Synthesis and Performance Evaluations of SAPO-34 Membranes for the Separation of Tritiated Water

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 alumino phosphate (SAPO-34) molecular sieve zeolite membranes were synthesized on tubular supports 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 that correspond to the range anticipated in a nuclear fuel processing system that includes both acid and water streams recycling. 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 separation factors calculated from the measured tritium concentrations ranged from 0.83-0.98. The HTO concentration was three orders of magnitude lower than prior experiments performed with simulated feed containing HDO (>100 ppm) using deuterated water where high separation factors (>10) were obtained using SAPO membranes on alumina disk supports. Although the membrane performance characterization results for HTO 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. Several new approaches are proposed, such as tuning the diffusion coefficient of HTO, and optimization of membrane thickness that may help achieve preferential transport of tritium (HTO) resulting in a substantially more concentrated permeate.

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FIGURES

TABLES

ACRONYMS

Al_2O_3	alumina
Bq	Becquerel
CECE	combined electrolysis and catalyst exchange
D_2O	deuterium oxide
DPA	di-*n*-propylamine
FTIR	Fourier Transform Infrared Spectroscopy
GPU	gas permeation unit (cm^3/cm^2-sec-cm Hg)
HDO	heavy (or deuterated) water
H_2O	water containing only hydrogen-1
H_3PO_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 (3.7×10^7 Bq)
PMR	palladium membrane reactor
P_2O_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 (PMR), and the highly energy intensive cryogenic distillation.[4-11] An alternative technology utilizing zeolite molecular sieve membranes was evaluated, which may demonstrate significant, low energy improvement over the available technologies for tritium separation. 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 compared to CECE, cryogenic distillation or PMR systems.

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.

SAPO-34 is a neutral uncharged zeolite material.[10] It has been reported that the self-diffusion of several isotopic species of water such as H_2O, HDO/D_2O (heavy water) and HTO/T_2O (tritiated water) can be significantly modified in cation exchanged zeolite or molecular sieve sorbents.[9] The self-diffusion coefficients of H_2O 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, 13] The goal in the proposed future studies is to evaluate the feasibility of separating tritium by taking advantage of the differences in adsorption and diffusion rates through cation exchanged zeolite molecular sieve membranes.

In the previous milestone reports, it was shown that a high HDO (deuterated water) separation factor of >10 using SAPO-34 membranes could be achieved.[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 prepared on the inside surface of a tubular alumina support to 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 200 to 1,000 Ci/m^3 or 0.2-1 mCi/mL. The HTO concentration at the upper end of the range was used in this study. On a comparative basis, these concentrations are at least three orders of magnitude lower than HDO concentration in deuterated water experiments.

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, H_3PO_4 (to produce the P_2O_5 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 $1.0\ Al_2O_3{:}1.0\ P_2O_5{:}0.32\ SiO_2{:}1.0\ TEAOH{:}0.8\ DPA{:}\ 52\ H_2O$. For membrane synthesis, α-alumina disks and tubular supports were first seeded by three rounds of mechanical coating/rubbing with a concentrated SAPO-34 seed crystal suspension (5 wt.%). The solution composition was $1.0\ Al_2O_3 : 3\ P_2O_5 : 0.6\ SiO_2 : 3.0\ TEAOH : 111\ H_2O$. 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 of the single-gas permeation tests (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 characterize the 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 HTO concentration is estimated to be 1-2%, and the error in the calculated HTO permeance is <5%. Analysis of deuterated water was performed using Fourier Transform Infrared Spectroscopy (FTIR) and is described in detail elsewhere.[12]

The separation factor of HTO over H_2O is defined as:

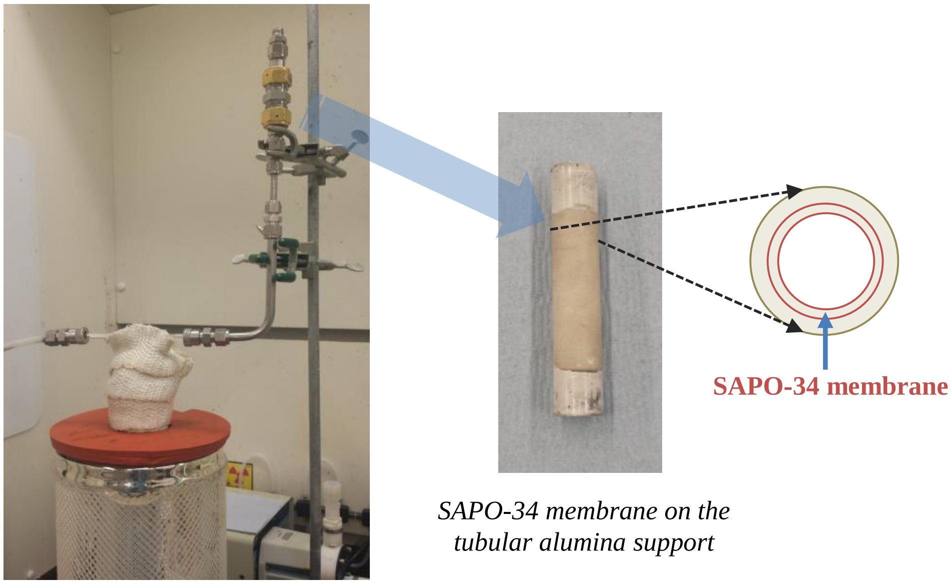
$$\alpha_{HTO/H_2O} = \frac{C_{HTO}^{P}/C_{H_2O}^{P}}{C_{HTO}^{F}/C_{H_2O}^{F}}$$

where, C_{HTO}^{P} and $C_{H_2O}^{P}$ are concentrations of HTO and H_2O 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 tubular molecular sieve zeolite membranes is shown in Figure 1. 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. The vapor pressure of water at this temperature is nearly zero.

