Hydrogen Isotopic Exchange Reaction in a Trickle-Bed

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1. Introduction

The CECE (Combined Electrolysis Catalytic Exchange) with a hydrophobic catalyst is ideally suited for extracting tritium from water because of its high separation factor and mild operating conditions. This process for different hydrogen isotope applications has been developed by AECL [1]. A laboratory scale CECE was built and operated at Mound Laboratory [2]. Belgium and Japan have also developed independently similar processes which are based on a hydrophobic catalyst [3].

The CECE column is composed of an electrolysis cell and a liquid phase catalytic exchange column. The liquid phase catalytic exchange columns having various structures were developed; and it has been recognized that a multistage type and a trickle-bed type are promising. The multistage type gave more successful results than the trickle-bed type. However, the structure of the column is complicated. The trickle-bed type has a significant advantage in that the structure of the column is quite simple: the hydrophobic catalysts or the catalysts and packings are packed within the column. This structure would lead us to a smaller column height than the multistage type [4].

This paper deals with the experiment for the hydrogen isotope exchange in a trickle-bed reactor packed with a hydrophobic catalyst and the design of the catalytic column for the CECE to tritium recovery from light water.

2. Catalytic Exchange Column

2.1 Hydrogen Isotopic Exchange Reaction

The isotopic exchange of tritium between liquid water and hydrogen gas occurs in two stages.

$$HTO_v + H_2 \quad\rightleftharpoons\quad H_2O_v + HT \qquad (1)$$

$$H_2O_v + HTO_l \quad\rightleftharpoons\quad H_2O_l + HTO_v \qquad (2)$$

The first reaction occurs only at the catalyst sites while the second takes place at any gas-liquid interface. With a hydrophobic catalyst both can occur simultaneously in a single trickle bed reactor. The "wet-proofing" repels the liquid water allowing the reactant and product gases to diffuse readily to and from the catalyst surface. To ensure that the second reaction does not become rate limiting, the catalyst bed is mixed with a hydrophilic packing to increase the gas-liquid interfacial area.

2.2 Performance of Trickle-bed

Neglecting the presence of the water vapor and considering a small height of the catalyst packing dZ (m) where the mol fraction of tritium in the gaseous hydrogen is y and the mol fraction of tritium in the liquid water is x, the tritium exchange rate per unit column area can be written as :

$$-Vdy = K_y a(y-y^*)\, S\, dZ \qquad (3)$$

Where V : hydrogen gas flow rate (m^3/s)
   $K_y a$: overall exchange rate constant (m^3/s/m^3)

Rearrangement and integration over the total column, with the assumption that G/k is constant throughout the column, yields the next expression for the catalyst packing height Z

$$Z = \frac{V/S}{K_y a} \int_{out}^{in} \frac{dy}{y - y^*} \qquad (4)$$

Since a hydrogen isotope exchange is classified as an equimolar counter diffusion, NTU (Number of Transfer Unit) and HTU (Height of a Transfer Unit) are defined as:

$$NTU\ (N_{OG}) = \int_{out}^{in} \frac{dy}{y - y^*} \qquad (5)$$

$$HTU\ (H_{OG}) = \frac{V/S}{K_y a} \qquad (6)$$

Therefore, equation (4) is simplified to:

$$Z = H_{OG} \cdot N_{OG} \qquad (7)$$

At a low tritium concentration, both the equilibrium and operating lines are linear and thus Equation (5) can be simplified in terms of a log-mean driving force.

$$NTU\ (N_{OG}) = \int_{out}^{in} \frac{dy}{y - y^*} = \frac{y_{in} - y_{out}}{\overline{\Delta y_L}} \qquad (8)$$

Where, $\overline{\Delta y_L}$ is the logarithmic mean value of the driving concentration difference y-y*:

$$\overline{\Delta y_L} = \frac{(y - y^*)_{in} - (y - y^*)_{out}}{\ln \dfrac{(y - y^*)_{in}}{(y - y^*)_{out}}} \qquad (9)$$

One overall exchange transfer unit corresponds thus to the height of a catalyst packing required to effect a HT concentration change in the hydrogen just equal to the average driving force given by equation (8). The $K_y a$ as determined from Equation (3) neglects the tritium carried by the water vapor. At ambient temperatures where the humidity is low, this assumption causes less than a 1% error. At high temperatures where the partial pressure of water becomes significant, this simple expression is only an approximate.

