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A NEW APPROACH TO HEAVY WATER UPGRADING TECHNOLOGY

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Abstract

Heavy water is an integral part of the Heavy Water Reactors (HWRs) and in particular, the CANDU family of reactors. Due to the high cost of heavy water and the radiological effect associated with tritium-contaminated heavy water, efforts are made to minimize the loss of heavy water by collecting any water from liquid leakages, spills, and vapour recovery. High isotopic purity is important in the efficient operation of HWRs, hence the need to continuously cleanup and periodically upgrade the collected heavy water

This paper explains Tyne Engineering's embracing of the modularized and more economical Combined Electrolysis and Catalytic Exchange (CECE) process as an alternative to the larger distillation methods of heavy water upgrading. The salient advantages and disadvantages of the CECE process for heavy water upgrading are discussed.

With the costing and modular construction/installation experience of Tyne Engineering, the CECE upgrading process has become less expensive and more attractive. The improved AECL proprietary catalysts, the availability of tritium compatible electrolyzer, the reduction in cost, and the simplicity of the process will certainly add value to the HWRs' attractiveness, and hence determine the process of heavy water upgrading for the present and the future.

1. Introduction

1.1 History of heavy water

Deuterium was discovered in 1931 by an American chemist Harold Urey who won the Nobel Prize in Chemistry in 1934 for this discovery [1]. In 1933, heavy water was produced by Lewis and MacDonald [2] using electrolysis. Realizing the potential of heavy water in science, engineering and medicine, the need to produce heavy water in large quantity became increasingly necessary.

The first industrial heavy water production plant was built by Norsk Hydro in Vemort near Rjukan, Norway in 1933. By 1935, the plant was producing 99% pure heavy water for commercial use. In 1943, Canada joined the heavy water producing group when it built and operated an electrolytic heavy water plant in Trail, British Columbia, as part of the Manhattan project. Other notable heavy water plants at that period were the Glace Bay and Port Hawkesbury in Nova Scotia, and the LaPrade in Bécancour, Quebec. Though the construction of

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the LaPrade plant was completed, the plant never went into operation before it was mothballed and its parts later sold. In 1979 when the Bruce Heavy Water Plant was commissioned in Douglas Point near Tiverton, Ontario, it was (and would still be) the world's largest heavy water production plant. This plant was shut down in 1997. Since then, attention has moved to heavy water management rather than production. One of the management procedures is to clean contaminated heavy water and to upgrade it if its isotopic purity is less than required

1.2 Uses of heavy water

As stated earlier, heavy water finds use in various facets of human life, some which are outlined below

At the Sudbury Neutrino Observatory in Sudbury Ontario, heavy water has been used in Neutrino detection, providing the medium for producing and visualizing the Cerenkov radiation.
Heavy water is used as doubly labeled water for mean metabolic rates in plants and animals In doubly labeled water the oxygen in the heavy water is ^{18}O. Also, the deuterium content of heavy water is used for the preparation of specifically labeled isotopologues of organic compounds. In FTIR detection of protein spectra, D_2O is used in order to shift the protein spectra from that of amide I region.

Heavy water finds by far its largest use in the nuclear industry as neutron moderator. The use of heavy water in this regard is further explained below

1.3 Heavy water in the nuclear industry

A number of nuclear power plants depend on heavy water to operate. Typical are the Pressurized Heavy Water Reactors (PHWR) and the CANDU family of reactors. For these reactors and reactors that use natural or partially enriched uranium as fuel, heavy water plays a very important role in the functioning of the reactors. These reactors use heavy water as coolant or as moderator, or both.

Using heavy water in nuclear plants comes with its associated problems such as size of containment building, and high heavy water inventory and cost. It is reported that the initial heavy water consumption cost in a nuclear plant could be as much as 20% of the plant's capital cost. The initial investment into heavy water for the Darlington plant was about 11% of the final capital cost or about 29% of the initial planned capital cost [3]. Because of this cost, every CANDU station owner makes efforts to minimize wastage of heavy water during the reactors operations.

