U.S. Department of Energy
Hanford Site

22-AMRP-000878 March 24, 2022

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Addressees:

EVALUATION OF TRITIUM REMOVAL AND MITIGATION TECHNOLOGIES FOR WASTEWATER TREATMENT DOE/RL-2022-09, REVISION 0, AND HANFORD FEDERAL FACILITY AGREEMENT AND CONSENT ORDER (TRI-PARTY AGREEMENT) MILESTONE M-026-07D

This letter transmits the 2022 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment, DOE/RL-2022-09, Revision 0, thereby completing Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) Milestone M-026-07D, due March 31, 2022.

If you have any questions, please contact me, or your staff may contact Mark French, Director, Project and Facilities Division, on (509) 373-9863.

Sincerely,

Thomas K Teynor for

William F. Hamel, Assistant Manager
for the River and Plateau

AMRP:MSF

Attachment

cc: See page 2

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Attachment
22-AMRP-000878

2022 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment
DOE/RL-2022-09 Revision 0

(27 pages including cover sheet)

DOE/RL-2022-09
Revision 0

2022 EVALUATION OF TRITIUM REMOVAL AND MITIGATION TECHNOLOGIES FOR WASTEWATER TREATMENT

Date Published
March 2022

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

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Executive Summary

This report contains the 2022 update evaluation of alternative tritium mitigation techniques to control tritium in liquid effluents and groundwater at the Hanford Site. A literature review was completed and updated information is provided on the latest technology developments for control of tritium in wastewaters. This report was prepared to satisfy Tri-Party Agreement (Ecology et al., 1989, *Hanford Federal Facility Agreement and Consent Order*[1]) Milestone M-026-07D. Tritium separation and isolation technologies are evaluated periodically to determine their feasibility for implementation to control Hanford Site liquid effluents and groundwaters to meet the 40 CFR 141.66, "National Primary Drinking Water Regulations,"[2] drinking water maximum contaminant level for tritium of 20,000 pCi/L and/or DOE O 458.1, *Radiation Protection of the Public and the Environment*[3] as low as reasonably achievable policy.

This report provides the latest tritium removal technology developments for the 2015 to 2021 period. Since the 2014 evaluation (DOE/RL-2014-10, *2014 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*)[4], there are five developments related to tritium separation and control with potential application in mitigating tritium contaminated wastewater. These developments include the existing Modular Detritiation System (MDS®) and two new novel approaches using graphene oxide and zeolite membranes. There are also developing technologies in advanced water distillation and nano filtration.

Since 1995, a state-approved land disposal site has received tritium-contaminated effluents from the Hanford Site Effluent Treatment Facility.

[1] Ecology, EPA, and DOE, 1989, *Hanford Federal Facility Agreement and Consent Order*, 2 vols., as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington. Available at: https://www.hanford.gov/page.cfm/TriParty/TheAgreement.

[2] 40 CFR 141, "National Primary Drinking Water Regulations," *Code of Federal Regulations*. Available at: https://www.ecfr.gov/current/title-40/chapter-I/subchapter-D/part-141.

[3] DOE O 458.1 Chg 3, 2011, *Radiation Protection of the Public and the Environment*, U.S. Department of Energy, Washington, D.C. Available at: https://www.directives.doe.gov/directives-documents/400-series/0458-1-border-admc3/@@images/file.

[4] DOE/RL-2014-10, 2014, *2014 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0086036.

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Tritium in this effluent is mitigated by storage in slow-moving groundwater to allow extended time for radioactive decay before the water reaches the Columbia River site boundary. By this method, tritium in the state-approved land disposal site is isolated from the general environment and human contact until it has decayed to acceptable drinking water standard levels.

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Terms

ALPS	Advanced Liquid Processing System
CECE	combined electrolysis catalytic exchange
DOE	U.S. Department of Energy
DWS	drinking water standard
ETF	Effluent Treatment Facility
IAEA	International Atomic Energy Agency
LTA	Linde Type A zeolite
MDS	Modular Detritiation System
PNNL	Pacific Northwest National Laboratory
SALDS	state-approved land disposal site
TRA	Technical Readiness Assessment
TRL-6	Technology Readiness Level 6

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Elements and Compounds

D_2O	deuterium oxide (heavy water)
GOx	graphene oxide
H_2	hydrogen gas
H_2O	water (light water-protium oxide or protinated water)
HDO	deuterated water
HTO, T_2O	tritiated water
K	potassium
N_2	nitrogen gas
Na	sodium
O_2	oxygen gas
SAPO-34	silica alumino phosphate

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1 Introduction

Tritium was generated as a product and a byproduct in reactor fuel at the Hanford Site by the U.S. Defense Program in nuclear reactor operations from 1944 to 1989. The bulk of this tritium was released to the ground from reprocessing facilities in the 200 Area Central Plateau in the form of tritiated waste in process condensate. Releases to the ground have greatly decreased since the last fuel was processed through the fuel separations plant in 1989. Tritium inventories remain in the Hanford Site groundwater and in the underground waste storage tanks, 100-KW Basin water, and waters stored at the 200 East Area Liquid Effluent Retention Facility. Concentrations of tritium in Hanford Site groundwater continue to decline as a result of natural decay and dispersion. Tritium decays with a 12.3-year half-life into helium.

