Techno-economic Analysis of Advanced Zeolite Membranes for the Concentration of Tritiated Water

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SUMMARY

This report describes the techno-economic analysis of advanced molecular sieve zeolite membranes to separate and concentrate tritiated water (HTO) from dilute HTO-bearing aqueous streams. In the first phase of this effort, several monovalent and divalent cation-exchanged silicoalumino phosphate (SAPO-34) molecular sieve zeolite membranes were synthesized on disk supports and characterized with gas and vapor permeation measurements. In the second phase, Linde Type A (LTA) zeolite membranes were synthesized on disk and tubular supports. The pervaporation process performance was evaluated for the separation and concentration of tritiated water.

Techno-economic analysis (TEA) on SAPO-34 and LTA membrane based technologies was completed. However, compared to the SAPO-34 membranes, LTA zeolite membrane performance both with respect to separation factor and permeance was superior and encouraging. LTA zeolite membranes were selected as the preferred option for comparison with the Combined Electrolysis and Catalyst Exchange (CECE) process for the concentration of tritiated water from dilute HTO-bearing aqueous solutions. It is estimated that the total energy cost to process 10 L/min of tritiated water for the membrane cascade system is substantially lower compared to the CECE process. A preliminary capital cost estimate for the membrane based system and the CECE process is also reported.

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FIGURES

TABLES

ACRONYMS

CECE	combined electrolysis and catalyst exchange
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
HTO	tritiated water
ISS	isotope separation system
ITER	international thermonuclear experimental reactor
LSA	liquid scintillation analyzer
LTA	Linde type A zeolite
NaA	Sodium exchanged LTA zeolite
KA	Potassium exchanged LTA zeolite
LUDOX	colloidal silica
PMR	palladium membrane reactor
SAPO-34	silicoalumino phosphate zeolite
XRD	X-ray diffraction

TECHNO-ECONOMIC ANALYSIS OF ADVANCED ZEOLITE MEMBRANES FOR THE CONCENTRATION OF TRITIATED WATER

1. INTRODUCTION

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 in nuclear enterprises such as light and heavy water power reactors, nuclear fuel cycle, and the International Thermonuclear Experimental Reactor (ITER).[1-3] In nuclear fuel reprocessing, process water and acid water streams are recycled and accumulate tritiated water which must be managed to control release to the environment.[4]

A novel separation process that utilizes molecular sieve membranes capable of preferentially separating tritium from dilute HTO-bearing aqueous streams is under investigation. The use of membranes for radioactive decontamination and tritium separation is detailed in the literature,[5-7] 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.[8-14] 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.

An alternative technology utilizing zeolite molecular sieve membranes was evaluated, which may demonstrate significantly lowered energy requirement 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.

In previous reports, the performance of silicoalumino phosphate (SAPO) zeolites and Linde Type A (LTA) zeolites for the separation and concentration of tritiated water was reported.[15, 16] In this research ion exchanged SAPO-34 and LTA membranes prepared on alumina disk and tubular supports were evaluated to determine the feasibility of concentrating tritiated water from high volume dilute aqueous solutions.

As discussed in the earlier reports[15, 16], CECE is one of the available alternatives to the membrane process for the concentration of the tritiated water. 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.[9, 10] Most of the reports and publications are on applications related to Canadian Heavy Water Reactors (HWR), fusion reactors such as the International Thermonuclear Experimental Reactor (ITER), and tritium concentration from a pool of water surrounding the fuel rods in Light Water Reactor (LWR).[1-3] However, it has not been implemented for the detritiation of high volume HTO-bearing aqueous streams. CECE process has several limitations such as high energy requirements, and may not be well-suited to treat large volume dilute solutions since the treatment cost is directly dependent on processing volume. The process also requires careful balance of concentration profiles in the tall columns (10-30 m high) packed with a hydrophobic catalyst and inert packing material to promote isotopic exchange between the aqueous solution and gaseous hydrogen. Although the reported separation factor for protium/hydrogen separation is as high as 5, the process is more complex and requires tall catalyst beds to achieve the tritium discharge concentration of < 100 µCi/kg.

The typical concentrations of the tritiated water from different sources are summarized in **Table 1**. The tritiated feed water concentration in a LWR and HWR/ITER applications is typically 1-2 mCi/L. This is significantly lower than the estimated tritium build-up in a water recycle application in nuclear fuel processing where concentrations are estimated to range from 200 -1000 mCi/L. The HTO concentration of approximately 1000 mCi/L, which is at the upper end of the estimated range of tritium build-up for nuclear processing applications, was used in this study.

Table 1. Typical tritiated water concentrations from different sources

Source	HTO Concentration (mCi/L)
Light water reactor (LWR)	1-2
Nuclear fuel processing	200-1000
Heavy water reactor (HWR)/ITER	1-2
This study	1000

In this report, the techno-economic analysis of zeolite membrane-based modular system for the concentration of tritiated water is discussed along with a comparison with the CECE process flowsheet. There are only limited reports available in open literature where economics of the CECE process is discussed in terms of direct numbers. The provided information is limited and indirect such as the energy requirements, and electrolysis cell specifications and capacity.[2, 17-19] Rae[17] compared economic attractiveness of the different processes for the heavy water production based on the separation factor and energy requirement. It was shown that while the electrolysis process required about 700 GJ/kg D_2O, CECE process needed about 460 GJ/Kg of D_2O. The total energy cost comparison of CECE with membrane process.is discussed in Section 3.2 In addition to the energy cost, a preliminary estimate of the capital cost for both CECE and membrane-based process is also provided in this report.

