AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

A BRIEF SURVEY OF PROCESSES FOR HEAVY WATER PRODUCTION

by

R. K. RYAN

ABSTRACT

A brief review is given of methods for the production of nuclear grade heavy water, including water electrolysis, distillation, and chemical exchange processes.

Present world production comes mainly from the U. S. A., however Canadian plants will shortly produce much of the world supply. These plants use the H_2O/H_2S process, the only one developed to industrial scale. Sufficient development of the NH_3/H_2 process has proceeded for its use industrially.

Heavy water production as a by-product of established industries appears attractive provided a process matched to the feed supply is available. There are many possible processes that have not been developed.

CONTENTS

Page No:

1. INTRODUCTION

The heavy water inventories for various reactors differ as shown by Cochran (1966) in a chart of heavy water inventory per MWe versus unit ratings (reproduced in Figure 1). Cochran, discussing the chart, suggested:

> "Curve 1 represents heavy water inventory resulting from a recent Canadian heavy water reactor design optimization for a range of unit ratings. This curve appears compatible with the majority of known heavy water reactor designs.
> However, there are exceptions at considerably lower inventory levels. Bohunice* has an inventory of 0.5 short tons per MWe because of its low burnup, about 3,000 MWd/tonne. The boiling light water reactor with 1.42 per cent. UO_2 enrichment, according to paper AECL-2010,** would have an inventory of about 0.34 short tons per MWe. Accordingly, curve 2 represents a possible minimum inventory level that may be encountered in the future".

Estimates of heavy water requirements for any country thus depend on the size and number of reactors to be built. Assuming initial reactor installations would be in the range 200 to 500 MWe, the heavy water inventory would be 0.8 to 1.0 short tons/MWe, if natural uranium is assumed to be the fuel.

2. SOURCES

Theoretically any hydrogen-containing compound is a potential source of deuterium and, hence, heavy water. However, many compounds have insufficient hydrogen content to be used economically as a source of deuterium. One of the important requirements for a source of nuclear grade heavy water is a pure feed material.

Very large quantities of feed material are necessary to recover rather small quantities of heavy water since the deuterium content of natural hydrogen sources, for example H_2O and CH_4, is only about 0.015 mole per cent. (Rae 1965, Bebbington and Thayer 1959). The quantity of feed material is further increased by the inefficiency of recovery in some processes. For example, in the GS (Girdler-Spevak or Girdler-Sulphide) process only 20 per cent. of the deuterium present is recovered (Becker 1962). The only feed materials available in sufficient quantity are hydrogen, ammonia, methane and water and typical examples of the quantities required to separate 100 short tons of D_2O per year are given in Table 1.

---

* A 150 MWe heavy water power reactor in Czechoslovakia for completion in 1968.

** Pon et al. (1964).

3. SEPARATION METHODS

The several methods available for the separation of deuterium from the feed, include electrolysis, distillation, and chemical exchange.

The separation factor (α) is defined as the ratio of the heads abundance ratio to the tails abundance ratio (Appendix 1). Separation factors for several possible processes are compared in Table 2. With other factors equal, the process with the higher separation factor is the better process. Although the separation factor is of great importance since it determines plant size, flow rates, etc., there is no correlation between α and the economic prospects of a process. The energy consumption and plant cost have to be carefully weighed in each case.

Becker (1962) in discussing the recovery of deuterium found water electrolysis too costly for pre-enrichment but suitable for final concentration because the process is simple and easily controlled. Water distillation also is useful only for final concentration, but low temperature hydrogen distillation, which has a high separation factor, is attractive provided the difficulties associated with the low temperatures are overcome. He found that chemical exchange methods are most economic, particularly the GS process, which has been run industrially at Savannah River. The H_2O/H_2 and H_2/NH_3 exchange processes are preferable because of their higher theoretical separation factor, but are not so highly developed.

3.1 Water Electrolysis

Water electrolysis has a high separation factor (Table 2). However, the energy requirements are very high. Some of the energy may be recoverable by fuel cells, but generally the process can only be used where power costs are extremely low and even then only for final concentration (Bebbington et al.1964). Alvarez (Alvarez et al.1964) and Otero (Otero and Gispert, 1964, Otero et al., 1965) are developing electrolytic cascades and burners and are piloting this process.

3.2 Distillation

Four different distillation processes are of interest. Water distillation is only of interest for final concentration where simplicity and operational safety rather than economics are of paramount importance. Proctor and Thayer (1962) described an improved vacuum distillation method. The other three processes are (a) hydrogen distillation, (b) methane distillation, and (c) ammonia distillation.

3.2.1 Hydrogen distillation

Hydrogen distillation has a high separation factor, but its disadvantage is the extremely low boiling point of liquid hydrogen, about 20°K.

Flynn (1960) described a pilot plant for the distillation of hydrogen to produce deuterium, which was built in 1958 at the National Standards Laboratories cryogenic engineering laboratory at Boulder. The preliminary concentration stage, which was the only one piloted, consisted of a 6 inch diameter tower with an equivalent D_2O production rate of 45 lb/8,000 hour year. Stouls (1965), in a patent described an apparatus for the production of deuterium by hydrogen distillation. At Nangal in India (Table 3) a hydrogen distillation plant for the production of deuterium is operated in association with a fertilizer plant (Gupta 1965).

