

# Separation of Tritiated Water from Water Using Composite Membranes

J. B. Duncan  
Westinghouse Hanford Company

D. A. Nelson  
Pacific Northwest National Laboratory

Date Published  
December 1995

To Be Presented at  
ESP Technical Exchange Meeting  
Gaithersburg, Maryland  
January 14-19, 1996

To Be Published in  
*Proceedings*

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management



**Westinghouse  
Hanford Company**

P.O. Box 1970  
Richland, Washington

Management and Operations Contractor for the  
U.S. Department of Energy under Contract DE-AC06-87RL10930

---

Copyright License By acceptance of this article, the publisher and/or recipient acknowledges the  
U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

Approved for public release

**LEGAL DISCLAIMER**

---

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

---

This report has been reproduced from the best available copy.

Printed in the United States of America

DISCLM-2.CHP (1-91)

## **Separation of Tritiated Water from Water Using Composite Membranes**

### **Task Description**

The work in this task involves the use of composite membranes to remove tritium from contaminated water at DOE sites. Experience with membrane systems in industry indicates that they are inherently energy efficient. Furthermore, membrane technologies such as reverse-osmosis have been well developed for desalination and other industrial/municipal applications. Aromatic polyphosphazenes were chosen as the polymeric material for the membranes being investigated because they have excellent radiological, thermal, and chemical stability. The FY-96 effort is directed toward empirical delineation of a potential mechanism, providing a statistical approach to data acquisition, further mass balance determination, and a preliminary design for the module staged array.

### **Technology Needs**

Although processes for the removal of tritiated water (e.g., combined electrolysis-catalytic exchange) are available, most require intensive capital or energy expenditures. Thus, the considered remediation of tritiated water from Department of Energy sites involves migration with time through geological formations. Although this is quite logical because of tritium's short half-life (12.3 years), regulatory agencies have requested more emphasis for separation technology, due to the inherent uncertainties in geologic strata. Any defects would accelerate ground water flow and allow a plume of tritiated water quicker access to a river and ultimately to human and animal ingestion. Sites currently with either point source or groundwater containing tritiated water are Hanford, Savannah River, INEL, LLNL, BNL, and Mound.

### **Scientific Background**

During earlier studies [1] of barrier materials for hydrogen isotopes, it was observed that the permeability of tritium was lower than deuterium or hydrogen through brominated acrylonitrile-butadiene copolymer. From this work, it was proposed that this difference was a result of the lower diffusivity by virtue of the larger molecular mass of tritium. Hollow fiber polyimide membranes have been used to separate tritium from moist air in support of fusion research [2]. Cellulose acetate membranes have been used to separate deuterium oxide (200 ppm enriched) from light water ( $H_2O$ ) under pervaporation conditions (reduced pressure at the downstream) [3]. Pervaporation was more effective ( $\alpha = 1.08$ ) at lower temperatures and pressures (20°C and 6 Torr). Transition to an ultrafiltration mechanism was proposed for higher temperatures and pressures. Similar presumed mechanism change was shown to occur with the separation of 50%  $D_2O$  from  $H_2O$  with downstream pressures of 260 Torr and temperatures of 65°C [4]. An extension of this research used polytetrafluoroethylene (PTFE) membranes for both H/D and  $^{16}O/^{18}O$  separations within water.[5] The separation of the oxygen-isotopes was greater than those for the hydrogen-isotopes, which suggest different mechanisms for the pervaporation processes. For similar

temperatures and pressures, the hydrophobic membrane gave enhanced separation compared to a cellulose acetate membrane. Preliminary engineering calculations have been reported for the separation of D<sub>2</sub>O from H<sub>2</sub>O using the PTFE membranes in counter-current cascades [6].

Polyphosphazenes were chosen as the polymeric material for the membranes in the current investigation because they have been shown to possess excellent isothermal stability to 320°C [7] and selected types, especially poly[bis(phenoxy)phosphazene] or PPOP, were permeable to alcohols [8]. Furthermore, these polymers are chemically resistant to various solvents and are film-forming thermoplastics [9]. Of interest to the current research, polyphosphazenes with aryloxy side groups provided very low scission or cross-linking yields when exposed to gamma-radiation, [10] especially if no halogen or alkyl-groups were substituted on the aryl-group.

