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Management of Tritium at Nuclear Facilities



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MANAGEMENT OF TRITIUM AT NUCLEAR FACILITIES

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MANAGEMENT OF TRITIUM AT NUCLEAR FACILITIES

FINAL REPORT OF A
CO-ORDINATED RESEARCH PROGRAMME ON
HANDLING OF TRITIUM-CONTAMINATED EFFLUENTS AND WASTES

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1984

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FOREWORD

This final report summarizes the results and conclusions of technical studies performed in connection with a four-year IAEA Co-ordinated Research Programme, begun in 1978, on the handling of tritium-contaminated effluents and wastes. Although many related studies are continuing, e.g. on tritium removal from aqueous effluents, immobilization of tritium and tritium-bearing waste, some firm conclusions on the overall concept were drawn by the programme participants and are reflected in this report.

Co-ordinated research programmes are initiated by the IAEA to investigate specific technical areas that are believed to merit international attention, such as the management of tritium-bearing wastes. In these programmes the IAEA seeks to co-ordinate research among principal investigators at various institutes to develop appropriate answers to technical concerns. The technical work is performed at the participating institutions, technical reports are interchanged, and the results are reported and discussed among the participants at IAEA-sponsored meetings held at one- to two-year intervals. Related international meetings provide opportunities for additional discussions. Specifically, the following five meetings included participants of the IAEA Co-ordinated Research Programme:

- (1) International Symposium on Management of Gaseous Wastes from Nuclear Facilities, organized jointly by the International Atomic Energy Agency and the Nuclear Energy Agency of the OECD, and held in Vienna, Austria, 18–22 February 1980
- (2) American Nuclear Society (ANS) Topical Meeting on Tritium Technology in Fission and Isotopic Applications, held in Dayton, Ohio, 28 April–1 May 1980
- (3) International Symposium on Metal Hydrogen Systems, held in Miami, Florida, 13–15 April 1981
- (4) International Conference on Radioactive Waste Management, Canadian Nuclear Society, held in Winnipeg, Manitoba, 13–15 September 1982
- (5) International Conference on Radioactive Waste Management, International Atomic Energy Agency, Seattle, Washington, 16–20 May 1983

V. Morozov of the IAEA's Division of Nuclear Safety and Environmental Protection began this programme and organized the first meeting. His successor, V. Tsyplenkov of the Division of Nuclear Fuel Cycle, assumed his responsibility

as the Project Officer, organizing and co-ordinating the work, including the preparation of the Final Report. The text of the Final Report was compiled by W.J. Holtlander of the Atomic Energy of Canada Ltd, Chalk River Nuclear Laboratories. Assistance in drafting the Final Report was provided especially by H. Brücher, N.S. Sunder Rajan and A. Bruggeman.

It is hoped that this report will be of value in helping Member States to consider their future research activities and policy with regard to management of tritium at nuclear facilities.

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1. INTRODUCTION

1.1. BACKGROUND

There are several aspects to the topic of tritium in the nuclear fuel cycle: e.g. its source, its behaviour when released to the environment, its management (such as trapping instead of release), conditioning, storage and disposal. Nuclear power plants and fuel reprocessing facilities are the major sources of tritium release to the environment, and with the continuing development of nuclear power, increasing attention will be given to improved treatment methods for tritium. The amount of tritium that will be produced and handled in future fusion reactors is several orders of magnitude greater than that produced during the generation of an equivalent amount of energy from fission reactors. Much of the technology now being developed for handling tritium produced by fission reactions will be applicable to fusion installations.

1.2. OBJECTIVES OF CO-ORDINATED RESEARCH PROGRAMME

The environmental aspects of tritium behaviour and technological interests in handling tritiated effluents and wastes are reflected in past and present programmes of the International Atomic Energy Agency. These aspects have been discussed at various IAEA meetings on management of radioactive wastes. The Technical Committee meeting held in December, 1978, in Vienna dealt particularly with topics on handling of tritium-bearing effluents and wastes. That meeting resulted in the publication of the IAEA Technical Reports Series No.203 [1], which outlines the state of the art of tritium management technologies and identifies areas where further data or studies are required.

In response to the recommendations made to the IAEA, a co-ordinated research programme (CRP), Handling Tritium-Bearing Effluents and Wastes, was initiated by the IAEA in 1978. The scientific background of this programme and directions of its development were discussed at the first research co-ordination meeting at Chalk River Nuclear Laboratories in May, 1979. The primary objectives of the programme were to co-ordinate ongoing studies in Member States and to disseminate and exchange information concerning the treatment, concentration, removal, storage, and disposal of tritium from effluents and wastes. Additional meetings were held in Jülich, Federal Republic of Germany, in 1980 and in Trombay, India, in 1982. The list of participants at the three meetings appears at the end of the report.

The studies carried out by the CRP participants revealed a variety of national approaches to resolve the problems of handling tritium-contaminated effluents and wastes. The management of tritium-bearing wastes arising from operations of heavy water reactors and reprocessing of LWR fuel was given the highest priority.

1.3. SCOPE OF REPORT

This report presents extended summaries of the work the participants have done over the three years in the framework of the CRP. Because the scope of the investigations extended over more than one topic, the results have been put together in sections which contain more detailed information. The subjects covered include production of tritium in nuclear power plants (mainly heavy water and light water reactors), as well as at reprocessing plants (Section 2); removal and enrichment of tritium at nuclear facilities (Section 3); conditioning methods and characteristics of immobilized tritium of low and high concentration (Section 4); and some potential methods for storage and disposal of tritium (Section 5). In these sections some work done by investigators who did not participate in the CRP earlier is also reviewed to give more depth to this report.

Finally, the conclusions from the three-year programme are presented and possible activities in the field are recommended (Section 6).

1.4. RELATIONSHIP WITH OTHER DOCUMENTS

This report is not comprehensive because of the limited number of participating Member States. Additional information on behaviour and management of tritium is available in various earlier publications. The behaviour of tritium in the environment was the subject of a symposium [2] organized jointly by the IAEA and the NEA/OECD in 1978. There are two reviews [3, 4] of the sources of tritium associated with the nuclear fuel cycle and environmental aspects of tritium. Within the framework of the Commission of European Communities (CEC) programme in the field of radioactive waste management, candidate materials for the immobilization of tritium were identified; considerations as to how they would be used in an immobilization scheme were given in a survey by H.A.C. McKay [5]. In addition, studies were undertaken on the isotopic enrichment and separation of tritium from aqueous effluents [6, 7] at the Belgian Nuclear Research Centre, SCK/CEN.

2. HANDLING OF TRITIUM

In nuclear power plants tritium is produced by ternary fission in the fuel and by nuclear reactions between neutrons and components of the nuclear power plant. Some of the tritium-producing reactions are ${}^2\text{H}(n, \gamma){}^3\text{H}$, ${}^{10}\text{B}(n, 2\alpha){}^3\text{H}$, ${}^7\text{Li}(n, n\alpha){}^3\text{H}$, ${}^6\text{Li}(n, \alpha){}^3\text{H}$, and ${}^3\text{He}(n, p){}^3\text{H}$. Heavy water moderated reactors are the major producers of tritium through neutron absorption by deuterium where the production rate is approximately $2400 \text{ kCi} \cdot \text{GW}(\text{e}) \cdot \text{a}^{-1}$ [1]. In comparison, the projection from ternary fission ranges from 15 to $30 \text{ kCi} \cdot \text{GW}(\text{e}) \cdot \text{a}^{-1}$ [1], from other nuclear reactions is less than $10 \text{ kCi} \cdot \text{GW}(\text{e}) \cdot \text{a}^{-1}$, depending on the reactor type.¹

2.1. NUCLEAR POWER PLANTS

2.1.1. Heavy water reactors

In Candu PHWRs heavy water is contained in two separate systems, the moderator and the coolant. Practically all of the tritium is produced and resides in the moderator system, which operates near atmospheric pressure and approximately 70°C . The coolant circuit operates at 300°C and 9.6 MPa. Leakage of tritiated heavy water from these systems is the source of tritium effluents. Tritium-contaminated effluents consist of airborne and aqueous effluents; thus, control and recovery of heavy water leakages are essential components of design and operation of heavy water reactors, for reasons of both safety and economics. Table I illustrates the results of heavy water leak measurements in a Candu nuclear power station [8].

Chronic low-level escape of tritiated heavy water gives rise to airborne tritium contamination. Distribution between water- and airborne tritium release values varies, depending on many factors. In addition to careful design to minimize leakage, the principal component of airborne contamination control is the placement of the majority of heavy water systems within the reactor containment envelope. The design, operation and maintenance of this envelope ensure that these contained systems are a minimal source of both environmental emissions and occupational exposures. Heavy water systems which must be accessible at power are located either in shielded rooms within containment or outside containment, mostly in confinement rooms.

Reactor containment is fitted with a closed-cycle heavy water recovery system to recover heavy water as well as to keep tritium levels to acceptable occupational levels. Confinement rooms may be either purged with air or fitted

¹ $1 \text{ Ci} = 3.70 \times 10^{10} \text{ Bq}$.

TABLE I. HWR D₂O LEAKAGE PATTERN – BRUCE GENERATING STATION A

Component	Total station chronic D ₂ O leakage (%)	Leaks (%)	
		<0.1 g/d	>0.1 g/d
Tube and pipe fittings	5.4	100	0
Instrumentation and control components	1.4	78	22
Flanges	28.1	56	44
Valves	59.8	78	22
Sight glasses	0.8	57	43
Other	4.5	–	–

with air dryer systems. Station air quality is maintained via purge ventilation designed to move air from the least contaminated to the most contaminated areas [9].

The leakages from both moderator and coolant systems are collected in tanks. Water from the moderator systems is either fed directly back to the moderator pumping system (if isotopic purity of heavy water is high enough) or sent to a cleanup system before upgrading by water distillation. The top product from the distillation unit contains less than 0.5% D₂O and is a source of tritiated waste. The tritium concentration in this stream depends on the tritium concentration in the recovered water; for recovered water at 5 Ci/L the tritium concentration in the top product would be less than 25 mCi/L.

The average daily airborne tritium emission for the Pickering A station was 43 Ci in 1981 and 51 Ci in 1980. For the Bruce A stations the corresponding numbers were 250 and 120 Ci/d. The aqueous emissions were 21 Ci/d in 1981, 35 Ci/d in 1980 for Pickering A and 55 Ci/d (1981) and 66 Ci/d (1980) for Bruce A.

Contamination of reactor components and housekeeping materials such as rags and mops by spilled heavy water is a source of solid wastes. Other tritium-contaminated wastes include sample bottles from laboratories, plastic personnel suits and vermiculite in air respirators. These low-level wastes are stored in monitored in-ground concrete trenches which are surrounded by compacted granular backfill and provided with a system of subsurface drainage pipes. Diffusion through concrete and leakage through small cracks in the concrete

and the sealants in construction joints are considered to be principal escape mechanisms for tritium. In the event of a leak, the escaped tritium will largely be intercepted and collected by the subsurface drainage system, with a much smaller proportion seeping into the highly impervious subsoil and the ground-water system.

In India, emission of tritium to the environment is mainly from the PHWRs at the Rajasthan Atomic Power Station (RAPS). The low-level tritiated liquid effluents are discharged to the Solar Evaporation Facility along with other low-level waste streams generated at the station. The facility is based on non-boiling-type, ambient-temperature evaporation. The specific activities are of the order of 2 to 6 Ci/L of wastes, including those received from heavy water upgrading plants. The evaporation rate is dependent on temperature, humidity and wind velocity profiles over time. These parameters are favourable at this site all year round. It has been observed that in addition to evaporation, exchange of tritiated water with the atmospheric water vapour is a predominant mechanism for disposal of tritium to the atmosphere [10].

The concentrated tritium from tritium recovery plants is a special product and is unlikely to be considered as waste because of its commercial value. Tritium recovery plants have been committed in Canada by Ontario Hydro and by Atomic Energy of Canada Ltd at the Chalk River Nuclear Laboratories. One plant is operating in France at the Institute Laue-Langevin, Grenoble. Details of the processes used in these plants are presented in Section 3.

2.1.2. Light water reactors

In both boiling water and pressurized water reactors tritium is produced mainly by ternary fission ($15\text{--}20 \text{ kCi}\cdot\text{GW}(\text{e})\cdot\text{a}^{-1}$) and by neutron reactions with natural deuterium, lithium and impurities present in water $<1 \text{ kCi}\cdot\text{GW}(\text{e})\cdot\text{a}^{-1}$. The tritium concentrations in water are in the low-level range of 0.3 mCi/kg. In BWRs the proportion of the activity released with the off-gases is 10 to 50% and that released in liquid phase is 50 to 90%. In PWRs 99% of the moderator and coolant activity is present in liquid phase, and 1% is in gaseous phase. Because of their low concentration, both gaseous and liquid tritiated effluents are released to the air after proper dilution, so the releases are much below the release levels permitted.

2.1.3. Other types of reactors

In other reactors, such as AGRs, HTRs and FBRs, tritium is produced only as a fission product and is in the range of about $17 \text{ to } 25 \text{ kCi}\cdot\text{GW}(\text{e})\cdot\text{a}^{-1}$.

2.2. REPROCESSING PLANTS

2.2.1. General

The amount of tritium passing to the fuel reprocessing plant (FRP) depends on the type of fuel as well as on the cladding materials used in different reactor types. During operation of the reactor some of the tritium diffuses out of the oxide fuel, permeates the cladding, and subsequently enters the coolant. From there it is finally discharged to the environment with normal aqueous or gaseous waste streams. The remaining tritium is expected to reach the reprocessing plant with the spent fuel.

LWR fuel (from PWRs and BWRs) with stainless steel cladding may contain only half of the tritium produced in the fuel, whereas Zircaloy-clad fuel is expected to carry almost all the tritium to reprocessing; this is because the tritium which diffuses out of the fuel will be retained almost entirely in the Zircaloy as zirconium tritide.

On the other hand, from AGRs and FBRs with stainless steel cladding, only minor amounts are expected to pass to reprocessing.

The distribution of tritium in HTRs, and hence the amounts passing to the FRP, is somewhat uncertain, depending on lithium impurities in the graphite and ^3He impurities in the helium coolant.

Based on worldwide nuclear power generation and current reprocessing technology, reprocessing of LWR fuel is expected to be dominant in nuclear fuel reprocessing for the next several decades. The throughput of a commercial-size LWR fuel reprocessing plant serving an installed electrical power of 50 GW(e) (corresponding to 1400 t of heavy metal per year) is estimated to be 0.5 to 1 MCi tritium per year.

2.2.2. Tritium in conventional Purex flowsheet

Plants for reprocessing LWR fuel presently use a Purex flowsheet to remove fission products and recover fissile and fertile material. During head-end operation, the fuel elements are chopped into small pieces that are fed into a dissolver, where the fuel is dissolved out by means of concentrated nitric acid.

The dissolver liquor, which contains uranium, plutonium, and fission products (FP), is fed into a solvent extraction system. In a first contactor the uranium and plutonium are extracted into the organic phase (tributyl phosphate in kerosene), scrubbed, and subsequently fed into a second contactor. The bulk of the fission products remains in the aqueous phase which is routed to high active waste treatment for concentration and solidification. In the second and third contactors, the product materials uranium and plutonium are separated and re-extracted, respectively.

TABLE II. SIMPLIFIED DISTRIBUTION OF TRITIUM IN CONVENTIONAL FUEL REPROCESSING

Operation	Process stream	Fraction of T in process stream (% of inventory)	Chemical form
	Fuel element	100 ^a	
Chopper	Fuel element pieces	>99.99	HTO, HT
	Off-gas	<10 ⁻³	
Dissolver	Aqueous phase	~40	HTO, TNO ₃
	Cladding	~60 ^b	ZrT
	Off-gas	<0.5	HT
Extraction	Aqueous phase	>35	
	Organic phase	<5	
Re-extraction	Aqueous phase	<4.9	
	Organic phase	~0.01	
	Pu product	~0.1	
	U product	~0.01	

^a Corresponds to 350 to 700 Ci/t at 30 GW·d/t.

