Combined Heavy Water Upgrading And Detritiation For CANDU Applications

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Abstract

Integrating heavy water upgrading with detritiation in CANDU® stations has the potential to provide cost savings and simplicity in comparison to stations with separate heavy water upgrading and detritiation systems. This paper presents results of a concept study into alternative processes for managing heat transport and moderator system water quality, including a new non-cryogenic isotope separation process being developed by Special Separations Applications, Inc. (SSAI) and General Electric (GE) for tritium removal. Overview descriptions are presented for the process design and process characteristics are described.

1. Introduction

All pressurized heavy water moderated reactors (PHWR), such as current CANDU® reactors, have the inherent hazard of radioactive tritium formation resulting from neutron capture by deuterium within the moderator and heat transport systems [1]. High concentrations of tritium within the working fluids of commercial reactors pose significant radiological risks to personnel and the environment.

A CANDU® 600 type reactor nominally produces 1.75×10^6 Ci/y of tritium, with approximately 95% of the tritium formed within the moderator heavy water (D_2O). Tritium in heavy water contributes 30-50% of the annual radiation dose received by operation personnel and represents up to 20% of the radioactivity released from the reactor to the environment [2]. Tritium discharges to the environment from current PHWR power stations are up to 20 times higher than light water reactors [3].

To date, two approaches have been employed by PHWR Utility companies to reduce operational tritium concentrations, namely:

- Dilution of the tritium concentration by addition of virgin heavy water (leading to storage of tritiated heavy water) and,
- Detritiation of heavy water in a centralized facility serving multiple reactors, by means of a Tritium Removal Facility utilizing cryogenic distillation technology.

The first approach is an unsustainable mitigation. It leads to consumption of a very expensive and rare commodity (virgin heavy water) while accumulating quantities of a hazardous liability.

The use of cryogenic distillation technology for detritiation of heavy water has proven to be complicated, expensive and susceptible to low reliability, mainly due to complications associated with the cryogenic process. Recently, a new non-cryogenic isotope separation process called Trit*Ex® has been developed by Special Separations Applications Inc (SSAI) and General Electric (GE) for tritium removal. This process uses a combination of isotope separation techniques, which leads to the following:

- Simpler delivery (design and build) and operation as compared to cryogenic distillation;
- Order of magnitude lower hydrogen and tritium inventories than cryogenic distillation;
- Smaller footprint building with economics permitting installation at every CANDU® station;
- Inherently safer technology due to small flammable and radioactive inventory, low complexity, ambient temperature process and absence of liquid cryogen hazards, such as high pressures generated due to evaporation of liquid cryogen material upon system warm-up.

Within an operating PHWR, light water ingress, primarily from atmospheric moisture, contaminates (downgrades) the heavy water reducing its moderating performance. Water distillation systems, commonly referred to as heavy water upgraders (HWUs), are employed at all CANDU® reactor stations to remove this light water. The light water waste product from HWUs is low in deuterium content and even lower in tritium content, since tritium is more easily separated from light water by water distillation than deuterium. Tritium is therefore recovered together with deuterium in the current upgrader process.

The rate of generation of tritium in heavy water is proportional to the neutron flux and the time spent within the reactor core. The heavy water in the heat transport system passes through the power reactor core quickly and in relatively small quantity, whereas the heavy water within the moderator, spends much more time inside the core, and thus has much higher levels of tritium. The large differences in tritium concentration typically leads to the heavy water from the moderator and the heat transport systems being managed independently and subsequently two water distillation systems are employed in the HWU process plant.

With the new Trit*Ex® process, detritiation is simplified, making it feasible to detritiate at each PHWR. This new possibility allows novel solutions to heavy water management, with potential for significant capital, operating and decommissioning cost savings.

2. Detritiation Process Overview Description

The combination of different isotope separation techniques operating in series for the enrichment of tritium has been employed at the GE Tritium Waste Treatment and Enrichment (WTE) facility at Cardiff, UK [4]. In this application light water contaminated with tritium, generated from the oxidation of tritiated mixed organic and aqueous waste material, is detritiated using a combination of water distillation followed by thermal diffusion [5] as illustrated in Figure 1.