The feed volume was in the range of 2 to 10 mL. Pervaporation experiments were performed at room temperature (~ 25 ˚C). The effective membrane area of the 1-2 inch long tubular membrane ranged from 6.5 to 12.5 cm^2. 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.



SAPO-34 membrane on the tubular alumina support

Figure 1: Pervaporation system with a tubular membrane for the recovery of deuterated/tritiated water.

3. RESULTS AND DISCUSSION

The results of the pervaporation experiments with tubular SAPO-34 zeolite membranes for the separation of HTO and HDO over H_2O are summarized in Table 1. The concentration of HTO in the feed solutions for experiments with disk membranes (Run # D1-1 D1-2, D1-3) and tubular membranes (Run # T1-1, T1-

2) was ~ 1 mCi/mL. Run nomenclature D1, D2 shows experimental results with 2 different disk membranes, and T1, T2 describes experiments performed on tubular membranes. The tritiated water as received from Perkin Elmer is at neutral pH (Run # D1-1). The pH of process water and acid water recycle streams at nuclear facilities can range from about 2 to 7. Run # T1-1 and T1-2 show the results at pH values in the range of 4 and 5.5 when spiked with nitric acid. Experiments at pH of 2 were not performed on tubular SAPO membranes due to concern of chemical stability at low pH. Run # D1-2 and D1-3 performed on SAPO-34 disk membranes illustrate the concern for stability at low pH. As can be seen, the HTO permeance at pH 4 to 7 was in the range of 190 to 687 GPU compared to a substantially higher value of 1643 GPU obtained at pH 2 (Run # D1-2).

Table 1 also shows the results of deuterated water separation on disk membranes. It can be seen that at the typical concentrations of HDO, which are several orders of magnitude higher than HTO, resulted in substantially higher HDO concentration in permeate. These experiments were performed on disk 2. The calculated separation factor ranged from about 2 to 10 (Run # D2-1, D2-2).

As shown in Table 1, separation factors of HTO/H_2O were slightly below 1.0 indicating that HTO did not preferentially permeate over H_2O. 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/H_2O separation tests. Additionally, the neutral uncharged SAPO-34 zeolite has no preferential affinity to HTO over H_2O. However, results from Run # D2-1 and D2-2 show that high separation factors were obtained for the concentration of deuterated water. Thus, selective HTO transport over H_2O may be anticipated at higher HTO concentrations. Unfortunately, such high concentrations are not typical of those encountered in process water and acid recycle in nuclear fuel processing. The tuning of H_2O diffusivity may enable preferential adsorption and transport of HTO over H_2O resulting in higher HTO concentration in permeate compared to the feed concentration.

The stability of SAPO-34 at low pH can be improved with appropriate modifications to the synthesis procedures. This is planned as part of the future studies in progress to prepare robust membranes with long-term chemical stability.

An important requirement for the economic viability of a membrane-based separation system is high permeance to deliver high throughput and process efficiency. HTO and H_2O permeance is a critical measure that will impact the capital and operating cost. Tubular module configuration offers a significant advantage due to the high packing density and ease of scalability. Table 1 shows the HDO, HTO and H_2O permeance of disk and tubular zeolite membranes. It can be seen that vapor permeance of tubular zeolite membranes was 2 to 4 higher compared to disk membranes. The permeance of Kr and Xe is included to show high quality and integrity of SAPO-34 membranes in Table 2. The calculated Kr/Xe selectivity ranged from about 5 to 9.

One of the approaches 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 (Co^{2+}, 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 Co^{2+}.[9] 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 modification and optimization of the 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 Runs	D1-1	T1-1	T1-2	D1-2	D1-3	HDO Runs	D2-1	D2-2
Note	pH 7 (disk 1)	pH 5.5 (tube 1)	pH 4 (tube 1)	pH 4 (disk 1)	pH 2 (disk 1)		pH 7 (disk 2)	pH 7 (disk 2)
HTO in Feed (ppm)	0.111	0.108	0.113	0.108	0.114	**HDO in Feed** (ppm)	350	165
HTO in Feed (mCi/mL)	1.108	1.081	1.127	1.081	1.135	**Total Permeate** in 24hr (mL)	0.18	0.49
HTO in Retentate (mCi/mL)	1.135	1.108	1.103	1.054	1.108	**HDO in Permeate** (ppm)	3630	320
HTO in Permeate (mCi/mL)	0.919	1.035	0.962	0.946	1.108	**H_2O Permeance** (GPU)	21	262
HTO Permeance (GPU)	-	687	412	190	1643	**HDO Permeance** (GPU)	245	580
Separation Factor	**0.83**	**0.96**	**0.85**	**0.88**	**0.98**	**Separation Factor**	**10.5**	**1.9**

Table 2: Permeance of Disk and Tubular SAPO-34 Membranes

Permeance (GPU)	D1	D2	T1	T2
Xe	1.4	1.5	2.5	2.3
Kr	11.8	12.5	12	11.7
H_2O (pH 7)	352	212	627	873
H_2O (pH 4)	-	190	402	-

4. FUTURE STUDIES

In order to increase separation factor of HTO/H_2O, several approaches will be pursued in the next milestone period. 1) 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. 2) 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. 3) Incorporation of molecular sieve carbon coating could be useful to reduce H_2O transport compared to HTO with superior chemical compatibility, particularly under acid recycle conditions.

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