The *Hanford Site Groundwater Monitoring Report* (e.g., DOE/RL-2020-60) describes the monitoring results for *Resource Conservation and Recovery Act of 1976* treatment, storage, and disposal units; *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* groundwater operable units; and *Atomic Energy Act of 1954* requirements. The U.S. Department of Energy (DOE) operates an extensive groundwater monitoring program at the Hanford Site, collecting thousands of samples from hundreds of wells each year. The latest report issued in September 2021 reported the monitoring results for 2020 (DOE/RL-2020-60). This report shows that concentrations of tritium are declining in many of the River Corridor and Central Plateau wells as the plumes attenuate naturally by radioactive decay and dispersion.

Since 1995, a state-approved land disposal site (SALDS) has received effluents from the Hanford Site Effluent Treatment Facility (ETF) (Figure 1). Most of the tritium discharged to the SALDS from 2015 to 2020 came from the K Basins wastewater, 242-A Evaporator process condensate, and treated pump and treat groundwater streams. Discharge to the SALDS allows natural radioactive decay to reduce tritium content as it migrates in groundwater before entering the Columbia River.

The numerical groundwater flow and contaminant transport model of the SALDS tritium plume was last updated in fiscal year 2018 (RPP-RPT-61178, *Results of Tritium Tracking and Groundwater Monitoring at the Hanford Site 200 Area State Approved Land Disposal Site, Fiscal Year 2018*). The model included tritium migration and fate predictions based on both the latest calibration of the groundwater model and the latest information regarding the forecast operation of the 200 West Area pump and treat system.

The modeling results showed that some locations along the northern margin of the 200 West Area are expected to exhibit measurable concentrations of SALDS-derived tritium by the year 2030, although the model indicates that concentrations would be below the drinking water standard (DWS) of 20,000 pCi/L. The eastern end of the tritium plume is also predicted to migrate to the south toward the 200 West Area pump and treat extraction wells by 2030. The maximum tritium concentration in the SALDS proximal wells in 2015 to 2021 was 60,300 pCi/L. As of 2020, tritium from the SALDS has not been detected in any of the tritium-tracking wells, although several wells have had increased tritium concentrations due to reinjection of effluent from the 200 West Area pump and treat system.

