[Form 2 (to be reported to Committee on Countermeasures for Contaminated Water Treatment and to be disclosed to public)

Technology Information	
Area	2 – Treatment of Contaminated Water
Title	2-1 Requirements for tritium removal technologies
Submitted by	Candu Energy Inc., SNC-Lavalin, Atomic Energy of Canada Ltd., Canadian Nuclear Partners (Ontario Power Generation)

1. *Overview of Technologies (features, specification, functions, owners etc.)*

Candu Energy Inc, Atomic Energy of Canada Ltd and SNC Lavalin are proposing a feasibility study for tritium-removal technologies, taking into consideration the wastewater treatment requirements, to select the best available technology to minimize, as far as practicable, the impact on the environment (including worker dose, public dose and non-human biota dose) whilst taking into account a wide range of factors, including cost-effectiveness, technological status, operational safety, social and environmental factors, and schedule.

The following tritium removal and D_2O production (hydrogen-isotope separation) technologies will be assessed:

- Technology No. 1: Water Distillation Process
- Technology No. 2: Ammonia Process
- Technology No. 3: Vapor Phase Catalytic Exchange-Cryogenic Distillation
- Technology No. 4: Liquid Phase Catalytic Exchange-Cryogenic Distillation
- Technology No. 5: Combined Electrolysis Catalytic Exchange Technology-Cryogenic Distillation
- Technology No. 6: Bithermal Hydrogen-Water Process
- Technology No. 7: Girdler-Sulfide Process
- Technology No. 8: Ammonia Hydrogen Process
- Technology No. 9: D_2O production for CANDU Reactors

<u>Technology No. 1: Water Distillation Process</u>

<u>Description</u>

Water distillation separation is based on the small difference in vapor pressure between water species containing different hydrogen isotopes (e.g., DTO, HTO). At 60°C (20 kPa), the H_2O vapour pressure is about 1.056 times that of HTO. Thus the equilibrium liquid mole fraction of HTO is 1.056 higher than the gas phase mole fraction. Water distillation is the simplest separation process. Water is boiled and condensed at opposite ends of a contacting tower, which is filled with a highly wettable packing, usually made of phosphor bronze. By countercurrent contacting of ascending vapor and descending liquid, tritiated water is depleted from the overhead product and enriched in the lower section of the column. It is common for a tritium removal process to have the equivalent of some hundreds of equilibrium contacts (i.e., increments of packing in which the exiting liquid and vapour are in equilibrium with each other), which increase the column length. Two-stage distillation (i.e., two columns) reduces the overall size of the column. Usually, a small fraction of the water in the reboiler is removed and sent to a second distillation column for further concentration.

Technology No. 2: Ammonia Process

Description

The ammonia process is based on extraction of tritium (or tritiated wastewater) into gaseous ammonia with subsequent separation of isotopic forms of ammonia mixture NH_3 $-NH_2T$ in distillation column [Ref: A.I. Egorov, V.M. Tyunis, Deactivation Of Tritium Containing Waters By Rectification Methods]. When using ammonia, the effects of separation of hydrogen and tritium are essentially slightly higher compared to water distillation process. The process is simple. The gaseous ammonia extracts tritium from streaming downs tritiated wastewater in an exchange column to form isotopic forms of gaseous ammonia mixture NH_3 $-NH_2T$. The detritiated wastewater is recovered at the bottom of the exchange column. The isotopic forms of gaseous ammonia mixture NH_3-NH_2T flows to a distillation column. By countercurrent contacting of ascending vapor and descending liquid, tritiated ammonia (NH_2T) is depleted from the overhead product and enriched in the lower section of the column and ammonia gas is recovered at the top section of the distillation column. Ammonia gases are recirculated back to the exchange column. The tritium concentrate is drawn from the still of distillation column.

