

Tritium Separation from High Volume Dilute Aqueous Streams

Fuel Cycle Research & Development

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SUMMARY

This report describes the synthesis and evaluation of molecular sieve zeolite membranes to separate and concentrate tritiated water (HTO) from dilute HTO-bearing aqueous streams. Several silico aluminophosphate (SAPO-34) molecular sieve zeolite membranes were synthesized and characterized with gas and vapor permeation measurements. The pervaporation process performance was evaluated for the separation and concentration of tritiated water.

Experiments were performed over a range of tritiated water concentration covering the range of concentration anticipated in nuclear fuel processing where potentially both acid and water streams are recycled. The permeate was recovered under vacuum. The tritium concentration ranged from 0.5 to 1 mCi/mL which is about 0.1 mg/L or 0.1 ppm. The HTO concentration was three orders of magnitude lower than experiments performed with simulated feed containing HDO (>100 ppm) using deuterated water where high separation factors (>10) were obtained using SAPO membranes. Separation factor calculated from the measured tritium concentrations ranged from 0.83-0.98. Although the membrane performance characterization results were lower than expected, they can be explained on the basis of low feed volume and three orders of magnitude lower HTO concentration compared to HDO concentration in deuterated water. We have identified several new approaches, such as tuning the diffusion coefficient of HTO, that may help achieve preferential transport of tritium (HTO) resulting in a substantially more concentrated permeate.

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ACRONYMS

Al ₂ O ₃	alumina
Bq	Becquerel
CECE	combined electrolysis and catalyst exchange
D ₂ O	deuterium oxide
DPA	di- <i>n</i> -propylamine
FTIR	Fourier Transform Infrared Spectroscopy
GPU	gas permeation unit (cm ³ /cm ² -sec-cm Hg)
HDO	heavy (or deuterated) water
H ₂ O	water containing only hydrogen-1
H ₃ PO ₄	phosphoric acid
HTO	tritiated water
ISS	isotope separation system
ITER	international thermonuclear experimental reactor
LSA	liquid scintillation analyzer
LTA	Linde type A
LUDOX	colloidal silica
mCi	milli Curie (3.7 x 10 ⁷ Bq)
PMR	palladium membrane reactor
P ₂ O ₅	phosphorus pentoxide
SAPO-34	silico alumino phosphate zeolite
SiO ₂	silica
TEAOH	triethyl aluminum hydroxide
XRD	X-ray diffraction

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

TRITIUM SEPARATION FROM HIGH VOLUME DILUTE AQUEOUS STREAMS

1. OBJECTIVE

The release of tritium [usually as tritiated water (HTO)] from nuclear facilities poses a serious hazard to the environment necessitating tritium abatement on aqueous streams generated from various nuclear operations. There are several sources of tritium generation in nuclear processing such as light and heavy water reactors, and the International Thermonuclear Experimental Reactor (ITER).

A novel separation was proposed that utilizes molecular sieve membranes capable of preferentially separating tritium from high volume dilute HTO-bearing aqueous streams. The use of membranes for radioactive decontamination and tritium separation is detailed in the literature,¹⁻³ but the proposed approach of utilizing molecular sieve membranes on robust high-surface area supports has not been reported. Traditional tritium separation technologies include combined electrolysis and catalytic exchange (CECE), palladium membrane reactor, and the highly energy intensive cryogenic distillation.⁴⁻¹⁰ An alternative technology utilizing zeolite molecular sieve membranes was evaluated, which may demonstrate significant, low energy improvement over the available technologies for tritium separation. It was recently shown that silico alumino phosphate (SAPO-34) layered on porous alumina supports can perform separations by taking advantage of the differences in the rates of adsorption, molecular weight, and kinetic diameter of the molecules being separated.¹¹

In the previous milestone report, we have shown a high HDO (deuterated water) separation factor of ~17 using SAPO-34 membranes.¹² The separation factor is the ratio of concentration of HDO in the permeate over the feed concentration and is further discussed in section 2.3. The research described in this report was designed to assess HTO separation with the same SAPO-34 membranes and determine their feasibility for tritiated water treatment. In nuclear fuel reprocessing process water and acid water streams are recycled and are contaminated with tritiated water. The HTO concentration can be in the range of 0.2-1 mCi/mL or 200 to 1000 Ci/m³.

