deuterium extraction plant was made.
In addition to the installed cost of all the primary equip-
ment and secondary heat exchangers, coolers, pumps and
compressors, the estimate included costs of a steam gener-
ating plant (to power compressors and pumps an to supply
process heat), a refrigeration system, cooling tower system,
instruments, electrical substation, spare parts, start up
and training expenses, as well as working capital. In summary
the cost estimate indicated (for 330 operating days/year):

| | |
|---|---|
| Fixed Plant Investment | $11,983,000 |
| Working Capital | 803,000 |
| Total Investment | $12,786,000 |
| Non-capitalized operating costs | $ 1,824,000 |

Since the rate of heavy water production equivalent
to the deuterium recovered is 133,600 lb/yr. (66.8 tons
$D_2O$/year), the unit cost of producing heavy water by the
ammonia-hydrogen process designed here (not including the
small additional cost for final concentration and oxidation
of deuterated ammonia to heavy water) can be represented
by

$$\text{Unit Cost of Heavy Water, \$/lb.} = 13.65 + 95.70\,r \qquad (1.2)$$

where r = annual fixed charge rate against total invest-ment.

For fixed charge rates of 10%/yr to 25%/yr, which are considered to cover the range of the fixed charge rates that might apply for government or private ownership, the cost of heavy water would be:

| Annual Fixed Charge Rate, r | Cost of Heavy Water $/lb |
|---|---|
| 0.10 | 23.2 |
| 0.15 | 28.0 |
| 0.20 | 32.8 |
| 0.25 | 37.6 |

The estimated cost of recovering deuterium by the process described here is therefore approximately the same as the USAEC sale price for heavy water of $28.50 per pound. This conclusion is not very favorable since much development work and expense would be required to bring the process described here into production.

However, as discussed previously, early termination of the support of this study did not leave sufficient time for process optimization. The cost estimates given are based on only one set of operating conditions, arbitrarily selected, in order that at least one cost estimate could be included in this final project report. Based on probabilities it seems unlikely that the first set of operating conditions, arbitrarily selected, would produce optimum economics. Therefore, considering that the estimated cost

of heavy water produced by this initial process design
is about the same as the present USAEC price, the process
may indeed warrant additional design and economic studies
to determine its potential relative to the hydrogen sulfide
process currently used for the production of heavy water,
especially if a demand for new heavy water capacity
develops.

Specifically, studies of the effect of (a) decreasing
the reference pressure selected for the exchange towers,
(b) increasing the reference temperature, pressure, degree
of conversion, and catalyst selected for the ammonia crack-
ing furnace, (c) increasing the plate efficiency in the
exchange towers, (d) considering the ammonia synthesis
and deuterium extraction plants to be designed and built
as a unit, and (e) larger scale production, all should be
carried out in order to compare the ultimate potential
of the chemically-refluxed ammonia-hydrogen exchange process
with the water-hydrogen sulfide exchange process.

## 2.0 INTRODUCTION

### 2.1 Ammonia-Hydrogen Exchange Process Description

Under the general sponsorship of the U.S. - Canada Cooperative Agreement, an investigation has been carried out on the ammonia-hydrogen exchange process for the recovery and concentration of deuterium. Canada is developing, and has made substantial plant committments to, heavy water moderated nuclear reactors for power generation. While three heavy water plants are now under construction in Canada using the hydrogen sulfide-water chemical exchange process, there is interest in reducing the cost of heavy water from the present price of $28.50 per pound, set by the United States Atomic Energy Commission effective May 10, 1968. So far, the only economical method of large-scale heavy water production has been the dual-temperature hydrogen sulfide-water chemical exchange process. The ammonia-hydrogen exchange process, however, has always been recognized as a potential commercial rival, especially now in the wake of renewed interest in larger and more efficient ammonia plants.

The ammonia-hydrogen exchange reaction is
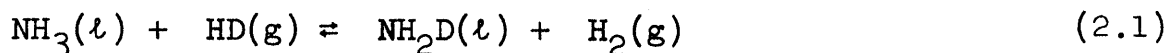
$$NH_3(\ell) + HD(g) \rightleftharpoons NH_2D(\ell) + H_2(g) \qquad (2.1)$$

The reaction must be operated at high pressure because of the low solubility of hydrogen in liquid ammonia and requires catalysis. Clayes, Dayton and Wilmarth (1) found that potassium

amide,$KNH_2$,catalyzes this reaction. Bigeleisen (2) measured the exchange rate as a function of temperature in practical contacting equipment and found it large enough to be of practical interest.

With the exception of the water electrolysis process the separation factor for this process and its temperature coefficient are the highest of all hydrogen-deuterium separation processes considered to date. The separation factor, for concentration of deuterium in the liquid phase, ranges from 3.7 at $20^{\circ}C$ to 8.3 at $-70^{\circ}C$ (3).

In the ammonia-hydrogen ($NH_3$-$H_2$) exchange process, hydrogen gas and liquid ammonia are brought into contact with each other to effect a net transfer of deuterium from the gas phase into the liquid ammonia. There are two ways of accomplishing this net transfer. First, in the bithermal version (see Fig. 1), the transfer is brought about by running two exchange towers at different temperatures in a fashion similar to the hydrogen sulfide-water ($H_2S$-$H_2O$) dual temperature process. Second, in the monothermal version (see Figs. 2 and 3), the exchange tower is run at a constant temperature, but enriched ammonia liquid is cracked into hydrogen and nitrogen at one end of the exchange towers and these gases provide gaseous reflux for the tower. The depleted hydrogen gas at the other end of the exchange towers is synthesized with nitrogen into ammonia to provide the liquid reflux to the exchange towers. For the second process, facilities for

Synthesis Gas to Ammonia Plant

Depleted Deuterium Content

```
                        ┌──────────────────┐
                        │                  │
                        │   Cold Tower     │
                        │   H – D          │
                        │   Exchange       │
                        │                  │
                        └──────────────────┘
```
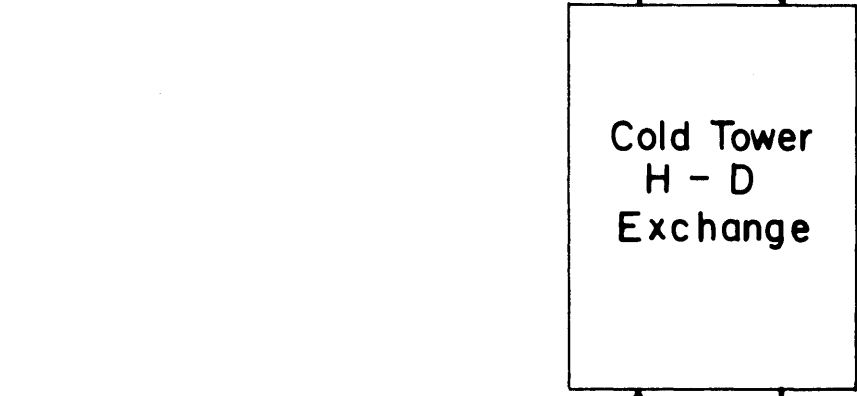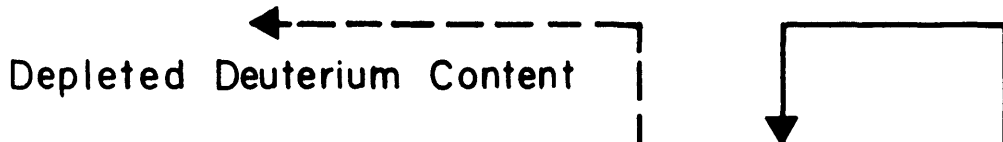
Product Synthesis Gas

Enriched Deuterium Content
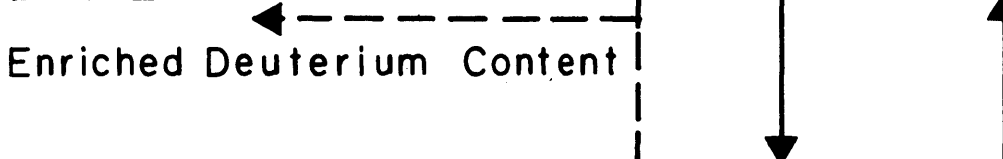
Circulating
Ammonia
+ Catalyst

```
                        ┌──────────────────┐
                        │                  │
                        │   Hot Tower      │
                        │   H – D          │
                        │   Exchange       │
                        │                  │
                        └──────────────────┘
```

Feed Synthesis Gas

Normal Deuterium Content

FIGURE 1

AMMONIA HYDROGEN
EXCHANGE – BITHERMAL

FIGURE 2.
CHEMICALLY REFLUXED
AMMONIA HYDROGEN
EXCHANGE – MONOTHERMAL I

Depleted

Ammonia Product

Main NH$_3$ Synthesis

Reflux NH$_3$ Synthesis

Ammonia Makeup

Ammonia Reflux

Depleted Synthesis Gas

Primary H – D Exchange

Secondary H – D Exchange

Catalyst Recycle

Enriched NH$_3$ + Catalyst

Gas Purification

H$_2$ + N$_2$ Gas Reflux

Catalyst Recovery

Feed Synthesis Gas Normal Deuterium Content

NH$_3$ Cracking

Enriched Ammonia Product
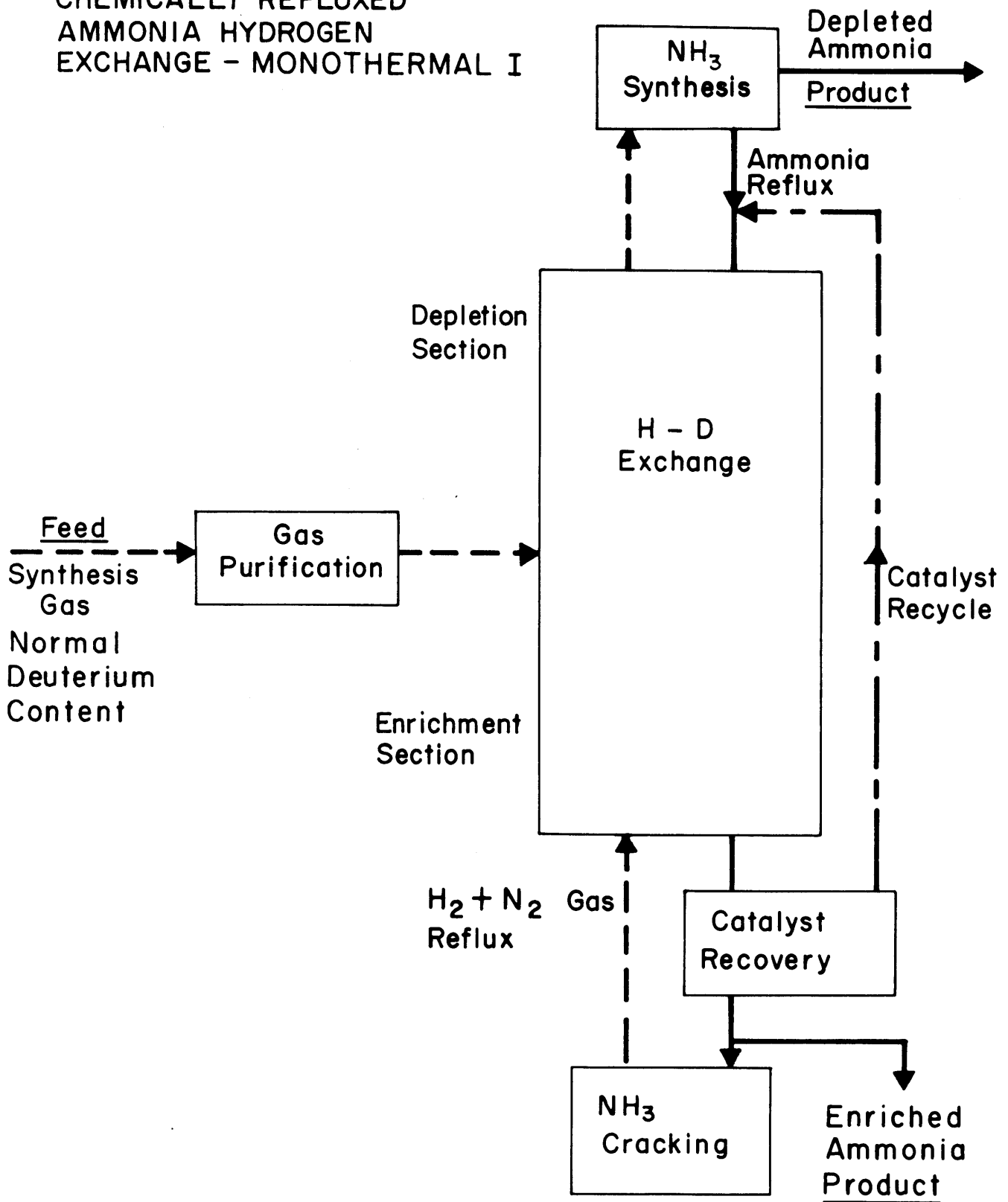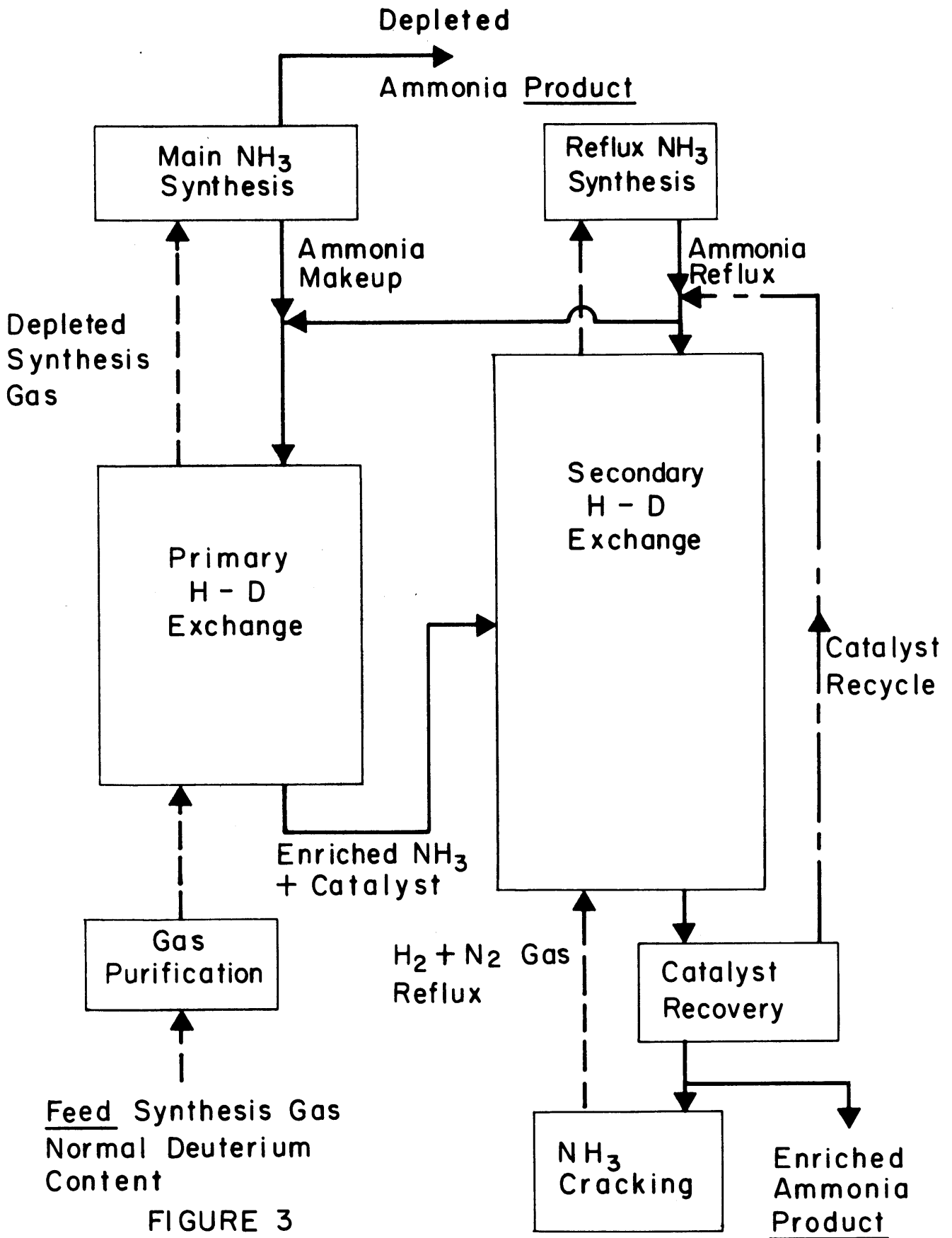
FIGURE 3
CHEMICALLY REFLUXED
AMMONIA HYDROGEN
EXCHANGE – MONOTHERMAL II

ammonia synthesis and cracking are necessary.

