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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE EXTRACTION OF TRITIUM FROM HEAVY
WATER

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Canada

TITLE

PROCESS FOR THE EXTRACTION OF TRITIUM
FROM HEAVY WATER

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ABSTRACT OF DISCLOSURE

A process for the extraction of tritium from a liquid heavy water stream comprising contacting the liquid heavy water with a countercurrent gaseous deuterium in a column packed with a water-repellent catalyst such that tritium is transferred by isotopic exchange from the liquid heavy water stream to the gaseous deuterium stream, passing the gas enriched in tritium from the column through means for removing tritium therefrom and returning the gas lean in tritium to the column, and obtaining a liquid heavy water output from the column, said heavy water being reduced in tritium content.

This invention relates to a process for the extraction of tritium from a liquid heavy water stream.

Nuclear power reactors of the type using heavy water (D_2O) as coolant and moderator incur a progressive build-up of tritiated heavy water (DTO) in the D_2O and this can lead to problems of controlling radiation exposure at the nuclear power stations. This D_2O impurity is produced continuously in the reactor as the D_2O is subjected to neutron irradiation. In present Canadian nuclear generating stations, the average tritium levels are the order of 1 curie per kg of D_2O in the primary heat transport systems and over 10 curies per kg of D_2O in the moderator systems and these levels are rising. Thus the tritium, while present in comparatively minute quantities, because of its radioactivity nonetheless poses significant radiation problems wherever D_2O leaks occur or where it is purged from the system.

At the present time tritium oxide (or "tritium water") can be enriched by various processes such as vacuum distillation or electrolytic cascade (several stages of water electrolysis). However, these processes are not very suitable because of high toxicity of tritium oxide, safety risks, low separation factor for water distillation, or high power consumption for the electrolyzers. A more practical method is to either convert the tritiated heavy water to the elemental form, for example, by water electrolysis or to extract tritium from water by catalytic exchange with a deuterium stream.

A process for removing protium and tritium from heavy water by vapour-phase catalytic exchange is described in United States Patent No.3,505,017 issued to E. Roth on April 7, 1970. Although the process described and claimed in this patent includes the steps of tapping



the heavy water contained in a nuclear reactor and subjecting said tapped heavy water to an isotope exchange reaction with gaseous deuterium, it is obvious from the disclosure that the "tapped heavy water" is heavy water vapour. Because the exchange is between water vapour and gas, the two streams flow to the exchange column concurrently and the process must operate at elevated temperatures (80° to 400°C using catalysts). This process involves the use of evaporators and condensers at each equilibrium exchange step and this is most
10 disadvantageous.

A process for hydrogen isotope concentration between liquid water and hydrogen gas is described in United States Patent No. 3,981,976 issued September 21, 1976 to W.H. Stevens and assigned to Atomic Energy of Canada Limited. This patent points out that the process may be used to reduce the tritium concentration, present as DTO, in heavy water that has been used in an operating nuclear reactor. This is achieved by increasing the concentration of tritium in liquid water by donation from gaseous deuterium derived
20 from the liquid water. The deuterium is produced from heavy water in a deuterium gas generator.

It is an object of the present invention to provide a process for extraction of tritium from liquid heavy water that operates at or near ambient temperatures and pressures.

It is another object of the invention to provide a process for removal of tritium from liquid heavy water that extracts, rather than concentrates, tritium from heavy water.

30 It is another object of the invention to provide a process for extraction of tritium from liquid heavy water that operates without the need for evaporating

and condensing heavy water at each equilibrium stage.

It is another object of the invention to provide a process for extraction of tritium from liquid heavy water that does not require a deuterium gas generator.

These and other objects of the invention are achieved by a process for the extraction of tritium from a liquid heavy water stream comprising: contacting the heavy water with a countercurrent gaseous deuterium stream in a column packed with a water-repellent catalyst such that
10 tritium is transferred by isotopic exchange from the liquid heavy water stream to the gaseous deuterium stream.