2. MATERIALS AND METHODS

2.1 SAPO-34 and ion exchanged SAPO-34 membrane synthesis

SAPO-34 crystals were first synthesized prior to the preparation of SAPO-34 membranes. The substrates were seeded using smaller-size SAPO-34 crystals via the steam-assisted conversion (SAC) method. The seed crystals were added to a synthesis mixture and well-intergrown SAPO-34 membranes were then prepared from the post-SAC substrates. The seeded substrate was placed vertically in a Parr autoclave and hydrothermal growth was carried out at 483 K for 6 h. The membranes were calcined at 823 K for 6 h in stagnant air using a slow 0.5 K/min heating and cooling rate to avoid potential cracks caused by rapid temperature changes. The acetate salts of various ions (Li^+, Na^+, K^+, and Co^{2+}) dissolved in ethanol and chloride salts of divalent cations (Mg^{2+} and Sr^{2+}) were used to introduce cations in H-SAPO-34. For barium cation exchange, barium chloride dissolved in methanol was prepared. A more detailed description of the synthesis and separation performance on tritiated water samples was reported by Bhave, et al.[15]

2.2 Synthesis of sodium (NaA) and potassium (KA) exchanged LTA zeolite membranes on tubular supports

NaA membranes were prepared by secondary growth on tubular-type α-alumina supports (10 mm O.D, 7 mm I.D. and 1.5 mm thickness, Inopor GmbH). The substrates were seeded using the NaA crystals *via* dip coating method. The tubular substrate was dip-coated for 30 sec, followed by drying at 333 K for 24 hours to obtain the seed coated tubular alumina support. To improve the formation of tubular NaA zeolite membrane on the alumina support, each membrane was synthesized twice (double-stage synthesis). Synthesized membranes were washed thoroughly with DI water for 12 hours. The synthesized NaA zeolite membranes were ion-exchanged with 1 M aqueous solution of potassium chloride for 1 hour and the ion-exchange procedure was repeated three times. A more detailed description of the synthesis and separation performance on tritiated water samples was reported by Bhave, et al.[16]

2.3 Characterization of ion-exchanged SAPO and LTA membranes

The X-Ray Diffraction (XRD) analysis and permeation measurement results showed that high quality membranes were synthesized which are well suited to evaluate the tritiated water vapor sorption and diffusion through the zeolite pores.[15] The characteristic peaks associated with LTA structure are detected in the XRD pattern and it is confirmed that no other competing phases are formed during synthesis. The bulk compositions of the as-synthesized NaA and cation-exchanged KA membranes were determined using EDX analysis of the Na, K, Si and Al content. Different from the membrane synthesized on the macroporous disk support (CoorsTek), seed/gel penetration is not found inside the support material, which is due to the small pore size (~ 100 nm) of top layer of the tubular substrate. The thickness of the membrane was estimated to be ~ 2.5 μm.

2.4 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%.

The separation factor of HTO over H_2O is defined as:

$$Separation\ factor = \alpha = \frac{(C_{HTO}/C_{H_2O})_{enriched\ phase}}{(C_{HTO}/C_{H_2O})_{depleted\ phase}}$$

where, C_{HTO} and C_{H_2O} are concentrations of HTO and H_2O.

While for SAPO-34, the enriched phase was permeate and depleted phase was feed, for LTA, the enriched phase was feed and depleted phase was permeate.

$$\textbf{\textit{Ideal Selectivity}} = \boldsymbol{S_P} = \textit{Permeance of HTO (GPU)/Permeance of } H_2O \textit{ (GPU)}$$

The permeance (in mol/m^2/s/Pa, or alternatively in gas permeation units, 1 GPU = 3.348×10^{-10} mol/m^2/s/Pa) of any species is obtained from the pervaporation equation:

$$N_i = \overline{P_i}\left(x_i p_i^* - y_i P_p\right)$$

Here N_i is the experimentally obtained flux of species i, x_i and y_i are its mole fractions in the feed and permeate respectively, p_i^* is the saturation vapor pressure of the species at the system temperature, P_p is the permeate-side pressure, and $\overline{P_i}$ is its permeance through the membrane.

Since, in the case of LTA membranes, HTO in feed was retained/concentrated by molecular sieving and selective permeation of the H_2O across the membrane, ideal selectivity definition was modified as shown below.

$$\textbf{\textit{Ideal Selectivity}}=\boldsymbol{S_F}= \textit{Permeance of } H_2O \textit{ (GPU)/Permeance of HTO (GPU)}$$

2.5 Pervaporation experiments

The schematic of the typical pervaporation system used for the permeation and separation measurements on disk molecular sieve zeolite membranes is shown in **Figure 1**. For the testing of the tubular membrane, a separate membrane cell was fabricated. 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 1.5 to 3 mL. Pervaporation experiments were performed at room temperature (~ 25 ˚C). The effective membrane area of the disk membrane (1inch diameter) and tubular membrane (1 in long, 0.28 in diameter) was 2.85 cm^2 and 5.6 cm^2, respectively. The feed HTO concentration was approximately 1 mCi/mL (1 Ci/L). This is consistent with the anticipated HTO concentration in the process water and acid recycle streams generated during the processing of used nuclear fuel.