Technology No. 3: Vapor Phase Catalytic Exchange (VPCE)-Cryogenic Distillation

Description

The vapour phase catalytic exchange (VPCE) process is used in the separation of tritium from tritiated water by reacting the water as superheated steam with tritium-lean hydrogen and separating the reaction products in a back-end cryogenic distillation (CD) [Ref: A. Busigin, S.K. Sood, Optimization of Darlington Tritium Removal Facility Performance: Effects of Key Process Variables, CANTEACH.CANDU.ORG website]. The VPCE front-end process comprises an evaporator, a superheater and a catalytic reactor, which are interconnected in series. These exchange hydrogen gas with a cryogenic distillation unit, that separates hydrogen isotopes by distillation at approximately 20K

Technology No. 4: Liquid Phase Catalytic Exchange (LPCE)-Cryogenic Distillation

Description

In the Liquid Phase Catalytic Exchange (LPCE)-Cryogenic Distillation (LPCE-CD) process an LPCE column is used to transfer the tritium from the light water to a recirculating e gas stream. A multi-column cryogenic distillation system both strips tritium from the recirculating hydrogen gas stream and concentrate the tritium to near-pure HT or T_2 for immobilization on titanium sponge. Tritiated light water is fed to the top of the LPCE where it counter-currently contacts the tritium depleted hydrogen gas returning from the cryogenic distillation system. H_2O leaving the LPCE column is tritium depleted.

Technology No. 5: Combined Electrolysis Catalytic Exchange (CECE)Technology-Cryogenic Distillation

Description

Combined electrolysis catalytic exchange (CECE) is one of several processes based on use of the hydrogen/water exchange equilibrium reaction that favors formation of liquid HTO when liquid H_20 is contacted with tritiated hydrogen (HT) gas.

The CECE process consists of countercurrent gas/liquid exchange columns packed with catalyst beds, with an electrolytic cell at the bottom to convert water into hydrogen and tritiated hydrogen gases and an overhead catalytic recombiner at the top to convert the hydrogen and oxygen gases into water.

Light tritiated water is fed mid-way down the countercurrent gas/liquid exchange column. Light water and hydrogen are depleted in tritium above the feed point and enriched in tritium below the feed point. Product water (tritium depleted light water) is taken from the top of the countercurrent gas/liquid exchange column (recombiner product*)*. A small hydrogen gas stream enriched in tritium is taken from the electrolytic cells for further processing or storage.

The CECE process can be easily tailored to achieve any particular DF and tritium enrichment by adjusting the length of the countercurrent gas/liquid exchange columns column stripping and enriching sections, respectively. If desired, the tritium-enriched stream can be further concentrated in a back-end cryogenic distillation system before storage. Such concentration, however, may not be necessary.

Technology No. 6: Bithermal Hydrogen-Water (BHW) Process

Description

The bithermal hydrogen-water (BHW) process is based on the same hydrogen/water exchange reaction as the CECE process and may be able to use similar catalysts. However it does not require electrolysis of the feed water, but instead relies on a recycled stream of hydrogen coupled with dual temperature separations columns. This process consists of cold-stripping and cold-enriching columns and hot-enriching and hot-stripping columns stacked in a vertical orientation with hydrogen gas flowing upward countercurrent to the aqueous streams.

Tritiated water to be treated is introduced between the cold-stripping and cold-enriching columns. In the upper "cold stripper" section, non-tritiated water is used to absorb tritium from the circulating hydrogen. The resulting hydrogen gas, essentially free of tritium is recirculated to the hot-stripping column to remove tritium from the wastewater to be discharged. The tritium-rich product stream is withdrawn from between the cold and hot enrichment columns. The columns are operated at high atmospheres pressure to achieve maximum separation factors.

Technology No. 7: Girdler-Sulfide (GS) Process

Description

The Girdler-Sulfide process is essentially used as a production method for making heavy water for CANDU reactors. Like the bithermal-hydrogen water process, the Girdler Sulfide process uses cold and hot columns and a recirculating gas to drive the separation process. However, in the GS process hydrogen sulfide is the recirculating gas and no catalyst is required.