3.2.2 Methane distillation

British American Oil Company is developing methane distillation as a source of heavy water. Methane distillation is useless at atmospheric pressure (separation factor = 1.0002). However, the factor increases at elevated pressure, being largest at about 600 p.s.i.a. (Pogorski 1965). Further improvements are obtainable by application of magnetic and electric fields and also by use of additives to give ternary systems. There is no problem from very low temperatures as required in the hydrogen distillation process, and the process may actually make use of high pressure liquefied methane if available, for example, in U. S. A. where helium is recovered from natural gas (C.N.T. 1966a). Shamsul Huq (1966) discussed this process for use in conjunction with fertilizer production from natural gas.

3.2.3 Ammonia distillation

Barr and Drews (1960) discussed ammonia distillation as a possible process for deuterium recovery. The vapour pressure and latent heat of ammonia compared with water would be advantageous in this distillation if the separation factor were large enough. However, it is too low for economic deuterium recovery. (Table 2).

3.3 Chemical Exchange Processes

Chemical exchange depends upon minor differences in the chemical properties of isotopes causing a shift in equilibrium of chemical reactions. Examples are:

$$H_2O_{(\ell)} + HDS_{(g)} \rightleftharpoons HDO_{(\ell)} + H_2S_{(g)} \qquad .....(1)$$

$$NH_{3(\ell)} + HD_{(g)} \rightleftharpoons NH_2D_{(\ell)} + H_{2(g)} \qquad .....(2)$$

$$H_2O_{(\ell)} + HD_{(g)} \rightleftharpoons HDO_{(\ell)} + H_{2(g)} \qquad .....(3)$$

Exchange processes are of two types, monothermal and bithermal (Figure 2).

Monothermal processes allow the recovery of most of the deuterium in the feed as the gas is produced by chemical decomposition of the liquid and then contacted with the incoming liquid, the temperature of the reaction being chosen to give a sufficiently large separation factor. The economic limitation on this process is the cost of the chemical decomposition step, for example, ammonia decomposition is feasible while water decomposition is not.

Bithermal processes use the difference between separation factors at two temperatures. The overall recovery of deuterium from the feed is limited by the temperature levels used. Bithermal processes require two contactors while monothermal processes require a contactor and a reaction vessel which means that a similar complexity of equipment is needed for both processes.

Barr and Drews (1960) described a large number of possible reactions. However, only a few have been studied extensively, the GS process (H_2S/H_2O exchange), the NH_3/H_2 exchange, and the H_2O/H_2 exchange. Separation factors are given in Table 2.

3.3.1 H_2S/H_2O exchange (GS process)

This process has been highly developed, being the process used at Savannah River for many years (Table 3) and that proposed for the Canadian plants at Glace Bay and Pointe Tupper (Table 4). The process is ionic and has been well described (Rae 1965, 1966; Bebbington and Thayer 1959, Spevak 1949, C. A. Laws 1964). Proctor and Thayer (1962) suggested ways to improve the GS process, reducing both the investment costs and the operating costs. Corrosion in the process is discussed by Thayer and DeLong (1962). Major variables affecting production and costs are given in Table 5 (Bebbington et al. 1964). A very sensitive method of control for the GS process was found to be the ratio of deuterium concentrations on the mid-plates of the hot and cold columns (Morris and Scotten 1962).

3.3.2 H_2/NH_3 exchange

This process has a more favourable separation factor than the GS process (Table 2). However, the reaction is not ionic and a catalyst is needed. Potassium amide is the common catalyst. However, Lafrancois et al. (1962) claimed

improved performance using cesium and rubidium amide catalysts. This process may be either monothermal or bithermal. (Figure 2). The small plant at Mazingarbe in France (Table 3) is of monothermal type (Rae 1966) and has been discussed by Lafrancois (1964). He suggested that the bithermal exchange may become economically preferable if the low temperature tower is held at -70°C or lower.

Rae (private communication) has indicated that assessments by A.E.C.L. of heavy water processes have shown that the NH_3/H_2 process does not appear as attractive as at first thought. Pilot plant studies will be undertaken when it is clear which process offers the most promise of worthwhile cost reductions.

3.3.3 H_2O/H_2 exchange

A bithermal process using liquid phase exchange is thermodynamically favourable. However, a better catalyst than Pt on colloidal charcoal is needed (Rae 1965). This process is being given some attention in Germany where Friedrich Uhde GmbH (Dortmund, West Germany) in co-operation with Degussa and Karlsruhe Nuclear Research Centre have built a single stage dual temperature system using a Pt on activated charcoal catalyst suspended in water. The French have also studied this using colloidal Pt catalyst (Laws 1965). Halpern and James (1966) have studied Ru-III Cl_3 as a catalyst in the D_2/H_2O exchange reaction.

4. PRESENT WORLD PRODUCTION

Table 3 lists heavy water plants in operation and under construction, indicating owners, location, and capacity. Table 4 shows some proposed plants.

The main world supply of heavy water is manufactured at Savannah River, U. S. A. by the GS process. Only part of the plant is in operation and the older Dana plant is out of operation.

In Canada A.E.C.L. has licensed two plants for the production of heavy water by the GS process. Deuterium of Canada has almost completed a 200 short tons D_2O/year plant at Glace Bay, Nova Scotia, which may be extended to 500 short tons D_2O/year, while Canadian General Electric has won the contract for the second plant to be located on the Cape Breton side of the Straits of Causo at Pointe Tupper, Nova Scotia (C.N.T. 1966b). Both Canadian plants have power plants nearby which will supply steam and electric power at a low fixed price.

