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2001 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management
Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

United States Department of Energy
P.O. Box 550
Richland, Washington 99352

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COGEMA Engineering Corporation

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ABSTRACT

This report contains the 2001 biennial update evaluation of separation technologies and other mitigation techniques to control tritium in liquid effluents and groundwater at the Hanford site. A thorough literature review was completed, and national and international experts in the field of tritium separation and mitigation techniques were consulted. Current state-of-the-art technologies to address the control of tritium in wastewaters were identified and are described. This report was prepared to satisfy the Hanford Federal Facility Agreement and Consent Order *(Tri-Party Agreement) Milestone M-29-05H (Ecology, EPA, and DOE 1996). Tritium separation and isolation technologies are evaluated on a biennial basis to determine their feasibility for implementation for the control of Hanford site liquid effluents and groundwaters to meet the* U.S. Code of Federal Regulations *(CFR), Title 40 CFR 141.16, drinking water maximum contaminant level (MCL) for tritium of 0.02 μCi/l (~2 parts per quadrillion [10^{-15}]) and/or DOE Order 5400.5 as low as reasonably achievable (ALARA) policy.*

The objectives of this evaluation were to (1) status the development of potentially viable tritium separations technologies with regard to reducing tritium concentrations in current Hanford site process waters and existing groundwater to MCL levels and (2) status control methods to prevent the flow of tritiated water at concentrations greater than the MCL to the environment. Current tritium releases are in compliance with applicable U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy requirements under the Tri-Party Agreement.

Advances in technologies for the separation of tritium from wastewater since the 1999 Hanford Site evaluation report include: (1) construction and testing of the Combined Industrial Reforming and Catalytic Exchange (CIRCE) Prototype Plant by Atomic Energy Canada Limited (AECL). The plant has a stage that uses the combined electrolysis catalytic exchange (CECE) and a stage that uses the bithermal hydrogen-water process. The testing is still ongoing at the time of the development of this evaluation report, therefore, final results of the testing are not available; (2) further testing and a DOE sponsored American Society of Mechanical Engineers (ASME) peer review of a tritium resin separations process to remove tritium from wastewaters; and (3) completion of the design of the water detritiation system for the International

Thermonuclear Experimental Reactor (ITER). The system uses a variation of the CECE process, and is designed to process 20 l/hr of feed.

The primary advance in technologies to control tritium migration in groundwater are the implementation of phytoremediation as a method of reducing the amount of tritium contaminated groundwater reaching the surface waters at Argonne National Laboratory, and initiation of a project for phytoremediation at the Savannah River Site.

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LIST OF TERMS

AECL	Atomic Energy of Canada, Limited
BNL	Brookhaven National Laboratory
CECE	Combined Electrolysis Catalytic Exchange
CIRCE	Combined Industrial Reforming and Catalytic Exchange
Deprotinate	To remove light water (H_2O from heavy water (D_2O)
Deuterium	An isotope of hydrogen – the nucleus contains one proton and one neutron
Deuterated water	Water which contains at least one deuterium atom
DOE	Department of Energy
DTLPCE	Dual-temperature liquid-phase catalytic exchange
ETF	Effluent treatment facility
Heavy water	Water that contains 2 deuterium atoms and one oxygen atom
HETP	Height equivalent of a theoretical plate
HLW	High-level Waste
LPCE	Liquid Phase Catalytic Exchange
MCL	Maximum contaminant level
Phreatophyte	A deep-rooted plant that obtains its water from the water table or the layer of soil just above it
Phytoremediation	Remediation using plants to perform the remediation
Protium	Ordinary hydrogen – the nucleus contains only a proton
SALDS	State-Approved Land Disposal Site
SOE	Solid oxide electrolyte
SRS	Savannah River Site
TAWRS	Tritium Aqueous Waste Recovery System
T/D	Tritium/Deuterium
T/H	Tritium/Hydrogen
Tritiated Water	Water that contains 1 tritium atom and one ordinary hydrogen atom
Tritium	A radioactive isotope of hydrogen – the nucleus contains one proton and 2 neutrons. Tritium has a half live of 12.3 years.
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
TRS	Tritium Resin Separation
VPCE	Vapor Phase Catalytic Exchange

SCIENTIFIC SYMBOLS AND ABBREVIATIONS

Units of Measure

Unit	Definition
Ci	curie
µCi	microcurie (10^{-6} curie)
pCi	picocurie (10^{-12} curie)
hectare	10,000 m^2
°K	Kelvin (absolute temperature)
l	liter
m	meter
mm	millimeter (10^{-3} meter)

Elements and Compounds

Hydrogen Isotopes	Atomic Mass
H (^1H) protium	1.008
D (^2H) deuterium	2.014
T (^3H) tritium	3.017

D_2	deuterium molecule
D_2O	deuterium oxide (heavy water)
DT	tritiated deuterium
DTO	tritiated deuterium oxide
H_2	hydrogen molecule
H_2O	water (light water-protium oxide or protinated water)
HD	deuterated hydrogen
HDO	deuterated water
HT	tritiated hydrogen
HTO	tritiated water
T_2	tritium molecule

Elemental Bonds

C-H	carbon-protium bond
C-T	carbon-tritium bond

1.0 INTRODUCTION

Tritium was generated as a by-product 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 fuel reprocessing facilities on the 200 Areas plateau in the form of tritiated water in process condensates. Tritium releases to the ground have greatly decreased since the last fuel was processed through the fuel separations plant in 1989. Tritium in these previously discharged liquid effluents has migrated into the groundwater toward and into the Columbia River. Tritium decays with a 12.3-year half-life, and it is estimated that the tritium inventory at the Hanford site from processed fuel has decayed to about 1.6×10^5 Ci to date (based upon decay from value in 1997 report (Jeppson 1997)).

