MLM-3260(OP)

Second Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, Dayton, Ohio, 30 April - 2 May 1985; aslo Fusion Technology Special Supplement, September, 1985

A LOW TEMPERATURE DISTILLATION SYSTEM FOR SEPARATING MIXTURES OF PROTIUM, DEUTERIUM, AND TRITIUM ISOTOPES

Michael C. Embury and Reed A. Watkins
Monsanto Research Corporation
Mound*
Miamisburg, Ohio 45342
(513)865-4195

Richard Hinckley and Arthur H. Post, Jr.
Arthur D. Little, Inc.
Cambridge, Massachusetts

ABSTRACT

A low temperature (24 K) distillation system for separating mixtures of hydrogen isotopes has been designed, fabricated, and delivered for use as the main component of the Hydrogen Isotope Separation System (HISS) at Mound. The HISS will handle feed mixtures of all six isotopic species of hydrogen (H_2, HD, HT, D_2, DT, T_2) and will enrich the tritium while producing a stackable raffinate. Arthur D. Little, Inc. (ADL) was the prime contractor for the distillation system. The design and fabrication techniques used for the HISS distillation system are similar to those used for previous stills which were also designed and built by ADL. The distillation system was tested with mixtures of protium and deuterium at the ADL shop. This system, as well as the feed, product, and raffinate handling systems are presently being installed at Mound where integrated testing is scheduled next calendar year.

INTRODUCTION

The current work at Mound in hydrogen isotope distillation comes from the need to replace the capacity of existing thermal diffusion columns to recover tritium. This involves the separation of tritium from a number of gas sources. Cryogenic distillation technology was selected for this purpose.

Cryogenic distillation of hydrogen isotopes has been applied to heavy water production,[1,2] moderator cleanup of heavy water reactors,[3,4] and to fusion fuel cycles.[5-7] Several demonstration or production plants have been built.[1,3,4,8-11]

The HISS distillation system is part of a total tritium recovery plant currently installed at Mound. The distillation system is a general purpose recovery and enrichment processor and was not designed for a specific function and feeds, such as in a fusion fuel cycle or a heavy water detritiation plant. The unit described in this paper receives feed from thermal diffusion column raffinate, recovery streams from aqueous wastes, and other process units. Distillation systems designed for tritium recovery have applications at any facility handling large amounts of tritium such as fusion power plants where process losses can have a large impact on inventory.[12]

PROCESS DESCRIPTION

The feed gases to HISS will be mixtures of protium, deuterium, and tritium isotopes, as well as helium and other impurity gases. The tritium concentration in the feed gas from different sources is expected to range from one to twenty or more atom percent. The product specification requires a stream enriched to 90 atom percent tritium which is suitable for additional processing. The raffinate stream is to contain no more than 770 MBq/h (0.5 Ci/d) at design feed rates. The raffinate stream will be released to the atmosphere with a negligible impact on the environment.

The HISS distillation system comprises three interconnected packed columns with three room temperature equilibrators as seen in Figure 1. Two separate feed streams enter the cascade which enables the system to accommodate the wide range of feed concentrations. A high tritium product stream and a single low tritium raffinate exit from the cascade. The packed distillation columns are operated at approximately 24 K and provide a separation due to the differences in the relative volatilities of the six isotopic species of hydrogen. The order of relative volatilities from highest to lowest is H_2, HD, HT, D_2, DT, T_2, so that in a single column of sufficient length H_2 would appear at the top and T_2 at the bottom with the other species distributed throughout the column in the above order. The equilibrators are chemical

*Mound is operated by Monsanto Research Corporation for the U. S. Department of Energy under Contract No. DE-AC04-76DP00053.