Smaller quantities are produced in Norway, India, Switzerland, and France. The processes used in these plants vary greatly.

5. INDUSTRIES CAPABLE OF PRODUCING BY-PRODUCT HEAVY WATER

Table 6 indicates some industries with which a by-product heavy water plant could be associated.

If heavy water is to be produced from any feed material other than water, then to be economic the material used must be converted into a form suitable for sale. As Table 1 shows, the production of rather small quantities of heavy water needs enormous quantities of feed material: thus the market for the saleable product must be of equivalent size. Unless a new market can be opened up, an already operating process would have to be used to produce by-product heavy water. This strictly limits the heavy water production. An industry which provides any pre-enrichment may, if large enough, have certain advantages.

Purity of the deuterium source stream may be the most important economic consideration for a by-product heavy water plant. Other conditions of the feed stream may be advantageous, for example, methane which has already been liquefied to separate helium.

6. ADDITIONAL POSSIBLE PROCESSES FOR HEAVY WATER PRODUCTION

Barr and Drews (1960) have listed possible processes for heavy water production. (See Table 7). They considered some of these processes attractive enough for further study. The H_2/H_2O-hydrazine exchange reaction may prove attractive if, as they suggest, the hydrazine acts as a catalyst similar to the amide in the H_2/NH_3 reaction. If a more effective catalyst is found, the PH_3/H_2O exchange reaction may prove of value. They suggest that 30 to 40 per cent. greater capacity may be obtained in the same size towers as used for the GS process. HI/H_2O, HCl/H_2O, and HBr/H_2O are considered but they all appear to be less attractive than a GS plant. The possibility of deuterium being evolved instead of hydrogen in an electrolysis reaction appears attractive. There is no method presently available for doing this. However, ionic resonance effects may prove useful.

7. SUMMARY

The more important processes for the recovery of heavy water have been reviewed briefly. There are many practical problems in these processes such as efficient energy recovery, which have not been considered. The optimum process will combine a high separation factor, large throughput per unit size, and efficient energy recovery.

Choice of processes must depend on the feed material source. However, it must be remembered that the H_2O/H_2S process is the only one that has been developed on an industrial scale and the NH_3/H_2 process has been developed sufficiently to consider its use industrially. No other process is so fully developed.

Of the large number of possible processes few have been discussed in the literature.

8. ACKNOWLEDGEMENTS

The author wishes to acknowledge valuable discussion with Dr. R. C. Cairns and Mr. M. G. Baillie in the preparation of this report. The assistance of Mr. R. C. Hirst in conducting part of the literature search is appreciated.

9. REFERENCES

Alvarez, J., Gispert, M., Maria, A., Otero, J. L., and Rojas, J. L. (1964).- Studies on the production of heavy water at J.E.N. Third United Nations International Conference on the Peaceful Uses of Atomic Energy. A/Conf 28/P/496.

Barr, F. T., and Drews, W. P. (1960). - The future of cheap heavy water. Chem. Eng. Prog. 56 (3):49.

Becker, E. W. (1962). - Heavy water production. I.A.E.A. Review Series. No.21.

Bebbington, W. P., Proctor, J. F., Scotten, W. C., and Thayer, V. R. (1964).- Production of heavy water in U. S. A. Third United Nations International Conference on the Peaceful Uses of Atomic Energy. A/Conf 28/P/290.

Bebbington, W. P., and Thayer, V. R. (1959). - Production of heavy water. C.E.P. 55 (9):70-78.

Cochran, D. R. (1966). - The role and requirements of heavy water in Canada and the World. Paper presented at the C.N.A. Conference, Winnipeg, Canada, May 30, 31 and June 1, 1966. 66-CNA-301.

C.N.T. (1966 a). - The newest variant. Canadian Nuclear Technology, Jan. - Feb. 1966.

C.N.T. (1966 b). - Canso N. S. site for heavy water plant. Canadian Nuclear Technology, July-Aug. 1966. p. 30.

Flynn, T. M. (1960). - Pilot plant data for hydrogen isotope distillation. C.E.P. 56 (3):37-42.

Gupta, S. N. (1965). - India chooses Candu for Kalpakkam. Canadian Nuclear Technology 4 (3):25.

Halpern, J., and James, B. J. (1966). - Homogeneous catalysis of D_2/H_2O exchange by Ru(III) Cl_3. Evidence for heterolytic splitting of H_2. Can. J. Chem. 44 : 671-75.

Lafrancois, B., Lerat. J. M., and Roth, E. (1964). - Study on the production of heavy water in France. Third United Nations International Conference on the Peaceful Uses of Atomic Energy. A/Conf 28/P/91.

Lafrancois, B., Sack, H., Vaniscotte, C., and Dirian, G. (1962). - Caesium and rubidium catalysts in deuterium enriching process. Canadian Patent 637,772 (March 6, 1962).

Laws, C. A. (1964). - Why the GS process still tops competitors. C.N.T. 3 (1):36-40.

Laws, C. A. (1965). - Heavy water : Western deuterium's new track. C.N.T. 4 (2):39.

Morris, J. W., and Scotten, W. C. (1962). - Control of the dual temperature exchange process for the manufacture of heavy water. C.E.P. Symposium Series 58 (39): 26-38.

Otero, J. L., and Gispert, M. (1964). - Study on the production of heavy water. Description of the J.C.N.-E.I.A. installation at Sabinanigo. Energia Nucl. (Madrid) 8 (32):4-11 abstracted in N.S.A. 19-26740.