The recovery of tritium from tritiated water was investigated in a Los Alamos National Laboratory technical report with the use of palladium membrane reactor/isotope separation system (PMR/ISS).⁶ The report also discusses the techno-economic analysis of the process to recover 200 grams of tritium stored in a relatively small volume of 1800 L. Birdsell and Willms have reported the tritium recovery from tritiated water with a two-stage PMR, where tritium was recovered from a container of Pt/ α -Al₂O₃ catalyst loaded with approximately 1.7 mg/L (17 Ci/L).⁷ Although the PMR based technology may be well suited for tritium recovery from concentrated solutions, it is unsuitable and not cost effective for large volume dilute aqueous solutions. The PMR/ISS process requires operation at high temperatures (>500 °C) and the recovery cost from a liter of tritium containing waste water can range from \$24,000 to \$100,000 per gram of tritium.⁵

Tritium removal from light and heavy water reactors is described with the application of combined electrolysis and catalyst exchange in U.S. and Canadian patent applications.^{5,6} CECE is generally recognized as the current state of the art for decontamination of tritium in light water and heavy water (HDO) nuclear power reactors where HDO is used both as a reactor moderator and coolant. The typical concentrations of HTO reported are in the range of 0.54 to 1 Ci/kg of tritiated water. For the CECE process, the processing cost for tritium recovery/concentration is directly proportional to the volume and also requires careful balance of concentration profiles in the column which is packed with a hydrophobic catalyst and inert packing material to promote isotopic exchange between aqueous solution and gaseous hydrogen.

Membrane-based tritium concentration, the subject of this effort, may offer several advantages over the current state of the art. The membrane system is relatively easy to fabricate and directly scalable to handle large volume dilute streams with low operating cost. The low cost operating features include separation and concentration at ambient temperature and low pressure with no moving parts compared to CECE, cryogenic distillation or PMR system.

The self-diffusion of several isotopic species of water such as H₂O, HDO/D₂O (heavy water) and HTO/T₂O (tritiated water) has been reported.^{9,11} The self-diffusion coefficients of H₂O and HTO in sorbents such as zeolite 4A can differ by several orders of magnitude depending on the type of cations (Co, Ni, Cs, etc.) that replace Na in the zeolite structure.⁹ The goal in this proof of concept study is to evaluate the feasibility of separating tritium by taking advantage of the differences in adsorption and diffusion rates through the zeolite molecular sieve membranes.

2. MATERIALS AND METHODS

2.1. SAPO-34 membrane synthesis

SAPO-34 crystals were first synthesized prior to the preparation of SAPO-34 membranes. Aluminum as aluminum isopropoxide, H₃PO₄ (to produce the P₂O₅ group), and deionized (DI) water were mixed and stirred for 3 h. LUDOX[®] colloidal silica was then added and mixed for another 3 h. triethyl aluminum hydroxide (TEAOH) and di-n-propylamine (DPA) were added to the homogeneous solution and stirred for 4 days as an aging step. The crystals were synthesized at 210°C for 24 h by the hydrothermal synthesis method, and the crystallized seeds were washed and dried. The molar composition of the resulting SAPO-34 crystals was 1.0 Al₂O₃:1.0 P₂O₅:0.32 SiO₂:1.0 TEAOH:0.8 DPA: 52 H₂O. For membrane synthesis, α -alumina support disks were first seeded by three rounds of mechanical coating/rubbing with a concentrated SAPO-34 seed crystal suspension (5 wt.%). The solution composition was 1.0 Al₂O₃ : 3 P₂O₅ : 0.6 SiO₂ : 3.0 TEAOH : 111 H₂O. The membranes were grown under hydrothermal conditions for 24 h at 210°C, by placing the seeded support disks into the autoclave along with the synthesis solution. The obtained membranes were washed, dried, and calcined at 550°C (holding time of 6 h) and with heating/cooling ramp rates of 0.5 °C/min.