### Technical Approach

The FY-95 effort at PNNL has shown that the poly[bis(phenoxy)phosphazene] based membrane can consistently achieve 30% reduction, single pass, from a challenge of 3  $\mu\text{Ci/L}$  (KE-Basin water). The FY-96 effort is directed primarily at a basic understanding of the HTO separation. Thus, a series of mass balance experiments will be conducted to confirm the preliminary FY-95 results. Experiments will follow statistically experimental parameters. Designed experiments will also examine factors which might impact the HTO separation, such as pH, ion type/concentration, and temperature. Assistance is expected from the University of Idaho and the University of Washington for spectroscopic data concerning the possible mechanism of the HTO separation. Similarly, we shall be assisted by SpinTek Membrane Systems in the study of water permeation through the membranes. Several critical factors must be determined if the system is to be modularized. We expect to examine N-Basin water (39  $\mu\text{Ci/L}$ ) during FY-96 as well as water with a much higher tritium content. The experiment(s) with water in the mCi/L or higher range will require considerable coordination with other PNNL (regulatory and technical) personnel as well as the possibility of other DOE sites. The data from this experiment is crucial since it will allow us to determine further design parameters for the staged array system. Once most of the mechanism information and membrane property data is obtained, we shall calculate the hypothetical separation of the isotopomeric water in the cascade.

### Accomplishments

The major milestones of this project are directed at several issues which need resolution. These include a statistical approach to experimental design and mass balances, calculations from a designed module staged array, and a determination of the mechanism of the HTO separation. A statistical design of experiments has been accomplished and work toward providing the necessary information is underway. Thus, we have deionized and distilled 10 gallons of KE-Basin water (3  $\mu\text{Ci/L}$ ) and used that HTO for initial experiments. Twenty gallons of N-Basin water (39  $\mu\text{Ci/L}$ ) will also be prepared for similar use. Experiments were conducted with 10% carboxylated poly(diphenoxy)phosphazene and poly(diphenoxy)phosphazene, unannealed, using distilled KE-Basin water (3  $\mu\text{Ci/L}$ ). The experiments indicated that HTO separation is quite variable and reached 18% depletion with

only one carboxylated membrane under deionized water conditions. This confirms the variability from many previous experiments with unannealed membranes. The annealed membranes have also been examined under similar conditions (4°C and distilled KE-Basin water), but the scintillation results indicate little, if any, HTO depletion. However, the pressure stability required to maintain permeation with the annealed membranes is constant in contrast to the continual pressure fluxations needed for the unannealed membranes.

The same set of experiments (2 membranes and 4°C) were performed with distilled KE-Basin HTO containing 0.001 M Na<sub>2</sub>SO<sub>4</sub>. Both membrane types provided HTO separation, with the carboxylated membrane showing up to 17% HTO depletion. Of interest was the ability of this membrane to operate for 4 hrs, yet provide HTO depletion. We are currently examining membrane experiments with 0.01 M and 0.1 M Na<sub>2</sub>SO<sub>4</sub> as well as similar calcium salt concentrations. These data will be reported at the ESP Technical Exchange. Although the initial experiments have not been completed, the present data suggest that hydration shell involvement may be a significant part of the HTO separation mechanism.

Work is proceeding with Liumar Technologies of Ottawa, Ontario. They are determining the coating conditions of the poly(diphenoxy)phosphazene with material from Ethyl Corp. They are also attempting to establish the nanofiltration characteristics of the membrane using various molecular weight polyethylene oxides. Similarly, we are collaborating with the University of Idaho and the University of Washington (Center for Process Analytical Chemistry) to help further define the HTO separation mechanism by spectroscopic technique.

## **Benefits**

Waters containing unacceptable tritium concentrations (above environmental release limits or drinking water standards) are released at DOE sites, including Hanford, Savannah River, INEL, LLNL, BNL, and Mound. One example involves the C-018H Treatment Facility at Hanford (to treat 242-A evaporator wastewater) which will discharge 1.4 M gallons of treated condensate containing tritium averaging 6.3 μCi/mL through 2015. Currently, water from some test wells at Hanford contain tritium concentrations approaching 6x10<sup>7</sup> pCi/L. The Tri-Party Agreement requires the tritiated water in the K-East Basin (spent nuclear fuel storage) be treated or relocated. There are no currently acceptable removal options for tritium remediation other than migration with time through geologic formations. This proposed research is the first step to develop a process that will reduce the risk to the environment and public, reduce the costs for ultimate disposal for the tritium-containing water, and provide a way to recover the tritium in a concentrated form for disposal or use.

Tritium is also found in nuclear power plants in Canada and the U.S., as well as the Savannah River Site, as a result of neutron capture within the heavy water moderator/coolant. Light water coolant also contains increasing concentrations of tritiated water (HTO and related species) in a similar ppm range due to neutron emission/capture (uranium fission). This technology would go far to mitigate tritiated water as a point source pollutant for light water reactors. Also, there is a possibility that this membrane separation process would be of use in the future fusion effort.