^b Depends mainly on local fuel rod temperature.

Following the route of tritium in reprocessing, a certain fraction is bound in Zircaloy cladding. According to recent studies [11], about 60% of the total inventory may be expected in the cladding, the actual figure being dependent on fuel rod temperature rather than local burnup. The tritiated cladding waste can be fixed in drums with cement and disposed of.

The bulk of residual tritium leaves the first contactor together with fission products in the aqueous phase as tritiated water (HTO) and tritiated nitric acid (TNO₃). A small percentage of the total inventory appears as tritiated molecular hydrogen (HT), and as HTO in various off-gases. Another small percentage follows the organic route in the dissolved and entrained aqueous phase.

Common acid and water recovery systems for the different extraction cycles, cross-contamination due to recycling, and other effects result in tritium contamination of practically all the process streams in the standard Purex flowsheet. Table II shows a simplified distribution of tritium during LWR reprocessing based on a standard Purex flowsheet.

2.2.3. Process modifications to confine tritium

From the dissolver onwards, the tritium in the fuel is repeatedly diluted isotopically as fresh water and nitric acid are introduced. As a result, the present mode of operating reprocessing plants produces very large volumes of aqueous tritiated effluents, which are of the order of 100 m³/t of heavy metal.

In locations where tritiated water can be discharged to the atmosphere (e.g. sun evaporation in India) and for coastal sites where it can be discharged directly to the sea using the enormous dilution effect (United Kingdom, France), this process is feasible. However, for densely populated inland sites, recovery of tritium might be required in the future.

Concepts for concentrating the tritium into smaller volumes of waste water have been reported and reviewed [5, 11, 12]. This can be achieved as follows.

- (1) Segregation of tritium in the first aqueous cycle in the head-end. The procedure includes a separate tritiated acid- and water-recovery system and scrubbing of the organic phase of the first contactor with non-tritiated scrub acid to remove the dissolved and entrained tritiated aqueous phase.
- (2) Concentration of tritium in a small volume of water. This is done by partial recycling of the water and nitric acid. This has an adverse operating effect of raising the tritium level in the first aqueous cycle.

By these means a volume of effluent can be reduced to the order of 1 m³/t heavy metal, which can be disposed of. Figure 1 shows schematically the distribution of tritium in the first aqueous cycle of a modified Purex flowsheet with recycling, scrubbing and separate acid recovery.

Voloxidation is an alternative head-end process to promote the release of gaseous fission products from oxide fuels by further oxidation at an elevated temperature. The process was intended as a method of removal of tritium, iodine, krypton, and xenon from irradiated fuel, but has so far only been partially successful with respect to iodine and noble gas removal [13].

However, voloxidation can be used to remove the tritium from the fuel before dissolution, thus avoiding isotopic dilution during reprocessing. Figure 2 shows the conceptual flowsheet. The process consists essentially of oxidation of UO₂ to U₃O₈ in a stream of air or oxygen to break down the lattice and release the trapped gases. This can be obtained by heating the chopped fuel at about 550°C for several hours in a rotating furnace. Between 2 and 20 L HTO/t of heavy metal may be expected with a tritium concentration in the range of 100 to 10 Ci/L; the release of gaseous tritium should be less than 0.1% [14]. The enriched tritiated water (about 30 m³/a for the 1400 t/a reprocessing plant) can be converted into the less toxic HT form by electrolysis and discharged to the atmosphere.

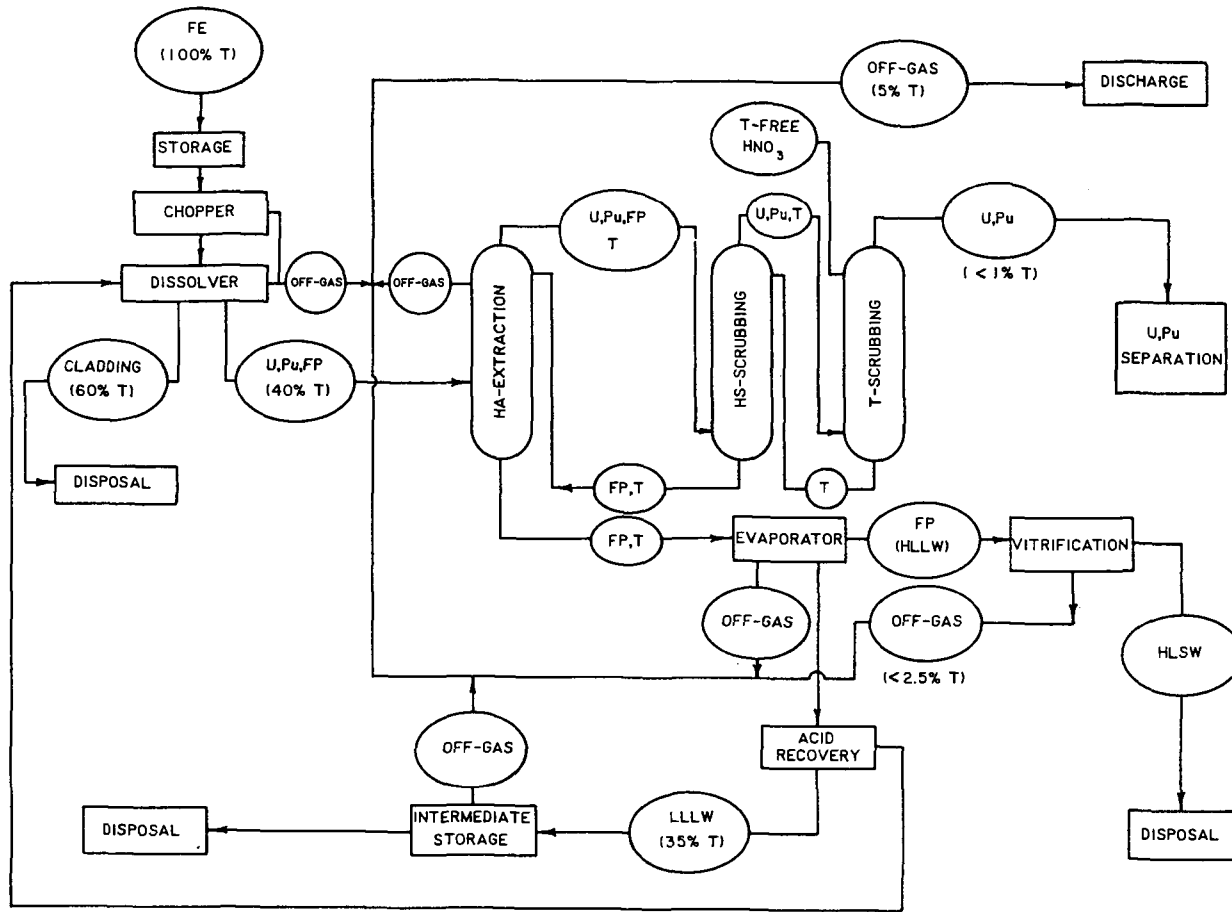


FIG.1. Distribution of tritium in the first aqueous cycle of a modified Purex flowsheet (T content given in percentage of total throughput).

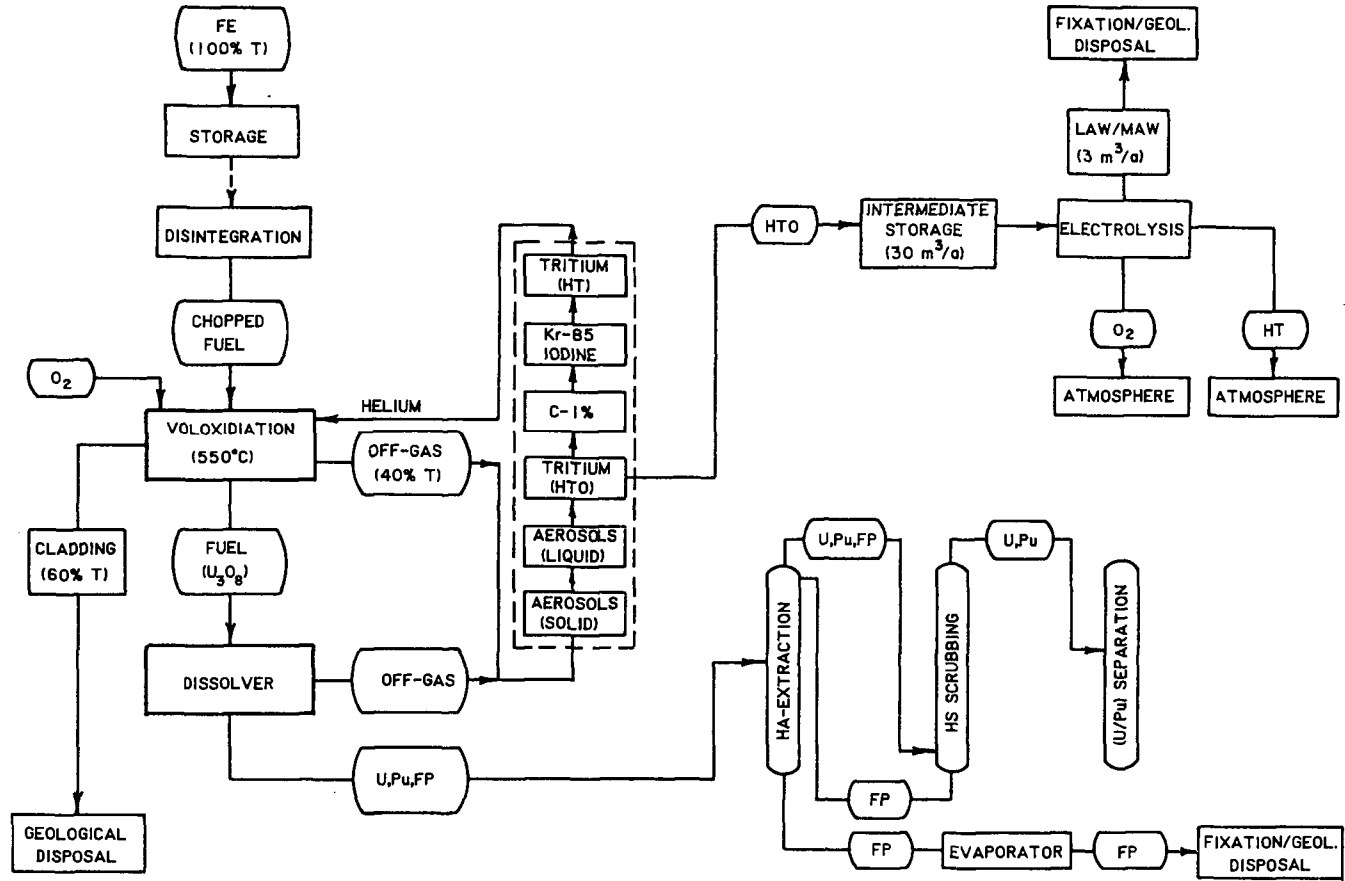


FIG.2. Release of gaseous tritium to the atmosphere (voloxidation).

The voloxidation process has not yet been fully developed. The main drawbacks may be (1) engineering problems (e.g. temperature control, size of equipment, abrasion and corrosion, criticality control); (2) behaviour of the voloxidized fuel in the dissolver; and (3) behaviour of the remaining volatile radionuclides (carbon, ruthenium, krypton, iodine).

3. TRITIUM SEPARATION AND ENRICHMENT

3.1. GENERAL PRINCIPLES

This section deals with processes for isotopic separation and enrichment of tritium before further conditioning for storage or disposal. In most tritium-containing streams and effluents the concentration of tritium is very low. For example, DTO:D₂O ratios are of the order of 10^{-5} in heavy water reactor (PHWR) moderators and HTO:H₂O ratios are of the order of 10^{-7} in the aqueous effluents of a reprocessing plant in which segregation and recycling of tritium have already been practised.

The general objective of the technique is to produce a product stream that is sufficiently enriched in tritium (volume reduction factor, VRF) to be economical for storage or disposal and a waste stream that is sufficiently depleted in tritium (decontamination factor, DF) to be recycled in the system or to be discharged to the biosphere. This objective may be met by a variety of processes and process combinations referenced elsewhere [5, 15]. As indicated in Ref.[1], the choice of a particular process depends on many factors that are application- and even case-specific. The most likely methods are, with one exception, based on technologies already developed for separation of deuterium from protium: water distillation, hydrogen distillation, electrolysis, isotope exchange between hydrogen and water vapour, and isotope exchange between hydrogen and liquid water.

In water distillation, the tritium-containing molecule becomes enriched in the liquid phase and depleted in the gaseous phase. The separation factor is very small and large columns with high energy consumption are needed. The separation factor decreases with increasing temperature and distillation is carried out at temperatures slightly above ambient and subatmospheric pressure. It is a simple and well-known technology and does not require the handling of hydrogen gas, with its fire and explosive hazards. However, it has the disadvantage of concentrating tritium in the more radiotoxic aqueous form.

Tritium separation by hydrogen distillation is also a well-known method, based on the same principle as water distillation but with a much higher separation factor. Because of the low boiling point of hydrogen, operation at cryogenic temperatures is necessary and the costs of refrigeration become very important. Nevertheless it is considered the least expensive alternative among the developed methods and it is possible to obtain pure tritium as T_2 . Tritium must, however, be fed in the molecular hydrogen form.

In electrolysis of tritium-containing water, tritium is concentrated in the aqueous phase and the cathodically formed hydrogen is depleted in tritium. Of all the well-known techniques this process has the highest separation factors; variations are possible, depending primarily on temperature and to a lesser extent on cell design and feed impurities. To achieve the necessary DF and VRF, several stages are required, and energy and investment costs are high. Inherent leakage limits the tritium concentration in cells to an acceptably safe level.

In isotope exchange between hydrogen and water vapour, tritium concentration in the water is favoured. The separation factor is high and is given by the equilibrium constant of the exchange reaction and decreases with increasing temperature. A catalyst is needed to attain a sufficiently high exchange rate. For effective separation and enrichment of tritium either a monothermal process with phase conversion or a bithermal process based on the difference in the equilibrium constant at different temperatures can be used. One monothermal technique is well known, but it suffers from both a low separation factor (since it operates at the higher temperature) and difficulties in obtaining a counter-current flow with several stages of evaporation exchange and condensation.

The development in Canada [16], Belgium [7], the Federal Republic of Germany [17], and Japan [18] of sufficiently active hydrophobic catalysts has allowed the exchange of tritium to be carried out between hydrogen and liquid water. This process is very similar to the preceding one but without the disadvantages cited. Monothermal or bithermal versions may become competitive with hydrogen distillation, but further development and demonstration are required.

Combinations of the previous techniques are possible and could even be advantageous. Eventually other methods, especially those based on new techniques such as the selective multiple photon dissociation of CF_3T or other suitable molecules studied in the United States, Japan, Canada and Belgium, could also become useful [19–21].

The decision on whether or not to separate and enrich tritium, and, if so, the choice of the VRF and DF, must be based on a number of factors, including cost of the process less the market value of the enriched product (where applicable); decrease in cost for immobilization, transport and storage or disposal of the tritiated waste; and radioecological benefit from a decrease in occupational, local and global exposure. On these grounds separation and enrichment of tritium in the moderator and coolant systems of heavy water reactors

appears worthwhile. Treatment of the effluents from those reprocessing plants where alternative management schemes such as direct disposal into the ocean or on-site, deep-well injection are not possible may also be worthwhile.

3.2. TRITIUM REMOVAL FROM HEAVY WATER REACTORS

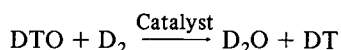
The ultimate method of decreasing tritium releases and occupational exposure in heavy water reactors is the removal of tritium from the moderator and coolant systems. Taking into account the large amounts of tritium in heavy water reactors, it is worthwhile to produce a small amount of a highly concentrated tritium stream that will either be stored for later use or disposed of. Cryogenic distillation of $D_2/DT/T_2$ is the only developed large-scale process available for the enrichment of tritium. The product is in the chemical form of tritiated water and does not suffer from radiolysis. Other possible enrichment processes are gas chromatography and thermal diffusion, but these have only been demonstrated on a scale much smaller than required and scale-up may be impractical.