2.2. Membrane characterization

The SAPO-34 seed crystals and membrane were characterized by X-ray diffraction (XRD), and the synthesized membranes were tested for single-gas permeation in which the driving force is a pressure gradient. The XRD patterns were analyzed solely to confirm the previously known and established phase identification of the synthesized seed crystals. After each single-gas permeation test (using xenon or krypton) the membrane was degassed at 100°C in a vacuum. The chamber at the permeate side of the membrane was evacuated, then closed, and target gas was introduced to feed side. During the test, pressure at the feed and permeate sides were recorded over time. This data was used to calculate the

membrane permeance and selectivity from a single gas permeation unit. This helps determine the desirable membrane properties in terms of selectivity and presence of defects.

2.3. Analysis of tritiated water samples

The analysis of HTO concentration in the feed and permeate from the pervaporation system was performed using a Liquid Scintillation Analyzer (LSA). The concentration (radioactivity) was measured in Becquerel/mL (Bq/mL). The error in the measurement of HDO concentration is estimated to be 1-2%, and the error in the calculated HTO permeance is <5%.

The separation factor of HTO over H₂O is defined as:

$$\alpha_{HTO/H_2O} = \frac{C_{HTO}^P / C_{H_2O}^P}{C_{HTO}^F / C_{H_2O}^F}$$

where, C_{HTO}^P and $C_{H_2O}^P$ are concentrations of HTO and H₂O in the permeate, respectively, and C_{HTO}^F and $C_{H_2O}^F$ are concentrations in the feed solution.

2.4. Pervaporation tests

The schematic of the pervaporation system used for the permeation and separation measurements on molecular sieve zeolite membranes is shown in Figure 1.¹³ The system consisted of a feed reservoir, a membrane test cell, and a cold trap to recover the condensed vapor on the permeate side of the membrane. The cold trap consisted of liquid nitrogen-cooled vessel. In some earlier experiments a mixture of dry ice and isopropanol was used, which reached a temperature of -77°F. The vapor pressure of water at this temperature is nearly zero.

The feed volume was in the range of 5 to 10 mL. Pervaporation experiments were performed at room temperature (~ 25 °C). The effective membrane area of the 1 inch diameter disk was 2.85 cm². The feed HTO concentration was varied from 0.5 mCi/mL to 1 mCi/mL (1 Ci/L). This range of concentration is consistent with the anticipated HTO concentration in the process water and acid recycle streams generated during the processing of used nuclear fuel.

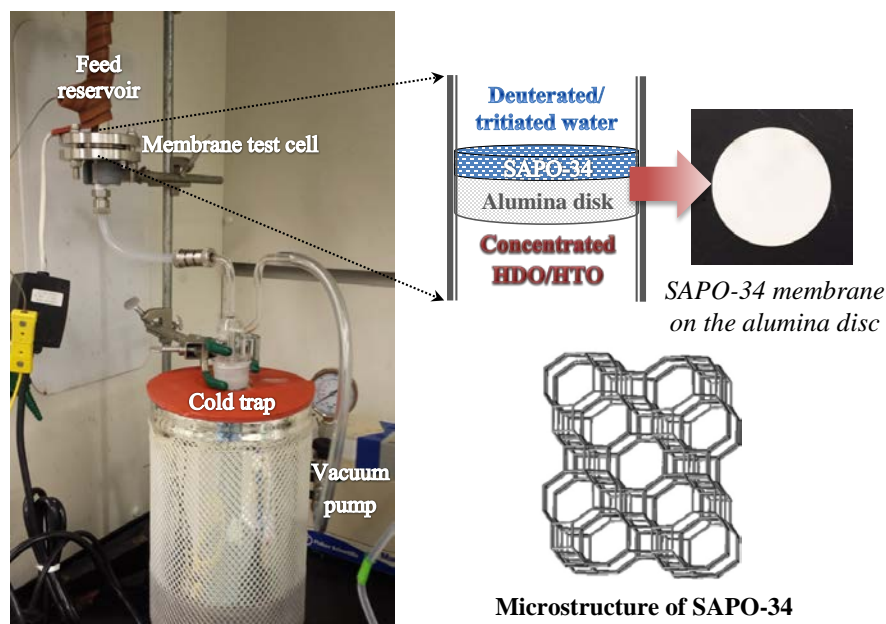


Figure 1: Pervaporation system for the recovery of deuterated/tritiated water.

