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2004 Evaluation of Tritium Removal and Mitigation Technologies for Wastewater Treatment

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

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

Project Hanford Management Contractor for the
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February 2004

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ABSTRACT

This report contains the 2004 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. Updated information on state-of-the-art technologies to address the control of tritium in wastewaters was identified and described. This report was prepared to satisfy the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) Milestone M-26-07A (Ecology, EPA, and DOE 1996). 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 U.S. Code of Federal Regulations (CFR), Title 40 CFR 141.16, drinking water maximum contaminant level (MCL) for tritium of 20,000 pCi/L and/or DOE Order 5400.5 as low as reasonably achievable (ALARA) policy.

Objectives of this evaluation were to (1) update status 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) update status of control methods to prevent the flow of tritiated water at concentrations greater than the MCL to the environment.

Since the 2001 Hanford Site evaluation report there have been a number of developments related to tritium separation and control with potential application in mitigating tritium contaminated wastewater. These are primarily focused in the areas of 1) development and demonstration of catalytic processes using hydrogen/water exchange to separate tritium from water, 2) development of a sorbent based process to separate tritium from water, 3) evaporation of tritium contaminated water for dispersion in the atmosphere, and 4) use of subsurface barriers to minimize the transport of tritium in groundwater.

Continuing development efforts for tritium separations processes have been primarily to support the international fusion reactor program and the nuclear power industry. While these are significantly different than the Hanford application, the technology could potentially be adapted for Hanford wastewater treatment. In the area of catalytic hydrogen/water based separations, improved processes have undergone successful demonstration by Atomic Energy Canada Limited (AECL)

at the Chalk River facility and also at the Combined Industrial Reforming and Catalytic Exchange (CIRCE) Prototype Plant located at Hamilton, Ontario Canada. Similar processes are proposed for installation at the Joint European Torus (JET) facility operated by the United Kingdom (UK) Atomic Energy Authority at Culham Oxfordshire, UK and at the proposed International Thermonuclear Experimental Reactor (ITER) facility.

Treatment processes to reduce tritium levels below the drinking water MCL have not been demonstrated for the scale and conditions required for treating Hanford wastewater. In addition available cost information indicates treatment costs for such processes will be substantially higher than for discharge to SALDS or other typical pump and treat projects at Hanford. Actual mitigation projects for groundwater with very low tritium contamination similar to that found at Hanford have focused mainly on controlling migration and on evaporation for dispersion in the atmosphere. Phytoremediation (use of plants) has been applied to remove tritium contaminated ground water to reduce movement of contaminated plumes that could contaminate surface water.

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LIST OF TERMS/ACRONYMS

AECL	Atomic Energy of Canada, Limited
BLIP	Brookhaven Linear Accelerator Isotope Producer
BNL	Brookhaven National Laboratory
CECE	Combined Electrolysis Catalytic Exchange
CFR	United States Code of Federal Regulations
CIRCE	Combined Industrial Reforming and Catalytic Exchange
Deprotinate	To remove light water (H_2O) from heavy water (D_2O)
Deuterium	An isotope of hydrogen with one proton and one neutron
Deuterated water	Water which contains at least one deuterium atom
DOE	U. S. Department of Energy
DWS	Drinking Water Standard
EPRI	Electric Power Research Institute
ETF	Effluent Treatment Facility
GS	Girdler Sulfide
Heavy water	Water that contains 2 deuterium atoms and one oxygen atom
ITER	International Thermonuclear Experimental Reactor
JET	Joint European Torus
LERF	Liquid Effluent Retention Facility
MCL	Maximum contaminant level
MSI	Molecular Separations Incorporated
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
SRS	Savannah River Site
TAWRS	Tritium Aqueous Waste Recovery System
T/D	Tritium/Deuterium
T/H	Tritium/Hydrogen
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
TRS	Tritium Resin Separation
Tritium	A radioactive isotope of hydrogen – the nucleus contains one proton and 2 neutrons. Tritium has a half-life of 12.3 years.
UK	United Kingdom
VLB	Viscous Liquid Barrier

SCIENTIFIC ABBREVIATIONS AND CONVERSIONS

Units of Measure

Unit	Definition
°C	degrees centigrade
Ci	curie = 3.7×10^{10} Becquerel (Bq)
cm	Centimeter
µCi	microcurie (10^{-6} curie)
µCi/L	microcuries per liter
µCi/mL	microcuries per milliliter
gal	gallon
gal/yr	gallons per year
gpm	gallons per minute
hectare	10,000 m^2
°K	degrees Kelvin (absolute temperature)
kA	kiloamps
kg	kilograms
km	kilometer
kWh	kilowatt hour
L	liter
L/s	Liters per second
L/h	Liters per hour
m	meter
mL	milliliter
mL/min	milliliters per minute
mm	millimeter (10^{-3} meter)
mrem	milliroentgen equivalent mammal
pCi	picocurie (10^{-12} curie)
pCi/L	picocuries per liter

Elements and Compounds

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

Pure tritium with a mass of 1.03 grams is equivalent to 10,000 Ci

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, T_2O	tritiated water
T_2	tritium molecule

Abbreviations

g	gas
l	liquid
Kd	distribution coefficient

1.0 INTRODUCTION

Tritium (T) 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. Releases to the ground have greatly decreased since the last fuel was processed through the fuel separations plant in 1989. Tritium in previously discharged liquid effluents has migrated into the groundwater, and in some cases toward and into the Columbia River. Significant tritium inventories remain in Hanford Site groundwater and in underground waste storage tanks, spent-fuel storage basin waters, and water stored at the Liquid Effluent Retention Facility (Jeppson et al. 1997). Hanford tritium concentrations are relatively low (<30,000,000 pCi/L or 0.003 parts per billion by weight) but in many cases exceed the 20,000 pCi/L drinking water standard (DWS) for tritium (40 CFR 141.16). Tritium decays with a 12.3-year half-life producing helium. It is estimated that the tritium inventory at the Hanford site from processed fuel has decayed to about 1.4×10^5 Ci to date, based upon decay from the value in the 1997 report (Jeppson et al. 1997).

Since 1995, a state-approved land disposal site (SALDS) has received effluents from the Hanford site Effluent Treatment Facility (ETF) that are essentially free of all contaminants except tritium. The majority of tritium discharged to the SALDS comes from process condensates from the 242-A Evaporator when it is processing wastes from underground storage tanks, fuel basin water stored at the Liquid Effluent Retention Facility (LERF), and other miscellaneous wastes. Discharge to SALDS allows natural radioactive decay to substantially reduce tritium content before the wastewater enters the Columbia River. Computer modeling results predict a relatively long travel time (many times the half life) for tritium bearing effluents discharged to SALDS to reach the Columbia River. The models indicate that tritium above drinking water standards will not reach the Columbia River in detectable quantities. (Ecology 2000)

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 million pCi/L to less than 20,000 pCi/L (RL-MW023, *Technology Needs/Opportunities Statement* [HST 1991]). 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.