Tritium recovery from heavy water reactors consists of two separate processes: one which transfers tritium from the tritiated heavy water to tritiated deuterium, followed by a cryogenic distillation process for separation of deuterium and tritium. The transfer processes that are being or will be used are vapour-phase catalytic exchange (VPCE) and liquid-phase catalytic exchange (LPCE); others include direct electrolysis (DE) and combined electrolysis catalytic exchange (CECE) and are described briefly.

3.2.1. Vapour-phase catalytic exchange (VPCE) and cryogenic distillation

This process was developed by the French Commissariat à l'énergie atomique. Sulzer Brothers Ltd, Winterthur, Switzerland, is licensed to market the process commercially and has built a small plant in Grenoble, France, that has operated since 1972 [22]. This process will also be used in the tritium removal system of Ontario Hydro in Canada.

In this process, the D_2O/DTO feed is vaporized, superheated and brought into direct contact with a recirculating, low tritium concentration D_2 gas stream (from the cryogenic distillation system) over a catalyst bed to promote the following exchange:



The water is then condensed and flows to the evaporation of the next stage. Several evaporation/catalytic exchange/condensation stages are used to achieve

the desired detritiation. After final condensation the detritiated heavy water is returned to the reactors.

The tritiated deuterium stream is purified by the removal of oxygen, nitrogen and other gaseous impurities and is then fed to the cryogenic distillation system. The detritiated deuterium gas from the first cryogenic distillation tower is recirculated to the VPCE front-end. Concentrated tritium is bled off periodically from the bottom of the last distillation tower and packaged for storage or disposal.

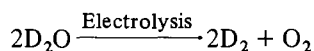
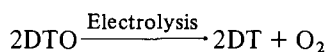
In this process concentrated tritium is handled in its elemental state and the maximum tritiated water concentration handled is that of the heavy water feed.

3.2.2. Liquid-phase catalytic exchange (LPCE) and cryogenic distillation

In the liquid-phase catalytic exchange tritium transfer process [23] the isotopic exchange reaction is carried out between liquid water and deuterium gas rather than water vapour, as in the VPCE process. The use of a hydrophobic catalyst developed by Atomic Energy of Canada Ltd (AECL) [16, 24, 25] or other similar catalysts subsequently developed [7, 17, 18] enables the reaction to be carried out using liquid water, thus providing a counter-current process and avoiding the necessity of evaporation, superheating and condensation of the feed. The LPCE process is coupled to cryogenic distillation in the same manner as in the VPCE process. The first industrial application of the LPCE process will be in the tritium extraction plant being built by AECL at the Chalk River Nuclear Laboratories (CRNL).

3.2.3. Direct electrolysis (DE) and cryogenic distillation

Tritiated heavy water from the reactor units is fed to electrolytic cells, where it is decomposed into an oxygen gas stream and a D₂/DT gas stream.



The D₂/DT stream is purified and fed to the cryogenic distillation system as before. The deuterium gas returning from cryogenic distillation is recombined with the oxygen generated in the electrolytic cells to form detritiated heavy water, which is then returned to the reactor units.

3.2.4. Combined electrolysis catalytic exchange (CECE) and cryogenic distillation

The CECE process was developed at Chalk River Nuclear Laboratories [26] and it uses a proprietary hydrophobic catalyst to promote exchange of deuterium

and tritium. Tritiated heavy water from the reactor units is fed to the catalytic column and allowed to flow downwards counter-currently to a rising stream of D_2/DT gas generated in electrolytic cells. Tritium moves from the gaseous D_2/DT stream to the liquid D_2O/DTO stream.



The liquid stream enriched in tritium is collected in the electrolytic cells at the bottom of the catalytic column. A portion of the concentrated DT/D_2 gas from the electrolytic cell is directed to the cryogenic distillation systems for tritium extraction. Since deuterium gas evolves preferentially to tritium in the electrolytic cell, the cell solution becomes enriched with tritium.

The deuterium gas stream (depleted in tritium) from the cryogenic distillation column is fed back to the bottom of the catalytic column. Gas leaving the top of the catalytic column is depleted in tritium and is oxidized by the oxygen stream from the electrolytic cells in a recombiner or burner to form detritiated heavy water, which is returned to the reactor units. Detritiation factors of many orders of magnitude are possible. This process is also being developed in the USA, Belgium and Japan [7, 18, 27].

3.2.5. Applications of transfer processes

There are advantages and disadvantages to each of the four transfer processes. The LPCE is favoured because of its simplicity and its operation at low pressures and temperatures. It is easier to make the equipment leak-tight and is safer because the tritium-in-water concentration is not increased beyond the feed concentration from the reactor system. The CECE process is more complex and requires handling of tritiated water at a concentration substantially higher than the feed concentration from the reactor. In applications of tritium recovery from water containing very low tritium concentrations, this enriching feature of the CECE system is considered most economical. Both the LPCE and CECE schemes have been evaluated on laboratory and pilot plant scales. The direct electrolytic conversion of tritiated D_2O to tritiated D_2 is somewhat more complex than LPCE and a low-inventory cell for the D_2O application is not yet proven. The VPCE is proven but has the disadvantage of operating at high temperature and is more complex because of the repeated evaporation and condensation cycles required. The size of the cryogenic distillation unit for a given decontamination factor depends on the transfer process and increases in the sequence CECE, DE, VPCE, LPCE.

There is only one operating plant for extraction of tritium from a heavy water reactor. This installation, at the Institute Laue-Langevin in Grenoble, France, began operation with tritiated heavy water in August 1972. It was designed to

maintain the tritium concentration of heavy water at 1.7 Ci/L by an annual extraction of 0.16 MCi using vapour-phase catalytic exchange followed by hydrogen distillation. The installation has been described in detail by Damiani and Pautrot [22].

In Canada two tritium removal systems (TRSs) to serve heavy water reactors have been committed, one by Ontario Hydro and the other by Atomic Energy of Canada Ltd.

In August 1980, Ontario Hydro committed a TRS for construction at Pickering Generating Station to meet a commissioning date of 1985.

The Ontario Hydro tritium removal system processes heavy water at the rate of 360 kg/h. About 8 MCi/a of tritium will be extracted at a steady-state condition.

The capital and annual operating cost of the TRS will be offset by the following advantages [9].

- (1) The capacity factor at the station would be expected to be lower if a TRS were not installed.
- (2) Lower tritium levels will also mean savings in maintenance costs – radioactivity levels within reactor buildings will be lower, allowing technicians to work longer and more efficiently. As a result of the installation of the TRS, the station's internal annual dose will be lower.
- (3) The tritium and its decay product ^3He are items of commercial value.

In October 1981, AECL committed a tritium extraction plant for construction at the Chalk River Nuclear Laboratories. This plant is expected to be in operation in 1986 and to be capable of extracting approximately 0.5 MCi/a of tritium from the AECL research reactors. It will be the first industrial demonstration of the LPCE process for the front-end tritium transfer step. A preliminary design of the process was described by Harrison [28].

The concentrated tritium produced from both of the Canadian plants will be immobilized as titanium tritide and packaged for storage as described in Ref.[29] and Section 4.

3.2.6. Description of the Ontario Hydro tritium removal system [30]

The feedwater, taken downstream from the moderator purification system, is degassed and purified before it enters the vapour-phase catalytic exchange (VPCE) process. In the VPCE process a tritium transfer, from heavy water to deuterium gas, takes place over a catalyst. The heavy water product, depleted in tritium, flows into a tank from which it is returned to the reactor systems.

The tritium-enriched deuterium passes through a dryer unit (to remove traces of heavy water) and an adsorber unit (to remove traces of oxygen and nitrogen). The D_2/DT gas stream enters the distillation unit, where the hydrogen

isotopes are separated by distillation at liquid hydrogen temperature. Tritium-lean deuterium gas is recirculated to the VPCE columns.

For the heavy water from Pickering reactors, the production of nearly pure tritium requires a concentration factor of over seven orders of magnitude. This is accomplished by using a series of cryogenic distillation columns.

The distillation unit is divided into two sections: one low-tritium column (LTC), and three high-tritium columns (HTC-1, HTC-2, HTC-3).

To maintain separation between low- and high-tritium content systems, the two distillation sections are located in separate cold boxes.

The cryogenic unit is provided with several safety features which protect it against over-pressure and reduce the potential for tritium release. Expansion tanks are provided so that, in the event of loss of insulation or refrigeration, pressure increase from the evaporation of liquid deuterium/tritium would be limited. In addition, loss of power or refrigeration activates isolation of the low- and high-tritium sections to prevent migration of tritium from the high- to the low-concentration columns.

The tritium gas from the cryogenic unit will be immobilized as a solid metal tritide of titanium, packaged and stored on the station site. Storage as an immobilized solid tritide was selected as being the safest, most volume-efficient, long-term technique.

An air cleanup system (ACS) is designed to detritiate the atmosphere in the building enclosing the tritium removal system in case of acute leakage of tritium. The system is actuated by monitors sensing tritium in any particular area of the building. Dampers in the ventilation system isolate the affected area and the air is directed to the ACS. In a catalyst bed, hydrogen isotopes are converted to water. The ventilation air is then cooled and dried in molecular sieve dryers to recover the tritiated water. The decontaminated air from the ACS is normally discharged to the environment by the stack. However, if residual activity is present, this entire air stream is recycled for decontamination.

3.3. TRITIUM SEPARATION FROM AQUEOUS REPROCESSING PLANT EFFLUENTS

Because of their importance, LWR fuel reprocessing effluents are the basis of this section. At present there has been no attempt to trap or retain tritium at reprocessing plants. Although high-temperature treatments such as the voloxidation process discussed in the previous section allow the removal of tritium from the spent fuel before dissolution, a normal chop-and-leach process is still preferred. Starting with dissolution, the tritium in the fuel is repeatedly diluted isotopically as aqueous reagents are introduced. As explained in Section 2, several schemes have been presented to confine the tritium to as small a volume

as possible and it can be expected that at future reprocessing plants the volume of tritiated aqueous effluents may be reduced to 5–0.5 m³/t LWR fuel processed [5], with a tritium level of about 50–100 Ci·m⁻³. In many cases, however, further reduction of the waste volume will be required and isotopic enrichment and separation of tritium by one of the methods described in Section 3.1 will have to be carried out.

A recent study [5] has shown that a complete immobilization scheme for tritium in a reprocessing plant must, in most cases, include: (1) segregation/recycling in the reprocessing plant; (2) isotopic separation; (3) immobilization; and (4) storage/disposal.

Segregation/recycling is necessary to reduce volume because the cost of subsequent stages would otherwise be prohibitive. Further volume reduction by isotopic enrichment is nearly always economically beneficial because it reduces the cost of immobilization and storage or disposal. Possible exceptions are schemes in which segregation is by voloxidation and those that are based on immobilization as tritiated cement.

Before enrichment, pre-treatment of the tritiated water may be required to remove the remaining nitric acid, possible organic impurities and traces of fission products, and actinides. Neutralization followed by distillation or ion exchange and activated carbon beds could be applied.

As noted in Section 3.1, the optimum degree of enrichment depends on many parameters. In many isotope separation processes costs are determined chiefly by throughput and decontamination factor.

If tritium is enriched as tritiated water, radiolysis will generally set an upper limit, at about 0.03% enrichment, corresponding to 10⁶ Ci·m⁻³ [5]. In many cases there will be no need to use such a high degree of enrichment, and processes that yield a volume reduction factor of 100 could be sufficient.

The decontamination factor when detritiating aqueous reprocessing effluents in the future will probably be in the range of 10–10³. For some detritiation processes the costs rise drastically with the DF required, and DFs as low as 2 or 3 have been proposed together with a recycling of the decontaminated stream to the reprocessing plant.

Unless the depleted stream is recycled, the requirement for a high DF tends to favour processes with high T/H separation factors to minimize the number of stripping (decontamination) stages; consequently, water distillation is at a considerable economic disadvantage. The costs for electrolysis also rise severely if a stripping cascade must be used. The cost of hydrogen distillation or of monothermal H₂/H₂O exchange is less dependent on DF.

In comparison with the other tritium separation and enrichment processes, the exchange of tritium between hydrogen and liquid water is not fully developed. Studies in several countries have, however, advanced far enough to consider the application of a monothermal exchange process. In this case the catalytic requirements are much smaller and the larger part of the operating costs are in fact due

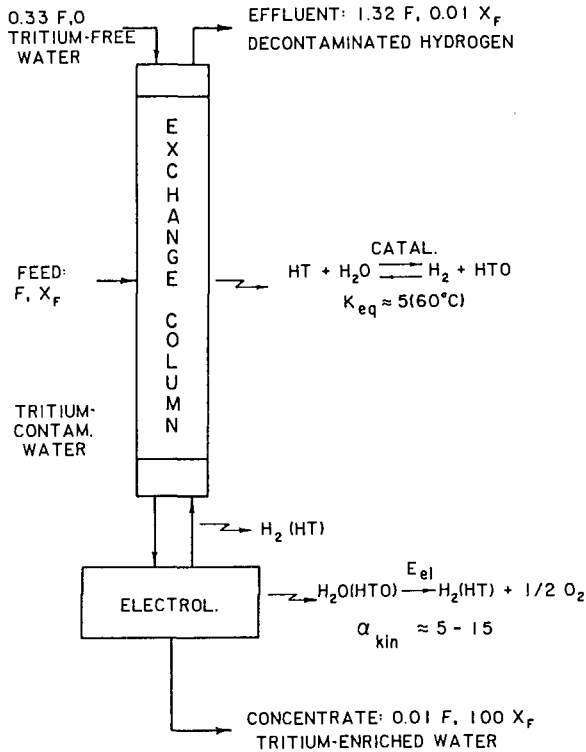


FIG.3. ELEX process for detritiation of water.

to the electrolysis process used for phase conversion. Nevertheless, although appropriate hydrophobic catalysts are developed, they are not yet commercially available and the required gas/liquid/solid contacting at low specific liquid flow rate could still benefit from further chemical engineering development.

Since 1978, within the framework of the Commission of the European Communities' indirect action programme on management and storage of radioactive wastes, the Belgian Nuclear Research Centre, SCK/CEN, has been developing the ELEX process for tritium separation from aqueous reprocessing effluents. This process, as is the CECE process described in Section 3.2, is a combination of water electrolysis and tritium exchange between hydrogen and water, the exchange being promoted by a hydrophobic catalyst [7]. Analogous processes are being studied in Canada, the USA, Japan and the Federal Republic of Germany [17, 18, 26, 27].

Figure 3 gives a schematic illustration of the ELEX process. It comprises an electrolyser for production of hydrogen and a packed-bed reactor for tritium exchange between counter-current flows of hydrogen gas and liquid water. As the liquid water trickles down the column it becomes more and more enriched in tritium. The hydrogen gas is depleted in tritium as it flows from the bottom to the top of the column. The tritium-contaminated water is fed into the exchange column at the point where its tritium content corresponds to the tritium content of the water that has been added at the top of the column. The tritium-depleted hydrogen stream at the top of the column can be vented and a small tritium-enriched water fraction is removed as condensate from the electrolyser for immobilization and storage.

Initially the R&D work at SCK/CEN concentrated on the separate constituent steps of the ELEX process. Electrolytic separation factors were experimentally determined and after the development of an appropriate hydrophobic catalyst, studies in counter-current, packed-bed reactors to optimize the overall tritium exchange rate were carried out.

A $10 \text{ mol} \cdot \text{h}^{-1}$ integrated bench-scale detritiation unit was built with a 1.5 kW electrolyser, two 2 cm dia. exchange columns containing the Belgian hydrophobic catalyst, and a recombiner. In this installation the ELEX process was successfully demonstrated by detritiating more than 1 m^3 of water containing up to 100 Ci/m^3 of tritium, which is the feed concentration expected for application of the process in a reprocessing plant. The process decontamination factor was always larger than 100. The volume reduction factor was between 10 and 15, but this factor will become much higher when the present electrolyser is replaced by the low-volume one now under construction at SCK/CEN.