In both cases, for large heavy water production rates, the heavy water plant must be associated with a large source of hydrogen. At a deuterium concentration of 132 ppm in the hydrogen of the synthesis gas feed to an ammonia plant, complete recovery of the deuterium would result in a heavy water production of only 0.466 lb $D_2O$/ton $NH_3$ product. Thus, a 1000 ton/day ammonia plant could produce a maximum of 77 tons of $D_2O$/yr. Until recently process hydrogen streams were too small to feed large heavy water units. More than twenty ammonia plants of 1000 ton/day or greater capacity have been committed in USA (4, 5, 6)and three are committed in Canada (6). These plants are the most common large sources of hydrogen, and they are being grouped together sometimes as three units to feed ammonia pipelines (7). Hydrogen alone, rather than the mixture with nitrogen to feed these large ammonia producers, will be produced at the Great Canadian Oil Sands plant at a rate equivalent to 50 tons $D_2O$/year (8, 9). In Texas pipeline hydrogen at 100 million $ft^3$/day (10) could produce nearly 100 tons/year. Although it contains nitrogen as a diluent, synthesis gas has been chosen as the reference feed stream for this study due to its greater availability.

The bithermal ammonia-hydrogen exchange process shown in Figure 1 employs neither a synthesis nor a cracking section. Deuterium concentration is made possible because of the different separation factors for the exchange reaction, Eq. (2.1),

in the two towers of different temperatures. The theory
of dual temperature exchange reactors is described by
Bendict and Pigford (_11_). The simple flow sheet of the bi-
thermal system shows an enriched synthesis gas stream at the
hot tower exit and a depleted gas stream at the cold tower
outlet. The liquid ammonia and the potassium amide catalyst
are continuously recirculated, with deuterium content being
increased in the cold tower and decreased in the hot tower.

Figure 2 shows a simple diagram of the monothermal ex-
change plant. The purified synthesis gas (3:1 hydrogen to
nitrogen mole ratio) which is the feed for the ammonia plant
is first sent into the deuterium exchange section, where it
is stripped of most of its deuterium before passing to the
ammonia synthesis plant. In the exchange tower the feed
synthesis gas of normal deuterium content from the main
plant plus deuterium-enriched cracked gas from the cracking
section flow upward counter-current to a stream of liquid
ammonia. In the presence of potassium amide catalyst dissolved
in the ammonia, deuterium is transferred from the gaseous
phase to the liquid ammonia according to Equation (2.1).

Part of the ammonia synthesized is liquefied and refluxed
into the exchange tower while the rest is withdrawn as the
main ammonia product, which is depleted in deuterium content.

The ammonia-catalyst stream which leaves the bottom of
the exchange tower is enriched in deuterium. The non-volatile
catalyst is concentrated in an ammonia evaporating chamber,

stripped of deuterium, and then returned to the liquid ammonia stream at the top of the exchange tower.

Part of the catalyst-free enriched ammonia stream leaving the catalyst recovery system is withdrawn as product for further enrichment and eventual oxidation to heavy water. The deuterium concentration in this stream depends on process design and operating conditions. The rest of the enriched ammonia is cracked to form the reflux gas stream.

An alternative process is presented in Figure 3, which shows two synthesis sections having a combined capacity equal to that of the plant in Figure 2. As shown, this arrangement could also involve a second exchange tower to strip the deuterium from the synthesis gas feed so that inerts in the feed gas would not affect operations in the major exchange tower from which the enriched ammonia product is withdrawn. The obvious disadvantage of Figure 3 is the greater cost incurred in maintaining two separate synthesis plants and two exchange towers, even if the over-all capacity remained the same.

## 2.2  Historical Development of the $NH_3$-$H_2$ Exchange Process

Many interesting studies on the ammonia-hydrogen exchange as a primary process have been conducted through the years. The object of all these studies was to see if the $NH_3$-$H_2$ exchange process, whether monothermal or bithermal, could effectively compete commercially against the established dual-temperature water-hydrogen sulfide exchange process.

Most of the early studies have dealt with the bithermal process.

In 1951, Thompson and Cohen released a very optimistic report (12), claiming a price of $18 per pound heavy water based on bithermal production. A few years later, however, Martin and Barr (13) repudiated their findings by stating that the liquid-vapor equilibrium data and the plate efficiency of 40% used by Thompson and Cohen were unduly and unreliably over-optimistic. Martin and Barr were completely negative regarding the ammonia-hydrogen exchange process even to the point of discouraging further laboratory work on the process without first seeking basic improvements of significant value.

Then, in 1958, the British firm Constructors John Brown introduced a bithermal version (14) which had an estimated heavy water production cost of $21.50 per pound. No pilot plant, however, has been built based on their report. Atomic Energy of Canada, Ltd., conducted their own bithermal study (15), but reached less optimistic conclusions.

For the monothermal version, the French have done much process development. The French paper (16) released at the 1964 Geneva Conference on Peaceful Uses of Atomic Energy reported some pilot-plant findings, as well as a recommended flow sheet for a monothermal plant. More insight into the French developments is obtainable from two British patents, Nos. 950,200 and 952,335, granted to the French experimenters.

The first patent   No. 950,200 (17), deals with an efficient method of recovering and recycling the potassium amide catalyst.  The second one, No. 952,335 (18), is essentially a patent on the monothermal set-up explained in the Geneva paper (16).

The French have constructed a 20 ton per year monothermal plant at Mazingarbe, France.  A description of their plant costs and process economics has not been released.  The French, in their 1958 analysis (19), were not very optimistic about being able to produce heavy water below $28 per pound.

More recently a news item (20) reported that the French are initiating a campaign to export heavy-water plants based on the ammonia-hydrogen exchange process used in their Mazingarbe plant.  The same article claimed the French say their process can produce deuterium for about 10% less than the hydrogen-sulfide process used in the U.S. and Canada. Three later news articles (21, 22, 23) indicated the French were discussing the sale of an ammonia exchange plant to the Indian A.E.C.

As an added item of interest, a brief news report in December 1957 (24) mentioned that the Russians have built an ammonia-hydrogen exchange plant of an estimated 30 to 40 tons $D_2O$ per year capacity.  Unfortunately, no details were given, and no other confirmation of this announcement has been found.

2.3    Scope of This Study

2.3.1  Chemical Reflux from Ammonia Synthesis and Cracking

Considering the greater simplicity and anticipated lower capital costs for the monothermal system as shown in Figure 2, emphasis was given in this study to the development and evaluation of a preliminary plant design based on that system. The major portions of the plant requiring design are the exchange section (including gas purification and catalyst recovery equipment), the ammonia synthesis sections, and the ammonia cracking section.

For adequate design of the plant, three sets of physico-chemical data have been correlated and presented as Supplements A, B, and C in a companion volume to this report (25). These three sets are:  A, Liquid-Vapor Equilibrium of the System $NH_3-H_2-N_2$; B, Enthalpies of the Three Gases; and C, Thermodynamic Equilibrium for Ammonia Synthesis and Cracking. These data were used in the development of mass and energy balances and in sizing of equipment during the process design.

Due to the low solubility of hydrogen in liquid ammonia, the transfer efficiencies of the gas-liquid contactors (sieve trays) employed in the exchange towers are quite low. A method of predicting tray efficiencies for the ammonia-hydrogen system was developed and is presented in Supplementary Report D (25).

The time available for this study before contract close-out due to termination of funding of the U.S.-Canada Cooperative

Agreement did not permit plant and economic optimization. However, in order to give a rough estimate of the cost of recovering deuterium from ammonia synthesis gas using chemically refluxed (monothermal operation) ammonia-hydrogen exchange, a set of operating conditions was arbitrarily selected, a process design developed, and a cost estimate prepared (with the assistance of an industrial firm experienced in processing gases and liquids at low temperatures) using this design as a basis. The reader should keep the limitations imposed by this required "one-shot" approach in mind when reading the following sections.

2.3.2  Other Studies

In addition to the scope of work related to the ammonia-hydrogen exchange process as discussed in the process section, two other studies were carried out during the course of this project.

Since the transfer efficiencies of the sieve trays employed in the design of the deuterium exchange system were so low (see Supplementary Report D(25)), a design study of the use of stirred gas-liquid contactors for deuterium exchange was conducted. Cost information on large stirred gas-liquid contactors was not available, so that the process design and evaluation discussed in this report was based entirely on conventional tray tower design. In Supplementary Report D(25), a design method is presented for estimating the stage transfer efficiency for the ammonia-hydrogen system as a function of

residence time in the contactor. Stage efficiencies of 50 to 60%, compared to about 2% for sieve trays, appear to be feasible. The number and volume of transfer stages could therefore be significantly reduced by using stirred contactors, at the expense, however, of more complicated equipment with recovery parts and additional energy requirements.

Another study, reported in Supplementary Report F($\underline{25}$), involved a survey of the possibilities of using chemically-generated reflux in the water-hydrogen sulfide exchange process for the extraction of deuterium from water. A search was made for an element or stable chemical radical M whose oxide $MO_n$ and sulfide $MS_n$ could take part in the reaction

$$\frac{1}{n} MO_n + H_2S \rightleftarrows \frac{1}{n} MS_n + H_2O \tag{2.2}$$
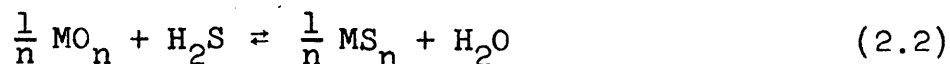
with an equilibrium constant favoring formation of oxide at one temperature and sulfide at another. No sulfide-oxide pair was found with equilibrium constants much greater than unity at one feasible temperature and much less than unity at another. The most favorable sulfide-oxide pair found, $MoO_2$-$MoS_2$, had an estimated thermal energy requirement greater than that required by the conventional dual temperature water-hydrogen sulfide exchange process. Consequently, further investigation of the chemically refluxed water-hydrogen sulfide process was not carried out.

### 3.0 PROCESS AND EQUIPMENT DESIGN

### 3.1 Relation Between Deuterium Plant and Ammonia Synthesis Plant

### 3.1.1 Original Ammonia Plant

To facilitate cost estimation, it has been assumed that the deuterium extraction plant will be built after and added to an existing ammonia synthesis plant, without materially altering the amount of ammonia available for sale. The rate of production of synthesis gas is assumed to remain the same after the deuterium extraction plant is added, so that the cost of producing synthesis gas need not be estimated or charged against deuterium extraction.

Although a somewhat more economical operation would have been found if the ammonia synthesis plant and the deuterium extraction plant had been designed as an integrated unit, instead of designing the deuterium extraction plant to be added to an existing ammonia plant, design of an integrated unit would have taken more time than was available to this study.

Figure 4 illustrates the synthesis compressor requirements and inlet and outlet flow rates for synthesis section of the original ammonia synthesis plant to which the deuterium extraction plant is to be added. The design capacity of this plant is 919.6 tons of ammonia per stream day.

Feed for this plant consists of 9576 pound moles per hour of synthesis gas containing 7096 moles per hour (74.1%) of hydrogen. This gas enters the primary compressor V-101 at 381 psia and 100°F and is compressed in the first case of the

Ammonia Synthesis Section
919.6 T/D

Recycle Gas
44,735 m/hr total
105 °F
2025 psia

Synthesis Gas
7097 m/hr H₂
9576.0 m/hr total
100°F      339°F      46°F
381 psia   945 psia   935 psia

Compressed Feed Gas
5431 m/hr total
155 °F
2145 psia

Ammonia for Sale
4508 m/hr total
920 T/D
-28°F
65 psia

V-101 Primary & Recycle Compressor
13,240 HP
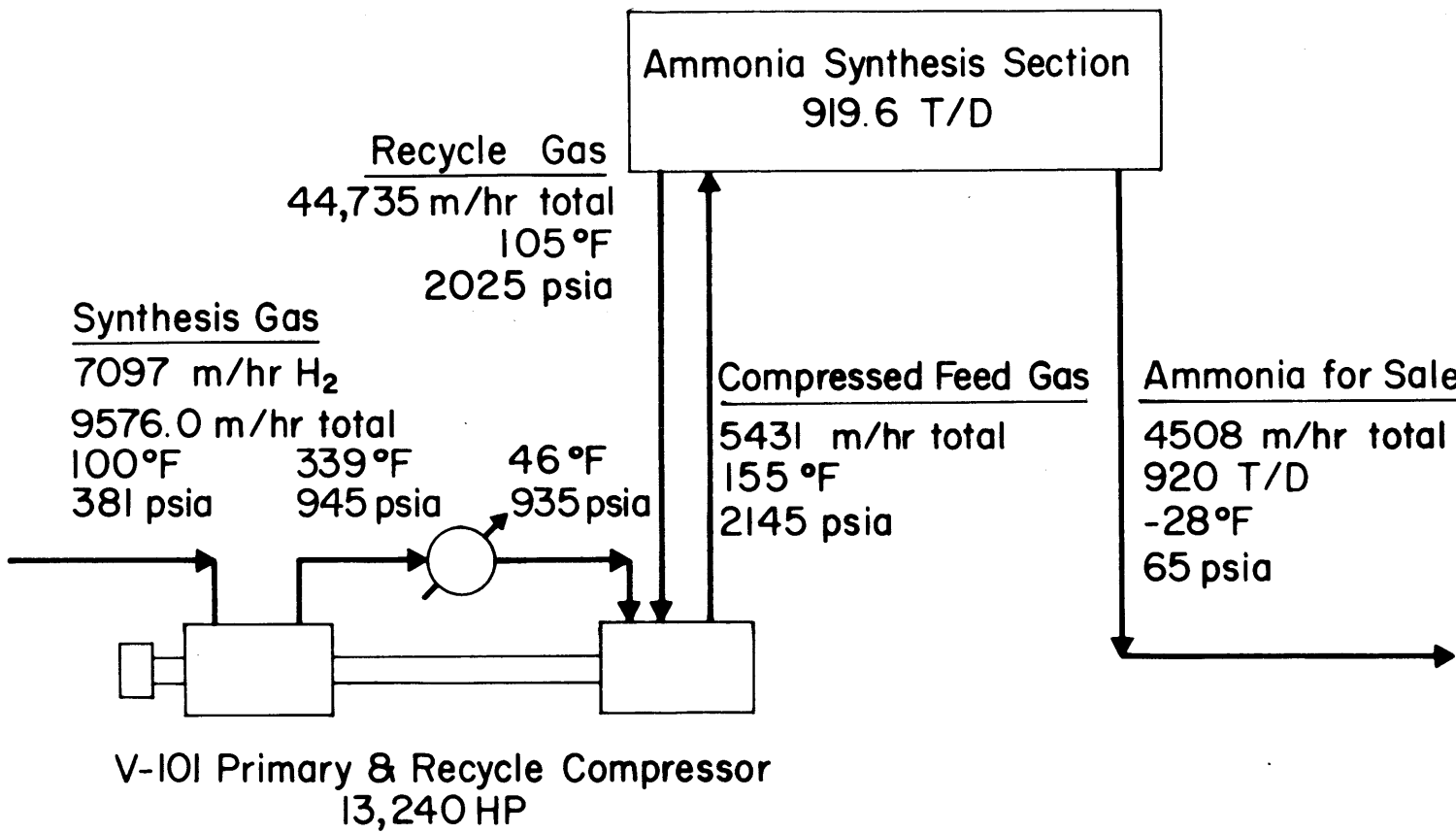
FIGURE 4.
ORIGINAL AMMONIA
SYNTHESIS PLANT

-22-

compressor to 945 psia and then cooled to $46^\circ$F. The gas is compressed to 2025 psia in the first three wheels of the second case of the compressor, where it is joined by 44,735 moles per hour of recycle gas from the synthesis reactors. The combined streams totalling 54,311 moles per hour are compressed to 2145 psia and $155^\circ$F and used as feed for the ammonia synthesis section. The calculated compressor power input is 13,240 HP for an isentropic efficiency of 68.8%.

Product ammonia at the rate of 4507.8 moles per hour is delivered at $-28^\circ$F and 65 psia.

Figure 5 is a detailed flow diagram for a synthesis section of an ammonia plant starting from the synthesis gas compressor up to the final product. The cost estimate for ammonia synthesis was based on this type of plant. The flow quantities in the diagram have been normalized to an ammonia output of 1000 pounds. The feed required is 1100.3 pounds, analysis of which is reported in Table 3-1. The difference of 100.3 pounds between feed and ammonia product leaves at various points as purge gas, mostly methane and argon.