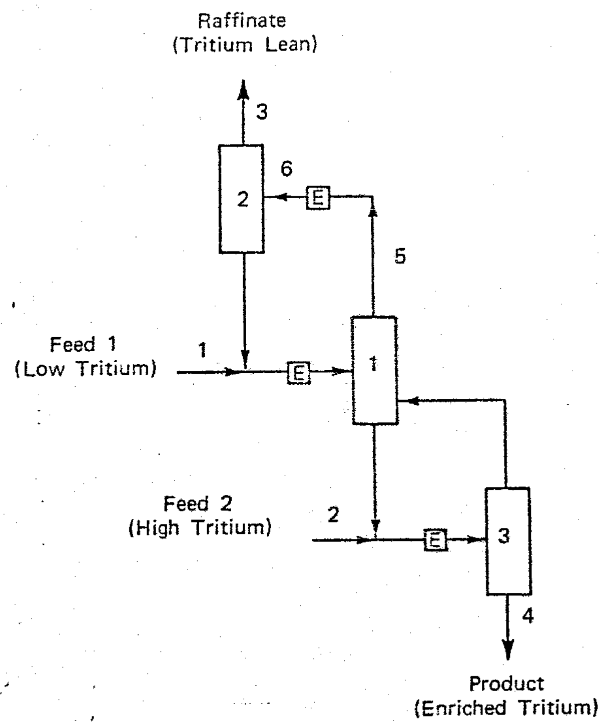

Figure 1 - HISS distillation system.

reactors filled with a precious metal catalyst which promote the following equilibrium relationships:

$$H_2 + D_2 = 2HD \quad K_{H,D} = 3.26 @ 300K \quad (1)$$

$$H_2 + T_2 = 2HT \quad K_{H,T} = 2.58 @ 300K \quad (2)$$

$$D_2 + T_2 = 2DT \quad K_{D,T} = 3.82 @ 300K \quad (3)$$

In HISS the equilibrators are used primarily to reduce certain stream concentrations of HT and DT by forming other species according to the above equations. The strategic location of the equilibrators and the use of recycle streams enable the desired separation with only a three-column system. The effectiveness of the HISS configuration of columns and equilibrators (Fig. 1) can be seen from the results of computer simulations for a typical case presented in Table 1. The two feed streams contain tritium at concentrations of 2.3% and 25.0% and produce a tritium stream enriched to 98% total tritium with a raffinate stream containing only 370 MBq/h (0.24 Ci/d).

With the use of recycle streams, the feed streams are, in effect, processed several times by the columns and equilibrators, thus providing a much greater overall separation than would be achieved by a single pass arrangement. By proper adjustment of column performance (reflux rate and pressure) and bottoms and distillate flowrates, the effect of the equilibrators can be enhanced as well. This is most evident in HISS in the low tritium recycle loop between columns 1 and 2. The base case calculations show that the distillate from column 1 will contain 163 ppm of HT as seen from Table 2. This concentration of HT in a large and predominately D_2 stream is "swamped" by the D_2 in the equilibrator, converting the HT into other isotopic combinations. The resulting HT concentration in the feed to column 2 is thus reduced by a factor of nearly 1000. Because the tritium effluent to the stack is mostly in the form of HT, the amount of tritium in the raffinate stream will be markedly reduced.

The design basis for the feed streams to HISS is approximately 0.0022 m^3/hr. However, additional simulation work at Mound has shown that this system will handle feed rates several times the design rate with no decrease in product concentration, although the tritium concentration in the raffinate increases slightly with the increased gas load. The only hardware change required are flowmeters sized to handle the increased gas loads.

SYSTEM DESIGN

Hydrogen distillation at near one atmosphere pressure requires that the columns operate at a nominal temperature of 20-24 K. In addition to the design requirements imposed by the cryogenic temperatures, the process gas contains radioactive tritium, which imposes an additional set of constraints. As a result, all materials and components were selected or designed to be compatible with low temperatures and tritium service, and the overall system design concepts included maximum reliability, safety, and ease of operation and maintenance. All tritium-containing piping and vessels are doubly contained, with the vacuum jacket or glovebox as the outer containment. All critical heaters and temperature sensors located within the vacuum shell are redundant, and expansion volumes and passive pressure relief devices are present to protect against overpressure due to loss of refrigeration.

The three distillation columns (having inside diameters of 26.1, 16.6, and 10.2 mm) are filled with helical wire packing known as Heli-Pak.[a] The column reboilers are designed to minimize tritium inventory in the liquid phase and contain copper fins and a central plug to achieve this result. The condensers are cooled by helium streams at approximately 18 K from a Koch Process Division, Model 1420 refrigerator with the helium flowing in tubes soldered to the exterior of the condenser proper. This technique provides a double wall separation between helium and tritium to ensure that no tritium is carried to the external helium refrigerator. Copper fins are used within the condensers to

[a] Available from Reliance Glass Works, Inc., 17 Gateway Road, Bensenville, Illinois 60106.