Otero, J. L., Gispert, M., and Rojos, J. L. (1965). - Studies on the production of heavy water. II. Pilot plant for electrolysis and burners. Energia Nucl. (Madrid) 9:90-4, abstracted in N.S.A. 19-44576.

Pogorski, L. A. (1965). - Method of production of deuterated methanes and heavy water. Canadian Patent 711,458.

Pon, G. A., Lewis, W. B., Haywood, L. R., Primeau, D. B., Phillips, G. J., and Merlo, E. E. (1964). - AECL-2010.

Proctor, J. F., and Thayer, V. R. (1962). - Economics of heavy water production. C.E.P. 58 (4):53-61.

Rae, H. K. (1965). - AECL-2503.

Rae, H. K. (1966). - AECL-2555.

Shamsul Huq, A.K.M. (1966). - AECD/CH/8.

Spevak, J. S. (1949). - NYOO-85.

Stouls, L. (1965). - Methods for the production of deuterium by distillation of hydrogen. U.S. Patent 3,216,800.

Thayer, V. R., and De Long, W. B. (1962). - Materials of construction for the dual temperature exchange process for producing heavy water. C.E.P. Symposium Series 58 (39):86-93.

Walter, S., and Schindewolf, U. (1965). - Enrichment of D through high pressure isotopic exchange between H_2 and liquid NH_3 in a hot-cold installation. Angew. Chem. Interm. Ed. Engl. 4:597. (July 1965) abstracted in N.S.A. 19-44574.

TABLE 1

FEED VOLUME REQUIREMENTS TO PRODUCE 100 SHORT TONS OF D_2O PER YEAR

Feed Material	Feed Volume Requirements	% D_2O Recovery	References
Hydrogen	10^8 S ft^3/day	Unknown	Rae 1965
Methane	2.55×10^7 S ft^3/day	100%	
Ammonia	1,500 short tons/day	Unknown	Rae 1965
Water	1.48×10^6 Imp.gal/day	20%	C.N.T.1966a

TABLE 2

SEPARATION FACTORS OF D_2O PROCESSES

Method	Process	Theoretical Separation Factor
Electrolysis	Water electrolysis	6 - 10
Distillation	Water distillation	1.05
	Hydrogen distillation	1.60
	Methane distillation 15 p.s.i.	1.0002
	Methane distillation 660 p.s.i.	Not available
	Ammonia distillation	1.036
Chemical exchange	H_2S/H_2O dual temperature exchange	1.22
	H_2/NH_3 dual temperature exchange	1.42
	H_2/H_2O dual temperature exchange	1.44

TABLE 3

HEAVY WATER PLANTS IN OPERATION AND UNDER CONSTRUCTION

Process	Owner	Location	Capacity Short tons D_2O/year
H_2/steam exchange and electrolysis	Norsk Hydroelektrick Koaelstofaktieselskb	Rjukan and Glam Fjord Norway	20
H_2 dist. + elect. pre-enrichment	Fertilizer Corp. India	Nangal, India	14
	Enser Werke AC	Domat/Eng, Switzerland	3
H_2S/H_2O exchange	U.S.A.E.C.	Aiken S.C., U.S.A.	180
	Deuterium of Canada	Glace Bay, N.S.	200 *
NH_3/H_2-exchange	C.E.A.	Mazingarbe, France	20

* Under construction

TABLE 4

HEAVY WATER PLANTS PROPOSED

Process	Location	Capacity Short tons D_2O/year
H_2S/H_2O exchange	CGE, Pointe Tupper, N. S.	500
	Deuterium of Canada, Glace Bay, N.S.	200 *
	Nangal or Bihar, India.	200
Electrolytic (Pt cat. exch.)	Sabinanigo, Spain **	0.55 short tons/year
H_2 distillation or H_2/NH_3 exchange or CH_4 distillation	Nat. Gas Fertilizer Factory, Fenchuganj, Pakistan	14.61 short/tons year
H_2/NH_3 exchange	Germany - Semi-industrial †	-

* Deuterium of Canada proposes to increase the size of plant to 500 short tons year.

** Otero and Gispert (1964).

† Walter and Schindewolf (1965).

TABLE 5

VARIABLES AFFECTING PRODUCTION AND COSTS - GS PROCESS

Variable	Effect on Production Rate
A ± 1½% deviation from the optimum liquid to gas flow ratio	1% decrease
1°C decrease in cold tower temperature	1½% increase
1°C increase in hot tower temperature	1% increase
Gas flow rate	Directly proportional
Gas quality (%H_2S)	Directly proportional
An increase of 15 p.s.i. in gas pressure	1% increase

TABLE 6

INDUSTRIES CAPABLE OF PRODUCING BY-PRODUCT HEAVY WATER

Material	Industry
Water	Naturally available
Hydrogen	Blue water gas and water gas shift Gas industry NH_3 synthesis CH_3OH synthesis Petroleum industry Chlorine production Electrolytic cleaning
Ammonia	NH_3 synthesis Fertilizer Urea production HNO_3 production Explosives
Methane	Naturally available HCl production NH_3 production

TABLE 7

POTENTIAL PROCESSES EXAMINED (From Barr and Drews 1960)