Significant tritium inventories exist in Hanford site facilities, such as in the underground waste storage tanks, Hanford site spent-fuel storage basin waters, and water stored at the Liquid Effluent Retention Facility. Since 1995, a state-approved land disposal site (SALDS) has received effluents from the Hanford site Effluent Treatment Facility (ETF) that are free of all contaminants except tritium. The tritium comes from process condensates from the 242-A Evaporator when it is processing wastes from underground storage tanks, N Basin water stored at the Liquid Effluent Retention Facility (LERF), and other miscellaneous wastes. Water from fuel-storage basins is expected to be processed through the ETF as part of the Hanford cleanup. If a viable tritium removal process can be identified, evaluation for implementation at Hanford will be recommended.

The SALDS is the prescribed location because it has been determined, by groundwater sample results evaluation and groundwater flow modeling, that the tritium at the 500-pCi/l level or above will extend a maximum horizontal distance of less than 1.5 km from the SALDS location (Barnett et al. 1997). In 1991, the U.S. Department of Energy, Richland Operations Office (Site Technology Coordination Group [STCG]), issued a notice of the need to reduce tritium concentrations in Hanford site wastewaters from 2-3 µCi/l to less than 0.02 µCi/l (RL-MW023, *Technology Needs/Opportunities Statement* [HST 1991]). The goal was to implement the technology in 2004 to correspond with the scheduled startup of the Hanford site high-level waste vitrification process. (See footnote below.[1])

A Hanford site Fiscal Year 1999 *Waste Tank Science Need*, RL-WT047-S (RL 1999), was issued, that called for identification of viable processes for reducing tritium concentrations in Hanford site wastewaters. These wastewaters include (1) pool water from spent-fuel storage basins, (2) Effluent Treatment Facility effluents, and (3) Hanford site groundwaters at the 200 East Area cribs and in the groundwater plume from the 200 East Area to the Columbia River. Each of the spent-fuel storage basins contains 3.8 to 5.8 million liters (1 to 1.5 million gallons) of tritium-contaminated water. Groundwater in the 200 East Area has been sampled and analyzed and was found to have tritium concentrations of up to 3.4 µCi/l near cribs that received

[1] The startup of the HLW vitrification process has been delayed and is now scheduled for hot commissioning in 2008 with start of hot services in 2011 (DE-AC27-01 RV14136, 2001).

process water from the fuel reprocessing facility. The groundwater tritium concentrations near the Columbia River from the old Hanford town site to the 300 Area are at >0.02 μCi/l.

The status of tritium mitigation technology reviews was documented in previous Hanford site reports DOE/RL-94-77 (Allen 1994), DOE/RL-95-68 (Allen 1995), and DOE/RL-97-54, Rev. 0 (Jeppson et al. 1997), and DOE/RL-99-42, Rev. 0 (Jeppson 1999).

This document provides a status of previously identified technologies along with any new technologies. Separation technology development for removal of tritium from wastewaters to meet environmental release limits is being conducted in several countries. Work is currently being done in Canada by Ontario Hydro and Atomic Energy of Canada, Limited (AECL), in Japan by Nagoya University and the Japan Atomic Energy Research Institute, and in the U.S. by MSI, Oak Ridge National Laboratory (ORNL), and at the Savannah River Site.

2.0 REMOVAL AND MITIGATION TECHNOLOGIES FOR TRITIUM IN WASTEWATERS

Tritium separation technologies are split into two areas for discussion. Section 2.1 discusses large-scale industrial processes for separation of hydrogen isotopes from water. Section 2.2 discusses pilot-plant and laboratory-scale processes for separating tritium from protinated water (H_2O). Other tritium mitigation technologies for groundwater are included in Section 2.3.

2.1 HYDROGEN-ISOTOPE SEPARATION TECHNOLOGIES USED BY INDUSTRY ON A LARGE SCALE

Hydrogen-isotope-separation technologies used on an industrial scale include those hydrogen-isotope-separation processes that separate deuterated water (HDO) from H_2O and/or tritiated water (HTO) from HDO. There are no industrial scale processes operating for removing HTO from H_2O.

2.1.1 Water Distillation

Water distillation for separation of HDO from H_2O is a safe and well-established process that has been used on an industrial scale for many years. Water-distillation facilities have operated to deprotinate heavy water in the United States, Canada, and Europe. Water distillation also is used on a large scale to remove HTO from HDO in large-scale industrial applications. Isotope separation by water distillation is based on the differences in vapor pressure for the various waters.

Since the process is relatively simple and well-established, no data was found beyond that given in the 1999 evaluation report, DOE/RL-99-42, Rev. 0 (Jeppson 1999).

2.1.1.1 Process Description. The process was described in detail in the 1999 evaluation report (Jeppson 1999). Therefore, it will not be described in detail again.

2.1.1.2 Application at the Hanford Site. The evaluation in 1999 was based upon a tritium concentration in the water of 2,000,000 pCi/l. However, the latest estimate for the waste from ETF is 5,000,000 pCi/l. And, although the concentration in many of the groundwater sampling wells during Fiscal Year 2000 were about 2,000,000 pCi/l, several wells showed greater contamination, with the worst contamination being approximately 8,300,000 pCi/l (Hartman 2001).

This means the facility would need to be designed to achieve a decontamination factor of approximately 420 rather than 100 to allow the drinking water standards to be met. Note that the increase in column height required to achieve the larger separation factor would significantly increase the cost of the columns.

The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed.