Table 3-1

Mole Percentages of Quantities at Various Points on
Synthesis Plant Flow Diagram, Figure 5

|  | $H_2$ | $N_2$ | $CH_4$ | A | $NH_3$ |
|---|---|---|---|---|---|
| Feed to V-1 | 74.0 | 24.7 | 1.0 | 0.3 | 0.0 |
| From converters Y-1 | 54.9 | 18.2 | 11.2 | 3.7 | 12.0 |
| Sep. S-2, Vapor | 63.3 | 20.9 | 10.2 | 3.5 | 2.1 |
| Sep. S-2, Liquid | 0.3 | 0.1 | 0.2 | 0.0 | 99.4 |
| Purge from S-3 | 47.0 | 18.0 | 20.3 | 3.8 | 10.9 |
| Purge from S-4 | 61.0 | 20.2 | 12.5 | 4.1 | 2.2 |
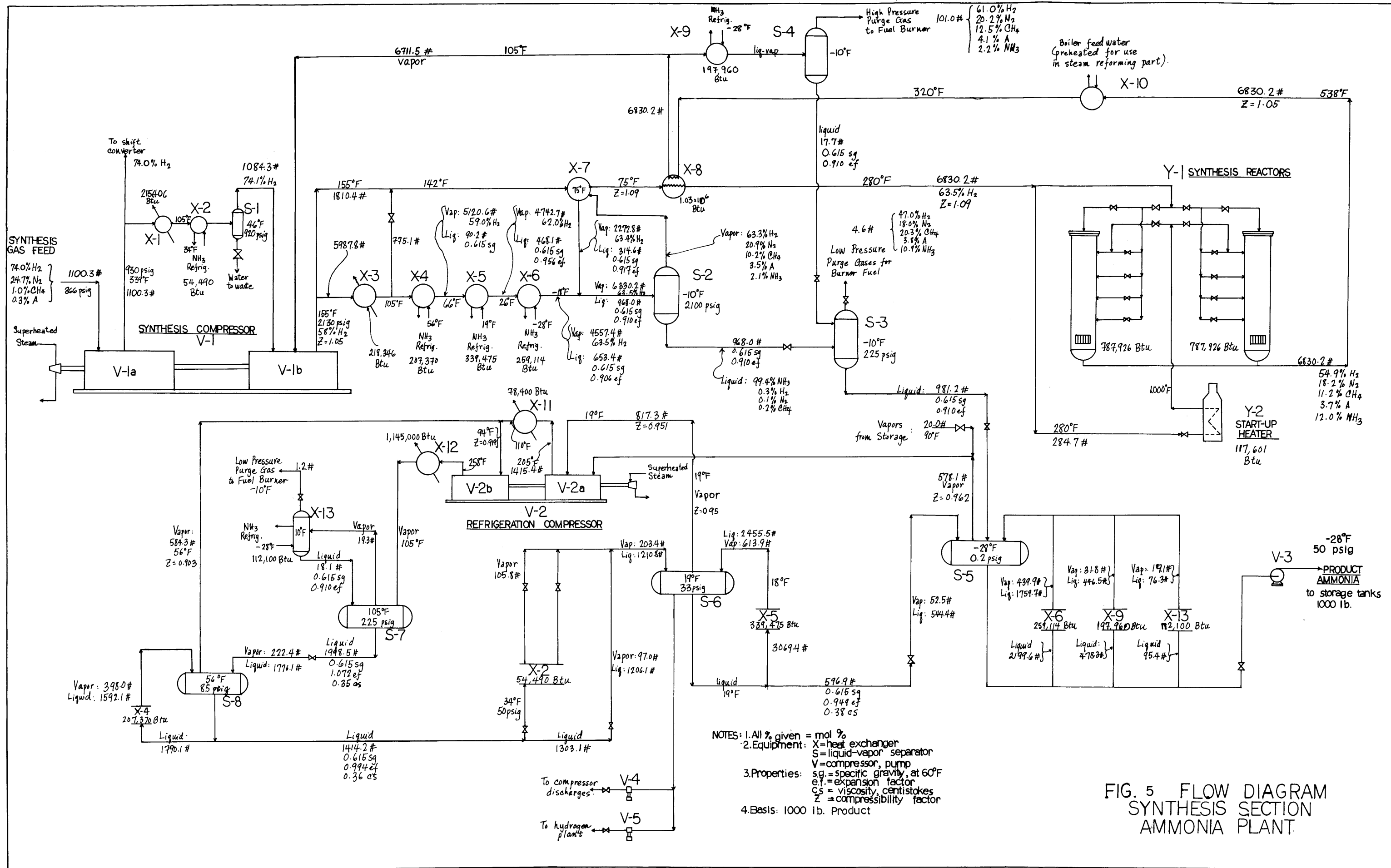
FIG. 5 FLOW DIAGRAM
SYNTHESIS SECTION
AMMONIA PLANT

Four wheels in the first case of centrifugal compressor V-1 (part V-1a on Figure 5) compress synthesis gas from 366 to 920 psig. The gas is then cooled to 46°F by water, followed by ammonia refrigeration, and is compressed in three of the four wheels of the second case of compressor V-1 (part V-2b), where it is joined by 6711.5 pounds of product from the ammonia converters Y-1a and Y-1b. The fourth wheel of the second case takes the combined streams to 2130 psig. The compressed gas is next cooled to -10°F in heat exchangers X-3, X-4, X-5, X-6, and X-7, and liquid ammonia is separated in S-2 at 2100 psig and -10°F. 6830.2 pounds of combined feed and recycle gas is preheated to 280°F by heat exchange against converted product gas in X-8 and is used as feed to the catalyst-filled converters Y-1a and Y-1b. Catalyst temperature is held at about 790°F by spaced injection of feed gas as quench. Converter product is cooled to 538°F in heat exchangers built into the converters, and to 320°F in boiler feed water preheater X-10.

Separators, notably S-2 and S-3, produce a liquid stream of essentially pure ammonia, which is led off into the refrigeration section. This section consists of a refrigeration compressor and a series of separators and heat exchangers. Ammonia refrigeration required by the synthesis gas in the upper part of the flow sheet Figure 5 is provided by the refrigeration section itself. As such, heat exchangers X-2, X-4, X-5, X-6, X-9, and X-13 appear twice in the flow sheet, once to indicate the flow of the synthesis gas as it cools down, and again to show the flow of the ammonia refrigerant. At the end of the line, liquid ammonia at -28°F and 50 psig is withdrawn as final

product to be stored and sold.

## 3.1.2  Combined Ammonia and Deuterium Extraction Plant

Figure 6 shows schematically how a deuterium extrac-
tion plant would be added to the ammonia synthesis plant of
Figure 4, whose components are shown as broken lines in Fig-
ure 6. The main units of the deuterium extraction plant added
in Figure 6 are the deuterium exchange section, the ammonia
cracking section, an added ammonia synthesis section with ca-
pacity of 481.8 tons per day and the recycle compressor V-102.

This flowsheet takes as feed synthesis gas at the same
flow rate and conditions as Figure 4. Hydrogen in feed gas
is assumed to contain 132 atoms of deuterium per million atoms
of hydrogen (132 ppm D). This feed gas is compressed to 945
psia in the first case of the compressor V-101 exactly as in
Figure 4. Conditions in the second case are changed from Fig-
ure 4, however, because this case cannot be used to compress
recycle gas as well as feed since recycle gas in this flowsheet
contains only 13.2 ppm D. Gas from the second case is compres-
sed to 2145 psia, as in Figure 4. In order to avoid surging
in the fourth wheel of the second case of the primary compressor
when it is no longer called on to handle the synthesis section
recycle gas, it is considered necessary to recycle feed synthe-
sis gas around the fourth wheel as shown in Figure 6. While
a detailed design might indicate the possibility of some power
savings without encountering surging, the power consumed by
V-101 was taken to be 13,240 HP as shown for the original plant
in Figure 4. This consideration is one area where the design

Added Ammonia Synthesis
Section, 481.8 T/D

Original Ammonia
Synthesis Section
919.6 T/D

**Recycle Gas**
68,172 m/hr
105 °F
2025 psia

**Compressed Feed Gas**
82,750 m/hr
105.9 °F
2145 psia

**Depleted Ammonia**
13.2 ppm D
7148 m NH$_3$/hr
-28°F
65 psia

**V-102 Recycle Compressor**
3400 HP

13.2 ppm D
278 m/hr NH$_3$
10,638 m/hr H$_2$
14,578 m/hr total
49 °F
2112 psia

**Ammonia for Sale**
13.2 ppm D
4465 m NH$_3$/hr
911 T NH$_3$/D

③

**Bypass of
Deuterium
Plant**

**Depleted
Ammonia
Reflux**
13.2 ppm D
2660 m NH$_3$/hr
-28°F
65 psia

**Synthesis Gas**
132 ppm D
7097 m/hr H$_2$
9576 m/hr total

**Synthesis Gas**
132 ppm D
7097 m/hr H$_2$
9576 m/hr total

②

100 °F
381 psia

339 °F
945 psia

46 °F
935 psia

237 °F
2145 psia

①

Deuterium
Exchange
Section

**Enriched
Ammonia
Product**
13,200 ppm D
42.6 m/hr
8.7 T NH$_3$/D
(66.8 T D$_2$O/yr)

**V-101 Primary Compressor**
13,240 HP

**Enriched
Synthesis Gas
Reflux**
13,200 ppm D
92 m/hr NH$_3$
3553 m/hr H$_2$
4830 total

2454 m/hr NH$_3$
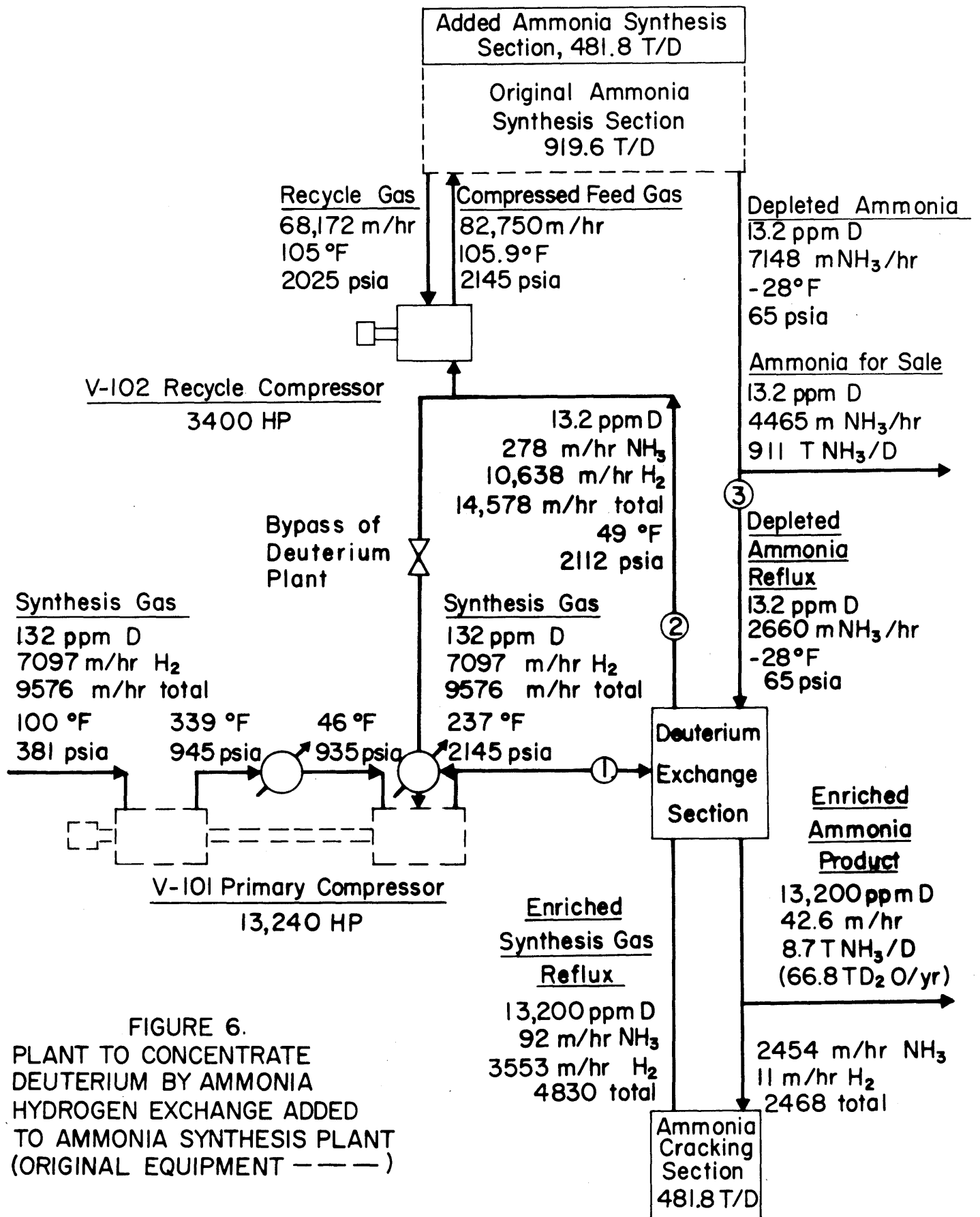11 m/hr H$_2$
2468 total

Ammonia
Cracking
Section
481.8 T/D

FIGURE 6.
PLANT TO CONCENTRATE
DEUTERIUM BY AMMONIA
HYDROGEN EXCHANGE ADDED
TO AMMONIA SYNTHESIS PLANT
(ORIGINAL EQUIPMENT ———)

of an ammonia plant and deuterium recovery plant simultane-
ously could result in savings of both capital and operating
costs for the primary compressor, V-101, when recycle duty
for the synthesis plant is shifted to added compressor V-102.

Details of the process used in the deuterium exchange
section and the ammonia cracking section, to the right of
point (1) and below points (2) and (3), will be described in
detail in Section 3.2.  In outline, what happens is as follows.
Purified feed synthesis gas containing 132 ppm D is passed
through a system of gas-liquid contactors at $-4^{\circ}F$ and 2139 psia,
in which the gas phase is predominantly synthesis gas
($3 H_2 : 1 N_2$) and the liquid phase is predominantly a dilute
solution of potassium amide ($KNH_2$) in ammonia.  The $KNH_2$
catalyzes the deuterium exchange reaction

$$NH_3(\ell) + HD(g) \quad \rightleftarrows \quad NH_2D(\ell) + H_2(g) \qquad (3.1)$$
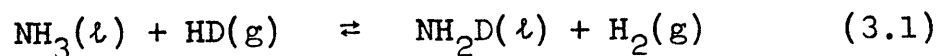
which has a separation factor of around 5 favoring concentra-
tion of deuterium in the liquid phase.  These gas-liquid con-
tactors are refluxed with 2660 moles per hour of liquid ammonia
and 4830 moles per hour of synthesis gas containing 3553 moles
per hour of hydrogen.  In the deuterium exchange section up-
flowing synthesis gas is stripped of deuterium till the efflu-
ent synthesis gas contains 13.2 ppm D.  The downflowing ammonia
is enriched in deuterium until the ammonia leaving the bottom
of the contactor contains 13,200 ppm D.  42.6 moles per hour
(8.7 tons per day) of this enriched ammonia is withdrawn as
product, and the remainder of the enriched ammonia, 2431 moles
per hour, is sent to the cracking section to provide enriched

synthesis gas reflux. This section cracks 481.8 tons of ammonia per day.

Deuterium in the 8.7 tons/day of enriched ammonia product may be concentrated further by fractional distillation to yield slightly less than 8.7 tons of normal ammonia for sale, plus highly enriched ammonia to be converted to heavy water. The deuterium content of the enriched ammonia product would produce

$$\frac{8.7 \times 0.0132 \times \frac{3}{2} \times 20 \times 330}{17} = 66.8 \text{ tons}$$

$D_2O$ per year, assuming 330 stream days operation per year.

Synthesis gas containing 13.2 ppm D arrives at the recycle compressor V-102 from the top of the exchange section at $49°F$ and 2112 psia at a flow rate of 14,578 moles per hour of which 10,638 moles per hour is hydrogen. This gas is compressed to 2145 psia in the recycle compressor along with 68,172 moles per hour of recycle gas. Power consumption of V-102 is 3400 HP. Volumetric capacity at 2025 psia is 3300 cfm; after gas at 2112 psia is added, capacity is 3870 cfm. It is then converted to ammonia containing 13.2 ppm D in the two ammonia synthesis sections, the original unit with a capacity of 919.6 tons per day, and an added unit with a capacity of 481.8 tons per day, to resynthesize the ammonia dissociated in the cracking section.
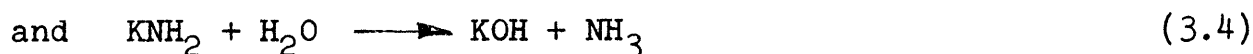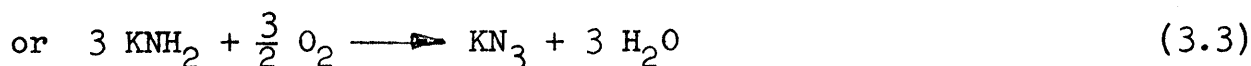
Of the 919.6 tons per day synthesized in the original unit, 910.9 leave the plant as depleted ammonia for sale and 8.7 leave as enriched product ammonia.