The current report is one in a series concerning tritium mitigation technologies. DOE/RL-94-77 (Allen 1994) provided an initial evaluation of tritium treatment and disposal options. Periodic updates on status of tritium mitigation technology have been published since that time: DOE/RL-95-68 (Allen 1995), DOE/RL-97-54, Rev. 0 (Jeppson et al. 1997), DOE/RL-99-42, Rev. 0 (Jeppson 1999), and DOE/RL-2001-33, Rev. 0 (Penwell 2001). The current report provides an update of developments in the area of tritium mitigation technology since the 2001 update. The earlier reports should be consulted for additional background information that is not repeated herein.

2.0 SUMMARY

A literature search was conducted and experts working in the field were consulted to update information in earlier reviews related to processes for removing tritium from Hanford Site wastewaters to meet the drinking water maximum concentration limit (MCL) of 20,000 pCi/L. Separation processes have been identified, described, and evaluated for application to the Hanford site wastewaters, including spent-fuel basin waters, ETF effluent, and groundwater. Other potentially applicable methods for mitigation of tritium contaminated wastewater or groundwater at the Hanford Site are also discussed.

Development work since the last update report has continued on separations processes based on catalytic exchange of hydrogen isotopes between elemental hydrogen gas and water, the combined electrolysis and catalytic exchange (CECE), and bithermal hydrogen-water processes. Catalytic exchange technology has been developed and demonstrated primarily for applications that support the fusion reactor program and for operation of heavy water moderated fission reactors, but could potentially be adapted for treating large volumes of groundwater and waste water with trace tritium contamination. However, the cost is expected to be relatively high.

Tests of a sorption based process have demonstrated some separation of tritium from wastewater but did not successfully demonstrate feasibility of the overall process. The developer of the process indicates problems have been resolved and the process is ready for use to remove tritium from wastewater. However, the process lacks large scale demonstration and available information indicates treatment costs are relatively high.

Treatment processes to reduce tritium levels below the drinking water MCL have not been demonstrated for the scale and conditions required for treating Hanford wastewater. In addition available cost information indicates treatment costs for such processes will be substantially higher than for discharge to SALDS or other typical pump and treat projects at Hanford.

Significant new developments and implementation work identified to mitigate bulk wastewater and groundwater with trace tritium contamination are limited to actions to restrict or alter groundwater movement by pumping or barriers and evaporation for air dispersions (thermal evaporation and "phytoremediation", or use of plants to uptake and evaporate groundwater).

3.0 REMOVAL AND MITIGATION TECHNOLOGIES FOR TRITIUM IN WASTEWATERS

Section 3.1 discusses industrial processes for separation of hydrogen isotopes in water. Section 3.2 discusses developmental processes for separating tritium from protinated water (H_2O). Other tritium mitigation methods for contaminated water are included in Section 3.3. Available information on relative costs is discussed in Section 3.4.

3.1 INDUSTRIAL HYDROGEN-ISOTOPE SEPARATION TECHNOLOGIES

Hydrogen-isotope-separation technologies used on an industrial scale include processes that separate deuterated water (HDO and D_2O) from H_2O and/or tritiated water (HTO) from HDO and D_2O. None of these processes are used on a large commercial scale for separating very low concentrations of tritium from light water to meet the MCL concentration. Processes discussed in this section would require some work to be adapted to the Hanford wastewater treatment requirements, but this is considered to be a moderate extrapolation from past successful applications of the processes.

3.1.1 Water Distillation

Isotope separation by water distillation is based on the small differences in vapor pressure between water species containing different hydrogen isotopes. Water distillation for separation of HDO and D_2O 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 to remove HTO from HDO and D_2O.

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

3.1.1.1 Process Description

The process was described in detail in the 1999 evaluation report (Jeppson 1999) and therefore is not described in detail herein.

3.1.1.2 Application at the Hanford Site

Distillation has not been used to treat large volumes of wastewater as needed for the Hanford application. As discussed in earlier evaluations, the technology is expected to work, however, the cost is expected to be high. The volatility of tritiated water is only slightly less than protinated water resulting in the need for a large number of separation stages. A large reflux ratio is required (about 30) resulting in liquid and vapor flows in the columns that are about 30 times the feed rate. If steam is used to heat the reboiler, the required steam consumption would be about 30 times the rate of water fed to the treatment process, resulting in high costs for steam

or fuel. A new dedicated steam boiler would be required because of uncertain capacity and longevity of the existing steam supply system (Ortiz 2003).

3.1.2 Combined Electrolysis Catalytic Exchange

Combined electrolysis catalytic exchange (CECE) is one of several processes based on use of the hydrogen/water exchange equilibrium reaction (Equation 1) that favors formation of HTO when liquid H_2O is contacted with tritiated hydrogen (HT) gas (Sienkiewicz and Lentz 1988).

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

A catalyst is required for the reaction to proceed at an appreciable rate, and development of improved hydrophobic catalysts in recent years has been key to commercialization of the process. These catalysts may be used for CECE and other processes based on Equation 1. The CECE process requires electrolysis of all feed water plus some deionized water used for stripping (approximately 1.4 times the feed flow is electrolyzed). The CECE process has a high isotopic separation factor and near ambient temperature and pressure operating conditions.