In drawings which illustrate an embodiment of the invention,

Figure 1 is a flow diagram of the extraction process, and

Figure 2 is a representative equilibrium diagram for the process,

Referring to figure 1, a liquid heavy water feed is passed through a purification stage 10. Depending
20 on the quality of the feedwater, the feedwater purification stage will include a filtering system to remove suspended solids, an ion-exchange system to remove ionic compounds and a standard degassing system to remove dissolved gases such O_2 and N_2 . If the feedwater is contaminated with oil or other organic materials, it will be purified by charcoal adsorption or chemicals methods. Normally, the heavy water withdrawn from reactor systems is relatively clean and will be passed only through a filtering and an ion-exchange system. The tritium to deuterium (T/D) atom ratio (X_0) in the heavy
30 water stream is in the order of parts per millium (typically 0.1 - 10 ppm) and the principle tritium-deuterium species, are DTO and D_2O . After purification, the liquid

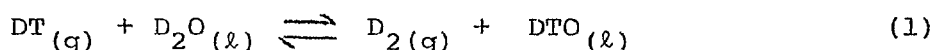
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stream is fed to the top of a catalytic isotope exchange column 11 in which the tritium is extracted from the liquid stream by contacting it with a counter-flowing gaseous stream of DT - D₂ in the column packed with a water-repellent catalyst. The process is operative with any type of catalyst that is water-repellent but the preferred type is that described in United States Patent No. 3,888,974 issued June 10, 1975 to W.H. Stevens and assigned to Atomic Energy of Canada Limited. This catalyst consists of at least one
10 catalytically active metal selected from Group VIII of the Periodic Table having a substantially liquid-water-repellent organic resin or polymer coating thereon which is permeable to water vapour and hydrogen gas. This type of catalyst is also described in the aforementioned Patent No. 3,981,976 and United States Patent No. 4,025,560 issued May 24, 1977 to John H. Rolston et al and assigned to Atomic Energy of Canada Limited. After passing through the column the detritiated liquid heavy water (T/D = X_n) is returned to the nuclear reactor or other source.

20 The deuterium gas (T/D = y_0) entering the bottom of the column 11 is lean in tritium (DT component) and after leaving the column is enriched in tritium (DT). This gas (T/D = y_1) is purified in gas purification stage 12 and sent to a cryogenic distillation stage 13 that lowers the concentration of the DT-T₂ in the gas after which it is returned to the bottom of the column 11. The feedgas purification system for the cryogenic unit is designed to remove traces of impurities which condense and solidify as the temperature of the feedstream drops (moisture, CO₂, N₂, O₂,
30 CO). Typically, the feedgas purification train includes molecular sieve driers, regenerative heat exchangers and cryogenic silica gel or charcoal adsorbers. Distillation

stage 13 gives as output a concentrated DT-T₂ gas stream which would normally be withdrawn into suitable containers. The cryogenic D₂ distillation stage 13 may be replaced with other isotopic separation processes such as thermal diffusion or gas chromatography.

The overall reaction in the catalytic isotope exchange column can be represented as follows:



The equilibrium constant K for the above reaction (expressed in terms of equilibrium mole fractions of the reaction species) is as follows:

$$K = \frac{[\text{D}_2(g)] [\text{DTO}_{(l)}]}{[\text{DT}_{(g)}] [\text{D}_2\text{O}_{(l)}]} \quad (2)$$

Since at low concentrations of DT and DTO, the mole fractions of D₂ and D₂O are nearly constant and approach unity, the above equation (2) can be simplified as follows:

$$K = \frac{\text{T/D atom ratio in the liquid DTO-D}_2\text{O phase}}{\text{T/D atom ratio in the gaseous DT-D}_2\text{ phase}} \quad (3)$$

provided the liquid phase is in equilibrium with the gas phase.

Equation (3) is also used commonly to define the separation factor α for the exchange of isotopic species between the liquid and gas phases. Therefore, $K = \alpha$ in this case.

The equation for K based on partition function ratios given by Bron J et al in the paper "Isotopic Partition Function Ratios Involving H₂, H₂O, H₂S, H₂Se, and NH₃", Z. Naturforsch, Vol. 28a, pgs 129-136, 1973 is as follows:

$$\ln k = 0.05352 + 0.29362 (300/T) + 0.46241 (300/T)^2 - 0.27574 (300/T)^3 + 0.06280 (300/T)^4 \quad (4)$$

where T = Temperature, Kelvin.

This shows that the separation factor at ambient temperature is approximately 1.6 ($\alpha = 1.6387$ at 25°C).

These very useful separation factor levels are obtained in the present process provided that:

- (1) water-repellent catalysts are used,
- (2) the atom ratio T/D in gas entering the column, y_0 , is smaller than the atom ratio T/D in the liquid entering the column, x_0 , that is $x_0 > y_0$.