For D_2O production, the method is an isotopic exchange process between H_2S and H_2O that produces heavy water over several steps. Each of a number of steps consists of two sieve tray columns. One column is maintained at 30°C and is called the cold tower and the other at 130°C and is called the hot tower. Deuterium extraction is done based on the difference in separation between 30°C and 130°C. The GS process can also be used for tritium extraction based also on the difference in separation between 30°C and 130°C.

Hydrogen sulfide gas is circulated in a closed loop between the cold tower and the hot tower (although these can be separate towers, they can also be separate sections of one tower, with the cold section at the top). Demineralised and deaerated water is fed to the cold tower where deuterium migration preferentially takes place from the hydrogen sulfide gas to the liquid water. This "enriched" water from the cold tower is fed to the hot tower where deuterium transfer takes place from the liquid water to the hydrogen sulfide gas. An appropriate "cascade" setup accomplishes enrichment. Using one tower instead of a cascade is possible, but in practice it never occurs, as the tower size and process inventory would be much larger.

Normally in this process, water is enriched to 15–20% deuterium. Further enrichment to "reactor-grade" heavy water (> 99% deuterium) is done in a vacuum distillation unit. For detritiation of Fukushima wastewater, the tritium would migrate with the deuterium.

Technology No. 8: Ammonia Hydrogen Process

Description

For D_2O production, the ammonia-hydrogen exchange process extracts deuterium from synthesis gas through contact with liquid ammonia in the presence of a catalyst. The synthesis gas is fed into exchange towers and to an ammonia converter. Inside the towers the gas flows from the bottom to the top while the liquid ammonia flows from the top to the bottom. The deuterium is stripped from the hydrogen in the synthesis gas and concentrated in the ammonia. The ammonia then flows into an ammonia cracker at the bottom of the tower while the gas flows into an ammonia converter at the top. Further enrichment takes place in subsequent stages and reactor grade heavy water is produced through final distillation. The synthesis gas feed can be provided by an ammonia plant that, in turn, can be constructed in association with a heavy water ammonia-hydrogen exchange plant (or detritiation plant). The same ammonia-hydrogen chemical exchange process could be used to extract tritium from tritiated wastewater.

Technology No. 9: D_2O production for CANDU Reactors and wastewater transport to existing D_2O production plants

Description

Chemically, there is more deuterium present in the Fukushima wastewater than tritium. As such, any process that detritiates the Fukushima water is also a D_2O production process. Since the detritiation processes described above are also D_2O-production processes, then D_2O production for operating CANDU plants should be explored as part of the study. The D_2O production pathway that will be explored is to produce a low-purity D_2O stream of 1-10%, and make arrangements for that low-purity stream to be accepted by operating CANDU plants as makeup water. The option of pretreatment of wastewater followed by tanker delivery to existing D_2O-production plants (Girdler-Sulfide plants or ammonia plants) and detritiation plant (e.g., Darlington TRF) will also be investigated. These recycle options would eliminate the need to store the Fukushima tritium product.

Overall Issues and Challenges for the Implementation of these Technologies.

Wastewater production rates would need to be reduced and/or additional temporary storage put in place to provide sufficient time to build one of the plants described under Technologies 1 to 8. If sufficient space is not available on the Fukushima site to construct such a plant, it may in addition be necessary to locate it elsewhere and arrange to transport the water (e.g., by tanker ship). In addition, the energy demands of Technologies 1 to 8 must be evaluated against local capabilities to deliver power.

More details are provided for each technology in Section 2.