1.4 Heavy water production technology

Various methods have been used in the production of heavy water. Most notable according to Chris Waltham [4] are:

1. Distillation of water or hydrogen - a process that requires many stages and a large amount of energy

2. Electrolysis of water. Also involves multi-stage and heavy on electrical energy requirement.
3. Hydrogen/water catalytic exchange, the "Trail Method". The method can be used in dual-temperature mode

$$H_2O + HD \longleftrightarrow HDO + H_2 \quad (1)$$

4. The Dual-Temperature Sulphide Process

$$H_2O_{liq} + HDS_{gas} \longrightarrow HDO_{liq} + H_2S_{gas} \quad (2)$$

Water distillation and water electrolysis have been quite prominent among these methods. Each of the methods comes with its advantages and disadvantages, but it is not the purpose of this paper to duel on these as they have been adequately covered by various authors [5-7]

2. Heavy water upgrading

In its simplest definition, Heavy Water Upgrading could be said to be the removal of the light water content of the heavy water. In a more scientific definition, heavy water upgrading could be defined as the replacement of the protium content of the water with deuterium. In the nuclear industry, heavy water upgrading could be defined as improving the isotopic of heavy water to meet reactor grade specification. Whichever way it is defined, heavy water upgrading results in a product that meets the requirements for use as moderator or as both moderator and coolant in Heavy Water Reactors.

Due to the high cost of heavy water and the radiological effect associated with tritium-contaminated heavy water, efforts are made to minimize the loss of heavy water by collecting any water from liquid leakages, spills, and vapour recovery. In the course of recovering these liquids and the airborne heavy water vapour, light water is also recovered along with the heavy water. Since fuel burnup is known to decrease by about 0.5% for every 0.01% downgrading of D_2O isotope, it becomes necessary, therefore, to concentrate the recovered heavy water fractions to meet the reactors isotopic requirements and hence improve fuel burnup.

In today's heavy water upgrading process, much as the isotope purity is important, the cost of achieving the specified purity is of paramount importance. This has led to attempts at improving existing processes and development of practical new processes. The water distillation (DW) method of upgrading is the most common in the nuclear industry. The general process involves direct vacuum distillation of heavy water in packed columns; with the D_2O moving towards the bottoms while the overheads carry away the H_2O. Recently though, a lot of work has been reported on an alternate process using electrolysis in combination with a catalyst packed column [8-10]. This process called the Combined Electrolysis and Catalytic Exchange (CECE) process has shown a lot of potential and is further discussed below.

2.1 The Combined Electrolysis and Catalytic Exchange (CECE) process

CANDU Reactors require high isotopic grade water to ensure efficient operation. During normal reactor operation, some light water gets into, and some heavy water escapes from, both the Moderator and the Primary Heat Transport System. In the course of recovering the lost heavy water and the airborne heavy water vapour, light water is also recovered along with the heavy water. It becomes necessary therefore to concentrate the pools of heavy water and also the recovered heavy water fractions to meet the reactors requirements.

2.1.1 Process description

For the purpose of this paper, the CECE Heavy Water Upgrading System consists of two Separate Upgraders. One system maintains the purity of heavy water in the Primary Heat Transport System (PHTS) and the other maintains the purity of heavy water in the Moderator. Since the upgrader does not include detritiation, it is best to individually upgrade the PHT and the Moderator streams.