Table 1

Simulation Results for the HISS, Selected Streams From Design Base Case

	Feed 1 1	Feed 2 2	Raffinate 3	Product 4
Flow (g.mol/s)	7.130E-6	1.968E-5	2.162E-5	5.198E-6
(m^3/h)*	0.00057	0.00159	0.00174	0.00042
Mole Fractions				
H_2	0.01275	0.00051	0.00011	~0
HD	0.17756	0.02983	0.10452	<0.1 ppm
HT	0.00421	0.00914	4.4 ppm	<0.1 ppm
D_2	0.76480	0.53432	0.89536	1.5 ppm
DT	0.04012	0.36154	<0.1 ppm	0.03952
T_2	0.00056	0.06466	<0.1 ppm	0.96048
Tritium Concentration or Rate	2.3%	25%	370 MBq/h (0.24 Ci/d)	98%

*Volume flow at "standard conditions" of 273.15 K (0°C) and 101.325 kPa (1 atm).

Table 2

Stream Data For Column 1 Distillate and Column 2 Feed HISS Design Base Case

	Column 1 Distillate 5	Column 2 Feed 6
Flow (g.mol/s)	1.309E-3	1.309E-3
(m^3/h)*	0.106	0.106
Mole Fractions		
H_2	3.8 ppm	1.8 ppm
HD	0.00225	0.00242
HT	163 ppm	0.2 ppm
D_2	0.99755	0.99738
DT	36 ppm	198 ppm
T_2	<0.1 ppm	<0.1 ppm

*Volume flow at "standard conditions" of 273.15 K (0°C) and 101.325 kPa (1 atm).

provide ample condensation area for column reflux. The column assemblies can be seen in Figure 2, while the design parameters for each column are presented in Table 3.

All joints in the process piping within the vacuum enclosure are welded. An automatic welder was used for about 550 tubing welds; about 150 welds were made manually. The three columns are attached to a central support and this assembly wrapped with multilayer insulation. The column assembly is enclosed within a copper thermal radiation shield cooled by liquid nitrogen. The radiation shield also is wrapped with multilayer insulation to reduce nitrogen usage.

The stainless steel vacuum shell measures 5.8 m long by 0.76 m diameter. It is fitted with two pairs of flanges to permit access to temperature sensors located in the condensers and reboilers of the columns. Vacuum pumping after cooldown is provided by a triode ion pump to ensure a totally enclosed secondary containment system. A pod attached to the main vacuum shell houses helium control valves, heaters, and temperature sensors all wrapped with multilayer insulation. A flanged head provides access to the heaters and sensors. An expansion tank is also contained within the pod, located outside the multilayer insulation.

