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THE CHALK RIVER TRITIUM EXTRACTION PLANT

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The Chalk River Tritium Extraction Plant for removal of tritium from heavy water is described. Tritium is present in the heavy water from research reactors in the form of DTO at a concentration in the range of 1–35 Ci/kg. It is removed by a combination of catalytic exchange to transfer the tritium from DTO to DT, followed by cryogenic distillation to separate and concentrate the tritium to T_2. The tritium product is reacted with titanium and packaged for transportation and storage as titanium tritide. The plant processes heavy water at a rate of 25 kg/h and removes 80% of the tritium and 90% of the protium per pass. Catalytic exchange is carried out in the liquid phase using a proprietary wetproofed catalyst. The plant serves two roles in the Canadian fusion program: (1) it produces pure tritium for use in fusion research and development, and (2) it demonstrates on an industrial scale many of the tritium technologies that are common to the tritium systems in fusion reactors.

1. Introduction

Tritium is produced in heavy water fission reactors by neutron capture by deuterium. The rate at which tritium is produced is dependent on the neutron flux and the volume of heavy water. In CANDU power reactors this production rate is approximately 0.2 grams of tritium per MW(e) per year. In research reactors the production rate is lower because of smaller volumes of heavy water exposed to the neutron flux. With increasing time of reactor operation the tritium concentration reaches an equilibrium value, where the rate of production equals the decay rate of the tritium. The time to reach equilibrium varies with reactor design, but is of the order of several years.

The presence of tritium in the heavy water contributes to the radiation dose of the reactor staff and radioactive emissions of the facility. Tritium dose is controlled through design and operation procedures which minimize leaks and limit exposure to the tritiated water. Experience over many years of operation has shown these procedures are effective in keeping doses far below allowable limits. A further method of dose control is to remove tritium from the heavy water and maintain the tritium concentration below the equilibrium value. This method of control is being adopted at Chalk River Nuclear Laboratories (CRNL) and by Ontario Hydro.

2. Technical program

2.1. Objectives

The Chalk River Tritium Extraction Plant (TEP) was built for two reasons. The first was to extract tritium from the heavy water in the NRU research reactor, a heavy water moderated and cooled reactor that has been in operation since 1957. The second was to demonstrate, on an industrial scale, new technologies needed for hydrogen isotope separation that had been developed at the laboratories over a number of years [1,2,3]. A third reason, subsequent to the decision to proceed, was to produce pure tritium for applications in fusion and for commercial applications such as self-powered lights and labelled compounds.

2.2. Role in fusion program

The plant has two major roles in the fusion program. The first is the supply of tritium for use in fusion experiments and the second is as a test bed and demonstration of hydrogen isotope separation and related technologies that will be required in the fueling systems of fusion devices. The related technologies are those associated with the safe handling of pure tritium, including methods of packaging and storage, the accurate

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measurement of quantities and purity, its dosimetry and environmental effects. Tritium technologies required for the extraction of tritium from water have many similarities to the requirements for fueling a tritium-burning fusion machine. The operation of the TEP provides a demonstration of these technologies on an industrial scale which will reduce the amount of development and demonstration required for fusion tritium systems.

2.3. *Technologies investigated / demonstrated*

The technologies involved include catalytic isotopic exchange between liquid water and deuterium, cryogenic distillation for isotope separation, packaging of T_2 as a metal hydride, electrolytic generation of D_2, catalytic trickle bed recombination of D_2 and O_2 and accountability of tritium and deuterium. One important objective, in addition to detritiating water and recovering the tritium is to demonstrate the safe and reliable operation of a tritium process system.

2.4. *Status of work*

Commissioning of the process systems is underway. After complete cold testing without tritium, tritiated water feed is planned for introduction during 1990.

2.5. *Major results*

Development in support of the plant has covered a number of areas:
- development and fabrication of wetproofed catalyst,
- operating pilot scale isotopic exchange columns, recombiners,
- development of packaging and storage containers for pure tritium,
- development of expertise in handling pure tritium gas,
- establishment of a high level tritium laboratory,
- development of process tritium monitors,
- design of specialty components for the plant, including the liquid phase catalytic exchange (LPCE) column, recombiner, uranium beds, tritide storage packages,
- testing and evaluation of plant components, e.g. Nova Magnetics deuterium gas blowers, water feed pumps, process tritium monitors, product gas chromatograph,
- software development for process control and analysis,
- training of plant operating staff,
- development of an area tritium monitor with HT/HTO discrimination,
- measurement and modelling of health effects of HT on people, and
- measurement and modelling of HT behavior in the environment.

2.6. *Future plans*

When satisfactory operation is established and the NRU water and water from shutdown reactors is processed, the plans are to evaluate other advanced forms of wetproofed catalysts and to investigate alternative process systems for the extraction and concentration of tritium from water.