A pilot detritiation installation has been designed, is being constructed and may be considered the last step before industrial application. This pilot consists of an 80 kW electrolyser and a 10 cm dia. exchange column with enriching and stripping sections, installed in a ventilated enclosure. Later it will be supplemented with a pre-treatment unit for the removal of HNO_3 and fission products. This unit will have a maximum total tritium inventory of 1000 Ci and will be used in 1983 to demonstrate the ELEX process at the following design conditions: (1) throughput, $0.15 \text{ m}^3 \text{ H}_2\text{O (HTO)}/\text{d}$; (2) feed concentration, 100 Ci/m^3 of tritium; (3) volume reduction factor, 100; and (4) process decontamination factor, 100. The first experiments will be carried out using a modified commercial electrolyser. In future work a new electrolyser of Belgian design will be put into operation.

4. CONDITIONING

4.1. CONDITIONING REQUIREMENTS

When conditioning of tritium-bearing effluents is required, there are two major requirements to be met. The first is that the tritium must be in a form or package such that the leakage rate will not cause an unacceptable radiation dose either to the workers at a storage facility or to the general population for the period of time it is stored or until it has decayed to a negligible level. The second requirement is that of an acceptable cost.

4.2. CONDITIONING METHODS

4.2.1. Conditioning of low-level, tritium-bearing aqueous wastes

Several solidifying media can be used for incorporating tritium-bearing wastes. The candidates are inorganic hydrates, metal hydrides, organic polymers and cement [5, 31]. However, the most widely investigated material for immobilization of low-level tritiated wastes in many countries is cement, and several investigators are currently engaged in more detailed evaluation of this method [32–35]. The main reason that makes cement attractive for immobilization of these wastes is that it is an accepted material for the fixation of wastes containing other radionuclides [36, 37], and tritium-bearing wastes are sometimes mixed with other activation and fission products.

Tritium-containing water is held in a hardened cement paste as: (1) water of hydration of cement compounds; (2) water adsorbed in the gel formed by the compounds; and (3) water present in capillary voids in the cement structure.

Portland cement fixes chemically about 0.25 g water/g cement if the hydration reaction proceeds completely [38]. The favourable factors for choosing cement are the hydration property of the cement and the development of coatings which form a barrier to permeation in the set cement block. Cement in the form of concrete is also a good radiation shield if other radionuclides are present. It has favourable mechanical properties for packaging, handling, transportation and storage and it is also inexpensive.

Factors that are important in the cementation of aqueous tritiated wastes are water:cement ratio and additives. The application of coating materials on the tritiated cement blocks assists in retaining tritium.

4.2.1.1. Water:cement ratio. The pore structure of the hardened cement paste in general depends on the weight ratio of water to cement [39]. The penetration of water through the pore structure extending through the body of the matrix

plays an important role in the leaching of tritium. When incorporating tritiated water into the cement, the water:cement ratio must be kept sufficiently low to ensure that all the water is fixed. A typical water:cement ratio is 0.33. Untreated concrete exposed to moisture loses its tritium initially very rapidly: 2–25% in the first week, 30–45% in the first month, followed by a slower release. In a year the release will be 50–70% [32]. The inclusion of additives in the cement blocks requires a higher water:cement ratio, approximately 0.40 [33].

4.2.1.2. *Additives.* Gypsum [32], sand, silica, vermiculite, and portland cement aggregate have been used as additives to cement [33]. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) loses part of its water of crystallization at 128°C and is capable of taking back that water when hydrated. Vermiculite (expanded mica) is a sodium aluminosilicate with calcium and magnesium as exchangeable ions whose addition might help in the uptake of other radionuclides. Silica gel, an amorphous gel of dehydrated silicic acids, will bind water to metastable forms of $\text{SiO}_2 \cdot \text{H}_2\text{O}$, $2\text{SiO}_2 \cdot \text{H}_2\text{O}$, etc. The silica gel particles and cement aggregate particles could trap the tritiated water escaping as evaporable water from the newly formed tritiated cement blocks. Sand particles, other than contributing to mechanical strength, may not provide any additional benefits.

The effect of adding sand, silica, portland cement aggregate, and vermiculite with 10%, 20% and 30% loadings with respect to portland cement was investigated by subjecting them to leaching in distilled water and synthetic sea water. The blocks were made with 100 g of portland cement, 40 mL of tritiated water, and 10, 20 or 30 g of the additives. The cast was broken on the third day, the block was cured in a humid chamber for 28 d, and the upper and lower sides were polished and used for leaching. For a total activity loading of $0.53 \mu\text{Ci}$ of tritium and a total leaching period of 34 d, the additives could be classified as two series in increasing order of tritium leachability for distilled water and synthetic sea water.

Sea water:

$$\text{Si}_{10} < \text{V}_{20} < \text{C}_{\text{Ag}30} < \text{C}_{\text{Ag}20} < \text{C}_{\text{Ag}10} < \text{S}_{30} < \text{Si}_{20} < \text{V}_{10}$$

$$\text{V}_{10} < \text{Si}_{30} < \text{V}_{30} < \text{S}_{10} < \text{S}_{20}$$

Distilled water:

$$\text{Si}_{10} < \text{C}_{\text{Ag}30} < \text{C}_{\text{Ag}10} < \text{S}_{10} < \text{V}_{20} < \text{S}_{30} < \text{V}_{10} < \text{S}_{20} < \text{V}_{30} < \text{Si}_{20} < \text{Si}_{30}$$

where C_{Ag} = portland cement aggregate
 Si = silica
 S = sand
 V = vermiculite

TABLE III. PERCENTAGE LEACHING OF TRITIUM FROM TRITIATED CEMENT BLOCKS

Coating	1 day	10 days	1 month	1 year
Uncoated cement	4-9	20-30	30-40	50-70
Painted				
epoxy resin 0.015-0.03 g/cm ²	0.1-1	1.5-8	5-20	35-50
epoxy resin with primer	0.02-0.03	0.2-0.3	0.6-0.9	7-11
Paraffin	-	1.5	2	-
Bitumen	-	7.5	10	-

TABLE IV. COATING MATERIALS USED

1. Four coats of epoxy paint with overnight drying interval in between.
2. One coat of epoxy paint; one coat of epoxy putty-cum-trowelling compound; three coats of epoxy paint.
3. One coat of epoxy paint; one coat of epoxy putty; three coats of chlorinated rubber paint.
4. Four coats of chlorinated rubber paint.
5. Three coats of epoxy putty.
6. Four coats of polysulphide primer.
7. One coat of primer; three coats of polysulphide.
8. One coat of red oxide, zinc chromate primer; one coat of epoxy coal-tar pitch paint.
9. One coat of Tarstil-Tar special grade and one coat of Shalimastic HD.
10. Three coats of coal-tar-based paint.
11. Coal-tar epoxy (one coat of epoxy and three coats of coal-tar epoxy).
12. Pipcothane (one coat of primer (30% vinyl acetate resin) and three coats of paint, pipcothane).

4.2.1.3. *Cement coating.* The use of coating materials to reduce the leaching of tritium from the tritiated cement blocks has been studied by many investigators [40, 41]. The integrity test [42] for solidified cement matrices under deep-sea conditions shows that the application of waterproof paint to the exposed surface of the solidified waste, to form cured film, can prevent the formation of cracks.

TABLE V. DETAILS OF BLOCKS USED FOR LEACHING

Block no.	Coating material	Distilled water leaching		Sea water leaching	
		Thickness of coating material (mg/cm ²)	Surface area (cm ²)	Thickness of coating material (mg/cm ²)	Surface area (cm ²)
1	Nil (control)	–	101.8	–	110.2
2	Epoxy	144.7	110.02	136.99	113.87
3	Shalimastic HD	186.09	116.23	249.07	116.23
4	Anticor	276.88	122.18	228.30	126.19

Table III gives a summary of the results obtained with different coatings [32]; paraffin and bitumen coatings were made by dipping the cement blocks into the coating, whereas other materials were brushed on the surface.

Work done in India, using a diffusion cell for preliminary screening of commercially available coating material (listed in Table IV), shows low diffusion rates for three coating materials. These were Anticor (CNSL epoxy coal-tar pitch paint, manufactured under licence as per IP 127126, patented by the Research Designs and Standard Organisations, Ministry of Railways, India); Shalimastic HD (conforming to American Bureau of Reclamation Specification “Cold-Applied Coal-tar Paint CA50”); and epoxy paint (Apcodur CF693, a two-pack air-drying epoxy paint in which a polyamide is used as the hardener). These three coating materials were used for extensive leach studies. Tritiated cement blocks with 100 g cement, 40 mL tritiated water and 20 g vermiculite were made and then cured in a humid chamber for 28 d. After an application of the coating material, the cement blocks were ready for leaching on the 45th day from casting. The coated blocks were subjected to leaching in distilled water and synthetic sea water. The results are expressed by a plot of the incremental leach rates (R_n) as a function of time, in days $[t_n - (t_n - t_{n-1})/2]$ [43].

$$R_n = \frac{a_n/A_0}{(F/V)t_n}$$

where R_n = leach rate, $\text{cm}\cdot\text{d}^{-1}$

a_n = radioactivity leached during period $(t_n - t_{n-1})$

A_0 = initial radioactivity loaded into specimen

F = surface area of specimen, cm^2

V = volume of specimen, cm^3

t_n = time, d

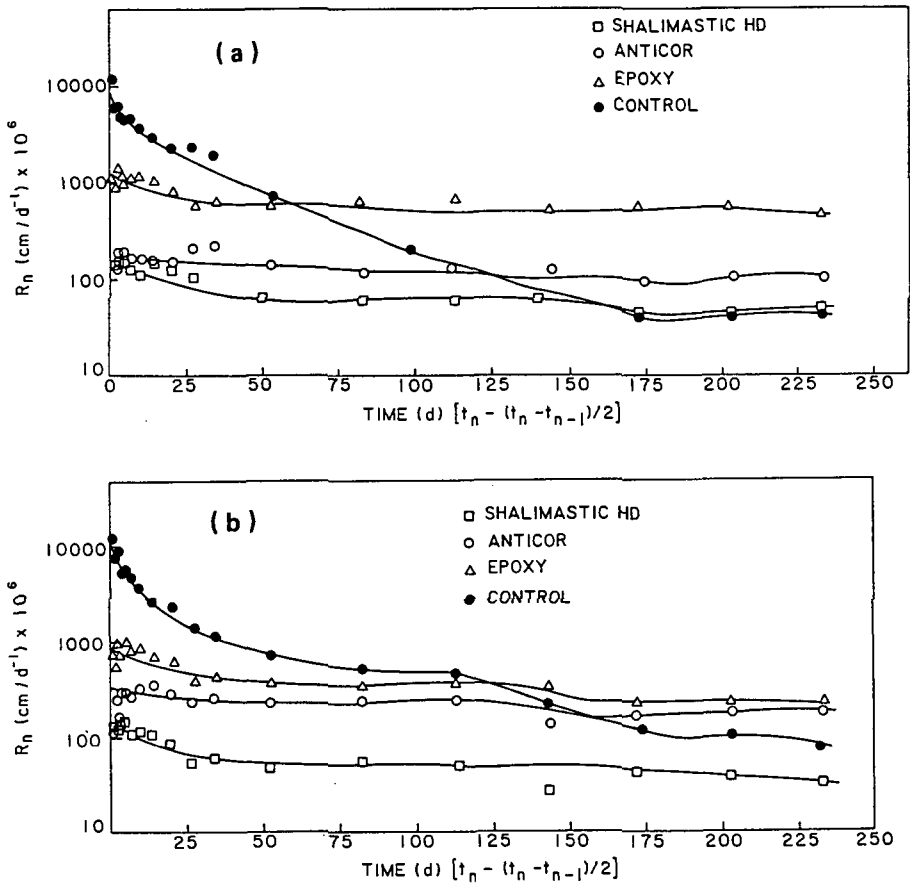


FIG.4. (a) Leach rates for coated blocks in distilled water;
 (b) leach rates for coated blocks in sea water.

Details of the blocks and the thickness of the coating material are given in Table V.

Figure 4 depicts the leach rates for the uncoated and coated blocks in distilled water and sea water.

Tables VI and VII give the cumulative leaching data for the coated and uncoated blocks (total activity loaded 254.64 μCi) in distilled water and sea water, respectively.

A Shalimastic HD-coated block was left in water for two years, and it was seen that the coating retained its original form.

TABLE VI. CUMULATIVE LEACHING OF TRITIUM FROM COATED AND UNCOATED CEMENT IN DISTILLED WATER (%) (*Total activity loaded: 255 μ Ci*)

Details of coatings	Time (days)										
	1	11	31	67	97	129	157	187	217	247	278
Uncoated block	1.5	7.4	14.0	18.0	—	20.0	—	20.0	20.0	20.0	20.0
Epoxy	0.1	1.0	3.0	6.0	8.0	11.0	13.0	15.0	16.0	18.0	—
Shalimastic HD	0.02	0.2	0.5	0.8	1.0	1.0	1.0	2.0	2.0	2.0	—
Anticor	0.02	0.2	0.7	1.0	2.0	2.0	3.0	3.0	4.0	4.0	4.0

TABLE VII. CUMULATIVE LEACHING OF TRITIUM FROM COATED AND UNCOATED CEMENT BLOCKS IN SEA WATER (%) (*Total activity loaded: 255 μ Ci*)

Details of coating	Time (days)									
	1	11	31	67	97	129	157	187	217	247
Uncoated block	1.4	7.0	12.0	15.0	17.0	18.0	19.0	19.0	19.0	20.0
Epoxy	0.1	1.0	4.0	4.0	5.0	7.0	8.0	9.0	10.0	—
Shalimastic HD	0.02	0.2	0.4	0.6	0.8	1.0	1.0	2.0	1.0	1.0
Anticor	0.03	0.3	0.8	1.0	2.0	2.0	3.0	3.0	3.0	4.0

The leaching data on the three coated cement blocks for a period of eight months and a visual observation of the Shalimastic HD-coated block in distilled water for two years make Shalimastic HD a promising candidate for such studies. The details of the coating procedure for Shalimastic HD were as follows. Three coats of primer were applied on the cement block. The primer, Tarstil special, is a coal-tar pitch-based, anticorrosive paint conforming to IS:290/1961, type B. Over this, three coats of Shalimastic HD were applied with a minimum 24 h drying time between each coat, in a dry air atmosphere.

4.2.1.4. Immobilization in polymer-impregnated cement. An evaluation of the possible use of a polymer-impregnated cement for immobilization of low-level, tritium-bearing aqueous wastes concluded they would be unsuitable in tritium recovery plants [44] because a substantial portion of tritiated water incorporated in the cement remains mobile and the efficiency of polymer impregnation of the composite as a barrier to tritium was not found satisfactory. However, work carried out in Finland [32] shows a leaching of only 0.07 to 0.1% activity from a polymer-impregnated cement block for 10 d.

4.2.2. Conditioning of concentrated tritium

The product from the tritium enrichment and recovery processes discussed in Section 3 requires immobilization and packaging before storage or disposal. The product from tritium recovery plants associated with heavy water reactors will be either T_2 or a mixture of D_2 , DT and possibly T_2 . Tritium recovered from a CECE unit or a reprocessing plant may be either light water containing $\gtrsim 10$ Ci/kg or tritiated hydrogen containing $\gtrsim 10$ Ci/m³, depending on whether the product was taken in the aqueous form from the electrolysis cell or the gaseous phase after electrolysis. If the product is taken as tritiated water, the methods described in Section 4.2.1 could be used. If tritiated hydrogen is taken, then the conditioning methods described in this section could be used. Economics will influence the decision. Tritium in the fuel cladding hulls is a second source of tritium from reprocessing plants. Because tritium in this form is immobilized as a solid it may be cemented and stored with other wastes in, for example, a salt dome (Section 5) or it could be recovered [45] and conditioned using the methods discussed in this report.