Candu Energy, AECL, SNC Lavalin and OPG Expertise in Heavy Water, Tritium Removal and Tritium Management Technologies

Candu Energy , Atomic Energy of Canada Ltd, SNC Lavalin and OPG (Candu consortium) have extensive experience in evaluating, developing and deploying heavy water production technology, detritiation technology and tritium management technology that could be applied to Fukushima's tritium issues:

- Decontaminating heavy water in CANDU reactors by extracting the tritium:
  The Candu consortium designed the Wolsong Tritium Removal Facility in Korea, and has performed feasibility studies for multiple reactor operators.
  The Candu consortium operates and supports the largest civilian detritiation plant in the world at Darlington, Canada.
- Decontaminating light water by extracting tritium:
  The Candu consortium is actively involved in design work for ITER.
  The consortium has designed a system to treat spent-fuel-bay water.
  The consortium has conducted feasibility studies on groundwater decontamination for various clients.
- Decontaminating air streams in power plants by removing HTO vapour:
  This technology is part of every standard CANDU reactor.
- Decontaminating solid waste by stripping tritiated water:
  Used by some facilities to simplify subsequent processing of the waste.
- Evaporation of tritium-contaminated water, with solidification of any solids:
  Designed and operated by the Candu consortium, it is a robust process for dealing with complex wastes.

Other expertise in tritium management include:

- Environmental monitoring and assessment, including environmental risk assessment
- Public and environmental dose modeling and assessment, including pathways analysis
- Health physics evaluations and programs
- Occupational monitoring, assessment and protection
- Effluent and waste monitoring and control for all tritiated species (gaseous, liquid and solid)
- Equipment and plants for removing tritium from gases, liquids and solids
- Repair, decontamination and decommissioning of tritiated facilities
- Long-term management of tritiated wastes
- Commercial applications of tritium

2. Notes (Please provide information if possible)

- Technology readiness level (including cases of application, not limited to nuclear industry, time line for application)

- Challenges

- Others (referential information on patent if any)

Technology No. 1: Water Distillation Process

Benefits

The process is simple and based on equipment used in various chemical-process industries. Heat is applied at the bottom; cooling at the top. There are few rotating components and the unit is almost totally sealed. Large-scale water distillation facilities are operating in CANDU nuclear power plants.

Issues/Challenges

The limitation of water distillation lies in the quantities of water that must be evaporated.
Because the separation factor (1.056) is relatively small, the internal flows between the boiler and the condenser must be very high in comparison with the feed flow. Consequently, achieve the required minimum detritiation factor of 100 the equipment would be large and energy consumption high. To reduce the overall energy consumption, mechanical vapor recompression could be utilized to heat the reboiler. Good purification of the water feed is also required to eliminate chemical contaminants that could corrode or coat the packing.

Project Examples of Application and Readiness

Water distillation has not been used as a detritiation process to treat large volumes (400 m^3/d) of wastewater with low tritium activity (10^6Bq/L). This process is primarily used at large scale to reprocess the small escapes of D_2O in CANDU reactors and for commercial production of O-18 enriched water. This process was, however, used for detritiation at a pilot scale in Japan Tokai Reprocess (JAEA) and to recover deuterium from light water for Manhattan project (USA).

Intellectual Property/Patent Aspects

Sulzer Brothers holds rights to the preferred column packing, but alternative packings are available.

Technology No. 2: Ammonia Process

Benefits

Same as water distillation process. In addition, the process does not require the same degree of feedwater purification as the other processes.

Issues/Challenges

This technology has not been demonstrated in pilot plant. A method must be provided for disposition of the concentrated tritiated ammonia stream. Ammonia is classified as toxic and dangerous for the environment.

Project Examples of Application and Readiness
No pilot-scale and large-scale plants for this ammonia process have been constructed yet.

Intellectual Property/Patent Aspects
No specific patent issues

Technology No. 3: Vapor Phase Catalytic Exchange-Cryogenic Distillation

Benefits
A large-scale detritiation plant is operating in Canada.

Issues/Challenges
The VPCE process is complex and operating cost is high. A cryogenic distillation is required for this technology. The VPCE process was used in the Darlington TRF because it was felt by the designers (in 1985) that LPCE was not sufficiently demonstrated.

The feed stream has to be treated to remove any organic volatiles and inorganic contaminants.