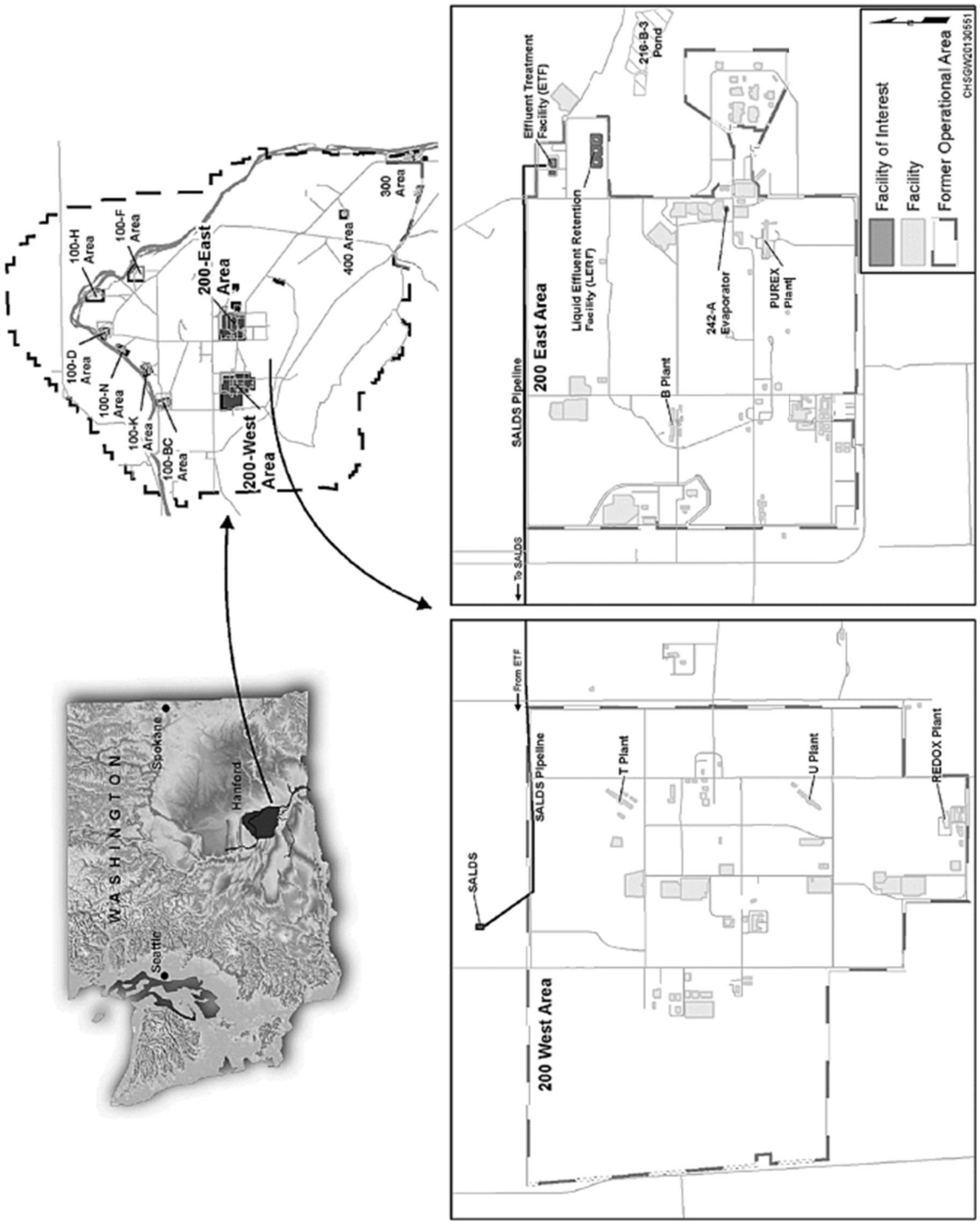

Figure 1. Location of the SALDS

Currently, the chosen alternative for handling tritium in the ETF effluent is to discharge this water to the subsurface at the SALDS and allow the tritium to decay into nonradioactive helium before it reaches the Columbia River. This pump and recharge (or soil column discharge) concept is discussed in the previous 2014 update report (DOE/RL-2014-10, *2014 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*). Although it would be desirable to have an alternative process that could actively separate tritium from water in the environment, the much larger cost-to-benefit ratio makes this approach unrealistic. Therefore, currently discharge to the subsurface is the only cost-effective method to handle tritium in feed to the ETF (Ecology, 2014, *State Waste Discharge Permit Number ST0004500).*

Under the 200-ZP-1 record of decision (EPA et al., 2008, *Record of Decision, Hanford 200 Area, 200-ZP-1 Superfund Site, Benton County, Washington*), which specifies operation of the 200 West Area pump and treat system as the selected remedy for removal of contaminants from groundwater, the preferred alternative for tritium treatment is monitored natural attenuation.

In 1991, the DOE Richland Operations Office (Site Technology Coordination Group) issued a notice of the need to reduce tritium concentrations in Hanford Site wastewaters from 2 to 3 million pCi/L to less than 20,000 pCi/L (DOE/RL-98-01, *Hanford Science and Technology Needs Statements, 1999*). *Fiscal Year 1999 Waste Tank Science Need* (RL-WT047-S) was issued that required identification of viable processes for reducing tritium concentrations in Hanford Site wastewaters.

This current report is one in a series of the following documents concerning new developments in tritium mitigation technologies:

- DOE/RL-94-77, *Tritiated Wastewater Treatment and Disposal Evaluation for 1994*, provided an initial evaluation of tritium treatment and disposal options
- DOE/RL-95-68, *Tritiated Wastewater Treatment and Disposal Evaluation for 1995*
- DOE/RL-97-54, *1997 Evaluation of Tritium Removal and Mitigation Technologies for Hanford Site Wastewaters*
- DOE/RL-99-42, *1999 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*
- DOE/RL-2001-33, *2001 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*
- DOE/RL-2004-11, *2004 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*
- DOE/RL-2009-18, *2009 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*
- DOE/RL-2014-10, *2014 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment*

This current report provides an update of developments in tritium removal and mitigation technology since the 2014 document update (DOE/RL-2014-10). The earlier reports should be consulted for additional background information that is not repeated herein. In addition to these documents, letters providing annual updates on tritium removal technology developments were submitted to state and federal regulators from 2010 to 2018. This current report includes technology development information provided in attachments to the 2015 to 2018 letters.

2 Tritium Removal and Mitigation Technology Developments

This report is a periodic review by DOE of tritium mitigation, with particular applicability and reference to the tritium-contaminated groundwater in the Central Plateau. As stated in DOE/RL-2014-10:

Tritium separation and isolation technologies are evaluated periodically to determine their feasibility for implementation to control Hanford Site liquid effluents and groundwaters to meet the 40 CFR 141.661 drinking water maximum contaminant level for tritium of 20,000 pCi/L and/or DOE Order 5400.52 as low as reasonably achievable policy.

There are few recent developments in tritium remediation techniques. Much of the relevant literature over the past 30 years focuses on methodology used in separation of hydrogen isotopes in heavy water, combined with electrolysis catalytic exchange (CECE), while other techniques have been assessed with various levels of success and applicability. A summary of tritium removal and mitigation technologies is presented in Table 1. The status of maturity and applicability of each technology listed is shown in relation to each of the updated reports dating back to 1994. This report discusses those technologies that have had developments since the 2014 update (shaded in blue in Table 1). The status of maturity and applicability for all other technologies discussed in previous reports have not changed from the 2014 report (last column of table). Except for the soil column discharge concept, the technologies listed cannot reasonably be applied on the scale required to address Hanford Site tritium contamination in liquid effluents and groundwater. At the Hanford Site, treated effluent containing tritium is discharged to the soil column via the SALDS.