3. RESULTS AND DISCUSSION

The results of the pervaporation experiments with SAPO-34 zeolite membranes for the separation of HTO and HDO over H₂O are summarized in Table 1. The concentration of HTO in the feed solutions for Run # 1, 2, 3, 4 and 5 was ~ 1 mCi/mL. The tritiated water obtained from PerkinElmer does not contain deuterium. Therefore, 150 ppm HDO was spiked in the feed solution for Run #2 to simulate the natural D₂O concentration in the processing waste stream from nuclear facilities. Run #3 was performed with the feed solution spiked with 2500 ppm HDO, based on the assumption that HTO could permeate more favorably along with HDO across the membrane. In previous experiments, higher HDO concentrations resulted in obtaining substantially higher HDO concentration in the permeate with separation factor >10 (Run # 6, 7)

As shown in Table 1, separation factors of HTO/H₂O in the first three runs (Run # 1, 2, 3) were below 1.0 indicating that HTO did not preferentially permeate over H₂O. This can be attributed to very low concentration of HTO in the feed which is about 3 orders of magnitude lower than HDO concentration in the feed for HDO/H₂O separation tests. The low feed volume (2-3 mL) of tritiated water contacting the SAPO-34 membrane also contributed to the low saturation coverage with HTO under current pervaporation conditions, resulting in low tritium permeation rate. When HDO concentration was varied in the feed by spiking from 0 ppm to 2500 ppm, there was no significant increase in HTO/H₂O separation factor as shown in Table 1, indicating that addition of HDO has negligible effect on HTO separation in SAPO-34 membranes. However, results from Run # 6 and 7 show that high separation factors were obtained for the concentration of deuterated water. Thus, selective HTO transport over H₂O can be anticipated at higher HTO concentrations and complete saturation of zeolite membrane with tritiated water.

In addition, the influence of pH in the feed solution on tritium separation with SAPO-34 membrane was investigated to simulate process water and acid recycle streams. Run #4 shows the results of pervaporation with the feed solution of pH 4 that was spiked with concentrated nitric acid. Although the separation factor was still <1, the amount of tritium adsorbed in the membrane was significantly reduced, suggesting that high concentration of hydrogen ion in the feed could reduce the loss of tritium in the membrane pores caused by adsorption. Run # 5 was performed using tritiated water at pH 2. The amount of adsorbed HTO was further reduced, and the measured permeate HTO concentration was the same as the retentate concentration resulting in a slightly higher separation factor of 0.98. The stability of SAPO-34 at low pH will be investigated, and appropriate modifications to the synthesis procedures are planned to prepare membranes with long-term chemical stability in acidic tritiated water feedstocks.

In order to improve tritium selectivity of the SAPO-34 membrane, it may be necessary to add a pretreatment step to allow the membrane to reach equilibrium state with tritiated water on adsorption sites prior to pervaporation tests. If tritium adsorption in the membrane layer could be minimized by pre-saturation step, it may be possible to obtain HTO separation factors in the range of 1.3~2.3. The membrane could be fully saturated by placing in a desiccator with ammonium chloride solution containing tritium for 14 days at ambient temperature.⁹

Another approach to increase the preferential diffusion of HTO is to vary the self-diffusion coefficient of water in zeolite pores by incorporating cations such as cobalt or cesium (Co²⁺, Cs⁺). According to the literature,⁹ diffusion coefficient of water can be tuned by several orders of magnitude when the zeolite structure was exchanged with other cations mentioned above. This is based on the hypothesis that one should expect slower diffusion of water when monovalent cation such as Na⁺ is replaced with smaller divalent cation such as Co²⁺.⁸ This is due to the fact that small-size polyvalent cations on zeolite framework sites interact strongly with water dipoles, allowing a more compact packing and ordering of water molecules in the pores. Reducing membrane thickness could be another approach to reduce

adsorption and increase permeance of HDO. These approaches would allow us to modify and optimize characteristics of SAPO-34 membranes in terms of both adsorption and diffusion selectivity.