3.2 <u>Description of Process in Deuterium Exchange and</u>
<u>Ammonia Cracking Sections</u>

Figure 7 is a process flowsheet for the deuterium ex-
change and ammonia cracking sections of the plant.  Detailed
data on flow rates, compositions, pressures and temperatures
for the points in this flowsheet designated by circled numbers
are given in Table 3.2.  Points (1), (2) and (3) correspond
to the points correspondingly numbered on Fig. 6.

3.2.1 <u>Feed Preparation</u>

Synthesis gas feed flowing at 9579 lb moles/hr at
point (1) must be cooled and treated for removal of oxygen
and water down to concentrations under 0.1 ppm.  This ex-
treme purification is necessary in order to prevent loss
of $KNH_2$ through the reactions

$$2 \text{ } KNH_2 + \frac{3}{2} O_2 \longrightarrow KNO_2 + KOH + NH_3 \qquad (3.2)$$

$$\text{or} \quad 3 \text{ } KNH_2 + \frac{3}{2} O_2 \longrightarrow KN_3 + 3 \text{ } H_2O \qquad (3.3)$$

$$\text{and} \quad KNH_2 + H_2O \longrightarrow KOH + NH_3 \qquad (3.4)$$
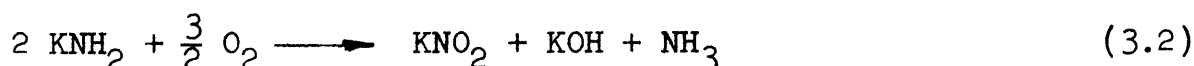
Loss of potassium amide is costly, and possible for-
mation of potassium azide $(KN_3)$ represents an explosive hazard.
Since synthesis gas from reformed natural gas is reported (26)
to contain well under 0.1 ppm oxygen no special provision for
oxygen removal has been provided.  The feed synthesis gas
is expected to contain 0.017% water vapor and up to 10 ppm
carbon monoxide and carbon dioxide.  The water vapor is re-

FIGURE 7: PROCESS FLOWSHEET
FOR EXCHANGE AND CRACKING SECTIONS
LEGEND FOR MAIN COMPONENTS OF STREAMS

— — — 3H₂ : 1N₂
——— AMMONIA
—×—×—× KNH₂ AND AMMONIA
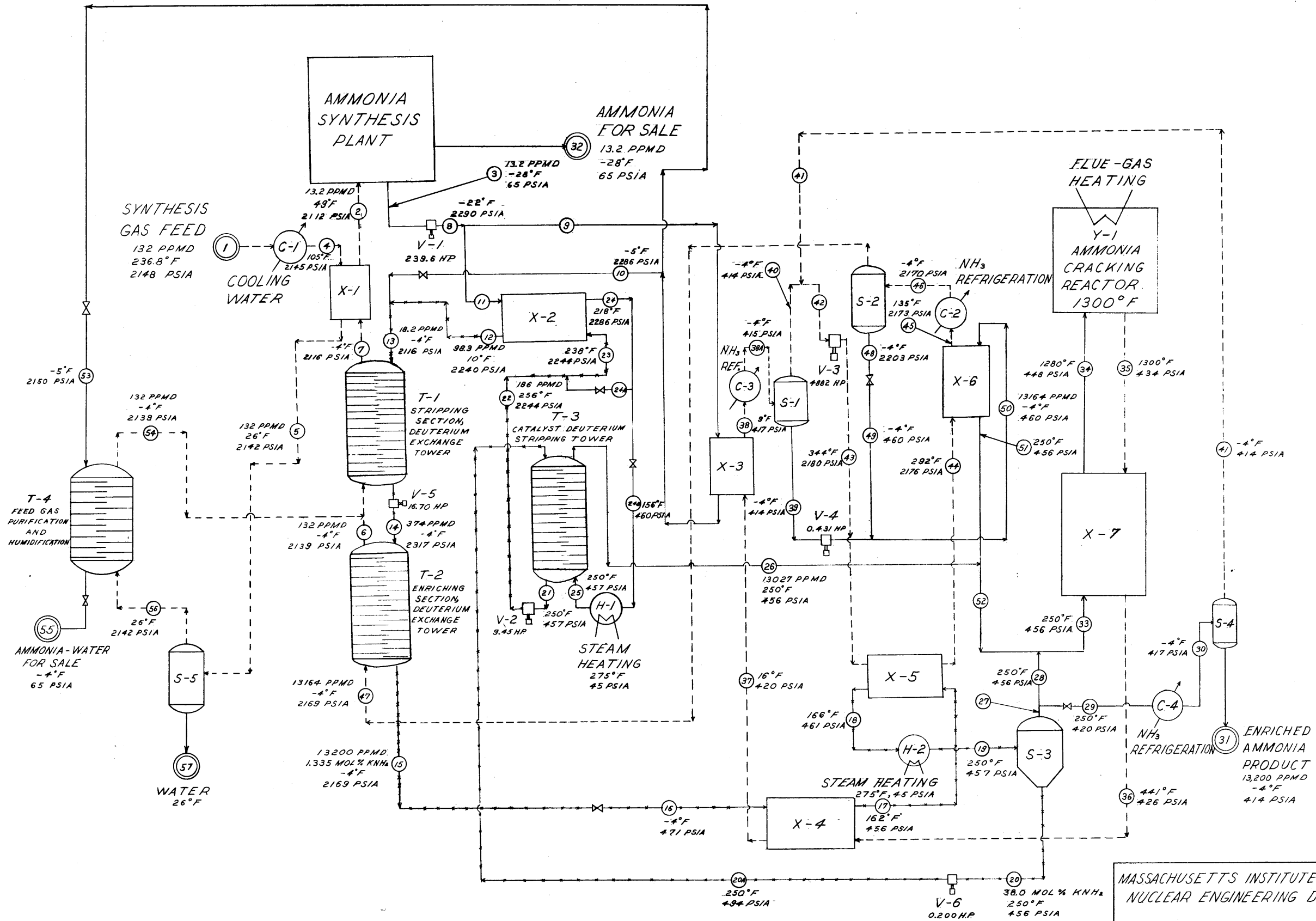
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NUCLEAR ENGINEERING DEPART.

## TABLE 3.2 FLOWSHEET CONDITIONS, FIGURE 7

### Sheet 1

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | FLOW RATE, POUND MOLES/HOUR | | | KNH$_2$ (H$_2$O) | TOTAL |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | NH$_3$ | H$_2$ | N$_2$, etc. | | |
| 1 | 236.8 | 2148 | V | 13.2 | | 7096.93 | 2480.59 | (1.63) | 9579.15 |
| 2 | 49 | 2112 | V | 13.2 | 277.99 | 10638.47 | 3661.07 | | 14577.53 |
| 3 | -28 | 65 | L | 13.2 | 2945.74 | | | | 2945.74 |
| 4 | 105 | 2145 | V | 132 | | 7096.93 | 2480.59 | (1.63) | 9579.15 |
| 5 | 26 | 2142 | V | 132 | | 7069.93 | 2480.59 | (1.63) | 9579.15 |
| 6 | -4 | 2139 | V | 132 | 92.11 | 3553.39 | 1184.79 | | 4830.29 |
| 7 | -4 | 2106 | V | 13.2 | 277.99 | 10638.47 | 3661.07 | | 14577.53 |
| 8 | -22 | 2290 | L | 13.2 | 2945.74 | | | | 2945.74 |
| 9 | -22 | 2290 | L | 13.2 | 2788.61 | | | | 2788.61 |
| 10 | - 5 | 2286 | L | 13.2 | 2339.11 | | | | 2339.11 |
| 11 | -22 | 2290 | L | 13.2 | 157.13 | | | | 157.13 |
| 12 | 10 | 2240 | L | 98.3 | 134.68 | | | 33.67 | 168.35 |
| 13 | - 4 | 2116 | L | 18.2 | 2473.79 | | | 33.67 | 2507.46 |
| 14 | - 4 | 2317 | L | 374 | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.40 |
| 15 | - 4 | 2169 | L | 13200 | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.4 |

Table 3.2 (cont'd)  Sheet 2

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | FLOW RATE, POUND MOLES/HOUR | | | KNH$_2$ (H$_2$O) | TOTAL |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | NH$_3$ | H$_2$ | N$_2$, etc. | | |
| 16 | − 4 | 471 | Mixture | 13200 | | | | | |
| | | | L | | 2473.34 | 2.44 | 1.10 | 33.67 | 2510.55 |
| | | | V | | 0.73 | 8.31 | 2.81 | | 11.85 |
| | | | Total | | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.40 |
| 17 | 162 | 465 | Mixture | 13200 | | | | | |
| | | | L | | 1100.03 | | | 33.67 | 1133.70 |
| | | | V | | 1374.04 | 10.75 | 3.91 | | 1388.70 |
| | | | Total | | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.4 |
| 18 | 166 | 461 | Mixture | 13200 | | | | | |
| | | | L | | 876.52 | | | 33.67 | 910.19 |
| | | | V | | 1597.55 | 10.75 | 3.91 | | 1612.2 |
| | | | Total | | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.4 |
| 19 | 250 | 457 | Mixture | 13200 | | | | | |
| | | | L | | 54.94 | | | 33.67 | 88.61 |
| | | | V | | 2419.13 | 10.75 | 3.91 | | 2433.79 |
| | | | Total | | 2474.07 | 10.75 | 3.91 | 33.67 | 2522.40 |
| 20 | 250 | 456 | L | 13200 | 54.94 | | | 33.67 | 88.61 |
| 20A | 250 | 494 | L | 13200 | 54.94 | | | 33.67 | 88.61 |
| 21 | 250 | 457 | L | 186 | 54.94 | | | 33.67 | 88.61 |
| 22 | 256 | 2244 | L | 186 | 54.94 | | | 33.67 | 88.61 |

Table 3.2 (cont'd)  Sheet 3

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | NH₃ | H₂ | N₂, etc. | KNH₂ (H₂O) | TOTAL |
|--------|---------|------------|-------|-------|-----|-----|----------|------------|-------|
| | | | | | FLOW RATE, POUND MOLES/HOUR | | | | |
| 23 | 238 | 2244 | L | 98.3 | 134.68 | | | 33.67 | 168.35 |
| 24 | 218 | 2286 | L | 13.2 | 157.13 | | | | 157.13 |
| 24A | 218 | 2286 | L | 13.2 | 79.74 | | | | 79.74 |
| 24B | 156 | 460 | Mixture | 13.2 | | | | | |
| | | | L | | 13.03 | | | | 13.03 |
| | | | V | | 64.36 | | | | 64.36 |
| | | | Total | | 77.39 | | | | 77.39 |
| 25 | 250 | 457 | V | 13.2 | 77.39 | | | | 77.39 |
| 26 | 250 | 456 | V | 13027 | 77.39 | | | | 77.39 |
| 27 | 250 | 456 | V | 13200 | 2419.13 | 10.75 | 3.91 | | 2433.7 |
| 28 | 250 | 456 | V | 13200 | 2376.50 | 10.75 | 3.91 | | 2391.16 |
| 29 | 250 | 420 | V | 13200 | 42.63 | 0.19 | 0.06 | | 42.88 |
| 30 | - 4 | 417 | L | 13200 | 42.63 | 0.19 | 0.06 | | 42.88 |
| 31 | - 4 | 414 | L | 13200 | 42.63 | 0.03 | 0.01 | | 42.67 |
| 32 | -28 | 65 | L | 13.2 | 4201.86 | | | | 4201.86 |
| 33 | 250 | 456 | V | 13164 | 2952.10 | 11.81 | 4.32 | | 2968.23 |
| 34 | 1280 | 448 | V | 13164 | 2952.10 | 11.81 | 4.32 | | 2968.23 |
| 35 | 1300 | 434 | V | 13164 | 590.32 | 3554.48 | 1185.21 | | 5330.01 |

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Table 3.2 (cont'd)   Sheet 4

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | FLOW RATE, POUND MOLES/HOUR | | | KNH₂ (H₂O) | TOTAL |
|--------|---------|------------|-------|-------|-----------------|----------|----------|------|-------|
| | | | | | NH₃ | H₂ | N₂, etc. | | |
| 36 | 441 | 426 | V | 13164 | 590.32 | 3554.48 | 1185.21 | | 5330.01 |
| 37 | 16 | 420 | Mixture | 13164 | | | | | |
| | | | L | | 24.38 | | | | 24.38 |
| | | | V | | 565.94 | 3554.48 | 1185.21 | | 5305.63 |
| | | | Total | | 590.32 | 3554.48 | 1185.21 | | 5330.01 |
| 38 | 9 | 417 | Mixture | 13164 | | | | | |
| | | | L | | 86.04 | 0.09 | 0.04 | | 86.17 |
| | | | V | | 504.28 | 3554.39 | 1185.12 | | 5243.84 |
| | | | Total | | 590.32 | 3554.48 | 1185.16 | | 5330.01 |
| 38A | – 4 | 415 | Mixture | 13164 | | | | | |
| | | | L | | 251.94 | 0.21 | 0.09 | | 252.24 |
| | | | V | | 338.38 | 3554.27 | 1185.12 | | 5077.77 |
| | | | Total | | 590.32 | 3554.48 | 1185.21 | | 5330.01 |
| 39 | – 4 | 414 | L | 13164 | 251.94 | 0.21 | 0.09 | | 252.24 |
| 40 | – 4 | 414 | V | 13164 | 338.38 | 3554.27 | 1185.12 | | 5077.77 |
| 41 | – 4 | 414 | V | 13200 | 0.16 | 0.05 | | | 0.21 |
| 42 | – 4 | 414 | V | 13164 | 338.38 | 3554.43 | 1185.17 | | 5077.98 |
| 43 | 344 | 2180 | V | 13164 | 338.38 | 3554.43 | 1185.17 | | 5077.98 |
| 44 | 292 | 2176 | V | 13164 | 338.38 | 3554.43 | 1185.17 | | 5077.98 |
| 45 | 135 | 2173 | V | 13164 | 338.38 | 3554.43 | 1185.17 | | 5077.98 |

Table 3.2 (cont'd)  Sheet 5

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | FLOW RATE, POUND MOLES/HOUR NH$_3$ | H$_2$ | N$_2$, etc. | KNH$_2$ (H$_2$O) | TOTAL |
|--------|---------|-----------|-------|-------|------|------|------|------|-------|
| 46 | - 4 | 2170 | Mixture | 13164 | | | | | |
|  |  |  | L |  | 246.27 | 1.04 | 0.38 | | 247.69 |
|  |  |  | V |  | 92.11 | 3553.39 | 1184.79 | | 4830.29 |
|  |  |  | Total |  | 338.38 | 3554.43 | 1185.17 | | 5077.98 |
| 47 | - 4 | 2169 | V | 13164 | 92.11 | 3553.39 | 1184.79 | | 4830.29 |
| 48 | - 4 | 2169 | L | 13164 | 246.27 | 1.04 | 0.38 | | 247.69 |
| 49 | - 4 | 460 | Mixture | 13164 | | | | | |
|  |  |  | L |  | 246.19 | 0.23 | 0.10 | | 246.52 |
|  |  |  | V |  | 0.08 | 0.81 | 0.28 | | 1.17 |
|  |  |  | Total |  | 246.27 | 1.04 | 0.38 | | 247.69 |
| 50 | - 4 | 460 | Mixture | 13164 | | | | | |
|  |  |  | L |  | 498.13 | 0.44 | 0.19 | | 498.76 |
|  |  |  | V |  | 0.08 | 0.81 | 0.28 | | 1.17 |
|  |  |  | Total |  | 498.21 | 1.25 | 0.47 | | 499.93 |
| 51 | 250 | 456 | V | 13164 | 498.21 | 1.25 | 0.47 | | 499.93 |
| 53 | - 5 | 2150 | L | 13.2 | 449.50 | | | | |
| 54 | - 4 | 2139 | V | 13.2 | 186.16 | 7095.82 | 2480.19 | | 9762.17 |
| 55 | - 4 | 65 | Mixture | 13.2 | | | | | |
|  |  |  | L |  | 263.34 | 0.03 | 0.01 | (0.66) | 264.04 |
|  |  |  | V |  |  | 1.08 | .39 | | 1.47 |
|  |  |  | Total |  | 263.34 | 1.11 | .40 | (0.66) | 265.51 |

Table 3.2 (cont'd)   Sheet 6

| STREAM | TEMP °F | PRESS psia | COND. | ppm D | FLOW RATE, POUND MOLES/HOUR | | | | |
| | | | | | NH$_3$ | H$_2$ | N$_2$, etc. | KNH$_2$ (H$_2$0) | TOTAL |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 56 | 26 | 2141 | V | 132 | | 7096.93 | 2480.59 | (0.66) | 9578.18 |
| 57 | 26 | 2141 | L | | | | | (0.97) | 0.97 |

moved by: (1) Cooling to $105^{\circ}F$ by exchange against cooling water in exchanger C-1 and then to $26^{\circ}F$ by exchange against effluent depleted synthesis gas leaving the stripping tower T-1 at $-4^{\circ}F$; (2) removing condensed water in separator S-5; and (3) then scrubbing the synthesis gas in Tower T-4 counter-current to a stream 449.5 lb moles/hr of liquid ammonia (depleted in deuterium) at point (53). Since the liquid ammonia in T-4 does not contain $KNH_2$ catalyst, there should be negligible deuterium exchange. Tower T-4 will: (1) remove the remaining water vapor; (2) humidify the synthesis gas with ammonia vapor; (3) cool the gas to $-4^{\circ}F$; (4) reduce the $CO_2$ content of the feed gas to less than 1 ppm by the formation of ammonium carbamate.

$$2NH_3 + CO_2 \rightleftharpoons NH_2CO_2NH_4 \qquad (3.5)$$

Solid carbamate is reported to form readily provided the partial pressures of $NH_3$ and $CO_2$ exceed the decomposition pressure for ammonium carbamate (1 atm at $60^{\circ}C$ and 7 atm at $100^{\circ}C$) (27); at the low temperature and high pressure present in T-1, carbamate should form and be removed in the liquid ammonia stream at point (55). This ammonia (53.7 tons/day) containing 0.25 mole % water is sold as liquid ammonia along with the main stream of depleted ammonia product, 857.2 tons/day (point (32) on Figure 7), to form the total depleted ammonia product of 910.9 tons $NH_3$/day.