According to equations (7) and (8) experimental data obtained in specific working conditions in a countercurrent trickle-bed reactor with a given height of a catalyst packing Z allows us to deduce the height of an overall exchange transfer unit H_{OG}, for these conditions. Afterwards the height of s catalyst packing Z required under the same conditions for a required separation duty can be calculated using these same equations. In stead of H_{OG} one can also use $K_y a$, the overall exchange rate constant defined by equation (3). The relationship between $K_y a$ and H_{OG} is given by equation (6).

3. CECE Process

When under constant feed conditions the effluent tritium concentration of the liquid and gas have been stabilized, the amount of tritium leaving the column per unit of time must equal the amount of tritium entering it Neglecting the presence of the water vapor a tritium balance over the countercurrent trickle-bed reactor yields:

$$L (x_{out} - x_{in}) = G (y_{in} - y_{out}) \qquad (10)$$

Where   L : water flow rate (mol/s)
   G : hydrogen flow rate (mol/s)
   x : mol fraction of tritium in water
   y : mol fraction of tritium in hydrogen

Even at higher temperatures, when larger amounts of water vapor are present, equation (10) can be used as an overall tritium balance on the condition that the hydrogen feed is presaturated by the outlet water and that the condensate from the outlet hydrogen is added to the water feed.

The heart of the process is the catalytic exchange columns containing the hydrophobic catalysts; these remain active under wet conditions, thus simplifying the reactor design to a trickle bed rather than separated beds, which are normally used in vapor phase exchange. Figure 1 gives a schematic illustration of the CECE process. It comprises essentially an electrolyser for the production of hydrogen and a countercurrent packed-bed reactor for the tritium exchange between the

hydrogen gas and the liquid water. As the liquid water trickles down the column it becomes more and more enriched in tritium. The hydrogen gas, which is already depleted in tritium relative to the electrolyte from which it evolved, becomes more and more depleted in tritium when it flows from the bottom to the top. The tritium contaminated water is fed into the exchange column at the point where its tritium content corresponds to the local tritium content of the originally tritium free water that has been added at the top of the column.
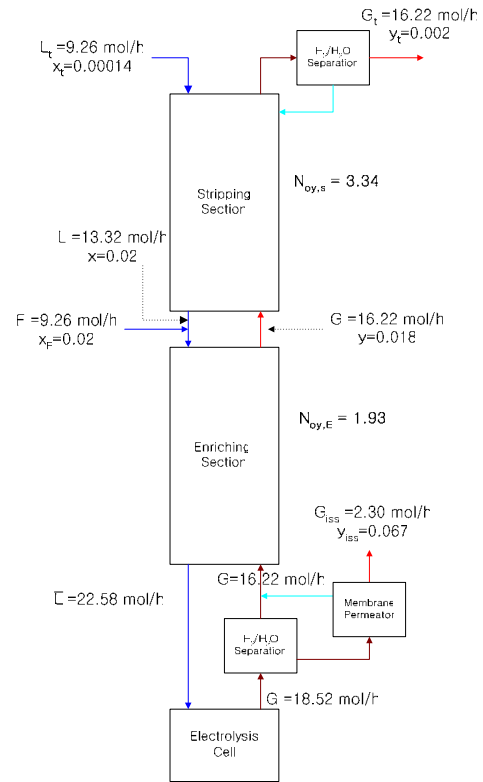

Figure 1. CECE process for detritiation.

Acknowledgement

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