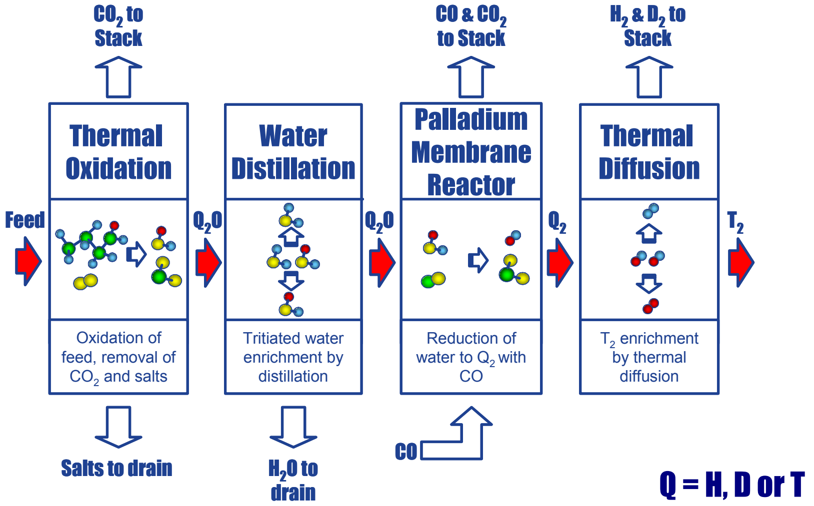


Figure 1: GE's Process for Removing Tritium from Light Water Block Diagram

For heavy water applications, water distillation has limited effectiveness due to similarity in volatility of the oxides of deuterium and tritium. At the typical water distillation temperature of 55°C, the water distillation elementary separation factor for D_2O-HDO is 1.051 compared to 1.012 for DTO-D_2O. This makes water distillation unattractive as the main technology for recovery of tritium from heavy water [6]. The novel Trit*Ex® process [7] is designed to remove tritium from heavy water by gaseous diffusion followed by thermal diffusion.

For a single CANDU® 600 reactor, approximately 25 kg/h of D_2O moderator water must be detritiated over 7,000 h/y in order to maintain the moderator tritium concentration at 10 Ci/kg. Without detritiation, the moderator tritium level will rise to a steady state value of about 95 Ci/kg. At steady state, tritium production is the same as the tritium decay rate plus losses. The initial rate of rise in moderator tritium level is 4 to 5 Ci/kg per year.

On this basis, a tritium removal system must extract about 1.75x 10^6 Ci (182g) per year of tritium. On an hourly basis, at 25 kg/h and 10 Ci/kg concentration, 250 Ci/h must be removed, which is only a tiny 0.026 g/h (1.6 std cm^3/min) of T_2 gas. The discrepancy in scale between the 25 kg/h (water basis) feed at the front-end and tiny back-end T_2 product flow, suggests the use of different technologies for front-end and back-end isotope separation. In a conventional cryogenic distillation plant, a single separation technology is used throughout, resulting in a significantly over-scaled backend. An unfortunate consequence of back-end over-scaling is that the tritium inventory in the isotope separation system is more than an order of magnitude greater than in a more scale-appropriate back-end technology. The high tritium inventory of cryogenic distillation has a large negative impact on overall safety of the process and potential dose to the public in the unlikely event of a serious release

Scale-down of cryogenic distillation is limited for reasons of column hydraulic operability. When producing 99% tritium the smallest achievable cryogenic distillation tritium inventory is about 1.2 gram, with several grams being more practical. A thermal diffusion column has an order of magnitude smaller tritium inventory and is much simpler to operate when compared to cryogenic distillation, at small tritium throughput.

The key isotope separation technologies - gaseous diffusion and thermal diffusion - used in the Trit*Ex® process are well established. The process introduces the novel concept of linking the two technologies in series which establishes major improvements and simplifications in the application of gaseous diffusion technology in particular.

As Figure 2 illustrates, the input and output species to the Trit*Ex® process is elemental hydrogen as with cryogenic distillation. As such, to detritiate heavy water, a front-end technology is required. For the process shown in Figure 2, a Liquid Phase Catalytic Exchange (LPCE) column is employed. However, other front end technologies such as Electrolysis (E), Vapor Phase Catalytic Exchange (VPCE) or Palladium Membrane Reactor (PMR) may be used, depending upon scale and application requirements. The main advantage of using LPCE is that no additional technology (i.e. recombiner) is required to convert the detritiated deuterium gas back into heavy water.