PROCESS NUMBER	PROCESS NAME	COMMENTS
Chemical Exchange Processes (See also Processes Nos. 55-80, 95, 96, 98)		
1	Hydrogen/water dual-temperature exchange	Might have good potentiality if the exchange could be made to go fast enough. No promising adaptations so far.
2	Ammonia/hydrogen dual-temperature exchange	Independent study made of this system. No advantage over the H_2S/H_2O process.
3	Phosphine/water dual-temperature exchange	Reaction rate probably too low, but separation efficiency higher than that of the H_2S/H_2O process.
4	Diborane/hydrogen exchange	Separation factors for this system not known. Unless it has unusual characteristics it will not be outstanding because of the high refrigeration load.
5	Hydrogen sulfide/water dual-temperature exchange	Target for comparison. See also Process No. 98.
6	Methane/hydrogen exchange	Exchange data on all show low reaction rate, extensive decomposition, or both. However, incentive for such a process is great since methane in natural gas is the largest single source of hydrogen next to water.
7	Ethane/hydrogen exchange	
8	Propane/hydrogen exchange	
9	Butane/hydrogen exchange	
10	Isobutane/hydrogen exchange	
11	Cyclohexane/benzene-hydrogen exchange	Involves isotope exchange equilibria in a hydrogenation-dehydrogenation reaction. Slow rates and high heat of reaction probably make it not economical.
11A	Cyclohexane or benzene-hydrogen exchange	Avoids the high heat of reaction, but quick, easy equilibration not expected.
12	Glycol/water exchange	Separation factor close to unity at all temperatures.
13	Aromatics/ammonia exchange	Separation factor probably low.
14	Acetone/hydrogen exchange	Separation factor probably good, but exchange rate low.
15	Mercaptan/water exchange	Suggested during the 1941-45 development work. No new information obtained. The process might still be attractive.

(continued)

TABLE 7 (Continued)

Chemical Exchange Processes (See also Processes Nos. 55-80, 95, 96, 98) (continued)

PROCESS NUMBER	PROCESS NAME	COMMENTS
16	Enols and ketones/hydrogen exchange	Separation factors probably good, but exchange rates low.
17	Potassium amide/hydrogen and substituted amines/hydrogen exchange	Expected to have about the same separation factor as the ammonia-hydrogen system. Choice of the proper amine substituent may avoid the high vapour pressure associated with ammonia, which makes high-pressure operation necessary. See also Process No. 95.
18	Ion-Exchange resin/water exchange	Separation factor likely to be poor.
19	Thorium hydride/hydrogen exchange	Exchange rate probably too slow to be of interest.
20	Potassium hydride/hydrogen exchange	
21	Sodium hydride/hydrogen exchange	
22	Cesium hydride/hydrogen exchange	Slow exchange rate; inventory costly and limited.
23	Rubidium hydride/hydrogen exchange	
24	Uranium hydride/hydrogen exchange	Exchange apparently rapid, and counter-current fluid solids tower could be used. However, large inventory would be expensive, and the separation factor probably not exceptionally good. See also Process No. 96.
25	Gadolinium hydride/hydrogen exchange	Separation factor probably low. Supply of Gd and Ce limited.
26	Lithium hydride/hydrogen exchange	
27	Cerium hydride/hydrogen exchange	

Once-Through Decomposition Reactions

PROCESS NUMBER	PROCESS NAME	COMMENTS
28	Decomposition of water by alkali metals	Generally unsuited to tower or cascade operation. Some might be useful for concentration of feed to existing operation. See Process No. 88.
29	Decomposition of water by calcium carbide	
30	Decomposition of water in methane-steam reforming	
31	Bacteriological decomposition and utilisation	

(continued)

TABLE 7 (Continued)

Processes Involving Electrolysis (See also Processes Nos. 83 and 84)

PROCESS NUMBER	PROCESS NAME	COMMENTS
32	Lowering overvoltages in an electrolytic process by the use of solutes	Could improve electrolytic process which already looks good, but would not make unattractive process economic. Probability of success low.
33	Reoxidizing hydrogen with metallic oxides to make pure metal by-products	Secures by-product credits for an electrolytic process, but limited by metals production rate.
34	Electrolysis through osmotic diaphragm	Considered in connection with Process No. 83.
35	Trail-type operation at electrolytic chlorine plants	Somewhat less attractive than the Trail operation, which does not compete with large scale H_2S/H_2O plants.
36	Simple reversible electrolysis	Little promise for the originally proposed process using two liquid phases. See process No. 83.

Adsorption Processes (See also Processes Nos. 85-88)

PROCESS NUMBER	PROCESS NAME	COMMENTS
37	Hydrogen on palladium	Inventory costs too high.
38	Hydrogen on platinum	
39	Hydrogen on platinum reforming catalyst	Detailed study of the char system (Process No. 44) made. General conclusion was that H_2 adsorption systems might be attractive if good separation factor obtained without going too low in temperature but that reaching this goal is unlikely. Char system would require separation factor of at least 100 at -400°F, or 50 at -260°F.
40	Hydrogen on hydroforming catalyst	
41	Hydrogen on aromatizing catalyst	
42	Hydrogen on alumina	
43	Hydrogen on silica gel	
44	Hydrogen on char	
45	Liquid-liquid extraction of water	Triethylamine was attractive solvent but separation factor and mass transfer rate were low.
46	Liquid nitrogen absorption of hydrogen	Other work was to be done in this field, so no evaluation made.

