SEPARATION OF TRITIATED WATER USING GRAPHENE OXIDE MEMBRANE

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Fuel Cycle Research and Development
Material Recovery and Waste Form Development Campaign

GJ Sevigny, RK Motkuri, DW Gotthold, LS Fifield
Pacific Northwest National Laboratory
AP Frost, W Bratton
Kurion

June 2015

FCRD- MRWFD-2015-000773
PNNL-24411

SUMMARY

The objective of this study is to demonstrate in proof-of-principle tests a process to remove low concentrations of tritium from large volumes of tritium-contaminated water so the water can be reused or discharged to the environment.

In future nuclear fuel reprocessing plants and possibly for nuclear power plants, the cleanup of tritiated water will be needed for hundreds of thousands of gallons of water with low activities of tritium. This cleanup concept utilizes graphene oxide laminar membranes (GOx) for the separation of low-concentration (10^{-3}-10 µCi/g) tritiated water to create water that can be released to the environment and a much smaller waste stream with higher tritium concentrations. Graphene oxide membranes consist of hierarchically stacked, overlapping molecular layers and represent a new class of materials.

In order to demonstrate the feasibility of GOx membrane-based isotopic water separation, Pacific Northwest National Laboratory (PNNL) demonstrated under fiscal year 2014 and 2015 work scope the relative transport of H_2O, D_2O, and HTO in different ways. First, the transport rate was measured using the mass loss over time of GOx membrane-covered containers of H_2O, D_2O, and HTO. Second, PNNL used an existing membrane test system to quantify the relative permeability of H_2O and D_2O. Third, a distillation system was modified to demonstrate transport of water vapor through the GOx membrane and to determine the tritiated water selectivity.

Three different thicknesses (5, 10, and 17 µm) of each membrane were tested. Each GOx membrane was fitted onto the opening of a 20 mL glass vial into which 10 g of D_2O, H_2O, and D_2O/H_2O mixture were loaded. The results showed that H_2O permeated faster than D_2O for all types of GOx membranes. GOx membranes with nanoflake size (about 100 nm) did not show a membrane thickness effect. However, a membrane thickness dependence on permeation rate was observed for the larger flake size SKU-HCGO-W. The average separation factor based on permeation rate of D_2O divided by H_2O was about 0.93 with a low of 0.87.

The permeation rate test was performed with a 2-µm-thick cast Asbury membrane using mixed gas permeability testing with zero air (highly purified atmosphere) and with air humidified with either H_2O or D_2O to a nominal 50% relative humidity. The membrane permeability for both H_2O and D_2O was high with N_2 and O_2 at the system measurement limit. The H_2O vapor permeation rate was 5.9×10^2 cc/m^2/min (1.2×10^{-6} g/min-cm^2), which is typical for graphene oxide membranes.

To demonstrate the feasibility of such isotopic water separation through GO_X laminar membranes, an experimental setup was constructed to use pressure-driven separation by heating the isotopic water mixture at one side of the membrane to create steam while cooling the other side. Several membranes were tested and were prepared using different starting materials and by different pretreatment methods. The average separation result was 0.8 for deuterium and 0.6 for tritium. These results indicate the process may need 250 x250 stages to reduce the initial concentration by 99%. Enhanced separation may be obtained using thicker membranes but at the expense of a lower permeation rate. Higher or lower temperatures may also improve separation efficiency but neither has been tested yet.

A rough estimate of cost compared to current technology was also included as an indication of potential viability of the process. The relative process costs were based on the rough size of facility to accommodate the large surface area of the membranes and the energy needed to evaporate the water and pass through the membranes as compared to the currently used combined electrolysis and catalytic exchange process. The water treatment costs ranged from $60/L to $180/L that included the combined annual energy operating costs and capitalization of the building over 10 years. The cost for combined electrolysis and catalytic exchange process system are estimated to be $2/L to $20/L. The membrane treatment costs could be reduced exponentially with better separation efficiency and compact membrane systems with higher surface area.

CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

The authors would like to acknowledge the efforts of Yongsoon Shin for the fabrication of the graphene oxide membranes and comments on the testing reporting efforts. Authors would also like to thank and acknowledge Wendy Bennett and Bruce McNamara for help with membrane testing in the laboratory and Herman Cho for laboratory measurements of deuterium water concentrations.

The authors are grateful for the financial support from the Office of Nuclear Energy's Fuel Cycle Technologies Program. Terry Todd (INL) and James Bresee (DOE) provided programmatic oversight.

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute.

ACRONYMS

CECE	combined electrolysis and catalytic exchange
GOx	graphene oxide laminar membranes
PNNL	Pacific Northwest National Laboratory
RGA	residual gas analyzer

1. INTRODUCTION

In future nuclear fuel reprocessing plants and possibly for nuclear power plants, the cleanup of tritiated water will be needed for hundreds of thousands of gallons of water with low activities of tritium. This cleanup concept utilizes graphene oxide laminar membranes (GOx) for the separation of low concentration (10^{-3}-10 μCi/g) tritiated water to create water that can be released to the environment and a much smaller waste stream with higher tritium concentrations. Graphene oxide membranes consist of hierarchically stacked, overlapping molecular layers and represent a new class of materials. Recent research by Nair et al. (2012) and Pacific Northwest National Laboratory (PNNL) has demonstrated that GOx membranes are leak-tight to most gases, but readily transport water vapor.

The physical structure of the 2D laminate GOx materials provides extremely long diffusion path lengths (~10,000 times the membrane thickness). The hydrophilic oxygenated nature of GOx provides it with extremely high proton conductivity (~0.01 S/cm) (Karim et al. 2013), reflecting an extensive interaction of H-bonding in the material. Ongoing research at PNNL is combining experimental and theoretical tools to understand and control the selective transport of water through GOx membranes, but the current understanding is that H_2O does not transport through the membrane by simple diffusion. Rather, the molecular selectivity derives from H_2O molecules proton hopping through the chemical functionality between the GOx lamina. This mechanism should provide isotopic selectivity (Hankel et al. 2012) much greater than a mechanism relying only on the mass difference between water and tritiated water.

Working on the premise that transport through GOx membranes is regulated by the repeated forming and breaking the O-H bonds, we can estimate the relative frequency of molecular hopping will be controlled by the O-H or O-T bond vibrational frequency. This means that it will be possible to achieve atomic-like isotope selectivity between tritiated water and molecular water (viz. kinetic isotope effect) (Webtheimer 1960). Additionally, the long path length and multi-step breaking and reforming of –OH bonds may provide an even higher selectivity. The potential for such attractive selectivity improvement is to be determined in the proof-of-principle test.

In order to demonstrate the feasibility of GOx membrane-based isotopic water separation, PNNL demonstrated under fiscal year 2014 and 2015 work scope the relative transport of H_2O, D_2O, and HTO in different ways. First, the relative transport rate was measured using the mass loss over time of GOx membrane-covered containers of H_2O, D_2O, HTO, and mixtures of the isotope concentrations of the remaining liquids. Second, PNNL used an existing membrane test system to quantify the relative permeability of H_2O and D_2O. Third, a modified distillation system was used to determine separation efficiency for the hydrogen isotopes. The system was modified to include a membrane for steam to pass through at an elevated temperature.

2. OBJECTIVE

The objective of this study is to demonstrate in proof-of-principle tests a process to remove low concentration tritium from large volumes of tritium-contaminated water in an effort to reuse or discharge the water to the environment. The removed tritium could be concentrated in a much smaller volume (e.g., 1/100th) that can be further separated to produce relatively pure tritium or stabilized for disposal. If successful, the final embodiment would be a multi-stage membrane separation that would remove tritium from large volumes without the huge energy demand needed for electrolyzed water in the catalyzed electrochemical exchange process currently in use in other countries.

3. EXPERIMENTAL TESTING

3.1 Static Diffusion Tests

Procedure: GOx membranes were prepared using commercial and custom-made GOx dispersions with different flake sizes by a vacuum filtration technique. A modified Hummer’s method was used to prepare the raw materials and produce small membranes (Kovtyukhgova et al. 1999). Three different thicknesses (5, 10, and 17 µm) of each membrane were tested. Each GOx membrane was fitted onto the opening of a 20 mL glass vial into which 10.0 g of D_2O, H_2O, and D_2O/H_2O mixture were loaded. All sample vials (Figure 1) were placed inside a fume hood and the weight loss of each vial was measured periodically. The blank test (no GOx membrane) was conducted in the same condition (air flow within the hood: 180 cfm. Each test was repeated three times.

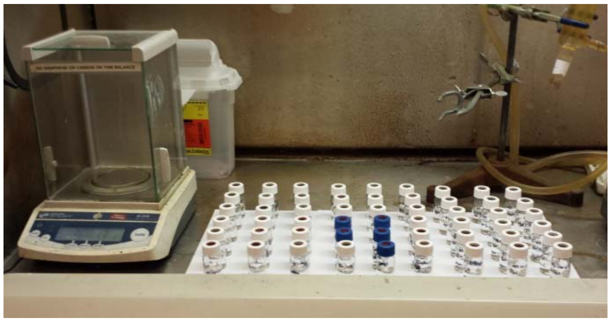


Figure 1. Gas diffusion test vials

The results showed that H_2O permeated faster than D_2O for all types of GOx membranes. GOx membranes with nanoflake size (about 100 nm) did not show a membrane thickness effect. A membrane thickness dependence on selectivity was observed, however, for the larger flake size SKU-HCGO-W. This is explained by the longer traveling time of D_2O molecules through the thicker membrane with larger flake size resulting in slower permeation than H_2O as shown in Table 1 and Figure 2.

Table 1. Permeation for NANO and SKU samples.