Project Examples of Application and Readiness
Ontario Power Generation (OPG) owns and operates the world's largest commercial tritium removal facility at its Darlington nuclear station. The Darlington Tritium Removal Facility (DTRF) has been detritiating water since 1989 to support CANDU-type Pressurized Heavy Water Reactors (PHWR) in Ontario, as well as other heavy water users. The DTRF can process up to 2.5 thousand tonnes (2,500 Mg) of heavy water a year, producing tritium with purity greater than 98%. OPG stores the tritium and markets it globally, for end-uses not associated with nuclear weapons.

The operation of the DTRF follows the same Nuclear Safety Culture as a commercial nuclear power plant with efforts to ensure exceptional radiological protection and environmental safety as well as industry-leading conventional safety. The areas of DTRF operating expertise include tritium handling, water detritiation, cryogenic distillation, tritium storage on metal getters, tritium isotope separation, atmospheric detritiation and tritium dosimetry.

Intellectual Property/Patent Aspects
Sulzer Brothers have rights to portions of the Darlington design. There are a limited number of potential suppliers in the world of large-scale CD equipment suitable for this use.

Technology No. 4: Liquid Phase Catalytic Exchange-Cryogenic Distillation

Benefits

A large-scale LPCE-CD plant is operating by KOPEC in Korea (i.e., Wolsong Tritium Removal Facility).

Issues/Challenges

The LPCE is somewhat simpler that VPCE, but shares most of its challenges. A cryogenic distillation is required for this technology.

The feed stream has to be treated to remove any organic volatiles and inorganic contaminants.

Project Examples of Application and Readiness

A LPCE type pilot plant (as front-end for Combined Electrolysis Catalytic Exchange (CECE) process) to recover tritium from heavy water was demonstrated at the Chalk River Laboratories (Ontario, Canada).

A large-scale LPCE-CD plant is operating in Korea with a plant capacity of 800 m^3/a (i.e., Wolsong Tritium Removal Facility).

Intellectual Property/Patent Aspects

AECL and KOPEC have rights to portions of the WTRF design. There are a limited number of potential suppliers in the world of large-scale CD equipment suitable for this use.

Technology No. 5: Combined Electrolysis Catalytic Exchange Technology-Cryogenic Distillation

Benefits

The CECE process has a high isotopic separation factor (2 to 7) at near ambient temperature and pressure operating conditions. A catalyst is required for the reaction to proceed at an appreciable rate, and development of improved hydrophobic catalysts in recent years has been key to commercial success of the process.

Only CECE has demonstrated a detritiation factor (DF) in excess of 100, which is the minimum required for Fukushima based on the data provided. Given more detailed information on concentrations and volumes, it may be possible to accommodate a DF lower than 100. This will assess in the feasibility study.

Issues/Challenges

The CECE has only been demonstrated at small scale (120 L/d). No commercial facility able to treat 400 m^3/d is available. Operating cost (energy consumption) is high.

The feed stream has to be treated to remove any organic volatiles and inorganic contaminants.

A method must be provided to dispose the concentrated tritiated water stream. A tritium enriched waste stream will be produced in addition to tritium depleted water or hydrogen. This enriched stream can be in the form of HT in hydrogen gas from the electrolytic cell or water with elevated tritium compared to the feed water. The HT could be loaded on a metal as a hydride and tritiated water could be disposed as a grouted waste form or stored as liquid.

Project Examples of Application and Readiness

AECL has developed a commercial water-stable wetproofed exchange catalyst for this process. The CECE process has been the subject of active development work over the last 30 years at the Chalk River Laboratories. The work includes catalyst development and testing, improvements to electrolytic cells, optimization of system and component designs, and industrial prototype construction and operation. Most of this work is aimed at tritium separation for heavy water reactors.

A two part demonstration of the CECE process was successfully completed at the Chalk River Laboratories. The first part was to demonstrate upgrading of heavy water and the second part demonstrated a detritiation decontamination factor of over 1,000 and as high as 50,000 treating tritium contaminated heavy water.

The CECE process for light water detritiation has been proposed for removing tritium in the spent fuel bay water at a research reactor facility. This project is at the conceptual design.