Diffusion Processes

PROCESS NUMBER	PROCESS NAME	COMMENTS
47	H_2 diffusion through porous barrier	No evidence that any of these processes (47-52 would be attractive. Successful aplication of diffusion separations has been to more valuable materials, with higher starting concentration (e.g. U-235).
48	H_2 diffusion through vapor-barrier	
49	Thermal diffusion (Clusius-Dickel)	

(continued)

TABLE 7 (Continued)

PROCESS NUMBER	PROCESS NAME	COMMENTS
Diffusion Processes (continued)		
50	Ion diffusion through exchange resin	No evidence that any of these processes would be attractive. Successful application of diffusion separations has been to more valuable materials, with higher starting concentration (e.g. U235).
51	Liquid thermal diffusion	
52	Hydrogen diffusion through palladium	
Distillation Processes (See also Processes Nos. 90-94, 97)		
53	Rotating-cone column for low pressure drop in water distillation	Water distillation excluded from this study, but idea might be useful for maintaining good separation factor by low pressure.
54	Falling-drop condensation in hydrogen distillation	To control fouling of exchangers by CO ice, but technique not necessary if reversing exchangers perform satisfactorily.
Additional Exchange Processes		
55	Benzene/hydrogen chloride exchange	Exchange rate and separation factor low.
56	Enols and ketones/water exchange	Separation factor probably close to unity.
57	Alizarin/hydrogen exchange	Separation factors about same as in ammonia/hydrogen system. The lower vapour pressures might help if exchange rates were good.
58	o-Anisidine/hydrogen exchange	
59	o-Toluidine/hydrogen exchange	
60	Dimethylglyoxime/hydrogen exchange	Separation factor no better than for water/hydrogen system.
61	Hydrogen chloride/hydrogen exchange	Poor separation factor.
62	Indole/water exchange	Separation factors about same as for ammonia/water exchange, which is close to unity.
63	Methyl indole/water exchange	
64	Pyrrole/water exchange	Separation factors for these systems also probably small.
65	Indene/water exchange	
66	Hydrogen sulfide/methyl alcohol exchange	Avoids hydrate formation problems in H_2S/H_2O system, but these apparently not serious. No improvement in exchange efficiency.

(continued)

TABLE 7 (Continued)

PROCESS NUMBER	PROCESS NAME	COMMENTS
Additional Exchange Processes (continued)		
67	Amyl alcohol/water exchange	Separation factor close to unity.
68	Methyl alcohol/water exchange	
69	Ethanethiol/water exchange	Separation factor about same as for H_2S/H_2O system.
70	Nitrophenol/water exchange	Separation factors expected to be low.
71	Phenol/water exchange	
72	Resorcinol/water exchange	
73	Sugars water/exchange	
74	Vinyl acetic/acid water exchange	
75	Acetylene/water exchange	Separation factors for these base-catalyzed reactions expected to be low.
76	Chloroform/water exchange	
77	Complex cobalt and copper-ammonia salts/water exchange	Between water vapor and a water solution of the salt. Separation factors probably low.
78	Aniline hydrochloride/water exchange	Low separation factor expected.
79	Mono- and dimethylamine hydrochloride/water exchange	
80	Halogen acid/water exchange	Not economical unless solubilities and humidities obtainable can be demonstrated to be much lower than assumed in this study.
81	Sodium sulfate decahydrate/water exchange	Negligible separation effect.
Partially Concentrated Sources (See also Process No. 88)		
82	Hydrogen residues from hydrogenation	No great possibilities seen for this system Hydrogen throughput unlikely to be large enough to give a considerable production of deuterium.
Additional Electrolysis Processes		
83	Diaphragm-separated reversible electrolysis	Little hope for making an economical process of this system. However, the idea is of considerable technical interest.
84	Direct electrolytic release of deuterium	Could be attractive if a separation factor of 10 or better were demonstrated for the preferential release of deuterium. Might be achieved by using pulsating direct current at a deuterium ion resonance frequency.

(continued)

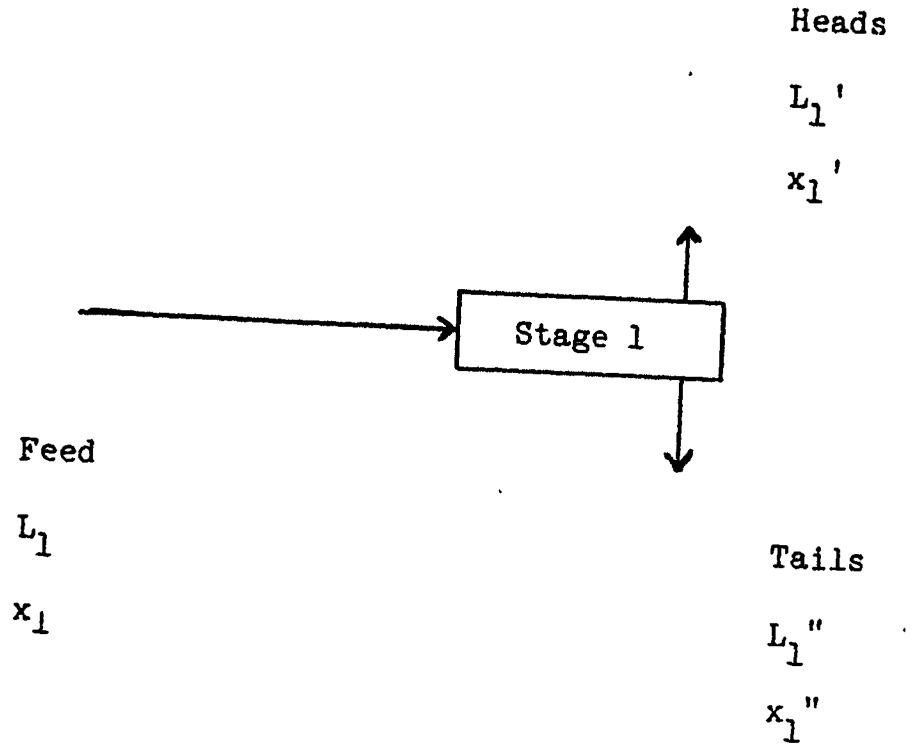
TABLE 7 (Continued)