GOx membrane	Flake size (µm)	Thickness (µm)	$H_2O^{(a)}$	$D_2O^{(a)}$	$H_2O+D_2O^{(a)}$ mixture	D_2O/H_2O ratio	Mix/H_2O ratio
NANO-GO-S	0.09±0.01	10	-62	-55	-58	0.89	0.93
NANO-GO-S	0.09±0.01	17	-63	-57	-59	0.91	0.93
SKU-HCGO-W	0.5-5	5	-61.0±2.0	-54.7±1.3	-57.0±1.0	0.90	0.93
SKU-HCGO-W	0.5-5	10	-60.7±5.7	-51.7±1.7	-52.0±2.0	0.85	0.85
SKU-HCGO-W	0.5-5	17	-52.7±3.7	-46.0±6.0	-47.7±4.3	0.87	0.90

(a) Average number of three measurements [-g/hr ×10,000]

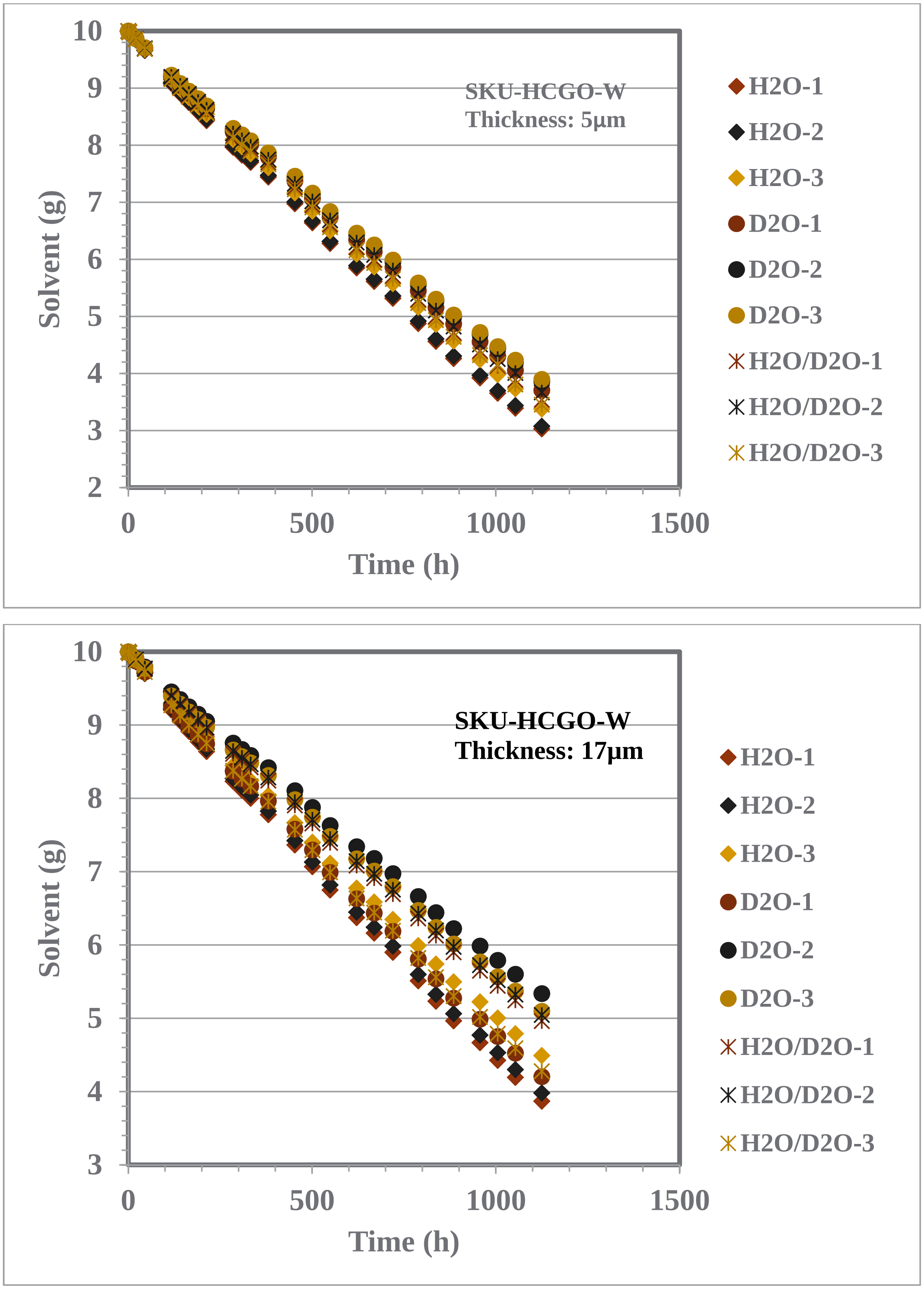


Figure 2. Test data for thin (top) and thick (bottom) GOx membranes made from commercial SKU graphene

The BC-GOx, custom-made membrane showed a similar result: H_2O permeates faster than D_2O, and permeation slopes (H_2O vs. D_2O) showed a bigger difference in the thicker membrane (17 µm) than in the thinner (5 µm) membrane (see Table 2 and Figure 3 and Figure 4).

Table 2. Solvent permeation for BC-GOx samples

GOx membrane	Flake size (µm)	Thickness (µm)	H_2O*	D_2O*	H_2O+D_2O* mixture	D_2O/H_2O ratio	Mix/H_2O ratio
BC-GOx	5-15	5	-61.6±2.7	-56.0±3.0	-56.0±1.0	0.910	0.909
BC-GOx	5-15	10	-55.7±1.3	-50.7±1.7	-55.3±2.3	0.910	0.993
BC-GOx	5-15	17	-60.0±2.0	-50.7±2.7	-54.7±2.7	0.846	0.912

Throughout all our experiments, we realized differences of intrinsic properties of the solvents were dominant (density, boiling point, viscosity, and heat of vaporization of H_2O and D_2O) in the permeation experiment. Comparison of GOx membranes with large flake size (0.1 µm vs. 500 µm) or with different thickness (1 to 2 µm vs. 100 µm) is required to have realistic effect (to overcome the intrinsic effect of solvents). We attempted to provide a reference point for these intrinsic effects by measuring both evaporation from an open container (no membrane) and through different commercial filtration membranes (polycarbonate, PTFE, PVDG and polypropylene). The open container test show no measureable difference between H_2O and D_2O, though the evaporation rate was very high and non-linear, indicating that airflow was likely a major factor. With the filter membranes, there was some selectivity also observed, with a D_2O/H_2O ratio around 0.9 independent of material or thickness.

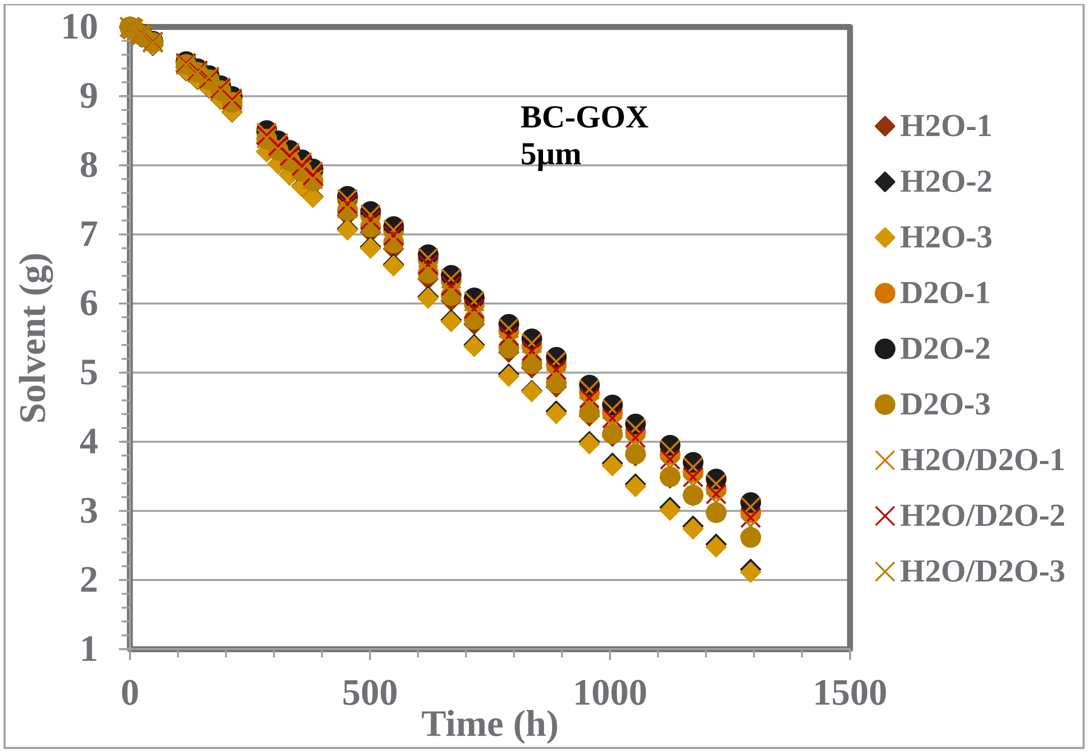


Figure 3. Test date for thin GOx membranes made from in-house processed graphite

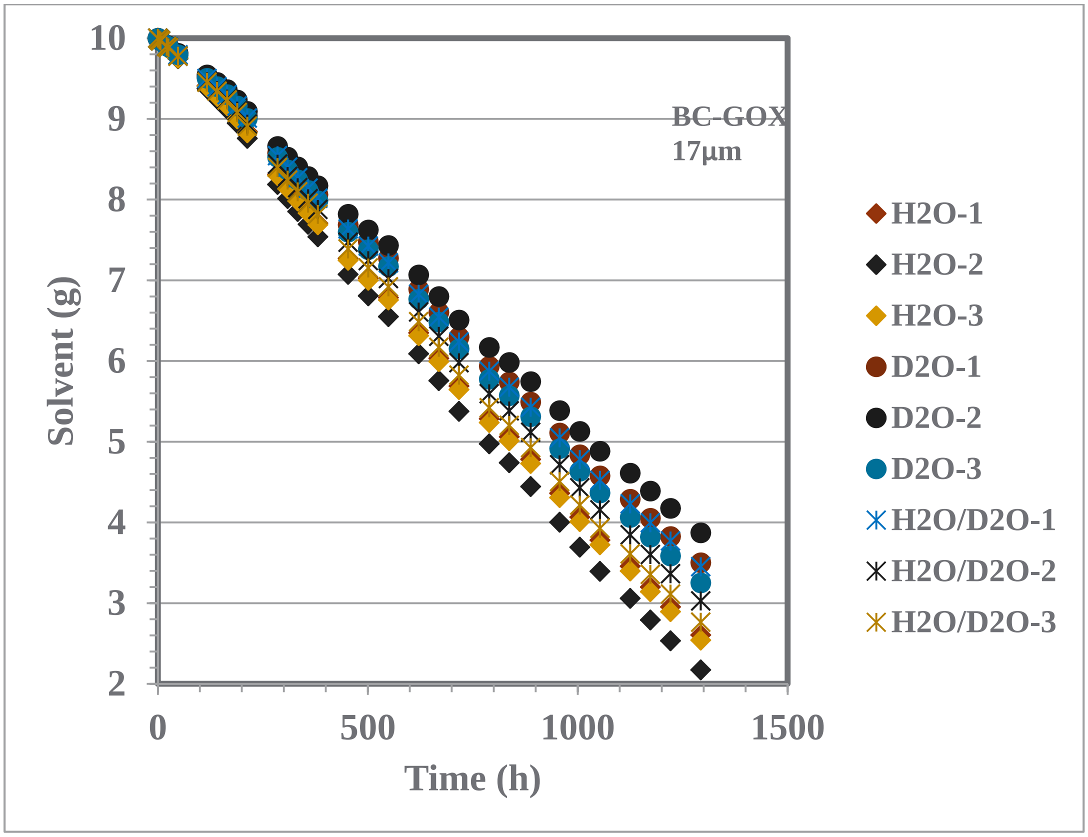


Figure 4. Test date for thick GOx membranes made from in-house processed graphite