2.1.2 Combined Electrolysis Catalytic Exchange

The combined electrolysis catalytic exchange (CECE) process has a high isotopic separation factor and near-ambient temperature and pressure operating conditions. The CECE process is based on a catalyst-enhanced equilibrium reaction (Eq. 1) that favors the formation of HTO, a type of tritiated water, when liquid H_2O is contacted with tritiated hydrogen (HT) gas (Sienkiewicz and Lentz 1988). The hydrophobic catalyst (platinum coated with Teflon[2]) was developed by AECL and the Chalk River National Laboratory (CRNL).

$$HT\ (g) + H_2O\ (l) \Leftrightarrow HTO\ (l) + H_2\ (g). \qquad (1)$$

This process requires the electrolysis of all feed water plus some deionized water used for stripping (approximately 1.4 times the feed flow is electrolyzed). An early version of this process (Ellis et al. 1982) was used to remove tritiated water from liquid wastewaters to reach discharge-level concentrations of <0.02 μCi/l in the Tritium Aqueous Waste Recovery System (TAWRS) at the U.S. Department of Energy (DOE) Mound Facility.

One type of CECE pilot plant was built and operated in Japan to recover tritium from light water. The plant capacity was 3.6 l/day of feed, and HTO was concentrated by a factor of 10^4 (Isomura et al. 1988). This type of process was used in connection with the FUGEN fusion reactor (located in Japan) for 13 years. A larger version of this plant has been designed for use with the International Thermonuclear Experimental Reactor (ITER), a fusion reactor. The facility will use 2-10 cm diameter columns, and is designed to operate at a feed rate of 20 l/h. The facility location and the construction schedule for the Water Detritiation System for ITER are not finalized at this time. Construction will probably be during or after 2003.

Another variation of the basic CECE process, which uses Vapor Phase Catalytic Exchange (VPCE) is used by AECL. The AECL uses the process in two heavy-water plants to remove tritium from deuterated (heavy) water. One plant is at Darlington in Ontario, Canada, and the other is in Grenoble, France. AECL claims that the process can achieve a tritium decontamination factor of 10^7 and a volume reduction factor of 100.

AECL has constructed and is performing tests of a CECE pilot plant as part of its Prototype CIRCE Plant (PCP) demonstration project. The pilot plant uses a 7.5 kA electrolysis cell and a 2-inch diameter column with a total water flow of approximately 1.5 l/h, but, further data was not provided. During testing, for maximizing detritiation, a detritiation factor exceeding 30,000 has been achieved (Miller 2001). However, at this time, the testing is not complete, and has not been officially documented.

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[2] Teflon is a trademark of E. I. duPont de Nemours & Company, Inc.

This process was included for consideration in the 1997 and 1999 Hanford site tritium technology evaluation reports (Jeppson et al. 1997, Jeppson 1999). The 1997 report referenced an evaluation of this process (Fulbright et al. 1997) that indicates a cost estimate of about $2.6/l ($10/gal) to process the tritiated water at a rate of 1.6 l/s (25 gal/min) with a tritium concentration of 40 μCi/l. The 1999 report referenced a more recent evaluation (Miller 1999) That indicates a preliminary cost estimate of about $0.32/l ($1.2/gal) for treating 1.3 l/s (20 gal/min) of water with a tritium concentration of 200 μCi/l (with no hydrogen recovery credit). The main difference in the two estimates was for capital equipment. The Savannah River Site (SRS) estimated capital equipment at $339 million for the 1.6 l/s case, and AECL estimated it at $20 million for the 1.3 l/s case. There have been no more recent evaluations of the costs.

2.1.2.1 Process Description. A schematic drawing of a CECE process is shown in Figure 1. The process consists of countercurrent gas/liquid exchange columns with packed catalyst beds, an electrolytic cell, and a hydrogen/oxygen recombiner. The catalyst beds comprise ceramic packing material coated with platinum and Teflon such that they are hydrophobic. The volume of catalyst required for the above process as evaluated Miller (1999) is 8.1 m^3 for exchange catalyst and 3.2 m^3 for recombiner catalyst with lifetime service expectancies of 5 years. The volume of catalyst required for the above process as evaluated by Fulbright et al. (1997) was about 40 m^3 for the exchange catalyst with no recombiner catalyst indicated and with catalyst lifetime service expectancy of 10 years.

2.1.2.2 Application at the Hanford Site. An evaluation conducted by the AECL for the Savannah River Site concluded that this concept should be considered as a viable process for detritiating water (Miller 1999). The estimated cost projection for this concept was considerably lower than that projected for the CECE process in a 1997 evaluation (Fulbright et al. 1997). The recent projections indicate a cost for treating 1.3 l/s (20 gal/min) of 200 μCi/l feed to reduce the concentration to <0.02 μCi/l at about $0.32/l ($1.2/gal) over a 20-yr period. This compares to the earlier cost estimate of $2.6/l ($10/gal) for treating 1.6 l/s (25 gal/min) of 40 μCi/l feed to reduce the concentration to <0.02 μCi/l. The difference is significant and puts the CECE process in a more feasible position if the AECL capital equipment costs are reasonable.