Table 1. Summary of Tritium Removal and Mitigation Technologies

Technology	Year Report Prepared							
	1994	1995	1997	1999	2001	2004	2009/ 2014	2022
Distillation	D, h	--	D, h	D, h	D, h	D, h	D, h	D, h
Gaseous diffusion	D, h	--	--	--	--	--	--	--
Laser isotope separation	T, h	T, h	T, h	--	--	--	--	--
Electrolysis	D, h	D, h	D, h	--	--	--	--	--
Combined electrolysis and catalytic exchange	D, h	D, h T, l	D, h T, l	D, h T, l	D, h T, l	D, h T, l	D, h T, l	D, h T, l
Combined electrolysis catalytic exchange with vapor phase catalytic exchange	--	--	--	--	D, h	--	--	--
Membrane separation process	T, l	T, l	T, l	--	--	--	--	See note[a]
Cryogenic distillation	D, h	D, h	D, h	D, h	D, h	--	--	See note[a]
Bithermal catalytic exchange	--	D, h T, l	--	D, h T, l	D, h T, l	D, h T, l	D, h T, l	D, h T, l

Table 1. Summary of Tritium Removal and Mitigation Technologies

Technology	Year Report Prepared							
	1994	1995	1997	1999	2001	2004	2009/ 2014	2022
Isotopic exchange, air sparge	--	T, l	--	--	--	--	--	--
Finely divided nickel catalyst	--	O	--	--	--	--	--	--
Separation by Metanetix, Inc.	--	O	--	--	--	--	--	--
Substituted naphthalene	--	O	--	--	--	--	--	--
Crown ether complexes	--	O	--	--	--	--	--	--
Girdler-sulfide process	--	--	D, h	D, h	D, h	D, h	D, h	D, h
Palladium Membrane Reactor	--	--	--	--	--	--	D, h	D, h
GE® Integrated Systems[b]	--	--	--	--	--	--	D, h	D, h
Liquid phase catalytic exchange with solid oxide electrolyte	--	--	D, h	D, h T, l	D, h T, l	--	--	--
Liquid phase catalytic exchange with high-temperature steam electrolysis (Hot Elly)	--	--	D, h	--	--	--	--	--
Sulfur resin ion exchange	--	--	O	--	--	--	--	--
Metal hydride exchange	--	--	T, h	--	--	--	--	--
Soil column discharge	D, l, h	--	D, l, h	D, l, h	D, l, h	D, l, h	D, l, h	D, l, h
Barrier formation	--	--	O	D, l, h	D, l, h	D, l, h	D, l, h	D, l, h
Air sparging	--	--	T, l		--	--	--	--
Dual-temperature liquid-phase catalytic exchange	--	--	--	D, h	--	--	--	--
Tritium resin separation process	--	--	--	T, l	T, l	T, l	T, l	T, l

Table 1. Summary of Tritium Removal and Mitigation Technologies

Technology	Year Report Prepared							
	1994	1995	1997	1999	2001	2004	2009/ 2014	2022
Kinetic-isotope effect for concentrating tritium	--	--	--	T, l	T, l	--	--	--
Pumping and recharging	--	--	--	D, l	D, l	D, l	D, l	D, l
Phytoremediation	--	--	--	--	D, l	D, l	D, l	D, l
Evaporation	--	--	--	--	--	D, l	D, l	D, l
Modular Detritiation System (MDS®)[c]	--	--	--	--	--	--	--	--
Graphene oxide (GOx) laminar membrane separation	--	--	--	--	--	--	T, l, h	T, l, h
Zeolite membrane separation	--	--	--	--	--	--	--	T, h
Advanced Water Distillation	--	--	--	--	--	--	--	T, l, h
Nano filtration	--	--	--	--	--	--	--	T, h

a. Specific technologies using this treatment method are provided in the table.

b. GE® is a registered trademark of the General Electric Company.

c. MDS® is a registered trademark of Kurion, Inc.

D = Demonstrated or developed technology that has been successfully applied in the field

T = Testing or theoretical stage of development

O = Observation indicates a potential process needing funding to continue

Applicability:

l = Technology is applicable to larger wastewater volumes having lower levels of tritium (less than 1.0E-05 Ci/L)

h = Technology is applicable to smaller wastewater volumes having higher levels of tritium (greater than 1.0E-05 Ci/L)

2.1 Modular Detritiation System

The Modular Detritiation System (MDS®) was developed by Kurion, Inc. in 2013 as a tritium removal technology based on advancements in the CECE process modified for light water detritiation. The method flows light tritiated water through a liquid phase catalytic-exchange column flushed with deionized water, sorbing the tritium on a proprietary metal hydride.

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The MDS is a viable technology for tritium removal in high-volume, low-concentration waste streams, providing a low energy, low-cost alternative to the conventional CECE tritium removal technology. The MDS technology releases only clean oxygen gas (O_2) and hydrogen gas (H_2) with no liquid effluent.