3.2 Permeation Rate Tests

A 2-um-thick cast Asbury membrane was evaluated using mixed gas permeability testing with zero air (highly purified atmosphere) and with air humidified with either H_2O or D_2O to a nominal 50% relative humidity. The measurement system is shown schematically in Figure 5. The source gas flows past one side of the membrane and permeate is collected with a sweep gas (He) that is carried to a residual gas analyzer (RGA). Gases on both sides of the test cell vent to atmosphere so the ΔP across the membrane is near zero and the only driving force is the relative partial pressure of the gases. The membrane under test is held against a porous metal frit to provide physical support and sealed with silicone O-rings.

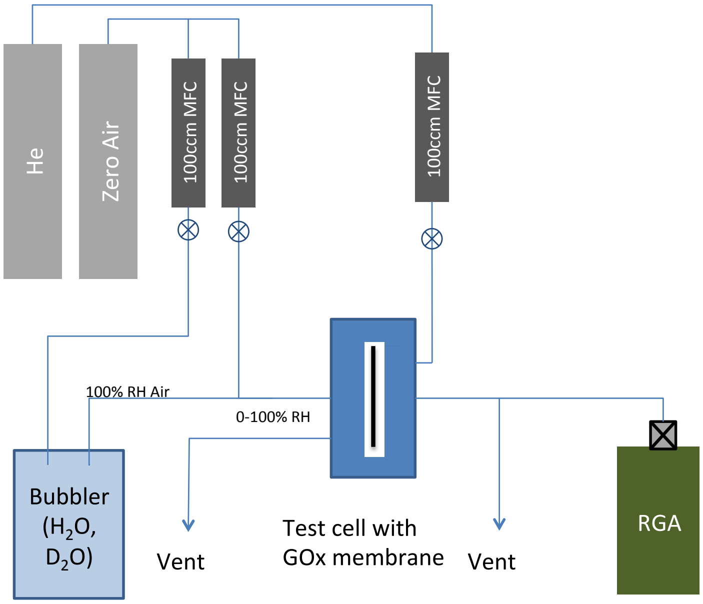


Figure 5. Schematic diagram of membrane test fixture

The RGA (and SRS RGA100) is a quadrapole mass spectrometer with a 0.1 AMU resolution up to 100 AMU and measures the partial pressure for each mass. Figure 6 shows the data for four different high-resolution scans, including a background scan with dry gas, a scan with H_2O humidified gas, and two different scans with D_2O gas. In each scan, the system was allowed to run with dry air for 8 to 12 hours to minimize the free water in the system and then the supply gas was switched to run through the bubbler to be humidified. Typically, the system reached steady state in 3 to 4 hours, and then the high-resolution scan was taken. For this series, the same membrane was left mounted in the test cell for the entire set of scans.

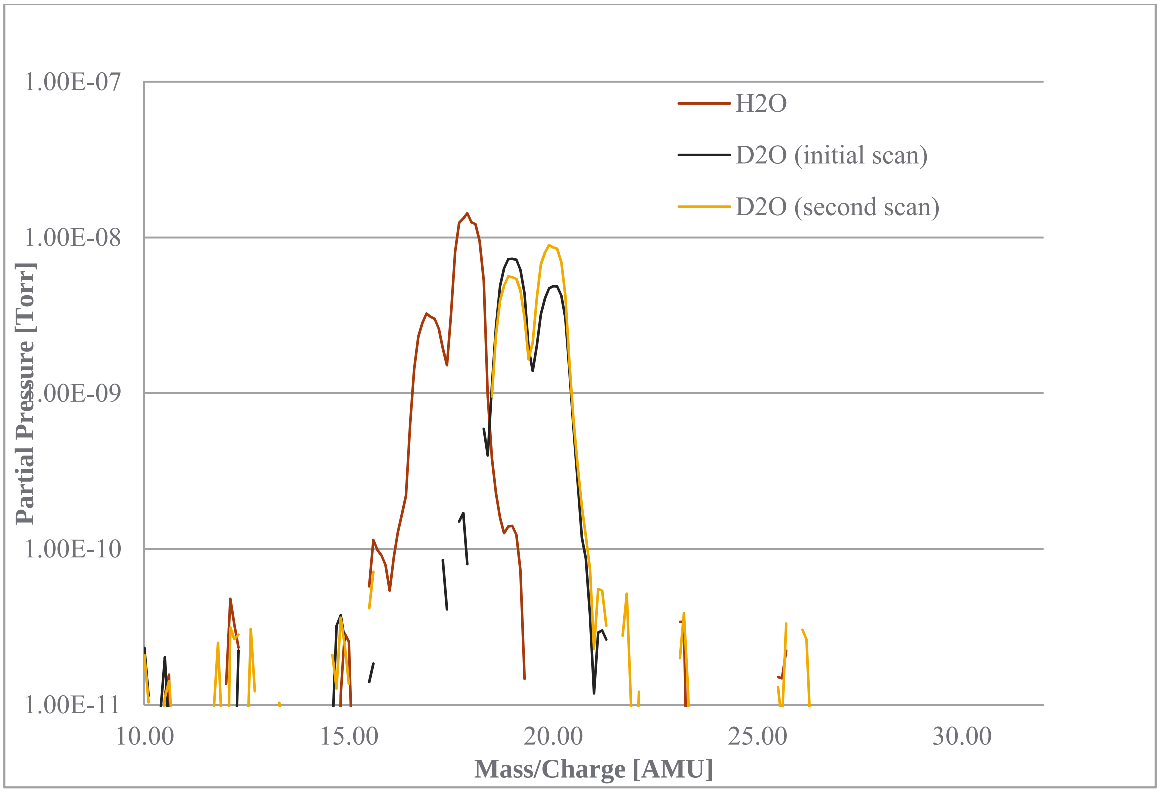


Figure 6. RGA partial pressure traces for three different high resolution scans. Humidified air (H_2O), humidified air (D_2O), and a second D_2O humidified air scan. The background for dry air has been subtracted, eliminating the N_2 (28) and O_2 (32) peaks that would normally be observed.

The membrane exhibited high selectivity for both H_2O and D_2O with N_2, and O_2 at the system measurement limit. The H_2O vapor permeation rate was 5.9×10^2 cc/m^2/min, which is typical for graphene oxide membranes using this test setup. The membrane water permeation rate was compared to a Nafion® membrane and the GOx permeation was approximately twice as high at room temperature. The D_2O permeation was two to five times lower, but varied some between the two measurements, between 1.1×10^2 and 2.4×10^2 cc/m^2/min. In order to accurately quantify the permeation, the relative sensitivity of the RGA system was tested using H_2O and D_2O humidified air with no membrane, and while the data has large variations, it did show that the RGA was at least as sensitive to the D_2O as the H_2O. Additional work will be needed to further quantify the background and sensitivity of the RGA to D_2O to eliminate equipment variability as the source of the high observed selectivity. Additionally, the increased permeation of the D_2O over time (between the first and second scans) indicates that there may be a saturation effect.

3.3 Distillation Tests

To demonstrate the feasibility of such isotopic water separation through GO_X laminar membranes, we constructed an experimental setup using pressure-driven separation by heating the isotopic water mixture at one side of the membrane while cooling at other side. The water isotope mixture (reservoir) was heated at elevated temperatures to generate water vapor, which was allowed to transport through the membrane and then cooled in a cold trap. The schematics and the experimental setup are shown in Figure 7.

For this study, the GOx membranes were prepared via modified Hummer's method (Kovtyukhgova et al. 1999). The first set of experiments was performed by using the GOx membrane where the graphene oxide was purchased from Aldrich and named "GOx-A." The second set of experiments was performed by using the PNNL-improved method, named "GOx-BC-improved."

For water permeation tests, the reservoir was filled with a D_2O-H_2O mixture and heated at 88 to 100 ^{o}C while the transfer line containing the membrane was heated about 5 to 10 ^{o}C above the reservoir temperature. The complete system was evacuated during startup to avoid any gases in the line that would not readily permeate the membrane. The system was allowed to heat slowly and the condenser was cooled to about 2 to 5 ^{o}C using a cold chiller solution.