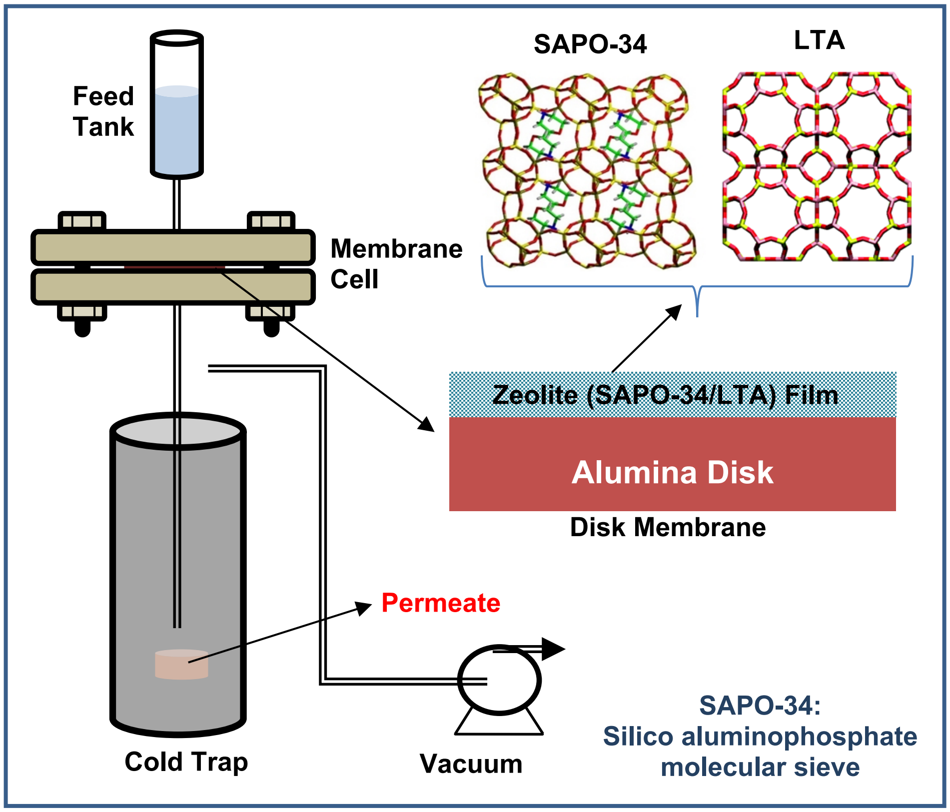

Figure 1. Schematic of the pervaporation system for the separation of tritiated water

3. RESULTS AND DISCUSSION

The rationale for the synthesis and evaluation of cation exchanged SAPO-34 is described by Bhave et al.[15] **Table 2** shows the results of pervaporation experiments with monovalent (K^+, Li^+, Na^+) cation exchanged SAPO-34 zeolite membranes. The separation factor (HTO/H_2O) for the tritiated water separation with neutral SAPO-34 zeolite membrane was 0.83 which indicates that HTO did not preferentially permeate through zeolite pores over H_2O. The calculated H_2O permeance was lower than HTO permeance resulting in the ideal selectivity value of 0.99 (<1). However, upon cation-exchange, the ideal selectivity for HTO/H_2O separation was higher than 1 for all cases. Among the various SAPO-34 membranes evaluated in this research, monovalent cation-exchanged SAPO membranes performed better compared to divalent cation exchanged membranes. While the feed volume was in the range of 1-3 mL, the collected permeate varied between 0.1-1 mL depending upon the run time (0.5-30 hrs) and the type of membrane. The permeance, separation factor and ideal selectivity shown in **Table 2** and **3** are determined based the specific experimental conditions.

Table 2. Separation characteristics of SAPO-34 and cation exchanged SAPO-34 membrane

Membrane	pH	Radioactivity (mCi/mL)		Permeance (GPU)		Separation factor (α)	Ideal Selectivity (S_P)
		Retentate	Permeate	HTO	H_2O		
SAPO-34	7	1135	946	115.83	116.01	0.83	0.99
K-SAPO-34	7	1162	1189	2087.12	1701.52	1.023	1.23
Li-SAPO-34	7	1165	1122	2134.47	1849.56	0.96	1.15
Na-SAPO-34	7	1178	1135	1827.97	1583.27	0.96	1.15

In the aluminosilicate framework of LTA, there is a negative charge available for each aluminum atom providing a significantly high exchange capacity of one cation per aluminum atom. In addition, the pore size of LTA zeolite can be decreased to about 0.3 nm, for example when exchanged with potassium.[20] These identified differences resulting in varied interactions with cation exchanged LTA zeolite surface oxygen atoms and manipulated pore sizes could be utilized to enhance the HTO/H_2O selectivity. Interestingly, NaA zeolite (Na-LTA) has been already used in many commercial plants for the selective removal of water from solvents.[21]

Evaluations with LTA zeolite membranes synthesized on alumina disk supports gave poor results both in terms of separation factor and vapor permeance. To overcome these difficulties an engineered asymmetric tubular alumina support with a thin smooth top layer of about 100 nm pore size was used to prevent gel penetration resulting in a thinner LTA layer. This approach enabled the preparation of high permeance LTA membranes with a higher HTO/H_2O separation factor. To further confirm the quality of the membrane, a characterization step was added to perform ethanol-water separation experiments prior to evaluations on tritiated water. The measured ethanol-water separation factor was > 50, and H_2O permeance of > 20,000 GPU.

