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Tritiated Wastewater Treatment and Disposal Evaluation for 1995

W. L. Allen, Ph.D.
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EXECUTIVE SUMMARY

A second annual summary and analysis of potential processes for the mitigation of tritium contained in process effluent, ground water and stored waste is presented. It was prepared to satisfy the Hanford Federal Facility and Consent Order (Tri-Party Agreement) Milestone M-26-05B.

Technologies with directed potential for separation of tritium at present environmental levels are organized into two groups. The first group consists of four processes that have or are undergoing significant development. Of these four, the only active project is the development of membrane separation technology at the Pacific Northwest Laboratory (PNL). Although research is progressing, membrane separation does not present a near term option for the mitigation of tritium.

A second grouping of five early stage projects gives an indication of the breadth of interest in low level tritium separation. If further developed, two of these technologies might prove to be candidates for a separation process.

At the present, there continues to be no known commercially available process for the practical reduction of the tritium burden in process effluent.

Material from last year's report regarding the occurrence, regulation and management of tritium is updated and included in the appendices of this report. The use of the State Approved Land Disposal Site (SALDS) for disposal of tritiated effluent from the 200 Area Effluent Treatment Facility (ETF) begins in the fall of 1995. This is the most significant event impacting tritium in the environment at the Hanford Site this coming year.

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LIST OF TERMS

AECL	Atomic Energy of Canada Limited
CECE	Combined Electrolysis Catalytic Exchange Process
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
DWS	*Drinking Water Standards*
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ETF	Effluent Treatment Facility
ICRP	International Commission on Radiological Protection
LERF	Liquid Effluent Retention Facility
PNL	Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction
NRC	U.S. Nuclear Regulatory Commission
REDOX	reduction oxidation
SALDS	State Approved Land Disposal Site
SRS	Savannah River Site
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*

SCIENTIFIC SYMBOLS AND ABBREVIATIONS

Units of Measure

Unit	Definition
L	Liter
m	Meter
g	Gram
h	Hour
K	Degree Kelvin (absolute temperature)
°C	Degree Centigrade
Ci	Curie
Bq	Bequerel
Gy	Grey (100 rads)
Sv	Sievert (100 rems)

Magnitude Modifiers

Symbol	Unit	Amount
K	Kilo	10^3
M	Mega	10^6
T	Tera	10^{12}
m	milli	10^{-3}
μ	micro	10^{-6}
p	pico	10^{-12}

Elements and Compounds

Symbol	Definition
H or ^1H	Hydrogen
D or ^2H	Deuterium
T or ^3H	Tritium
He	Helium
H_2	Hydrogen, elemental
D_2	Deuterium, elemental
T_2	Tritium, elemental
HD	Mixed isotopic hydrogen, elemental
HT	Mixed isotopic hydrogen, elemental
DT	Mixed isotopic hydrogen, elemental
H_2O	Water
D_2O	Deuterium oxide or heavy water
T_2O	Tritium oxide
HDO	Mixed isotopic water
HTO	Mixed isotopic water (tritiated water)
DTO	Mixed isotopic water
^{129}I	Iodine-129
^{90}Sr	Strontium-90

1 INTRODUCTION

This report is the second annual assessment of tritium separation technology at the Hanford Site. This assessment is mandated by the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) as Milestone M-26-05B (Ecology et al. 1994), which states:

> "Submit to EPA and Ecology an evaluation of development status of tritium treatment technology that would be pertinent to the cleanup and management of tritiated wastewater (e.g., the 242-A Evaporator Process Condensate liquid effluent) and tritium contaminated groundwater at the Hanford Site."

The information presented updates the material discussed in *Tritiated Wastewater Treatment and Disposal Evaluation for 1994* (DOE 1994). This material includes more recent events and information regarding tritium in the environment and separation processes for tritium. Refer to the 1994 report for background material.

1.1 TRITIUM BACKGROUND INFORMATION

Summaries of tritium information that appeared in the 1994 report have been updated and are included in Appendices A, B, and C, by topic, as follows:

Appendix A:	Tritium Information
Appendix B:	Tritium in the Environment
Appendix C:	Tritium at the Hanford and Savannah River Sites.

Appendix D is a Tritium Fact Sheet that summarizes tritium information included in Appendix A, B and C. This fact sheet was included in the information submitted to Ecology in obtaining the State Waste Discharge Permit for the 200 Area ETF.

Chapter 6 contains a bibliography of general reference works about or including tritium.

1.2 PREPARATION OF THE 1995 TRITIUM REPORT

First, a phone network of individuals in government and business having a concern or interest in tritium was established. Calls to individuals in the network helped provide the most current information regarding tritium. As a result of

contacts in the network, two meetings dealing with tritium separation technology were conducted at the Hanford Site this year.

Second, recent publications and scientific journals, including abstracts and papers published in association with technical meetings and symposia, were searched for references to tritium. All relevant publications for 1994 to 1995 were reviewed. Where historical continuity was important, volumes from 1993 and even 1992 were examined. In addition, several online abstract services were searched for current information on tritium.

As a part of this program, The International Program Support Office at the Pacific Northwest Laboratory (PNL) was commissioned to review international publications for reference to tritium.

Appendix E contains a complete listing of publications and databases searched.

2 TRITIUM SEPARATION TECHNOLOGIES

As a product and as a waste of the nuclear age, tritium provides a significant challenge both in terms of science and of policy. As an isotope of the element hydrogen, the chemical and physical properties of tritium differ only slightly from hydrogen. When tritium is manufactured for strategic or other uses, processing operations for manipulation and isolation employ properties that are common to all hydrogen isotopes. When tritium is mixed with any chemical form of hydrogen, all of its characteristics except its radioactivity are masked by hydrogen. The separation of tritium from hydrogen in this condition requires the use of small differences in the physical and chemical properties that exist between tritium and hydrogen. This specialized area of separation technology is referred to as isotopic separation.

A report prepared for the Department of the Environment of the United Kingdom provides a review of the issues associated with tritium removal (Kisalu 1991). The report includes a large section on the recovery of tritium from spent radioluminous light sources. The report concludes, as does this report, that present costs for removing tritium from aqueous wastes outweigh the potential reduction in hazard.

2.1 ISOTOPIC SEPARATIONS, BACKGROUND

In general, when designing a purification or separation process, there is a large array of processing techniques from which to choose. In most cases, the application of the appropriate separation technology provides a reduction of specific impurities by factors ranging from 500 to 10,000. Filtration, coagulation, ion exchange, and reverse osmosis are all single-stage unit operations that accomplish these types of separations. Processing units function well for chemical and physical separations because of the large differences in the properties between the system and the impurity. However, when the differences in properties between the system and the impurity become as small as they are between hydrogen and tritium, a single-stage separation unit only reduces the contaminant level by a very small factor. In order to achieve a practical level of separation, several stages are linked in a process series called a "cascade" design.

Single-stage isotopic separations produce two product streams. One stream contains slightly less of the isotope of concern and the other stream contains slightly more. The ratio of the isotopic content in the two streams is called the "separation factor." The separation factor, the feed rate, the incoming isotopic concentration, and the desired isotopic purity in the outgoing stream are key engineering criteria for the design of a facility for isotopic separations.

Generally, the lower the separation factor (i.e., the closer the number is to 1.0), the higher the number of separation stages required to achieve an overall degree of separation. In the case of tritium, the "clean" discharge must be less than the 40 CFR §141, *Drinking Water Standards* (DWS), for tritium (20,000 pCi/L). The concentration of tritium in high-level tritiated waste must ultimately be determined by factoring the processing costs of the high-level waste stream against the disposal costs for the volume of waste generated.

2.2 COMMERCIAL APPLICATIONS FOR SEPARATION OF HIGHLY CONCENTRATED TRITIUM

Currently, tritium separation is practiced commercially in association with heavy water moderated nuclear reactors and in nuclear fusion research. These separation processes are found where tritium occurs in high concentration and is produced or handled as a pure product stream. High concentration isotopic separations are often referred to as "enrichment." Those businesses or agencies that have the need to process high level tritium have adopted or developed the required separation technology.

The transfer of existing technology for the separation of tritium in areas of environmental concern has <u>not</u> yet been successful because of the high cost of processing large volumes of very dilute tritium. However, two commercial processes utilized world-wide are included here to illustrate the tritium enrichment process.

2.2.1 Heavy-Water-Moderated Nuclear Reactors

The Canadian Deuterium Uranium (CANDU) nuclear reactor design uses heavy water (D_2O) as a moderator/coolant. The high neutron flux in the reactor core converts some of the deuterium to tritium. The Combined Electrolysis Catalytic Exchange (CECE) process, designed by Atomic Energy of Canada Limited (AECL), is used to separate T_2O from D_2O (Section 2.4.1). Two plants using this process are in operation, one at Darlington, Ontario, Canada, and the other at Grenoble, France. Typically, heavy water, with as much as 1 Ci/L tritium, is processed to reduce radioactivity in the cooling loop. The output stream is gaseous deuterium depleted in tritium by a factor of 100 to 200. The enriched stream is further processed by cryogenic distillation providing essentially pure tritium which is then sold to the manufacturers of self-illuminating light sources.

2.2.2 Nuclear Fusion Research

Fusion energy research and strategic weapons utilize tritium in its pure form. When tritium from these operations is recycled, it must be separated from helium and deuterium. Since this stream is already in the gaseous form and at a fairly high concentration, tritium is purified by cryogenic distillation. The Princeton Plasma Physics Laboratory and The Los Alamos National Laboratory use cryogenic distillation in their fusion research with tritium.

2.3 TECHNOLOGY FOR SEPARATION OF ENVIRONMENTAL TRITIUM

Tritium that is a by-product of past nuclear operations is found in the environment and in stored process waste. Tritium found in ground water, waste storage tanks and spent fuel basins is in the form of HTO. In this form, it is often referred to as "tritiated water." Typically, tritium in this form has a concentration of a few millionths of a curie per liter. This concentration is about two orders of magnitude above the DWS of 20,000 pCi/L.

Since environmental tritium occurs as dilute HTO in water, methods for separating hydrogen isotopes that apply to hydrogen gas cannot be used. These methods are not applicable primarily because of the cost of converting large quantities of water to elemental hydrogen. As a result, electrolysis, cryogenic distillation, and gaseous diffusion are eliminated from serious consideration as options for separation.

Present nuclear operations generate and discharge tritium within the limits of established regulatory permitting systems. As such, nuclear power plants and fuel reprocessing facilities have no need for tritium separation. The presence of tritium in stored waste and ground water resulting from past operations at DOE sites (See Appendix C) leaves DOE as a "stand alone" party with needs and interest in low-level tritium separation. As a result, DOE has funded and directed the development of technology for tritium separation. Presently, The Efficient Separations and Processing Integrated Program (ESPIP) within the DOE Office of Environmental Management has designated tritium separation as a target technology for development (Kuhn 1995).

2.4 CANDIDATE TECHNOLOGIES

Four separation technologies have been proposed as potential process options for separating low-level tritium from treated liquid effluent. These technologies are in various stages, ranging from those being actively developed to those seeking funding for further work. Work on one system has been

discontinued because of poor results. Each of these technology development projects has received at least some direction and funding from the DOE. A summary of information regarding these technologies is given in Table 2.1.

2.4.1 Combined Electrolysis and Catalytic Exchange

Although it was designed for high-level tritium, the CECE process has been recommended as a candidate for environmental tritium. The process has been tested and developed for the recovery of tritium from high-level aqueous waste at the DOE Mound facility (Sienkiewicz and Lentz 1988).

A proposed flowsheet for the CECE process is shown in Figure 2-1. In this process, tritiated feed water is introduced at a point between a stripping and an enricher column. Hydrogen generated by electrolysis passes up through both columns. The proprietary catalyst in the columns establishes an exchange equilibrium between the hydrogen and water phases. As a result, tritium is reduced in the hydrogen phase and concentrated in the water phase. Electrolysis further concentrates tritium at this point in the process. Water vapor that is carried with the oxygen stream is condensed and removed as the concentrated HTO stream. "Clean" hydrogen gas is the "detritiated" stream from the process. It is important to note that the entire volume of the clean stream must be removed in the form of hydrogen gas.