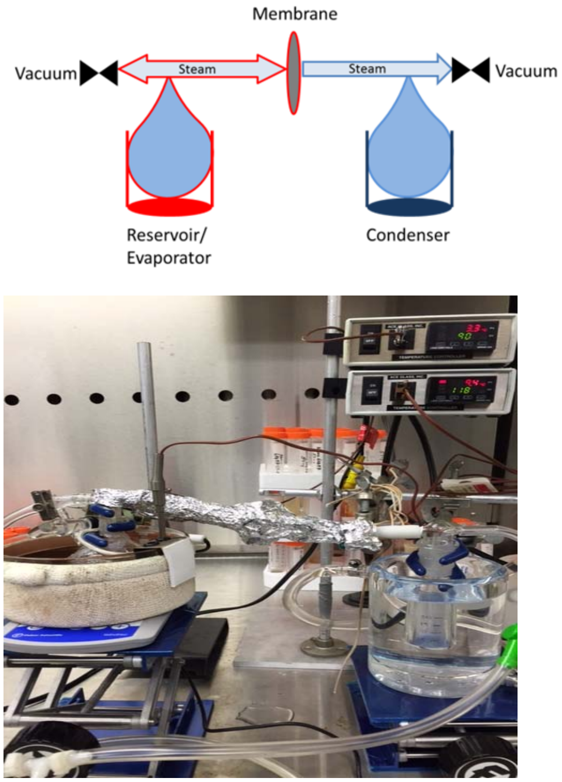


Figure 7. The schematic (top) and the experimental setup (bottom) of water isotope separation.

The first set of experiments was done without inserting any membrane and demonstrated the expected quick transportation rate of water vapor from the reservoir/evaporator to the condenser. Then the membrane was introduced under the conditions described above and water samples were collected after the condenser. The samples were subjected to ^{2}H-NMR studies to see the concentrations of isotopes in the mixture and comparing them to the samples in the evaporator which were treated as standard solutions. The results are presented in Table 3. RKM-1 is considered as a reference material and was prepared by mixing 10% D_2O in water. RKM-3 and RKM-5 are the main samples collected in the condenser with the membranes GOx-A and GOx-improved fabrication methods. RKM-3 and -5 showed a decrease in the concentration of deuterium. The decrease is ~18% in both the samples, which reflects the active engagement of GOx membranes for removing/trapping deuterium from the mixture. From the results, it is interesting to note that both GOx membranes showed similar performance and separated deuterium from the water mixture.

Table 3. ^{2}H-NMR studies on the D_2O-H_2O transport rates and separation

	Temp	Membrane	% D_2O	moles/min cm^2	g/min-cm^2	Outlet/Inlet concen.
RKM-1[(a)]		BC-GOx				1.00
RKM-3	88-95°C	BC-GOx A	10	2.90E-06	5.22E-05	0.82
Bruce 1	90-95°C	BC-GOx A	10	3.25E-04	5.85E-03	0.92
RKM-5	88-95°C	BC-GOx improved	10	2.54E-06	4.57E-05	0.82
RKM-7	88-95°C	BC-GOx	10	3.38E-06	6.09E-05	0.81
RKM-9	88-95°C	BC-GOx	3	3.67E-06	6.61E-05	0.51
RKM-11	110-115°C	Asbury	2	2.17E-05	3.90E-04	0.91
RKM-12	110-115°C	Asbury	2	2.44E-05	4.39E-04	0.98
Trit-1			10 mCi/l			0.38
Trit-2			10 mCi/l			0.64
Permeation using RGA	23°C		0	2.64E-06	4.75E-05	NA

(a) Original solution

T – Tests with tritium solution with initial concentration of 10 mCi/L

The transport rates in this study were slow, partially because of the small size of the filter used. The separation took a few days in most cases. The slow rate may be compensated by using larger pressure differentials or different operating temperatures; however, this was not demonstrated. Increasing the temperature at the evaporator side will improve the kinetics, but large surface areas will still be needed for production units. The initial setup consisted mostly of glassware, so the evaporator temperature could not be manipulated above 100 °C due to concerns about internal pressure limits. Subsequently, an improved, second stainless steel setup was constructed with a reservoir connected to the condenser through the membrane. With the new setup, temperatures of 110 °C were achieved without any problems. Initially, both sides of the membrane were connected to a pressure gauge to observe the pressure, but these lines caused condensation during heating. So finally they were removed and a 2 psi pressure relief valve close to the condenser side was inserted for safety. The experimental setup is shown in Figure 8. The new setup was used for tests RKM 7, 9, 11, and 12.

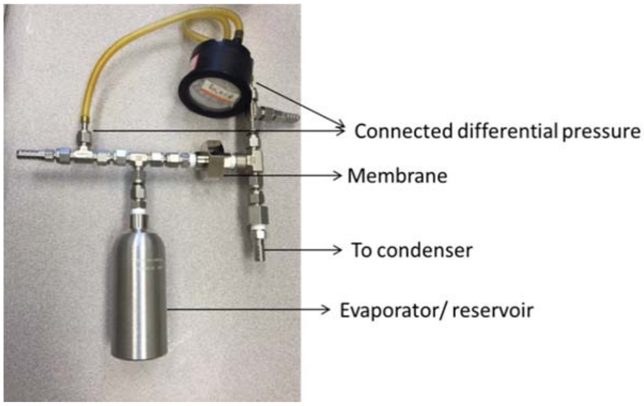


Figure 8. Improved stainless steel experimental setup

A evaporative test with deuterium-enriched water was also conducted in a separate piece of equipment with similar features as an acceptance test for performing tests with tritium. The system operated under similar conditions but with a different GOx membrane. The results for test "Bruce 1" showed a 92% reduction in the deuterium content and the condensate was collected at a higher rate than the previous tests. No obvious tears in the membrane were observed, but the high transport rate indicates the membrane may have developed a flaw. The other tests with tritium were completed with new membranes. It is difficult to observe visual flaws in the membrane and some membranes may have been damaged during assembly. For the membranes to be used routinely, their durability must be increased. The initial tritium test failed because of a crack in the glassware and the system required modification to prevent leaks of tritium from the test system. The results of two subsequent tritium tests are provided in Table 3 and show an increase in the separation efficiency over deuterium, as expected. The condensate to starting solution ratio was 0.4 for the first test and 0.64 for the second test with the same membrane indicating a good separation efficiencies, but there may be some saturation effects. The increase may also occurred because of the increase in the evaporator solution. The original evaporator solution was not recoverable to verify an increase in the remaining evaporator water. The second test was performed to ensure that any holdup of clean water in the initial membrane did affect the results, although the water content of the membranes is very small.

3.4 Testing Summary

Separation efficiency indicated using the static test and evaporative test system shows comparable rates of approximately 80% for H/D separation. This is similar to the square root of the H/D molecular weight ratio. The separation for the T/D was about 60%, which is also similar to the square root of H/T molecular weight ratio. The permeation rate of water vapor is in the range of 5e-5 moles/min-cm^2.

The cost to set up a system with multiple stages appears to be more than the cost of the current baseline technology without significant improvements in separation efficiency and permeation rate.

Membrane improvements include an outer hydrophilic coating to allow direct contact with water and to provide additional strength.

4. HIGH LEVEL ECONOMIC COMPARISONS

This section provides an overview of the analyses performed in economic comparison report prepared by Kurion (Frost 2015). The comparison used a nominal separation rate of 67% for a single stage and a permeation rate of 5×10^{-5} g/min-cm^2. For a more detailed comparison, see Attachment A.

The graphene oxide membranes tested have the potential in terms of reduced energy for the purification of low concentrated tritiated waters compared to more conventional technologies. The current footprint and system size requirements for purification are such that improvements are still required to advance the technology. Areas of improvements should include the separation factor and additional improvements in methods for pleating the membranes such that an increased surface area of membrane per unit of volumetric space can be achieved. If a pleating factor of 20 can be achieved, then this technology could be much more space efficient and the initial building costs (i.e., space requirements) for the system could become much more reasonable. Reduced initial facility costs when combined with current energy requirements lead to a potential technology application that could have a sufficient business case in the future.

The separation unit would be a multi-stage system driven in the steam phase and the sizing for each unit in the stage would be controlled by the treatment rate and the mass fraction that must be treated in each unit (the majority of the mass would be treated along the diagonal of a square system arrangement). An initial boiler will be needed to convert the contaminated water into steam. Once converted to steam, it will flow through the system. However, as with any steam system, the steam will condense at startup as it comes in contact with the cold pipes and equipment. To preserve the membranes and ensure that the contaminated water is treated, it may be necessary to start up the system with clean water until it is heated to its process temperature. Since this energy will be small over the course of a year, it will be neglected in this analysis. Additional heat will be necessary to overcome heat losses in a system of any significant size. For the purposes here, the process steam is assumed to be reheated by 10 °C for each stage.

Table 4 presents estimate energy usage and costs based on the degree of decontamination obtained by the facility. The 90 x 90 stage reduces the concentration of the initial concentration by 90% whereas the 250 x 250 reduces the initial concentration by 99%. A comparative for energy consumption was made to systems based on combined electrolysis and catalytic exchange (CECE) where the water undergoes electrolysis followed by a liquid catalytic exchange process. The graphene approach uses between 2.3 and 4.5 kW·hr/L of water treated. Typical estimates for CECE are between 7.2 kW·hr per liter of water treated (DOE 2009) and 8.45 kW·hr/L of water treated (Boniface 2014). This represents a saving of about one-half to one-third of the annual energy operating costs.

Table 4. Estimated energy costs and membrane surface area

Facility Size	Stages	Required Membrane Surface Area (m^2)	Annual Energy Required[(a)] (kW·hr)	Estimated Energy Cost per Liter[(b)] ($/L)
1,000,000 L/yr	4 x 4	37,000	1.1 million	0.08
1,000,000 L/yr	90 x 90	0.94 million	2.3 million	0.16
1,000,000 L/yr	250 x 250	2.6 million	4.5 million	0.32

(a) The annual energy is based on an 80% overall facility efficiency (a 20% downtime is assumed to determine the process rate and membrane surface area). The water is assumed to begin at 15 °C and be heated to steam at 300 °C at atmospheric pressure

(b) Energy costs are assumed to be $0.07/kW·hr

The other major cost element besides energy is initial facility design and fabrication. Facility design for this process is complex, and it consists of individual units in each stage that will be of varying sizes. To design such a facility, it is assumed that modular subunits will be designed and used to assemble each unit.

One such construct assumes that a modular subunit would be able to hold a membrane approximately 30 cm in diameter (see Table 5). Such a subunit would consist of 0.07 m^2 of membrane area and take up approximately 0.03 m^3. It would treat 42 mL of steam per minute (about 6 millionths of the total quantity of 1,000,000 L of water per year). This excludes the supporting equipment (steam vents, steam traps, pressure regulators, facility ventilation, heat trace, etc.), which is estimated as an additional 1 m^3 per unit.