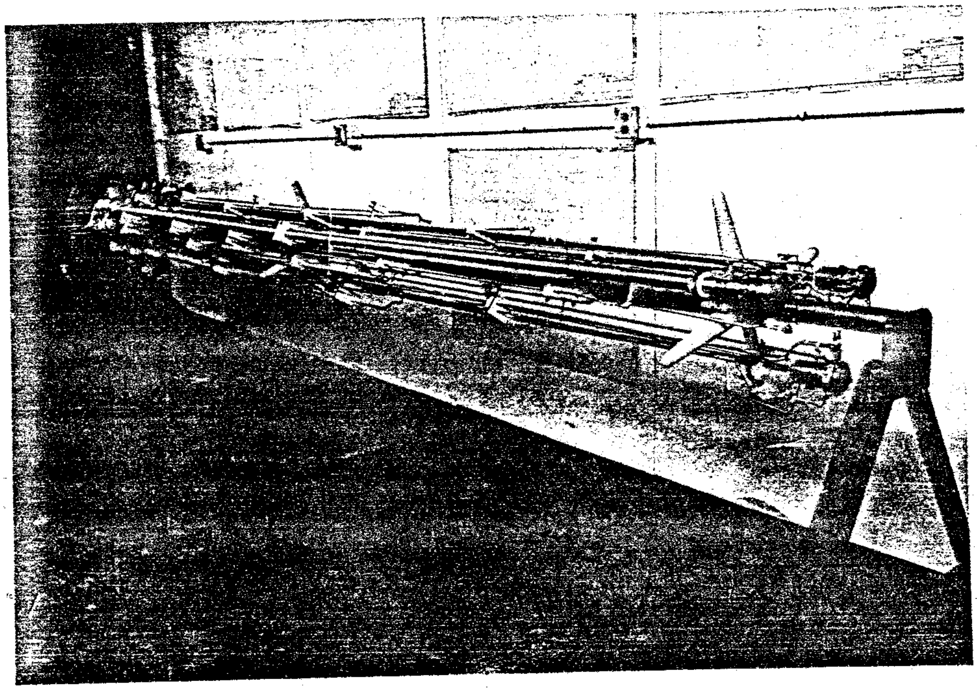

Figure 2 - Distillation columns mounted on center support during assembly with reboilers shown at right.

Table 3

Column Design Parameters

	Column 1	Column 2	Column 3
ID (mm)	26.1	16.6	10.2
Packed Length (mm)	3.66	3.66	3.66
HETP (mm)	65	65	65
Heli-Pak Type	No. 3008	No. 3008	No. 3013
Packing Holdup (%)	9.5	9.5	10.7
Vapor Velocity (mm/s)	80	15	54
Main Feed Stage(s)	28, 51	16	35
Recycle Feed Stage	4	-	-
Reflux Ratio (L/D)	18.9	86.2	50
Condenser Temperature (K)	23.9	23.7	24.2
Condenser Pressure (kPa)	111	107	107
Condenser Cooling Load (W)	29.8	2.3	3.2
Helium Supply Temperature (K)	17	17	17
Reboiler Temperature (K)	24.3	23.8	25.2
Reboiler Heat Duty (W)	30.9	2.3	3.3
Reboiler Liquid Level (mm)	12.7	12.7	12.7
Tritium Inventory (g)	2.73	0.0	7.39

A glovebox welded to the circumference of the vacuum shell houses all valves, instrument sensors, equilibrators, pumps, room temperature piping, and other components as seen in Figure 3. All joints for process piping inside the glovebox are either welded or are "VCR" fittings manufactured by Cajon Inc. All valves and other components requiring maintenance are installed with VCRs on all process connections.

A graphic control panel shown in Figure 4 is provided to facilitate operation and training. Instrumentation includes five digital pressure readouts, three differential pressure readouts, three digital liquid level readouts, six digital temperature readouts, and eight mass flow readouts for the process system. Eleven additional digital temperature readouts for the helium refrigeration system are available within the panel. A vacuum readout for the cold box, ion pump control, and liquid nitrogen level indicator and automatic refill control are also present. Control components include ten servo-controlled valves, five manually controlled heaters, and two variable speed positive displacement doubly-contained pumps. Six automatic valves on the process system provide for recycle and containment in the event of any separation problem.

A rigorous Quality Assurance Plan was defined at the beginning of the project and closely followed until the distillation system was shipped. Included in the documentation were materials certifications, welding records, and test results. A stringent nondestructive testing program called for all welds to be radiographed, dye penetrant tested, and helium leak tested to 1×10^{-10} Pa.m^3/s. The welds were cold shocked three times to liquid nitrogen temperature before the testing. Additional procedures were included for subassemblies. The entire process piping assembly was cooled to operating temperature and helium leak tested to better than 1×10^{-9} Pa.m^3/s with 790 kPa helium in the piping.

SYSTEM OPERATION AND CONTROL

The distillation system described above is designed to run continuously 24 hours a day, seven days a week with manual supervision present only for a single eight-hour shift, five days a week for feed preparation and maintenance. The system delivered to Mound provides for complete manual control and local automatic control with manual setpoint. Thirty-eight variables are monitored for alarm conditions, and, if the system becomes unstable, a programmable logic controller (PLC) will divert the system operation to a total recycle condition until an operator is present to regain control.