As shown in Figure 2, the atom ratio T/D in liquid entering the column, x_0 , is greater than the atom ratio T/D in the gas entering the column, y_0 , that is $x_0 > y_0$; the atom ratio T/D in the gas leaving the column, y_1 , is greater than in the gas entering the column, that is, $y_1 > y_0$. As tritium is stripped from the liquid phase $x_0 > x_n$, where x_n is T/D ratio in the liquid leaving the column. Figure 2 represents a simplified graphical determination of the number of equilibrium stages required to achieve a given extraction of tritium from the liquid-phase (frequently referred to as the McCabe-Thiele diagram). It involves alternative use of two plots: one representing a materials balance for each equilibrium stage, referred to as the operating line, and the other representing the equilibrium T/D ratio in the liquid phase (x) and in the gas phase (y), referred to as the equilibrium curve. A material balance for the exchange tower can be expressed by the following equation representing the terminal points of the operating line, that is, x_0 and y_1 at the top of the tower and x_n , y_0 at the bottom of the tower:

$$L(x_0 - x_n) = G(y_1 - y_0)$$

where L and G are molar liquid and gas flow rates, respectively,

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To achieve the transfer of tritium from the liquid to the gas phase, the operating line must always be below the equilibrium curve ($x_0 > y_0$, $y_1 > y_0$ and $x_0 > x_n$).

1 claim

1. A process for the extraction of tritium from a liquid heavy water stream containing 0.1 to 10 ppm of tritium comprising:
 - a) passing the liquid heavy water from which tritium is to be extracted through a purification stage,
 - b) contacting the purified heavy water with a countercurrent gaseous deuterium stream in a column packed with a catalyst, consisting of at least one catalytically active metal selected from Group VIII of the Periodic Table and having a substantially liquid-water-repellent organic resin or polymer coating thereon which is permeable to water vapour and hydrogen gas, such that tritium is transferred by isotopic exchange from the liquid heavy water stream to the gaseous deuterium stream,
 - c) passing the gas enriched in tritium from the column through a gas purification stage,
 - d) passing the purified gas through a cryogenic distillation stage to remove tritium therefrom and returning the gas lean in tritium to the column, and
 - e) obtaining a liquid heavy water output from the column, said heavy water being reduced in tritium content.