Table 5. Estimated subunit size and membrane cost

Subunit Treatment Size	Membrane Surface Area	Subunit Volume	Estimated Cost
42 mL/min	0.07 m^2	0.03 m^3	$0.42 for membrane

The land area required for this type of system is significant and is approximated to be between 100 and 300 acres for 90 to 250 stages in the system. The space requirements for the graphene membrane approach are significantly larger than CECE processes. As an example, the Detritiation Facility for the ITER reactor was designed at 20 by 80 m with a height of 34 m to house a system that was capable of processing 20 kg/hr (Laesser 2008).

The building costs, including membrane production costs, are estimated to be between $600 million and $1.8 billion for 90 to 250 stages. When combined with annual energy operating costs and capitalization of the building over 10 years, the water treatment costs range from $60/L to $180/L. It should be noted that the lower bound only treats the water to 10% of initial concentration, while the larger value treats the water to 1% of the original concentration. Although the costs of the membranes are included in the facility costs, the costs are much smaller than the estimated building costs, such that the membrane costs become inconsequential.

Table 6. Estimated facility size and cost

Stages	Number of Units	Number of Subunits	Facility Footprint[(a)] (m^2)	Estimated Facility Costs[(b)]	Estimated Membrane Cost	Facility Costs
4	16	520,000	5,200	$25M	$200,000	$25M
90	8100	13 million	130,000	$600M	$5.6M	$600M
250	62,500	37 million	370,000	$1.7B	$15.6M	$1.7B

(a) Footprint estimated based on assuming a 3-m-tall facility.

(b) Assumed construction and land costs of $428/ft^2 including necessary monitoring and analytical equipment. Based on Virginia Building Construction Costs Database queried 03/07/14 using average of wet and research laboratory values.

Reports of comparable CECE systems typically have capital plant costs in the range of $350 million for a system that can treat 100,000 m^3 annually. Therefore, the typical capital costs (i.e., non-operating costs) are $50 to $75 million depending on the capital amortization period (Boniface 2014). This translates into building costs of 0.50 to 0.75 dollars per liter. Total operating costs of CECE systems range from $2/L to highs of $20/L for systems with high removal capacities.

5. CONCLUSIONS

Based on the testing performed and the economic analyses, the following conclusions can be made.

- The graphene oxide membranes tested have the potential in terms of reduced energy for the purification of low concentrated tritiated waters compared to more conventional technologies
- The large flake GOx membranes have a higher separation efficiency than the small flake material.
- The separation efficiency for tritiated water was approximately 60%. However very large membrane areas are still needed for the separation of large volumes of water to obtain a high separation efficiency process.
- Transport mechanisms did not appear to be based on tritium/protium atomic weight ratios (but closer to square root of atomic weight ratios).
- The current footprint and system size requirements for purification are such that improvements are still required to advance the technology. Areas of improvements include better separation factor and additional improvements in methods for increasing the membrane strength so pleating the membranes or forming tubes would increase the surface area per unit of volume, thus reducing the facility size and cost.
- Facility costs are most significant factor for this technology and estimated costs are higher than CECE technology without improvements to surface area per unit volume or increased processing rates. Better separation efficiency exponentially would reduce the separation stages needed and consequently the facility size.

6. REFERENCES

Boniface HA, J Robinson, NV Gnanapragasam, I Castillo, and S Suppiah. 2014. "A Practical Process for Light-water Detritiation at Large Scales." In *The 19th Pacific Basin Nuclear Conference* (PBNC2014-282), Vancouver, British Columbia, Canada, August 24 through 28, 2014.

DOE. 2009. *Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*. DOE/RL-2009-18, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, WA.

Frost A and W Bratton. 2015. *Design Analysis of Tritium Graphene Oxide Membrane System*. KUR-BATT04-001-RPT-001, Rev A, Kurion, Richland, WA.

Hankel M, Y Jiao, A Du, SK Gray, SC Smith. 2012. "Asymmetrically Decorated, Doped Porous Graphene as an Effective Membrane for Hydrogen Isotope Separation." *J. Phys. Chem. C* 116:6672–6676.

Karim MR, K Hatakeyama, T Matsui, H Takehira, T Taniguchi, M Koinuma, Y Matsumoto, T Akutagawa, T Nakamura, S-I Noro, et al. 2013. "Graphene Oxide Nanosheet with High Proton Conductivity." *J. Am. Chem. Soc.* 135(22):8097-8100.

Kovtyukhova NI, PJ Ollivier, BR Martin, TE Mallouk, SA Chizhik, EV Buzaneva, and AD Gorchinskiy. 1999. "Layer-by-Layer Assembly of Ultrathin Composite Films from Micron-Sized Graphite Oxide Sheets and Polycations." *Chem. Mater.* 11:771-778.

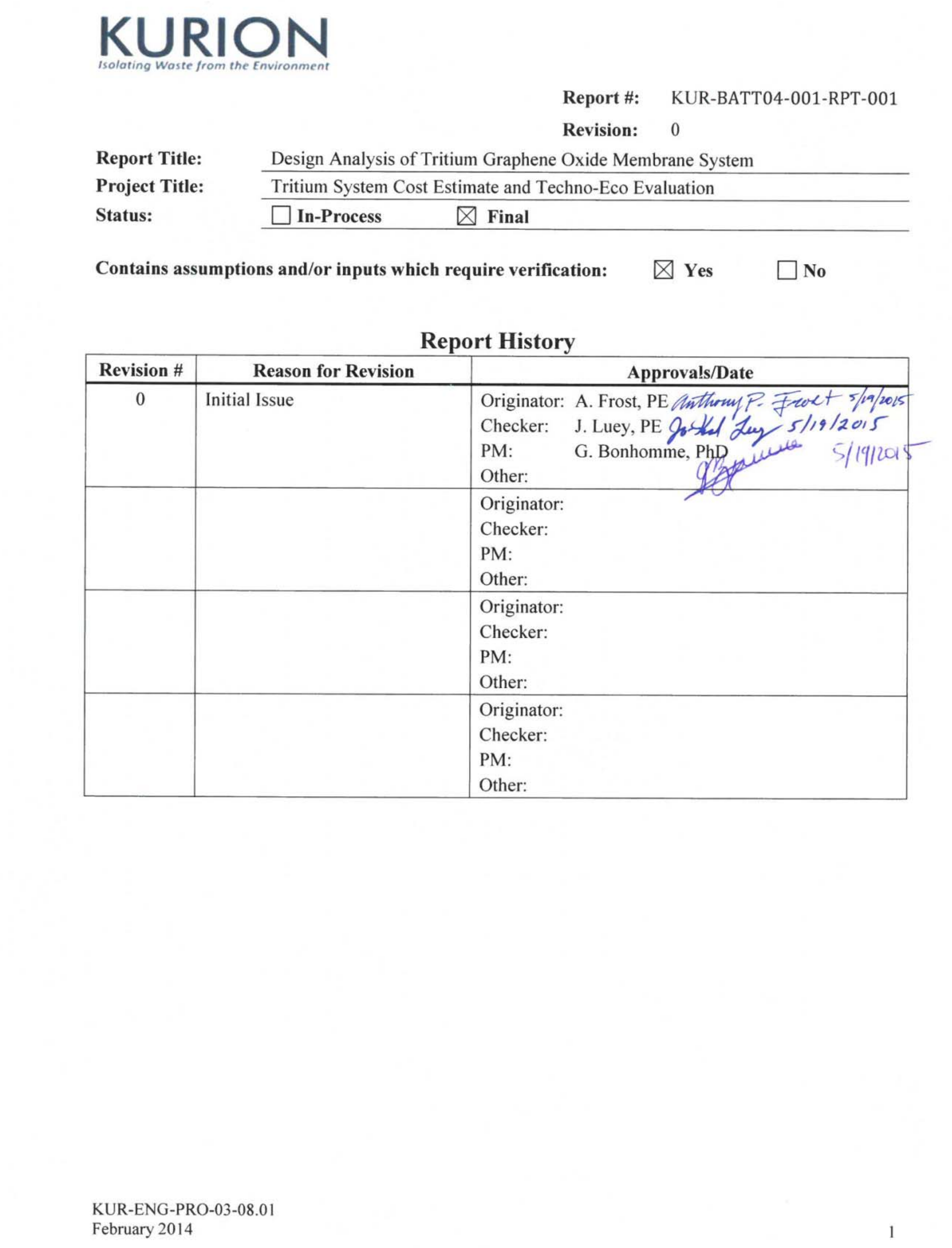
Laesser R. 2008. A few topics addressed in Working Group 7 (tritium Plant) during the ITER Design Review.

Nair RR, HA Wu, PN Jayaram, IV Grigorieva, and AK Geim. 2012. "Unimpeded Permeation of Water through Helium-Leak-Tight Graphene-Based Membranes." *Science* 27, 335(6067):443-444.

Webtheimer FH. 1960. *The Magnitude Of The Primary Kinetic Isotope Effect For Compounds Of Hydrogen And Deuterium*. The James Bryant Conant Laboratory, Harvard University, Cambridge, Massachusetts.

ATTACHMENT 1

DESIGN ANALYSIS OF TRITIUM GRAPHENE OXIDE MEMBRANE SYSTEM



KURION
Isolating Waste from the Environment

Report #: KUR-BATT04-001-RPT-001
Revision: 0

Report Title: Design Analysis of Tritium Graphene Oxide Membrane System
Project Title: Tritium System Cost Estimate and Techno-Eco Evaluation
Status: ☐ **In-Process** ☒ **Final**

Contains assumptions and/or inputs which require verification: ☒ **Yes** ☐ **No**

Report History

Revision #	Reason for Revision	Approvals/Date
0	Initial Issue	Originator: A. Frost, PE Anthony P. Frost 5/19/2015 Checker: J. Luey, PE 5/19/2015 PM: G. Bonhomme, PhD 5/19/2015 Other:
		Originator: Checker: PM: Other:
		Originator: Checker: PM: Other:
		Originator: Checker: PM: Other:

KUR-ENG-PRO-03-08.01
February 2014 1

KUR-BATT04-001-RPT-001, Rev. 0 May 20, 2015

Executive Summary

A review of an innovative graphene membrane approach for separation of tritiated water to create clean water and a much smaller waste stream has been conducted by the Pacific Northwest National Laboratory (PNNL). The graphene membrane approach utilizes a series of membranes that fundamentally pass water in the vapor phase, but have a much lower permeability for tritiated water vapor. Because of the permeability differences, the approach can be utilized to separate tritiated water from the non-tritiated water. The graphene process is less energy intensive than the traditional liquid Combined Electrolysis and Catalytic Exchange (CECE) process since the graphene process does not require the water to be cracked (cracking is the process of breaking a compound into simpler molecules; for water, cracking is the process of severing the molecular bond between Hydrogen and Oxygen). Preliminary estimates are the energy costs of the graphene process are half the CECE process. The drawback of the graphene approach is that a very large area of membrane is required to effectively separate large quantities of low concentration water. For a 1-million liter per year plant, the land requirements are estimated between 30 and 100 acres depending on the level of concentration reduction required. If methods for placing more membrane surface area into a smaller volume (such as pleating or small diameter tubes) can be determined, then the costs related to the facility area are significantly reduced and the graphene approach has promise as an economical tritium separation approach.