There are uses of tritium such as fusion reactor fuel or self-powered lights that may dictate storage for only a short term. In other circumstances disposal (until negligible activity remains, 100–200 years) may be appropriate. In conditioning the tritium these two possibilities must be considered.

4.2.2.1. Potential storage methods

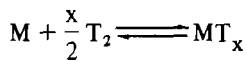
Packaging as a gas. The simplest packaging technique is a metal cylinder with tritium gas either compressed or at subatmospheric pressure. This is a simple,

well-established technology and there are a number of designs of tritium gas containers in use. These packages are normally fabricated from stainless steel with primary and secondary containers, both designed to contain the tritium safely. Various designs are for differing quantities of tritium, up to approximately 1.5 MCi. These containers have usually been designed for transportation, rather than storage, and are equipped with overpacks.

In a gas container filled initially with T_2 the pressure increases with time from radioactive decay to ^3He , with the pressure ultimately reaching twice the filling pressure. For storage, permeation of tritium through the wall of the vessel and the effect of helium on the strength of the steel must be considered. For austenitic stainless steel at 75°C , it has been shown that there is no significant permeation of tritium through the wall. For an initial T_2 pressure of 100 atm and a temperature of 200°C , helium embrittlement has been shown to be no problem [46–48].

The disadvantage of gas storage is the potential for leakage through valves. The advantage is that the tritium is easily recoverable for use at any time.

Packaging as metal hydrides. Tritium in the T_2 form can be immobilized as a solid by the reaction with a suitable metal to form a solid metal hydride:



The reaction is reversible by heating, so the tritium may be recovered. For storage, the metal tritide would have to be packaged in a suitable container. The advantages of metal tritides are that they are solids with a high capacity for tritium and, with the proper choice of metal, have a low equilibrium pressure of tritium. The disadvantages are that they require a processing step and the cost of the metal. This cost may not be significant in comparison with the value of the tritium or the costs of separation and concentration of the tritium. The characterization of metal tritides for transport, storage and disposal of tritium has been reported by Bowman, Carlson and De Sando [49].

Packaging as tritiated organic compound. Organic compounds are composed primarily of carbon and hydrogen atoms. Replacement of hydrogen atoms with tritium is a possible means of immobilizing tritium. Organic compounds with strong covalent bonds between the carbon and hydrogen, such as in paraffin-like oils, have extremely low hydrogen-isotopic exchange rates with water, very low solubility in water, and are generally unreactive chemically. Their major drawbacks are their flammability and radiation-induced decomposition. Only organic compounds that are of a higher molecular weight and are non-volatile are considered for tritium storage. The following polymers have been suggested [13]: polyacetylene, phenol-formaldehyde resins, polyacrylonitrile, and polystyrene.

The technology for the production of non-tritiated forms of these materials is established for commercial applications; however, in the case of making their tritiated versions, several complications arise. The route for production usually involves several steps with many stages of reactions. Each of these steps requires catalysts and/or special conditions to promote the desired reactions. The reactions, in general, do not go to completion and various side reactions occur. In the tritium application all of these extraneous products which contain tritium must be retained and recycled. While the end product polymer has desirable properties as a tritium storage compound, its preparation is complex and may be impractical. An outline of possible steps required in the preparation of these polymers is described by Burger and Trevorrow [15] and by McKay [5].

Other packaging methods. Ion implantation of tritium into receptor materials such as alumina, carbon, silicon carbide, and boron nitride has been proposed by Nelson and Whitmell [50], who suggested that a moving foil belt be used with the receptor material, deposited on both sides of the foil, being fed tritium by two ion guns. They estimated that a storage rate of 500 Ci/d using 10% tritium could be achieved with the foil moving at approximately 30 cm/min and with ion beam currents of 100 mA in both ion guns.

4.2.2.2. *Immobilization of tritium as metal tritides*

Many metals react with hydrogen to form solid hydrides but only transition metals have the required properties for a tritium storage applications. The properties of these metal hydrides that make them suitable are very low dissociation pressures at normal temperatures, high capacity for tritium, ease of preparation, and stability in air and water at storage temperatures. The hydrides of zirconium, titanium, hafnium, and yttrium [15], as well as erbium, have been suggested as useful for tritium storage. Uranium hydride has been used for many years for short-term tritium storage. The dissociation pressures of titanium and zirconium hydrides are less than 10^{-15} Pa at 25°C and less than 5 kPa at 500°C, but at 1000°C these hydrides are completely dissociated, whereas hydrides of yttrium and erbium are extremely stable with dissociation pressures less than 100 Pa even at 1000°C. Titanium and zirconium hydrides would be suitable for recoverable storage, whereas the hydrides of erbium and yttrium would be more suited for non-recovery of the tritium. Because uranium hydride is pyrophoric in air, it is less suitable for long-term tritium storage.

For all practical purposes there is no tritium partial pressure above these compounds at temperatures expected for storage, $\leq 100^\circ\text{C}$. This means that rupture of the storage container would not result in tritium release. Another advantage of metal tritides is their large capacity for tritium. The density of hydrogen in some metal hydrides is similar to or greater than that of liquid hydrogen [51].

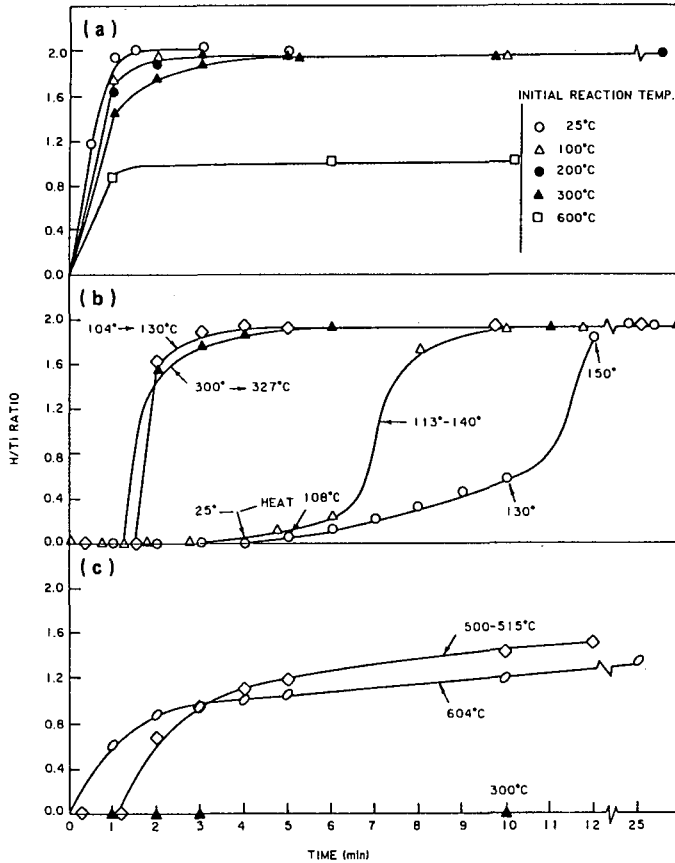


FIG. 5. (a) Formation of titanium hydride from titanium sponge;
 (b) formation of titanium hydride from titanium chips (vacuum-annealed at 1000°C);
 (c) formation of titanium hydride from titanium plate (vacuum-annealed at 1000°C).

The recovery of tritium from tritides by heating (450° to 600°C for Ti and Zr) is not as convenient as simply opening a valve on a gas cylinder, but it does provide a simple method for separating the decay product (^3He) from the tritium. Helium-3 has a significant commercial value.

The development of immobilization and packaging technology for concentrated tritium was studied by Atomic Energy of Canada Ltd as a contribution to the IAEA Co-Ordinated Research Programme on Handling Tritium-Bearing Effluents and Wastes. Some of this work has been published [52, 53] and a summary of it is reported here. Some work in this area has also been reported by Ontario Hydro [54].

For the direct hydriding reaction to proceed quickly the metal surface must be clean and the hydrogen must be pure. The work has been done with titanium and zirconium in the form of metal sponge, turnings and rod or plate. The metal surface is cleaned by being heated in vacuum (vacuum-annealing) for a period of time to dissolve the surface oxide, then cooled to the desired reaction temperature. The hydrogen is purified either by being passed through a hot palladium-silver alloy membrane or by absorption/desorption on a uranium metal bed.

Zirconium and titanium have been hydrided to different hydrogen:metal ratios under various reaction conditions. The rate of formation of titanium hydride from titanium sponge, chips and plate is illustrated in Fig.5. For each of the metal forms, the metal was vacuum-annealed at 1000°C for a period of one-half to two hours. The choice of 1000°C was arbitrary in these initial experiments. Figure 5 shows the effect of the initial reaction temperature on the formation of titanium hydride from 1–2 g samples of titanium sponge. The reaction rate is fast with the reactions complete in less than 5 min, even with an initial reaction temperature as low as 25°C. The reaction temperatures quoted are initial ones because the reaction is exothermic and the temperature increases as the reaction proceeds. The reaction at 600°C is limited to a hydrogen:metal ratio of 0.9 because of the pressure/temperature/composition relationship for the titanium-hydrogen system. All reactions were done using initial hydrogen pressures of ~100 kPa for two reasons: the first was that the apparatus was glass, and the second was that this pressure was adequate to process the expected quantity of tritium from a recovery plant.

The reaction rate of titanium chips or plate is slow compared with that of the sponge. At an initial reaction temperature of 25°C the chips did not react, but on heating, the reaction started at ~100°C and proceeded quickly above 130°C, as shown in Fig.5. When a sample was initially heated to 100°C before the hydrogen was admitted, a 5 min induction period was noted before any reaction was observed. A previously hydrided sample reacts much faster on the second hydriding because of the increased surface area resulting from the hydriding-dehydriding procedure. For a fast reaction of titanium chips or turnings an initial reaction temperature of ~300°C is required for the first hydriding. Temperatures of 500–600°C are required for titanium plate or bars. An increase in the initial reaction temperature of the blocks results in shorter induction periods and a faster initial reaction, but the higher temperatures limit the reaction to a hydrogen:metal ratio less than 2 because of the pressure/temperature/composition relationship for the system.

The rate of the hydride formation reaction at various reaction temperatures depends on the surface area of the sample, as might be expected. Sponge samples with a high surface-area-to-volume ratio react more quickly at a lower temperature than the turnings and bars. Because of the bulk form of the turnings and

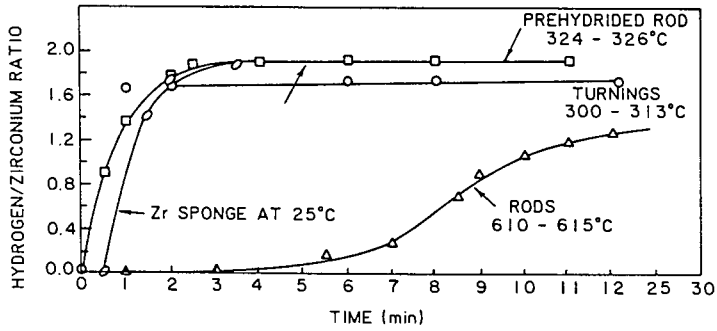


FIG.6. Formation of zirconium hydrides (vacuum-annealed at $\sim 1000^{\circ}\text{C}$).

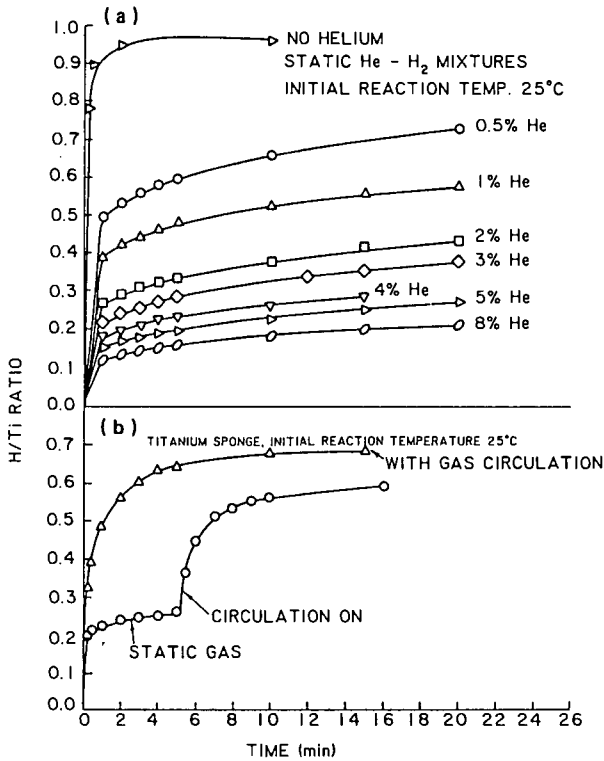


FIG.7. (a) Effect of helium on formation of titanium hydride from titanium sponge;
 (b) effect of recirculation of gas.

bars, diffusion of the hydrogen into the metal is believed to be the rate-controlling step [55] in the reaction and hence higher temperatures are required. The distance that the hydrogen must diffuse in the sponge is much smaller than that for the bulk samples because of the large surface area and porous nature of the sponge. The amount of hydrogen diffusing into a metal cylinder depends inversely on the square of the distance [56] and hence a more complete penetration of hydrogen at a particular time and temperature (i.e. a faster hydriding rate) is noted for sponge compared with that for the bulk samples. Similar results were observed with various zirconium samples, as shown in Fig.6.

The minimum annealing temperature required for rapid hydriding of titanium sponge was determined to be $\sim 400^{\circ}\text{C}$. Annealing at 300°C resulted in a negligible hydriding rate at 25°C , whereas annealing at temperatures of $400\text{--}1000^{\circ}\text{C}$ resulted in fast reactions at 25°C . Temperatures between 400 and 500°C are sufficient to dissolve the surface oxides into the bulk metal [57].

Hydriding reactions using deuterium with and without trace quantities of tritium showed equal rates of reaction, within experimental scatter, to those observed with hydrogen, thus implying that there is not a large kinetic isotopic effect.

The major difference in the chemistry with tritium compared with hydrogen or deuterium is the effect of ^3He from tritium decay. This helium is known to inhibit the hydriding reaction [58]. To simulate this effect, samples of titanium sponge were hydrided with hydrogen-containing helium, using the standard hydriding procedure. The results are shown in Fig.7. In the presence of helium there is an initial rapid absorption of hydrogen followed by a very much slower rate of reaction. With as little as 0.5% He, only half of the hydrogen is reacted quickly; the remainder reacts at a very slow rate. This effect is thought to be the result of a blanketing effect of the metal surface by the helium, preventing access to the surface by the hydrogen. To reduce this blanketing effect the procedure and apparatus were modified to allow circulation of the gas over the metal surface. This greatly improved the rate of reaction so that complete reaction of the hydrogen in a mixture containing initially 6% He occurred in about 10 minutes.

The possibility that the observed effect was due to oxygen as an impurity in the helium had been suggested [59]. The effect of oxygen and helium impurities in the hydrogen was studied in both static and dynamic (circulation of the gas over the metal) experiments and the results are summarized in Fig.8. These results clearly show that the reduction in the hydriding rate observed in static reactions is due to helium and that oxygen concentrations up to $910\ \mu\text{L/L}$ have little effect.

The hydride property of most interest for tritium storage is stability at expected storage and accident conditions. The compounds should be unreactive in air and resistant to leaching of the tritium out of the sample in water.