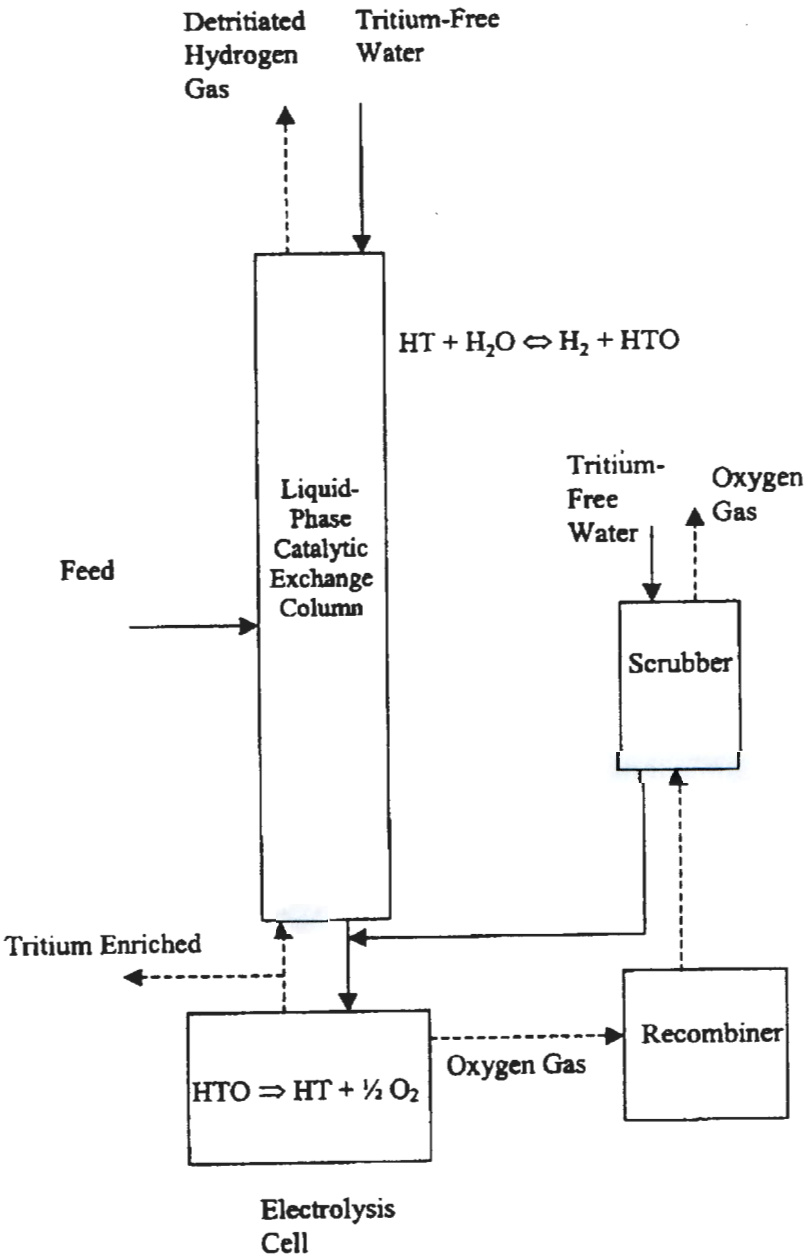
The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed.

This process requires a moderate amount of the costly hydrophobic catalyst, considerable cost for the electrolytic cells, considerable energy for electrolytic decomposition of about 1.4 times the feed volume of water, and hydrogen gas at near-atmospheric pressures for the separation. For the AECL evaluation, tritium is enriched in the form of HT in hydrogen gas from the electrolytic cell and must be loaded on a metal as a hydride or converted to water and dispositioned as a grouted waste form. This stream is very small. But, the cost of dispositioning the waste will depend upon the method, and could be significant. One possibility, would be further concentration then loading it on a metal as a hydride and sending it to the SRS tritium facility for further purification and use as part of the national tritium inventory.

The tritium-depleted stream is in the form of hydrogen gas and can be collected for liquefaction and sold as a by-product. If sold at about $700/metric ton it would provide a reduced processing

cost of about \$0.05/l (\$0.2/gal). A market for this hydrogen would have to be established before credit could be assumed for this potential by-product.

Figure 1. Combined Electrolysis Catalytic Exchange Process.



2.1.3 Other Hydrogen Isotope Separation Processes

2.1.3.1 Hydrogen Isotope Distillation and Water Electrolysis. Hydrogen-Isotope distillation (cryogenic distillation) requires converting the total wastewater stream to hydrogen and oxygen gases, separating the gases, and then processing the hydrogen gas through several stages of cryogenic separations to concentrate tritium by a factor of about 100.

The process requires electrolysis of the total wastewater stream, which although energy intensive is less than that for the CECE process that requires electrolysis of approximately 1.4 times the wastewater feed stream. The electrolysis is followed by cryogenic distillation of the hydrogen gas. The processing concept was determined to be unfeasible in the 1997 evaluation (Jeppson et al. 1997). No new developments have increased the acceptability of this concept since the 1997 evaluation. In fact, since the previous reports were based upon a lower maximum tritium concentration than the maximum found in *Hanford Site Groundwater Monitoring for Fiscal Year 2000* (Hartman 2001), several more theoretical stages would be needed for the cryogenic distillation columns to allow the most concentrated wastes to meet the drinking water standards.

The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants. The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed.

2.1.3.2 Girdler Sulfide Process. This process is a mature process, and scale-up of this process is feasible. Because the process is mature, there have been no further developments associated with the acceptability of this process. Although feasible, the process has major safety concerns associated with it. The safety concerns are focused around the high-pressure (20 atm) for the process. Therefore, leaks that might develop would release tritiated gas and toxic and corrosive hydrogen sulfide gas into the atmosphere.

The 1999 report stated that this process was determined to be the most economical separations process considered [$0.05/l ($0.2/gal) for the 1.6 l/s (25gal/min) flowrate] in the Fulbright et al. (1997) evaluation. In the Miller (1999) evaluation, the Girdler sulfide process was judged to cost somewhat more than the CECE process or a bithermal hydrogen-water process. Costs of about $0.5/l ($2/gal) (Miller 1999) were determined for this process to reduce tritium concentrations from 200 μCi/l to <0.02 μCi/l at a flow rate of 1.3 l/s (20 gal/min). There have been no further developments that would impact the costs, therefore, no further cost estimates were developed.

The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed.

2.1.4 Bithermal Hydrogen-Water Process

The bithermal hydrogen-water process was discussed in the 1999 evaluation report (Jeppson 1999). As stated in the 1999 evaluation report, the process (Miller 1999) was evaluated to be only slightly more costly than the CECE process.

This process is the second stage of the prototype CIRCE plant mentioned in the discussion associated with the CECE process. Testing is still in process. Therefore, no information has been released at the time this report was being prepared. Information currently provided by AECL does not provide the size of the bithermal hydrogen-water stage of the process.