3.2.2 Ammonia Reflux

The other stream entering the exchange section from the ammonia synthesis plant shown in Figure 6 is the depleted

ammonia reflux stream flowing at 2946 lb. moles/hr at point (3). Initially at $-28^{\circ}F$ and 65 psia, this is compressed to 2290 psia in pump V-1, which raises its temperature to $-22^{\circ}F$. Most of this ammonia, 2789 lb. moles/hr, is heated to $-5^{\circ}F$ in heat exchanger X-3, where it is used to cool cracked synthesis gas to $9^{\circ}F$. The balance of the depleted ammonia, 157 lb.moles/hr in stream (11) is heated to $218^{\circ}F$ in exchanger X-2. 77.4 lb. moles/hr in stream (24B) is used to strip deuterium from catalyst in tower T-3 as described later in Section 2.4. The rest of the depleted ammonia at $218^{\circ}F$, stream (24A), 79.7 lb. moles/hr, is used to dilute stream (22), a saturated solution of $KNH_2$ in depleted ammonia at $256^{\circ}F$, to avoid precipitation of stream (23) as it is cooled in heat exchanger X-2.

The mixed stream (23) at $238^{\circ}F$ is cooled to $10^{\circ}F$ in exchanger X-2 by heat exchange against the depleted ammonia in stream (11). Reflux for tower T-1 at $-4^{\circ}F$, point (13), is obtained by mixing depleted ammonia from stream (10) with the solution of depleted $KNH_2$ in depleted ammonia from stream (12). Part (449.5 lb.moles/hr) of stream (9) is diverted to tower T-4 as stream (53) as discussed in Section 3.2.1, leaving the remainder as reflux to tower T-1 as stream (10).

3.2.3 Deuterium Exchange Towers

The desired concentration of deuterium in the exchange towers T-1 and T-2 is made possible through the deuterium exchange reaction

$$HD(g) + NH_3(\ell) \underset{\rightleftharpoons}{\overset{KNH_2}{}} H_2(g) + NH_2D(\ell) \tag{3.6}$$
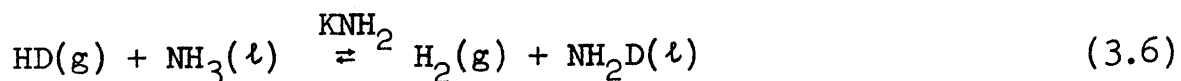
This reaction takes place in the liquid phase in the presence of dissolved $KNH_2$ as catalyst. The $KNH_2$ concentration is essentially constant at 1.335 mole % through both towers T-1 and T-2. At the temperature of $-4^\circ F$ and the pressure of around 2150 psia at which these towers operate, the separation factor for concentration of deuterium relative to hydrogen in the liquid phase is approximately 5.0.

Referring first to the deuterium stripping tower T-1, gas phase feed to the bottom of the tower consists of synthesis gas feed (54), at $-4^\circ F$ plus 4830.3 lb. moles/hr of effluent gas (6) from enriching tower T-2 at $-4^\circ F$. Both streams are saturated in ammonia vapor, contain 132 ppm D, and are at a pressure of 2139 psia. Liquid phase feed to the top of the tower (13) is the solution of depleted $KNH_2$ in depleted ammonia at $-4^\circ F$ described in Section 3.2.2. This stream contains 18.2 ppm D.

As the gas stream flows up through the tower, it transfers HD to the downflowing liquid phase, where the above exchange reaction converts HD to $NH_2D$. When the gas phase reaches the top of the tower at (7) its deuterium content has been reduced to 13.2 ppm D and its pressure is down to 2116 psia. This gas, flowing at 14577.5 lb. moles/hr, is heated to $49^\circ F$ in exchanger X-1, where it cools incoming synthesis gas to $26^\circ F$.

Leaving X-1 at (2) at 2112 psia, this stream is sent
to the ammonia synthesis plant when it is converted to ammonia
containing 13.2 ppm D.

The liquid flowing down through tower T-1 becomes
progressively richer in deuterium. It leaves the tower at
$-4^{\circ}F$ and 2139 psia, containing 374 ppm D.

This liquid is picked up by transfer pump V-5 and
is compressed to 2317 psia so that it can flow to the top
of the enriching tower T-2, where the pressure is 2139 psia.
As this liquid flows down through T-2 counter to upflowing
synthesis gas, it is enriched further in deuterium to 13,200
ppm D as it leaves the bottom of the tower at (15). The
ammonia in this stream is vaporized from $KNH_2$ as described
next in Section 3.2.4, a portion of the ammonia is withdrawn
as enriched product, and the remainder is cracked as described
later in Section 3.2.5 to provide gas phase reflux for tower
T-2.

Gas phase reflux (47) containing 13164 ppm D enters
the bottom of tower T-2 at $-4^{\circ}F$ and 2169 psia. As it flows
up it transfers HD to the downflowing liquid, when it leaves
the top of the tower at (16) at $-4^{\circ}F$ and 2139 psia its D
content has been reduced to 132 ppm.

Towers T-1 and T-2 are described in more detail in
Section 4.

3.2.4  Catalyst Recovery

Before the liquid leaving exchange tower T-2 at (15)
can be cracked, it is necessary to recover the $KNH_2$ catalyst

from it. Before this catalyst can be returned to the top of exchange tower T-1 its deuterium content must be reduced enough to prevent serious mixing loss upstream of (13). The manner in which these two functions are performed will be described in this section.

2522.4 lb. moles/hr of liquid leaving T-2 at $-4°F$ is dropped in pressure to 471 psia at (16). The stream is heated to $250°F$ and most of its ammonia is vaporized by passage successively through heat exchangers X-4, X-5 and H-2. Heat for X-4 is obtained by cooling cracked synthesis gas stream (36) from $441°$ to $16°F$. Heat for X-5 is obtained by cooling compressed synthesis gas stream (43) from 344 to $292°F$. Heat for H-2 is obtained by condensing 13282 lb/hr of saturated steam at $275°F$ and 45 psia. This steam is supplied from the turbine drives for the cooling water pumps, which are driven by steam at 600 psig and $750°F$ and exhaust at 30 psig (45 psia) and $275°F$. The conditions of the mixed ammonia and $KNH_2$ stream as it flows through X-4, X-5 and H-2 are given in Table 3.3.

Table 3.3

Condition of Ammonia Streams in X-4, X-5, and H-2

| Stream | Enters | Leaves | $°F$ | psia | Moles/Hour Vapor | Solution | Mol % $KNH_2$ in Solution |
|--------|--------|--------|------|------|-------|----------|----------|
| 16 | X-4 | --- | -4 | 471 | 11.8 | 2510.6 | 1.34 |
| 17 | X-5 | X-4 | 162 | 465 | 1388.7 | 1133.7 | 2.97 |
| 18 | H-2 | X-5 | 166 | 461 | 1612.2 | 910.2 | 3.70 |
| 19 | S-3 | H-2 | 250 | 457 | 2433.8 | 88.6 | 38.0 |

Stream (19) leaving H-2 goes to separator S-3 where 2419 lb. moles/hr of ammonia vapor plus a little hydrogen and nitrogen is taken off as overhead (27) and 88.6 lb. moles/hr of a saturated solution containing 38.0 mol % $KNH_2$ in ammonia at $250^{\circ}F$ is taken off as bottoms (20). The $KNH_2$ solution is compressed to 494 psia by transfer pump V-6 and sent to the top of the catalyst deuterium stripping tower T-3, at 456 psia and $250^{\circ}F$.

In tower T-3, deuterium is transferred from the liquid phase to a counterflowing stream of ammonia vapor through the liquid phase reaction.

$$KNHD(\ell) + NH_3(\ell) \rightleftharpoons KNH_2(\ell) + NH_2D(\ell) \qquad (3.7)$$

and the liquid-vapor equilibrium

$$NH_2D(\ell) + NH_3(g) \rightleftharpoons NH_3(\ell) + NH_2D(g) \qquad (3.8)$$
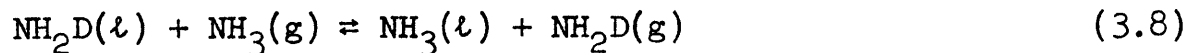
The deuterium separation factor for each of these reactions at $250^{\circ}F$ was assumed to be 1.00. The liquid phase reaction was assumed to proceed rapidly, because $KNH_2$ and liquid ammonia are both partially ionized into $NH_2^-$; consequently the theoretical and actual heights of a transfer unit were assumed to be equal.

The vapor entering the bottom of tower T-3 at (25) is ammonia containing 13.2 ppm D which has been vaporized and super-heated to $250^{\circ}F$ in H-1. As this ammonia vapor flows up through T-3 counter to the downflowing saturated solution

of $KNH_2$ in liquid ammonia, there is no net transfer of ammonia from liquid to vapor, because the liquid is at its boiling point of 250°F at tower pressure of 456 psia. Deuterium is transferred however, from liquid to vapor, with equivalent transfer of hydrogen from vapor to liquid. Consequently, ammonia vapor flowing up tower T-3 is enriched in deuterium, leaving with 13,027 ppm D at (26), while the liquid solution of $KNH_2$ flowing down the tower is depleted in deuterium, leaving with 186 ppm D at (21). The enriched ammonia vapor from the top of T-3 at (26) is sent on to be cracked.

The 88.6 lb. moles/hr of a solution of 38 mole % $KNH_2$ in ammonia at 250°F at (22) is diluted to 20.0 mole % at (23) with 79.7 lb. moles/hr of ammonia at 218°F from stream (24A), so that when the mixed stream is cooled in X-2 to 10°F, $KNH_2$ does not crystallize out. Cooling fluid for X-2 is the 157.1 lb. moles/hr of liquid ammonia at 2290 psia and -22°F of stream (11). The result this operation is to obtain at (12) 168.4 lb. moles/hr of a solution of 20.0 mole % $KNH_2$ in ammonia at 10°F containing 98.3 ppm D. This solution is mixed with 2339.1 lb. moles/hr of ammonia in stream (10), to obtain liquid reflux for tower T-1 at -4°F with 18.2 ppm D. The pressure of this stream is 2139 psia at the base of T-1 and 2116 psia at the top.

3.2.5 Enriched Ammonia Product

Of the overhead vapor (27) from the ammonia separator S-3, 42.9 lb. moles/hr are withdrawn at (29), cooled from

250 to $4^{\circ}$F in C-4 with ammonia refrigeration, and condensed

liquid ammonia is drawn off the bottom of separator S-4 at (31).

A small amount of uncondensed $H_2$ and $N_2$ in the overhead (41)

from S-4 is returned to tower T-2 via compressor V-3. The

liquid ammonia from the bottom of S-4 at (31) is the product

of the deuterium extraction plant. It contains 42.6

lb. moles per day of ammonia, enriched to 13,200 ppm deuterium,

plus a very small amount of hydrogen and nitrogen.

### 3.2.6  Ammonia Cracking

The feed to the ammonia cracking reactor Y-1 is made

up of 2391.2 lb. moles/hr of vapor (28) overhead from

separator S-3 containing 13,200 ppm D, 77.4 lb. moles/hr of

enriched ammonia vapor (26) from the top of the catalyst

deuterium stripping tower T-3 containing 13,027 ppm D, and

499.9 lb. moles/hr of recycle ammonia vapor from vaporizer

X-6 (51) containing 13164 ppm D. These three streams combine

to make 2968.2 lb. moles/hr of ammonia vapor (33) at $250^{\circ}$F

and 456 psia. This is heated to $1280^{\circ}$F in heat exchanger

X-7 by countercurrent exchange against cracked ammonia gas

entering at $1300^{\circ}$F.

Ammonia vapor (34) at $1280^{\circ}$F and 448 psia is passed

through the ammonia cracking reactor Y-1, where 80.0% of the

entering ammonia is cracked to synthesis gas, 3 $H_2$ : 1 $N_2$.

Gas in the reactor is held at an average temperature of $1300^{\circ}$F

and an average pressure of 441 psia (30 atm). The

58.4 million BTU per hour of heat needed for the endothermic

cracking reaction is provided by a combustion heated furnace surrounding the reactor tubes containing catalyst. Gases flowing through the reactor experience a pressure drop of 14 psia.

The mixture of 5330.0 lb. moles/hr of $H_2$, $N_2$ and uncracked ammonia leaving the reactor Y-1 at (35) at $1300°F$ and 434 psia is cooled to $441°F$ at (36) in X-7 by heat exchange against incoming ammonia feed vapor. The cracked mixture is cooled further to $16°F$ at (37) in X-4 by heat exchange against the cold solution of $KNH_2$ in ammonia leaving tower T-2. It is cooled to $9°F$ at (38) in X-3 by heat exchange against liquid ammonia stream (9) at $-22°F$, and then finally to $-4°F$ by external ammonia refrigeration in C-3. This cold mixture passes to separator S-1, where liquid ammonia is taken off as bottoms (39) and $H_2$ while $N_2$ and uncondensed ammonia vapor are taken off as overhead (40). The overhead is combined with a small amount of vapor (41) from product separator S-4 to form 5078.0 lb. moles/hr of gas at (42), at $-4°F$ and 414 psia.

This gas (42) is compressed to 2180 psia in compressor V-3, where 5300 horsepower is expended. This is the principal power demand of the deuterium extraction process. Compressed gas (43) is cooled by successive heat exchange in X-5 to $292°F$ against the solution of $KNH_2$ in ammonia, in X-6 to $135°F$ against boiling liquid ammonia bottoms from S-1 and S-2, and in C-2 to $-4°F$ against external ammonia refrigeration.

Mixed liquid and vapor (46) leaving C-2 at $-4°F$ passes to separator S-2. Overhead vapor (47) goes to tower T-2 as enriched vapor reflux containing 13164 ppm D. Liquid ammonia bottoms (48) is combined with liquid ammonia bottoms (39) from S-1 which is compressed in recycle pump V-4 to 460 psia. The combined stream of 499.9 lb. moles/hr of recycle liquid ammonia (50) is vaporized and heated to $250°F$ in heat exchanger X-6. This stream (51) of recycle ammonia vapor joins ammonia (28) vaporized from $KNH_2$ and ammonia vapor (26) from the catalyst deuterium stripping tower T-3 to make up the stream (33) fed to the cracking system, of which 2952.1 lb. moles/hr is ammonia.