Page ii

Contents

Figures

Tables

Terms

CECE	Combined Electrolysis and Catalytic Exchange
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
GOx	Graphene Oxide Laminar Membrane
IAEA	International Atomic Energy Agency
ITER	International Thermonuclear Experimental Reactor
METI	Japan Ministry of Economy, Trade and Industry
PNNL	Pacific Northwest National Laboratory

1.0 Introduction

Tritium in the environment is an emotionally debated matter in public dialogue world-wide that has a scientific parallel as illustrated by the wide range of drinking water standards from country to country. In a groundbreaking precedent, based on a tritium release in his home state, then Senator Obama, dismissed arguments that tritium leaks posed no health threat and proposed the *Nuclear Release Note Act of 2006* because this "is not about whether tritium is safe, or at what concentration or level it poses a threat [but] about ensuring that nearby residents know whether they may have been exposed to any level of radiation" (Source: NY Times). Recent scientific debate includes:

- The U.S. Environmental Protection Agency (EPA) has decided to reevaluate standards for tritium in water under new rulemaking. The reevaluation was driven by rising concerns at the EPA that the effect of low-energy beta radiation from tritium is actually more efficient at causing cancer than originally thought. This is because it imparts 100 percent of its energy into cellular structures versus high-energy radiation that pass through cells. (Source: February 7, 2014, *Scientific American* article "Is Radioactive Hydrogen in Drinking Water a Cancer Threat".)
- In a September 2013 report, the Atomic Energy Society of Japan declared that the only two options to deal with tritium leading to a low environmental impact was tritium removal and/or concentration by an isotopic exchanger, or dilution and environmental release of tritium. This unfortunately ignored that, despite diluting the contaminated water to the site concentration release limit of 6×10^4 Bq/L, the annual site permit radioactivity limit of 2.2×10^{13} Bq/yr would require the Tokyo Electric Power Company to release the tritiated water over more than 40 years.
- In a March 2014 presentation to the METI Task Force in Tokyo, The Institut de Radioprotection et de Sûreté Nucléaire concluded that "uncertainties remain in the marine and terrestrial ecosystems" with regards to the studies performed to understand tritium behavior in the environment in order to have a more realistic dose assessment for human and biota.

The key, then, is whether an economically attractive technological alternative exists that can be reliably matured rather than simply releasing tritium into the environment. "Economically attractive" means its costs are deemed to offset reparations to certain industries and stakeholders and the indirect costs of loss of trust by the public in nuclear energy and institutional promises. As a result, the U.S. Department of Energy (DOE) Northeast division has had Pacific Northwest National Laboratory (PNNL) investigate a new graphene membrane approach for separation of tritiated water to create clean water and a smaller waste stream. This report presents a preliminary cost and energy analysis of the new approach for comparison with traditional CECE tritium separation approaches.

2.0 Graphene System Design

It is estimated that in the future, nuclear fuel reprocessing plants will be required to clean-up tritiated water. The estimated volumes will be hundreds of thousands of gallons of water with low activities of tritium. More economical processes that are currently available and designed for low-activity water will likely be needed to process this quantity of low-activity water (10^{-3} to 10 uCi/g).

The PNNL concept utilizes Graphene Oxide Laminar Membranes (GOx) for the separation of low concentration (10^{-3} to 10 uCi/g) tritiated water to create clean water and much smaller waste stream with much higher tritium concentrations. Graphene oxide membranes are laminar membranes consisting of hierarchically stacked, overlapping molecular layers that are a new class of materials. Recent research by

Nair et al. and at PNNL has demonstrated (GOx) membranes to be leak-tight to most gases, but readily transport water vapor.

The physical structure of the 2D-laminate materials provides extremely long diffusion path lengths (~10,000 times the membranes thickness). The hydrophilic oxygenated nature of GOx provides it with extremely high proton conductivity (~0.01 S/cm), reflecting an extensive interaction of H-bonding in the material. Ongoing research at PNNL is combining experimental and theoretical tools to understand and control the selective transport of water through GOx membranes, but the current understanding is the H_2O does not transport through the membrane by simple diffusion. Rather, the molecular selectivity derives from H_2O molecules proton hopping through the chemical functionality between the GOx lamina. This mechanism should provide isotopic selectivity much greater than a mechanism relying only on the mass difference between water and tritiated water (PNNL 2015, *Separation of Tritiated Water from Water using Graphene Oxide Membrane*).

Working on the premise that transport through GOx membranes is regulated by the repeated forming and breaking the O-H bonds, we can estimate the relative frequency of molecular hopping will be controlled by the O-H or O-T bond vibrational frequency. This means that it will be possible to achieve atomic-like isotope selectivity between tritiated water and molecular water (vis. kinetic isotope effect). Additionally, the long path length and multi-step breaking and reforming of O-H bonds may provide an even higher selectivity. The potential of such attractive selectivity improvement is to be determined in the proof-of principle test.

A series of tests conducted by PNNL utilizing a 10 percent deuterium solution showed that a decrease in deuterium of almost 18% in both samples, which reflects the active engagement of the GOx membranes for removing and trapping deuterium from the mixture. All tests were done in the steam phase with minimal pressure difference across the membranes. The permeation rates during the tests were approximately 5×10^{-5} g/min-cm^2 (PNNL 2015).

To facilitate scale-up of the experimental tests, a numerical model was created to simulate the process with multiple stages of refinement and some feedback looping to process and entire volume of low-activity water. The model is based upon a steady-state separation of the tritiated water within each stage of the operation assuming an HTO/H_2O hold-up rate of 67% and a permeation rate equal to those measured in the deuterium tests.

Initially, a boundary condition is drawn that assumes steady-state conditions where conservation of mass may be applied to one chamber with the membrane as the boundary. As a mass of steam flows into the membrane at a steady initial concentration, the concentration of tritiated water vapor (HTO) inside the chamber increases as tritium is "held up." A mass of the high HTO concentration must be drawn off at a steady rate to prevent the concentration from rising to a point where the steam passing through the membrane is no cleaner than the inlet concentration. Lastly, the concentration of the steam passing through the membrane is two-thirds smaller than the steady-concentration inside the chamber due to the HTO hold-up rate (HTO is assumed to pass through the membrane at two-thirds the speed as H_2O). See Figure 1.

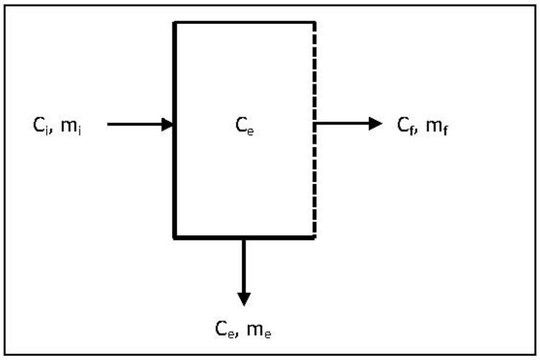


Figure 1: Steady-State Diagram of Membrane

To develop a mathematical model that determines the final concentration, C_f, of the "clean" steam and the equilibrium concentration, C_e, of the "dirty" steam, a mass flow ratio must be assumed. If the mass of steam leaving the chamber through the membrane is high, then the equilibrium concentration will increase due to the hold-up of the tritium. If the mass of steam leaving the chamber as "waste" is high, then the equilibrium concentration will be lower (and, therefore, the "clean" concentration will be lower). Unfortunately, the optimal balance is difficult to ascertain since the trade-off in volume is not favorable (i.e., a large volume of slightly "dirty" water and low volume of "clean" water may be obtained or a large volume of slightly "clean" water and low volume of "dirty" water may be obtained).

The relationships described above can be used to develop an equation that determines the concentrations of C_e and C_f based on the initial concentration assuming an HTO hold-up rate and m_f:m_i ratio:

$$\dot{m}_i = \dot{m}_e + \dot{m}_f$$ **Equation (1)**

$$x = \frac{\dot{m}_f}{\dot{m}_i}$$ **Equation (2)**

$$w = \frac{2}{3}$$ **Equation (3)**

$$C_f = wC_e$$ **Equation (4)**

$$\dot{m}_i C_i = \dot{m}_e C_e + \dot{m}_f C_f$$ **Equation (5)**

where:

$\dot{m}_i$	mass flow inlet of steam (kg H_2O/min)
$\dot{m}_e$	mass flow outlet of steam at increased HTO concentration (kg H_2O/min)
$\dot{m}_f$	mass flow outlet of steam at decreased HTO concentration (kg H_2O/min)
x	proportion of mass flow passed through membrane as "clean" steam (unitless)
w	hold-up rate of HTO with respect to H_2O (unitless)
C_i	initial inlet concentration of steam (kg of HTO/kg of H_2O)
C_e	outlet concentration of steam at increased HTO concentration (kg of HTO/kg of H_2O)
C_f	outlet concentration of steam at decreased HTO concentration (kg of HTO/kg of H_2O)

Combining the equations to solve for the equilibrium concentration reached in the chamber (i.e., the outlet concentration of steam at an increased HTO concentration, C_e):