2.1.4.1 Process Description. This process consists of cold-stripping and cold-enriching columns and hot-enriching and hot-stripping columns stacked in a vertical orientation with hydrogen gas flowing upward countercurrent to the aqueous streams, as shown in Figure 2. The tritiated water to be treated is introduced between the cold-stripping and cold-enriching columns. There are three conditions that are important to achieving the to maximizing separation factors, the hydrophobic catalyst (the same catalyst used for the CECE process), temperature control to enhance the stripping and enriching conditions, and high pressure.

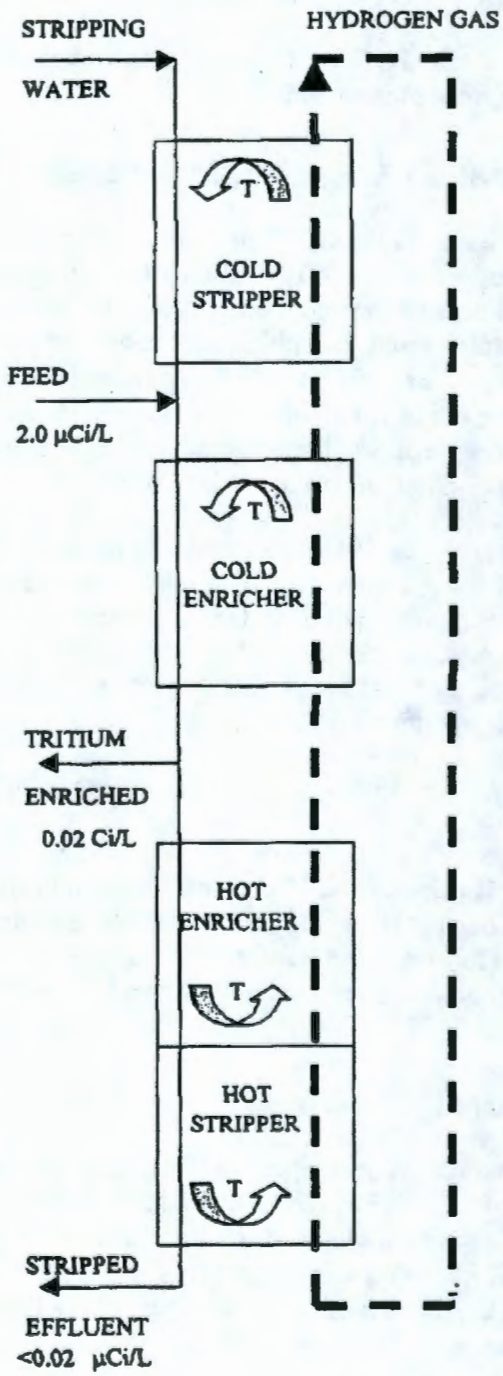
Nontritiated water is used to strip tritium from the circulating hydrogen in the cold-stripping column. The hydrogen gas stripped of tritium is recirculated to the hot-stripping column to remove tritium from the wastewater to be discharged. The tritium-rich product stream is withdrawn from between the cold and hot enrichment columns. The columns are operated at near 49 atmospheres of pressure to achieve maximum separation factors. The hot temperature enrichment and stripping column sections are operated at about 443 °K (170 °C), and the cold-stripping and cold-enrichment column sections are operated at about 323 °K (50 °C).

2.1.4.2 Application at the Hanford Site. This process does not require energy to change phases of the feed stream, but does require heating to moderately high temperatures. The feed stream does not have to be converted to elemental gases. The process is capable of reducing the tritium concentration (feed of 8.3 μCi/l) to below the maximum contaminant level (MCL) (0.02 μCi/l) for discharge of the depleted stream to the ground and can provide a tritium-rich stream of >20,000 μCi/l to provide a manageable tritium-rich stream. The AECL has stated that this process can be designed to process 300 to 500 l/min with no obvious difficulty.

The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants. The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed.

Concerns with this process include (1) the containment of tritiated water and tritiated hydrogen gas under high pressure, (2) safety with the use of high-pressure hydrogen gas in the process, and (3) the fact that the process has not been used on a large industrial scale. In addition, the process is much more sensitive to control of the process flows than is the CECE process. Costs for this process are expected to be similar to the costs for the CECE process.

Figure 2. Bithermal Hydrogen-Water Process.



2.2 HYDROGEN-ISOTOPE SEPARATION TECHNOLOGIES ON A LABORATORY OR PILOT-PLANT SCALE

The following technologies are in the laboratory or demonstration stages of development for separation of tritiated water from protinated water.

2.2.1 Liquid Phase Catalytic Exchange with Solid Oxide Electrolyte

This process, which is a variation of the CECE process, was described in the 1997 and 1999 evaluation reports (Jeppson et al. 1997, Jeppson 1999). The process was stated to be effective and have low total energy consumption. The solid-oxide electrolyte (SOE) cell does not require energy for electrolysis and recombination but does require energy to vaporize water and heat it to a high temperature of 1198 °K (925 °C). The specialized catalyst and the high temperature are used to drive the thermodynamics to allow the water to be electrolyzed. Overall, it uses considerably less energy than standard electrolytic cells. However, this process uses a costly hydrophobic catalyst to allow the electrolysis to occur.

The 1999 evaluation report (Jeppson 1999) stated that the process had been demonstrated only on a very small scale (2 l of water feed at 500 μCi/l to give a depleted stream of 0.005 μCi/l and an enhanced tritium concentration stream of 50,000 μCi/l). The 1999 report also stated that a larger scale liquid-phase catalytic exchange (LPCE) with the SOE system had been designed and was scheduled to be demonstrated. Although research into this technology is continuing, no further information could be obtained for this technology.

2.2.1.1 Process Description. The 1999 evaluation report (Jeppson 1999) provides a description of the process.

2.2.1.2 Application at the Hanford Site. The process has not been demonstrated at a size beyond laboratory scale. The process would have to be demonstrated at a larger scale to be considered a viable process for use at the Hanford site. Also, there are safety concerns associated with the high temperature and moderate pressure required to allow the catalytic electrolysis to proceed.