The report on management of tritium wastes in Great Britain provides a cost estimation for a process similar to the Canadian CECE process (Kisalu et al. 1991). The report provides a speculative projection for the cost of a CECE plant. This cost projection was derived by extrapolating a known base cost of about $3,000,000 U.S. dollars[1] for a 6 L/hr pilot plant to a 170 L/min (45 gal/min) size using a logarithmic scaling factor. The report projects a capital cost of $600,000,000[1] for a 170 L/min (45 gal/min) tritium treatment facility that would be coupled to a PUREX-type operation in the fuel reprocessing plant at Sellafield. This seems to be a high cost for a facility to process 170 L/min (45 gal/min), but there are no other numbers with which it can be compared for validation.

AECL has not provided any cost estimates for using this process for treating low-level tritium.

---

[1]Based on an exchange rate of $1.55 U.S. dollars per British pound.

2.4.2 Bithermal Catalytic Exchange

Bithermal processes for separating hydrogen isotopes are common. Chemical exchange processes reviewed in literature (Vasaru 1993) commonly utilize a hydrogen-containing species that is cycled through a counter-current flow of water. A low-temperature column enriches tritium in an aqueous stream and a high-temperature column enriches tritium in the vapor phase. See Figure 2-2, for a process flow sheet.

Original work on a bithermal hydrogen/water exchange process was published by researchers in Japan (Kitamoto et al. 1985). Professor Vincent Van Brunt in the Chemical Engineering Department of the University of South Carolina further developed the process for DOE at the SRS (Schwirian-Spann et al. 1994). The Efficient Separations and Processing Integrated Program (ESPIP) within the DOE, Office of Environmental Management, supported the work by Van Brunt.

The bithermal process uses the same catalytic exchange process developed by AECL for use in the CECE process. The main difference is that the two columns used in the process are maintained at different temperatures. Since the separation factor for tritium in the water/hydrogen system decreases with increasing temperature, a low-temperature column (25°C) is used to enrich tritium in the liquid (aqueous) phase and a high-temperature column (100° to 200°C) is used to enrich tritium in the gas (hydrogen) phase. Connecting the two columns as shown in Figure 2-2, provides a counter-current flow of water downward through the system and a recycling flow of hydrogen gas upward. A small electrolysis unit provides replacement hydrogen for the recycle stream and also increases the tritium enrichment in the aqueous discharge stream. In this system, hydrogen is a recycled stream. The two product streams are both water, one enriched and one depleted in tritium. Laboratory tests using the system resulted in a reduction of tritium concentration by a factor of 100.

Professor Van Brunt stated that this system, since it only requires a small amount of energy for electrolysis relative to the volume of water flowing through the system, is the best current candidate for economical enrichment of environmental tritium. But, in order for it to be useful, more efficient catalysts will need to be found and developed (Van Brunt 1994). In its present state of development, this technology is not a candidate for commercial application.

2.4.3 Laser Isotope Separation

Laser isotope separation technology has attracted a great amount of attention in the past 15 years. Initial indications were that a separation factor of 10,000 was possible for the extraction of tritium from tritiated water. Both Ontario

Hydro and Lawrence Livermore National Laboratory (Vasaru 1993) were involved in substantial research projects for laser isotope separation of tritium. An entire chapter in *Tritium Isotope Separation* (Vasaru 1993) is devoted to a description of this technology.

The laser isotope process shown in Figure 2-3, consists of two sections. In the first section, steam from evaporated tritiated water passes upward through a stripper column where tritium is transferred to a "working fluid". The enriched working fluid is then transferred to a reaction column where tritium is exchanged for hydrogen in CF_3H. The mixture of CF_3H and CF_3T in vapor form is exposed to a laser beam that selectively decomposes CF_3T forming C_2F_4 and TF. Chemical and physical methods are used to separate TF from CF_3H and C_2F_4. Condensate from the stripper column is the depleted stream.

In 1989, researchers at Ontario Hydro (Bartoszek et al. 1989) predicted that a plant based on this technology would cost about half that of the CECE plant operating at Darlington. The results of testing subsequent to these predictions, revealed that the complexities of the process (Woodall 1995) reduced the efficiency of the exchange and decomposition steps to a point where the process was no longer economical. All work on this technique was stopped at Ontario Hydro.

Currently, there is no other work underway on the development of laser isotope separation technology.

2.4.4 Membrane Separation

The ESPIP within the DOE, Office of Environmental Management, is funding a project at PNL to develop a polyphosphazine membrane system for tritium separation. The specific mission of the work is aimed at reducing tritium in the 105-KE Basin. The membranes used in the program had demonstrated the ability to retain levels of tritium in previous laboratory experiments (Nelson et al. 1994).

In the 1995 program, researchers at PNL continued testing laboratory manufactured polyphosphazine membranes using actual water from the 105-KE Basin in the 100 Area of the Hanford Site (Nelson et al. 1995). The membranes used are now subjected to an annealing process at 75-100°C. As a result, this year's tests show a consistent tritium reduction of about 40%. The researchers predict that production of their membrane system using commercial methods will improve tritium separation to around 50%.

The chemistry of the polyphosphazine membrane seems to be a significant factor in performance. Selected commercial nanofiltration membranes tested in the same system were found to deplete tritium by only 5%.

Separation of tritium continues to be better at 5°C than at any other temperature. This fact alone leads the scientists to believe that separation takes place at the membrane surface by some mechanism involving water aggregates or clusters that tend to hold HTO somewhat more strongly than they do H_2O.

2.4.4.1 Appropriate Waste Form. When dealing with a system for isotopic separation, the product is two streams: one enriched in tritium and the other depleted in tritium. The enriched, or waste, stream must be reduced in volume to a sufficient point that disposal or storage is cost efficient. The volume of the stream and the tritium level can be factored together to determine the optimal balance for minimal cost. Waste criteria for this stream and a method for its ultimate storage or disposal are issues that should be addressed as membrane separation technology becomes closer to a reality for remediating tritium. The cost analysis in the following section illustrates this importance.

2.4.4.2 Cost Analysis. A concurrent work at PNL (Villegas et al. 1995) developed cost estimate ranges for removing tritium from the 105-KE Basin utilizing preliminary information from the membrane research. Theoretical systems engineering cost equations were used to estimate the cost of treating the tritium in the Basin. The modeling calculations for total capital and operational costs to reduce the tritium by 90% ranged from $7,000,000 to $80,000,000, depending in the number of cells and the feed rate for the proposed system. The time frame for the operation was a year or less. The result would be to concentrate 90% of the tritium from the Basin into 85 m^3 of solidified waste.

The difficulty in this work is that, instead of using a countercurrent cascade design, they used a simple cascade design for their model. This design processes a stream from the 105-KE Basin sequentially through a series of membrane cells. The tritium concentration in the process stream was increased in each cell by a factor of 2.2. The final output is a process stream with a higher tritium concentration and lower volume. Presumably, this concentrated stream would be low enough in volume to allow it to be dispositioned properly and efficiently.

In the theoretical design, the depleted stream from each membrane cell was piped directly back to the 105-KE Basin. As a result, a design problem occurs because the tritium concentration is increasing in the feed to each sequential cell, but only the depleted stream from the first cell is actually lower in tritium concentration than the water in the Basin. "Depleted " streams from all stages higher than the first are actually higher in tritium than the Basin. Much of the separation work done by the system is lost because of this.

It would be informative to see this same computer simulation done using a feedback design. In this case, the depleted stream from each stage would be piped into the feed stream of the next lower separation stage. The efficiency of the

process would improve because some of the separation work done by previous stages would be retained by the system. Qualitatively, one would expect capital costs to increase because of increasing complexity, but operational costs should drop along with the volume of solidified waste produced because the process would become more efficient.

2.4.4.3 Future Development of Membrane Separation. The next stages of work on this concept will involve further definition and optimization of the reject stream by testing both turbulent and laminar cross-flow membrane design units. This information is required for the mathematical models used for further scale-up and design work. A larger membrane unit is being commercially prepared for testing at the 105-KE Basin this summer. Even with continued success in research, it will still be a number of years before a membrane process is ready for commercial development.

Table 2-1. Summary of Developed and Developing Processes.

Process: Status	Company/Lab: Contact	Process Description	Evaluation: Pros and Cons
Combined Electrolysis Catalytic Exchange (CECE) See Section 2.4.1 Commercially used for removal of high-level tritium from D_2O. Not developed for low-level tritium.	Atomic Energy Canada, Ltd. Chalk River Laboratories Chalk River, Ont., Canada Dr. Alistair I. Miller 613-584-3311 Ex 3207	Equilibrium exchange of hydrogen between H_2 gas and water is established using a proprietary water-proof catalyst. Tritiated water flows down over a catalyst bed while H_2 from water electrolysis moves up through column. Tritium concentrates in water phase. Longer column length gives better separation. Larger column diameter required for higher flow rates.	Pro: Process is well demonstrated commercially for removing high level tritium from D_2O at low flow rates. Con: Has not been demonstrated on low level tritiated water. "Clean" product stream is hydrogen, requiring conversion of water to H_2. No process economics available from AECL.
Bithermal Catalytic Exchange See Section 2.4.2 Laboratory tested. No field experience planned.	University of South Carolina Department of Chemical Engineering Columbia, South Carolina Prof. Vincent Van Brunt 803-777-3115	Chemistry identical to CECE process. H_2 recycled through low then high temperature catalytic exchange columns. Tritium concentrates in vapor phase in high temperature column and in liquid phase in low temperature column. Net effect is to produce low tritium water discharge from high temperature column and high tritium water discharge from low temperature column.	Pro: "Clean" stream is water with lower tritium. For this reason would potentially be lower cost than CECE. Con: Less efficient separation because of the bithermal columns. Needs to have more efficient catalyst for further development.
Laser Isotope Separation See Section 2.4.3 Extensively developed in the laboratory. Project cancelled because of poor results.	Ontario Hydro, Research Division 800 Kipling Ave. Toronto, Ont. Canada Dr. K. B. Woodall 416-231-4111	Tritiated water is evaporated. Resulting steam is passed through a caustic exchange column. Exiting steam is condensed to produce "detritiated" water. Enriched fluid is passed through second column where CF_3H vapor exchanges H for T. CF_3H/ CF_3T vapor is passed through laser beam. CF_3T preferentially decomposes to TF and C_2F_4. TF is separated and CF_3H recycled.	Pro: Has potential for highest separation factor. Con: Chemical process for transfer of tritium from water to CF_3H is very inefficient. Laser frequency for decomposition also needs to be better tuned.
Membrane Separation See Section 2.4.4 Laboratory development showing good promise. Development will continue.	Pacific Northwest Laboratory Richland, Washington Dr. David A. Nelson 509-376-0875	Laboratory Reverse Osmosis (RO) membranes are made from substituted polyphosphazines. Single stage laboratory RO units were tested with tritiated water resulting in retardation of tritium by membrane. Water passing through membrane has 40% less tritium than the feed.	Pro: Capital and operating costs expected to be similar to other RO operations. Con: Process is still in early stages of development.