The MDS uses a modular approach and allows for a flexible design to meet various facility sizes and processing needs (Whitcomb et al., 2017, "A Tritium Management Tool for Light Water Detritiation"). The modular approach uses commercially available equipment to deliver a factory quality and plug and process system, which minimizes impact to ETF operations. The modular system allows for operation over a wide range of tritium concentrations and flow rates.

2.1.1 Modular Detritiation System – Process Description

The MDS applies CECE to concentrate tritium in a reduced volume of water while producing clean hydrogen and oxygen gases. Tritiated water is converted to tritiated hydrogen gas using an electrolyzer. Oxygen produced by the electrolyzer is dried and released to the environment while the tritiated hydrogen gas is fed to a liquid phase catalytic exchange column. Isotopic exchange occurs in the liquid phase catalytic exchange column where hydrogen gas flows from the bottom to the top of the column and is released to the environment (Figure 2).

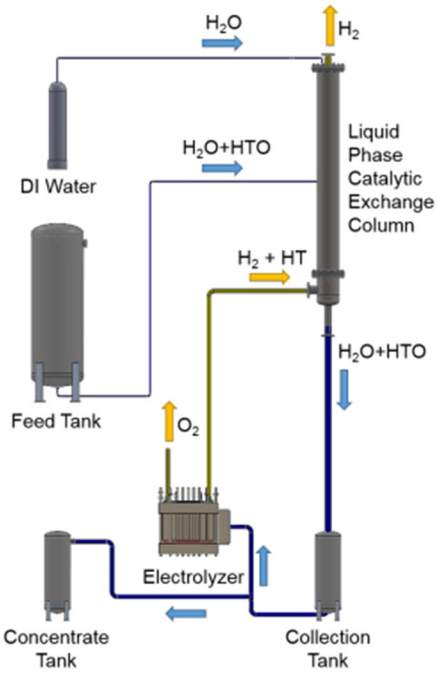

Figure 2. Simplified Diagram of the CECE System

2.1.2 Modular Detritiation System – Recent Developments

The MDS was fully licensed and permitted in March 2016 and passed acceptance testing. Veolia Nuclear Solutions built a full-scale prototype and operated the MDS at its Richland, Washington, tritium facility. The system was designed and developed in response to a potential application to water decontamination at the Fukushima Daiichi Nuclear Power Plant (hereinafter called the Fukushima Plant) in Japan. In 2020, it was determined that the only practical solution to deal with large, stored volumes of treated wastewater containing tritium at the Fukushima Plant was to release it into the Pacific Ocean (Normile, 2021, "Japan Plans to Release Fukushima's Wastewater into the Ocean").

The MDS technology was not going to be used to separate tritium from more than 560,000 tons of radioactive wastewater stored in nearly 1,000 steel vessels.

The MDS was tested under the internationally recognized Technical Readiness Assessment (TRA) in December 2016, achieving a Technology Readiness Level 6 (TRL-6) (Veolia Nuclear Solutions, 2016, "Veolia Nuclear Solutions' Prototype Tritium-Removal System Surpasses International Readiness Benchmark for Commercial Use"). TRL-6 is a National Aeronautics and Space Administration/Department of Defense TRA model adopted by the DOE Office of Environmental Management for evaluating technology maturity that includes a structured, criteria-based, and clearly documented assessment.

TRL-6 is a laboratory-scale demonstration of a representative prototype system that includes testing a prototype with real waste and a range of simulants. TRAs are procurement tools used to assess the commercial viability of promising new technology and have been modified for nuclear applications by the United States. TLR-6 status implies the technology performed successfully in engineering-scale testing and is now reliably ready for deployment in commercial applications. According to Veolia Nuclear Solutions marketing literature, the MDS, with its modular design, is easily scalable to achieve greater processing capacities, from just a few cubic meters per day to 400 m^3/day (about 75 gpm) and higher.

2.1.3 Modular Detritiation System – Application at the Hanford Site

The MDS was operated for over 1,000 hours during a 9-month period at Veolia Nuclear Solution's tritium facility in Richland, Washington. The status of the technology has not changed since the 2016 TRA (Veolia Nuclear Solutions, 2016). The MDS would require significant modification, and the current prototype is not designed to meet the flow requirements or detritiation factors necessary for use at the Hanford Site. Operating costs and actual tritium removal rates have not been released by Veolia Nuclear Solutions. However, a news release published in the December 2014 issue of *Science* (Normile, 2014, "The Trouble with Tritium") quoted a cost estimate of $1 billion to concentrate all of the Fukushima Plant's tritium-contaminated wastewater into 5 cubic meters of water. With 560,000 tons of wastewater to treat, the cost per liter of Fukushima Plant wastewater would be approximately $2/L.

Cost information is not available on the MDS Veolia Nuclear Solutions technology[1], although it is unlikely to be cost effective with the passive approach of tritium decay in slow-moving groundwater currently in effect at the Hanford Site. Eventual discharge to the Columbia River of the tritium-contaminated groundwater is predicted to be well below drinking water standards, having achieved sufficient decay to innocuous levels over a period of 10-12 half-lives (tritium half-life is 12.3 years).