Table 3 summarizes the results of the HTO/H_2O separation experiments carried out using K-LTA zeolite (KA) membrane fabricated on tubular alumina support. The results showed that a significant improvement in the HTO/H_2O separation factor and ideal selectivity was observed with different samples of K-LTA membranes. It was also interesting to note that the K-LTA membranes selectively permeated H_2O over HTO resulting in higher concentration of HTO in retentate compared to the permeate. While the separation factor (α_F) varied in the range of 1.38-2.79, ideal selectivity ranged between 1.15 to 2.33. Based on these results, we hypothesize that the mechanism of separation is a combination of molecular sieving and adsorption. However, further detailed studies are required to understand this phenomenon and the mechanism of separation.

Table 3. Separation of HTO with K-LTA zeolite membranes on tubular supports

	Membrane	pH	Radioactivity (mCi/L)		Permeance (GPU)		Separation Factor (α)	Ideal Selectivity (S_F)	%HTO in Permeate (mCi in permeate/mCi in feed)
			Feed	Permeate	HTO	H_2O			
1	**K-LTA-1-B1**	7	1054	378.0	8872	20657	2.79	2.33	4.79
2	**K-LTA-1-B1**	7	1081	783.8	9095	10474	1.38	1.15	19.6
3	**K-LTA-1-B2**	7	1027	675.6	4074	5171	1.52	1.27	26.35
4	**K-LTA-1-B2**	7	918.9	648.6	4983	5894	1.42	1.18	32.22
5	**K-LTA-1-B2**	7	1000	512.5	3423	5569	1.95	1.63	21.43

3.1 Performance comparison of SAPO and LTA membranes for the concentration of tritiated water

The two key performance metrics for the separation of tritiated water are vapor permeance and selectivity. A high separation factor would have a major impact on the separation efficiency as it will minimize the number of stages required to achieve the desired final concentration factor. On the other hand, a high vapor permeance is also essential for the economic viability as it has somewhat greater impact on the system size and cost. Efforts were focused both on optimization of permeation and separation properties of the synthesized zeolite membranes. Membrane process modeling and simulations for a cross-flow cascade system were conducted with target values of permeance and separation factor at 298 K for the design flow rate of tritiated water feed stream. The differential equations which include the flux of HTO and H_2O, separation factor and boundary conditions were solved using Matlab software. Since the pore size of the support layer (~100 nm) is much larger than that of the zeolite membrane layer (0.3 nm), the support layer resistance was neglected.

3.1.1 Case A: Concentration of tritiated water with SAPO-34 membranes

In this case, the observed HTO permeance is greater than H_2O permeance thus concentrating tritium (HTO) in the permeate. **Figure 2** shows the schematic of a cascade system for the concentration of tritiated water from high volume dilute HTO-bearing aqueous solutions.

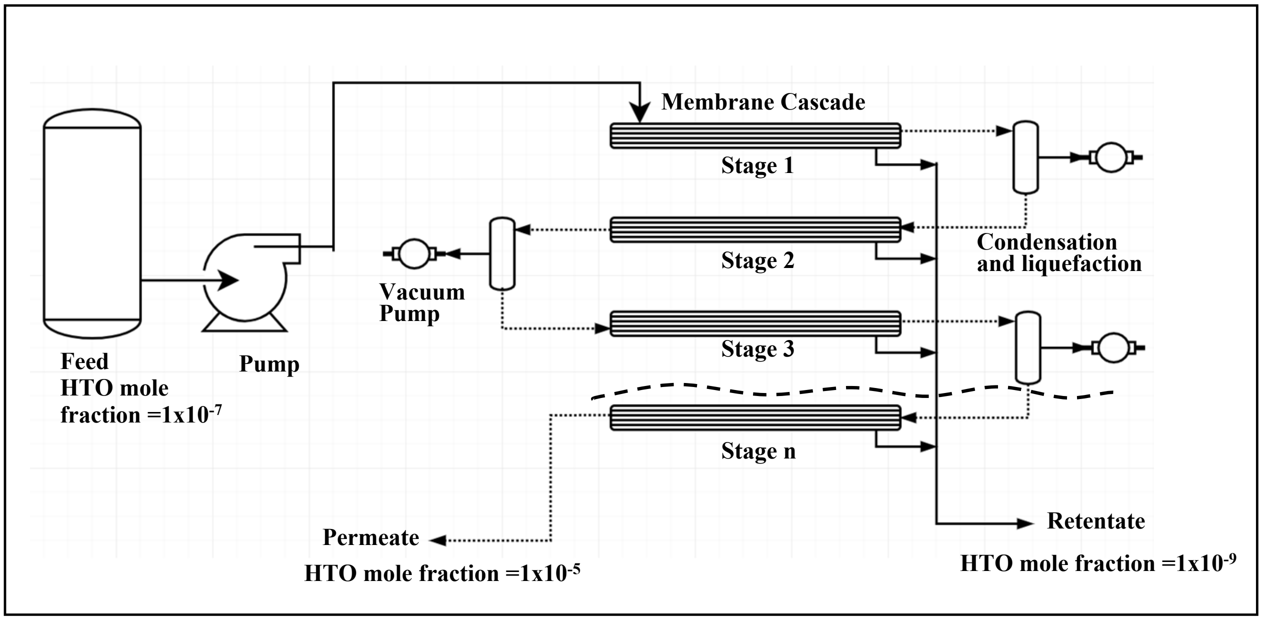

Figure 2. Schematic of a cascade system showing SAPO-34 membrane based concentration of tritiated water.

