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MEMBRANE MEDIATED SEPARATION OF TRITIATED WATER FROM
WATER WITHOUT PHASE CHANGE

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Introduction

This development effort at the Pacific Northwest Laboratory (PNL) has been directed toward the separation of tritium (via ^3HOH or HTO) from contaminated ground water with the use of membrane technology. Tritium contamination exists in both aquifers and water used for reactor cooling and represents both a technical and financial challenge for the Department of Energy. Currently, the primary option for the remediation low-level tritium is migration with time through geological formations. However, point sources containing tritiated water can be attacked by separation technology, thus directly addressing environmental concerns. The separation technology reported here is especially applicable to tritium contaminated water generated in nuclear fuel storage basins. At Hanford, the dual K-Basins contain 1000 metric tons of fuel with cooling waters; the K-East Basin contains 5.7 million liters of water at 11.1 MBq ($3 \mu\text{Ci/L}$). The K-West Basin contains 300,000 pCi/L also due to cannister leakage.

At the Savannah River Site, the L-Reactor Basin (15.2 million liters of water) and K-Reactor Disassembly Basins have held fuel rods for 5 years and many have corroded. Tritium levels are near that of the Hanford basins. At INEL, Building 603 stores more than 13,200 Kg of fuel rods in three pools of lesser volume than the Hanford or Savannah River Sites.

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Experience with membrane systems in industry indicates that they are inherently energy efficient. In the work at PNL, aromatic polyphosphazenes were chosen as the polymeric material for the membranes being investigated because they have been shown to possess excellent isothermal stability above 300°C and are quite robust under radiolysis conditions.

Description of the Actual Work

Based upon poly[bis(phenoxy)phosphazene] and its 10% carboxylated-derivative, the membranes were prepared by solvent casting on porous polyethylene terephthalate support. The membrane thicknesses were approximately 20 μM . The permeation tests used Hanford well water containing 4.14×10^5 Bq (HTO) and involved dead-end filtration. Two test cells were used, one constructed from cast aluminum and one an Amicon stirred cell. Both were configured so that well water could be used in the temperature range of 2° to 35°C. Pressure in the aluminum cell was held at 0.33 MPa, while the stirred cell could be operated from 0.07 to 0.41 MPa. At least 10 permeate water samples, of approximately 2 mL, were collected during each experiment. The reservoir contained 50 or 100 mL of well water. Efforts were made to establish a mass balance of tritium for each experiment. The membranes were also examined with a Desal Pilot Cell unit (Desalination Systems, Inc.) since it allows cross-flow conditions similar to that of reverse osmosis. The reservoir contains up to 75.7 L and the unit can be operated to 1.38 MPa. The tritium content of the samples was measured using a Beckmann LS800 scintillation counter.

Results

Experiments conducted with the membrane test cells indicated that the maximum depletion of HTO through the membranes was achieved with poly[bis(phenoxy)phosphazene], (PN_x), and PN_x containing 10% carboxylation in the 4-position of the aromatic rings, designated

PN_x(10%CO₂H). PN_x membranes have shown the ability to separate HTO at 4° to 23°C (up to 34% depletion), while the best separation temperature for PN_x(10%CO₂H) is below 10°C (up to 74% depletion). PN_x(5%CO₂H) membranes have properties intermediate between PN_x and PN_x(10%CO₂H). Membranes containing larger amounts of the carboxylic acid groups rapidly lose the HTO separatory ability.

Since this work was conducted using tritiated water at very low concentration, a material balance was conducted for several of the experiments. Table 1 is representative of the material balances obtained for membrane separations. The reservoir contents (feed, F) was 50 mL of HTO at 337.4 Bq/mL; the permeate (P) is represented by the values of Table 1; and the concentrate (C) is 31.4 mL at 427.091 Bq/mL. The tritium content is in reasonable agreement using $F = P + C$, since the analytical error for this series was about 3.4%. Experiments with deuterium oxide will be presented to confirm this type of membrane separation. The error for this series was 11.1 Bq/mL.

Table 1. Separation of HTO with Poly[bis(phenoxy)phosphazene] Membrane in an Amicon Stirred Cell at 7°C and 0.14 MPa

<u>Sample #</u>	<u>Volume (mL)</u>	<u>Bq/mL</u>
Standard		376.216
1	2.2	383.320
2	2.3	383.764
3	1.7	321.493
4	2.0	335.812
5	1.7	364.968
6	2.0	275.909
7	1.9	291.301
8	1.6	302.808
9	1.6	307.692
10	1.6	372.664
Membrane Top 11	31.4	427.091

Table 1. Separation of HTO with Poly[bis(phenoxy)phosphazene] Membrane in an Amicon Stirred Cell at 7°C and 0.14 MPa

A number of experiments were conducted with the Desal Pilot Cell unit (single pass) with two polyphosphazene membranes. HTO depletion was generally found to occur in the 7-10% range for both PN_x and $PN_x(10\%CO_2H)$ at 5-6°C and 0.33 MPa. However, the sample size was 1 L for these experiments rather than sequential 2 mL aliquots.

The reverse-osmosis concept was utilized to prepare a preliminary design for a membrane system to remove tritium from contaminated water contained in the K-East Basin at the Hanford Site. A cost estimate was generated using the preliminary design. The assumptions for the preliminary design and costs included a tapered design (cascade), 40% depletion of tritium per pass, final permeate must be less than 740,000 Bq/L, and the processing of the basin water to be completed within 2 years. The HTO treatment facility was estimated to have a capital cost of \$600,000 with an operating cost of \$100,000/y. If it is necessary to operate at low temperature (4°C), the capital cost of a chiller system would be \$200,000 with an operating cost of \$100,000/y.

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