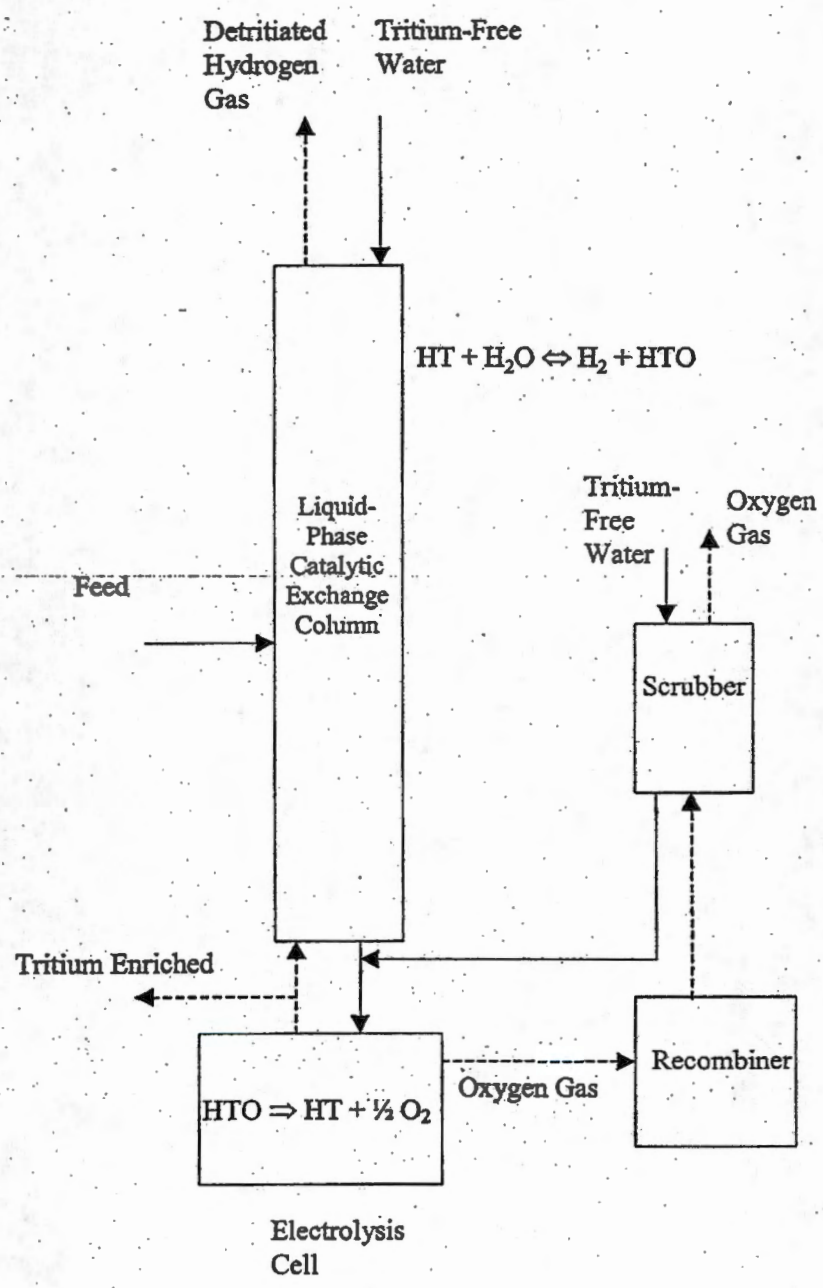
3.1.2.1 Process Description

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 electrolysis cell, and a hydrogen/oxygen recombiner (omitted if hydrogen production is desired). A platinum based solid catalyst is used that has been treated to make it hydrophobic (repels liquid water). The water to be treated is added in mid-column. As the water flows down, the tritium is transferred from the stream of hydrogen rising through the column producing a liquid enriched in tritium at the bottom and a hydrogen stream partially depleted in tritium that flows to the upper section of the column. Clean water is added at the top of the column. In the upper section, the clean water further reduces the tritium content of the rising hydrogen, resulting in a hydrogen stream exiting the top that is essentially free of tritium. The combined water stream (feed plus added clean water) drains from the bottom of the column to an electrolysis cell where it is electrolytically split into oxygen and tritiated hydrogen gas. The concentrated tritium stream can be taken from the bottom of the column either as tritiated water or as tritiated hydrogen gas depending on the desired form for the concentrated tritium containing product.

3.1.2.2 Process Development

An early version of this process was used to remove tritiated water from liquid wastewaters to reach discharge-level concentrations of 20,000 pCi/L in the Tritium Aqueous Waste Recovery System (TAWRS) at the U.S. Department of Energy (DOE) Mound Facility (Ellis 1982), (Sienkiewicz and Lentz 1988). System capacity was on the order of 2-liters per hour.

Figure 1. Combined Electrolysis Catalytic Exchange Process



A CECE type pilot plant to recover tritium from light water was built and operated in Japan for over 14 years in connection with the Fugen reactor. The plant capacity was 3.6 liters per day of feed, and HTO was concentrated by a factor of 10^4 (Isomura et al. 1988).

The CECE process has been the subject of active development work in recent years. The work includes catalyst development and testing, improvements to electrolytic cells, optimization of system and component designs, and industrial prototype construction and operation.

Hydrophobic platinum based catalysts were initially developed by AECL and the Chalk River National Laboratory (Sienkiewicz and Lentz 1988). Catalysts from additional developers have recently been subjected to testing (Cristescu et al. 2002) and (Braet and Bruggeman 2003). Active work on catalyst development/testing, process optimization, and demonstration testing have also been reported at other sites in Russia, Germany and the United Kingdom (UK); (Perevezentsev et al. 2002), (Cristescu et al. 2002), (Alekseev et al. 2003), (Alekseev et al. 2002), and (Fedorchenko et al. 2001).

A larger version of the process used at the Japanese Fugen reactor has been designed for use with the proposed International Thermonuclear Experimental Reactor (ITER), a fusion reactor (Iwai et al. 2002). The proposed system is designed to treat 20 kg per hour (about 20 L per hour) of water using a ½ meter diameter column. Facility location and the construction schedule for the ITER are not finalized at this time.

AECL constructed and completed a successful demonstration of the CECE process as part of its Prototype CIRCE Plant demonstration project at Hamilton, Ontario Canada (Miller 2003). 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 per hour. During testing, a detritiation factor exceeding 30,000 has been achieved (Miller 2001). A two part demonstration of the CECE process was also successfully completed at Chalk River (Miller et al. 2002), (Graham et al. 2002). The first part was to demonstrate upgrading of heavy water and the second part demonstrated a detritiation decontamination factor of over 1,000 and as high as 50,000 treating tritium contaminated heavy water.

A recent paper (Aleskeev et al. 2003) provides information on a CECE pilot plant at the Petersburg Nuclear Physics Institute that has been operated since 1995. The plant has processing capacity of about 4.5 kg per day (about 4.5 L per day) and has demonstrated tritium decontamination factors of 1,000 when operated with heavy water (a more difficult separation than with light water). Multiple operating modes and conditions have been tested.

A CECE treatment system is planned for the Joint European Torus (JET) facility operated by the UK Atomic Energy Authority at Culham Oxforshire (Perevezentsev et al. 2002), (Lasser et al. 2003). In support of the JET program, process development work is underway and a CECE test system is being installed at Tritium Laboratory Karlsruhe in Germany (Lasser et al. 2003).

The active development and implementation work at multiple sites indicates CECE is a viable process and may continue to improve over time.

3.1.2.3 Application at the Hanford Site

An evaluation conducted by the AECL for the Savannah River Site concluded the CECE process should be considered as a viable process for detritiating water (Miller 1999). Since that time there has been considerable development and demonstration of the process for different applications and the process appears technically feasible. As discussed below and in Section 3.4, cost for treating bulk quantities of wastewater with trace tritium contamination appears relatively high. With current Hanford Site average power cost of $0.0344 per kWh in fiscal year 2003 (Geiger 2003), power cost alone would be over $1 per gallon of water treated. This process requires a moderate amount of costly hydrophobic catalyst, considerable cost for electrolytic cells, and handling of hydrogen gas at near-atmospheric pressures for the separation. Confinement systems will be required for the concentrated tritium product for protection of workers, the environment and public. Detailed site specific cost estimates are not available and testing has not been performed with Hanford specific waste compositions.

Feed for this process needs to be water with low levels of organic and inorganic contaminants. Water that has been processed at ETF is likely to work well as a feed because this wastewater is essentially free of contaminants other than tritium. Full characterization and possibly testing work would be needed to determine if additional pretreatment is needed for specific candidate waste streams.

A tritium enriched waste stream will be produced in addition to tritium depleted water or hydrogen. This can be in the form of HT in hydrogen gas from the electrolytic cell or water with elevated tritium compared to the feed water. The HT could be loaded on a metal as a hydride or tritiated water could be dispositioned as a grouted waste form. This stream is small compared to the wastewater feed. Cost of dispositioning the waste will depend upon the method, and could be significant.