In this cascade system, the permeate from one stage, which is concentrated in HTO is fed to the next stage and so on until the required concentration of HTO is achieved in the final stage permeate. On the other hand, retentate from each stage is collected at the required concentration. Since the permeate quantity decreases as it goes from one stage to the next stage, the area required also decreases with stage numbers from 1 to n.

The preliminary economic analysis for the concentration of tritiated water was based on the following assumptions. The flow rate of tritiated water of 10 L/min with a feed HTO concentration of 10^{-7} mole fraction (10^{-5} mole%) which corresponds to HTO concentration of about 1000 mCi/L. The desired concentration factor is 100 which would result in a 100-fold concentrated permeate or 99% removal of HTO from the feed into the permeate.

Table 4 shows the material balance for the SAPO-34 membrane separation stages in the initial four in series where HTO permeance is 2000 GPU with separation factor of 1.5 (Case 1) and that of 3 (Case 2), respectively. It is not clear to observe the change in permeate rate or concentration between stages in Case 1 in the initial stages, since the membrane has low separation factor. However, from Case 2, we can clearly see the decrease in permeate flow rate and increase in HTO concentration from one stage to the next stage. The simulation was then conducted for the next steps in the same way, and then stopped when the HTO concentration in the permeate reaches 10^{-5} mole %.

Table 4. Material balance of initial 4 stages in series with the feed to each stage being the permeate stream of the previous stage (SAPO-34).

		Membrane Stage Number			
		1	**2**	**3**	**4**
Case 1 (α = 1.5)	Feed flow Rate [L/min]	10.0	10.0	10.0	10.0
	HTO mole fraction in feed	1.00e-7	1.00e-7	1.00e-7	1.00e-7
	Permeate Flow Rate [L/min]	10.0	10.0	10.0	10.0
	HTO mole fraction in permeate	1.00e-7	1.00e-7	1.00e-7	1.00e-7
	HTO mole fraction in retentate	1.00e-9	1.00e-9	1.00e-9	1.00e-9
	Area [m^2]	4.74	4.74	4.74	4.74
Case 2 (α = 3)	Feed flow Rate [L/min]	10	9.53	8.20	7.84
	HTO mole fraction in feed	1.00e-7	1.05e-7	1.10e-7	1.15e-7
	Permeate Flow Rate [L/min]	9.53	8.20	7.84	7.51
	HTO mole fraction in permeate	1.05e-7	1.10e-7	1.15e-7	1.20e-7
	HTO mole fraction in retentate	1.00e-9	1.00e-9	1.00e-9	1.00e-9
	Area [m^2]	9.02	8.61	8.23	7.89

Table 5. Preliminary estimate of membrane area and stages for the concentration of tritiated water for the case of cation exchanged SAPO-34 membranes with concentrated HTO in the permeate

Case	HTO permeance [GPU]	Separation Factor (α)	Total Stages	Total Area [m^2]
1	2000	1.5	4000	5000
2	2000	3	580	530

Table 5 illustrates the impact of key process parameters, namely, permeance and separation factor, on the number of stages and required total membrane area to achieve the desired HTO concentration factor. As can be seen, due to the significantly lower separation factors, the required total number of stages and the membrane area is substantially higher.

3.1.2 Case B: Concentration of tritiated water with LTA zeolite membranes

In the case of LTA membranes, the observed H_2O permeance is substantially greater than HTO permeate thus tritium (HTO) was concentrated on the retentate side. In this case, at each stage most of the feed is permeated through the membrane leaving the retentate at the required higher concentration. Accordingly, the retentate from each stage is collected as concentrate and permeate is fed to the next stage for further processing. Since, in this case a major portion of the feed in the first stage and permeate in the subsequent stages is permeated through the membranes leaving only a small fraction of the retentate, there was only a small drop was observed in the required membrane with increase in stage number from 1 to n.

Table 6. Material balance of initial 4 stages in series with the feed to each stage being the permeate stream of the previous stage (LTA).

		Membrane Stage Number			
		1	**2**	**3**	**4**
Case 1 (α = 1.5)	Feed flow Rate [L/min]	10.0	10.0	10.0	10.0
	HTO mole fraction in feed	1.00e-7	9.97e-8	9.94e-8	9.91e-8
	Permeate Flow Rate [L/min]	10.0	10.0	10.0	10.0
	HTO mole fraction in permeate	9.97e-8	9.94e-8	9.91e-8	9.88e-8
	HTO mole fraction in retentate	1.00e-5	1.00e-5	1.00e-5	1.00e-5
	Area [m^2]	0.702	0.702	0.702	0.702
Case 2 (α = 3)	Feed flow Rate [L/min]	10	9.98	9.97	9.96
	HTO mole fraction in feed	1.00e-7	8.32e-8	7.02e-8	5.98e-8
	Permeate Flow Rate [L/min]	9.98	9.97	9.96	9.95
	HTO mole fraction in permeate	1.00e-5	1.00e-5	1.00e-5	1.00e-5
	HTO mole fraction in retentate	8.32e-8	7.02e-8	5.98e-8	5.16e-8
	Area [m^2]	0.701	0.700	0.700	0.699