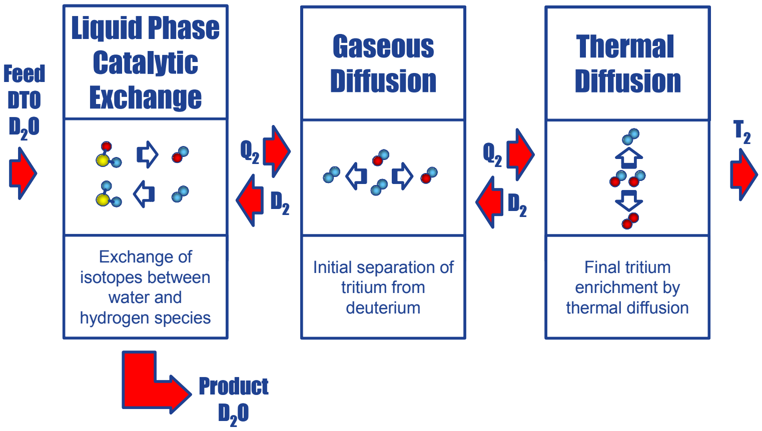


Figure 2: Trit*Ex® Process Block Diagram with LPCE Front End

3. Gaseous Diffusion

As discussed by London [8], gaseous diffusion using microporous membranes was first used to enrich ^{22}Ne. By 1936, its use had expanded to small-scale enrichment of isotopes such as ^{2}H and ^{13}C. Large-scale development occurred only from 1939 onwards for the separation of uranium isotopes using UF_6 as the working gas. Gaseous diffusion plants were built in the United Kingdom, the United States of America, China, the Soviet Union (now in Kazakhstan) and France. The majority of these have now closed or are expected to close because they are unable to compete cost-effectively with newer gas centrifuge technology, which requires much less energy to produce the same separation of heavy uranium isotopes.

The move away from gaseous diffusion is appropriate for heavy element separations, in which small separation factors and low diffusivity of heavy molecules require a large number of separation stages and large equipment. However, the converse is true for light elements, in particular for hydrogen isotopes. For lighter elements, gaseous diffusion separation factors are large – in many cases comparable to or larger than distillation separation factors. The diffusivity of light elements is also large, leading to high throughput and small equipment size.

Outside of isotope separation, gaseous diffusion using a microporous membrane has seen few applications in the chemical process industries due to the high capital cost of specialized membranes and compressors, in addition to the large number of stages required for clean separations. In the chemical process industries, membrane development has focused mostly on developing membranes with large separation factors for separating different chemical species. This research is not relevant, however, to membrane isotope separations, which use only a single chemical species.

Gaseous diffusion employs the phenomenon of molecular effusion to separate components. For a gas mixture at thermal equilibrium, the average kinetic energy of all molecules will be the same. Hence gas molecules with lower molecular weight will move at a faster speed, thereby impacting a vessel wall more frequently than heavier molecules relative to their concentration. If the vessel walls have tiny holes, so small such that only individual molecules can escape one by one (i.e. preventing bulk viscous flow) then the escaping gas will be enriched with the lighter gas. This flow of individual molecules through a porous material is called molecular effusion. The relative frequency at which different species enter the tiny holes is inversely proportional to the square root of their molecular weights; this ratio is the ideal separation factor for gaseous diffusion. Table 1 illustrates ideal separation factors for some different isotopologues of hydrogen and UF_6:

Species Pair	**Separation Factor**
DT, T_2	1.095
D_2, DT	1.118
D_2, T_2	1.225
$^{235}UF_6, ^{238}UF_6$	1.0043

Table 1: Gaseous Diffusion Separation Factors for some Hydrogen and UF_6 Isotopologue Pairs

GE and SSAI have developed a novel arrangement and operation of the gaseous diffusion technology that results in significantly fewer moving components. This advancement leads to significant capital cost and energy savings, reduced footprint and lower inventories of radioactive material.