The general approach to control is to enforce an overall material balance on each distillation column and on the system as a whole. Condenser pressures for the first two columns in the cascade are under automatic

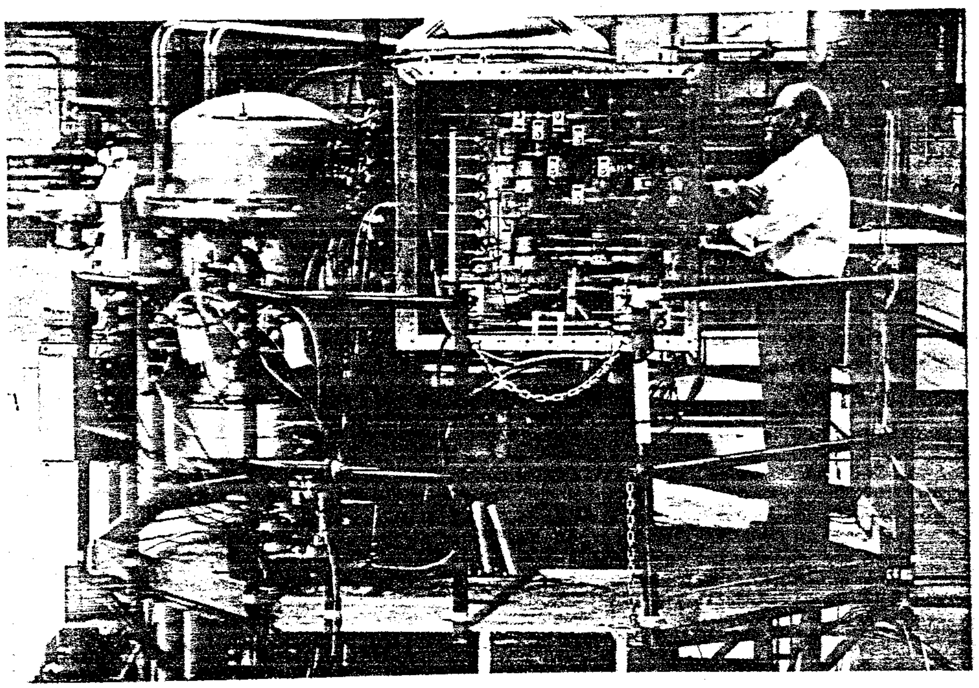

Figure 3 - Side view of distillation system glovebox with helium pod shown on left.

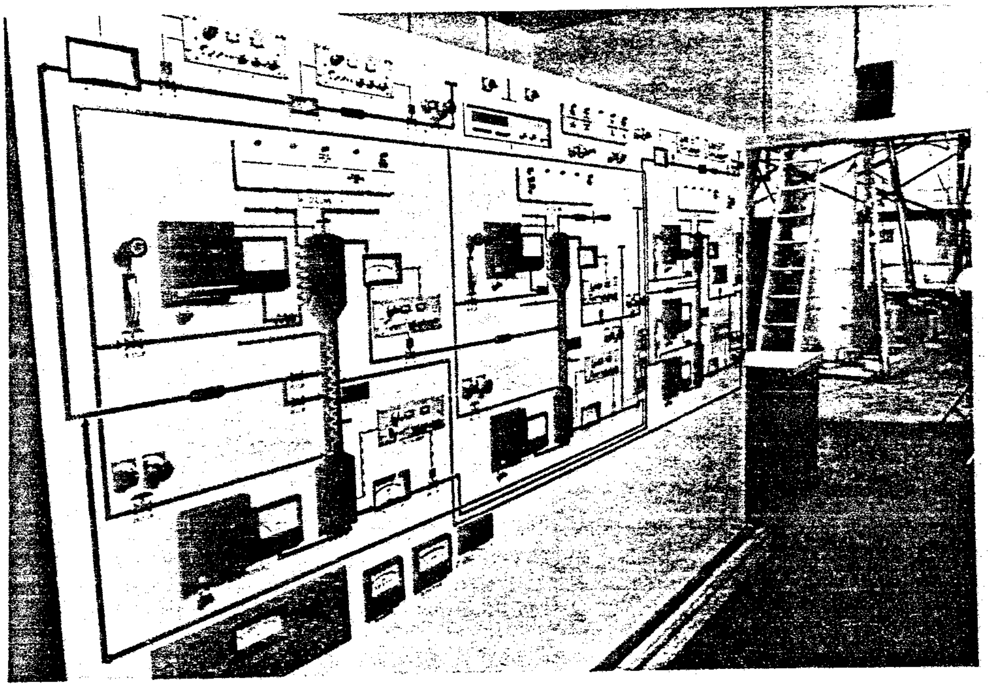

Figure 4 – HISS distillation system graphic control panel.