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Bithermal Catalytic Exchange See Section 2.4.2 Laboratory tested. No field experience planned.	University of South Carolina Department of Chemical Engineering Columbia, South Carolina Prof. Vincent Van Brunt 803-777-3115	Chemistry identical to CECE process. H_2 recycled through low then high temperature catalytic exchange columns. Tritium concentrates in vapor phase in high temperature column and in liquid phase in low temperature column. Net effect is to produce low tritium water discharge from high temperature column and high tritium water discharge from low temperature column.	Pro: "Clean" stream is water with lower tritium. For this reason would potentially be lower cost than CECE. Con: Less efficient separation because of the bithermal columns. Needs to have more efficient catalyst for further development.
Laser Isotope Separation See Section 2.4.3 Extensively developed in the laboratory. Project cancelled because of poor results.	Ontario Hydro, Research Division 800 Kipling Ave. Toronto, Ont. Canada Dr. K. B. Woodall 416-231-4111	Tritiated water is evaporated. Resulting steam is passed through a caustic exchange column. Exiting steam is condensed to produce "detritiated" water. Enriched fluid is passed through second column where CF_3H vapor exchanges H for T. CF_3H/ CF_3T vapor is passed through laser beam. CF_3T preferentially decomposes to TF and C_2F_4. TF is separated and CF_3H recycled.	Pro: Has potential for highest separation factor. Con: Chemical process for transfer of tritium from water to CF_3H is very inefficient. Laser frequency for decomposition also needs to be better tuned.
Membrane Separation See Section 2.4.4 Laboratory development showing good promise. Development will continue.	Pacific Northwest Laboratory Richland, Washington Dr. David A. Nelson 509-376-0875	Laboratory Reverse Osmosis (RO) membranes are made from substituted polyphosphazines. Single stage laboratory RO units were tested with tritiated water resulting in retardation of tritium by membrane. Water passing through membrane has 40% less tritium than the feed.	Pro: Capital and operating costs expected to be similar to other RO operations. Con: Process is still in early stages of development.

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Figure 2-1. Combined Electrolysis Catalytic Exchange Process.

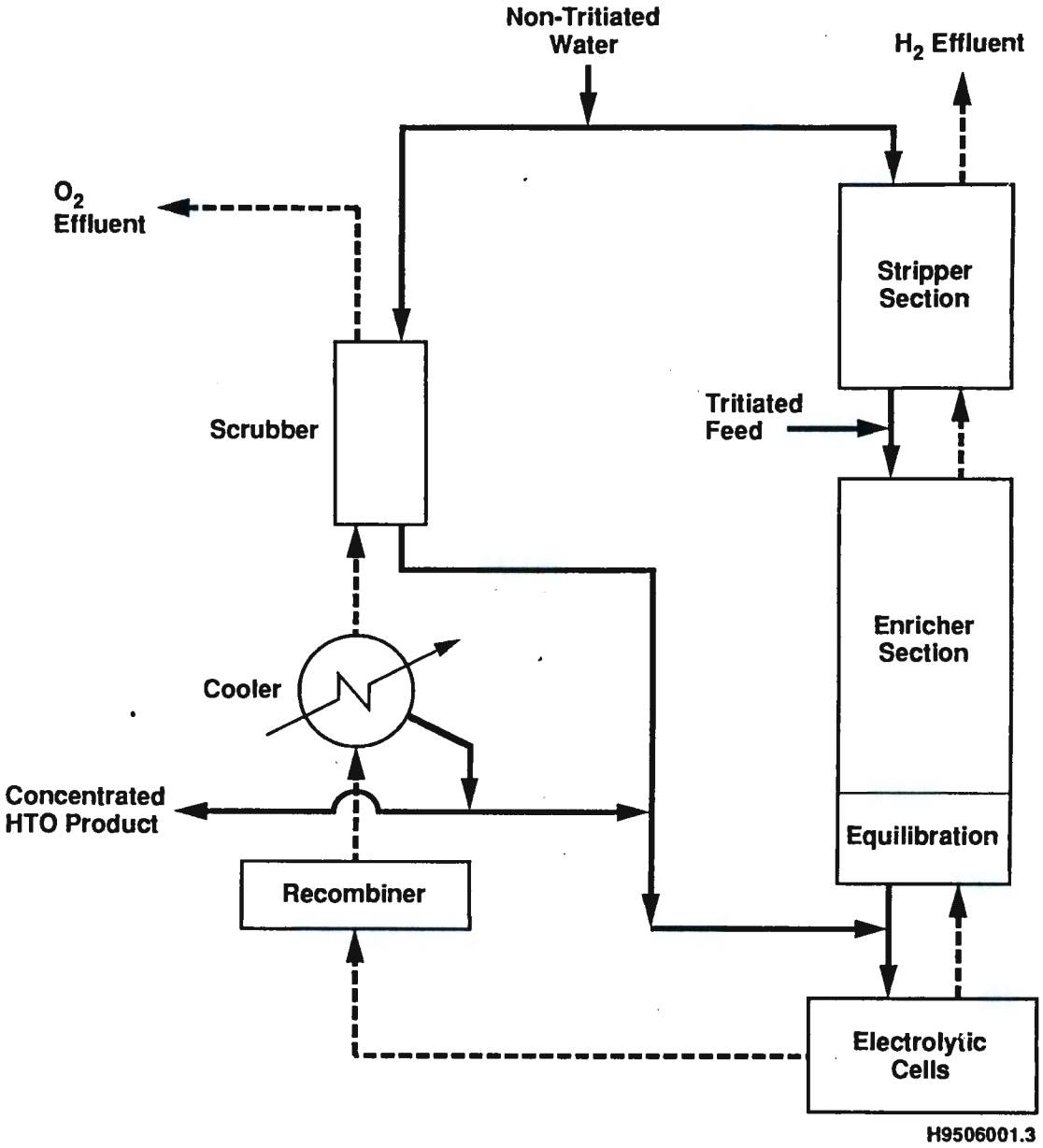
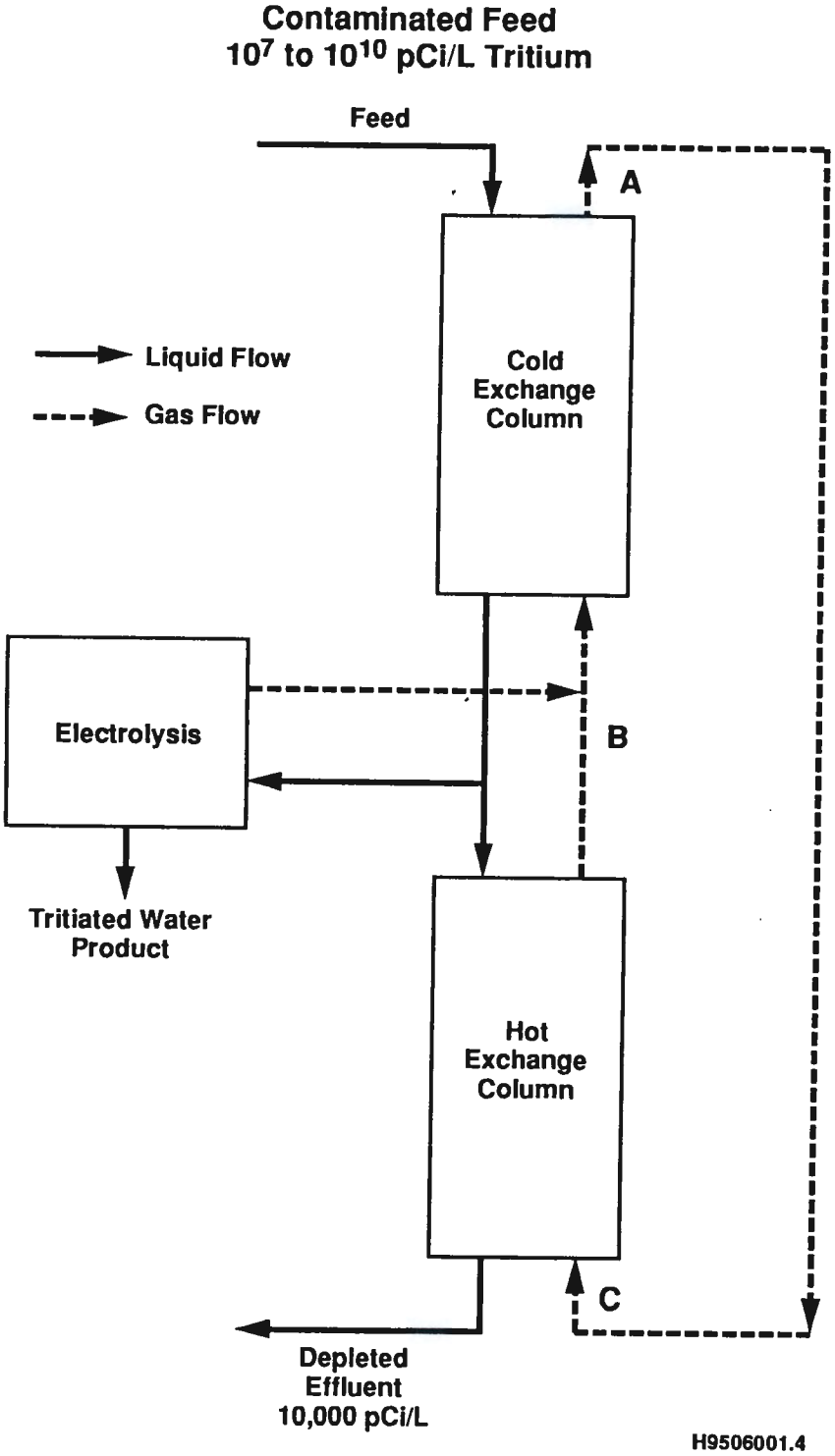


Figure 2-2. Bithermal Process.



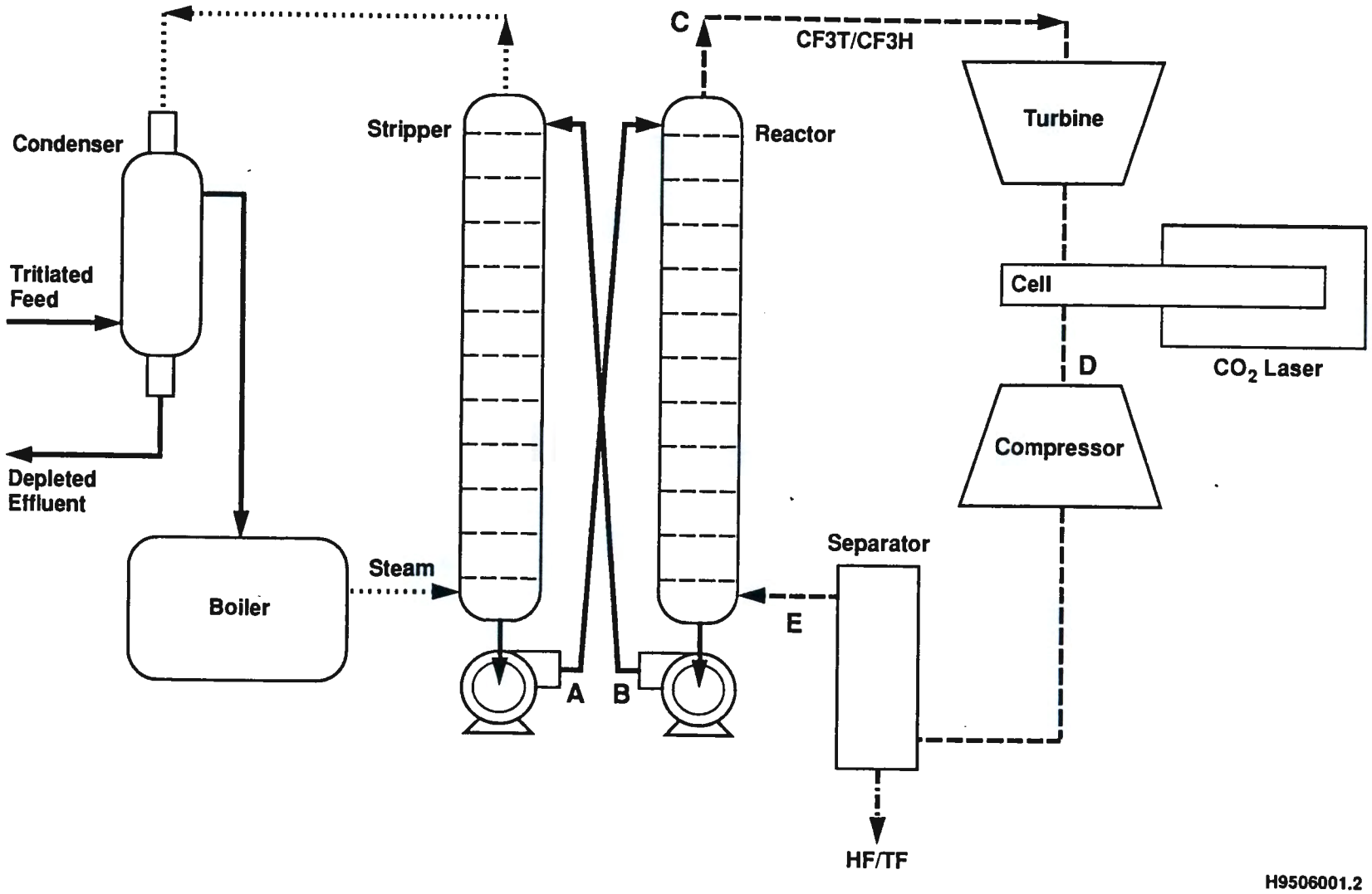


Figure 2-3. Laser Isotope Separation.