4. Thermal Diffusion

In 1938 Clusius and Dickel [9] developed a thermal diffusion column capable of substantial degrees of isotope separation. The separation takes place (usually in gaseous form) within a long vertical tube, heated internally by a hot wire at the axis of the tube and cooled externally. The outwards heat flux sets up a small difference in composition through the thermal diffusion effect, with the lighter component concentrating closer to the hot wire. Laminar flow convection currents are also set up, with the lighter hotter fluid moving upwards, and the heavier colder fluid moving downwards as illustrated in Figure 3. The counter-current flow multiplies the composition difference, produced by thermal diffusion, making significant degrees of separation possible from the top to the bottom of the column.

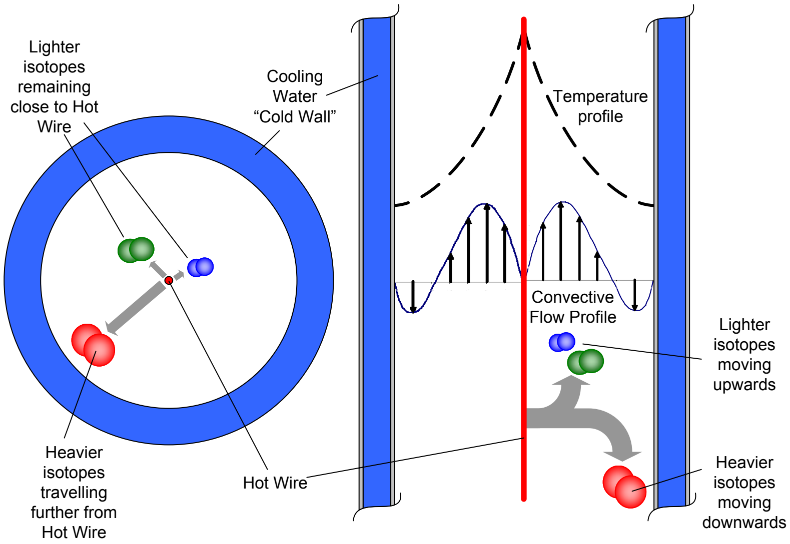


Figure 3: Thermal Diffusion Column Principle of Operation

Laminar flow is essential to a thermal diffusion column to avoid parasitic mixing that would otherwise undo the isotope separation effect. Unfortunately, the requirement for laminar flow limits the size and throughput of a single column, thus requiring many columns in parallel to achieve high throughputs. Thermal diffusion columns have had limited large-scale use over the years. As part of the Manhattan project, a liquid thermal diffusion plant [10] containing 2100 columns was used as a pre-enrichment process of ^{235}U. The plant had a limited operational life and was soon shutdown when the K-25 gaseous diffusion plant began operation due its significantly greater power consumption, as compared with gaseous diffusion.

For smaller throughputs, in which total power consumption is less significant, thermal diffusion column technology has considerable advantages over other isotope separation techniques:

- Overall simplicity of equipment, resulting in easy construction and operation
- Unrivalled reliability due to the absence of moving equipment
- Tiny separation stage height facilitating large separations in relatively small equipment

- Inherently safer technology arising from benign operating conditions and very low inventory.

Historically, thermal diffusion technology has been used within various laboratories for small-scale isotope separation. As part of the development of the Cardiff Tritium Waste Treatment and Enrichment Facility, GE has industrialized the technology, developed a computer simulation code for design and made large step improvements in operational control, secondary containment, online analysis and safety systems.

5 Trit*Ex® Tritium Removal Facility

A Trit*Ex® Tritium Removal Facility for a typical CANDU® application comprises the following major subsystems:

1. *Feed Storage System* – receives tritiated heavy water feed from the station and provides buffering.
2. *Heavy Water Degassing System* – removes dissolved gasses from the feed water.
3. *Liquid Phase Catalytic Exchange System* – detritiates heavy water by counter-current isotopic exchange with deuterium gas.
4. *Deuterium Drying System* – dries deuterium gas before feeding to the Gaseous Diffusion System.
5. *Deuterium Gas Storage System* – provides pressure control, gas buffering and gas storage during shutdown.
6. *Gaseous Diffusion System* – provides large-scale isotope separation.
7. *Palladium Membrane Reactor System* – a small system for D_2/DT gas purification and tritiated impurity detritiation before final tritium enrichment by thermal diffusion.
8. *Thermal Diffusion System* – provides final tritium enrichment by thermal diffusion to 99% tritium product quality.
9. *Tritium Immobilization System* – immobilizes tritium product in a removable 500 kCi Immobilized Tritium Container (ITC).
10. *Product Storage System* – receives detritiated water product and transfers product back to the station.