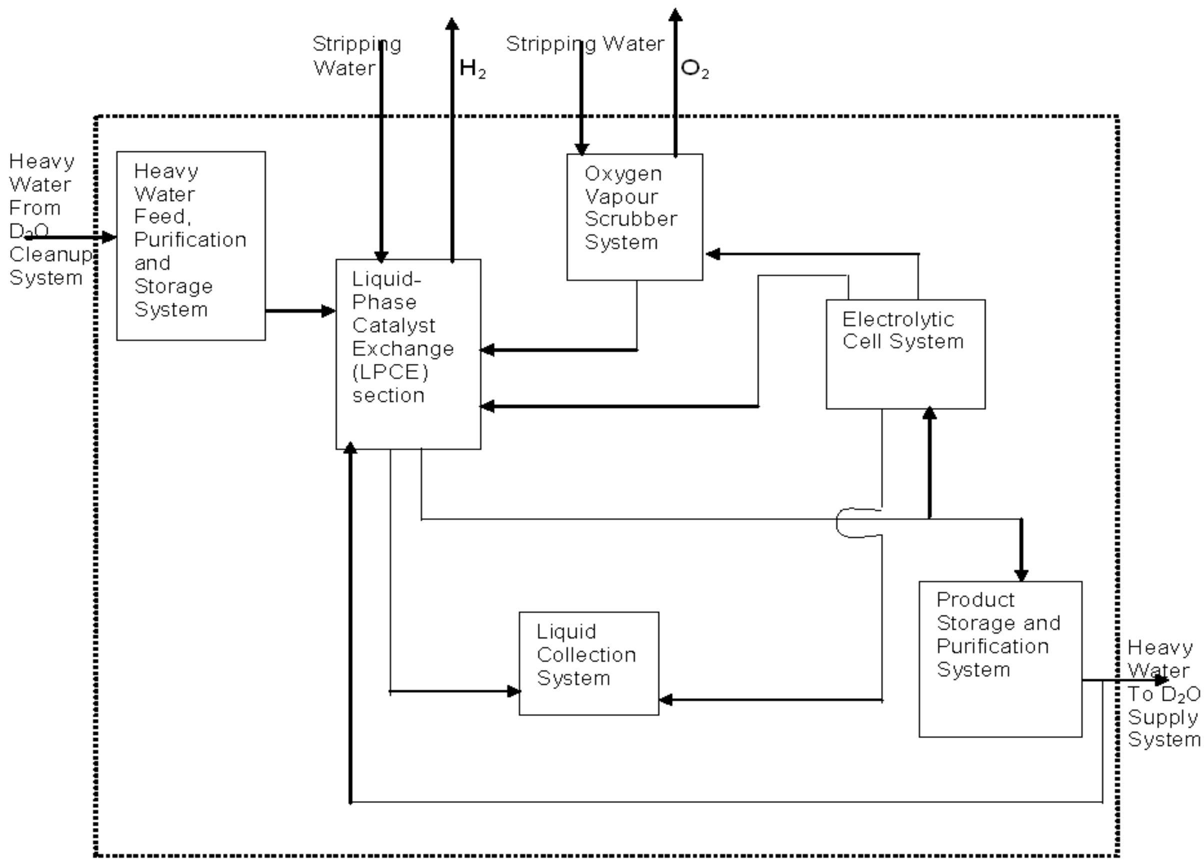

Figure 1 Simplified Block Diagram of the Upgrading Process

The CECE Process for Heavy Water upgrading is based on the isotope-exchange reaction between water and hydrogen isotopes in the presence of a catalyst. The process comprises two main stages:

1. The Electrolysis of heavy water in which deuterium (D_2) is generated;
2. The Liquid Phase Catalytic Exchange (LPCE) where the generated D_2 is exchanged with H_2 in the in-coming H_2O to enrich the depleted D_2O.

In the upgrading process, downgraded heavy water from the D_2O Clean-Up System is passed through polishing filters and then fed into a series of LPCE columns. Above the feed point, the heavier isotopes (deuterium and tritium) are stripped from the hydrogen gas by purified natural water fed to the top of the LPCE column. The stripping is reliant on the presence of special catalyst packing. The upward-flowing hydrogen gas, having been stripped of the heavier isotopes of deuterium and tritium is vented. The downward-flowing water, now enriched in D_2O is monitored for isotopic purity. By controlling the draw-off rate, the product isotopic content can be maintained at the required specification for transfer back to the heavy water management system. The rest of the bottoms product is sent to the electrolysis cells (E-cells) to generate the D_2 gas.