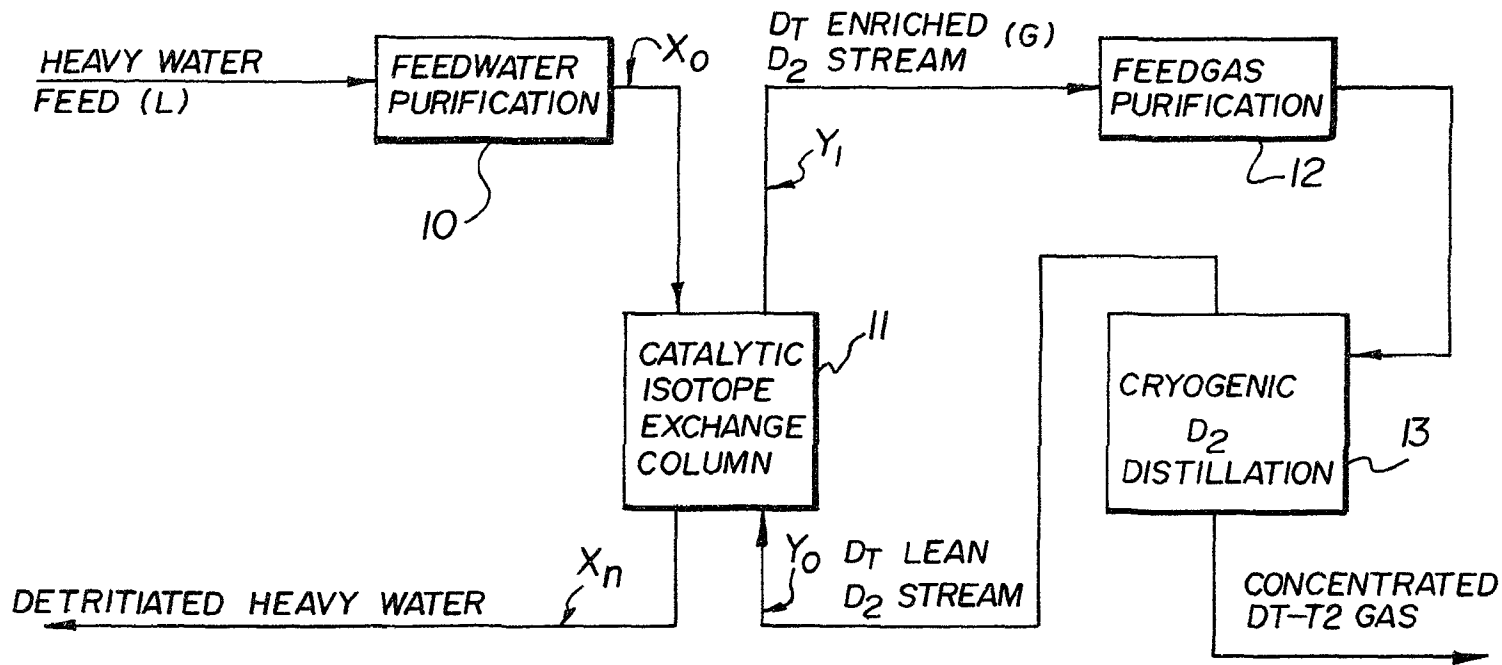


FIG. 1

Division of Chemical Process Design

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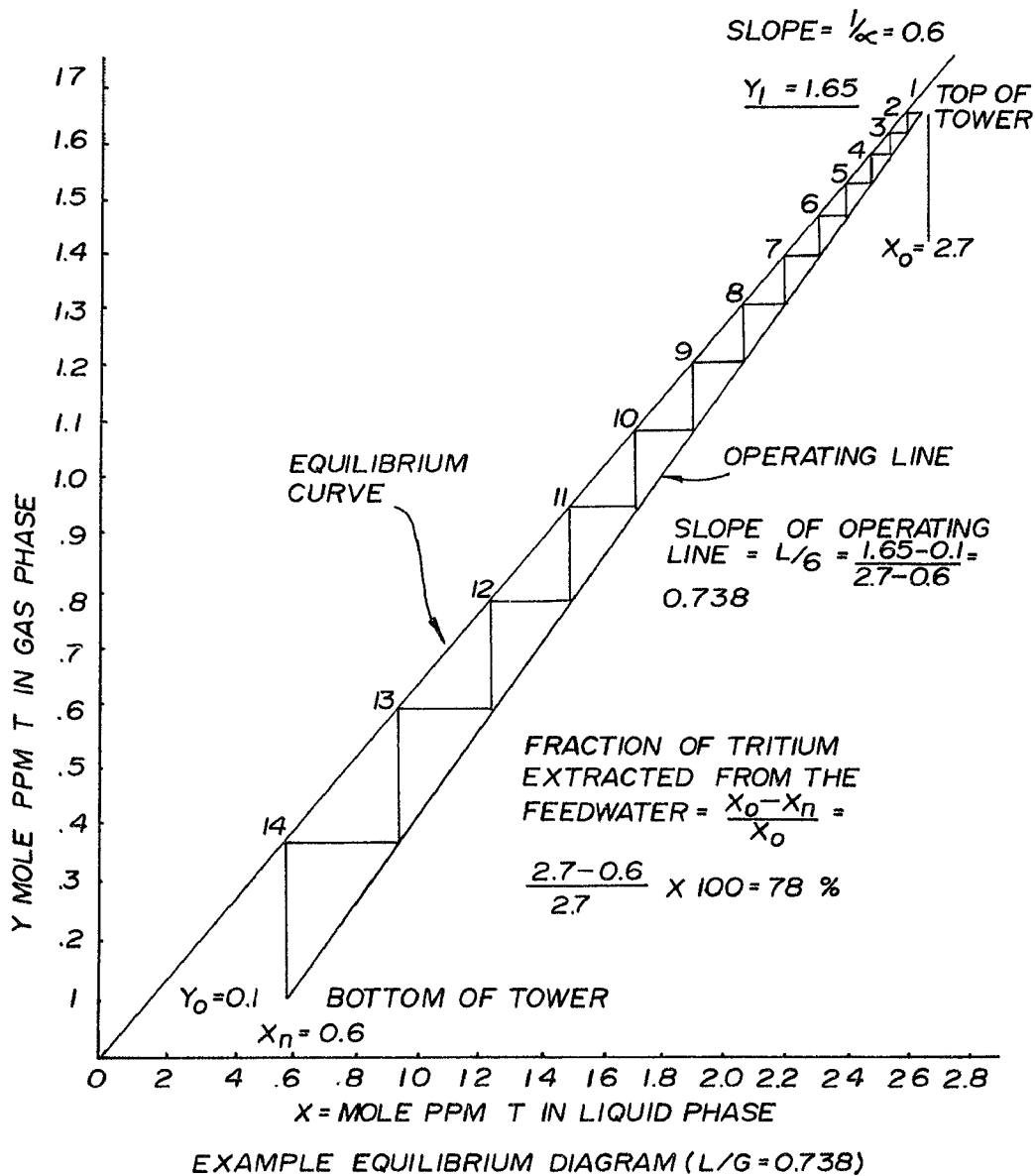


FIG. 2

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