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3 NEW DEVELOPMENTS

In an attempt to develop the broadest base of information about tritium research in its earliest stages, a standard library database search was supplemented by professional networking and inquiry. This approach resulted in the discovery of non-published information and interest in tritium separation in three new areas.

One published source, *Waste Management Research Abstracts Volumes 21 and 22* (IAEA 1992, 1993), contains abstracts from over 1,500 internationally sponsored research projects. Although tritium is indexed and appears as the focus of a few projects, none are related to separation technology. Likewise, *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, also contains no mention of tritium separation (Cecille et al. 1991). This indicates that overall scientific interest in developing technology for tritium separation is somewhat narrow.

Several new developments in tritium separation are reported here. A summary of information regarding these technologies is given in Table 3.1. Because these technologies are in very early stages of development, none of them would be considered ready for application or economic assessment at this time.

Since this is the only document known to review early stage research in tritium separation, the following section gives a detailed description of each technology. This is provided in hope that it may stimulate scientists in thinking of new and improved ways for efficient tritium separation and to broaden interest in tritium separation technology.

3.1 ISOTOPIC EXCHANGE

A recent paper (Slattery and Ingraham 1994) published the results of research dealing with isotopic exchange between tritiated water and water vapor. In their experimentation, the scientists bubbled air containing tritium-free water vapor through a container of tritiated water. The tritium in the system reaches an equilibrium state between the water and the vapor in the air in the same ratio predicted by the liquid/vapor separation factor for tritium (i.e., 1.05). After 50 days of continuous sparging at 35 L/min, tritium in a 30-L container was depleted by about 80%. The air containing tritiated water vapor was vented to the atmosphere.

As a result of these tests, the authors claim to have a "simple, low cost vapor sparging technique" for removing tritium from a contaminated body of water. Unfortunately, it is not that simple, especially when considering this process in a

larger technical scope. When tritium is at equilibrium between aqueous liquid and vapor phases, it would make no difference whether the water vapor removed was from vapor sparging or from simple distillation. The same result would be obtained if a body of water containing tritium were distilled. In this case, continuously replacing water removed as vapor with tritium-free water would likewise reduce the tritium in the reservoir. The paper did not discuss the issue of discharging tritium to the atmosphere.

3.2 ADSORPTION AND DESORPTION FROM FINELY DIVIDED NICKEL

In a recent paper, scientists in Japan reported working with finely divided nickel catalyst prepared by the Rainey procedure (Takeuchi et al. 1994). In this process, a 1:1 nickel/aluminum alloy is treated with aqueous sodium hydroxide. This dissolves the aluminum leaving a precipitate of finely divided nickel with hydrogen adsorbed to its surface. This catalyst is commonly used for many synthetic organic reductions.

When sodium hydroxide was dissolved in tritiated water, the scientists observed that the initial hydrogen evolved in the process contained only about a tenth the tritium that was in the water. When the moist catalyst residue was heated from 100° C to 1000° C, the hydrogen driven off was enriched in tritium by 3.6-fold. The total difference in tritium in the two streams is a factor of 36. This technical phenomenon may be similar to that operating in catalytic exchange processes (Sections 2.4.1 and 2.4.2), where platinum is used as a reversible absorber for hydrogen exchange between water and hydrogen gas.

The problem with this process is that after the nickel is heated to remove the tritium, it is no longer an active hydrogen adsorber. Without a reversible substrate, the process could not be operated continuously, making it difficult to design an operational system. Although this work does not currently provide a basis for reducing tritium in waste processing effluent, the ideas presented in this paper may stimulate research in related areas. It is possible that this research may lead to more applicable technologies, particularly in the areas of composition of exchange catalysts or electrodes for the electrolysis process.

3.3 SEPARATION REPORTED BY METANETIX, INC.

In January of 1995, Dr. Irving DeVoe, Chief Scientist of Metanetix, Inc., presented a seminar for scientists and engineers at the Hanford Site (DeVoe 1995). During the seminar, Dr. DeVoe summarized the results of tests using proprietary separation technology. In one experiment, tritiated water was used as a tracer for determining the free volume of a separation column containing a proprietary

medium. Surprisingly, tritium was held up on the column until approximately 12 bed volumes had been eluted. DeVoe concluded that the media has a stronger affinity for tritium than it does for normal hydrogen in the water. DeVoe speculated that coupling this technology with his patented "steady-state reactor" design (DeVoe 1993) might provide an economical operation for tritium removal. An interesting advantage to this system is that the desorption of tritium from the media can be accomplished using a cationic species with a higher affinity. This would produce a concentrated tritium stream. No work has been done to test or confirm this observation. Dr. DeVoe is seeking funding for further study in this area.

3.4 CHEMICAL EXCHANGE

Two uniquely different reports concerning chemical exchange of tritium and hydrogen were reviewed this year.

3.4.1 Naphthalene

Professor Vincent Van Brunt (Section 2.4.2) was at PNL for a roundtable discussion of tritium separation in December of 1994. He discussed preliminary tests using deuterated water that showed substituted naphthalene displayed a capacity to exchange and preferentially hold deuterium over hydrogen. The exchange required an acid catalyst and a surfactant to disperse the naphthalene derivative in deuterated water. Professor Van Brunt believes that tritium would be held even more strongly than deuterium. No further research has been done on this concept.

3.4.2 Crown Ether Complexes

A 1985 report revealed new chemistry for a liquid/liquid extraction process for separating tritium (Nishizawa 1985). In this process, tritium is exchanged between tritiated water and a primary amine salt (RNH_2T^+). In order to achieve a separation, the amine salt is extracted into a chloroform layer containing a cyclic ether which strongly complexes the amine salt. Total separation factor for tritium between the aqueous and organic layers was reported to be 50 when tertiary butyl amine was used. Such a degree of separation is unusually high compared to factors for chemical exchange which typically range from 1.2 to 4.0 (Vasaru 1993).

The experimentation and the calculations reported all appear to be scientifically sound. One wonders why there has been no follow-up work on such

a promising application. A possible reason is found in a report by Russian scientists describing similar tests with a system using carbon tetrachloride as the solvent and a substituted cyclic ether (Khomuev and Katal'nikov 1993). In this case, the reported separation factor for tritium was a maximum of 5.0. It is difficult to reconcile a difference of a factor of 10 in the results given in these two reports, particularly when the chemistry is so similar.

A U.S. company, IBC Advanced Technologies, Inc., is developing similar chemistry for more efficient removal of metals from aqueous waste streams (Izatt et al. 1993). In discussions with IBC, they indicated that IBC would examine the possibility of using their technology for tritium separation (Bruening 1995).

Table 3-1. Summary of Reported Early Stage Technology Research

Process: Status	Company/Lab: Contact	Technology Reported	Evaluation: Pros and Cons
Isotopic Exchange (see Section 3.1) Results of research reported in technical journal. Further status unknown.	Desert Research Institute Water Resources Center P.O. Box 19040 Las Vegas, NV 89109 Neil L. Ingraham	Air saturated with tritium-free water vapor was sparged into a container of tritiated water for a period of 80 days. The tritiated water was maintained at 24.5°C. After 50 days sparging at 35 L/min, the tritium in a 30 L vessel was reduced by 80%. Tritium containing air leaving the vessel was vented to the atmosphere.	Pro: Authors claim to have a low cost method for tritium remediation. Con: The tritium removed by the process is vented to the atmosphere as tritiated water vapor.
Finely Divided Nickel (see Section 3.2) Results of research reported in technical journal. Further status unknown.	Hydrogen Research Center Toyama University Toyama 930, Japan Toyosaburo Takeuchi	Aluminum in a 1:1 nickel/aluminum alloy was dissolved in tritiated water containing NaOH. Hydrogen evolved contained 1/10th the tritium level that was in the initial water. Hydrogen evolved when the solid residue was heated to 1000° C contained 3.6 times the tritium of the tritiated water.	Pro: The process gives good separation of tritium. Con: The process is not reversible; therefore, it would not lend itself to lower cost continuous processing schemes.
Metanetix, Inc. (see Section 3.3) Results of research reported in technical seminar. No further work is planned.	Metanetix, Inc. P.O. Box 505 Butte, MT 59703 Dr. Irving W. DeVoe 406-723-8292	Tritiated water was eluted through a separation column containing a treated media. 12 bed volumes of water were eluted from the column before the tritium front was detected. The test was repeated with identical results.	Pro: Simple process with potential for low operating and capital costs. Con: Results are for very limited testing.
Naphthalene (see Section 3.4.1) Results of research reported in technical seminar. It is not known if further work is planned or in progress.	University of South Carolina Department of Chemical Engineering Columbia, SC Prof. Vincent Van Brunt 803-777-3115	Substituted naphthalene was used as an exchange substrate for deuterium in D_2O. A surfactant and acid catalyst were required for exchange. The naphthalene derivative held deuterium preferentially to hydrogen. Prof. Van Brunt speculates that tritium will be similar. No details are available.	Pro: New area of chemical exchange. Con: Substantial amounts of naphthalene would be required unless a second reaction sequence can be developed to transfer tritium to another medium.
Crown Ether Complexes (see Section 3.4.2) Results of research reported in technical journals. Contact was made to create interest.	IBC, Advanced Technologies, Inc. P.O. Box 98 American Fork, UT 84003 Dr. Ronald L. Bruening 801-763-8491	Researchers in Japan and Russia reported tritium extraction into CCl_4 and $HCCl_3$ using tertiary amines and crown ethers. Separation factors reported were good. This information was supplied to a U.S. company specializing in this area of chemistry in order to create interest.	Pro: Appears to be an attractive system for processing. Con: Requires use of chlorocarbon solvents.

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4 CONCLUSIONS

A number of new developments have been reported and progress continues on research and development of methods for separating tritium. However, at the present no commercially feasible technology is available for low-level tritium.

Five new technologies for separating tritium were reported this year. Two of them have no technical potential for further development. An assessment of the technical potential of the remaining three will occur if any of them receive funding for further research.

The membrane separation process being developed at PNL continues to show potential. The results of testing larger scale, commercially prepared membranes will be crucial to establishing the parameters needed to determine their potential for future success.

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[2]SuperLig is a trademark of IBC Advanced Technologies, Inc., Provo, Utah.

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APPENDIX A
TRITIUM INFORMATION

A1 TRITIUM

"Tritium" is the third member of the hydrogen isotope series. Because it is an isotope, tritium differs from other members of the hydrogen series in the structure of its nucleus. The tritium nucleus consists of one proton and two neutrons resulting in an atomic mass of three. Its symbol is "^3H," but "T" is used more often as an abbreviation or as a scientific symbol.

The second hydrogen isotope is deuterium. Its scientific symbol is "^2H," but the abbreviation "D" is more commonly used.