This process was included for consideration in earlier 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 indicated a cost estimate of about $2.6 per L ($10 per gal) to process the tritiated water at a rate of 1.6 L/s (25 gpm) with a tritium concentration of 40 μCi/L. A more recent preliminary cost estimate by AECL (Miller 1999) indicated a treatment cost of about $0.32 per L ($1.2 per gal) for treating 1.3 L/s (20 gpm) of water with a tritium concentration of 200 μCi/L (with no hydrogen recovery credit). Volume of catalyst required for a 20 gpm capacity CECE process was estimated by Miller (1999) as 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 a 25 gpm capacity CECE process was estimated by Fulbright et al. (1997) at about 40 m^3 for the exchange catalyst based on scale up from relatively old data (Hammerli et al. 1978).

The Miller (1999) estimate listed above assumed power cost of $0.02 per kWh. The CECE process uses about 8 to 9 kWh of power per liter of feed processed. If power cost is assumed at $0.0344 per kWh, the estimated processing cost increases by about $0.13 per liter (about $0.50 per gallon) to about $0.45 per liter or $1.70 per gallon. These estimates would be further increased by costs for handling and disposal of the concentrated tritium product and other site specific project costs. The cost estimates cited were prepared for the Savannah River Site (SRS)

and were based on tritium concentrations about an order of magnitude higher than those expected at Hanford. The reduced separations efficiency required for Hanford could reduce the cost per gallon treated, but only slightly. All of the feed processed must be electrolyzed, so that power consumption is not substantially reduced by reduced separations efficiency requirements.

3.1.3 Bithermal Hydrogen-Water Process

The bithermal hydrogen-water process is based on the same hydrogen/water exchange reaction as the CECE process (Equation 1, see Section 3.1.2), and can use the same catalysts. However it does not require electrolysis of the feed water, but instead relies on a recycled stream of hydrogen coupled with dual temperature separations columns. The bithermal hydrogen-water process was discussed in the 1999 evaluation report (Jeppson 1999).

3.1.3.1 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. Tritiated water to be treated is introduced between the cold-stripping and cold-enriching columns. Three conditions are important to maximizing separation factors: 1) use of an active hydrophobic catalyst (the same catalyst used for the CECE process), 2) temperature control to enhance the stripping and enriching conditions, and 3) high pressure.

In the upper "cold stripper" section, non-tritiated water is used to absorb tritium from the circulating hydrogen. The resulting hydrogen gas, essentially free 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 pressure to achieve maximum separation factors. The hot 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).

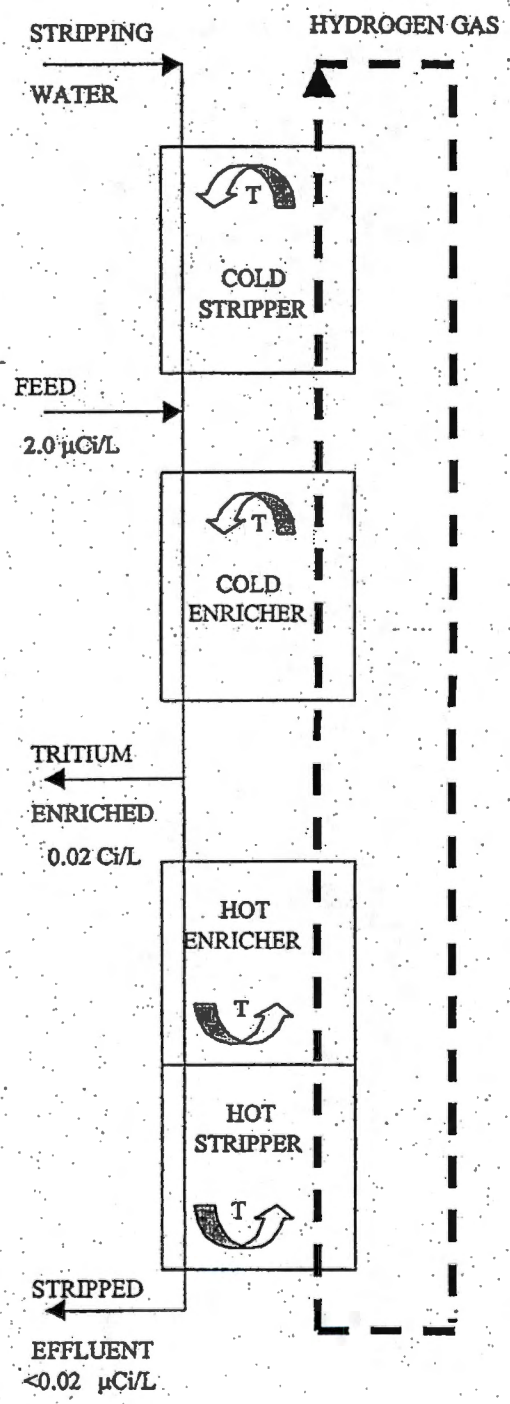
3.1.3.2 Recent Developments

The bithermal hydrogen-water process uses the same chemistry and the same catalysts used for the CECE process. Therefore much of the development work on the CECE process is directly or indirectly applicable to bithermal hydrogen-water. A prototype unit was installed and operated successfully at the Prototype Combined Industrial Reforming and Catalytic Exchange (CIRCE) demonstration project at Hamilton, Ontario Canada (Miller 2003).

3.1.3.3 Application at the Hanford Site

Existing applications for the bithermal hydrogen-water process are for treating heavy water, however, it appears feasible to adapt the technology for treatment of Hanford Site wastewater and groundwater. This process does not require electrolysis of the feed water to change phases of the feed stream, but operation with large volumes of hydrogen gas at high pressure, heating to moderately high temperatures and significantly higher recirculation flows compared to the CECE process. The process is expected to be capable of reducing tritium concentrations from levels

Figure 2. Bithermal Hydrogen-Water Process



typical of Hanford wastewaters to less than the MCL of 20,000 pCi/L for the depleted discharge stream while producing a small volume tritium-rich stream of >0.02 Ci/L. The AECL has stated that this process can be designed to process 300 to 500 liters per minute with no obvious difficulty.

Feed for this process needs to be water with low levels of organic and inorganic contaminants. Water that has been processed at ETF is likely to work well as a feed because this wastewater is essentially free of contaminants other than tritium. Full characterization and possibly testing work would be needed to determine if additional pretreatment is needed for specific candidate waste streams.

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. Because electrolysis of all the feed is not required, power costs are expected to be lower than for the CECE process. However the separations columns, catalyst beds, and the internal stream flows are much larger. As in the case of the CECE process, a method must be provided to disposition the concentrated tritiated water stream. As stated in the 1999 evaluation report, the process (Miller 1999) was evaluated to be only slightly more costly than the CECE process for the 20 gpm scenario they evaluated. Lower decontamination factors required at Hanford compared to SRS could tend to favor the bithermal hydrogen-water process because its costs are more sensitive to required separation efficiency. Total treatment cost (capital, utilities, labor, etc.) for this process are expected to be similar to the costs for the CECE process with the lowest cost option depending on capacity, operating duration, power cost, and other site specific factors.

3.1.3.4 Girdler Sulfide Process

Like the bithermal hydrogen water process, the Girdler Sulfide (GS) process uses cold and hot columns and a recirculating gas to drive the separation process. However, in the GS process hydrogen sulfide is the recirculating gas and no catalyst is required. The GS process is described in more detail in Jeppson et al. (1997). This mature process has been long used for heavy water production and is expected to be adaptable to Hanford Site wastewater treatment requirements. No significant recent developments were identified for this process and although it is expected to be feasible, the process has major safety concerns. The safety concerns are focused around the high-pressure (20 atm) and the highly toxic and corrosive gas hydrogen sulfide used in the process.