2.2 Graphene Oxide Membrane Separation

This concept uses graphene oxide (GOx) laminar membranes for separating low concentration, tritiated water so that the cleaned water can be released to the environment. The GOx membranes represent a new class of materials and consist of hierarchically stacked, overlapping molecular layers. The purpose of this cleanup concept is to remove low concentrations of tritium from large volumes of water contaminated with tritium.

[1] In 2021, Veolia merged with SUEZ, and continues to provide water treatment services throughout North America and elsewhere under the tradename Veolia North America.

2.2.1 Graphene Oxide Membrane Separation – Process Description

The GOx laminate materials provide diffusion path lengths approximately 10,000 times the membrane thickness. The GOx materials also have high proton conductivity because of its hydrophilic oxygenated nature. Research by Nair et al., (2012) and Pacific Northwest National Laboratory (PNNL) demonstrated that GOx laminar membranes do not leak most gases but can transport water vapor. Ongoing research is to understand and control the transport mechanism through the membrane. Water vapor is not transported through the membrane by simple diffusion but by molecular selectivity from water vapor molecules proton hopping between the membrane laminas. Based on the premise that transport through the membranes is regulated by forming and breaking of O-H bonds, the relative frequency of molecular hopping can be controlled, and isotope selectivity between tritiated water and molecular water can be achieved.

2.2.2 Graphene Oxide Membrane Separation – Recent Developments

The feasibility of separating water using GOx membranes was demonstrated by studying the relative transport of water (H_2O), deuterium oxide (D_2O), and tritium water (HTO) using different methods. These methods were studied by PNNL and Kurion (PNNL-24411, *Separation of Tritiated Water Using Graphene Oxide Membrane*) and are as follows:

- Estimate the relative transport rate by measuring the mass loss of GOx membrane containers of H_2O, D_2O, and HTO, and by using mixtures of the isotopic concentrations of the remaining liquids.
- Quantify the relative permeability of H_2O and D_2O using an existing membrane test system.
- Determine separation efficiency for the hydrogen isotopes using a modified distillation system.
- The relative transport rate was determined using three different thicknesses for each membrane tested. Each GOx membrane was fitted onto a 20 mL glass vial, which was loaded with 10 g of D_2O, H_2O, and a D_2O/ H_2O mixture. The results showed that H_2O transported faster than D_2O for all the membranes tested. The average separation factor based on permeation rate of the D_2O to H_2O and mixture to H_2O ratios ranged from 0.87 to 0.93.

The relative permeability of H_2O and D_2O was tested with a 2 μm thick cast Asbury membrane using mixed gas with zero air and with air humidified with either H_2O or D_2O to a nominal 50% relative humidity. The relative permeability for H_2O and D_2O was high with nitrogen gas (N_2) and O_2 gases. The H_2O vapor permeation rate was 5.9×10^2 cc/m^2/min and the D_2O permeation rate ranged between 1.1×10^2 and 2.4×10^2 cc/m^2/min.

Isotopic water separation efficiency through GOx laminar membranes was determined by heating the isotopic water mixture on one side of the membrane to create steam while cooling the other side. Several membrane materials were tested using different pretreatment methods. The average separation efficiency was 80% for D_2O and 60% for HTO.

2.2.3 Graphene Oxide Membrane Separation – Application at the Hanford Site

The GOx membranes tested for purifying low-concentrated tritiated waters have the potential to reduce energy consumption compared to conventional technologies, such as combined CECE. The GOx membrane approach is estimated to use between 2.3 and 4.5 kW · hr/L of water treated and the CECE approach is estimated to use between 7.2 and 8.45 kW · hr/L, which represents annual energy savings of about one-half to one-third. However, the cost element for the facility design, fabrication, and land area is significantly higher than for a comparable CECE system.

The combined annual energy operating and capitalization costs for treating tritiated water using GOx membranes is estimated to range from $60/L to $180/L for high removal capacities, compared to $2/L to $20/L for the combined costs of the CECE system.

The GOx membrane-based water separation technology is primarily focused on cleanup of tritiated water at nuclear fuel reprocessing plants. The GOx separation technology can treat tritiated water in the concentration range of 10^{-3} to 10 μCi/g (PNNL-24411). This concentration range equates to 1E+6 to 1E+10 pCi/L, which is approximately one to five orders of magnitude higher than maximum tritium concentrations currently in liquid effluent and groundwater at the Hanford Site. Separation of tritium from low-concentration wastewater discharged at the SALDS using the GOx membrane technology is not economically viable compared to the cost using conventional technologies such as the CECE system.

2.3 Zeolite Membrane Separation

A novel separation approach uses molecular sieve zeolite membranes capable of preferentially removing tritium from high-volume dilute tritium-bearing aqueous streams. One type of membrane, silica alumino phosphate (SAPO-34) layered on porous alumina supports, can separate tritium by taking advantage of the differences in the rates of adsorption, molecular weight, and kinematic diameter of the molecules being separated. The membrane system is claimed to be relatively easy to fabricate and scalable to handle large-volume dilute streams with low operating cost. Separation and concentration of tritium at ambient temperature and low pressure are low-cost operating features using molecular sieve zeolite membranes.