Table 6 illustrates the flow rates and concentration of HTO at each stream with LTA membrane. Different from SAPO-34 case, the simulation run at each stage is stopped when the concentration of HTO at retentate becomes 10^{-5} mole%. The number of stages and required area for the whole system can be

determined when the HTO mole fraction in permeate is diluted to 10^{-9} mole%. As can be seen from **Table 7**, the total vapor permeance of K-LTA can be an order of magnitude higher (in the range of 9,000-18,000 GPU) compared to SAPO-34 membranes. It is conceivable that with the high permeance LTA membrane and molecular sieving separation of tritiated water, a multistage cascade system would enable a cost-effective separation of tritiated water from high volume dilute HTO-bearing aqueous solution. **Figure 3** shows the schematic of a cascade system for the concentration of tritiated water.

Table 7. Preliminary estimate of membrane area and stages for the concentration of tritiated water for the case of cation exchanged LTA zeolite membranes with concentrated HTO in the retentate

Case	H_2O permeance [GPU]	Separation Factor (α)	Total Stages	Total Area [m^2]
1	9000	1.5	500	350
2	9,000	3	72	50
3	18,000	1.5	500	175
4	18,000	3	72	25

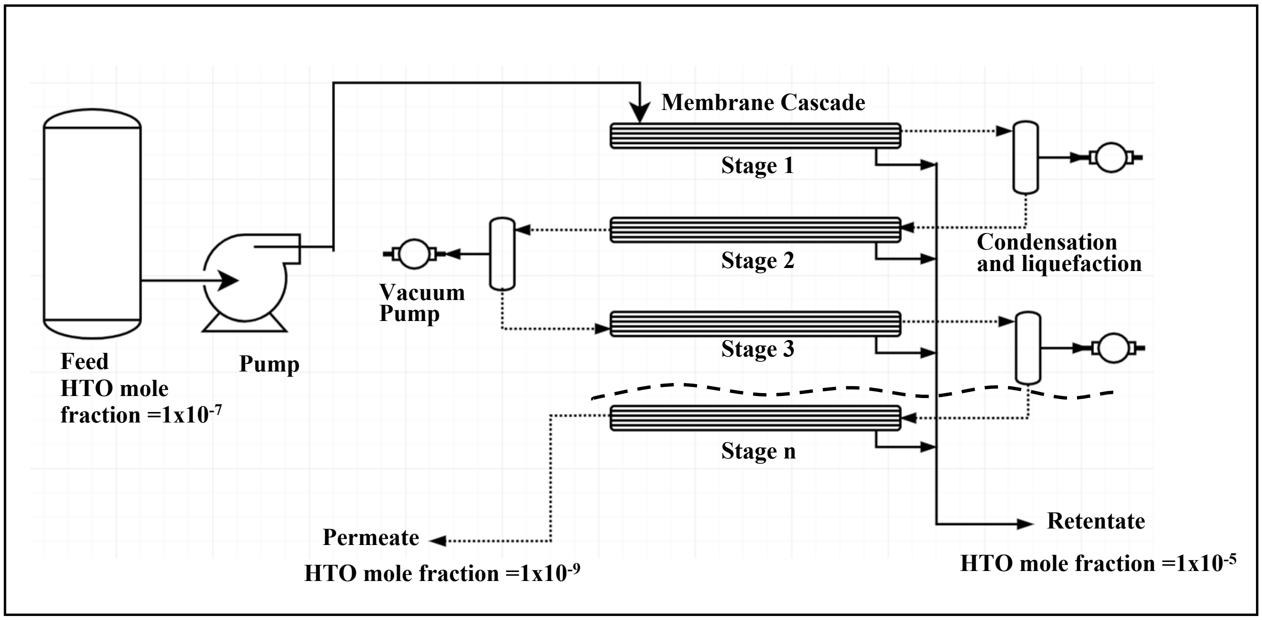

Figure 3. Schematic of a cascade system showing LTA membrane based concentration of tritiated water.

Table 7 shows that the required number of stages for the LTA zeolite membrane is significantly lower than that with SAPO-34 membranes at similar separation factors. This can be attributed to two main reasons. First, the substantially higher permeance with LTA membrane compared to the SAPO-34 at similar separation factors. And secondly, in the case of LTA membranes, since H_2O, which is the major component of the feed solution (>99.99%) is transported across the membrane, it would require a larger number of stages to achieve the final desired HTO concentration in the retentate. However, it should be noted that the membrane area for each stage will be relatively small (< 1m^2) as the volume of feed progressively decreases with the number of stages. Large-scale membrane-based systems such as for the dehydration of alcohols with LTA zeolite membranes with >1,000 m^2 membrane area are reported.[18]

Based on the configuration of the membrane cascade system and operational simplicity, the LTA membrane-based process appears to be more practical and promising.

3.2 Techno-economic comparison of the zeolite membrane and CECE processes for the concentration of tritiated water.

The estimated system cost for the membrane-based system will be driven by capital cost (three major components, namely, zeolite membrane elements in a housing, feed pump, vacuum pumps for each stage and a control system) and operating cost (electrical energy required for permeate condensation i.e. refrigeration and pumps, labor, maintenance and replacement).