In the Miller (1999) evaluation, the GS process was judged to cost somewhat more than the CECE process or a bithermal hydrogen-water process for the specific scenarios evaluated. Costs of about $0.5 per L ($2 per gal) (Miller 1999) were estimated to reduce tritium concentrations from 200,000,000 pCi/L to <20,000 pCi/L at a flow rate of 1.3 L/s (20 gpm). The lower tritium concentrations typical at Hanford are expected to reduce the cost only slightly. In an earlier study, this process was estimated to be the most economical separations process considered [$0.05 per L ($0.2 per gal) for a 1.6 L/s (25gpm) flow rate] (Fulbright et al. 1997).

Feed for this process needs to be water with low levels of organic and inorganic contaminants. Water that has been processed at ETF is likely to work well as a feed because this wastewater is

essentially free of contaminants other than tritium. Full characterization and possibly testing work would be needed to determine if additional pretreatment is needed for specific candidate waste streams.

3.1.4 Other Industrial Hydrogen Isotope Separation Processes

Other industrial processes have been used for hydrogen isotope separation as discussed in earlier evaluation reports. However, no new development work, evaluations, or implementation projects were identified. The earlier evaluation reports (Jeppson et al. 1997) and (Jeppson 1999) should be consulted for information on these processes.

3.2 DEVELOPMENTAL HYDROGEN-ISOTOPE SEPARATION TECHNOLOGIES

This section summarizes new information identified on developmental hydrogen isotope separation technologies that have not been demonstrated on an industrial scale.

3.2.1 Tritium Sorbent Process

A sorbent based tritium separation process developed by Molecular Separations Incorporated (MSI) was discussed in the 1999 and 2001 evaluation reports (Jeppson 1999), (Penwell 2001). Details of the process have evolved since the 1999 report; however, the basic technical approach remains the same. A solid sorbent material is used with water of hydration sites that are selective for tritiated water over protinated water. Tritiated water is selectively adsorbed onto the sorbent as it contacts the contaminated water, and the sorbent is periodically regenerated by heating. At the time the 1999 evaluation report was prepared, the process involved a moving bed of sorbent trickling through the exchange columns and then being regenerated outside of the columns. The process was later changed to use a fixed bed with the resin being regenerated in place, which is expected to be more amenable to scaling up to a larger process flow.

Since the 2001 report was prepared, pilot testing supported by the Electric Power Research Institute (EPRI) was performed by Duratek (EPRI 2002). The project developer (MSI) has also teamed with Calgon Carbon Corporation for commercial application of the technology (MSI 2003).

3.2.1.1 Process Description

There are several ways the process might be configured. The following outlines one approach, which is similar to the process used for the EPRI/Duratek pilot tests. Tritiated contaminated water is contacted with a bed of solid sorbent material. Tritiated water is preferentially adsorbed as water of hydration, and the tritium-depleted stream passes through the bed. This loading process is conducted at near 50 °C. The process typically involves multiple columns that the waste flows through in series. The number and size of the columns is determined by the flow rate and desired tritium decontamination factor. As with most adsorption and ion exchange processes, tritiated water adsorption on the sorbent bed is proportional to feed concentration and bed volume for a specified diameter column. In theory, the feed stream can be decontaminated

to essentially any desired tritium level if enough contact stages are provided. However, the very limited data currently available suggests that removal efficiency and sorbent capacity drop as the tritium concentration is reduced.

As the sorbent becomes loaded, tritium concentration in the discharge stream increases. When sorbent in a column is no longer effective, the column is taken offline and the bed is regenerated in place as follows:

- Free water is drained from the bed and recycled back to the column's tritiated water feed tank.
- The sorbent bed is heated to a moderate temperature (80 to 120°C) to remove remaining interstitial water and some lightly held hydration water. This water is also returned to the column's feed tank for reprocessing; the recycled waters constitute approximately 50 percent of the feed-flow stream.
- Finally, the column is heated to about 160°C and the more strongly bonded water is swept off the resin as water vapor. This stream, containing the bulk of the tritiated water, is absorbed in a solid molecular sieve bed (dryer) or is condensed and collected as liquid. The absorbed or condensed water is expected to be a small fraction of the original volume of feed and contains an elevated level of tritium compared to the feed. Gas from the dryer/condenser is recycled to a heater for reuse.

If additional volume reduction of the tritium concentrate is needed it may be rerun through the sorption process, using the same or auxiliary columns.

After regeneration, the column is placed back into service for another cycle. Cycling with the most recently regenerated column as the final column in the series would typically be used to maximize column loading efficiency and removal of tritium.

3.2.1.2 Process Development and Evaluation

Process development and testing work on sorbent based tritium separation has been performed by MSI, Washington State University, Clemson Environmental Technology Laboratory (Jeppson et al. 2000), and Duratek (EPRI 2002). The Clemson tests demonstrated tritium removal in bench scale sorption columns. Subsequent testing was sponsored by EPRI and performed by Duratek (EPRI 2002). Static contact beaker tests were performed, which demonstrated depletion of tritium from water that was contacted with the sorbent. This is assumed to have resulted from preferential adsorption of tritiated water on the sorbent. In the most favorable case reported, when 20 mL of tritiated water was mixed with 10 mL of sorbent the measured tritium concentration in the water dropped from 5.44 to 3.32 μCi/mL (38.87% reduction).

The following calculation illustrates the difficulty of this separation compared with ion exchange processes typically used for water treatment. A useful way to characterize sorbent performance is with a distribution coefficient (Kd), defined as follows:

$$Kd = X_{sorbent}/X_{solution} \qquad (2)$$

Where $X_{sorbent}$ is the equilibrium concentration in the sorbent bed of the component being sorbed and $X_{solution}$ is the corresponding concentration in solution of the same component. If it is assumed that the reduction in tritium concentration represents tritium deposited onto the sorbent at equilibrium, the equilibrium distribution factor (Kd) can be estimated from the data stated above as follows:

$$Kd = ((5.44-3.32\ \mu Ci/mL)*(20mL\ water)/(10mL\ sorbent*3.32\ \mu Ci/mL) \quad (3)$$

$$= 1.27$$

Similar tests using ion exchange media for ions such as cobalt or cesium show Kd values in the range of several thousand (EPRI 2002). The indicated Kd value for the tritium sorbent is orders of magnitude lower than typically found for ion exchange resins. This result is consistent with the relatively low bed capacity and removal efficiency seen with ion exchange column tests. Additional static tests indicated sorbent degradation may be caused by impurities in the water.

After completion of the beaker tests, six test sorption cycles were completed in a pilot plant test system using a 4.6 cm diameter by 1.7 m long sorption column with a nominal 125 mL/min flow capacity. Three different sorbent material formulations were tested for treatment of wastewater with about 6,000 µCi/L tritium. A maximum of two cycles were performed using the same bed of sorbent material. Reduction of tritium from the feed material was demonstrated, however, the reduction in tritium concentration was not large (<10%). Some process problems were encountered, and one of the sorbents had problems with physical breakdown. The process developer indicates that problems have been resolved and the process is ready for implementation (St. Genis 2003).