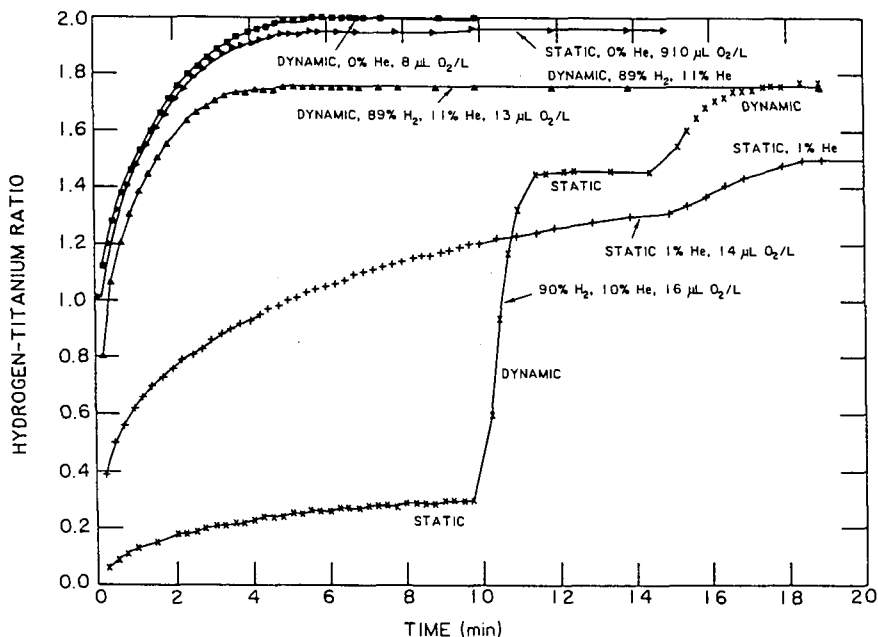


FIG.8. Hydriding reactions of titanium sponge effect of oxygen and helium.

None of the hydrides prepared are pyrophoric in air at room temperature. The reactivity of these hydrides at elevated temperatures has been investigated qualitatively by heating them on a hot stainless steel plate in air and observing the temperature at which they start to spark and/or burn. These observations showed that the samples do not burn in air, even at elevated temperatures, unless they are very finely divided. Of the various zirconium hydride samples, the lowest ignition temperature noted was 450°C for a fine powder of ZrH₂. Sponge samples of zirconium metal and hydride did not react until dropped on a hot surface of 560°C; when heated from 25°C to 800°C this material did not burn but rather showed a gradual colour change as it oxidized. Samples of titanium hydride prepared from sponge did not burn at any temperature up to 800°C. Slow changes in colour indicated a transformation of the hydride to the various oxides of titanium.

These observations are consistent with those summarized in the literature by Blackledge [60], which include an ignition temperature of 430°C for a finely divided powder of ZrH₂ suspended in air. The conclusion from these qualitative tests is that metal tritides prepared as described previously from sponge metals will not burn in air at expected storage conditions.

The leaching of tritium from samples of zirconium and titanium deuterides containing trace quantities of tritium has been observed in de-ionized water and

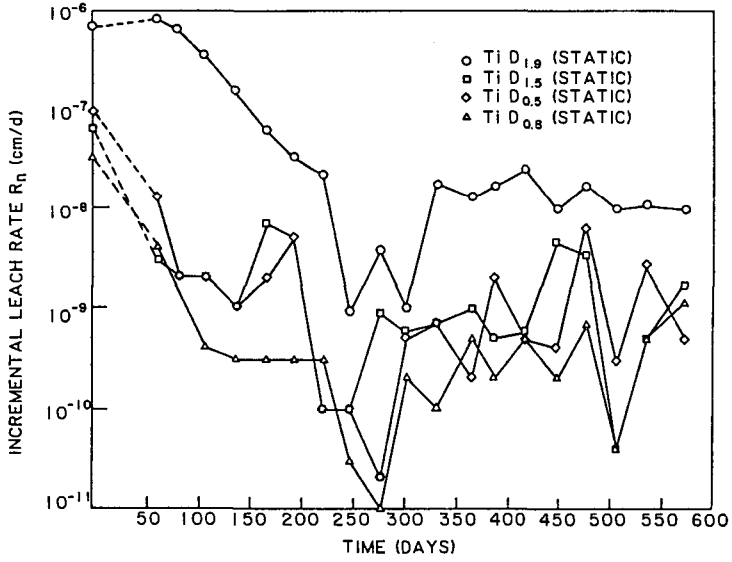


FIG. 9. Incremental leach rate versus time for titanium sponge samples.

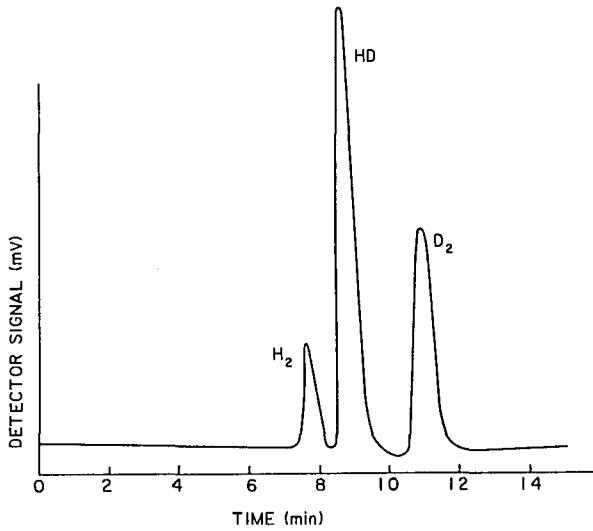


FIG. 10. Separation of H_2 , HD, D_2 on alumina column coated with ferric hydroxide (80–100 mesh, $3\text{ m} \times 1\text{ mm}$), 77 K, helium flow 98 mL/min.

various salt solutions for approximately 600 days [61]. In the leach test procedure, the IAEA standard leach test method [43] was followed as closely as possible.

The initial incremental leach rate (R_n), calculated using geometric surface area, ranged from 10^{-6} to 10^{-9} cm/d for the various zirconium and titanium sponge samples. These rates stabilized to 10^{-8} to 10^{-10} cm/d over the duration of the test period. The leach rate (cm/d) for the static testing of titanium sponge samples is shown in Fig.9. Although the hydrogen:metal ratio varied from 0.5 to 1.9, the leach rates are very similar. The cyclic behaviour shown is typical of that observed in all the data.

Samples of hydrided metal rods (approximately 0.6 cm dia.) had a leach rate which ranged from 10^{-10} to 10^{-11} cm/d at the end of the test period.

Cumulative fractional releases have also been calculated for the various tritiated samples. The fractional release (total amount of activity leached/total initial amount of activity) is less than 0.05% over 600 d.

The leach test data obtained from tritiated zirconium- and titanium-hydride sponge samples indicate that these metal hydrides are stable compounds and suitable for the immobilization of recovered tritium.

4.2.2.3. *Isotopic analysis of hydrogen*

When packaging tritium it is necessary to know the amount of tritium put in each container. To do this, the quantity of gas is measured by conventional pressure-volume-temperature measurements and the gas analysed for the fraction of tritium present. Three methods are being considered: gas chromatography, mass spectrometry and ion chambers. Preliminary evaluation of gas chromatography using the method of Genty and Schott [62] has shown that this method is feasible and the separation of hydrogen and deuterium isotopes on a 3 m ferric hydroxide treated alumina column at 77 K was achieved. This is shown in Fig.10. However, there has been a problem with stability of the column and deterioration of the resolution with time. A small quadrupole residual gas analyser has been installed and shown to provide adequate resolution for H_2 , HD and D_2 , and on the basis of work reported in the literature [63] is expected to be adequate for DT and T_2 . An ion chamber similar to the one that has been used successfully elsewhere [64] has been built but not yet evaluated.

4.2.2.4. *Packaging metal tritides*

A conceptual design of a primary container and a shipping package has been made to contain 0.5 MCi (19 PBq) of tritium as the metal tritide [65]. Schematic diagrams of the primary vessel and the transportation package are shown in Fig.11.

The primary vessel is a 6 L stainless steel container designed to contain the helium generated by the complete decay of the tritium. This vessel has been

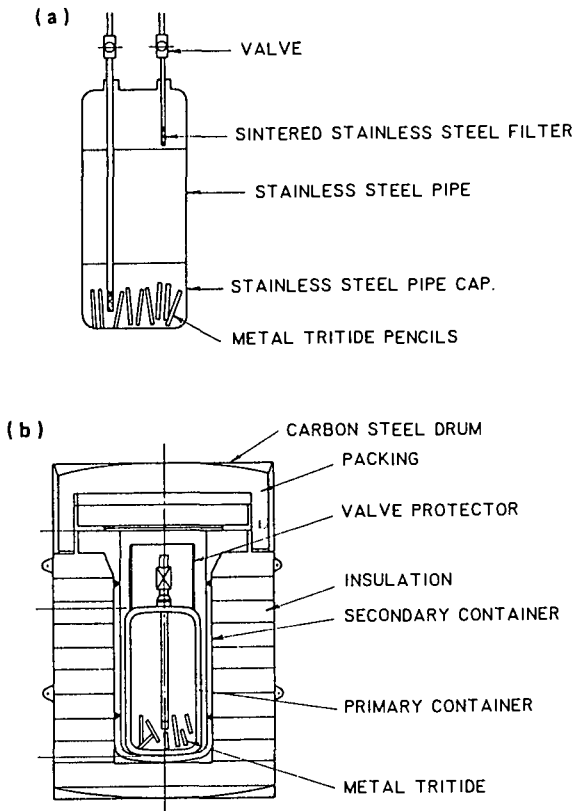


FIG. 11. (a) Conceptual design for metal tritide container;
 (b) conceptual design of a tritide transportation package.

designed to double as the reactor vessel in which the metal tritide is prepared and for this reason it is equipped with two valves to permit circulation of the gas during the hydriding procedure. To prevent escape of fine particles of the metal tritide that may be produced during the hydriding or subsequent decay of the tritium, the inlet and exit of the vessel are protected by sintered steel filters. Tests with a prototype primary vessel of this design have shown that the hydriding reaction can conveniently be carried out in this vessel.

For transportation it is expected that the primary container will be placed in a second stainless steel container with a flange closure and this two-container assembly will then be placed in a suitably sized drum packed with insulation to provide protection from heat in the event of a fire [65]. A similar package, but without the secondary container, has been designed by Ontario Hydro. Prototype transportation packages have been fabricated and are undergoing testing to provide the data necessary for licensing as type B packages.

Extensive evaluation of applicability of austenitic stainless steel for the containment of tritium has been carried out by Ells et al. [46–48]. They have shown for type 316L stainless steel at ambient storage conditions that the permeation of tritium into the vessel wall and subsequent decay of the helium will not jeopardize the integrity of the vessel. It was concluded that there would be negligible permeation of tritium (whether stored as a gas or a metal tritide) through the walls of a 6 mm, 316L stainless steel wall at ≤ 348 K. Even in the case of tritium gas at 1 MPa and 573 K for 12 h, the release of $<10^{-12}$ Ci was predicted.

Metal hydrides, while stable solids, must be packaged to provide multiple barriers to release and to provide convenience in handling. NUKEM, in the Federal Republic of Germany, uses a high-grade steel container for transportation of up to 1000 Ci of tritium as uranium tritide [66]. The steel vessel is equipped with an all-metal valve and is placed in a second container with the interspace filled with argon. The inner container is equipped with a heater to recover the tritium. In the USA, similar double-walled containers are used for shipping tritium as uranium tritide.

5. STORAGE AND DISPOSAL

5.1. GENERAL OPTIONS

Many alternatives for storage and discharge/disposal of tritium-bearing wastes have been reported. Any decision in favour of one or the other must take into account site-specific data. These data must include all parameters affecting possible pathways of the radionuclide to man, e.g. demography, meteorology, geology and hydrology, as well as the physical and chemical form in which tritium may be released. Tritium is normally released to the environment in liquid or gaseous form. The fate of the chemical form of the released tritium depends on environmental conditions.

Most of the tritiated water released will be stable and will reach man in this chemical form after isotopic dilution with environmental water. The radiological effects of HTO on man are relatively well known. According to the data of the ICRP [67, 68], tritiated water is assumed to be uniformly distributed among all soft tissue of the human body.

With the assumption that there is no relevant oxidation of HT to HTO in body tissue, the dose rate from gaseous tritium, HT, is expected to be about four orders of magnitude lower when compared with the dose rate from aqueous

tritium, HTO. However, recent results indicate that if tritium released as hydrogen is trapped in the soil there may be a rapid oxidation by bacteria in soil [69, 70], thus leading to an increased uptake of HTO by plants, which would again result in an increased dose rate to man in the vicinity of the point of emission. However, this effect must be investigated further.

Depending on environmental conditions, some of the released tritium might be used by hydrogen-utilizing bacteria [71] and converted to organic compounds. Decomposition of organically bound tritium might also produce a variety of organic tritium compounds which behave in the environment according to their chemical nature.

The ICRP has pointed out that the organic compounds of tritium might differ considerably in their behaviour from that of tritiated water, although this has not yet been adequately studied. Specific values of the annual limit on intake (ALI) for various chemical forms have not been given in Ref. [67], but the value for tritiated thymidine might be as much as 50 times smaller than that for tritiated water. The ICRP is keeping this matter under review.

5.2. ALTERNATIVES

Methods of storing and disposing of tritium have been discussed in the literature [1, 5, 15, 72]. Recovery and concentration plants at HWRs and FRPs generally produce tritium in hydrogen form (e.g. T_2), so this is the likely starting material for storage or disposal. Concentrated tritium in water form also arises, particularly from waste recovery operations in tritium-handling facilities. Other tritium-containing materials may also be produced but are more likely as by-products of tritium handling, and they would be expected to be substantially smaller in quantity.

Reprocessing plants produce two main tritium-bearing waste streams (see Section 2.2): the cladding waste where tritium can be found in the form of hydride ZrT_x , and an aqueous waste stream with low tritium concentration (≈ 100 Ci/m³). Methods for disposal of both waste streams are required.

5.2.1. Wastes from heavy water reactors

According to the discussion in preceding chapters, intermediate storage may be required for concentrated tritium from HWRs, either for disposal or for further use. For disposal purposes, the radionuclide is to be stored until radioactive decay has reduced the activity to a reasonable level. Each century gives a reduction by a factor of about 275. From a complete tritium-handling scheme a storage period of about one century was deemed sufficient [5].

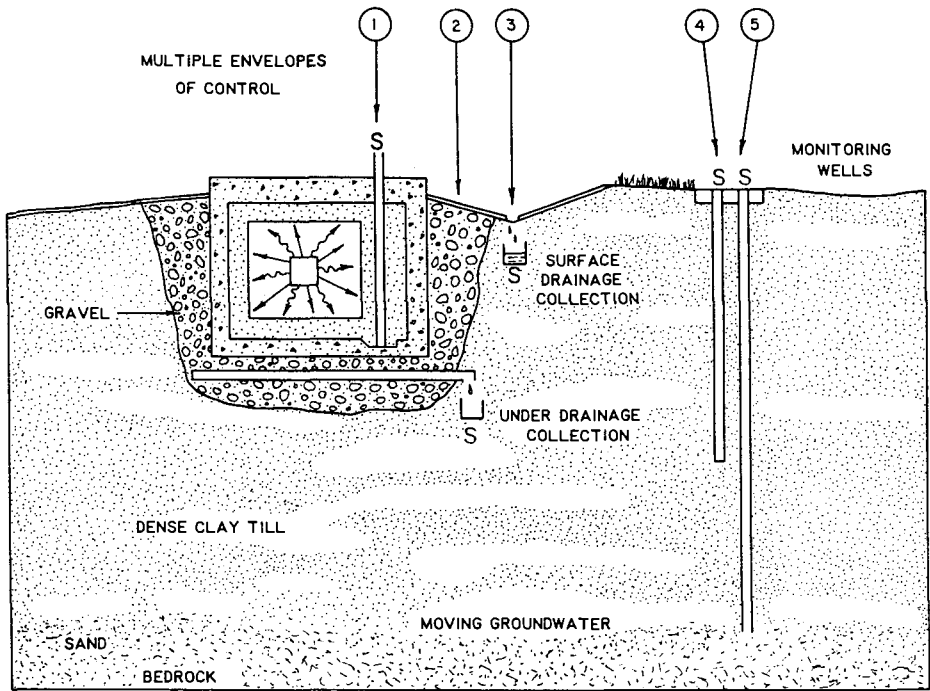


FIG.12. Schematic view of concrete trench.