A CECE type pilot plant to recover tritium from light water was built and operated in Japan for over 14 years in connection with the Fugen reactor. The plant capacity was 3.6 liters per day of feed, and HTO was concentrated by a factor of 10^4 (S. Isomura, K. Suzuki and M. Shibuya, Separation and Recovery of Tritium by Hydrogen Water Isotopic Exchange Reaction, Fusion Technology, 1988).

Intellectual Property/Patent Aspects

AECL holds rights to its CECE catalyst.

Technology No. 6: Bithermal Hydrogen-Water

Benefits

For heavy water production, a hydrogen-water BHW technology was successfully demonstrated by AECL at the prototype CIRCE (Combined Industrially Reformed hydrogen and Catalytic Exchange (CIRCE) demonstration project at Hamilton.

Because electrolysis of all the feed is not required, operating costs are expected to be lower than for the CECE process.

Issues/Challenges

This process has not been operated on a large industrial scale.

The separations columns, catalyst beds, and the internal stream flows are much larger than CECE. As in the case of the CECE process, a method must be provided to dispose the concentrated tritiated water stream.

Feed water for this process needs to contain low levels of organic and inorganic contaminants.

Operating cost is high.

Project Examples of Application and Readiness

For heavy water production, a hydrogen-water BHW technology was successfully demonstrated by AECL at the prototype CIRCE (Combined Industrially Reformed hydrogen and Catalytic Exchange (CIRCE) demonstration project at Hamilton.

Intellectual Property/Patent Aspects

AECL

Technology No. 7: Girdler-Sulfide Process

Benefits

Large scale plants are operating and could treat wastewater containing chloride. The feedwater does not require any pretreatment. In the GS process the exchange reaction is fast and occurs without a catalyst.

Issues/Challenges

Girdler-Sulfide process has not been used as a detritiation process to treat large volumes (400 m^3/d) of wastewater with low tritium activity (10^6Bq/L). It is only used at large scale for D_2O production. Its applicability for detritiation has to be assessed. The safety concerns are focused around the high-pressure (20 atm) and the highly toxic and corrosive hydrogen sulfide gas used in the process.

Operating cost is high.

Project Examples of Application and Readiness

Several D_2O-production plants exist with the required capacity. Presently, India has many heavy water production plants. The first of these to use the Girdler process is located at Rawatbhata near Kota, Rajasthan.

Intellectual Property/Patent Aspects

No specific patent issues

Technology No. 8: Ammonia Hydrogen Process

Benefits

The separation factor is high (2.8 to 6). Large-scale plants are operating.

Issues/Challenges

The ammonia hydrogen process has size limitations. To exploit the effect of temperature on separation factors, refrigeration is needed and the energy demands of the process are significant. Complex mechanical agitation is needed to provide adequate transfer rates.

Though less hazardous than H_2S, ammonia is also toxic. Safety issue with the use of high-pressure hydrogen gas in the process.

Operating cost is high.

The feedwater needs pretreatment.

Project Examples of Application and Readiness

Large-scale ammonia hydrogen plants have been built and successfully operated in India (Baroda, Hazira, Talcher, Tuticorin).

Intellectual Property/Patent Aspects

No specific patent issues

Technology No. 9: D_2O production for CANDU Reactors and wastewater transport to existing D_2O

production plants

Benefit

These approaches would eliminate the waste liability, not simply reduce it, without the costs and complexity of full detritiation at Fukushima site. Candu Energy and SNC Lavalin have strong credentials in international logistics for the transport of tritiated water, and close ties to the CANDU fleet. Ontario Power Generation (OPG) is the owner of the largest CANDU fleet in the world and operates the largest detritiation plant in the world (See Technology No. 3).

Issues/Challenges

Substantial international considerations for the transport of tritiated water.

Project Examples of Application and Readiness

See project examples for Technologies 3, 7 and 8.

Intellectual Property/Patent Aspects

See patents for Technologies 3, 7 and 8.