2.2.2 Tritium Resin Separation Process

The tritium resin separation process developed by Molecular Separations Incorporated (MSI) has generated much interest since it was initially discussed in the 1999 evaluation report (Jeppson 1999). The process methodology has changed from that provided in the 1999 report. However, the basics of the process remain the same. The company reported the process flowsheet was currently in the process of revision. Therefore, a flowsheet diagram will not be provided. However, the basics of the process will be discussed.

Essentially, the process uses an exchange material that has large values for the water of hydration and the sites for the water of hydration are selective for tritiated water over protinated water.

The tritiated water is selectively adsorbed onto the resin as the contaminated water flows around the resin.

At the time that the 1999 evaluation report was prepared, the process involved the resin trickling through the exchange columns and then being regenerated outside of the columns. That process would not tend to work well on a large scale. And, it would tend to significantly increase breakage of the exchange resin. The process was later changed to using a fixed bed with the resin being regenerated in place. That type of process is more amenable to scaling up to a larger process flow. Recent tests have shown breakage problems in the resin. The problem is probably because of the organic substrate and the swelling problems typically associated with organic resins that have large values for water of hydration. The heat associated with the hydration may also be a factor in the breakage. Therefore, current research is focused on the development of an inorganic substrate for the chemicals that perform the separation. Preliminary testing shows no swelling problems with the inorganic substrate (Furlong 2001).

There have been two recent evaluations of the process. The DOE had a peer review of the process performed by the American Society of Mechanical Engineers (ASME) (ASME 2001). The report for that peer review was issued to DOE in April. The report gave several areas where more information or more research was needed before they would recommend DOE spend money on the process. In addition, there was a recent set of tests and an associated evaluation performed for the Electric Power Research Institute (EPRI). The report documenting the research and evaluation has not been finalized as of the writing of this report.

2.2.2.1 Process Description. Tritiated water at low concentrations in protinated water is preferentially loaded on a proprietary resin bed as hydrated water, allowing the tritium-depleted stream to pass through the bed. Cation sites attached to the resins are employed to preferentially hydrate the tritiated water. This loading process is conducted at near 303°K (30 °C). The process would typically involve several columns that the waste would flow through in series. As with most adsorption and ion exchange processes, the tritiated water adsorption on the resin bed is proportional to feed concentration and resin-bed volume for a specified diameter column. And, above a certain flow rate (which has not been determined), the removal of tritium would be adversely affected by increases in the flow rate. Depleted tritiated water streams with a tritium concentration below the MCL are possible by using the appropriate resin-bed residence time to effect the necessary exchange.

When the resin in a column becomes loaded, the column is taken offline, and the resin is regenerated in place. The regeneration process first drains the free water, which is recycled back to the column's tritiated water feed tank, from the column. Then the resin is heated to a moderate temperature of 373°K (100 °C) to remove the remainder of the interstitial water and the lightly held hydration water. This water is returned to the column's feed tank for reprocessing; the waters constitute approximately 50 percent of the feed-flow stream. Finally, the column is heated to 403 °K (130 °C) and the more strongly bonded hydrated water (including the bulk of the tritiated water) is swept off the resin as water vapor with a heated nitrogen gas flow to a condenser. This water, containing the bulk of the tritiated water, is condensed and collected as liquid in a receiving tank. The volume of condensed water amounts to 0.25 to 0.5 percent of the original volume of feed and contains about 99 percent of the tritiated water. The gas from the condenser is recycled to a heater for reuse.

After regeneration, the column would be placed back into service as the final column in the series. The cycling with the most recently regenerated column as the final column in the series maximizes the removal of tritium.

2.2.2.2 Application at the Hanford Site. Due to changes in the process, the process is not at the point where scale-up and cost estimation are possible. In addition, there are currently many unknowns associated with the technology. Therefore, the ASME Peer Review Panel commissioned by the DOE to review the technology developed by MSI (ASME 2001) considered the technology to be in an early stage of research and development, requiring significant development to be completed for the technology to mature and prove itself.

The feed for this process will need to be water that has been processed to remove organic and inorganic contaminants. The water that has been processed at ETF should work well as a feed because the contaminants other than tritium have been removed. However, the resin is susceptible to competing ion exchange, if the feed contains active cations such as sodium in groundwater. The resin could be occluded with colloids and would adsorb certain organic compounds if they were present in the feed stream, which would reduce the overall effectiveness of the resin. Therefore, the feed stream must be cleaned of other contaminants, such as radionuclides, sodium, and organics, or must be cleaned before it is processed for tritium removal. However, the required feed purity has not been defined.

2.2.3 Dual Temperature Liquid Phase Catalytic Exchange

This process was discussed in the 1999 evaluation report (Jeppson 1999). There have been no updates on the research associated with this process. Therefore, it will not be discussed further.

2.2.4 Membrane Mediated Separation

No new information was found beyond that given in the 1999 evaluation report (Jeppson 1999).

2.2.5 Laser-Induced Tritium Separation

No new information was found beyond that given in the 1999 evaluation report (Jeppson 1999).

2.2.6 Kinetic Isotope Effects Methodology for Tritium Separation

There has been some work during the past two years to develop new technologies for separation of tritiated water from normal water using kinetic isotope effects. The new technologies use a formic acid/benzyl alcohol separation. The Tritium/Deuterium (T/D) separation factor appears to be about 38, and the Tritium/Hydrogen (T/H) separation factor is about 300. However, one of the developers of the method stated that he feels that the process would be acceptable for pilot plant scale separation, but not for large-scale separation.

2.2.6.1 Process Description. Development efforts to date for tritium removal include demonstration of proof-of-principle deuterium experiments and development of catalytic chemistry in redox active films involving surface-modified electrodes. Evaluation of C-H/C-T[3] kinetic isotope effects in the oxidation of several functionally different organic substrate bonds, and investigation of the magnitude of kinetic isotope effects to identify the most promising metal-catalyst system in solution, have been completed.