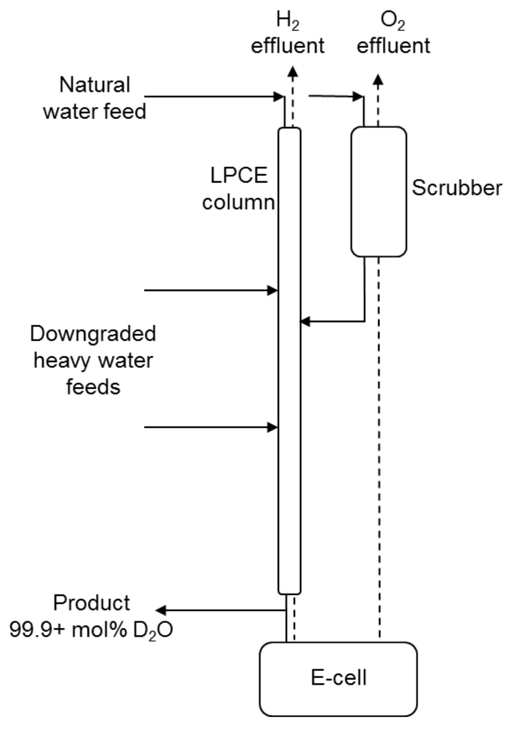

Figure 2 Simplified CECE Heavy Water Upgrading Process

The E-cells contain potassium hydroxide (KOH) which serves as the electrolyte. The heavy water content of the E-cells is split into two gaseous streams by electrolysis. The streams are the deuterium-rich hydrogen (D_2) stream and the oxygen (O_2) stream. While the electrolysis is taking place, isotopic separation of the protium, deuterium and tritium also occurs through kinetic electrode mechanism. Each of the two streams from the E-cell contain liquid entrainment that is then removed using a demister on each stream. The exiting O_2 stream from the demister passes through a recombiner where any remaining hydrogen isotopes are combined with oxygen forming the oxides. The humid oxygen vapour stream from the recombiner is sent to an Oxygen Vapour Scrubber (OVS) where it contacts the counter-current H_2O in the OVS packed bed. Bottom-liquid from the OVS column is fed to the LPCE column at a point where the concentration of this liquid is nearest to the LPCE internal concentration profile. The oxygen is then vented to atmosphere, having had its heavy water vapour removed.

2.2 Associated problems with the CECE process

The CECE process is not without its downside. However, the authors can attest that the effects of these are very minimal as explained below.

2.2.1 Hydrogen (H_2) safety

Hydrogen is a flammable fuel and has a wide flammability range of about 4 – 74% in air. Because of the possible associated hazards with hydrogen handling, several safety standards and codes such as the International Standard [11] and the National Standard of Canada [12] are available to help with the safe handling of the hydrogen gas. A typical schematic of safety assessment for hydrogen by HySafe [13] is shown below. This and other similar ones are readily available for use in ensuring safe handling of hydrogen