Table 1: Separation of HTO and HDO with SAPO-34 zeolite membranes

HTO	1	2	3	4	5	HDO	6	7
Note		150 ppm D ₂ O	2500 ppm D ₂ O	pH 4 2500 ppm D ₂ O	pH 2 2500 ppm D ₂ O			
HTO in Feed (ppm)	0.111	0.114	0.116	0.108	0.114	HDO in Feed (ppm)	2650	350
HTO in Feed (mCi/mL)	1.108	1.135	1.162	1.081	1.135			
HTO in Retentate (mCi/mL)	1.135	1.081	1.081	1.054	1.108	Total Permeate in 24hr (mL)	0.38	0.18
HTO in Permeate (mCi/mL)	0.919	0.946	1.000	0.946	1.108	HDO in Permeate (ppm)	47900	3630
HTO adsorbed in membrane (mCi)	-	0.168	0.222	0.086	0.068	H₂O Permeance (GPU)	778	782
HTO Permeance (GPU)	-	106	220	190	1643	HDO Permeance (GPU)	17900	9750
Separation Factor	0.83	0.83	0.86	0.88	0.98	Separation Factor	19.0	10.5

4. FUTURE STUDIES

In order to increase separation factor of HTO/H₂O, several approaches will be pursued in the next milestone period. 1) The pretreatment of SAPO-34 membranes will be performed by contacting the membrane in tritiated water for a longer period of time (1-2 weeks) to attain complete equilibrium of HTO in the pores of SAPO-34 membrane. 2) The effect of cation exchange such as Na, Cs, and Co in zeolite structure will be investigated to tune the self-diffusion coefficient of water versus HTO in modified SAPO-34. 3) Thinner zeolite membranes (< 5 μm) will be fabricated and evaluated to reduce HTO adsorption and increase permeance. In addition, tubular zeolite membranes which have higher surface area than disk membranes will be fabricated and evaluated to enhance HTO recovery.

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5. REFERENCES

- 1) Trznadel, G. Z., *Tritium removal from water solutions*, Desalination, 200, 737-738 (2006).
- 2) Ambashta, R. D., et al. *Membrane purification in radioactive waste management: a short review*, Journal of Environmental Radioactivity, 105, 76-84 (2012).
- 3) Rana, D., et al. *Radioactive decontamination of water by membrane processes- A review*, Desalination, 321, 77-92 (2013).
- 4) Butler, J.P. et al. *Apparatus for removal and recovery of tritium from light and heavy water*, US patent 4190515 (1980).

- 5) Bell, A.C., Perevenzentsev, A.N. *Method and apparatus for concentrating tritiated water*, European Patent Appl. EP 1,736,439 A2, December 27 (2006).
- 6) Drake, R.H., *Recovery of tritium from tritiated waste water cost-effectiveness analysis*, Los Alamos National Laboratory LA-UR-97-3767, June (1996).
- 7) Birdsell, S.A., et al. *Tritium recovery from tritiated water with a two-stage palladium membrane reactor*, Fusion Engineering and Design, 39-40, 1041-1048 (1998).
- 8) Embury, M.C., et al. *Tritium recovery by cryogenic hydrogen isotope distillation*, Proceedings of AIChE winter annual meeting, Miami, November 2-7 (1986).
- 9) Todorovic, M., et al. *The release of tritiated water from cobalt (II) exchanged 4A zeolite into surrounding water*, Environmental Pollution (Series B) 7, 193-204 (1984).
- 10) Crawford, P., et al. *Zeolite membranes for the separation of radioactive krypton and xenon*, Proceedings of the Annual Meeting of the American Nuclear Society, Reno, June 15-19 (2014).
- 11) Mills, R., *Self-diffusion in normal and heavy water in the range of 1-45°*, Journal of Physical Chemistry, 77(5), 685-688 (1973).
- 12) Bhave, R., et. al. *Tritium separation from high volume dilute aqueous solutions*, FCRD-MRWFD-2015-000391; ORNL/SPR-2015/316).
- 13) Wee, S., et al. *Membrane separation process-pervaporation through zeolite membrane*, Separation and Purification Technology, 63, 500-516 (2008).