Sorbent testing has been reported with tritium concentrations between about 300,000 and 6,400,000,000 pCi/L, as compared with Hanford waste concentrations between about 20,000 and 30,000,000 pCi/L. The limited available published data suggests that sorbent performance in terms of percentage removal efficiency and sorbent capacity is reduced at lower tritium concentrations.

An information brochure provided by MSI provides the estimated treatment costs listed in Table 1 and also indicates that Calgon Carbon Corporation has teamed with MSI.

Table 1 MSI Sorbent Based Water Detritiation Cost Projections (MSI 2003)

WASTE WATER VOLUME	TREATMENT COST VERSUS TRITIUM CONCENTRATION REDUCTION		
	10 Fold Reduction	100 Fold Reduction	2000 Fold Reduction
100,000 gal/yr	$5.00/gal	$7.00/gal	$11.00/gal
1,000,000 gal/yr	$4.00/gal	$5.00/gal	$7.00/gal
5,000,000 gal/yr	$3.75/gal	$4.50/gal	(not provided)

The cost projections include equipment, sorbent, and operating costs but do not include land, site preparation, or handling and disposal of the concentrated tritium product. The cost projections were also based primarily on data from tests using tritium concentrations higher than typical of Hanford wastes (St. Genis 2003). Test data indicate reduced performance at lower concentrations so some increase in cost might be expected for the Hanford case depending on the specific waste stream to be treated.

3.2.1.3 Application at the Hanford Site.

Proof of principle tests show that the sorbent selectively removes tritiated water from light water, however the overall process currently lacks documented large scale demonstration. The developer has teamed with a major industrial water treatment company and believes that the process is ready for implementation.

A feed specification is not available for the sorbent, and the effects of various potential feed impurities are not known. The sorbent is likely susceptible to competing ion exchange and may be subject to degradative attack by wastewater impurities. The sorbent 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. Preferably, water to be treated for tritium removal should have a low level of other impurities, but the required feed purity has currently not been defined. Full characterization and possibly testing work would be needed to determine if additional pretreatment is needed for specific candidate waste streams.

In summary, there are currently a number of unknowns associated with the technology, and the treatment cost projections appear relatively high for treating bulk quantities of Hanford wastewater with trace tritium contamination.

3.2.2 Other Developmental Processes

Earlier evaluations included additional developmental technologies for separation of hydrogen isotopes, including: Membrane mediated separation, laser induced tritium separation, kinetic isotope effects, and variations of the dual temperature liquid phase catalytic exchange processes. No significant developments were identified for these processes, and no new processes that are potentially applicable to Hanford wastewater were identified in the current review. See earlier evaluation reports for information on these processes.

3.3 OTHER TRITIUM MITIGATION TECHNOLOGIES FOR WASTEWATERS

There are several concepts for delaying movement of tritium contaminated groundwater plumes thereby maximizing the time before contaminated groundwater reaches site boundaries. These concepts are based upon the fact that tritium decays with a half-life of 12.3 years. Other methods involve evaporation or incineration of the tritiated water with releases directly to the atmosphere.

3.3.1 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. Treatment to remove contaminants other than tritium may be performed prior to recharge.

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 may continually increase. And, as the volume being extracted and recharged increases, the pumping system requirements grow each year. Therefore, this treatment methodology should usually be combined with methods to minimize the natural recharge to the aquifer.

The concept was used at the Savannah River Site between 1998 and 2003 and at Brookhaven National Laboratory between 1997 and 2000. The 1999 evaluation report (Jeppson 1999) discussed in detail the methods used at Savannah River and at Brookhaven. Therefore, the information will not be repeated.

Pump and recharge at the Savannah River Site was stopped in mid-2003 because of the high cost of groundwater treatment ($0.012 per L or $0.047 per gallon) and about a 50 to 70 % reduction of the tritium concentration (up to 50,000,000 pCi/L or 10 times the maximum tritium concentration in groundwater at Hanford) in the plume after five years of pumping and up-gradient recharging (Flach 2002, Blount et al. 2003, Blount 2003). Operating cost for the pump-treat-recharge was about $50,000 per day. Pump and recharge at Brookhaven was stopped in 2000 because the tritium levels in the vicinity of the extraction wells decreased to below the average minimum detection limit of the BNL Analytical Services Laboratory (343 pCi/L) (BNL 2002a, BNL 2002b). The decrease is a result of the combined effects of radioactive decay, dilution and dispersion.

3.3.1.1 Application at the Hanford Site

As stated in the 1999 report, groundwater pumping at the 20,000 pCi/L concentration front would cover a distance of over 40 km (Jeppson 1999, Hartman 2003). 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 and potentially treated to meet applicable state and federal limits except for tritium preclude this concept from being economically feasible.

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

3.3.2 Barrier Formation

Two types of subsurface barriers have been demonstrated at the DOE Sites. The frozen soil barrier concept was discussed in detail in the 1999 evaluation report. (Jeppson 1999). The information will not be repeated.

Another barrier technology termed Viscous Liquid Barrier (VLB) was selected by the Brookhaven National Laboratory for groundwater remediation. Groundwater monitoring near the Brookhaven Linear Accelerator Isotope Producer (BLIP) showed tritium and other radionuclide contamination had occurred before 1998. The VLB technology was developed at Lawrence Berkley National Laboratory with funding from DOE (EM-50). It used low-pressure permeation grouting to deliver a colloidal-silica grout to the subsurface. The grout gels in place and forms a barrier to liquid movement. The VLB in conjunction with a gunite cap around the surface soil of BLIP would minimize the volume of surface water percolating through the contaminated soils to the groundwater. The estimated volume of soil to be treated is approximately 85 m^3. Preliminary modeling results showed that if the flow rate though the activated soil can be reduced to less than 1 cm/yr, short-lived isotopes including tritium will not reach the aquifer at levels exceeding the drinking water standard (Heiser et al. 2000).

The VLB installation was completed in 2000 at a cost of about $436,000 (North-Abbot 2004, Heiser et al. 2000). The cost includes site characterization, grout compatibility and optimization testing, modeling, and barrier integrity verification and some planning documents. According to groundwater monitoring data, the actions taken to date have been highly effective in eliminating the BLIP source of groundwater contamination. Recent data on groundwater and soil collected during and after installation of the VLB indicate that grouting displaced soil pore water contaminated with tritium into the groundwater. The maximum tritium concentration in groundwater increased to 50,000 pCi/L from 1,000 pCi/L after grout injection. This limited tritium release is expected to be a one-time event and to dissipate quickly into the aquifer. Evaluation of barrier performance is continuing (Sullivan 2003).

3.3.2.1 Application at the Hanford Site

Application of the soil barrier technology is not economically feasible for tritium remediation in bulk groundwater because of the large volume of subsoil that would have to be frozen or injected with grout. The soil at Hanford is also different.

3.3.3 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 Effluent Treatment Facility (ETF) processing of wastewater. The ETF treated wastewater meets all applicable state and federal limits except for tritium (Ecology 2000). The majority of the tritium comes from processing liquid mixed wastes from single-shell and double-shell underground storage tanks and other radioactive miscellaneous wastes from the Hanford site. The waste discharge to SALDS is based on the average monthly flow and past performance allowed by State Waste Discharge Permit ST-4500. The permitted average monthly flow rate is 0.25 million gallons per day or up to 90 million gallons per year.

