Palladium Alloy Membrane Process for Purifying Hydrogen Isotopes

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1. Introduction

Tritium is a radioactive isotope of hydrogen and it has a half-life of 12.3 years; it decays to He-3 by emitting a low energy beta radiation with an average energy of 5.7 keV and a maximum energy of 18.6 keV. Transfer of environmental tritiated water to humans takes place via an inhalation, diffusion through the skin and ingestion. Radioactive waste containing tritium is continuously generated by the nuclear industry in, for example, nuclear reactor operations and a radioisotope production, and in medical research. Methods for removing tritium from liquid waste provide an alternative to the control of tritium emissions and a personnel exposure. Combined electrolysis and catalytic exchange process is a very effective method to remove small quantities of tritium from light or heavy waste water streams. The process consists of three main steps: (a) A front end step that exchanges the tritium to a less toxic hydrogen phase. This can be performed either through a chemical exchange in the presence of a platinum supported catalyst or through the decomposition of water. (b) A back end process that purifies the tritiated hydrogen gas which evolved from the electrolysis. This can be performed through a palladium alloy membrane separator. (c) A means of storing the concentrated gas safely. Uranium or ZrCo metal is used if storage is temporary; titanium is mainly employed for long term storage. To have a better knowledge of the tritiated hydrogen gas purification process, a mathematical model of the palladium alloy membrane has been used. This model is described herein, and the representative results of the model calculations are presented [1, 2].

2. Detritiation Process

In this section the overall detritiation process is shown in Figure1. As an illustration of the calculation, the material balance for the process is shown in Table1. The process treats four liters of tritiated water with a detritiation factor of ten. The process makes use of a hydrophobic catalyst in a liquid-phase exchange column. Tritiated water flows downward countercurrently to a rising stream of a tritiated hydrogen gas generated in the electrolytic cells. The liquid stream entering at the top of the catalyst column is made up of distilled water. The hydrogen stream from the electolyser is fed to the bottom of the column. As this hydrogen stream is enriched in heavier isotopes, a part of the stream is purified in a membrane permeator in which the water vapor and a small amount of oxygen gas are separated. The upstream hydrogen gas is vented to the atmosphere through a stack. This stream can also be fed to a fuel cell to provide a reflux to the process. Finally the purified waste hydrogen gas in the membrane permeator is safely stored in a metal getter bed.

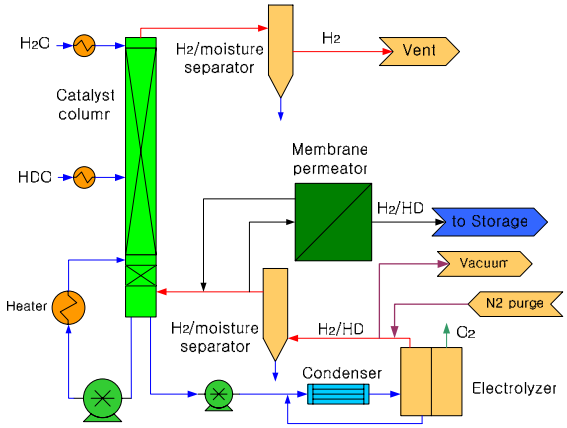

Figure1. Detritiation Process Schematic

Heavy water(HDO)	feed flow rate	L/day	4.00
		mole/h	9.26
	D content	ppm	20000
Light water(H_2O)	feed flow rate	L/day	4.00
		mole/h	9.26
	D content	ppm	140
H_2 exhausted	flow rate	mole/h	16.22
		L/min	6.05
	D content	ppm	2000
HD	flow rate	mole/h	2.30
		L/min	0.86
	D content	ppm	66964
Electrolyser	water throughput	mole/h	18.52
	H2 production rate	mole/h	18.52
		L/min	6.91
Membrane permeator	feed flow	mole/h	-
	permeate flow	mole/h	2.30
	bleed flow	mole/h	-
Detritiation factor			10.00

Table1. Detritiation Process Material Balance

3. Membrane Permeator

3.1 Palladium Alloy Membrane

The membrane is clearly the most important part of the separation process. Generally membrane materials are classified into three types: (a) Synthetic polymers; a vast source in theory although perfluoropolymers, silicon rubbers, polyamides and polysulphones are prominent, (b) Modified natural products; cellulose-based, (c) Miscellaneous; include inorganic, ceramic, metals, dynamic and liquid membranes [3, 4]. The authors selected the palladium alloy membrane for the hydrogen purification process by considering the membrane properties, such as the chemical resistance, mechanical stability, thermal stability, high permeability, and a stable operation. Hydrogen permeates through the palladium alloy membrane by adsorbing and dissociating into atoms at the metal surface, followed by a dissolution and diffusion of the hydrogen atoms through the metal under the influence of the pressure gradient applied. At the permeate side of the hydrogen atoms they recombine to the molecular form and desorb from the surface.

3.2 Solution-Diffusion Model

Sieverts and Kumbhaar observed that the solubility of hydrogen in the α-phase of the palladium has been found to be directly proportional to the square root of the hydrogen pressure [3]. This proportionality is due to the dissociation of hydrogen into atoms at the surface of the palladium. The flux of hydrogen, J, can be expressed in terms of the solution-diffusion model as

$$J = P\,[\sqrt{p'_{H2}} - \sqrt{p''_{H2}}\,] / \delta$$

where J is the flux, $cm^3/cm^2/s$, p'_{H2}, p''_{H2} are hydrogen pressures, bar, δ is the thickness of the palladium, cm, P is the permeability constant, cm^3. $cm/cm^2/s$ /√bar , $P = 6.52\times10^{-6}\exp(-6.38/RT)$.

3.3 Permeate Flow Calculation

The authors applied the solution-diffusion model to a palladium alloy membrane of Johnson Matthey Inc., to obtain the following useful equation for estimating the permeate flow, F.

$$F = K\,[\,\sqrt{p'_{H2}} - \sqrt{p''_{H2}}\,] \text{ in Model HP-2}$$

where F is the permeate flow, 0.859 SLPM, p'_{H2}, p''_{H2} are hydrogen pressures, ata, and K is a constant, 0.4 SLPM/√ata.

Finally Table2 shows the design concept of the membrane permeator for the detritiation process of Figure1.

Gas	Hydrogen Flow rate	Composition
Feed	1.159 SLPM	H_2O Vapor 2.3 vol. %(20℃ saturation), O_2 1ppm(PEM electrolyser)
Permeate	0.859 SLPM	H_2O ND, O_2 ND
Bleed	0.3 SLPM	+ H_2O Vapor
Membrane	Temperature 400℃	Feed: 4.6 ata, Permeate: 0 ata(for hydride)
	Material	Pd/Ag

Table2. Membrane Permeator Specification

3. Conclusion

The authors selected the palladium alloy membrane for the hydrogen purification process by considering the membrane properties, such as the chemical resistance, mechanical stability, thermal stability, high permeability, and a stable operation. The solution-diffusion model can be a useful tool for designing a membrane permeator. The authors applied the solution-diffusion model to a palladium alloy membrane to obtain the design parameters for the detritiation process.

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