Table 8. Energy and capital cost estimates for concentration of tritiated water using LTA membrane separation system.

Description	Value	Unit
Required processing flowrate =	10	L/min
Number of membrane stages =	72	
Membrane area =	50	m^2
Energy Cost		
Amt of permeate to be condensed (100 times concentration) =	1,026,720	kg/day
Total energy consumption = (accounting for latent heat of vaporization, specific heat of water, latent heat of fusion, specific heat of ice)	131,752,817	kJ/day
Energy required for refrigeration = (considering 50% loss)	1525	kWh
Cost of refrigeration ($0.1/kWh) =	$3,852	/day
Cost refrigeration (per year) =	$1,406,134	/year
Energy required for vacuum and pumping =	10	kWh/day/stage
Cost of energy for vacuum and pumping =	$131,400	/year
Total energy cost for membrane process =	**$1,567,534**	**/year**
Capital Cost		
Cost of the membrane module ($2,500/m^2) =	$125,000	
System cost (pumps, refrigeration, piping, instrumentation) and maintenance) =	$1,000,000	
Total capital cost for membrane system =	**$1,875,000**	

The zeolite membrane will be fabricated on multichannel inorganic supports with 2-4 mm diameter channels ranging from 20 to 60 per membrane element. The estimation of the energy and capital cost for the membrane separation and concentration of tritiated water with a processing capacity of 10 L/min is summarized in **Table 8**. It is estimated that the membrane module cost would range from $1500-2500/m^2

of membrane area, depending on the system size. This is based on the current market prices for membrane supports and includes the added cost of the zeolite membrane synthesis on ceramic support.

Table 9. Energy cost estimation for CECE process for different cases reported in the literature.

Description	Value	Unit
Case 1 Rae (1978)- Information provided: Amount of equivalent thermal energy required for 1 kg of D2O production using CECE process- 460 GJ/Kg D_2O		
Required processing flowrate =	10	L/min
Amt of D_2O produced =	2.246	kg/day
Amt of energy required for this D_2O =	1033.34	GJ
Cost of energy ($0.1/kWh) =	$1,196	/day
Cost of energy (per year) =	**$436,540**	**/year**
Case 2 Hammerli (1978) - Information provided: Energy required to produce pure D_2O (50 MWh/Kg of D_2O)		
Required processing flowrate =	10	L/m
Amt of D_2O produced =	2.246	kg/day
Energy required to produce pure D_2O =	50	MWh/kg D_2O
Total energy required =	112,320	kWh
Cost of energy ($0.1/kWh) =	$11,232	/day
Cost of energy (per year) =	**$4,099,680**	**/year**
Case 3 Rigers (1978)- Information provided: Electrolysis cell details for specific electrolysis capacity (for 3.528 L/day, a cell with 8 stacks of 50 amp and 16.8 V)		
Required processing flowrate =	10	L/min
Amt of D_2O produced =	2.246	kg/day
Wattage of one stack =	840	watt
Energy required =	82285.7	kWh
Cost of energy ($0.1/kWh) =	$8,228	/day
Cost of energy (per year) =	**$3,003,428**	**/year**
Case (4) Colella (2014)- Information provided: PEM electrolysis plant capacity and total electricity consumption (50.3 kWh/kg of H_2).		
Required processing flowrate =	10	L/min
Plant capacity (H2 production) =	1,500	kg/day
Equivalent H_2O electrolysis capacity =	540	kg/day
Electrical usage =	139.7	kWh/kg H_2O
Electricity usage =	75,450	kWh
Electricity for required plant capacity (600 kg/day) =	83,833	kWh
Cost of energy ($0.1/kWh) =	$8,383	/day
Cost of energy (per year) =	**$3,059,917**	**/year**

As shown in **Table 8**, the primary energy cost for the membrane system would be the electrical energy for vacuum pumps and refrigeration of the for the condensation of vapor permeate. Energy costs are estimated to be about $1,567,534/yr for a 10 L/min tritiated water treatment capacity. Based on the selectivity and vapor permeance in Case 2 (as shown in **Tables 7**), the average capital cost for the membrane system is estimated to be about $1, 125,000 for a 10 L/min tritiated water feed containing 10^{-5} mole% HTO.

As mentioned earlier, the published literature on CECE process provides limited specific information on the operating and capital cost. Thus, the available reported information such as the energy requirements and electrolysis cell specification for CECE process was used to estimate the total energy cost based on present electricity cost of $0.1/kWh. Four different cases of the CECE process are presented in **Table 9** with estimation of the total energy cost on yearly basis. Except the Case 1, the yearly operating cost for the CECE process (Case 2-4) was estimated to be significantly higher than that of the membrane process. The observed lower estimation with Case 1 could be attributed to the uncertainty in terms of the conversion of equivalent thermal energy to the electrical energy.

Figure 4 shows the simplified process flow diagram of the CECE process used for the detritiation of the light water.