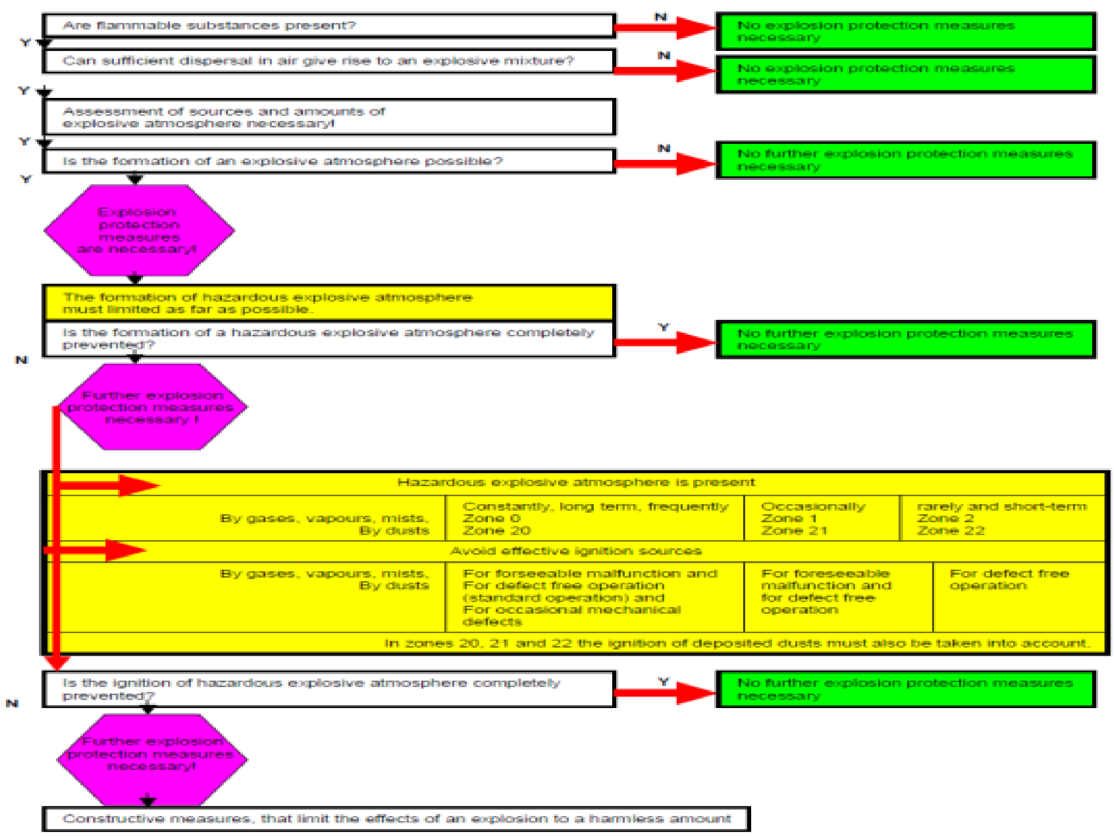

Figure 3 Schematic for the assessment and prevention of explosive risks [13]

2.2.2 Electrical power use

The major drawback for the CECE upgrader is the high electrical power usage. The authors have reviewed this in the light of its availability in the power generating environment, and in comparison with the chilled water and steam requirements of the DW process. With CECE upgrader, electrical power consumption of <500 kW for a CANDU-6 system should not be seen as a drawback that should warrant rejection of the process

2.2.3 Catalyst renewal

There is the possibility of the catalyst bed being reversibly poisoned by contaminants in the feed water. This problem is addressed in two main ways; by adequately pre-treating the feed water, and by including an *in situ* catalyst drying and regeneration system in the process to prolong the life span of the catalysts. The catalysts supplied by AECL are expected to remain active for at least five years, so annual replacement of less than 20% of the catalyst may be required. With the small total volume of catalyst, this is not a difficult operation.

2.2.4 Membrane electrodes replacement

Another potential issue for the CECE heavy water upgrading process is the need to replace the E-cell internals. Currently, there are e-cells that do not require membrane and electrode replacement in less than five years from operation. With their relatively small size and modest cost, replacement of <20% of the e-cell capacity each year is also not difficult.

2.3 Comparative advantages of the CECE process to other processes

The CECE process has a lot of advantages that make it attractive in today's heavy water upgrading. According to A.I. Miller and H.M. van Alstyne, "The CECE process is a highly effective technology for heavy-water upgrading" [14]
The CECE process has the following comparative advantage over water distillation

1. Lower Installed Cost - potentially half of the cost of the DW process
2. Factory-built Modules - Reduced site-work time to about 2½ years from Contract Effective Date (CED)
3. Minimal Seismic issues - considering the smaller, shorter and lighter equipment
4. Very low tritium emission - Environmental Consciousness
5. Reduced C-14 emission - Environmental Consciousness
6. No requirement for steam - Cost Saving, particularly during commissioning
7. Low cooling and chilled water requirements - Cost Saving
8. No Heavy Water loss in overheads - Cost Saving and Environmental Consciousness