### 3.3  Cracking Reactor .

Cracking Reactor Y-1 has been sized for the following conditions

|  | Inlet | Outlet |
|---|---|---|
| Temp, $°F$ | 1280 | 1300 |
| Pressure, psia | 448 | 434 |
| Pound moles/hr |  |  |
| $NH_3$ | 2952.10 | 590.32 |
| $H_2$ | 11.81 | 3554.48 |
| $N_2$ | 4.32 | 1185.21 |
| Total | 2968.23 | 5330.01 |

for a conversion of 80.0% cracked per pass. Heat input duty is 58.4 million BTU/hr. As we did not have a good idea of the cost of catalyst, reactor vessels, heating furnace or ammonia recycle operations, it is probable that the conditions

chosen for this initial design are considerably off optimum. The principal variables which should be considered in any more detailed study are pressure, pressure drop, temperature, cracking per pass and catalyst particle size.

For this particular design, TOPSOE type KM I R catalyst was chosen, with an equivalent diameter 4.6 mm. This is a triply promoted iron synthetic ammonia catalyst. Its reaction kinetics determined experimentally have been reported by Nielsen (29).

On the assumption that the cracking reaction in Y-1 proceeds isothermally at $1300^\circ F$, a catalyst volume of 7700 $ft^3$ was calculated as needed for the specified conversion. It is proposed that this catalyst be loaded into 490 tubes 6 inches in internal diameter, with a total packed length of 80 feet per tube. For mechanical reasons it will probably be desirable to use at least four shorter tube lengths in series. The required heat input of 58.4 million BTU per hour can be obtained by maintaining the outer wall of these tubes at $1350^\circ F$ in a furnace. The heat flux required at the inlet is about five times that at the outlet.

Calculations for such a multitube reactor predict the following conditions:

   Maximum heat flux, at inlet, 2838 BTU/hr $ft^2$

   Heat transfer coefficient, at inlet, 74 BTU/hr $ft^2 {}^\circ F$

   Temperature difference, tube to gas, at inlet, $38.4^\circ F$

   Mass velocity, 0.145 lb/sec $ft^2$

Superficial velocity, at outlet, 0.65 ft/sec

Pressure drop through bed, 1.95 psia.

As indicated in Section 2.3, time did not permit optimization studies of the design. The cost estimate indicates that the cracking furnace operating at $1300^{\circ}F$ requires a great deal of catalyst, has too low a heat flux, and is therefore unusually large for a tube-type furnace of the indicated heat duty. Consequently use of a higher cracking temperature is indicated. Kinetics calculations indicate that operations at a temperature of $1500^{\circ}F$ in the cracker would result in about a ten-fold reduction in catalyst requirements. Specific information on larger ammonia crackers operating at high pressures ( since at high temperatures, material strength is important) could not be obtained, but small (11 lb. mole $NH_3/hr$) commercially available ammonia dissociators operate at $1750^{\circ}F$ and 6 to 10 psig (28), further suggesting that the initial temperature selected here was too low. Additional information should be obtained concerning the catalyst as well. The Danish firm, Haldor Topsoe, participated in the design, construction and start-up of the ammonia dissociator for the French ammonia-hydrogen exchange plant at Mazingarbe, and thus undoubtedly has information of value on the ammonia dissociator for process described here. No details could be obtained from them or their New York office for use in this study.

## 3.4  Towers

This section presents a brief description of the design and purpose of tower systems T-1 through T-4. Design information for the four tower systems is presented in Table 3.4.

### 3.4.1  Deuterium Exchange Towers

Tower system T-1 is designed to reduce the deuterium content of streams (54) and (6) from about 132 ppm D to 13.2 ppm in stream (7). This system complex consists of three towers in series with 73 sieve plates in each. These sieve plates are of conventional single crossflow design with the active area 76% of the tray area. The number of plates is quite large due to the low efficiency of each plate. Three plates are used in the dissolution of gases in stream (13). The towers are 4 ft inside diameter with an operating pressure and temperature of about 2125 psia and -4°F. The liquid leaving the T-1 complex is compressed to 2317 psia from 2139 psia in V-5 before entering the T-2 system.

In the T-2 system the deuterium content of the liquid ammonia is increased from 374 ppm in stream (14) to 13,200 ppm in stream (15). The T-2 system consists of 4 columns, 75 sieve plates each, operating at a pressure of about 2150 psia and a temperature of -4°F. The sieve plates in T-2 are the same design as in T-1 except that the diameter is 2.5 ft instead of 4 ft. The gas in stream (47) has a lower deuterium content than the exiting liquid. This is due to:

Table 3.4
Tower Data Sheet

| Tower System | T-1 | T-2 | T-3 | T-4 |
|---|---|---|---|---|
| No. Columns in series | 3 | 4 | 1 | 1 |
| Type | Sieve | Sieve | Packed | Sieve |
| Inlet pressure (psia) | 2137 | 2169 | 457 | 2139 |
| Operating temp. ($^{\circ}$F) | -4 | -4 | 250 | -4 |
| Height (ft) | 156 | 150 | 90 | 40 |
| Inside diameter (ft) | 4.0 | 2.5 | 1.25 | 3.0 |
| Packing | -- | -- | 1" Berl saddles (ceramic) dumped | -- |
| Tray thickness (in) | 0.1 | 0.1 | -- | 0.1 |
| No. stage/column | 78 | 75 | 73.9 | 20 |
| Total No. stages | 234 | 300 | 73.9 | 20 |
| Tray spacing (ft) | 2 | 2 | -- | 2 |
| Tray flow type | Single Crossflow | Single Crossflow | -- | Single Crossflow |
| Downcomer | Segmental | Segmental | -- | Segmental |
| Weirs | Straight | Straight | -- | Straight |
| Weir height (in) | 4 | 4 | -- | 4 |
| Weir length (% tower dia.) | 77 | 77 | -- | 77 |
| Hole size (in) | 1/8 | 1/8 | -- | 1/8 |
| Hole area/tower area | 0.10 | 0.10 | -- | 0.10 |
| Liquid redistribution sections | -- | -- | 6 | -- |
| Liquid redistribution equipment | -- | -- | Flat plate Liq. thru. holes; Gas thru. risers. | -- |

Table 3.4  (cont'd)

| | T-1 | T-2 | T-3 | T-4 |
|---|---|---|---|---|
| Tower length between redistribution (ft) | -- | -- | 15.0 | -- |
| Packing support | -- | -- | Grating | -- |
| Plate efficiency $E_{mv}(\%)$ | 1.89 | 2.4 | -- | (5.0) |
| Flooding vel (fps) | 1.124 | .828 | -- | 1.32 |
| % Flooding | 75.3 | 86.7 | 41.6 | 75.9 |
| % Ave. Loading | -- | -- | 65.5 | -- |
| Flow Rates: | | | | |
| Internal (lb mole/hr) | 2581.51 | 2539.93 | 88.61 | 482.8 |
| External (lb mole/hr) | 2522.40 | 2522.40 | 88.61 | 449.5 |
| Dry Gas (lb moles/hr) | 14593.59 | 4830.30 | 77.39 | 9762.17 |
| Liquid Density lb/ft$^3$ | 42.9 | 42.90 | 47.57 | 41.34 |
| lb moles/ft$^3$ | 2.454 | 2.454 | 1.495 | 2.432 |
| Gas Density lb/ft$^3$ | 3.756 | 3.809 | 1.024 | 3.79 |
| lb moles/ft$^3$ | 0.434 | 0.440 | 0.0603 | 0.438 |
| Viscosity, (lb/ft hr) | | | | |
| liquid | 0.605 | 0.605 | 43.5 | 0.59 |
| gas | 0.04 | 0.04 | 0.036 | 0.04 |

a) part of gas comes from catalyst recovery tower T-3 whose exiting gas stream (26) has a deuterium content of 13,027 ppm.

b) gas from hydrogen dissolved in stream (13) has a much lower deuterium content of about 2500 ppm.
The liquid flows from system T-2 to a heat exchanger X-4 and evaporators X-5 and H-2 after being dropped in pressure. A concentrated amide solution (38 mole %) is removed in separator S-3 and is sent to the catalyst recovery section T-3.

The towers were designed using plate efficiencies shown in Table 3.4, which were calculated using the procedures presented in Supplementary Report D (25).

3.4.2 Catalyst Deuterium Stripping Tower

The liquid stream (20) enters tower T-3, which is 15 inches in diameter packed with 1 inch ceramic Berl saddles. The tower consists of six 15 ft. high sections. The packing in each section is on a grating type support. The top 2 ft. of each section's packing provides for good liquid distribution. The liquid is distributed by means of a flat plate in which the liquid flows through holes onto the packing while the gas goes through risers. The liquid is decreased in deuterium content from 13,200 ppm to 186 ppm when it leaves the column. The entering ammonia vapor, stream (24), on the other hand, increases its deuterium content from 13.2 ppm to 13027 ppm before leaving. The operating conditions are $250^{\circ}F$ and 457 psia.

### 3.4.3  Feed Gas Purification and Humidification

Tower system T-4 is designed to remove trace amounts
of water and carbon dioxide from the feed gas and to saturate
the feed gas with ammonia vapor.  The single tower consists
of 20 sieve plates each 3 feet in diameter.  The upward
flowing synthesis gas at (56) is scrubbed with depleted
ammonia from stream (53).  Since no exchange catalyst, $KNH_2$,
is present, exchange of deuterium between the two streams
is negligible.  As with towers T-1 and T-2, the low solubility
of carbon dioxide in liquid ammonia is expected to result in
low tray efficiencies for $CO_2$ removal; the entire tower T-4
serves the function of one equilibrium contact stage.

### 3.5  Heat Exchangers

The principal criteria in sizing the heat exchangers
was to utilize a minimum temperature approach of $20^{\circ}F$ in
each exchanger.  The arrangement shown in Figure 7 represents
the most acceptable among several flow patterns investigated.
The amount of external heating and refrigeration was kept
as low as possible, without making the flow patterns too
complicated.  Design information for the heat exchangers is
presented in Table 3.5.

Exchanger X-7 has the largest duty, heating the ammonia
(33) to $1280^{\circ}F$ prior to cracking; it is a gas-gas exchanger.
X-1 is also a gas-gas exchanger,  used to cool the feed
synthesis gas (1) down to $26^{\circ}F$.

### TABLE 3.5  HEAT EXCHANGER DATA SHEET

| UNIT NUMBER | HOT SIDE Composition mole % H₂ | N₂ | NH₃ | Flow Rate lb/hr | lbm/hr | Inlet °F | psia | Outlet °F | psia | COLD SIDE Composition mole % H₂ | N₂ | NH₃ | KNH₂ | Flow Rate lb/hr | lbm/hr | Inlet °F | psia | Outlet °F | psia | DUTY MBTU/hr | Est. MTD °F | NOTES | Area ft² |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X-1 | 74.1 | 25.9 | | 83750 | 9576.0 | 105 | 2142 | 26 | 2139 | 73.0 | 25.1 | 1.9 | | 128692 | 14577.5 | -4 | 2116 | 49 | 2112 | 5.354 | 41.7 | a | 1165 |
| X-2 | | | 80.0 | 4146 | 168.35 | 238 | 2244 | 10 | 2240 | | | (1) | | 2676 | 157.13 | -22 | 2290 | 218 | 2286 | 0.742 | 25.5 | b | 832 |
| X-3 | 66.7 | 22.2 | 11.1 | 50406 | 5330.0 | 16 | 420 | 9 | 417 | | | (1) | | 47496 | 2788.6 | -22 | 2290 | -5 | 0.771 | 0.852 | 24.2 | c | 234 |
| X-4 | 66.7 | 22.2 | 11.1 | 50406 | 5330.0 | 441 | 426 | 16 | 420 | | | (1) | 1.33 | 44026 | 2522.4 | -4 | 471 | 162 | 465 | 16.654 | | d | 3135 |
| | | | | | | | | | | | | | | | | | | | | 8.32 | 38.5 | e | |
| | | | | | | | | | | | | | | | | | | | | 8.34 | 147.5 | f | |
| X-5 | 70.0 | 23.4 | 6.6 | 46114 | 5078.0 | 344 | 2180 | 292 | 2176 | | | (1) | 1.33 | 44026 | 2522.4 | 162 | 465 | 166 | 461 | 1.84 | 156 | g | 235 |
| X-6 | 70.0 | 23.4 | 6.6 | 46114 | 5078.0 | 292 | 2176 | 135 | 2172 | | | (g) | | 8501 | 499.9 | -4 | 460 | 250 | 456 | 5.705 | | h | 865 |
| | | | | | | | | | | | | | | | | | | | | 1.57 | 61.4 | i | |
| | | | | | | | | | | | | | | | | | | | | 3.47 | 55.2 | j | |
| | | | | | | | | | | | | | | | | | | | | 0.67 | 84.4 | k | |
| X-7 | 66.7 | 22.2 | 11.1 | 50406 | 5330.0 | 1300 | 434 | 441 | 426 | | | (g) | | 50406 | 2968.2 | 250 | 456 | 1280 | 448 | 35.0 | 75.8 | l | 6600 |
| H-1 | | (H₂O) | | 1175.6 | | 275 45 sat. vap. | | 275 45 sat. liq. | | | | (g-1) | | 1318 | 77.39 mixture | 156 | 460 | 250 | 457 | 1.097 | | m | 200 |
| | | | | | | | | | | | | | | | | | | | | 0.090 | 119 | n | |
| | | | | | | | | | | | | | | | | | | | | 1.007 | 60.2 | o | |
| H-2 | | (H₂O) | | 13281.5 | | 275 45 sat. vap. | | 275 45 sat. liq. | | | | 98.1 1.33(N₂-H₂ trace) | | | 44026 | 2522.4 | 166 | 461 | 250 | 457 | 12.393 | 57 | p | 1450 |
| C-1 | 74.1 | 25.9 | | 83750 | 9576.0 | 236.8 | 2145 | 105 | 2142 | | | (H₂O) | | Cooling Water | | | | | | 8.863 | 53 | | 1000 |
| C-2 | 70.0 | 23.4 | 6.6 | 46114 | 5078.0 | 135 | 2173 | -4 | 2170 | | | 100 | | Ammonia Refrigeration | | | | | | 7.340 | 16 | | 1130 |
| C-3 | 66.7 | 22.2 | 11.1 | 50406 | 5330.0 | 10 | 417 | -4 | 415 | | | 100 | | Ammonia Refrigeration | | | | | | 0.575 | 50 | | 400 |
| C-4 | 0.44 | 0.14 | 99.42 | 728.1 | 42.88 | 250 | 420 | -4 | 417 | | | 100 | | Ammonia Refrigeration | | | | | | 0.484 | 80 | | 670 |

## TABLE 3.5 (cont'd)

### Notes

a)    Gas-gas exchange

b)    Liquid-liquid exchange

c)    Hot side condensing throughout, cold side remains liquid

d)    Consider two duties for X-4

e)    For heating $NH_3$-$KNH_2$ mixture to $162^\circ F$ liquid

f)    For vaporizing $NH_3$ at $162^\circ F$

g)    Consider the vaporizing cold stream at a constant temperature of $166^\circ F$

h)    Three duties for X-6

i)    For heating $NH_3$ to saturated liquid at $160^\circ F$

j)    For vaporizing $NH_3$ at $160^\circ F$

k)    For superheating $NH_3$ to $250^\circ F$

l)    Gas-gas exchange

Both X-5 and X-6 involve vaporizing a stream, with the heat being provided by the compressed synthesis gas stream (43). In X-5, the cold stream is ammonia being vaporized from the $NH_3$-$KNH_2$ mixture at 162 to 166°F. The cold stream in X-6 is the recycle ammonia from separators S-1 and S-2, which vaporizes at 160°F at the pressure of 460 psia and is then super-heated to 250°F. The closest temperature approach of 20°F occurs where liquid ammonia reaches its boiling point of 160°F on the cold side.

Exchanger X-3 condenses ammonia from synthesis gas on the hot side and warms liquid ammonia from -22°F to -5°F on the cold side. The main function of X-3 is to reduce the refrigeration on stream (37) and at the same time, to raise the temperature of stream (9) to -5°F.

X-2 is a liquid-liquid exchanger, cooling the $NH_3$-$KNH_2$ stream (23) from 238°F to 10°F and heating the pure ammonia (11) at -22°F to 218°F.

In X-4 both streams change phase within the exchanger. The hot stream is the cracked gases (36) entering at 441°F and leaving at 16°F, with about 4% of the ammonia liquified. The cold stream is the $NH_3$-$KNH_2$ stream (16) at 471 psia entering at -4°F and leaving at 162°F, with about 57% of the ammonia vaporized and a liquid phase of 2.97 mole % $KNH_2$.

Heaters H-1 and H-2 use exhaust steam from the cooling water pump drives at 45 psia and 275°F. The hourly steam rates are 1,176 lb./hr in H-1 and 13,282 lb./hr in H-2.