A1.1 PROPERTIES

In general terms, the chemical properties of an isotope series are almost identical. Chemical properties (Section A1.1.1) are dependent upon the electronic structure of an atom, which is the same in every isotopic series. Physical properties within an isotopic series differ only because of the variation in the mass of the nucleus of each isotope (Section A1.1.2). The most characteristic differences within an isotopic series occur in the radiological properties (Section A1.1.3).

A1.1.1 Chemical Properties

Like hydrogen, tritium gas burns in oxygen to form T_2O. Like water, T_2O can be electrolytically decomposed to form tritium gas and oxygen.

Differences in the chemical behavior of isotopes, called isotope effects, have been experimentally observed for the hydrogen series. For example, free tritium exchanges quite readily with bonded hydrogen. Because it is heavier than hydrogen, chemically bonded tritium is slightly more stable than hydrogen bonded in the same environment. This difference is illustrated by comparing the first ionization constants for H_2O and T_2O. For water (H_2O), the pKa for first ionization is 14.0 and for tritium oxide (T_2O) it is 15.2. The difference in these two values is a quantitative measure of T-O bond strength vs H-O bond strength. This variation between tritium and hydrogen forms the basis of chemical isotopic separation schemes (Sections 2 and 3).

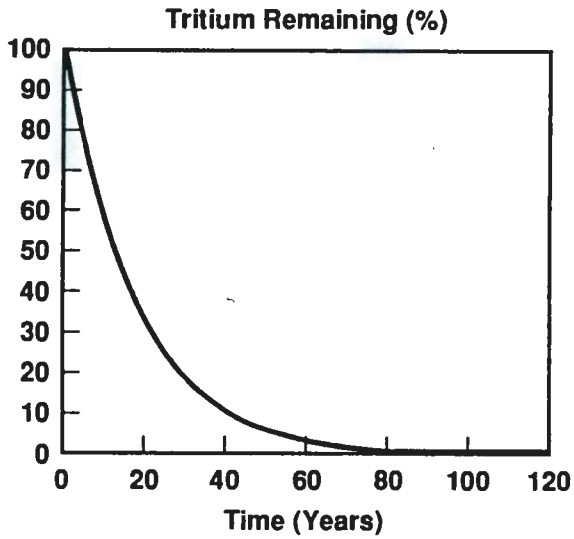
A1.1.2 Physical Properties

Relative to hydrogen, elemental tritium has a larger atomic mass. This causes its physical properties to be slightly different than hydrogen. For example, tritium boils at 25 K relative to 20 K for hydrogen. Tritium oxide (T_2O) boils at 101.5°C compared to 100.0°C for normal water (H_2O). The specific gravity of T_2O is also greater than the specific gravity of H_2O. Differences in physical properties have also been exploited for the separation of hydrogen isotopes.

A1.1.3 Radiological Properties

The tritium nucleus is unstable because of the high ratio of neutrons to protons. This instability causes tritium to radioactively decay with a half-life of 12.3 years. The product of this decay is ^3He and a low energy beta particle. Figure A-1 and Table A-1 show the decay rate for tritium. To aid in the process of mental arithmetic, tritium decay rate can be expressed as 5.5% per year. For longer decay times, 41 years is the time required for the amount of tritium to be reduced by 90%.

Figure A-1. Tritium Decay.



H9407028.1

Table A-1. Tritium Decay.

Tritium Remaining	Decay Time, Years
1.0	0
0.1	41
0.01	82
0.001	123
0.0001	164
0.00001	205

A1.2 ANALYSIS AND DETECTION

Because it is radioactive, tritium is readily detectable. Concentrations as low as 10 pCi/L in water can be detected under certain conditions. Liquid scintillation counting is a sensitive and sometimes rapid method for determining tritium in

aqueous samples. Mass spectrometry is most useful for distinguishing between compounds containing mixed hydrogen isotopes (e.g., HD, HT, and DT or HDO, HTO, and DTO).

For low-level tritium, detection accuracy is improved by increasing the specific activity of the sample (Dressel et al. 1994). Laboratory-scale electrolysis is used to increase the isotopic concentration of the low-level tritium. This enrichment, combined with longer counting times, improves sample accuracy where the tritium level is near the detection limit.

A1.3 COMMERCIAL USES FOR TRITIUM

Fusion power, if it is developed and used in the future, will be a major commercial application for tritium. Presently, tritium is used in radioluminous light sources. In these applications, beta emission from tritium activates a luminescent phosphor and causes the emission of light. This light is particularly useful for signs where there is no electrical power (e.g., glowing "EXIT" signs). Small amounts of tritium are also used as a radiotracer in medical and laboratory work.

A2 HEALTH RISKS ASSOCIATED WITH EXPOSURE TO TRITIUM

Nothing new regarding the health risks of tritium was reviewed in the last year. The information contained in *Tritiated Wastewater Treatment and Disposal Evaluation for 1994* (DOE 1994) is summarized here to provide the reader with some basic information. The December 1993 issue of *Health Physics* is devoted to risk assessment, dosimetry, and radiobiology of tritium. The information in Sections A2.1, A2.2, and A2.3 was taken primarily from the Okada and Momoshima (1993) article in that December 1993 issue.

A2.1 TOXICITY

The maximum energy of beta emission from tritium decay is 18.6 keV. This energy level produces a maximum track length of 6 μm for tritium beta travel in water. Because beta radiation can never penetrate the outer layers of skin, beta radiation from tritium decay only inflicts damage to humans when tritium is present inside the body.

Radioactivity by low energy beta emission is the only biological hazard characteristic of tritium. Because tritium, as HTO, is not distinguished from water by living systems, it does not concentrate in a specific organ, as does ^{129}I or ^{90}Sr. Also, like hydrogen, tritium possesses no intrinsic chemical toxicity.

A2.2 METABOLISM

When it is incorporated into a living system, tritiated water will partition into three biological components. The first biological component is Tissue Free Water Tritium (TFWT). In humans, TFWT is responsible for about 90% of a total absorbed dose. The remaining 10% of the tritium dose comes from the combined second and third biological components. Tritium, as HTO, has a biological half-life of about 10 days in the TFWT component.

The second component, organically bound tritium (OBT) results from the exchange of tritium with hydrogen bound to carbon. OBT has a biological half-life of 30 days. The third component is the OBT present in lipids and fatty tissue where the biological half-life is 450 days. The substantially lower exchange rate for tritium into this last component is the result of lower interaction of water with the "oily" surfaces of fatty tissues and lipids.

The biological half-lives for tritium in different body systems represent physical and chemical processes within the body and not the nuclear decay of tritium. As such, the half-lives represent the rate of exchange of tritium both into and out of the biological system components. These half-life values vary from individual to individual. Those reported above are assumed averages for the adult male.

When a person receives an internal dose of tritium, the National Council on Radiation Protection and Measurement (NCRP) recommends oral intake of 3 to 4 L/day of fluid (e.g., water, fruit juice, tea, coffee, or beer) to dilute and flush tritium out of body systems, particularly before it assimilates into the more isolated systems (Okada and Momoshima 1993).

The internal hazard from exposure to molecular tritium (HT or T_2) is even less than that of HTO. In humans, only 0.004% of any amount of HT inhaled is converted to HTO and retained in the body. This compares to 98 to 99% retention for inhaled HTO. Neither HT nor T_2 is absorbed through the skin, whereas HTO is taken into the body both by absorption and by inhalation. The relative dose effect for exposure to HT is about 1/10,000 that for HTO.

No apparent enrichment or bioconcentration of tritium in aquatic or terrestrial food chains has been reported.

A2.3 OCCUPATIONAL EXPOSURE LIMITS

For purposes of radiation protection, the International Commission on Radiological Protection (ICRP) established 3×10^9 Bq (about 0.08 Ci) as the annual limit for intake of tritiated water (ICRP 1991). The ICRP-established Derived Air Concentration (DAC) limit for HTO is 8×10^5 Bq/m^3 ($\sim$22 μCi/m^3) (ICRP 1978). Because tritium gas (T_2 or HT) is less radiotoxic than HTO and is much less likely to be absorbed into the body from an exposure, the DAC limit for tritium is 2×10^{10} Bq/m^3 (0.5 Ci/m^3) (ICRP 1978).

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APPENDIX B
TRITIUM IN THE ENVIRONMENT

B1 TRITIUM IN THE ENVIRONMENT

Tritium occurs in nature only to the extent that it is in equilibrium with amounts that are produced naturally by cosmic rays or are man-made as by-products of nuclear processes. The occurrence of man-made tritium in the environment and the regulation of tritium discharges was reviewed in depth (DOE 1994). The information from DOE (1994) is summarized and updated in the following sections.

B1.1 NATURALLY OCCURRING TRITIUM

Tritium occurs naturally in the environment as a result of processes in the upper atmosphere. Cosmic rays containing high energy protons and neutrons from the sun interact with nitrogen and oxygen nuclei producing tritium. Carbon-14, the basis for the radiocarbon dating process, is formed in the same way.

About 4 to 8 MCi of "natural" tritium are produced each year via this interaction. Based on those numbers, the natural global inventory of tritium is estimated to be 70 to 140 MCi (Vasaru 1993).

B1.2 MAN-MADE TRITIUM EMISSIONS

In addition to naturally occurring tritium, artificial sources also contribute to the global inventory. Atmospheric testing of thermonuclear devices from 1950 to 1963 released about 1 billion Ci of tritium.

B1.2.1 Reactor Produced Tritium

Nuclear reactors produce tritium as a by-product of operations. In 1989, Commercial power reactors world-wide released 700,000 Ci of tritium in liquid and gaseous discharges (UNSCEAR 1993). Of these releases, 70% (490,000 Ci) were from 11 heavy-water-moderated (HWM) reactors.

A 1994 report by the U.S. Nuclear Regulatory Commission (NRC 1994) presents a detailed summary of emissions from U.S. nuclear power stations. Total liquid discharges of tritium from these sources in 1991 was 38,000 Ci. The

average annual liquid emission of tritium is 500 Ci per plant. The highest emission, 5,000 Ci, was reported by two plants. Using the reported values for tritium emission and the corresponding volumes of water discharged, the average concentration of tritium in the effluent was calculated for each plant. Of 83 plants reporting, most had average tritium concentrations in their effluent less than 20,000 pCi/L. Five plants had average concentrations above 20,000 pCi/L, but less than 100,000 pCi/L. Two plants with the highest average tritium concentrations had values of 250,000 pCi/L and 600,000 pCi/L. These are still within the NRC limit of 1,000,000 pCi/L (see Section B-1.3.1).

Interestingly, Washington Public Power Supply System Plant 2, located Richland, Washington, reported 1.8 Ci of tritium in its liquid discharge in 1991. This discharge is permitted by the NRC. This amount of tritium in a total volume of 1.7 billion liters of water discharged represents a tritium concentration of 1,000 pCi/L. In the same year, the Trojan facility situated on the Columbia River 72 km (42 mi) NW of Portland, Oregon, discharged 198 Ci of tritium at a concentration of 2,400 pCi/L in liquid effluent.

B1.2.2 Nuclear Fuel Reprocessing

Tritium is also trapped in the fuel rods during nuclear reactor operation. Reprocessing this fuel releases tritium as both gaseous and liquid plant effluent. Worldwide, nuclear fuel reprocessing released 180,000 Ci of tritium in 1989.

In 1992, the Sellafield reprocessing plant in England reported emissions of 1,200 TBq (30,000 Ci) of tritium in gaseous and liquid form (BNFL 1993). The regulatory limit for tritium discharge from the plant is 3,500 TBq/year (95,000 Ci/year). By comparison, this same plant emits a total of 90 TBq (2,400 Ci) of all other radioactive materials. The report also states, "Tritium is, however, one of the least radiologically significant radionuclides per unit discharge and has low overall impact to the critical groups. Overall, the scale of marine discharges of radioactivity from Sellafield is comparable to that of Cap la Hague, in northern France, the only other major nuclear reprocessing plant currently operating in the Western world."