2.3.1 Zeolite Membrane Separation – Process Description

SAPO-34 is a neutral uncharged zeolite material. The self-diffusion of H_2O (water), HDO/D_2O (heavy water), and HTO/T_2O (tritiated water) can be significantly modified in cation exchanged zeolite or molecular sieve sorbents. Tritium is separated by taking advantage of the differences in adsorption and diffusion rates using cation exchanged zeolite molecular sieve membranes. These concepts can be extended to the use of ion-exchanged Linde Type A zeolite (LTA) membranes as an alternative to SAPO-34 zeolite membranes. LTA zeolites provide superior cation exchange capacity relative to the SAPO-34 materials, potentially increasing HTO permeance and selectivity.

2.3.2 Zeolite Membrane Separation – Recent Developments

Research was performed in two phases: the first phase using SAPO-34 zeolite membranes and the second phase using LTA zeolite membranes. In the first phase of the study, pervaporation experiments with SAPO-34 zeolite membranes were conducted for separating HTO and HDO from H_2O (ORNL/TM-2016/99, *Tritium Separation from High Volume Dilute Aqueous Streams*; and ORNL/TM-2016/248, *Synthesis and Performance Evaluations of SAPO-34 Membranes for the Separation of Tritiated Water*). The separation factor ranged from 0.83 to 0.98 for separating HTO from water and high separation factors were obtained for deuterated water.

In the second phase of the study, LTA zeolite ion-exchange membranes were evaluated as alternatives to the SAPO-34 zeolite membranes (ORNL/SR-2017/459, *Performance Evaluations of Ion Exchanged Zeolite Membranes on Alumina Supports*). Sodium and potassium exchanged LTA zeolite membranes were synthesized on flat disk and tubular alumina supports and the pervaporation process performance was evaluated for separating and concentrating the tritiated water. Several different SAPO-34 membranes were also fabricated and tested for HTO/H_2O separation. The study found that potassium-LTA membranes performed better than the SAPO-34 zeolite membranes and had a separation factor ranging from 1.3 to 2.79. This range compares to the separation factor range of 0.83 to 1.023 for the SAPO-34 zeolite membranes.

Two key performance metrics for the separation of tritiated water are selectivity and vapor permeance. Higher selectivity for HTO over H_2O has a major impact on the separation efficiency. Selectivity of LTA zeolite membranes on disk supports ranged from 0.80 to 0.95 and on tubular supports ranged from 1.07 to 2.33. This compares to a selectivity range of 0.99 to 1.23 for the SAPO-34 membranes.
Vapor permeance is also essential for economic viability because it has a greater impact on the system size and cost. The total vapor permeance in the potassium-LTA membrane was measured to be an order of magnitude higher than in the SAPO-34 membranes. Vapor permeance of tubular zeolite membranes is two to four times higher compared to vapor permeance of disk membranes. With the high permeance LTA membrane and molecular sieving, it is conceivable a multistage cascade system separating tritiated water from high-volume dilute aqueous solutions would be cost effective.

2.3.3 Zeolite Membrane Separation – Application at the Hanford Site

A membrane-based separation system for removing tritium from liquid effluents and groundwater is not economically viable. An important requirement for economic viability is high permeance to deliver a high throughput and process efficiency. Permeance of HTO and H_2O is a critical measure that will affect the capital and operating cost.

While membrane separation for removing tritium from wastewater has become a focus of recent development and testing, this technology focuses on small volumes of waste streams with heavy tritium contamination, such as nuclear fuel process water. The membrane separation technology can handle HTO concentration in the range of 200 to 1000 Ci/m^3 (ORNL/TM-2016/99). This concentration range equates to 2E+11 to 1E+12 pCi/L, which is approximately six to seven orders of magnitude higher than maximum tritium concentrations currently in liquid effluent discharged at the SALDS. Zeolite membrane separation has not been proven successful for separating tritium from high-volume, low-concentration wastewater that exists at the Hanford Site.

2.4 Advanced Water Distillation

Canadian company Laker TRF has developed a technology referred to as Advanced Water Distillation, with 80% less energy consumption than conventional water distillation (*World Nuclear News*, 2019, "Canadian Technology Offers Fukushima Tritium Option"). Laker TRF has a demonstration plant in Oakville, Ontario, and a larger multicolumn plant to be developed in Cambridge, Ontario.[2]
The technology relies on the vapor pressure differences of the isotopologues. As with the Veolia Nuclear Solutions MDS, Laker TRF targeted the Fukushima Plant liquids in storage that had most radioactive contaminants removed, with the exception of tritium. A byproduct of the Laker TRF distillation process is the stable heavy isotope oxygen-18, used in the radiopharmaceutical industry.