Coolers C-2, C-3, and C-4 all utilize external ammonia refrigeration, which is to be obtained from an addition to the refrigeration equipment of the original synthesis plant. In all three cases, the stream being cooled leaves at $-4^\circ F$.

Cooler C-1 employs process water to cool the feed synthesis gas (1) from $236.8^\circ F$. Another possibility considered was to eliminate C-1 and allow stream (1) to exchange heat with some other stream in the process, but this move was discarded because of severe complications in the flow patterns.

## 3.6    Pumps and Compressors

Design information relating to the pumps and compressors is contained in Table 3.6.

Most of the compressive work in the cracking section is provided by V-3, which compresses the synthesis gas from 414 to 2180 psia, ready to be returned to the exchange towers. An isentropic efficiency of 75% was assumed, while 80% was used for all other pump and compressors in Fig. 7. The work required is 5300 HP, and the synthesis gas, which enters at $-4^\circ F$, leaves at $344^\circ F$.

The reflux ammonia pump V-1 is also large, 218 HP, pumping the ammonia from the synthesis plant (3) from 65 to 2290 psia. The ammonia temperature rises from $-28^\circ F$ to $-22^\circ F$.

Pump V-5 carries the $NH_3$-$KNH_2$ mixture from the base of tower T-1 to the top of tower T-2. Pump V-2 raises the pressure of the concentrated catalyst stream (21) from 457

## TABLE 3.6  PUMP & COMPRESSOR DATA SHEET

| UNIT NUMBER | Composition, Mole % | | | | Flow Rate | | Inlet Conditions | | | | Outlet Conditions | | | | Eff'y | HP |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | $H_2$ | $N_2$ | $NH_3$ | $KNH_2$ | lb/hr | lbm/hr | psia | °F | lb/ft³ | cfm | psia | °F | lb/ft³ | cfm | | |
| V-1 | | | 100.0 | | 50171.8 | 2945.74 | 65 | -28 | 42.6 | 17.87 | 2190 | -22 | 42.3 | 18.00 | 0.80 | 239.6 |
| V-2 | | | 62.0 | 38.0 | 2787.6 | 88.61 | 457 | 250 | 47.6 | 0.976 | 2244 | 256 | 47.6 | 0.976 | 0.80 | 9.45 |
| V-3 | 70.00 | 23.34 | 6.66 | | 46114 | 5078.0 | 414 | - 4 | 0.768 | 1000.2 | 2180 | 344 | 2.294 | 334.9 | 0.75 | 5300 |
| V-4 | 0.08 | 0.03 | 99.89 | | 4294.0 | 252.2 | 414 | - 4 | 41.5 | 1.725 | 460 | - 4 | 41.6 | 1.720 | 0.80 | 0.431 |
| V-5 | 0.42 | 0.16 | 98.08 | 1.34 | 44121 | 2522.4 | 2139 | - 4 | 47.6 | 15.45 | 2317 | - 4 | 47.6 | 15.45 | 0.80 | 16.70 |
| V-6 | | | 62.0 | 38.0 | 2787.6 | 88.61 | 456 | 250 | 47.6 | 0.976 | 494 | 250 | 47.6 | 0.976 | 0.80 | 0.200 |
| V-7a-e (5 required) | 0.42 | 0.16 | 98.08 | 1.34 | 47253 | 2709 | 2124 | - 4 | 41.9 | 18.8 | 2166 | - 4 | 41.9 | 18.8 | 0.80 | 4.32 |
| V-102 | 73.0 | | 1.90 | | | 14577 | 2112 | 49 | | | 2145 | 105.9 | | | 0.7 | 3400 |
| | | | | | | 68172 | 2025 | 105 | | | | | | | | |

to 2244 psia, before cooling, dilution and return to tower T-1. Pump V-4 is used to recycle the liquid ammonia from separator S-1, while pump V-6 lifts the $NH_3$-$KNH_2$ mixture to the top of tower T-3.

In addition to the liquid pumps shown in the flowsheet, Fig. 7, five transfer pumps are needed to pump liquid from the bottom of one section of tower T-1 or T-2 to the top of the next section. These are designated V-7a through V-7e.

## 3.7    Separators and Drums

Design information concerning the separators and drums shown on Figure 3 is presented in Table 3.7.

## 3.8    Utilities

Design information concerning utility requirements is presented in Table 3.8.

## Table 3.7

### LIST OF SEPARATORS AND DRUMS

| UNIT NUMBER | Pressure psia | Temp. $^\circ F$ | Diam. ft | Height ft | Volume $ft^3$ |
|---|---|---|---|---|---|
| S-1 | 414 | - 4 | 6.50 | 16.0 | 531.0 |
| S-2 | 2169 | - 4 | 4.00 | 10.0 | 125.7 |
| S-3 | 456 | 250 | 6.00 | 13.5 | 381.7 |
| S-4 | 414 | - 4 | 1.50 | 2.0 | 3.53 |

## Table 3.8

### UTILITIES

COMPRESSOR DRIVES                                      HORSEPOWER

| | | |
|---|---|---|
| V-1 | Reflux Ammonia Pump | 218 |
| V-2 | Stripped Catalyst Pump | 9.5 |
| V-3 | Cracked Gas Compressor | 5300 |
| V-4 | Recycle Ammonia Pump | 0.5 |
| V-5 | Transfer Pump to T-2 Top | 16.7 |
| V-6 | Transfer Pump to T-3 Top | 0.2 |
| | Total | 5544.9 |


AMMONIA REFRIGERATION

| Unit | Cooling from | To | BTU/hr |
|---|---|---|---|
| C-2 | 135°F | -4°F | $7.340 \times 10^6$ |
| C-3 | 10°F | -4°F | $0.6549 \times 10^6$ |
| C-4 | 250°F | -4°F | $0.4838 \times 10^6$ |
| | | Total | $8.4787 \times 10^6$ |


STEAM at 45 psia

| Unit | Function | BTU/hr | lb/hr |
|---|---|---|---|
| H-1 | Ammonia Vaporizer | $1.097 \times 10^6$ | 1,175.6 |
| H-2 | $KNH_2$ Concentration | $12,393 \times 10^6$ | 13,281.5 |


HEAT above 1300°F for Reactor Y-1

$$58.4 \times 10^6 \text{ BTU/hr}$$

## 4.0 <u>COST ESTIMATES AND ANALYSIS</u>

### 4.1 <u>Procedures</u>

The purpose of this section is to present and discuss estimates of the added costs, both investment and operating, involved when a plant for the recovery of deuterium from ammonia synthesis gas by ammonia-hydrogen exchange is added to an existing ammonia synthesis plant. These cost estimates were developed largely through the cooperation of Air Products and Chemicals, Inc. Details of the cost estimates are presented in Appendix A of this report; following a brief description of the procedures, the results are presented in this section.

The process design presented in Section 3.0 assumes that the deuterium recovery plant is to be added to an existing 920 ton/day ammonia synthesis plant. The design calls for the addition of an ammonia synthesis section capable of synthesizing 482 tons/day of ammonia to provide the required liquid reflux to the deuterium exchange towers plus the addition of deuterium exchange and ammonia cracking sections.

The cost estimating procedure was carried out in two steps. First the costs associated with the required additional ammonia synthesis section were estimated, and then the costs associated with the exchange and cracking sections were estimated.

In 1967, information relating to the cost of synthesizing ammonia from synthesis gas was obtained from Air Products and Chemicals (30); this information was based on the ammonia synthesis plant owned and operated by Air Products in Michoud, Louisiana. The capacity of this plant is 610 tons/day of liquid

ammonia product. A summary of this information is presented
in Appendix A.1.1 of this report. The design and cost informa-
tion obtained from Air Products was used to estimate the costs
(capital and operating) of the equipment which must be added
to the existing 920 tons/day ammonia plant in order to produce
the required ammonia reflux. Details of the calculations are
given in Appendix A.1.2, but the general procedure was as
follows. Since the main compressor of the original plant
(V-101 in Figures 4 and 6) is more than adequate for the com-
bined plants, no added costs are involved for main compressors
when the deuterium recovery plant is added. However, the re-
cycle compressor, V-102, is new and adds an estimated $360,000
to the cost of the deuterium plant (see Table A.4). The re-
maining cost items in the 610 ton/plant were scaled down to
the required 482 ton/day capacity (see Appendix A.1.2).

In June 1969, when the process design presented in Sec-
tion 3.0 had been developed, Air Products and Chemicals again
(32) cooperated in this study by providing estimates of the
equipment and operating costs for the deuterium exchange and
ammonia cracking sections; see Appendix A.2 for details.

## 4.2    Results of Cost Estimates

A summary of estimated investment costs for the entire
plant associated with deuterium recovery is presented in Table
4.1; estimated operating costs are given in Table 4.2. The
unit cost of recovering deuterium by the process described
in this report is given in Table 4.3, expressed as dollars
per pound of $D_2O$ for various annual fixed charge rates.

## Table 4.1

## Summary of Capital Investment Associated With
## Deuterium Recovery by Chemical Exchange

| Plant Investment | $1000 |
|---|---|
| Ammonia Synthesis Section[a] | 2,052 |
| Refrigeration and Ammonia Recovery Section | |
|     Synthesis plant[a] | 800 |
| Deuterium Extraction Section[b] | |
|     Towers | 893 |
|     Separators | 43 |
|     Exchangers | 62 |
|     Heaters | 12 |
|     Coolers | 18 |
|     Compressors V-102 | 360 |
|             V-3 | 675 |
|     Pumps (V-1,2,4,5,6,7) | 112 |
|     Refrigeration System | 200 |
|     Cracking Reactor System | 1,500* |
|     Steam System | 1,000* |
|     Cooling Tower System | 200* |
| Construction Work | 1,550 |
| Instruments and Control Panelboard | 180 |
| Electrical Substation and Starter Equipment | 40 |
| Engineering | 700 |
| | 10,397 |
| Contractors Fee    4% | 416 |
| Spare Parts, Initial Supplies | 550 |
| Construction Interest | 450 |

Table 4.1 (Cont'd)
Sheet 2

Startup and Training Expenses                                170

    Fixed Plant Investment                               11,983

Working Capital

Cash Equivalent to 4 months operating costs                  608
    (See Table 4.2)

Catalyst Inventory                                           195

    Working Capital                                      803

    Total Investment                                  12,786

\*  Installed

a  See Table  A.3

b  See Table  A.4

Table 4.2

Annual Operating Costs Associated with Deuterium
Recovery by Chemical Exchange
Basis:  330 stream days/year

|  | $1000/yr |
|---|---|
| Labor | 430 |
| Natural Gas | 480 |
| Electricity | 27 |
| Steam | 114 |
| Catalysts, Chemicals, Lubricants | 80 |
| Make-up Water | 108 |
| Maintenance, Replacement Parts, etc. | 419 |
| Subtotal | 1,658 |
| General and Administrative Costs | |
| 10% of Subtotal | 166 |
| Non capitalized Operating Costs | 1,824 |

Table 4.3

Unit Cost of Recovering Deuterium by Chemical Exchange

Capital Charges = r x total investment

$$= r \times \$12.862 \times 10^6$$

Total Annual Costs $= 1.824 \times 10^6 + 12.786 \times 10^6 \ r$

Annual Equivalent $D_2O$ Production Rate = 66.8 tons/yr

$$= 133600 \text{ lb/yr}$$

Unit Cost of $D_2O$ = 13.65 + 95.70 r   \$/lb.

| Annual Fixed Charge Rate, r | Cost of $D_2O$ \$/lb $D_2O$ |
|---|---|
| 0.10 | 23.2 |
| 0.15 | 28.0 |
| 0.20 | 32.8 |
| 0.25 | 37.6 |

The estimated cost of recovery given in Table 4.3 ranges from $23.2 to $37.6 per pound of $D_2O$ for fixed charge rates of 10%/yr to 25%/yr, which were considered to cover the fixed charge rates that might apply for government or private ownership. Although the enriched product of the process described here is (arbitrarily) 13,200 ppm deuterium in liquid ammonia, the additional costs of further concentration and conversion to heavy water at 99.8 a/o deuterium will be relatively small compared to the costs shown in Table 4.3.

Thus the cost of recovering deuterium by the process described here appears to be approximately the same as the USAEC sale price for heavy water of $28.50 per pound. This conclusion is not very favorable since much development work and expense would be required to bring the process described here into production.

However, as discussed in Section 2.0, early termination of the support of this study did not leave sufficient time for process optimization. The cost estimates given are based on only one set of operating conditions, arbitrarily selected, in order that at least one cost estimate could be included in this final project report. Based on probabilities, it seems unlikely that the first set of operating conditions, arbitrarily selected, would produce optimum economics. Therefore, considering that the estimated cost of heavy water produced by this initial process design is about the same as the present USAEC price, the process may indeed warrant additional design

and economic studies to determine its potential relative to the hydrogen sulfide process currently used for the production of heavy water, especially if a demand for new heavy water capacity develops.

## 5.0 RECOMMENDATIONS FOR FURTHER WORK

In spite of the lack of optimization, an evaluation of the information presented in Tables 4.1 and 4.2 provides assistance in indicating the direction to head if additional studies of this process are considered in the future.

In selecting the operating conditions used in the process design described in Section 3.0, it was guessed that the benefits of low pressure in the cracking section would offset the penalties to be incurred in the pressure letdown required in order to recover the potassium amide catalyst and improve the equilibrium dissociation of ammonia into hydrogen and nitrogen. However, considering the high cost of the recompressor V-3 required to recompress the cracked gases to the pressure level in the exchange towers (pressure increase from 414 to 2180 psia across V-3) as well as the very large steam consumption of V-3 (40% of the output of the steam system in Table 4.1 and 25% of the natural gas consumption in Table 4.2 is used to power V-3), the optimum operating pressure in the cracking section may well be greater than the level of about 450 psia used in the process design discussed here. The effect of operating pressure in the cracking section on process economics therefore requires study.

Additional design work on the ammonia cracking reactor, Y-1, is also required. The design presented in Section 3.3 based on operation of the cracker at 1300°F. results in a very

large reactor, with a very low surface heat flux of 950 BTU/hr ft$^2$, and excessive structure to support all the tubing required. The estimated cost of the resulting furnace was prohibitively high. Consequently the cost estimate of $1.5 million was based on a reactor and furnace design for a mean heat flux of 15 - 20,000 BTU/hr ft$^2$, considered more normal for this service. To obtain this heat flux with 6-inch tubing would require that the cracking temperature be raised from 1300°F to about 1600°F. This change in cracking temperature will necessitate changes in process conditions for heat exchangers X-4, X-5, X-7 and H-2, but these are not expected to affect cost estimates appreciably.

A more detailed design and economic study of the cracking reactor is required to determine the optimum temperature, pressure, degree of conversion, pressure drop, and catalyst.

Development work on the requirements for feed gas purification and the purification process itself are required.

Determination of the contact efficiency of various types of gas-liquid contractors for the hydrogen-deuterium ammonia system is also required in order to place the design of the multi-plate exchange towers on a more firm basis. The number of theoretical transfer plates required for the exchange operation is quite low, but with transfer plate efficiencies of the order to 1 to 2%, as calculated in this study, the number of actual plates will be very sensitive to slight variations in plate efficiency.

In order to simplify the design and economic studies

which could be carried out in the time available, the deuter-
ium recovery plant described in Sections 3.0 and 4.0 was
assumed to be an addition to an existing ammonia plant. How-
ever, savings in the cost of producing both the depleted and
enriched ammonia products would result if the two plants were
constructed at one time. Since unit costs are generally lower
for systems of greater capacity, the investment for the com-
bined ammonia synthesis, refrigeration, steam supply, and cool-
ing water systems for an integrated facility could be less
than the combined investments for the two smaller systems re-
quired by separate ammonia and deuterium plants. Furthermore
investment and operating savings would result from the pur-
chase of a primary compressor, V-101, sized for the combined
process, so that recycle around the fourth wheel would not be
necessary (refer to Section 3.1.2). Savings in instrumenta-
tion and common facilities should also result. In addition,
again due to the laws of scale as they affect unit costs,
costs would be further reduced if larger plants capable of
producing 1500 to 3000 tons/day of depleted ammonia were to
be considered. An evaluation of a combined plant, for
optimized performance and large capacity, is required to com-
pare the ultimate potential of the ammonia hydrogen exchange
system with the current water-hydrogen sulfide process.