In principle, concentrated tritium can be stored as a liquid or a gas or in immobilized form, with each technique having its own advantages and disadvantages. The derived air concentration value for tritiated hydrogen is 2×10^4 times higher than for aqueous tritium [68], implying that the radiotoxicity of the water form is several orders of magnitude larger than that of tritiated hydrogen. It is therefore preferable to store concentrated tritium in the non-aqueous form if possible.

An adequate scheme for the fixation of enriched tritium gas prior to storage/disposal has been designed in Canada (Section 4) [29, 52, 53, 54, 73]. The concept includes preparation of tritides of a suitable metal (e.g. titanium or zirconium), a primary stainless steel container, and a transportation package meeting the IAEA regulations for type B packages.

Ontario Hydro presently operates a radioactive waste storage site [74] with four types of storage structures in use and under construction. These four types are concrete trenches (shallow, in-ground, reinforced structures), concrete tile holes (vertical tile facilities), quadricells (above-ground facilities), and a low-level storage building (above-ground, pre-stressed, concrete superstructure).

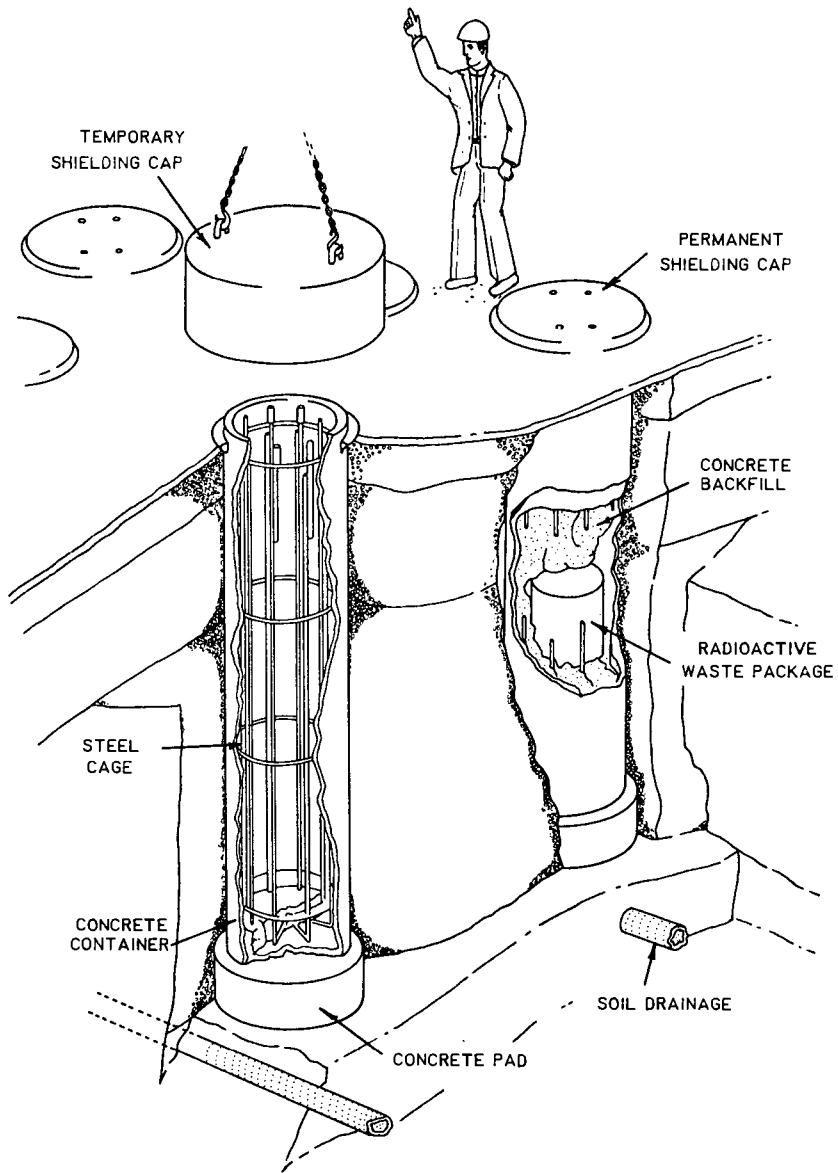


FIG.13. Schematic view of tile hole.

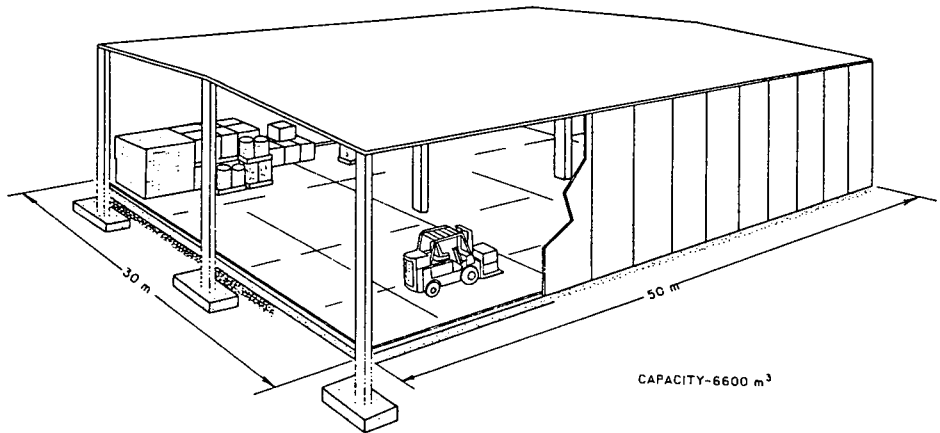


FIG.14. Perspective view of low-level storage building.

Figures 12–14 show schematic views of these structures. Preliminary evaluation of these existing facilities indicates that they would be suitable for storage of concentrated, immobilized tritium [73]. A facility designed specifically for the storage of concentrated and immobilized tritium will be used by Ontario Hydro.

5.2.2. Fuel reprocessing plant wastes

As stated in Section 2.2 in more detail, reprocessing plants produce two main tritium-bearing waste streams: namely, the cladding wastes and tritiated water.

Tritiated Zircaloy cladding can either be compressed for volume reduction or packaged as is in 200 L drums and fixed with cement. Both sheath activation products and associated fuel particles contribute a hazard that must be taken into account in handling the cladding. About 15 m^3 cladding wastes per 1 GW(e)-a are produced. In the classification scheme being developed in the Federal Republic of Germany [75] these are heat-producing, medium-level wastes which can be disposed of in geological repositories using a container meeting type B requirements.

Various alternatives for storage and discharge/disposal of tritiated waste water have been developed. For the following discussion, data from Table VIII will be assumed to be in agreement with Ref. [12]. Minor, but not negligible, contamination of the tritiated waste water with fission products, as well as with actinides, cannot be excluded; the actual figures depend on the specific waste water treatment system in the reprocessing plant.

TABLE VIII. ASSUMED DATA FOR DESCRIPTION OF TRITIATED WASTE WATER MANAGEMENT ALTERNATIVES

Reprocessing capacity ^a	(tHM/a)	1400
T-inventory of spent fuel elements	(MCi/a)	1
T-inventory of cladding	(MCi/a)	0.6
T-inventory of tritiated water	(MCi/a)	0.35
Volume of tritiated water ^b	(m ³ /a)	3000
T-activity of tritiated water	(Ci/m ³)	≈120
β/γ-activity of tritiated water	(Ci/m ³)	≤0.1
α-activity of tritiated water	(mCi/m ³)	≤0.3

^a Corresponding to 50 GW(e) capacity installed.

^b Recycling, T-scrubbing and separate acid recovery assumed.

Figure 15 summarizes various alternatives for the management of tritiated aqueous wastes. Using a conventional Purex flowsheet without recycling to minimize its volume, direct discharge into the sea and deep-well injection are suitable procedures.

Direct discharge to the sea uses the enormous isotopic dilution effect, thus avoiding potential hazards to operators and potential danger of concentrated tritium release to the environment. Discharge to the sea is being used in the United Kingdom (e.g. Windscale [76]), in France (La Hague [77]), and in Japan (Tokai-mura [78]) to dispose of the bulk of tritium in the fuel. However, in several countries there are strong pressures against this practice.

Discharge to the atmosphere in aqueous form may be another disposal alternative for tritiated effluents, if site-specific data allow for it. At present several tens of thousands of curies of tritium per year are being discharged to the atmosphere, e.g. at Windscale [79], and at the Savannah River Plant [80]. India uses the sun-evaporation technique to discharge tritiated water to the atmosphere.

At inland sites in densely populated areas, and with the growth of the nuclear industry, it may become unacceptable to discharge tritiated aqueous effluents directly to the atmosphere or to surface waters because of both radiological aspects and shrinking public acceptance. This is supported by studies such as that of UNSCEAR [71], indicating that 50% of the collective dose of the world's population results from global distribution of volatile radionuclides such as tritium, even though in absolute terms these doses are small compared with natural background radiation.

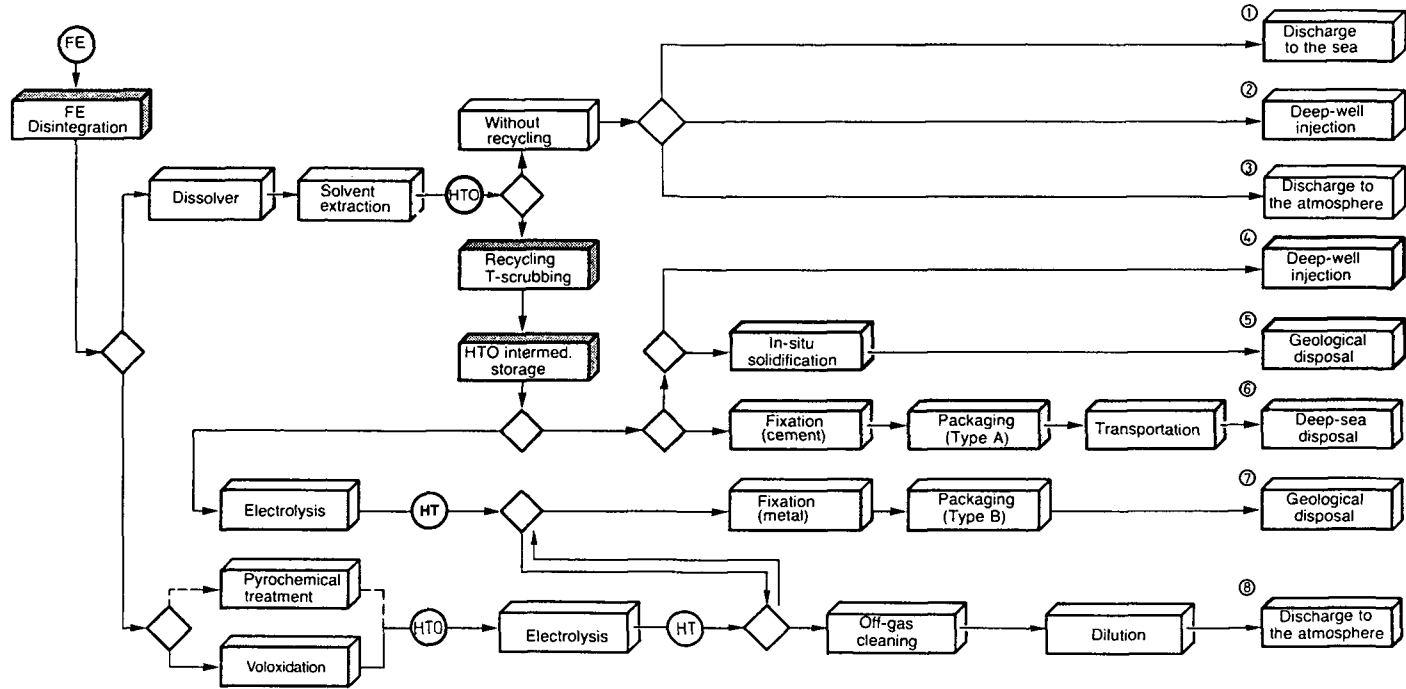


FIG.15. Tritium – waste management alternatives.

Using the dosimetry model of ICRP Publication No. 30 and site-specific data from a plant in the Federal Republic of Germany, the annual release of 0.4 MCi of tritium (which is all the tritium not bound in the Zircaloy cladding) would result in an effective dose equivalent rate of about 1 mrem/a to the most highly exposed individuals in the vicinity of the plant [81].

To estimate the maximum dose rate from a global distribution of a representative mixture of reprocessing plants, it has been assumed that 20 of these commercial-size reprocessing plants release 8 MCi/a tritium into the environment over 10 000 years. The resulting dose rate to an individual of the world's population after global distribution of the tritium would be less than 1 μ rem/a.

These results show that the maximum radiation dose is very much below the dose limit recommended by the ICRP (which is 500 mrem/a) and that the globally distributed exposure of future generations from a well established nuclear industry will remain very low indeed, even without taking measures of retaining tritium. However, according to the ALARA principle [82], doses should be kept as far below this dose limit as is reasonably achievable, taking into account social and economic considerations.

For a modified Purex flowsheet with reduced volume of tritiated waste water, this water can be injected into deep wells, solidified with cement in situ in a cavern which is not man-operated, or fixed with cement and dumped into the sea.

A totally different treatment route foresees conversion of the tritiated water to HT (by electrolysis), which can be fixed in a metal matrix, packaged and disposed of in a geological formation, or directly discharged to the atmosphere. Before electrolysis, an aqueous stream enriched in tritium can be produced by introducing a new head-end procedure in reprocessing: namely, voloxidation or pyrochemical treatment of the fuel before dissolution.

These alternatives are described in more detail in the following subsections.

5.2.2.1. *Deep-well injection* [12, 83]

Figure 16 shows a typical disposal well design. Liquid waste is injected through a deep borehole into a receiving stratum which may be located at a depth of 1000 m or more. Certain properties of the receiving stratum such as porosity, absence of faults (especially faults with a vertical orientation), and a capacity in excess of the expected volume of waste to be injected are required. Sandstone and limestone are typical types of rock suitable as the receiving stratum.

The presence of confining strata bounding the receiving stratum on top and bottom is an essential part of the required geology. They must possess integrity and thickness and be impermeable to water. Layers of clay and shale fulfil these requirements.

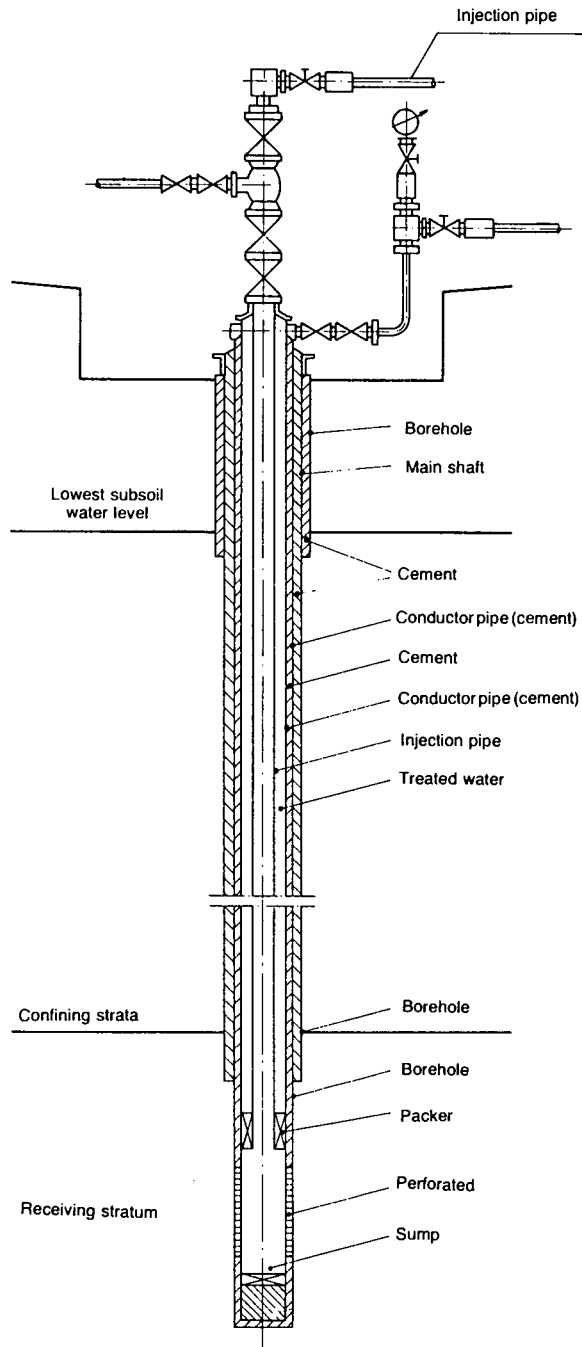


FIG.16. Typical disposal well design.