2.2.6.2 Application at the Hanford Site. As stated previously, this technology is not expected to ever develop into a large-scale process for removing tritium from water. Therefore, it is not applicable for treating the Hanford wastewaters or groundwater

2.3 OTHER TRITIUM MITIGATION TECHNOLOGIES FOR WASTEWATERS

2.3.1 Treatment Methods Based Upon Delaying Movement of the Contamination Plume to Offsite Areas.

There are several concepts for remediation of tritium contaminated groundwater plumes that are based upon maximizing the time before contaminated groundwater reaches site boundaries. The concepts are based upon the fact that tritium decays with a half-life of 12.3 years.

2.3.1.1 Pump and Recharge. The pump and recharge concept extracts tritium contaminated water from the ground and recharges it at a location where the movement of groundwater will take longer for the contaminated groundwater to reach site boundaries. The concept can work effectively.

However, there is a significant drawback to this methodology. Due to natural recharge of the contaminated aquifer, the volume of waste to be pumped and recycled continually increases. And, as the volume being extracted and recharged increases, the pumping system requirements grow each year. Therefore, this treatment methodology should always be combined with methods to minimize the natural recharge to the aquifer.

The concept is being used at both the Savannah River Site and at Brookhaven National Laboratory. The 1999 evaluation report (Jeppson 1999) discussed in detail the methods being used at Savannah River and at Brookhaven. Therefore, the information will not be repeated.

2.3.1.1.1 Application at the Hanford Site. As stated in the 1999 report, groundwater pumping at the 20,000 pCi/l concentration front would cover over 40 km (Jeppson 1999, Hartman 1999, Hartman 2001). The large distance of the front, the number of wells which would be required, and the large volume of water which would have to be pumped preclude this concept from being economically feasible.

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[3] C-H carbon-protium bond, C-T carbon-tritium bond

An additional factor that makes the concept not feasible at the Hanford site is the increase in volume that would need to be pumped each year. Although the recharge rate is low, the additional amount of water to pump each year would increase significantly because of the large volume of the contaminated plume.

2.3.1.2 Frozen Soil Barrier. The frozen soil barrier concept was discussed in detail in the 1999 evaluation report. (Jeppson 1999). As stated in that report, the concept of is not economically feasible due to the large volume of soil that would have to be frozen to use it as a barrier.

2.3.1.3 State Approved Land Disposal Site. The SALDS is located just north of the 200 West Area on the Hanford site and began receiving tritiated wastewater in December 1995. The SALDS receives effluents from the ETF that are free from all contaminants except tritium. The tritium comes from processing wastes from single-shell and double-shell underground storage tanks and other radioactive miscellaneous wastes from the Hanford site.

The SALDS is a prescribed location, because it is determined by groundwater evaluations to allow sufficient time for tritium to decay below MCL values before it drains to the Columbia River. SALDS is the prescribed location because it has been determined, by groundwater sample results evaluation and groundwater flow modeling, that the tritium at the 500 pCi/l level or above will extend a maximum horizontal distance of less than 1.5 km from the SALDS location (Barnett et al. 1997).

Discharges to the SALDS are listed in Table 1 by date, volume, and concentration of tritium.

Table 1. Tritiated Water Discharges to the State-Approved Land Disposal Site.

Year	Volume		Average Tritium Concentration *	Tritium
	(l)	(gal)	(μCi/l)	(Ci)
1995	2,237,000	591,000	6.2	13.8
1996	28,630,000	7,564,000	7.5	214.5
1997	57,445,000	15,177,000	0.61	35.1
1998	107,195,000	28,321,000	0.29	31.5
1999	88,266,000	23,320,000	.10	8.95
2000	91,306,000	24,123,000	.23	21.1

* The average tritium concentration is misleading because most years, the majority of the tritium is sent during a one to two month period. For example, most of the tritium for calendar year2000 was from a 2 month period, with the maximum average monthly concentration being 2.34 μCi/l.

2.3.2 Phytoremediation

Phytoremediation is the process of using plants to remediate contaminated areas; both soil and groundwater can be remediated. The process is being used at the Argonne National Laboratory and is also being planned for the Savannah River site.

In phytoremediation the plants take up nutrients from the contaminated soil and use the contaminated water to grow. The contaminants are concentrated in the leaves and/or stems, and the water is transpired into the atmosphere as part of the natural plant growth. The process is only good for near surface contamination and shallow aquifers.

The phytoremediation at Argonne National Laboratory is being performed on a site that is contaminated with tritium. However, the concentration of tritium in the groundwater meets the drinking water limits at the current time. The primary reason for performing the remediation is to stop the growth of the groundwater plume, and remove other contaminants that are in the soil and groundwater. The tritium is assumed to be transpired in the same concentration as its concentration in the groundwater (Negri 2001).

Of primary interest is not that tritium is being treated, but that the phytoremediation was designed so that in a few years, the rate of transpiration of the water will match the natural recharge to the aquifer. This will essentially stop the movement of the contamination plume (Quinn 2001).

Although detailed information on the phytoremediation project at the Savannah River site could not be obtained, the two primary goals with regard to tritium would be to reduce the volume of water (natural recharge) reaching the contaminated aquifers and reduce the volume of contaminated water reaching the surface water sources. The reduction of recharge, and the removal of water from the aquifers via the plant roots would increase the time for decay of the tritium while it is still in the ground. Although this will result in tritiated water being transpired into the atmosphere, this remediation method was considered acceptable at the Savannah River Site because of the distance to the nearest population center (Sullivan 2001).

2.3.2.1 Application at the Hanford Site This technology would not meet the needs of the Hanford site because of the aquifer depth. Also, phytoremediation for minimizing water entering a contaminated aquifer typically uses either hybrid poplars, or pine trees. Neither of those types of plants would be amenable to the natural environment on the Hanford site.