control by varying helium temperature, and reboiler heat control is set manually since the feed rates to the system will be constant for extended periods of time. This technique ensures that the distillate from the second column, which will be vented to the stack and must contain a minimal quantity of tritium, may be controlled by material balance or flow rate. Whenever the distillate is controlled by flow rate, the bottom product rate is controlled by constant liquid level. The third column control is based on tritium product purity, so that the bottom flow rate and product purity are the principal control variables, with condenser pressure control dependent on distillate flow rate and reboiler liquid level controlled by heat input.

Feed rates and feed compositions are expected to be relatively constant; a constant flow rate control, therefore, is provided but with no feedback trim or feedforward adjustment. If this operating mode proves satisfactory, it will ensure that the control system itself does not introduce unwanted transients.

The control philosophy for HISS provides for eventual supervisory computer control with setpoint adjustment based on periodic measurement of stream concentrations by gas chromatograph or tritium activity meter (TAM). This additional level of control may be necessary as a result of changing feed compositions, tighter product specifications, or other control problems resulting from the process dynamics of the system design.

SYSTEM TESTS

Prior to acceptance for shipment to Mound, the distillation system was tested in the fabrication shop at Arthur D. Little, Inc. In addition to helium leak tests, pressure tests, and component function tests, system operational tests were carried out with protium and deuterium. These tests included operation of the three columns at total reflux. Samples were analyzed with a gas chromatograph in order to observe the progress of separation in each isolated column. Exact measurements of column performance were not obtained under the conditions of the tests. The system was also operated with flow in the recycle loops to test all of the mechanical and electrical components.

After installation of the distillation system at Mound, a more extensive set of operating tests will be done. However, the primary purpose of the system will remain utilitarian rather than experimental.

REFERENCES

1. E. S. SELLERS and D. R. AUGOOD, "The Distillation Characteristics of Liquid Hydrogen," Trans. Instn. Chem. Engrs, 34, 53 (1956).

2. H. K. RAE, "Selecting Heavy Water Processes," ACS Symposium Series 68 (1977).

3. P. H. PAUTROT and M. DAMIANI, "Operating Experience with the Tritium and Hydrogen Extraction Plant at the Laue-Langevin Institute," ACS Symposium Series 68 (1977).

4. K. Y. WONG, T. A. KHAN and F. GUGLIEIMI, "Canadian Tritium Experience," Canadian Fusion Fuels Technology Project, Ontario Hydro (1984).

5. M. KINOSHITA, "A Cryogenic Distillation Column Cascade for a Fusion Reactor," Fusion Technology, 6, 629 (1984).

6. J. R. BARTLIT, R. H. SHERMAN, R. A. STUTZ and W. H. DENTON, "Hydrogen Isotope Distillation for Fusion Power Reactors," Cryogenics, 19, 275 (1979).

7. B. MISRA and V. A. MARONI, "Isotopic Enrichment of Plasma Exhausts from Controlled Thermonuclear Reactors by Cryogenic Distillation," Nucl. Technol., 35, 40 (1977).

8. R. H. SHERMAN, J. R. BARTLIT and D. K. VEIRS, "Experimental Results from Hydrogen/Deuterium Distillations at the Tritium Systems Test Assembly," Fusion Technology, 6, 625 (1984).

9. B. S. JOHNSON and F. G. RUST, "Low Temperature Still for Separation of Hydrogen Isotopes," E. I. duPont de Nemours & Co., Savannah River Laboratory, Aiken, SC, AEC Research and Development Report DP-732 (1962).

10 M. BENEDICT, T. H. PIGFORD and H. W. LEVI, Nuclear Chemical Engineering, Second Edition, McGraw-Hill, New York (1981).

11 K. D. TIMMERHAUS, D. H. WEITZEL and T. M. FLYNN, "Low Temperature Distillation of Hydrogen Isotopes," Chem. Engr. Prog., 54, 6 (1958).

12 J. L. ANDERSON and J. R. BARTLIT, "Unresolved Tritium Issues in the Magnetic Fusion Energy Program", presented at the Second ANS National Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications, Dayton, Ohio, April 30, 1985.