The ST-4500 permit condition S.10 requires a tritium tracking and groundwater monitoring plan. The DOE has agreed to monitor the tritium plume created by ETF discharge and update models used to predict travel time to the Columbia River. See Barnett et al. (1997) and Barnett et al. (2003) for discussion of modeling and monitoring results.

The ST-4500 permit indicates that previous computer model results predict tritium bearing effluents discharged to the ground at SALDS will take an extended period of time to travel with groundwater beneath the Hanford site before ultimate discharge to the Columbia River. Models and discharge scenarios indicate that tritium above the drinking water standard will not reach the Columbia River in detectable quantities. (Ecology 2000) During the long residence time in the aquifer, most of the tritium will decay to non-radioactive helium. An update to the earlier model calculations is planned for the near future.

Discharges to the SALDS are listed in Table 2 by date, volume, and concentration of tritium.

Table 2. Tritiated Water Discharges to the State-Approved Land Disposal Site.

Calendar Year	Volume		Average Tritium Concentration*	Tritium
	(L)	(gal)	(pCi/L)	(Ci)
1995	2,237,000	591,000	6,200,000	13.8
1996	28,630,000	7,564,000	7,500,000	214.5
1997	57,445,000	15,177,000	610,000	35.1
1998	107,195,000	28,321,000	290,000	31.5
1999	88,266,000	23,320,000	100,000	8.95
2000	91,306,000	24,123,000	230,000	21.1
2001	98,353,000	25,985,000	6,000	0.1
2002	23,367,000	22,071,000	105,000	8.8
2003	95,655,000	25,880,000	43,000	4.25

* The annual average tritium concentration is misleading because most years, the majority of the tritium comes from waste evaporation campaigns at the 242-A Evaporator which is sent during a one to two month period. For example, most of the tritium for calendar year 2000 was from a 2 month period, with the maximum average monthly concentration being 234,000 pCi/L. The majority of waste water to the SALDS is from treatment of Operable Unit UP-1 groundwater which normally contains less than 1,000 pCi/L of tritium.

3.3.4 Evaporation

One approach for disposing of wastewater and ground water is evaporation with dispersion into the atmosphere. Potential evaporation methods include:

- Boiling or Mechanical Evaporation. A variety of industrial equipment is available for evaporation by boiling, including conventional indirect contact types (boilers, evaporators) and direct contact types (for example incinerators).

- Solar evaporation. Use of solar heat and movement of air to evaporate water.

- Contact with an air stream. For example air can be bubbled through the water or water can be sprayed into the air.

- Phytoremediation. Plants take in the contaminated water through their roots and the majority of the water (including tritium) is evaporated. A fraction of the tritium is also retained in the plant matter until it decays. If the water source is at or near the surface, the plant may remove water directly from the source. Alternatively the water may be pumped to the plants (e. g. the contaminated water is used for irrigation).

Three evaporation methods (Solar Evaporation, Irrigation, and Mechanical Evaporation) were considered in the 1994 Hanford Site evaluation (Allen 1994). Of 11 tritium mitigation methods evaluated, the above three received the lowest rankings (Table 7-1 of (Allen 1994)). As discussed in the following, incineration and phytoremediation have recently been selected at other DOE sites for disposal or mitigation of wastewater with trace tritium contamination.

3.3.4.1 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 the Savannah River Site for tritiated water.

In phytoremediation the plants take up nutrients from the contaminated soil and use the contaminated water to grow. The plants can breakdown, trap and hold contaminants in the leaves and/or stems, and transpire the water into the atmosphere as part of the natural plant growth. The process is only good for near surface contamination, shallow aquifers, and irrigation. The transport of water in soil and vegetation and accumulation of biomass in the forest trees are considered the most important physical, chemical and biological transport processes for estimating partitioning of isotopes to vegetation and the amount of fixed tritium in a forest that has been exposed to tritiated irrigation water (Diabate and Strack 1993, Murphy 1993).

The turnover time of tritiated water in the conducting outer rings of the roots and stem and in the leaves is on the order of hours to several days. The turnover time of tritiated water in the inner, older rings of the roots and stem is on the order of days to years depending on the size of the tree. Approximately 60 percent of the tritium fixed during synthesis will remain in the biomass until released by decay or combustion after death of the tree. The remaining 40 percent will be exchanged with hydrogen in water (Blount et al. 2003).

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 et al. 2001). Work on phytoremediation has continued at Argonne National Laboratory, and a report covering results is to be issued early in 2004 (Negri 2003).

The phytoremediation project at the Savannah River site with regard to tritium is 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 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, Blount et al. 2003). The potential maximum exposed individual off site dose from a liquid release of 1200 Ci of tritium to the Savannah River is twice the dose for an airborne release of 1200 Ci of tritium (0.0060 mrem vs 0.0027 mrem). The total liquid-pathway population dose of 0.20 person-mrem is essentially the same as the airborne-pathway population dose (Blount et al. 2003).

A sheet pile dam for collection of water and forest irrigation system was installed in 2000 and 2001, respectively, for tritium remediation at a cost of about $1,500,000. Tritiated water behind the dam is used for irrigation of 25 acres of natural forest pines and hardwood trees located upgradient of the seepline. The irrigation supplements natural precipitation and evaporation. Annual operating cost is about $500,000 and about 7,570,000 liters (2,000,000 gallons) of tritiated water was used for irrigation of the forest in FY 2003 (Blount 2003).

3.3.4.2 Application at the Hanford Site

Phytoremediation does not meet the needs of bulk ground water clean up at the Hanford site because of the aquifer depth. Insufficient oxygen in the soil usually prevents root depth of plants and trees growing below about 1.2 m where most nutrient absorption occurs. Some pines found in Texas and mesquite (Keawe) have been known to send roots penetrating to depths of 3 m and 24 m respectively (Schnelle et al. 1989).

Table 3 shows the maximum tritium concentration and depth to groundwater. Depths range between 20 m and 100 m except at the Columbia River shoreline. Also, phytoremediation for minimizing water entering a contaminated aquifer typically uses either hybrid poplars or pine trees. Neither of these types of plants would be amenable to the natural environment on the Hanford site. The 1994 tritium technology evaluation scored irrigation (phytoremediation) as the poorest based on relative cost and risk (Allen 1994).

Table 3. Maximum Tritium Concentrations and Depth to Water at Hanford[1]

Area	Maximum Tritium concentration, pCi/L		Depth to Water, m
	Well	Shoreline[2]	
100 B/C	**30,600**	**45,000**	<1 to 30
100 D	16,300	**29,400**	<1 to 25
100 H	6,400	1,245	<1 to 12
100 F	3,800	1,470	<1 to 14
100 K	**588,000**	5,150	<1 to 22
100 N	**39,300**	**21,500**	> 1 to 21
200 W	**1,690,000**	-	50 to 100
200 E	**4,170,000**	**58,400**	65 to 100
400	13,000	-	45 to 50
600	-	-	-
300	12,100	-	<1 to 18
300 FF-5	**4,230,000**	-	<1 to 18
1100	432	-	2 to 30

Notes: 1) Source of information is Hartman (2003). Concentrations in **bold** type exceed the drinking water standard (MCL) of 20,000 pCi/L (0.020μCi/L).