The Table below shows some comparative requirements of the CECE and the DW processes

Table 1 Comparison of DW and CECE Upgrader

UTILITIES	**DW**	**CECE**
Heating Steam (kg/h)	2,000	0
Cooling Water (kg/h)	230,000	1,000
Chilled Water (kg/h)	14,000	300
Demineralized Water (kg/h)	0	60
Instrument Air (m^3/h)	45	45
Electrical Power (kW)	40	350
OTHERS		
Heavy Water Holdup (L)	12,000	8,000
Tritium Emission (Ci/a)	>5,000	<12
Column Diameter (mm)	800	150
Delivery Schedule from CED (yrs)	4	<2½

In addition, the use of the CECE process becomes more attractive when we consider the following aspects

2.3.1 <u>Engineering</u>

The main advantage here is the simplicity of the CECE process. In the CECE process, the plant is completely modular, which makes it simple, small and a more efficiently erected system. This results in a shorter startup time from Contract Effective Date (CED) as compared to most other processes. Based on Tyne's experience in modular manufacturing, the author estimates that it will take around 30 months from CED for the upgrader to be up and running.

2.3.2 <u>Environment</u>

The process is known for its low emission of hazardous materials thereby making it environmentally friendly. The CECE is designed to concentrate the heavier isotope of deuterium and tritium in the liquid phase. Hence the vented hydrogen (H_2) is depleted of these isotopes. Design and experimental results have shown that for the CECE process, the tritium content of the vented H_2 is usually in order of 0.13uCi/kg which is substantially lower than that achieved by the DW process. Also, the vented oxygen gas contains the original enriched ^{17}O present in the heavy water supply. The removal of the excess amount of this oxygen isotope ensures a reduced radioactive carbon (C-14) emission.

2.4 Costing the CECE upgrader

To effectively cost our proposed upgrader, the authors considered three major areas which are

1. Adequate and up-to-date Piping and Instrumentation Diagrams (P&ID)

2. Adequate specifications sheets for all major equipment
3. Modular plant layout and modular fabrication

These and Tyne Engineering's experience in the costing, building and commissioning similar process enabled the authors to obtain an EPC cost that shows the process to be more financially attractive. Skid-module construction and reduced on-site installation time extensively and effectively reduced the total cost and the fabrication/installation cycle.

3. The future

3.1 Using tritium compatible electrolyzer

The electrolyzer described for this write up is the alkaline-based electrolyzer. However Tyne Engineering is currently developing a PEM electrolyzer to mitigate some of the known shortcomings of the alkaline electrolyzer [15] This electrolyzer, which will be very compact, will reduce the footprint of the CECE process, and hence a general reduction in the cost. Since the electrolyzer is being developed with high tritium concentration in mind, its tritium compatibility will assure longer membrane life, thus less frequent replacement and ultimately further saving in operating cost.

4. Conclusions

Over 15 years ago, A.I. Miller [14] wrote "By deploying both CIRCE and CECE processes worldwide, this program will assure continuing supplies of heavy water for CANDU reactors that can meet any conceivable demand for heavy-water production at a cost that maintains the competitiveness of CANDU reactors" This statement remains perfectly valid. With demonstration tests on the CECE in the CECE Upgrading and Detritiation (CECEUD) by AECL-CRL and the positive results, and with the costing and modular construction/installation experience of Tyne Engineering for similar processes, the CECE upgrading process has become less expensive and more attractive. These and the improved AECL isotope exchange catalysts and the tritium-compactible electrolyzer make this process the heavy water upgrading choice for the present and the future. The reduction in cost, availability of tritium compatible electrolyzer, and the simplicity of the process will certainly add value to the HWRs' attractiveness.

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