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3.0 SUMMARY

A literature search was conducted and national and international experts were consulted to identify potentially viable processes for removing tritium from Hanford site wastewaters to the drinking water maximum concentration limit (MCL) of 0.020 μCi/l. Separation processes were identified, described, and evaluated for application to the Hanford site wastewaters, including spent-fuel basin waters, ETF effluent, and groundwaters. Other mitigation processes applicable to Hanford site groundwater containment also were identified, described, and evaluated for the prevention of tritium migration at concentrations above 0.020 μCi/l (the drinking water maximum concentration limit) to offsite locations.

Potentially viable separations processes identified, described, and evaluated in this report include (1) water distillation, (2) CECE , (3) bithermal hydrogen-water, (4) DTLPCE, (5) LPCE with SOE, (6) resin separation, and (7) membrane separations. The kinetic isotope effects process is not considered viable because it does not appear to ever be scalable beyond bench to pilot plant scale.. The processes described for preventing migration of tritium above the MCL limit include SALDS, pump and recycle, freeze barrier, and phytoremediation.

Currently no processes that can be scaled up for use in treating the wastewater and groundwater at the Hanford site are economically viable. Development work is continuing on several processes by various sponsors. At the current time, the processes either need more development to demonstrate economic viability or need more development to allow the processes to be scaled up for use in treating the wastewater and groundwater at the Hanford site.

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4.0 REFERENCES

40 CFR 141.16, "National Primary Drinking Water Regulations," *Code of Federal Regulations*, Title 40, Part 141.

Allen, W. L., 1994, *Tritiated Wastewater Treatment and Disposal Evaluation for 1994*, DOE/RL-94-77, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Allen, W. L., 1995, *Tritiated Wastewater Treatment and Disposal Evaluation for 1995*, DOE/RL-95-68, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

ASME, 2001, Technical Peer Review Report: *Separation of Tritium From Wastewater*, ASME/CRTD-RP-01-22, under contract to the U.S. Department of Energy, April 2001

Barnett, D. B., M. P. Bergeron, C. R. Cole, M. D. Freshley, and S. K. Wurstner, 1997, *Tritium Monitoring in Groundwater and Evaluation of Model Predictions for the Hanford Site 200 Area Effluent Treatment Facility*, PNNL-11665, Pacific Northwest National Laboratory, Richland, Washington.

Bushart, S, 2001, email to D. Penwell, Reply for "Reference for information recent tritium resin separation research", Electrical Power Research Institute, May 21, 2001

Contract, DE-AC27-01RV14136, *Hanford Waste Treatment*, Section.

DOE Order 5400.5, *Radiation Protection of the Public and the Environment*.

Ecology, EPA, and DOE, 1996, *Hanford Federal Facility Agreement and Consent Order*, 2 vols., Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

Ellis, R. E., J. E. Lentz, M. L. Rogers, and C. J. Sienkiewicz, 1982, *Final Report: Development of Combined Electrolysis Catalytic Exchange*, MLM-2952, Monsanto Research Corp., Miamisburg, Ohio.

Fulbright, H. H., A. L. Schwirian-Spann, K. M. Jerome, B. B. Looney, and V. Van Brunt, 1997, *Status and Practicality of Detritiation and Tritium Reduction Strategies for Environmental Remediation*, WSRC-RP-96-0075, Rev 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Furlong, L., 2001, email to D. Penwell, *MSI Tritium Separation Update*, Molecular Separations Inc. May 6, 2001

Hartman, M. J., 1999, *Hanford site Groundwater Monitoring for Fiscal Year 1998*, PNNL-12086, Pacific Northwest National Laboratory, Richland, Washington.

Hartman, M. J., 2001, *Hanford Site Groundwater Monitoring for Fiscal Year 2000*, PNNL-13404, Pacific Northwest National Laboratory, Richland, Washington.

HST, 1991, *RL-MW023, Technology Need/Opportunities Statement*, DOE/RL-98-01, Rev. 1, Hanford Science and Technology for the U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Isomura, S., K. Suzuki, and M. Shibuya, 1988, *Separation and Recovery of Tritium by Hydrogen Water Isotopic Exchange Reaction, Fusion Technology*, Vol. 14, p 518-523, September 1988.

Konishi, S., May 10, 1999, letter to D. W. Jeppson, *Bench-Scale Test For Integrated LPCE with SOE*, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.

Miller, A. I., 1999, *Tritium Treatment Technologies for Groundwater Remediation at Savannah River Site*, WSRC-OS-98-00127, prepared by Chalk River Laboratories and Atomic Energy of Canada, Limited, for Westinghouse Savannah River Company, Aiken, South Carolina.

Miller, A. I., 2001 email to D. L. Penwell, *Reply to Questions Regarding Tritium Removal Technologies.*, Atomic Energy of Canada, Limited, March 7, 2001

Negri, M. C., 2001, email to D. L. Penwell, *Reply for Questions Regarding Phytoremediation and Tritium*, Argonne National Laboratory, April 18,2001

Quinn, J. J., Negri, M. C., Hinchman, R. R., Moos, L. P., and Wozmiak, J. B. (Argonne National Laboratory), and Gatliff, E. G. (Applied Natural Sciences), 2001, *Predicting the Effect of Deep-Rooted Hybrid Poplars on the Groundwater Flow System at a Large-Scale Phytoremediation Site*, International Journal of Phytoremediation, Vol. 3., No. 1., p. 41-60, 2001

RL, 1999, *Fiscal Year 1999 Waste Tank Science Need*, RL-WT047-S, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Sienkiewicz, C. J., and J. E. Lentz, 1988, "Recovery of Tritium from Water," *Fusion Technology*, Vol. 14, pp 444-449, 1988.

Sullivan, T., 2001, Letter to G. Penny, Minutes of the Conference Call on Tritium Treatment Technologies, Brookhaven National Laboratory, January 30, 2001

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