2) Shoreline sampling includes aquifer sampling tubes, seeps and shoreline wells since the Fall of 2001. The 200 E area plume is monitored at the Hanford town site.

3.3.5 Incineration

Incineration or direct contact mechanical evaporation provides a controlled and measurable means of disposing of tritiated water though a stack. The Brookhaven National Laboratory used a low flow pumping system to remove the highest concentrations of tritium from the aquifer south of the High Flux Beam Reactor. Approximately 340,000 liters (90,000 gallons) of tritiated water (500,000 pCi/L) was transported to Oakridge National Laboratory for disposal at the GTS Duratek incinerator. Transportation and off site disposal cost of the tritiated groundwater was about $5.30 per liter ($20 per gallon). Low flow pumping, transportation, and incineration were stopped in early 2001 after removing the target 0.2 Ci of tritium from the aquifer. The DOE at Brookhaven made the decision to dispose of the tritiated groundwater offsite rather than construct and operate a treatment facility at Brookhaven (ROD 2000, Hauptmann 2003).

3.3.5.1 Application at the Hanford Site

Mechanical evaporation of tritiated water at Hanford was studied as an alternative to the SALDS (Brown 1993) and as treatment method of tritiated water disposal in (Allen 1994). Brown (1993) developed a rough order of magnitude cost estimate of $38,145,000 (includes project and 30 yr operation and maintenance costs) for mechanical evaporation of ETF wastewater and showed it cost considerably more than other disposal alternatives. Air disposal of ETF wastewater would impact site air emissions and effective dose to the on-site workers and offsite public. Air disposal received a very low ranking among tritium mitigation options evaluated in the 1994 report (Allen 1994).

3.4 RELATIVE COST OF MITIGATION OPTIONS

Costs for options to mitigate tritium in Hanford waste water will vary substantially depending on the technical process option selected. Costs can also be expected to vary substantially depending on site specific and project specific factors. Available cost estimate information for various technologies is identified in the sections that discuss those technologies. In most cases estimates have not been developed for specific Hanford treatment scenarios that might currently be considered. To develop more reliable cost estimates, specific scenarios would need to be defined, including wastes to be treated or otherwise mitigated, location, capacity, operating duration, applicable state and federal requirements for treated wastewater and concentrated product, etc. Despite these limitations, some general comments on relative costs can be made, as discussed below and summarized in Table 4.

- Separation is typically the most expensive overall mitigation option. For a large base-load type facility operated almost continuously, sized to treat the full stream currently discharged to the SALDS, and designed to reduce tritium content below the drinking water standard, the total treatment cost (capital, operation, utilities, and other project costs) is expected to be in the range of dollars per gallon, likely at least several dollars per gallon. The CECE, Bithermal Hydrogen-Water, and Girdler Sulfide Processes all appear to be viable candidate separation processes. Available information is not sufficient to determine a clear preference or ranking among these tritium separation processes. The preferred option may vary depending on power and steam costs, plant capacity, and base load versus cyclic or campaign type operations and other scenario/site specific factors. If

developed successfully, the sorbent based processes discussed in Section 3.2.1 may also be cost competitive with those listed above. However, based on current available information, sorbent based processes do not appear to offer a major breakthrough that will significantly reduce cost for tritium separation from wastewater. If developed successfully, sorbent based processes could have some advantages in terms of ease of operation, portability, and safety.

- For separations options that produce a concentrated tritium product, options for handling, storage, and disposal will significantly affect total cost.

- Cost estimates prepared to support selection of the current SALDS option suggest that the cost for mechanical evaporation will be on the order of tenths of a dollar per gallon, while costs for crib disposal (current SALDS approach) are on the order of cents per gallon. (Field 1991), (Brown 1993). These estimates were based on the assumption that the full stream currently discharged to SALDS would be treated.

- The cost for all mitigation options will tend to increase in terms of dollars per gallon for smaller processing capacity and intermittent operation.

- Costs for water treatment at existing Hanford site pump and treat projects provide additional perspective on typical wastewater treatment costs. Hanford 100 area projects and contaminants removed are as follows: 100-HR-3, hexavalent chromium; 100-KR-4, hexavalent chromium; and 100-NR-2, Strontium-90. Fully burdened treatment costs for these project averaged about $.05 per gallon for the six years ended in 2002 (see Section 5.0 of Kelty et al. 2003). Hanford 200 area projects and contaminants removed are as follows: 200-UP-1, uranium, technicium 99, carbon tetrachloride, and nitrate; and, 200-ZP-1, carbon tetrachloride. Fully burdened treatment costs for these projects averaged less than $.03 per gallon for the six years ended in 2002 (see Section 4.0 of Erb et al. 2003).

- Costs for options such as pumping, underground barriers, and phytoremediation are highly site specific.

- For mitigation of relatively small volumes, such as treatment or relocation of a relatively small-volume high-concentration wastes, mitigation process costs (equipment, and operation) are likely to be overshadowed by other project costs such as waste characterization, engineering, technology development/definition, safety evaluations and approvals, permitting, and overheads.

- For waste water that is already in the ground, it appears obvious that decay in place (simply leaving it there) is the lowest cost option for tritium mitigation. For wastewater discharged from the ETF, continued discharge to ground water via the SALDS is undoubtedly the lowest cost mitigation option. The tritium concentration in groundwater will gradually drop due to radioactive decay and dilution. For the contamination levels in SALDS discharge and in groundwater identified at Hanford, decay alone will reduce tritium concentrations below the drinking water standard in less than 100 years

Table 4. Relative Cost and Efficiency for Mitigation Approaches

Mitigation Approach	Typical Implement-ation or Technology	Efficiency	Cost Information	Comments
Separation treatment	CECE, bithermal hydrogen, GS, sorbent	Efficiencies to meet drinking water standard demonstrated for CECE, expected achievable by others with sufficient staging.	For large base load type facility costs expected to be in dollars per gallon range. Increased by smaller size, intermittent operation, or short operating life.	Handling and disposal of concentrated tritium stream will add additional costs
Decay	Discharge to slow moving ground water via Crib or percolation pond	Efficiency determined by travel time to release point. Models predict acceptable efficiency for SALDS	For large volume operated over a long period of time (such as SALDS) cost expected to be in cents per gallon range	Current SALDS approach
Decay	Upgradient pumping, barriers, or reduced inflow to delay release	Site specific and highly variable	Costs are site specific and highly variable. Massive barriers to control ground water movement at Hanford judged economically infeasible	Does not appear applicable to Hanford due to large areas and large perimeter
Mechanical evaporation	Boiler, incinerator	100 % of tritiated water can be evaporated	For large volume base load type facility cost is expected to be in tenths of a dollar per gallon range. Expected to be much higher for small volumes	Rated very poorly in initial option evaluations
"Natural" evaporation	Solar evaporation, evaporation by plants, irrigation	Solar evaporation could evaporate essentially 100 %, others highly variable	Costs are site specific and highly variable	Rated very poorly in initial option evaluations

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