The fact that this plant is on the British seacoast and that liquid discharges are piped out into the sea for rapid dilution allows the discharge of such radioactive effluent. The British government actively monitors total radioactivity discharged to the sea from this location. It also conducts an environmental monitoring program for the seacoast north and south of the Sellafield location (BNFL 1993).

B1.3 REGULATION OF TRITIUM EMISSIONS

Laws regulating the release of radioactivity into the environment vary from country to country. The limits of these emissions may be expressed by the amount of potential exposure to the radioactivity, as an amount of activity over time, or as concentration limits in air or liquid discharges. Usually, an overall dose limit is established for the public. From the dose limit, activity limits for emissions from specific sources can be derived.

The ICRP is an advisory body for international radiation protection. Maximum levels of radioactivity in plant effluent recommended by the ICRP do not carry the force of law, but they do serve as a basis for most of the radiation protection standards and permit limits established worldwide.

B1.3.1 U.S. Tritium Discharge Limits

The NRC, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) all have established limits for tritium emissions. Table B-1 contains a tabulation of these limits. Because of the

Table B-1. United States Regulatory Limits on Radioactive Exposure to the Public and Release of Tritium.

Regulation	Radiation Dose or Activity Concentration in Water
10 CFR §20[1] (NRC)	1.0×10^{-3} μCi/mL (1,000,000 pCi/L)
40 CFR §141[2] (EPA)	4 mrem/year (beta emitters) (total body or any organ)[3] (20,000 pCi/L)
WAC 173-200[4]	20,000 pCi/L

NOTE: These dose limits are for exposure to the general public and are not occupational exposure limits.

EPA U.S. Environmental Protection Agency.
NRC U.S. Nuclear Regulatory Commission.
CFR Code of Federal Regulations.
WAC Washington (State) Administrative Code.

[1]10 CFR §20, *Standards for Protection Against Radiation*, U.S. Nuclear Regulatory Commission, Washington, D.C.

[2]40 CFR §141, *Drinking Water Standards*, U.S. Environmental Protection Agency, Washington, D.C.

[3]EPA estimates that 20,000 pCi/L of tritium results in a total body or organ dose of 4 mrem/year.

[4]WAC 173-200, *Water Quality Standards for Ground Waters of the State of Washington*.

number of operating nuclear power-generating facilities in the United States, the NRC regulations have the broadest application.

B1.3.2 Tritium Discharge Regulation in Other Countries

In Canada this year, the Ontario Minister of Energy and Environment accepted the World Health Organization limit on tritium in drinking water of 7,000 Bq/L (190,000 pCi/L). In doing so, the Minister rejected a petitioned limit of 20 Bq/L (540 pCi/L), indicating that it was "unwarranted and fundamentally flawed" (Silver 1995). This was the only change in the regulation of tritium emissions in other countries that was reported in the last year.

The full compilation of limits is listed in DOE (1994) and will not be repeated here.

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APPENDIX C
TRITIUM AT THE HANFORD AND SAVANNAH RIVER SITES

C1 TRITIUM AT HANFORD

Tritium is found in a number of areas at the Hanford Site. Past practice disposal of wastewater resulted in the formation of several large ground water plumes containing tritium. The unconfined aquifer at the Hanford Site contains tritium plumes that encompass about 25% of the area between the Columbia and Yakima Rivers and the basalt base of the Rattlesnake Hills. Tritium is also found in controlled areas such as the 100K and 100N Basins and in tank waste. Solid waste disposal sites presently contain about 225,000 Ci of tritium (Coony 1994).

C1.1 GROUND WATER MONITORING

Under contract to the DOE, the Pacific Northwest Laboratory (PNL) monitors ground water at the Hanford Site. Under this program, ground water samples are periodically analyzed for radionuclides and other contaminants. The results of this monitoring program are reported annually. The most current of these data are presented in Dressel et al. (1994).

About 3,400 wells exist on the Hanford Site. Approximately 50% (1,676) are used in ground water monitoring (Chamness and Merz 1993). A map showing the location of these wells is shown in Dressel et al. (1994, p. 4.28).

Per Dressel et al. (1994):

> "Tritium is the most widely distributed radiological contaminant onsite. Tritium was present in many waste streams discharged to the soil column and is the most mobile radionuclide onsite. As a result, tritium reflects the maximum extent of contamination from Site operations in the groundwater and is the radionuclide most frequently monitored at the Hanford Site."

C1.1.1 Tritium in Ground Water

Relative to the information in Dressel et al. (1993) and DOE (1994), very little change has taken place. The annual sitewide environmental report shows the historical progression of the movement of ground water plumes containing tritium (Dirkes et al. 1994). It provides a good understanding of the impact of the decay

of tritium and its rate of movement in the aquifer. Figure C-1 (C-1a through C-1e) is taken from Dirkes (1994) to show the movement of tritium in ground water from 1964 to 1993.

C1.1.1.1 100 Area Tritium Plumes. The 100K, 100N, 100D, and 100F Areas all show tritium in ground water at concentrations above the DWS (Dressel et al. 1994). The highest reported tritium level in the 100K Area reactor site was 3,320,000 pCi/L in 1993. The same well reported a tritium concentration of 1,690,000 pCi/L in 1992. The reason for such a large shift appears to be that the 100K Area plume is quite narrow and that a slight shift in its position results in a significant rise or fall in the tritium level measured at the well location. The 199-KE-1 french drain appears to be the source of the tritium in this plume.

The 100N Area reactor site plume has shown little change since 1992. The maximum tritium concentration in 1993 was 104,000 pCi/L. The 1325-N liquid waste drain field appears to be the source of this plume. The 100F Area reactor site plume was reported to be 180,000 pCi/L in 1993. The reason for the increase from 1992 appears to be movement and leaching from the 118-F-1 burial ground. The 100D Area reactor site tritium plume is the lowest in concentration at 73,000 pCi/L. The concentration has not changed significantly since 1992.

C1.1.1.2 200 West Area Plumes. The major plume in 200 West Area is the result of past operations at the Reduction/Oxidation (REDOX) Plant. The historical pattern of tritium decay and slow movement of this plume are discussed in the DOE (1994). Monitoring results from the well near the apex of this plume show a continual decline in tritium that is consistent with the rate of decay of tritium (Figure C-2). Movement of the REDOX plume is expected to be slow because of the low hydraulic conductivity of the sediments in the area (Wurstner and Devary 1993, p 4.13). The maximum concentration of tritium found in this plume in 1993 was 3,590,000 pCi/L.

C1.1.1.3 200 East Area Plumes. The movement of the widespread tritium plume originating from the Plutonium-Uranium Extraction (PUREX) operations continues to be consistent with observations discussed previously (DOE 1994, Dressel et al. 1993). The history of this plume is described by Gerber (1993). The maximum concentration of tritium found in this plume in 1993 was 3,540,000 pCi/L. The most significant feature of this plume is that it borders on the Columbia River from a point upstream from the old Hanford Townsite to a point downstream from the Washington Public Power Supply System location. The tritium concentration at the riverbank is greater than 20,000 pCi/L for almost this entire length. At a point near the old Hanford Townsite, the tritium increases to 200,000 pCi/l. A riverbank spring at this location contains an average tritium concentration of 142,000 pCi/L.

Figure C-1a. 1964 Tritium Movement.

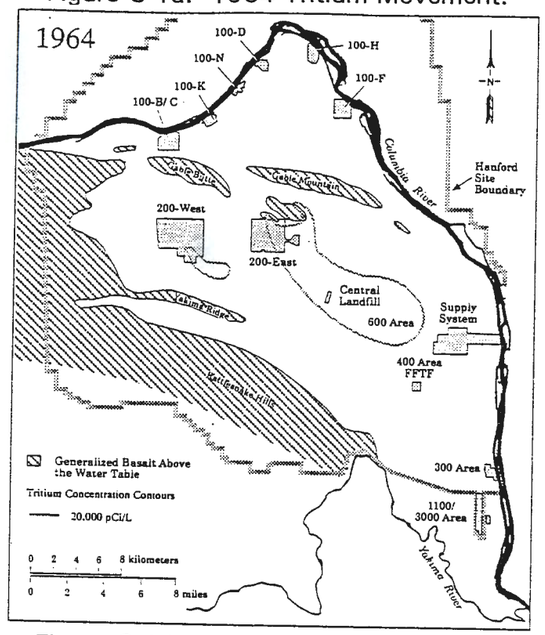

Figure C-1b. 1974 Tritium Movement.

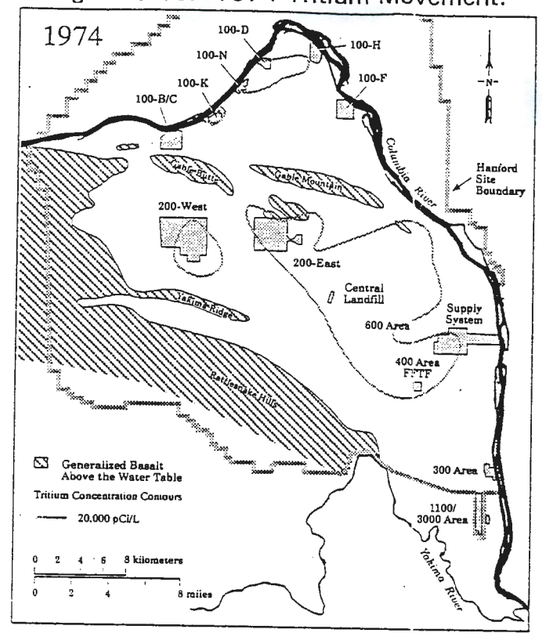

Figure C-1c. 1983 Tritium Movement.

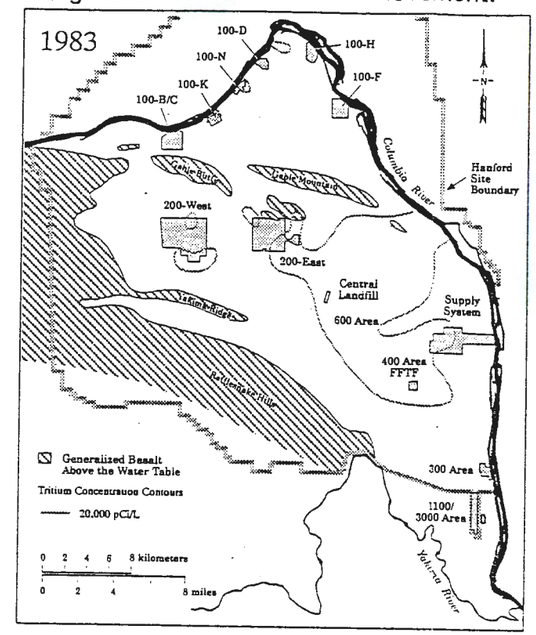

Figure C-1d. 1988 Tritium Movement.

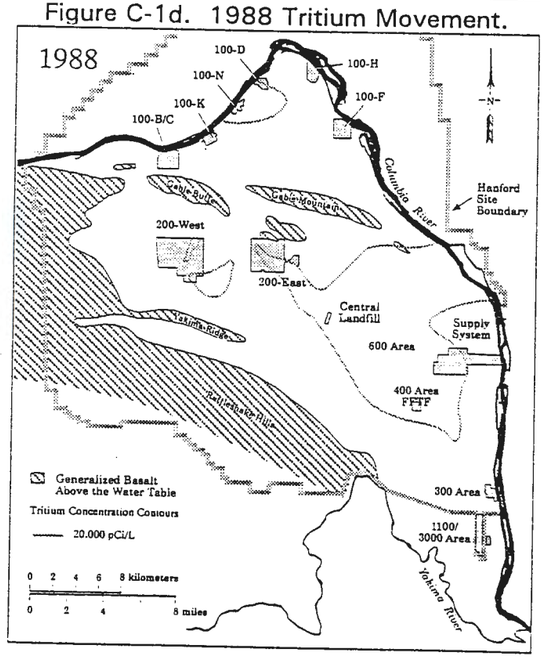

Figure C-1e. 1993 Tritium Movement.