## **Technology Transfer/Collaborations**

This work represents a collaborative effort between PNNL, Westinghouse Hanford Corp., and SpinTek Membrane Systems. Also, Atomic Energy Canada, Limited has expressed distinct interest in the membrane process and has entered into a proprietary agreement with PNNL. Similarly, two meetings with Ontario Hydro personnel have been conducted. PNNL has moved to expand the involvement of interested industries. In this regard, collaboration with Desalination Systems, Inc. was maintained throughout FY-95. Liumar Technologies Corp. has examined the polyphosphazene membranes for their proprietary applications and continue to provide us information concerning aqueous permeation. Separation Systems Technology, Inc. has also provided us considerable information concerning membrane properties needed for module design. SEG/Oak Ridge has discussed their need for this technology for application to commercial nuclear power facilities. We have obtained information concerning deuterium and tritium physical properties from both the All Russian Institute of Chemistry/Murmansk and the Association of Advanced Technologies/Minatom (Russia). To promote interest in this technology, we have presented the work before the Canadian Nuclear Society [11], the American Nuclear Society [12], and have a major publication about to issue [13]. A patent has also been issued [14].

## **Keywords**

Tritiated Water, Membrane, Polyphosphazene, Cross-Flow, Aqueous Separation

## **For further information, please contact:**

David A. Nelson  
Principal Investigator  
Pacific Northwest National Laboratory  
(509) 376-0875  
Email: david\_a\_nelson@rl.gov

James B. Duncan  
Principal Investigator  
Westinghouse Hanford Company  
(509) 372-0896  
Email: james\_b\_duncan@rl.gov

TTP Number: RL46C311 (also reference RL3420227)

## Bibliography

1. Nakagawa, T., M. Yoshida, and K. Kidokoro, "Development of Rubbery Materials With Excellent Barrier Properties to H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub>", *J. Membrane Sci.*, 52 (1990) 263.
2. Ito, H., T. Suzuki, T. Takanaga, Y. Matsuda, S. Konishi, Y. Naruse, and S. Hirata, "Separation of Tritium Using Polyimide Membrane", in Abstracts of the Fourth Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, Albuquerque, New Mexico, 1991, pp. 988-993.
3. Chmielewski, A. G., G. Zakrzewska-Trznadel, N. R. Miljevic, and W. A. van Hook, "Investigation of the Separation Factor Between Light and Heavy Water in the Liquid/Vapor Membrane Permeation Process", *J. Membrane Sci.*, 55 (1991) 257.
4. Chmielewski, A. G., J. Dlutowski, G. Zakrzewska-Trznadel, and N. Miljevic, "Hydrophilic Membrane as a Third Component in Light/Heavy Water Separation Process", *Nukleonika*, 34 (1989) 273.
5. Chmielewski, A. G., G. Zakrzewska-Trznadel, N. R. Miljevic, and W. A. van Hook, "<sup>16</sup>O/<sup>18</sup>O and H/D Separation Factors for Liquid/Vapor Permeation of Water Through an Hydrophobic Membrane", *J. Membrane Sci.*, 60 (1991) 319.
6. Chmielewski, A. G., A. Matuszak, G. Zakrzewska-Trznadel, W. A. van Hook, and N. R. Miljevic, "Cascades for Natural Water Enrichment in Deuterium and Oxygen-18 Using Membrane Permeation", *Separation Sci. Technol.*, 28 (1993) 909.
7. Maynard, S. J., T. R. Sharp, and J. F. Haw, "Thermal Degradation Chemistry of Poly(diphenoxyphosphazene)", *Macromolecules*, 24, (1991) 2794.
8. McCaffrey, R. E., R. E. McAtee, A. E. Grey, C. A. Allen, D. G. Cummings, A. D. Appelhans, R. B. Wright, and J. G. Jolley, "Inorganic Membrane Technology", *Separation Sci. Technol.*, 22 (1987) 873.
9. Allcock, H. R., R. L. Kugel, and K. J. Valan, "Phosponitric Compounds. VI. High Molecular Weight Poly(alkoxy- and aryloxyphosphazenes)", *Inorg. Chem.*, 5 (1966) 1709.
10. Babic, D., D. M. Souverain, V. T. Stannett, D. R. Squire, G. L. Hagnauer, and R. E. Singler, "The Radiation Cross-linking and Scission of Some Polyphosphazenes", *Radiat. Phys. Chem.*, 28 (1986) 169.
11. Nelson, D.A., J.B. Duncan, G.A. Jensen, and S.D. Burton, "Separation of HTO from Water Using Membrane Technology", in Proceedings of the 34th Conference of the Canadian Nuclear Society, Vol. 2, pp 73-83, 1994, Montreal, Quebec.
12. Nelson, D.A., J.B. Duncan, G.A. Jensen, and S.D. Burton, "Membrane Mediated Separation of Tritiated Water from Water Without Phase Change", *Transactions of the American Nuclear Society*, Vol. 71, 1994, pp 82-83.
13. Nelson, D.A., J.B. Duncan, G.A. Jensen, and S.D. Burton, "Isotopomeric Water Separations with Supported Polyphosphazene Membranes", *J. Mem. Sci.*, (1995), in press.
14. Nelson, D.A., G.A. Jensen, and J.B. Duncan, "Method and Apparatus for Tritiated Water Separation" USP 5,451,322 (1995).