In addition to the major subsystems, there are auxiliary systems for activation of ITCs, tritium accountancy, tritium product storage, liquid dump for shutdown and maintenance, and liquid sampling.

Notably absent from the process are any cryogenic systems, thereby eliminating impurity freezing problems, which are a recurring problem with cryogenic distillation systems. In addition, the gas purification requirements of gaseous diffusion are significantly less rigorous than with cryogenic distillation system, thereby eliminating a second and complex purification step after drying. Small amounts of impurities that enter the gaseous diffusion system are continuously removed to prevent any buildup.

5.1 Trit*Ex® Building

A dedicated building can be used to house the Trit*Ex® process. This building has five main areas, as illustrated in Figure 4, a description of the main areas follows:

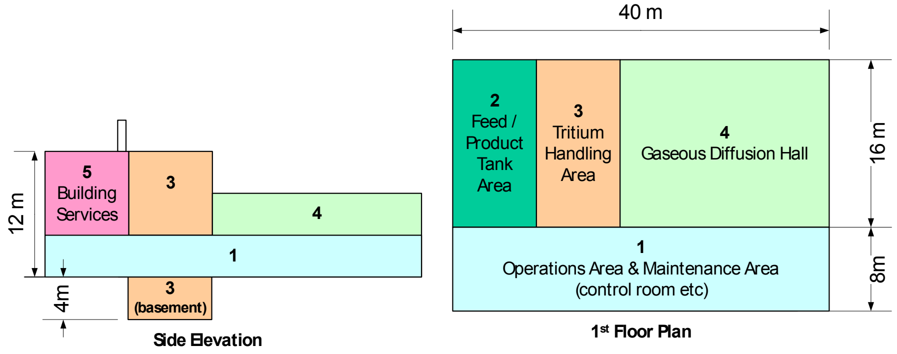


Figure 4: Conceptual Layout of Trit*Ex® Facility (based on 25 kg/h throughput)

1. *Operation and Maintenance area*
   This first floor area houses the access to the facility and the required amenities/services to support operation and maintenance of the process plant. This area includes: the local operational control room, support systems rooms (electrical switchgear rooms, control system room), personnel facilities (WC, change rooms, etc.), dedicated maintenance area including workbenches and local stores, analysis room for radioactive sample measurement and personnel monitoring and material shipping area.
2. *Feed and Product storage*
   This first floor area houses the tanks for holding the tritiated heavy water feedstock, the detritiated heavy water product and part-processed heavy water during periods of maintenance. Together with associated transfer pumps, these large tanks are located within dedicated bermed areas.
3. *Tritium Handling Area*
   This part of the facility extends from the basement to the third floor and houses the Thermal Diffusion system, Tritium Immobilization system, water/hydrogen conversion system (e.g. LPCE) and supporting systems such as ITC activation, calorimeter and the storage vault.
4. *Gaseous Diffusion Hall*
   This is the largest area in footprint and has an open two storey hall with an overhead crane used for initial installation, major maintenance work and final decommissioning. This hall houses the gaseous diffusion cascade including the compressors, membranes and associated secondary containment systems.
5. *Building Services Area*
   The Building Services Area extends over the second and third floors above the Feed and Product Storage area. Here the heating, ventilation and air conditioning systems are housed that provided the cascaded ventilation throughout the facility. The extract from the

ventilation system is discharged through a stack located on the roof the Building Services Area.

5.2 Trit*Ex® Utility and Energy requirements

The Trit*Ex® Facility is designed to run as an island, isolated as far a practicable from the PHWR station. Only non-critical, general site distributed utilities (e.g. compressed air, electricity, cooling water, etc) are connected to the facility.

The largest energy demand in a Trit*Ex® Facility is for the operation of deuterium gas compressors in the gaseous diffusion cascade. When comparing gaseous diffusion energy demand to that of cryogenic distillation (CD), the relevant point of comparison for CD is the energy required to provide refrigeration to condense saturated deuterium vapor (1.3 bara and 24.2 K typical conditions).