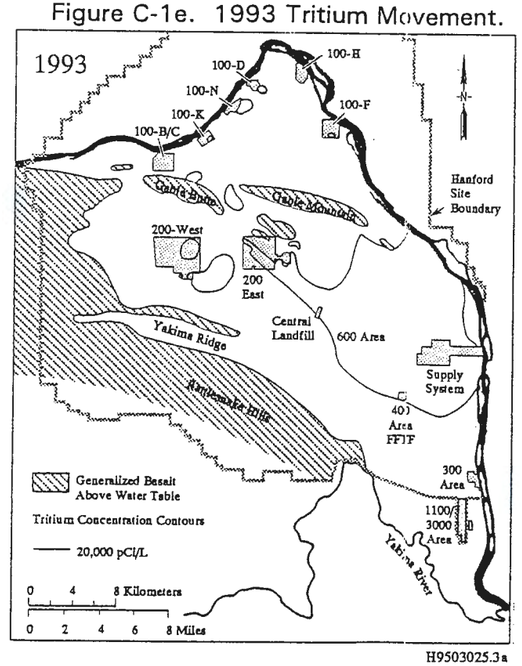

Figure C-1. Tritium Movement in Hanford Site Ground Water.

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Figure C-1a. 1964 Tritium Movement.

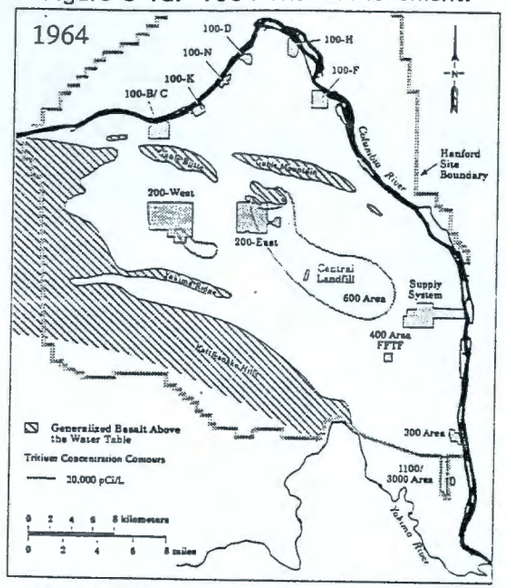

Figure C-1b. 1974 Tritium Movement.

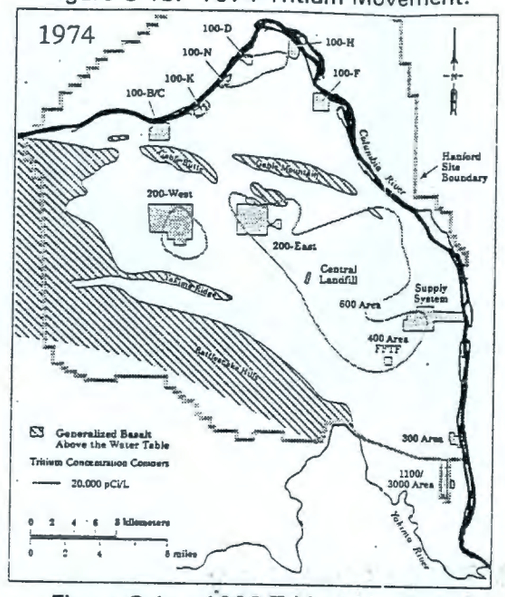

Figure C-1c. 1983 Tritium Movement.

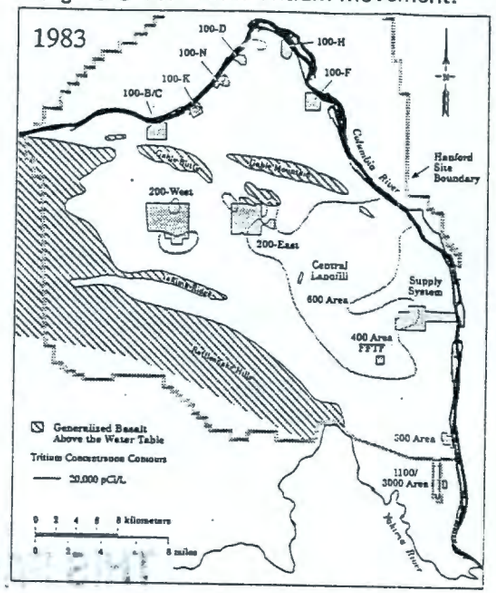

Figure C-1d. 1988 Tritium Movement.

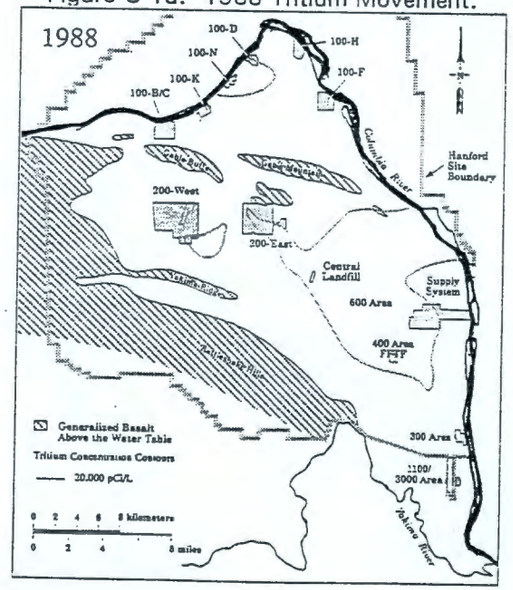

Figure C-1e. 1993 Tritium Movement.

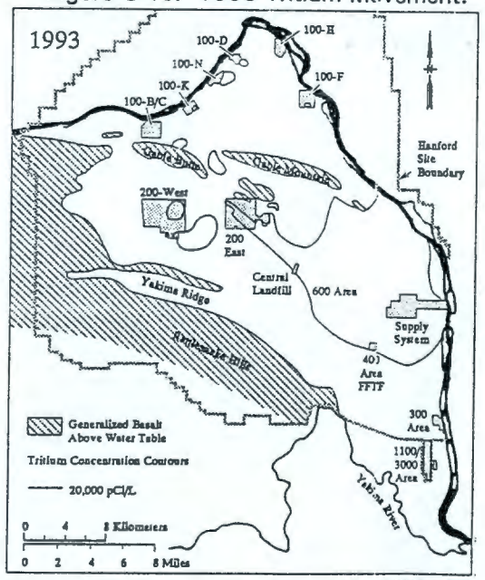

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Figure C-1. Tritium Movement in Hanford Site Ground Water.

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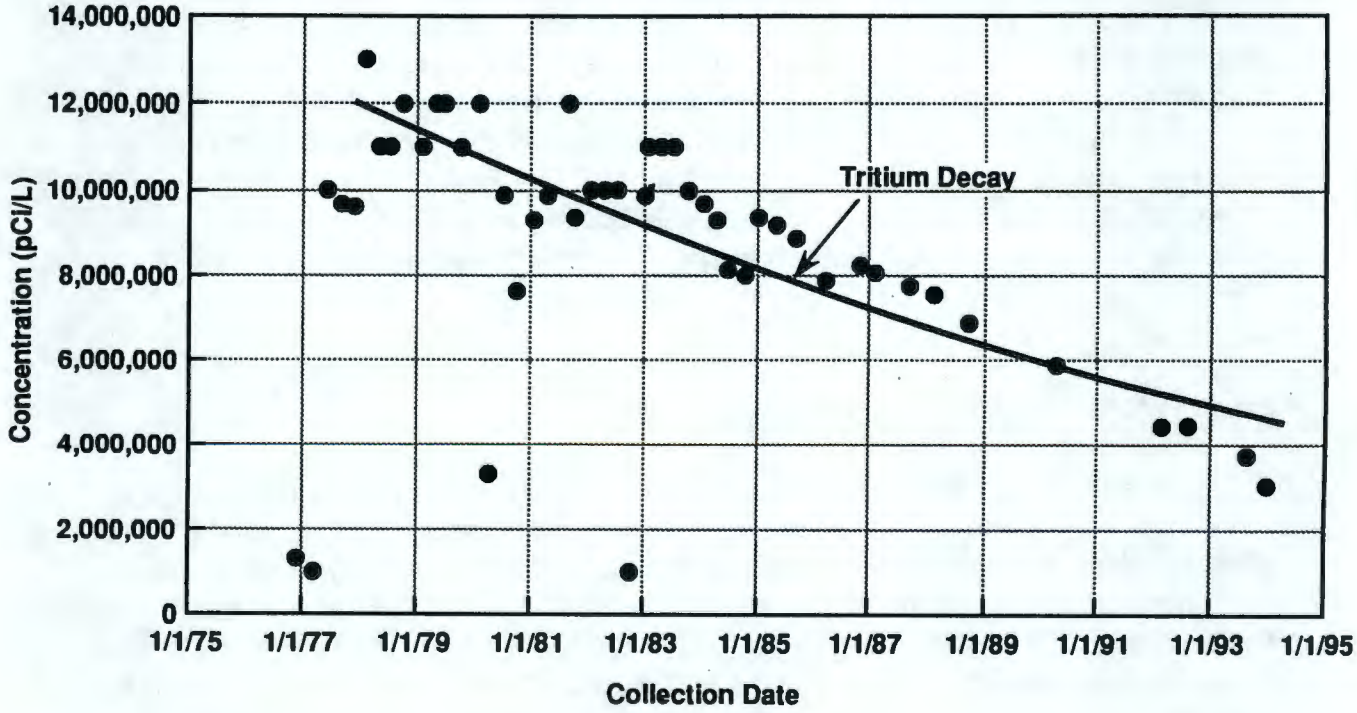
Figure C-2. Tritium Concentration Trend in Well 299-W22-9.



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C1.1.2 Ground Water Modeling

A three-dimensional flow and transport model for the unconfined aquifer of the Hanford Site ground water system is in the final stages of development at PNL. The work is sponsored by the Hanford Site Ground-Water Surveillance Project and is funded by the DOE. The initial report on this development was published in late 1993 (Wurstner and Devary 1993). When complete, the model will simulate ground water flow and contaminant transport both horizontally and vertically within the aquifer. The model will help determine the best location for future monitoring wells to intercept contaminant plumes and to predict the effects of various cleanup and land-use alternatives on contaminant movement in the aquifer.

This model will also aid the scientific and engineering community in understanding future movement and decay of present tritium plumes and will help in projecting the movement of tritium from the SALDS site. Specifically, this model will be useful for refining the present understanding of tritium movement in ground water that is presently based on older, less sophisticated modeling programs (DOE 1994).

C1.2 PONDS AND IMPOUNDMENTS

Water containing tritium is found in storage impoundments at both the 100K and 100N Basins. Additionally, tritium occurs in tank waste and is in process condensate produced by the 242-A Evaporator. Until the 200 Area ETF begins treatment operation, this water is held in the Liquid Effluent Retention Facility (LERF) basins adjacent to the treatment plant. The Fast Flux Test Facility (FFTF) Pond, located near the 400 Area, receives cooling and sanitary water from various facilities in the 400 Area. Tritium in the FFTF Pond was about 6,000 pCi/L in 1993 (Dirkes et al. 1994).

C1.2.1 Liquid Effluent Retention Facility Basins

The LERF basins were constructed to provide interim storage of process condensate from the 242-A Evaporator during construction phases of the ETF. As of May 1995, the basins contained about 25,000 m^3 (6.5 Mga) of condensate. Another evaporator run is scheduled for June before ETF startup and another about the time the ETF is scheduled to start operations. The weighted average tritium concentration presently in the basins is 8,500,000 pCi/L. This is somewhat higher than the 90% confidence level of 6.3 million pCi/L anticipated. However, tritium assays ranged from 3.3 million to 4.5 million pCi/L for the 94-1 campaign and from 9.3 million to 22 million pCi/L for the 94-2 campaign. These all fall within the range of concentrations used to calculate the 90% confidence level (McDonald 1992).