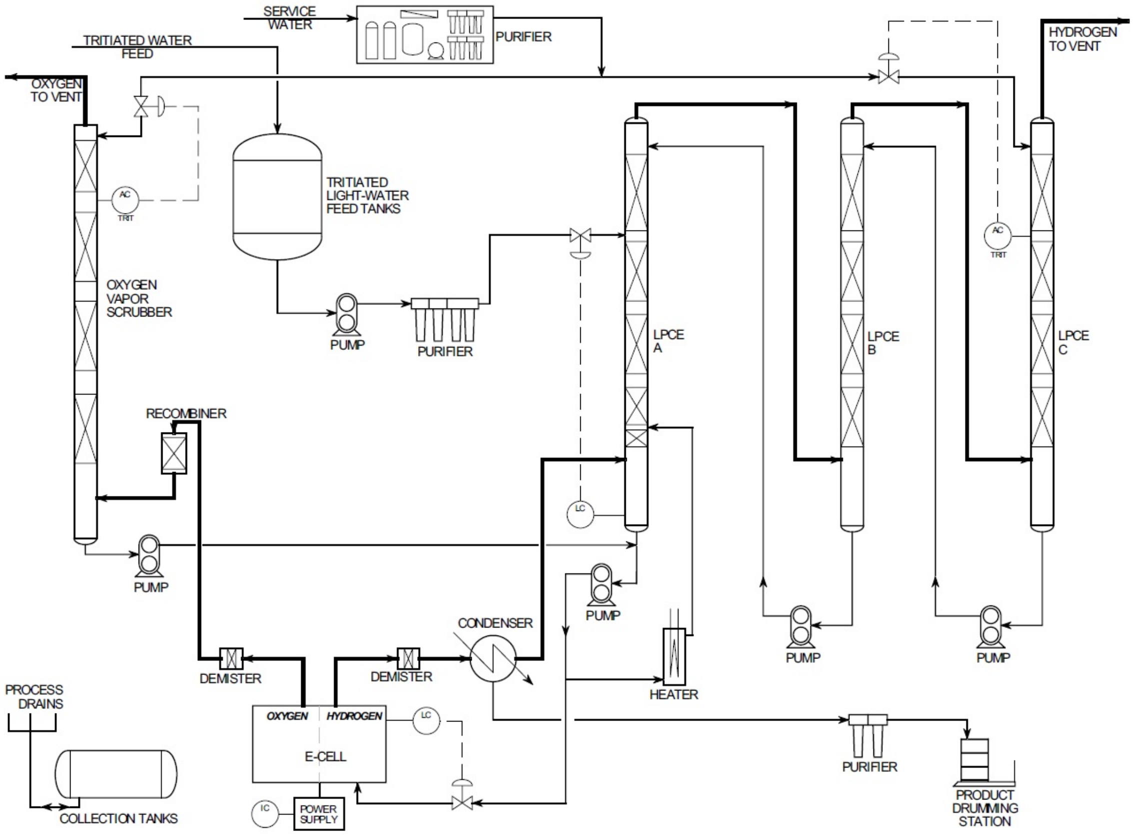

Figure 4. CECE process flowsheet for light water detritiation[3]

The membrane based separation system capital and operating cost was compared to the CECE process, where the processing cost for tritium recovery/concentration is directly proportional to the total volume. The process 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 the aqueous solution and gaseous hydrogen. For the preliminary estimation of the CECE process capital cost, the techno-economic details from PEM electrolysis process was used. The electrolysis capacity of the reported system in terms of H_2 production was 1500 kg H_2/day.[22] The preliminary estimation of the CECE capital cost was obtained by using the PEM electrolysis capital costs for water electrolysis, which appears to be closest approximation to the CECE process, and is presented in **Table 10**.

Table 10. Preliminary estimate of CECE process capital cost.[22]

Description	Value	Unit
PEM electrolysis H_2 production capacity =	1,500	kg/day
Amount of equivalent H_2O processing=	13,500	kg/day
	540	kg/h
Electricity usage =	54.6	kWh/kg
	81,900	kWh/day
	3412.5	kW
Capital cost (lower end of the range $450-900 /kW) =	$450	/kW
Capital cost for electrolysis =	$1,535,625	
The required CECE H_2O processing capacity =	600	kg/h
The equivalent capital cost for this capacity =	$1,706,250	
Capital cost for rest of the system (including catalyst column, etc.) =	$1,706,250	
Total capital cost for CECE process (at the lower end) =	$3,412,500	

It can be seen from Tables 8, 9, and 10 that the estimated capital and energy cost of the CECE process is higher than the membrane -based concentration of tritiated water. A more detailed techno-economic analysis will be performed in the future, if more representative CECE cost and performance data for the concentration of tritiated water become available.

4. CONCLUSIONS & FUTURE WORK

Based on the results of LTA and SAPO-34 membranes, it can be seen that LTA membrane performance was more encouraging, and has the potential for the economical separation and concentration of HTO from high volume dilute HTO-bearing aqueous solutions. The total capital and energy cost for a CECE process is estimated to be substantially higher compared to the membrane based concentration of HTO.

Several approaches will be pursued in FY18 to further improve the selectivity and separation factor of H_2O/HTO. (1) The effort on synthesis of improved ion exchange LTA zeolite membranes will be continued to further tune the diffusion coefficient of water versus HTO while reducing the membrane thickness. (2) The effect of Al-Si ratio in LTA (silicoaluminate) zeolites will be evaluated both to increase the selective adsorption and diffusion of H_2O over HTO and to increase the chemical stability in acid contaminated water recycle streams. (3) Perform evaluations to better understand the molecular sieving and adsorption mechanism.

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