The Advanced Water Distillation technology is unlikely to be deployed at the Fukushima Plant, given recent news reports on likely tritium release to the ocean (NTV News 24, 2021a; 2021b). The Tokyo Electric Power Company, owner of the Fukushima Plant, issued an International Atomic Energy Agency (IAEA)-supported position in December 2021 (IAEA 2021) that the company will be releasing the stored tritiated water to the ocean for dilution, apparently with IAEA oversight. The release of the stored water after treatment in the Advanced Liquid Processing System (ALPS) to remove other contaminants is the recently published resolution to the storage of large volumes of tritiated water in tanks at the Fukushima Plant.

[2] The parent company, Laker Energy Products Ltd., was acquired by BWXT in early 2020 with the Laker TRF technology likely included in the acquisition. Inquiries to BWXT remain unanswered to date.

2.5 Nano Filtration

As reported in *The Mainichi*, 2018, "Researchers Develop Technology to Remove Radioactive Tritium from Water," researchers at Kindai University, Japan, in conjunction with Toyo Aluminum K.K. and other private companies, have developed an aluminum filter with extremely tiny holes, 5 nanometers or less in diameter. The filter can trap vapors of tritium water, with a relatively high separation rate of almost 100% (*The Mainichi*, 2018). The researchers projected the technology would be used eventually in processing tritium-contaminated water stored at the Fukushima Plant.

Similar to the Advanced Water Distillation technology, the nano-filter developed in Japan is unlikely to be deployed at the Fukushima Plant, given recent news reports on likely tritium release to the ocean (NTV News 24, 2021a; 2021b).

2.6 Relative Cost Considerations of Mitigation Options

Relative costs of mitigation options for treating tritium in Hanford Site wastewater can vary substantially, depending on the technical process option selected and on site-specific factors and project objectives. Available cost information was not developed for specific Hanford Site wastewater treatment scenarios because this is not the scope of this technology development update. To develop accurate cost estimates, engineering studies would need to be performed to estimate facility size, energy consumption, and capital and operating costs. Cleanup goals would need to be defined and applicable state and federal requirements must be considered for treating tritiated wastewater and, if necessary, for disposing of the concentrated effluent. Despite this scope limitation, some general comments comparing tritium mitigation approaches and relative costs are summarized in Table 2. These mitigation approaches are compared relative to the current operating approach used at the Hanford Site, which is radioactive decay and groundwater dispersion at the SALDS.

Table 2. Comparison of Tritium Mitigation Approaches

Mitigation Approach	Technology	Efficiency	Cost Information	Comments
Radioactive decay and groundwater dispersion	Soil column discharge to slow-moving groundwater	Efficiency determined by travel time to release point; models predict acceptable efficiency for SALDS	Cost expected to be in the cents per gallon range for disposing of large volumes over long periods of time	Current approach at SALDS on the Hanford Site
Separation treatment	Modular Detritiation System	Advancements in the CECE system to concentrate tritium in a reduced volume of water	On the order of ~$2/L (~$8/gal) based on estimates for the Fukushima Plant	Fully licensed and permitted and achieved TRL-6 status for deployment in commercial applications
Separation treatment	Graphene oxide membrane	Average separation efficiency is 60% for tritiated water	Range of $60/L to $180/L for combined energy consumption and capitalization costs	Suited for treating tritium concentrations higher than that for Hanford Site wastewaters

Table 2. Comparison of Tritium Mitigation Approaches

Mitigation Approach	Technology	Efficiency	Cost Information	Comments
Separation treatment	Zeolite membrane separation (SAPO-34 and Linde Type A zeolites)	Efficiency determined by selectivity and vapor permeance	No cost information available, but not considered economically viable	Not suitable for treating large volume, low concentration wastewaters at the Hanford Site

CECE = combined electrolysis catalytic exchange
SALDS = state-approved land disposal site
TRL-6 = Technology Readiness Level 6

3 Summary

The MDS technology is the most promising tritium removal technology under development since the 2014 update (DOE/RL-2014-10). A full-scale demonstration of the technology occurred at the Veolia Nuclear Solutions tritium facility in late 2015. In early 2016, the MDS technology passed acceptance testing and was fully licensed and permitted. However, there is no known application of this technology for commercial use. This technology was being considered for treating large volumes of tritium-contaminated wastewater at the Fukushima Plant but was determined not to be a realistic solution. The MDS would require significant modification to meet the flow rate requirements or tritium removal rates necessary for use on a large scale at the Hanford Site.

Other tritium removal technologies that have received attention include the use of GOx and zeolite membranes. These membrane technologies primarily focus on separating tritium from wastewater produced at nuclear fuel processing plants. The GOx membranes have the potential to treat large volumes of low concentration tritiated waters at reduced energy consumption compared to conventional technologies. However, energy use combined with capitalization costs for facility design, fabrication, and land area are significantly higher. SAPO-34 and LTA zeolite membranes are novel approaches that have been studied recently for their potential for separating tritium from contaminated water. GOx and zeolite membranes are currently not economically viable for treating large volumes of tritiated water efficiently at the Hanford Site.

Advanced Water Distillation and nano filtration are two new technologies developed and targeted for treating tritium at the Fukushima Plant in recent years. However, it is unlikely these technologies will be deployed at the Fukushima Plant.

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