C1.2.2 105-KE Basin

The water in the 105-KE Basin has been considered an environmental risk because of its radionuclide content and because of its proximity to the Columbia River. A seismic barrier has been installed to reduce the possibility of a major spill, which could result if an earthquake were to cause a breach in foundational elements of the basin. An engineering evaluation of treatment/disposal options for the tritiated water in the basin was completed this year by the Foster Wheeler Environmental Corporation (WHC 1995). The report concludes that treatment and disposal of the 105-KE Basin water at ETF/SALDS is feasible.

C1.2.3 100N Basin

Water in the 100N Basin contains tritium at a concentration of about 30 million pCi/L. The total contents of the basin is about 300 Ci of tritium. Options for treatment and disposal of water from the 100N Basin are being developed.

C1.3 COLUMBIA RIVER

The results of monitoring for tritium and other radionuclides in the Columbia River are reported annually in the *Hanford Site Environmental Report*. The latest data are in Dirkes et al. (1994). Dirkes (1994) contains data on the Columbia River monitoring for 1980 to 1989. The tritium level in the Columbia River shows a continual decline over the past 14 years. Upstream at the Priest Rapids Dam, tritium was measured at 230 pCi/L in 1980 and 40 pCi/L in 1993. At the Richland Pumphouse, tritium was 280 pCi/L in 1980 and 90 pCi/L in 1993.

The difference between upstream and downstream measurements of tritium levels in the Columbia River remains constant at 50 and 60 pCi/L throughout the years reported (Dirkes 1994). In the annualized flow of the Columbia River as it passes the Hanford Site this difference in tritium levels equates to 5,000 Ci of tritium in 10^{11} m^3 of river water.

C1.4 OPERATION OF STATE APPROVED LAND DISPOSAL SITE

The most significant change to the ground water picture in the next year will be the startup of the 200 Area Effluent Treatment Facility (ETF) and the discharge of tritiated effluent at the State Approved Land Disposal Site (SALDS) location. The State Waste Discharge Permit for the 200 Area ETF was issued effective June 30, 1995.

Because of the low conductivity of the aquifer in the area of SALDS, tritium is not expected to appear in monitoring wells in the area north of 200 West for several years.

C2 TRITIUM AT THE SAVANNAH RIVER SITE

Although a number of other DOE sites have experienced tritium releases and contamination during operations, the SRS is the most significant. Historical operations at the SRS include nuclear reactors, fuel reprocessing, and tritium manufacture. These three sources all resulted in emissions of tritium.

C2.1 LIQUID RELEASES OF TRITIUM TO THE SAVANNAH RIVER

The *Savannah River Site Environmental Report for 1993* (Arnett et al. 1994) shows the most recent information regarding tritium contamination at SRS. The total amount of tritium released to Site streams at SRS in 1993 was 1,670 Ci.

Much of this was discharged as effluent from the SRS ETF. A total of 9,600 Ci of tritium was released to Site streams by migration from seepage ponds and the Solid Waste Disposal Facility. The tritium released into tributaries of the Savannah River is carried to the ocean by river flow. Above SRS, tritium in the Savannah River is about 70 pCi/L; below SRS tritium is 1,200 pCi/L. At Beaufort, South Carolina, 170 km (100 mi) below SRS, the tritium level has been diluted to 700 pCi/L. The calculated annual maximum dose for a person consuming 2 L/day from the Beaufort water plant is 0.04 mrem. This is 1.0% of the DWS of 4 mrem/yr.

C2.2 TRITIUM IN GROUND WATER

Tritium in surface water and in rainfall are problems at SRS not experienced at the Hanford Site. Rainfall in the H Area at SRS, where tritium is processed, contains tritium at a level of 40,000 pCi/L (Arnett et al. 1994).

There is a concern at the SRS that tritium in ground water may create plumes containing tritium and these plumes may be migrating under the Savannah River to adjacent areas in Georgia. Tritium levels as high as 2,000 pCi/L have been found in ground water samples taken from areas across the Savannah River from SRS. The Trans-Savannah River Flow Project was established to study the problem. Results to date indicate that rainfall is the cause, not subsurface migration (Arnett et al. 1994).

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APPENDIX D
TRITIUM FACT SHEET

Tritium

Tritium (T or ^3H) is the third isotope in the hydrogen series. As an isotope, it is not easily distinguished from normal hydrogen except by its radioactivity. Tritium arises in nature by the nuclear action of cosmic rays on the upper atmosphere. Man-made tritium is the result of the atmospheric testing of nuclear devices in the 1960's. Once formed, tritium is absorbed into atmospheric moisture that falls to earth as rain. As a result, tritium is present in very small amounts in all waters of the world. Tritium is also the unavoidable by-product of nuclear operations both for electrical power generation and for past production of strategic nuclear materials.

Radiological and Toxicological Properties

The radioactive decay of tritium produces a low energy beta particle (an electron) and a stable helium-3 atom. The time required for half the amount of tritium to decay is 12.3 years. Tritium is most often found as very dilute "tritiated water," HTO. In this form it is like normal water, H_2O. It possesses no chemical toxicity nor does it bioconcentrate in specific organs of the body. For these reasons, tritium has a much lower potential for adverse impact to the population and environment than many materials present in waste at the Hanford site.

Uses

The primary commercial use for tritium is as an activator in radio-luminous light sources. An example would be self-illuminating "EXIT" signs found in airplanes and buildings. Each sign contains about 25 Ci (0.0025 g) of tritium. Tritium is used as a tracer in biomedical research. It has also been added to ground water in low levels to allow scientists to study the direction and rate of flow of underground water systems.

Tritium in Treated Effluent

The 200 Area Effluent Treatment Facility (ETF) will have tritium in its liquid effluent. The design criterion for tritium activity in the ETF process stream is 6.3 microcuries per liter. A microcurie is one millionth of a curie, the standard U.S. unit for the measure of radioactivity. To put this into perspective, 4 million liters of effluent would contain the same amount of tritium that is in a single "EXIT" sign

described above. An estimated half-billion liters of treated effluent will be discharged from the ETF during its twenty-year operational lifetime. At the design level of 6.3 microcuries/L, this effluent would contain no more than 3300 Ci (about one-third of a gram) of tritium. This amount would be equivalent in volume to one raindrop in 20 Olympic size swimming pools.

Several alternatives for disposal of tritiated effluent from the ETF were proposed and studied. The study concludes that ground disposal of effluent at a site just north of the 200 W Area would provide the greatest protection for the public. The movement of ground water from this site was also studied using detailed modeling calculations. These calculations predict that effluent containing tritium discharged at this site would reach the Columbia river no earlier than the year 2125. By this time, decay will have reduced the amount of tritium in the effluent by a factor of one thousand (0.001).

Tritium in Ground Water

Because of past disposal practice, areas of ground water beneath the Hanford Site contain tritium. Situated throughout the Hanford Site, 1,600 ground water wells are regularly sampled and tested for tritium and other contaminants. Areas have been identified where tritium levels are greater than the drinking water standard (0.02 microcuries/L). Small tritium plumes in the 100 Area are the result of operations at the D, F, K and N reactor sites. A concentrated stationary plume SE of the 200 West area is from the Redox plant. A large diffuse triangular plume located between the Columbia River, the 200 East and 300 areas is from PUREX operations. Most of the tritium in the 200 East Area plume is expected to decay to the drinking water standard in 20 to 40 years.

Tritium in the Columbia River

Tritium in ground water from operations in the 100 and 200 East Areas is now seeping into the Columbia River. Underground seepage from these plumes contributed an estimated 4,600 Ci of tritium to the river in 1993. Over the past 14 years, the level of tritium in the Columbia River averaged 50 to 60 picocuries/L (a picocurie is one millionth of a microcurie) above the background level . The background level of tritium in the Columbia River has decreased from 280 picocuries/L in 1980 to 90 picocuries/L in 1993.

APPENDIX E
PREPARATION OF THE 1995 TRITIUM REPORT

Two main sources were used as a means for discovering current information regarding tritium for this year's report. First, a phone network of individuals in government and business with a concern or interest in tritium was established. Calls to individuals in the network helped provide the most current information regarding tritium. As a result of contacts in the network, two meetings dealing with tritium separation technology were conducted at the Hanford Site this year.

Second, recent publications and scientific journals, including abstracts and papers published in association with technical meetings and symposia, were searched for references to tritium. All relevant publications for 1994 to 1995 were reviewed. In addition, where historical continuity was important, related annual, quarterly, or monthly volumes from 1993 and even 1992 were examined.

The following journals and publications were reviewed:

Environmental Science and Technology
Fusion Technology
Health Physics
Nuclear Technology
Nuclear Waste News
Radiochemistry
Radiochemistry Acta
Radioactive Waste Management, Current Abstracts from 1994, 1995
Waste Management Symposia, from 1994, 1993.

In addition, several online abstracting services were searched for current information on tritium.

Chemistry Citation Index (Institute for Scientific Information)
Pollution & Toxicology (Cambridge Scientific Abstracts)
National Technical Information Service (NTIS)
Energy Data Base (Energy Technology Data Exchange)
Energy Data Base (International Atomic Energy Agency).

As a part of this program, The International Program Support Office at the Pacific Northwest Laboratory was commissioned to review international

publications for reference to tritium. Their search involved a monthly review of the following publications:

Atoms in Japan
Background Notes on the Countries of the World
Canadian Environmental Protection
Diplomatic List
Energy Balances of OECD Countries
Environmental Manager
Environmental Remediation Technology
Epa Journal
Genetic Engineering News
Haztech News
Hazmat World
Industrial Wastewater
International Journal of Radioactive Materials Transport
Key Offices of Foreign Services Posts
Meetings on Atomic Energy (IAEA)
Nagra Informiert
Nea Newsletter
Nuclear Energy (BNES)
Nuclear Energy Data
Nuclear Engineering International
Nuclear Europe
Nuclear Fuel
Nuclear Fuel Cycle
Nuclear Law Bulletin
Nuclear News (ANS)
Nuclear Waste News
Nucleonics Week
Nukem Market Report
Pollution Prevention
Post-Soviet Nuclear and Defense Monitor
Radioactive Exchange
Radioactive Waste Management and the Nuclear Fuel Cycle
Radwaste Magazine
Revue Generale Nucleaire
Waste Management
Waste Tech News
World Environmental Report

APPENDIX F
CONVERSION TABLES

Table F-1. Radioactivity Level Conversions.

pCi/L	μCi/L	Ci/L	μCi/mL
10^4	0.01	10^{-8}	0.00001
10^5	0.1	10^{-7}	0.0001
10^6	1	10^{-6}	0.001
10^7	10	10^{-5}	0.01
10^8	100	10^{-4}	0.1
10^9	1000	10^{-3}	1
10^{10}	10,000	10^{-2}	10
10^{11}	100,000	10^{-1}	100
10^{12}	1,000,000	1	1000

Table F-2. Fractions and Multiples of Units.

Multiple	Decimal Equivalent	Prefix
10^{12}	1,000,000,000,000	tera
10^9	1,000,000,000	giga
10^6	1,000,000	mega
10^3	1,000	kilo
10^2	100	hecto
10^1	10	deka
10^0	1	--
10^{-1}	0.1	deci
10^{-2}	0.01	centi
10^{-3}	0.001	milli
10^{-6}	0.000001	micro
10^{-9}	0.000000001	nano
10^{-12}	0.000000000001	pico
10^{-15}	0.000000000000001	femto

Table F-3. Units of Radiation Measure

Current System	Systeme International	Conversion
curie (Ci)	becquerel (Bq)	1 Ci = 3.7×10^{10} Bq
rad (radiation absorbed dose)	gray (Gy)	1 rad = 0.01 Gy
rem (roentgen equivalent man)	sievert (Sv)	1 rem = 0.01 Sv

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