PROCESS NUMBER	PROCESS NAME	COMMENTS
Additional Adsorption and Absorption Processes		
85	Adsorption of hydrogen on nickel	Conclusions of the study on Process No. 44 are pertinent. However, refrigeration would not be required.
86	Adsorption of hydrogen on calcium	
87	Adsorption of water on silica gel	Water adsorption on char may have favorable application as feed water concentrating process.
88	Adsorption of water on char	
89	Hydrogen absorption in water	Separation factor expected to be low.
Additional Distillation Processes		
90	Dual-temperature water distillation	Vapor recompression is more economical method of heat conservation.
91	Methane distillation	Less attractive than ammonia distillation (Process No. 94).
92	Silanes distillation	Not attractive without unusually good separation factors. Feed would have to be by equilibration with water, satisfactory form of which is not readily apparent.
93	Hydrogen fluoride distillation	
94	Ammonia distillation	Could be distinctly superior to water distillation, but this depends on confirmation of anomalous vapor presure of NH_2D.
Additional Exchange Processes, etc.		
95	Hydrazine-water/hydrogen exchange	Has promise. Separation factor of the order of the H_2O/H_2 and the NH_3/H_2 systems. Presence of hydrazine or substituted hydrazine might give useful exchange rates. See also Process 17.
96	Titanium hydride/hydrogen exchange	Reported to have reasonably good separation factor. Fluid solids exchange tower could be used See also Processes Nos. 19-27.
97	Zone-melting of water	Zone melting is the solid/liquid analog of batch distillation. No possibility of economical application seen.
98	Liquid-liquid hydrogen sulfide/water exchange	Study indicated that liquid/liquid hydrogen sulfide/ water exchange could not compete with the present vapor/liquid process.

APPENDIX I

DEFINITION OF SEPARATION FACTOR

Component definitions are shown in the following diagram:



where L = stream flow rate

x = atom fraction of recoverable isotope

Abundance Ratio $= \xi = \dfrac{x}{1-x}$

Separation Factor $= \alpha = \dfrac{\xi'}{\xi''}$

$$= \frac{x'}{(1-x')} \; \frac{(1-x'')}{x''}$$

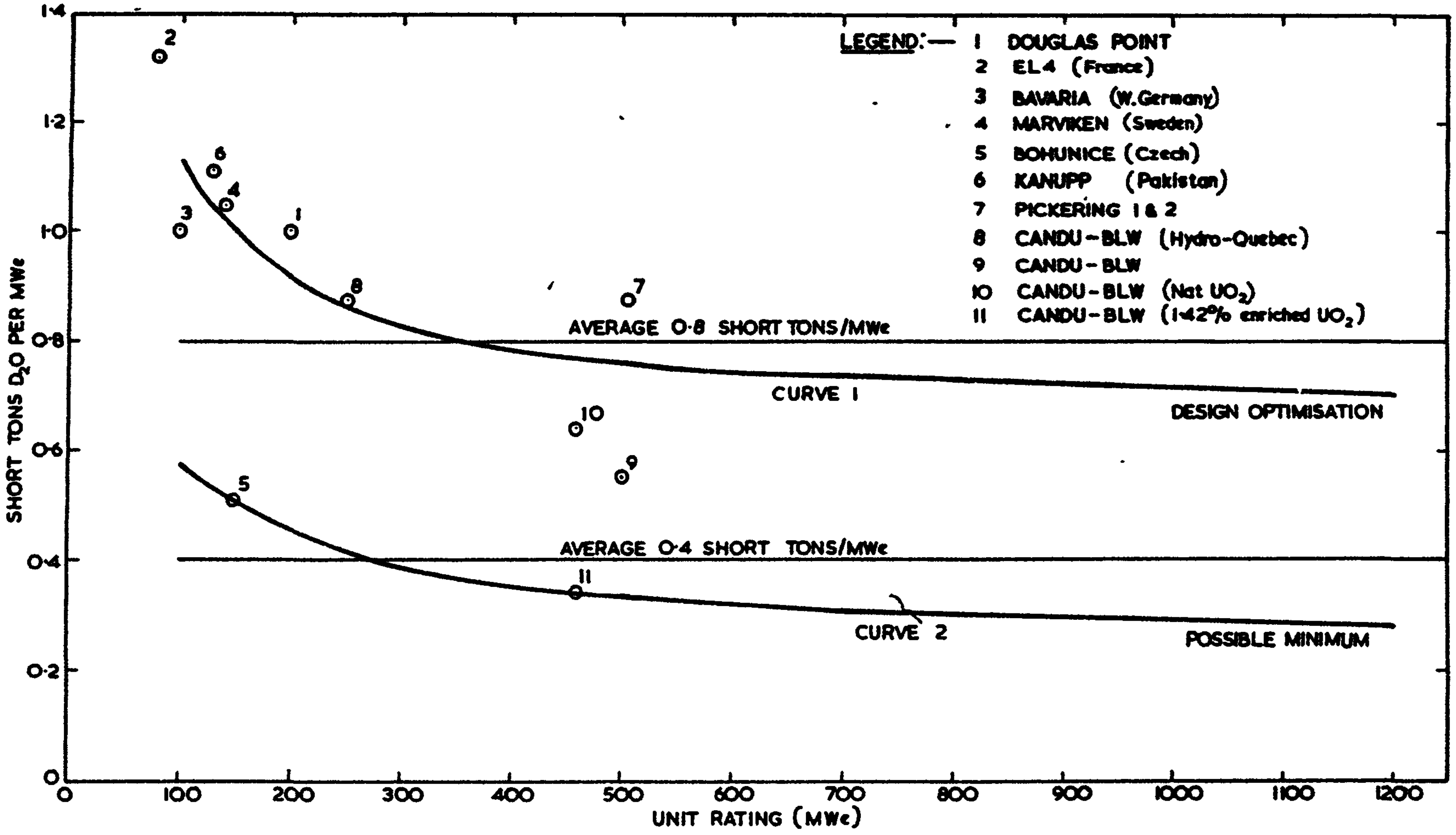
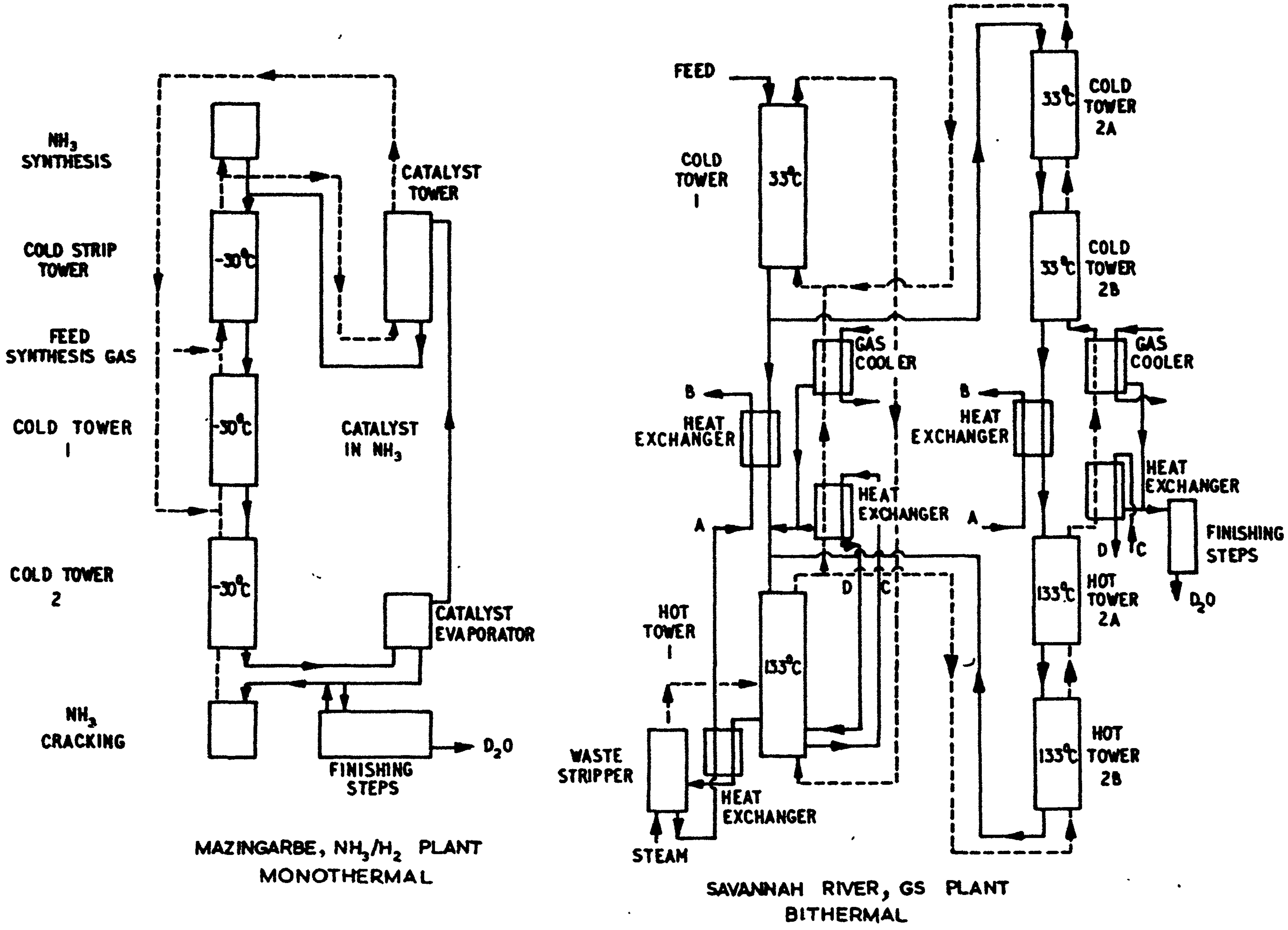


FIGURE 1. HEAVY WATER INVENTORY v. UNIT RATING IN MEGAWATTS (ELECTRICAL) (After Cochran, 1966)

P1065



MAZINGARBE, NH_3/H_2 PLANT
MONOTHERMAL

SAVANNAH RIVER, GS PLANT
BITHERMAL

FIGURE 2. CHEMICAL EXCHANGE PROCESSES

P1065