For a 25 kg/h throughput, assuming an LPCE front-end with a gas to liquid flow ratio of 3, and a cryogenic distillation stripping section reflux ratio of 9, the total condenser duty (not including heat ingress) is 12.1 kW. Ideal Carnot refrigerator power is 138 kW. A standard refrigerator will have approximately 33% Carnot efficiency, resulting in an energy demand of about 417 kW. Calculating the power of a comparable gaseous diffusion cascade is more complicated, since the power required is dependent on design trade-offs in compressor pumping speed, gas pre-cooling, membrane area, pressure ratio, number of compression stages, and cascade tapering. Simulation studies show that a comparable gaseous diffusion cascade will require approximately 200-250 kW of electrical power.

The energy efficiency of cryogenic distillation can be improved by heat pumping at cryogenic temperatures, but only at significant additional capital cost as well as equipment and operating complexity. It is far simpler to improve the energy efficiency of a gaseous diffusion cascade by simple measures such as chilling the gas prior to compression, optimal configuration of the gaseous diffusion cascade, and optimization of operating parameters such as pressure ratio, membrane area and cascade tapering.

Tests have been carried out at the GE Global Research Center in Niskayuna, NY during the first half of 2007 to obtain engineering data associated with the characteristics of the gaseous diffusion process for hydrogen isotope separation.

5.3 Trit*Ex® Operation Overview

This section provides an overview of a typical CANDU® tritium removal facility operation based on the Trit*Ex® process. Tritiated heavy water is pumped to the Trit*Ex® Facility in batch operations from the PHWR station's heavy water management system. The heavy water is then fed to a degassing column for D_2O steam stripping of dissolved gases before entering the water-to-hydrogen conversion step (e.g. LPCE, electrolysis, VPCE, etc.). After drying, the hydrogen species enter the gaseous diffusion cascade where the major volume reduction step is performed; here the tritium is concentrated. Following a further purification stage the tiny tritium rich flow enters the thermal diffusion (TD) system. The TD column for the Trit*Ex® process is shorter than the system installed at GE's WTE Facility, since only one column is required in comparison to the two installed at Cardiff. The TD system has the capacity to produce T_2 product from 70% to 99% depending upon end-user preference. The T_2 product is continuously drawn from the bottom of the column, into an Immobilized Tritium Container (ITC). Based on 25 kg/h throughput at steady state, approximately 4 ITCs are filled per year. The deuterium from the top of the TD column is recycled back to the gaseous diffusion cascade. Detritiated heavy water is stored in the product tanks. (LPCE and VPCE front-ends do not require a recombiner, whereas electrolysis does.) From here, the detritiated heavy water product is pumped back to the station's heavy water systems in batches. Facilities are provided for safely holding the tritium inventory from the process plant during periods of maintenance. Upon restart, this material is fed back into the Trit*Ex® process. Finally, immobilized tritium product is stored in the Tritium Storage Vault system.

5.4 Tritium Safe Handling Arrangements

Tritium is radioactive and flammable. It degrades materials and poses significant challenges when controlling contamination because of its high diffusivity and permeability. In order to manage operator and environmental risks to ALARA, the Trit*Ex® facility employs the use of defense in depth engineering controls including the following:

- High performance leak tight primary containment specially designed to GE's tritium compatible mechanical standards making the leaks highly unlikely whilst reducing tritium permeability and avoiding material radiation degradation
- Triple diaphragm compressors with two monitored interspaces, mitigating the risk of an uncontrolled release of tritium in the unlikely event of compressor diaphragm failure
- Inert secondary containment with IEC61508 [11] compliant SIL rated safety system devices providing demonstrable reliability and performance for mitigating breaches of primary containment
- Forced cascaded ventilation with online real-time tritium monitors providing last-line defense protection to the operators whilst demonstrating best practice in environment emission management
- Point-of-source abatement technology minimizing release of tritium and deuterium to the environment demonstrating execution of best practicable means and ALARA principles for emission reduction whilst helping to minimize economic loss through deuterium recovery.

In addition to the engineering controls, a Trit*Ex® Facility will have administrative and procedural controls in line with international expectations for a secure tritium facility.