APPENDIX A - COST ESTIMATE INFORMATION

A.1    Cost of Additional Ammonia Synthesis Plant Required
to Provide Chemical Reflux

A.1.1  Estimate for Ammonia Synthesis Plant of 610 ton $NH_3$/day
Capacity

On a visit to Air Products and Chemicals, Inc. on

September 9, 1967, M. Benedict obtained provisional informa-

tion on the cost of the ammonia synthesis and recovery section

of that company's ammonia plant at Michoud, Louisiana.  This

information was supplemented by more complete data forwarded

by Mr. J. H. Arnold of Air Products on September 27, 1967 (30).

The purpose of this section is to use the above

information to make an estimate of the cost of synthe-

izing ammonia to reflux an ammonia-hydrogen exchange tower

for deuterium recovery.

The plant to which this cost estimate applies takes

synthesis gas at $100^{\circ}F$ and 366 psig containing

$$H_2 \qquad 4762.8 \text{ lb moles/hr}$$
$$N_2 \qquad 1588.3$$
$$CH_4 \qquad 64.9$$
$$A \qquad \underline{20.3}$$
$$6436.3 \text{ lb moles/hr}$$

and converts to to 51,020 pounds of ammonia per hour.

Ammonia synthesis is carried out at 2130 psig.  Power

requirements are:

| | |
|---|---|
| Synthesis gas compression | 11,000 HP |
| (of which 1,000 HP is for recycle) | |
| Ammonia refrigeration | 5,000 HP |
| Total | 16,000 HP |

The estimated capital investment and annual operating
costs for the 610 ton/day ammonia synthesis plant are given
in Tables A.1 and A.2.

A.1.2  Estimate for Required 482 ton $NH_3$/day Plant

The process design and evaluation carried out in this
study assumes that the deuterium extraction plant will be
added to an existing complete ammonia synthesis plant, which
has a capacity of 920 tons $NH_3$/day before the addition.
The cost estimate to be made for this study concerns the
incremental costs associated with installing and operating
the deuterium plant.

The cost estimate for the 610 ton/day ammonia synthesis
plant described in the preceding section was used as the basis
for estimating those incremental costs associated with the
482 ton/day synthesis plant required to supply the liquid
reflux to the exchange towers.  Consequently those parts
of the Air Products plant which are not required in the
additional synthesis plant need to be eliminated, and the
cost estimates given above must be adjusted to reflect the
lower required capacity.

Compressor V-101, which is part of the original 920
ton/day plant, will satisfy the required capacity of the
combined plants (see Section 3.1.2), Compressor V-102 is a
new compressor whose cost must be charged against the deu-
terium plant operation.  Its cost was estimated by Air
Products (32).

## Table A.1

### Investment for 610 ton/day Ammonia Synthesis Plant

Plant Investment

| | |
|---|---|
| Synthesis gas compressors | $ 940,338 |
| Ammonia synthesis section, ex catalyst | 2,040,154 |
| Refrigeration and ammonia recovery section | 797,694 |
| Total, ex catalyst | $3,778,186 |
| Allowance for 10% cost increase since Air Products plant was built in 1965 | 377,819 |
| Equipment total | $4,156,005 |
| Spare parts, at 4% | 166,240 |
| Off-site facilities at 10% | 415,600 |
| Fixed plant investment | $4,737,845 |

Working Capital

Cash equivalent to four months operating costs $\frac{4}{12}$ (694,092) =     $ 231,364

Catalyst inventory     120,141

$ 351,505

Total Investment     $5,089,350

Note: Cost of generating synthesis gas at 366 psig is not included.

Table A.2

Operating Costs for 610 ton/day Ammonia Synthesis Plant

Annual Operating Costs   (330 stream days per year)

| | |
|---|---|
| Labor 4 shifts x $10,000/shift-year | $    40,000 |
| Steam (8 lb/hp hr) (16,000 hp) (24 hr/day) (330 day/yr) ($0.45/1000) | 456,192 |
| Catalyst (3 yr life) 120,141/3 | 40,044 |
| Maintenance, operating materials and make-up supplies 2% of fixed plant investment 0.02 (4,737,845) | 94.757 |
| Subtotal | $  630,993 |
| General and Administrative Costs 10% of subtotal | 63,099 |
| Non-capitalized operating costs | $  694,092 |

Plant costs were assumed to vary as the 0.75 power of plant capacity; this relationship was recommended as the result of a study of cost estimates of ammonia plants ranging in size from 300 to 3000 tons/day made by Oak Ridge National Laboratory (31). The estimated costs for the additional ammonia synthesis plant are given in Table A.3.

A.2     Cost of Deuterium Exchange and Ammonia Cracking Sections

Through the efforts of the Air Products and Chemicals, Inc., preliminary estimates of the various items of capital cost and annual operating costs for the deuterium exchange and ammonia cracking process is shown in Figure 7 and described in Section 3, have been prepared.

A summary of the Air Products cost estimates (32) of the various pieces of equipment and systems obtained from is presented in Table A.4. An estimate of the total plant capital costs for the deuterium exchange and ammonia cracking sections is presented in Table A.5. Additional design details (32) on which the estimates in Table A.3 are based are presented in Table A.6. Estimates of the annual costs of labor, maintenance, utilities, chemicals and water are given in Tables A.7 and A.8.

To be conservative, some of the quantities listed in these tables for computing the cost of utilities consumed are larger than the quantities calculated for the individual pieces of equipment (see Table 3.8). Also note that Table A.8 gives an estimate of the labor requirements for the entire plant.

## Table A.3

### Cost Estimates for Additional 482 ton/day
### Ammonia Synthesis Section

Investment

Synthesis Gas Compressor  V-102                          See Table A.4

Ammonia Synthesis Section, ex catalyst

$$2{,}040{,}154 \times \left( \frac{482}{610} \right)^{0.75} = \qquad\qquad \$1{,}710{,}000$$

    Cost increase allowance at 10%                         171,000

    Offsite facilities at 10%                                   171,000

                        Total                       $2,052,000

Refrigeration - Synthesis Section

$$797{,}694 \left( \frac{482}{610} \right)^{0.75} \qquad\qquad 666{,}000$$

    Cost increase allowance at 10%                          67,000

    Offsite facilities at 10%                                    67,000

                        Total                     $   800,000

Catalyst

$$\frac{482}{610} \times 120{,}141 \qquad\qquad \$ \quad 95{,}000$$

Spare Parts - Ammonia Synthesis and Refrigeration

    At 4% of Equipment Cost                                $   104,000

Annual Operating Costs

    Labor - estimated together with exchange and
              cracking sections. (See Table A.8)

    Steam - (for Ammonia synthesis only, since synthesis
              gas compression is included either in
              original 920 ton/day ammonia plant or in
              deuterium plant estimates)

Table A.3 (cont'd)
Sheet 2

Ammonia refrigeration

$\frac{482}{610}$ x 5000 HP = 4000 HP.

To be compatible with estimate of 610 ton/day
plant, assume this steam is purchased at
$0.45/1000 lb. from original steam plant.

(8lb/HP hr) (4,000 HP) (24 hr/day) x
(330 day/yr) ($0.45/1000 bl)        =        $ 114,000/yr

Maintenance, operating materials and
make-up supplies at 2% of fixed plant
investment
(0.02)(2,052,000 + 800,000 + 104,000)        $ 59,100/yr

Catalyst Makeup
95000/3        $ 32,000/yr

## Table A.4

### Estimated Costs of Equipment for Deuterium Plant

| Equipment | | Size | Unit Cost $1000 | Quantity | Total $1000 |
|---|---|---|---|---|---|
| Name | Number | | | | |
| Stripping Tower | T-1 | 156' x 4' 2 1/8" thick | 181 | 3 | 543 |
| Enriching Tower | T-2 | 150' x 2.5' 1 3/8" thick | 78 | 4 | 312 |
| Catalyst Tower | T-3 | 90' x 1.25' 1/4" thick | 7 | 1 | 7 |
| Purification Tower | T-4 | 40' x 3' 1 5/8" thick | 31 | 1 | 31 |
| Separator | S-1 | 6.5'x 16' 5/8" thick | 13 | 1 | 13 |
| | S-2 | 4' x 10' 2 1/8" thick | 18 | 1 | 18 |
| | S-3 | 6' x 13.5' 5/8" thick | 11 | 1 | 11 |
| | S-4 | 1.5' x 2' 5/16" thick | 1 | 1 | 1 |
| Exchanger | X-1 | 1165 $ft^2$ HP, C-Steel | 7 | 1 | 7 |
| | X-2 | 832 $ft^2$ HP, C-Steel | 5 | 1 | 5 |
| | X-3 | 234 $ft^2$ HP, C-Mo Steel | 3 | 1 | 3 |
| | X-4 | 3135 Mod P, C-Mp Steel | 12 | 1 | 12 |
| | X-5 | 235 $ft^2$ HP, CO-Mo Steel | 3 | 1 | 3 |
| | X-6 | 865 $ft^2$ HP, C-Mo Steel | 9 | 1 | 9 |
| | X-7 | 6600 $ft^2$ Mod P, C-Steel | 23 | 1 | 23 |

Table A.4 (cont'd)
Sheet 2

| Equipment Name | Number | Size | Unit Cost $1000 | Quantity | Total $1000 |
|---|---|---|---|---|---|
| Heater | H-1 | 200 ft$^2$ LP, C-Steel | 2 | 1 | 2 |
| | H-2 | 1450 ft$^2$ LP, C-Steel | 10 | 1 | 10 |
| Cooler | C-1 | 1000 ft$^2$ HP, C-Steel | 5 | 1 | 5 |
| | C-2 | 1130 ft$^2$ HP, C-Steel | 6 | 1 | 6 |
| | C-3 | 400 ft$^2$ HP, C-Steel | 3 | 1 | 3 |
| | C-4 | 670 ft$^2$ HP, C-Steel | 4 | 1 | 4 |
| Compressor | V102 | Centrifug. 1-Wheel | 360 | 1 | 360 |
| | V-3 | Reciproc.. | 675 | 1 | 675 |
| Pumps | V-1 | Reciproc. 25 BHP | 42 | 1 | 42 |
| | V-2 | Reciproc. 11 BHP | 6 | 1 | 6 |
| | V-4 | Reciproc. 1 BHP | 1 | 1 | 1 |
| | V-5 | Centrifug. 17 BHP | 12 | 1 | 12 |
| | V-6 | Reciproc. 1 BHP | 1 | 1 | 1 |
| | V-7 | Centrifug. 5 BHP | 10 | 5 | 50 |
| Refrigeration Systems | | 8.5 x 10$^6$ Btu/hr at -4$^o$F | | | 200 |

Subtotal Uninstalled Equipment      2,375

Table A.4 (cont'd)
Sheet 3

| Equipment | | Size | Unit Cost | Quantity | Total |
|---|---|---|---|---|---|
| Name | Number | | $1000 | | $1000 |
| Cracking Reactor | | $80 \times 10^6$ Btu/hr 40 ft tubes 15-20,000 Btu/hr/ft$^2$ | | | 1500* |
| | | Cracking catalyst | | | 100* |
| Steam System | | $1.35 \times 10^5$ lb/hr sat. steam Superheated by reactor gases | | | 1000* |
| Cooling Tower System | | 15,200 gpm 175 BHP | | | 200* |
| | | Subtotal, Installed Equipment | | | 2,800 |
| | | Total Equipment | | | 5,175 |

* Items for which estimates are for installed systems .
For all other items, estimates are for uninstalled equipment.

## Table A.5

### Estimated Plant Capital Costs for Deuterium
### Exchange and Ammonia Cracking Sections

|  | | $1000 |
|---|---|---|
| Equipment Cost (see Table A.3) | | 5,175 |
| Construction Work - Materials and Labor | | 1,550 |
| Civil | $160,000 | |
| Structural | 170,000 | |
| Mechanical | 930,000 | |
| Electrical | 90,000 | |
| Instrument | 110,000 | |
| Insulation \} Painting | 90,000 | |
| Instruments and Control Panelboard | | 180 |
| Instrument Air Compressor and Drier | | |
| Electrical Substation and Starter Equipment, etc. | | 40 |
| Engineering | | 700 |
| Total Installed Plant | | 7,645 |
| Contractors fee at 4% | | 305 |
| Spare Parts, Initial Supplies, etc. | | 400 |
| Construction Interest | | 320 |
| Start-up and Training Expenses | | 170 |
| Total Plant Capital Cost | | 8,840 |

## Table A.6

### Design Information on Compressor, Pumps, Refrigeration System, Reactor System, Steam System and Cooling Tower System

## Compressors and Pumps

|  | BHP | lb/hr. steam |
|---|---|---|
| V-102 | 3400 | 27000 |
| V-1 | 250 | 2500 |
| V-3 | 5300 | 40000 |
|  |  | KW |
| V-2 | 11 | 10 |
| V-4 | 1 | 1 |
| V-5 | 17 | 15 |
| V-6 | 1 | 1 |
| V-7 (5 req.) | 5 ea | 5 |

## Refrigeration System

### Deuterium Section

$8.5 \times 10^6$ Btu/hr at $-4^{\circ}$F

1000 BHP, 8500 lb/hr. steam

7000 gpm water cooling and condensing

Refrigeration for ammonia synthesis included in cost of ammonia plant.

## Reactor System

Design given in Section 3.3 appears inefficient and too expensive considering total heat duty and low heat flux. Cost estimate based on use of 40 ft. long tubes, 50 psi pressure drop, heat flux of 15,000 to 20,000 Btu/hr/ft$^2$ of tube I.D., and proper cracking catalyst. Include waste heat steam superheater.
$60 \times 10^6$ Btu/hr radiant duty $= 80 \times 10^6$ Btu/hr total duty.
Gas consumption $100 \times 10^6$ Btu/hr

Table A.6 (cont'd)

Sheet 2

**Steam System**

| | lb/hr steam | |
|---|---|---|
| V-102 | 27,000 | 600 psi, 750°F TT |
| V-3 | 40,000 | |
| V-1 | 2,500 | |
| Refrigeration | | |
| Deuterium Section | 8,500 | |
| Ammonia Section [a] | - | |
| | 78,000 | 600 psi, 750°F TT, exhaust to 3 1/2" vac. |
| Cooling Pumps | 16,500 | 600 psi, 750°F TT, exhaust to 30 psi, 275°F TT for heater duty. |
| Total | 94,500 | |

Superheat will be furnished by reactor flue gases

Furnish steam generator for 100,000 lb/hr to 600 psi: sat with boiler feed pumps, deaerator, water treating, etc.

Gas consumption = $150 \times 10^6$ Btu/hr

**Cooling Tower System**

| | gal/min. |
|---|---|
| Condense 78,000 lb/hr at 3 1/2" vac. = | 7500 |
| Ammonia refrig. system [a] | 7000 |
| C-1 cooler | 700 |
| | 15,200 |

Cooling pumps on steam

Cooling tower = 175 BHP = 150 KW

[a] Cost of steam, cooling towers, etc. for ammonia synthesis included in cost of ammonia synthesis section. (See Appendix A.1).

## Table A.7

### Estimated Annual Cost of Utilities, Chemicals, Maintenance

### Deuterium Plant

Basis:  8000 hr/yr

$1000/yr

| Natural Gas | Btu/hr | | |
|---|---|---|---|
| Reactor | $100 \times 10^6$ | | |
| Steam Boilers | $150 \times 10^6$ | | |
| Total | $250 \times 10^6$ at   $0.24/10^6$ Btu | | 480 |

| Electricity | Kw | |
|---|---|---|
| Cooling Tower Fans | 150 | |
| Instrument Air Compressor | 25 | |
| Pumps | 50 | |
| Compressor Auxiliaries | 30 | |
| Lighting | 80 | |
| Total | 335 Kwh/hr  at $0.01 | 27 |

| Catalysts, Chemicals, Lubricants | $1000/yr | |
|---|---|---|
| Catalysts     $ 100000/3 | 33 | |
| Lubricants | 5 | |
| Chemicals | 10 | |
| Total | 48 | 48 |

Makeup water

|  | | |
|---|---|---|
| 3% Makeup = 450 gpm  at $0.50/1000 gal | | 108 |
| = $13.50/hr | | |
| Total     Utilities and Supplies | | 663 |

Table A.8

Estimated Costs of Operating Labor and
Maintenance - Deuterium Plant

| Labor (Total, including added synthesis section) | | | | $1000/yr | $1000/yr |
|---|---|---|---|---|---|
| Superintendent | 1 | at | $15K | 15 | |
| Shift Super. | 4 | at | $12K | 48 | |
| Shift Operat. | 12 | at | $10K | 120 | |
| Maint. Men | 14 | at | $11K | 154 | |
| Loader and Shipper | 1 | at | $ 8K | 8 | |
| | | | | 345 | |
| Fringe Benefits | | 25% | | 85 | |
| Total | | | | 430 | 430 |

Maintenance Materials, Replacement Parts,
Contract Labor

Deuterium Plant                                             360

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