Combining Equations (5) and (4) and solving for C_e:

$$C_e = \frac{\dot{m}_i C_i}{\dot{m}_e + w\dot{m}_f}$$ **Equation (6)**

Further combining Equations (1), (2), and (6):

$$C_e = \frac{\dot{m}_i C_i}{(1-x)\dot{m}_i + xw\dot{m}_i}$$ **Equation (7a)**

$$C_e = \frac{C_i}{1 + (w-1)x}$$ **Equation (7b)**

If the outlet products are passed through "n" stages with the same "x" and "w" ratios, then the end concentrations and masses can be determined using the following equations:

$$C_{e,n} = \frac{C_i}{[1 + (w-1)x]^n}$$ **Equation (8)**

$$\dot{m}_{e,n} = (1-x)^n \dot{m}_i$$ **Equation (9)**

$$C_{f,n} = w^n \frac{C_i}{[1 + (w-1)x]^n}$$ **Equation (10)**

$$\dot{m}_{f,n} = x^n \dot{m}_i$$ **Equation (11)**

If we assume the reduction in concentration desired is defined as "z," then the number of stages required can be solved by rearranging Equation 10:

$$z = w^n \frac{1}{[1 + (w - 1)x]^n} \qquad \textbf{Equation (12a)}$$

$$n = \frac{\log z}{\log\left(\frac{w}{1 + (w - 1)x}\right)} \qquad \textbf{Equation (12b)}$$

The previous equations are only valid for a system with a single line of membranes. For a system with "n" cleaning stages and "m" concentrating stages, the mass flow for each concentration step can be determined from the following equations (the derivation of these equations is too involved for discussion here):

$$\dot{m}_{e,m,n} = \dot{m}_i \binom{n + m - 1}{m} x^{n-1}(1 - x)^m \; for\ m = 1 \cdots m - 1 \qquad \textbf{Equation (13a)}$$

$$\dot{m}_{e,m,n} = \dot{m}_i \binom{n + m - 2}{m - 1} x^{n-1}(1 - x)^m \; for\ m = m \qquad \textbf{Equation (13b)}$$

Similarly, the mass flow for each cleaning stage (i.e., mass flow through the membrane) is as follows:

$$\dot{m}_{f,m,n} = \dot{m}_i x^n \; for\ m = 1 \qquad \textbf{Equation (14a)}$$

$$\dot{m}_{f,m,n} = \dot{m}_i \binom{n + m - 2}{m - 1} x^n (1 - x)^m \; for\ m = 2 \cdots m \qquad \textbf{Equation (14b)}$$

Lastly, the concentrations can be determined for "n" cleaning stages and "m" concentrating stages as:

$$C_{f,m,n} = w^n \frac{C_i}{[1 + (w - 1)x]^{(n+m-1)}} \qquad \textbf{Equation (15)}$$

$$C_{e,m,n} = w^{n-1} \frac{C_i}{[1 + (w - 1)x]^{(n+m-1)}} \qquad \textbf{Equation (16)}$$

Utilizing these equations, a spreadsheet was developed to diagram a simple 4x4 system (i.e., a system with four cleaning stages and four concentrating stages). Assuming an HTO/H_2O hold-up rate of 67 percent, the following results are obtained with 62.1 percent of the mass being cleaned in each stage as shown in Figure 2.

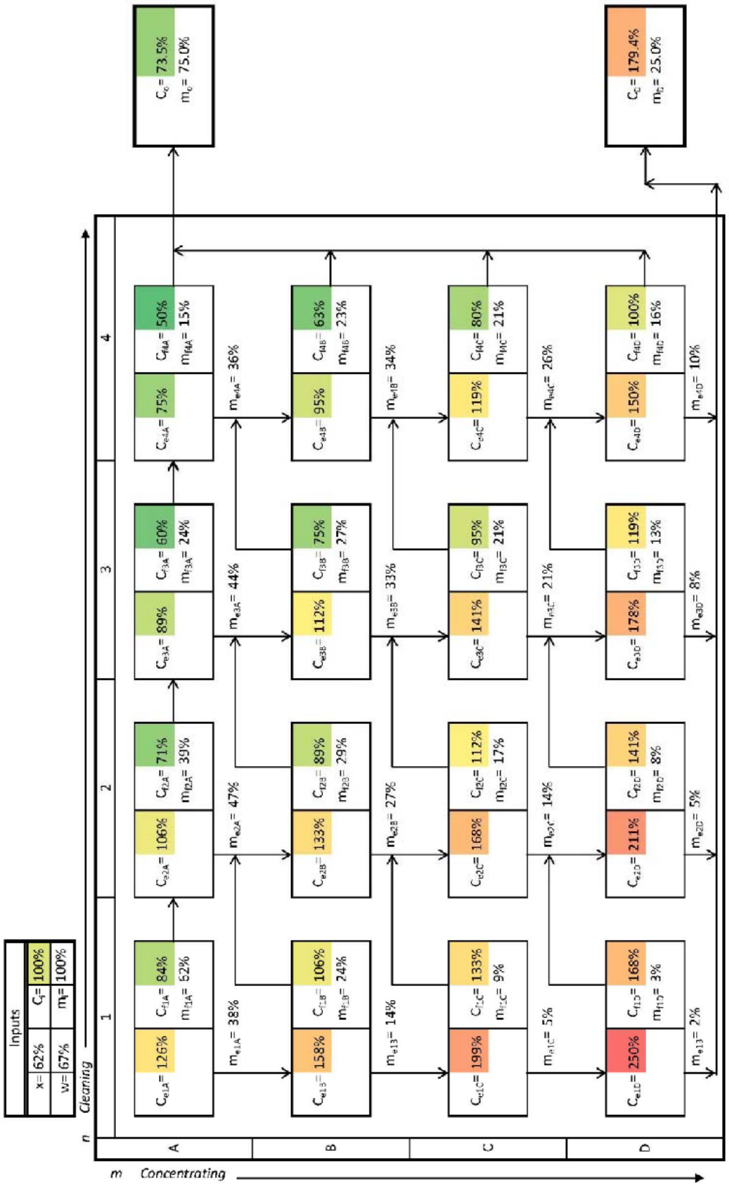


Figure 2: Staging Model Results for 4x4 System

Based upon the model run under these conditions, the initial concentration of the HTO water has been reduced to 73.5 percent of the starting concentration for 75 percent of the initial volume. The volume reduction has been good in the process as the volume of concentrated waste water is only 25% with a concentration 179% of the initial concentration. Many more stages are needed to reduce the concentration of the clean water materials to less than 10 percent of the initial concentration. The desired results may be reached by the addition of further stages.

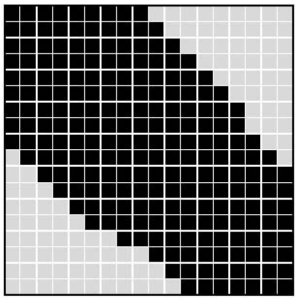


Figure 3: Representation of an Economized System

In addition to considering the flow sheet and determining the staging requirements, the size of each stage was considered. The stage size is a function of the volume of water to be processed over a given period of time. Provided a constant permeation rate for steam (590 mL/m^2/min) (PNNL, 2015), the surface area of the membrane for the system may be estimated if the desired flow rate is known. Provided a facility sized to treat 1,000,000 L/yr of contaminated water, the area of the GOx membranes is estimated to be 6520 m^2 for the first stage and 10,500 m^2 for each subsequent stage. Depending on the desired result, the complete facility may need approximately 250x250 stages: creating a need for approximately 2.6 million m^2 of the GOx membrane to fabricate the facility. It is estimated that 250x250 stages could treat 99 percent of the water to 1 percent of the initial concentration (resulting in a waste water concentration of 69 times the original concentration).

A facility of approximately 90x90 stages could treat 90 percent of the water to 10 percent of the initial concentration (resulting in a waste water concentration of 9.2 times the original concentration).

It should be noted that these models do not take into account physical size and are mathematical in nature. For example, the last stage of a 250x250 stage system will process a mass fraction of x^{250}, resulting in a mass that is likely so miniscule that no realistic system could be built to treat it. However, the mass of the system does collect along the center, which could create the opportunity to economize if some of the smaller mass stages are cut out and recycled into the system (see Figure 3). It is not obvious how such an economization would change the results of the simple mathematical constructs used to estimate plant design here. In future, a computer program could potentially be written to model systems with varying geometries, mass fraction splits, and HTO hold-up rates to determine an optimum plant design.

3.0 Cost and Energy Analysis

As described above, the system is driven in the steam phase and the sizing for each unit in the stage is controlled by the treatment rate and the mass fraction that must be treated in each unit (the majority of the mass is treated along the diagonal of a square system arrangement). An initial boiler will be needed to convert the contaminated water into steam. Once converted to steam, it will flow through the system. However, as with any steam system, the steam will condense at startup as it comes in contact with the cold pipes and equipment. To preserve the membranes and ensure that the contaminated water is treated, it may be necessary to start up the system with clean water until it is heated to its process temperature. Since this energy will be small over the course of a year, it will be neglected in this analysis. Additional heat will be necessary to overcome heat losses in a system of any significant size. For the purposes here, the process steam is assumed to be reheated by 10 °C for each stage.

Table 1 presents estimate energy usage and costs based upon the degree of decontamination obtained by the facility. As pointed out above the 90x90 stages reduces the concentration of the initial concentration by 90 percent whereas the 250X250 reduces the initial concentration by 99 percent. A comparative for energy consumption was made to systems based upon CECE where the water undergoes electrolysis followed by a liquid catalytic exchange process. The graphene approach uses between 2.3 and 4.5 kW·hr/L of water treated. Typical estimates for CECE are between 7.2 kW·hr per liter of water treated (DOE/RL-2009-18, *Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*) and 8.45 kW·hr/L of water treated (Boniface 2014, "A Practical Process for Light-water Detritiation at Large Scales"). This represents a saving of about one-half to one-third of the annual energy operating costs.

Table 1: Estimated Energy Costs and Membrane Surface Area

Facility Size	Stages	Required Membrane Surface Area (m^2)	Annual Energy Required (kW·hr)[a]	Estimated Energy Cost per Liter (\$/L)[b]
1,000,000 L/yr	4x4	37,000	1.1 million	0.08
1,000,000 L/yr	90x90	0.94 million	2.3 million	0.16
1,000,000 L/yr	250x250	2.6 million	4.5 million	0.32

[a] The annual energy is based on an 80% overall facility efficiency (a 20% downtime is assumed to determine the process rate and membrane surface area). The water is assumed to begin at 15 °C and be heated to steam at 300 °C at atmospheric pressure.