To reinforce the significant safety improvement provided by the Trit*Ex® process, Table 2 provides a straightforward comparison between conventional cryogenic distillation (based upon technology employed at the Darlington TRF) and the Trit*Ex® process. The values represent inventory held within the isotope separation section of the facility (it is assumed that other systems would be comparable). The basis used is 25 kg/h D_2O throughput and 99% T_2 product:

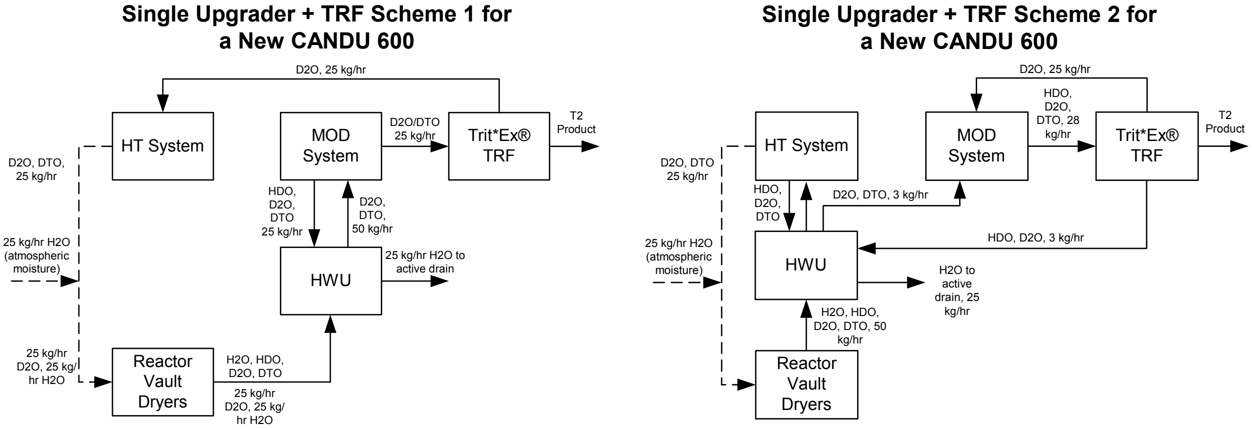
	Cryogenic Distillation	Trit*Ex®
Tritium inventory, kCi	120	3.6
Critical group public dose based upon full tritium inventory release, rem	2.3	0.068

Table 2: Inventory and Dose Risk Posed by Isotope Separation Technology (Inventories in both technologies will decrease if the tritium product quality is reduced)

6. Heavy Water Upgrading (HWU) and Trit*Ex®

Given the significant difference in tritium content (and the consequent containment requirements) of the moderator and heat transport systems, almost all CANDU® stations have separate HWUs for moderator and heat transport heavy water.

The affordability and simplicity of the Trit*Ex® process now makes it feasible to provide tritium removal at every station, rather than relying on a centralized facility, or simply living with high tritium concentrations. As the Trit*Ex® process is also capable of separating light water from heavy water, some of the upgrading load can be performed by the Trit*Ex® Facility. This concept is not completely new; the current Darlington Tritium Removal Facility can perform limited upgrading. Figure 5 illustrates how the Trit*Ex® process can be integrated into the overall station heavy water management, and eliminate an upgrader to offset the cost of the TRF.



Single Upgrader + TRF Scheme 1 for a New CANDU 600

Single Upgrader + TRF Scheme 2 for a New CANDU 600

Figure 5: Two Single Station Upgrader Schemes for Integrated Heavy Water Upgrading and Detritiation Using the Trit*Ex® Process

7. Conclusion

With the novel non-cryogenic Trit*Ex® process - combining for the first time gaseous and thermal diffusion technology - integrated heavy water upgrading and detritiation is now feasible and cost effective. Adding a TRF based on the Trit*Ex® process to an existing reactor is also greatly simplified.

In comparison to conventional cryogenic distillation technology, the Trit*Ex® process is inherently safer, less energy demanding and simpler to design, build and operate. This introduces the opportunity for each PHWR station to install a Trit-Ex® TRF facility at its own site, preventing the need for one, large, centralized facility, in which transportation risks and backlog would become issues. Based on recent water distillation and tritium removal system design and construction experience, GE is now able to offer the full range of technologies for tritium removal, integrated heavy water detritiation and traditional upgrading systems.

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