The liquid wastes (which should be compatible with the receiving rock matrices) are injected into the receiving stratum through a pipe, which is surrounded by one or more pipes of larger diameter. The annular gaps are filled with liquid (pressure compensation and/or leak detection) and with cement. Near the surface, adjacent fresh-water-bearing strata are protected additionally by another cement-sheathed pipe.

The disposal of liquid wastes by injection into deep wells was first practised with oil field brines from crude oil production. Injection of industrial wastes and municipal sewage followed.

Deep-well injection of liquid radioactive waste has been used in the USSR to dispose of low- and medium-level wastes. Between 1963 and 1970 about 10^6 m³ of liquid waste was injected with a flow rate of about 400 m³ per day [84]. For comparison, typical industrial flow rates range between 250 and 4000 m³ per day.

In the Federal Republic of Germany, an experimental demonstration of the injection of tritiated liquids was scheduled for the late 1970s at the Karlsruhe Nuclear Research Centre using a depleted oil field. However, because the field is again being used for oil production the experiment was cancelled. Investigation for another suitable site has begun.

In conclusion, there is an abundance of industrial experience and technology available which is applicable to the injection of tritiated liquid waste. The process is expected to have low specific costs, a relatively low radiation exposure to operating personnel, and a low release to the environment even in the case of accidents. It will be necessary to provide evidence that the escape of radionuclides from the storage horizon can be ruled out with reasonable certainty.

5.2.2.2. *In situ solidification*

The concept of in situ solidification has been investigated at the Karlsruhe Nuclear Research Centre in the Federal Republic of Germany [85]; Fig. 17 is a schematic drawing. The main feature of the concept is an in situ solidification of preconditioned low- and medium-level waste granules, together with tritiated water in non-man-operated salt caverns, thus avoiding shielding and container material. The steps in the process are:

- (1) Prefabrication of granules at the waste producer's site from medium- and low-level waste arisings and cement;
- (2) Transportation of the cured granules in shielded containers to the final repository;
- (3) Mixing of granules (60 vol. %) at the repository site with cement grout (40 vol. %) using tritiated waste water;
- (4) Transport by gravity of the mixture into a 75 000 m³ salt cavern at a depth of about 1000 m through a relatively thin pipe;

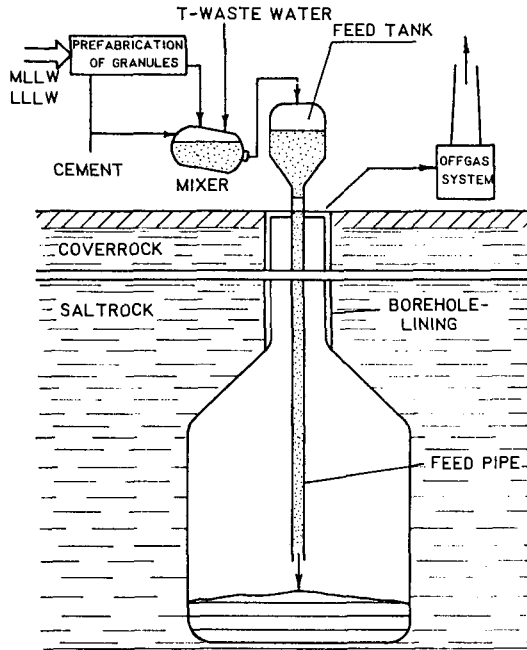


FIG.17. Concept of in situ solidification of radioactive wastes.

- (5) In situ solidification of the concrete in layers, each of which represents one filling campaign, and then finally backfilling of the open cavern space with inactive material.

Figure 18 illustrates the underground cavern system [12]; three different stages are shown: (a) under construction, (b) in operation, and (c) backfilled and sealed. A 75 000 m³ cavern would serve the MLW/LLW and tritiated waste arisings of a five-year operation of a 1400 t/a reprocessing plant. Caverns would be constructed either by solution mining or by drilling and blasting.

To demonstrate the technique, three small-scale caverns with a volume of 10 m³ each have been mined and filled with inactive simulated waste in the Asse salt dome in the Federal Republic of Germany. A large-scale experiment with inactive material is scheduled to start in 1984.

The conclusion is that the in situ concept offers the possibility of disposing of medium- and low-level waste together with tritiated liquor in a very simple configuration. Compared with the technique of drum disposal in a man-operated mine, as it is currently demonstrated in the Asse salt dome, the in situ technique promises low cost and a considerable reduction in doses to personnel.

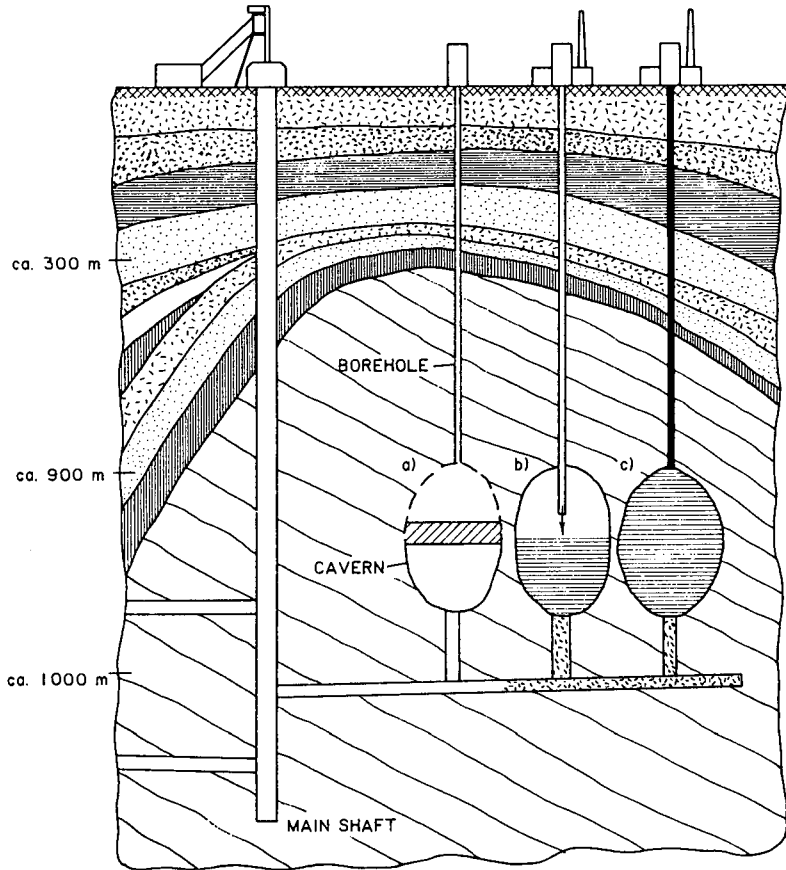


FIG.18. *In situ cavern system.*

However, the technique is relatively complicated and not all of its components are yet developed. Further R&D work is required.

5.2.2.3. *Deep-sea disposal*

A concept has been developed at the Jülich Nuclear Research Centre, Federal Republic of Germany, to dispose of solidified tritiated waste water in the deep sea. The scheme is illustrated in Fig. 19. Work has been carried out within the scope of a study entitled "Management of Tritiated Aqueous Waste – Technology and Safety" [12], which deals especially with alternatives 4, 5 and 6 from Fig. 15.

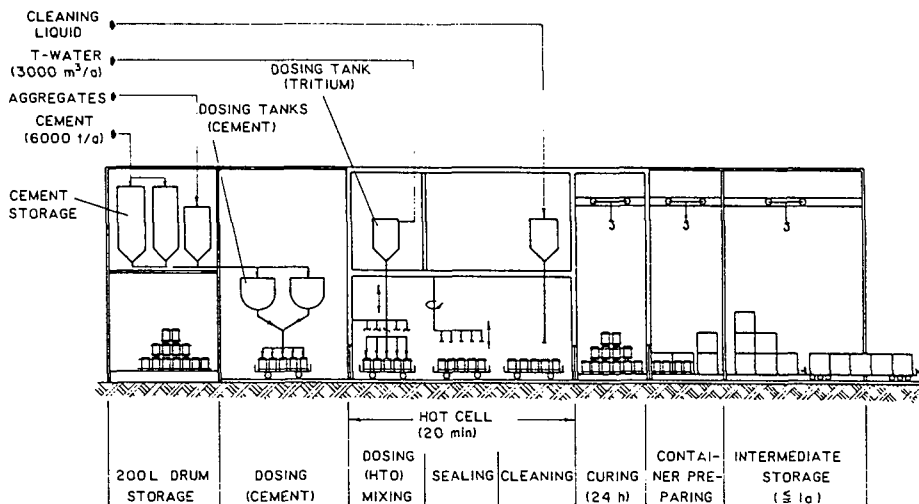


FIG.19. Deep-sea disposal of solidified tritiated water.

The cement and the aggregates are fed from dosing tanks into each of five 200 L drums in batches of 244 kg. Five drums with cement are transported to their respective positions in the hot cell on a special rail carriage where 122 L of tritiated water are proportioned into each drum and subsequently mixed with the cement using a planetary stirrer to form homogeneous cement grouts.

The drums are sealed, checked for contamination, decontaminated if necessary, and transported to the curing zone. After curing, 13 drums are loaded into a railway freight container and stored at an intermediate storage zone for not more than 12 months. The storage facility has a capacity of 1900 containers, thus providing the annual production of 24 700 drums from a 1400 t/a reprocessing plant. Railway transport to the harbour and sea transport (without containers) to the dumping site would take place once a year.

According to the data from Table VIII, the activity content of one 200 L drum would be about 13 Ci of tritium, less than 13 mCi β/γ -activity and less than 36 μ Ci α -activity. The dose rate on the surface of a drum would be of the order of 10^{-2} to 10^{-3} mSv/h. The drum itself meets the requirements for the type A package.

Transportation and dumping would take place in conformance with the international provisions applicable, i.e. the IAEA Transport Regulations [86, 87] and the London Convention [88], together with the NEA Guidelines [89] and IAEA Definitions [90].

The special advantages of the concept are its simplicity and the fact that all the components are state of the art. In addition, the deep sea ensures a safe isolation of tritium from the biosphere for the limited time period required. A disadvantage is the relatively high expenditure for packaging and transport of the large number of packages, resulting in relatively high specific costs.

However, according to the London Convention, the dumping of matter in the deep sea is only permitted if such matter cannot be disposed of on land without impairing the welfare of the general public or if such disposal would involve a disproportionately high expenditure. This means that dumping of solidified tritiated water in the deep sea cannot be applied unless proof has been furnished to the effect that land-based alternatives are not practicable, from a technical, economic, ecological or radiological point of view.

5.2.2.4. Fixation in metal hydrides and disposal

A high degree of immobilization would be required if the waste were highly enriched in tritium. Enrichment processes considered to be best suited for commercial operation are described in Section 3 of this report.

The gaseous hydrogen product may be fixed by a reaction with a suitable metal (e.g. titanium, zirconium) to form a metal hydride. Section 4 outlines this topic. About 15 t of Zr metal, or 2.4 m³, are required to completely bind the entire hydrogen gas as ZrH₂, which is contained in the waste water volume reduced to 3 m³ HTO/a. This method of incorporating the tritium in a metal lattice is presently regarded as being the safest procedure. The leaching rates are several orders of magnitude below those measured for cement.

Because of the high specific T-activity of about 200 Ci/L Zr, a type B package is prescribed for any transportation of tritium-bearing metal hydride pieces on public traffic ways.

The highly enriched metal tritide can be stored in an intermediate storage facility or disposed of in a final repository if further use of the tritium is not envisaged. In the literature [91], subsurface shafts, concrete-lined pits, sea-bed disposal, and geological repository are assumed to be feasible.

5.2.2.5. Discharge of gaseous tritium to the atmosphere

Because tritiated hydrogen has an estimated four orders of magnitude lower radiotoxicity than tritiated water, the Jülich Nuclear Research Centre has started a study to determine if a controlled release of tritiated hydrogen could lead to a reduction of global radiation exposure from reprocessing plants [92]. Electrolyzers would be used to generate tritiated hydrogen from aqueous wastes.

The capacity required for complete conversion of tritiated water from reprocessing into its gaseous state would be less than 1000 m³ H₂/h. Adaption

of conventional electrolysis techniques to the decomposition of tritiated water requires additional development.

The results of the radiological assessment which addresses the question of whether or not the release of gaseous rather than aqueous tritium can reduce the dose rate are listed in Refs [70, 92]. Based on a modified model proposed by Murphy [93], which assumes a rather rapid re-oxidation of HT to HTO by bacteria at the surface of the soil, it was concluded that the local individual dose rate due to HT release may be only one order of magnitude lower when compared with HTO release. However, this was very preliminary work and further experimental investigation is required to obtain definitive conclusions.

6. CONCLUSIONS AND RECOMMENDATIONS

This programme was useful in bringing together two different areas of tritium technology in the nuclear establishments: i.e. the handling and disposal of very dilute tritium streams in light water reactors and fuel reprocessing plants and the recovery, concentration, conditioning, and packaging of pure tritium from heavy water reactor systems. It has been demonstrated that current management practices limit tritium effluent releases to the environment to well below the regulated values. Current research and development programmes are investigating areas of new tritium management practices, such as effluent volume reduction in reprocessing plants, tritium recovery and packaging technology and investigations of alternative technologies to be applied where current practices cannot be used.

The radiotoxicity of tritium contained in the form of hydrogen is of the order of 10 000 times smaller than that of aqueous tritium. This means that any system that converts tritiated hydrogen to tritiated water to trap tritium and prevent its release to the environment must have retention efficiency of greater than 99.99% for there to be a net benefit over releasing the tritiated hydrogen. However, there is considerable uncertainty regarding the fate of the tritiated hydrogen in the environment; it is unstable and will convert to water at some rate that is dependent on many factors that have not been clearly identified or defined. It is recommended that studies be undertaken in this area to define the factors which contribute to the oxidation of tritiated hydrogen in the environment so that reasonable estimates of the potential radiation dose can be calculated from releases of tritium in the form of hydrogen.

Processes for recovery of tritium from aqueous systems have been demonstrated and their use is being expanded, which is an effective way to limit tritium releases.

The development of new isotopic exchange catalyst technology is providing improved processes. Research, development and demonstration in this area should continue.

Conditioning of concentrated tritium as metal tritides appears to be a satisfactory method with a low probability of escape of tritium to the environment. Careful monitoring is recommended of the performance of metal tritide-containing packages that will be used at new tritium recovery plants to provide reliable data.

Conditioning of dilute aqueous tritium in cement is an effective practice, provided the cement is packaged in such a way as to prevent isotopic exchange of tritium with free moisture. It would be useful to have available a conditioning method for low-concentration aqueous tritium that was as simple and inexpensive as is cement but with better retention of tritium without dependence on additional barriers. It is recommended that further work in this area be done.

When tritium is recovered from nuclear systems such as heavy water moderators and reprocessing plants and concentrated to high levels, e.g. pure tritium, then it would be desirable to have the tritium packaged in containers of a standardized design and to have some standard criteria for storage facilities.

The quantities of tritium in fission-based nuclear power are small in comparison with those expected in nuclear fusion. It is recommended that a symposium be convened on tritium technology in nuclear facilities with the object of giving the current state of the technology and identifying what developments will be required to meet the needs of fusion.

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