[b] Energy costs are assumed to be $0.07/kW·hr.

The other major cost element other than energy is initial facility design and fabrication. Facility design for this process is complex, and it consists of individual units in each stage that will be of varying sizes (note that the mathematical pattern is based on the binomial coefficient). To design such a facility, it is assumed that modular subunits will be designed and used to assemble each unit.

One such construct assumes that a modular subunit would be able to hold a membrane approximately 30 cm in diameter (see Table 2). Such a subunit would consist of 0.07 m^2 of membrane area and take up approximately 0.03 m^3. It would treat 42 mL of steam/min (about 6 millionths of the total quantity of 1,000,000 L of water per year). This excludes the supporting equipment (steam vents, steam traps, pressure regulators, facility ventilation, heat trace, etc.), which is estimated as an additional 1 m^3 per unit.

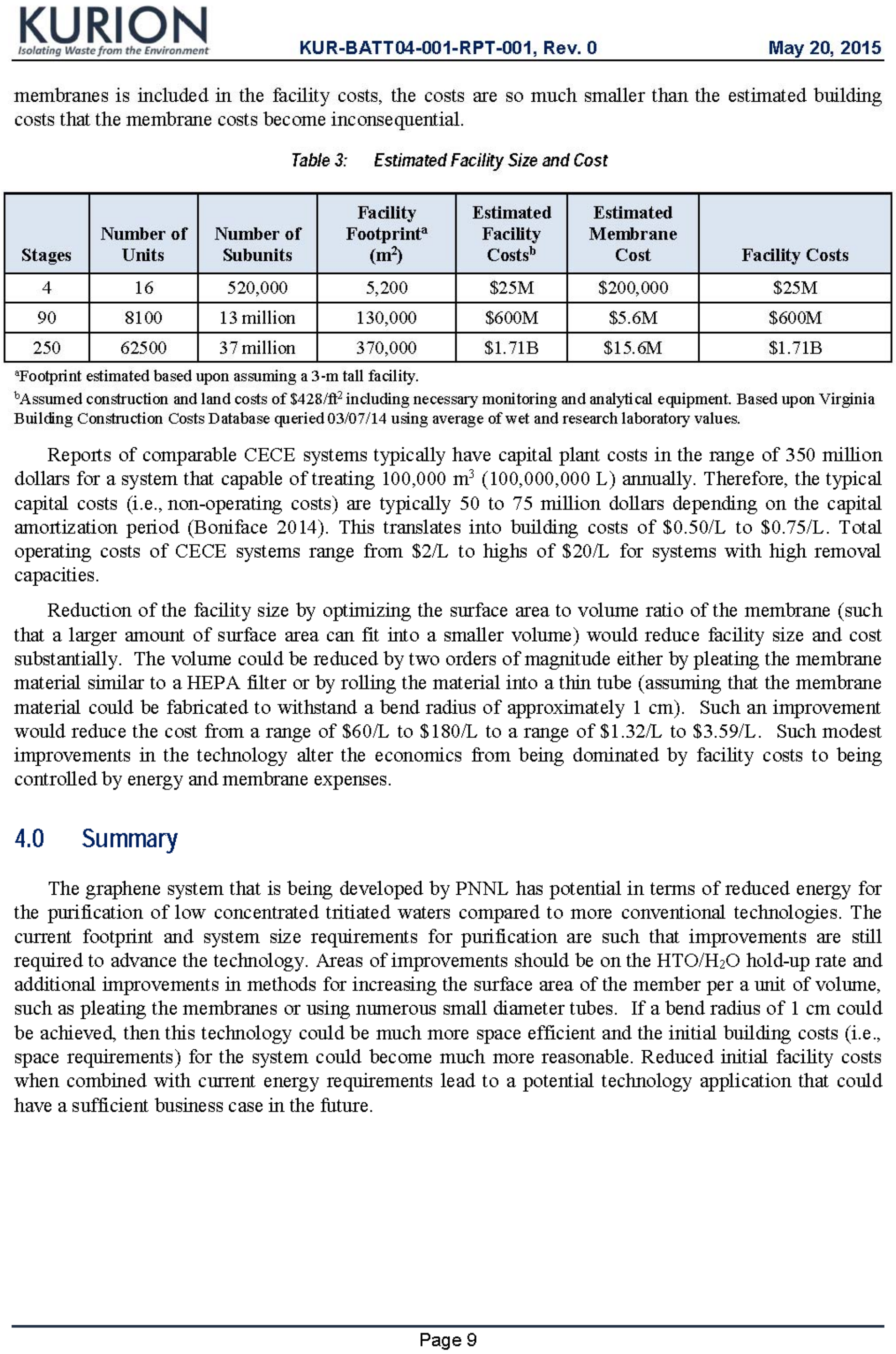
Table 2: Estimated Subunit Size and Membrane Cost

Subunit Treatment Size	Membrane Surface Area	Subunit Volume	Estimated Cost[c]
42 mL/min	0.07 m^2	0.03 m^3	\$0.42 for membrane

[c] Membrane costs are assumed to be \$6.00/m^2.

The land area required for this type of system is significant and is approximated to be between 100 and 300 acres for 90 to 250 stages in the system. The space requirements for the graphene membrane approach are significantly larger than CECE processes. As an example, the Detritiation Facility for the ITER reactor was designed at 20 m by 80 m with a height of 34 m to house a system that was capable of processing 20 kg/hr (Laesser 2008, "A few topics addressed in Working Group 7 (tritium Plant) during the ITER Design Review").

The building costs, including membrane production costs, are estimated to be between 600 million and 1.8 billion dollars for 90 to 250 stages. When combined with annual energy operating costs and capitalization of the building over 10 years, the water treatment costs range from \$60/L to \$180/L. It should be noted that the lower bound only treats the water to 10 percent of initial concentration, while the larger value treats the water to 1 percent of the original concentration. Although the cost of the



membranes is included in the facility costs, the costs are so much smaller than the estimated building costs that the membrane costs become inconsequential.

Table 3: Estimated Facility Size and Cost

Stages	Number of Units	Number of Subunits	Facility Footprint[a] (m^2)	Estimated Facility Costs[b]	Estimated Membrane Cost	Facility Costs
4	16	520,000	5,200	$25M	$200,000	$25M
90	8100	13 million	130,000	$600M	$5.6M	$600M
250	62500	37 million	370,000	$1.71B	$15.6M	$1.71B

[a] Footprint estimated based upon assuming a 3-m tall facility.

[b] Assumed construction and land costs of $428/$ft^2$ including necessary monitoring and analytical equipment. Based upon Virginia Building Construction Costs Database queried 03/07/14 using average of wet and research laboratory values.

Reports of comparable CECE systems typically have capital plant costs in the range of 350 million dollars for a system that capable of treating 100,000 m^3 (100,000,000 L) annually. Therefore, the typical capital costs (i.e., non-operating costs) are typically 50 to 75 million dollars depending on the capital amortization period (Boniface 2014). This translates into building costs of $0.50/L to $0.75/L. Total operating costs of CECE systems range from $2/L to highs of $20/L for systems with high removal capacities.

Reduction of the facility size by optimizing the surface area to volume ratio of the membrane (such that a larger amount of surface area can fit into a smaller volume) would reduce facility size and cost substantially. The volume could be reduced by two orders of magnitude either by pleating the membrane material similar to a HEPA filter or by rolling the material into a thin tube (assuming that the membrane material could be fabricated to withstand a bend radius of approximately 1 cm). Such an improvement would reduce the cost from a range of $60/L to $180/L to a range of $1.32/L to $3.59/L. Such modest improvements in the technology alter the economics from being dominated by facility costs to being controlled by energy and membrane expenses.

4.0 Summary

The graphene system that is being developed by PNNL has potential in terms of reduced energy for the purification of low concentrated tritiated waters compared to more conventional technologies. The current footprint and system size requirements for purification are such that improvements are still required to advance the technology. Areas of improvements should be on the HTO/H_2O hold-up rate and additional improvements in methods for increasing the surface area of the member per a unit of volume, such as pleating the membranes or using numerous small diameter tubes. If a bend radius of 1 cm could be achieved, then this technology could be much more space efficient and the initial building costs (i.e., space requirements) for the system could become much more reasonable. Reduced initial facility costs when combined with current energy requirements lead to a potential technology application that could have a sufficient business case in the future.

5.0 References

Biello, David, 2014. *Is Radioactive Hydrogen in Drinking Water a Cancer Threat.* Scientific American.

Boniface, H.A., J. Robinson, N.V. Gnanapragasam, I Castillo, and S. Suppiah, 2014, "A Practical Process for Light-water Detritiation at Large Scales", The 19th Pacific Basin Nuclear Conference (PBNC2014-282), Vancouver, British Columbia, Canada, August 24 through 28, 2014.

DOE/RL-2009-18, 2009, *Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Laesser, R., 2008, *A few topics addressed in Working Group 7 (tritium Plant) during the ITER Design Review*.

Maro, Denis. 13 March 2014. *Environmental behavior of tritium released by nuclear facilities in marine and terrestrial ecosystems: State-of-the-art and examples.* Institut de Radioprotection et de Súreté Nucléaire.

McIntire, Mike. February 3, 2008. *Nuclear Leaks and Response Tested Obama in Senate*. New York Times.

Nair, R.R., H.A. Wu, P.N. Jayaram, I.V. Grigorieva, and A.K. Geim, 2012, *Unimpeded Permeation of Water through Helium-Leak-Tight Graphene-Based Membranes*, Science 27, Vol. 335 No 6067, January, 2012, pp. 443-444.

PNNL, 2015, *Separation of Tritiated Water from Water using Graphene Oxide Membrane*, Draft Report M4FT-14PN0302168, Pacific Northwest National Laboratory, Richland, Washington.

Treatment of contaminated water stored in Fukushima Dai-ichi Nuclear Power Plant. September 10, 2013. Atomic Energy Society of Japan: Investigation Committee on the Nuclear Accident at the Fukushima Dai-ichi NPP.