3. Facilities

3.1. *Major characteristics*

3.1.1. *Process description*

The process, shown schematically in fig. 1 has been described previously in a number of papers [1,2,3]. The heavy water contains tritium in relatively low concentrations. Tritium concentrations in heavy water are normally quoted in units of Curies of tritium per kg of heavy water, where 1 Ci/kg = a ratio of 0.35 ppm T/D. The current tritium concentration in the NRU reactor water is about 18 Ci/kg. The process in this plant is designed to remove 80% of the T and 90% of the H in a single pass of water through the plant at a feed rate of 25 kg/h. In the process, tritium is transferred from the DTO form in the water stream to the DT form in deuterium gas by a catalyzed isotopic exchange process called the Liquid Phase Catalytic Exchange Process (LPCE), described by the following reaction:

$$DTO + D_2 \leftrightarrow D_2O + DT.$$

This is called the front end of the process and is carried out in a packed bed column with counter current flows of heavy water and deuterium gas. Tritium and deuterium are then separated by low temperature distillation of the liquified D_2–DT mixture in a train of cryogenic distillation columns. The tritium-lean D_2 stream is returned to the front and catalytic column and the T_2 product is removed from the end of the distillation train and packaged for storage. The catalyst used to promote the isotopic exchange reaction is a unique feature of the process used in this facility. It is the wetproofed platinum-on-carbon catalyst developed at

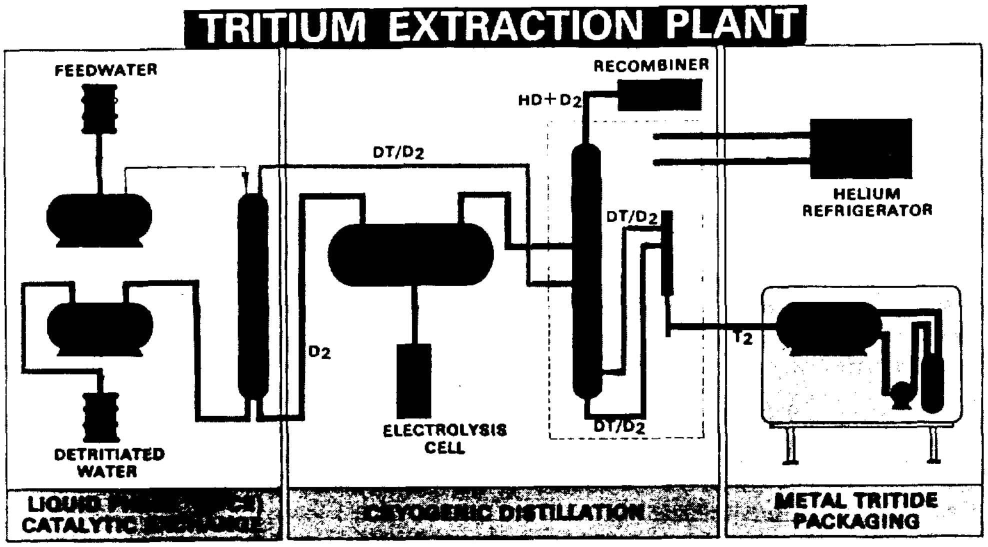

Fig. 1. Process schematic for Chalk River's Tritium Extraction Plant.

Chalk River for the hydrogen-water heavy water process [4,5]. The special property of this catalyst is the ability to retain its catalytic activity in the presence of liquid water. Conventional catalysts must remain dry to maintain their activity and therefore when used to catalyze this exchange reaction, the water must be in the vapour phase. The effectiveness of the wetproofed catalyst in this application means the process is greatly simplified and process equipment such as evaporators, superheaters and condensers in the front end are not required.

There are a number of auxiliary systems in addition to three main systems in the process, i.e., the front end tritium transfer process, the cryogenic distillation and the packaging. These include deuterium make-up which supplies the initial charge of D_2 gas to the plant and provides make-up quantities as required during operation, the off-gas system that recombines various deuterium streams with oxygen to form water, refrigeration and safety systems. Protium, as HD, is removed in a small stream from the top of the first distillation column and recombined in the off-gas recombiner to downgraded heavy water. This water is processed in a separate electrolytic upgrading plant on site to bring it back to reactor grade heavy water.

3.1.2. Technology demonstration

There are several areas of technology demonstration embodied in the plant. The major one is the use of the wetproofed catalyst in the LPCE process. These catalysts have been extensively tested in laboratory and pilot plant equipment, but this is the first plant scale demonstration on a continuous basis.

A modified version of the wetproofed catalyst is used for catalytic recombination of the deuterium and oxygen in the off-gas system. Employment of the wetproofed catalyst in this application allows the recombination reaction to be cooled by liquid water rather than be diluted by an inert gas, thereby requiring much smaller equipment [6].

Make-up D_2 for the plant is produced by the electrolysis of D_2O. This plant employs an electrolytic cell that was originally developed specially for electrolysing tritiated heavy water in a combined electrolytic catalytic exchange (CECE) process. The features of the cell are leak tightness and a low inventory of water. The cell was developed and built by Noranda Electrolyser Inc. under contract to Ontario Hydro and Atomic Energy of Canada Ltd. Application of the cell in this service will provide operational experience, even though the cell will not operate at the high tritium concentrations anticipated in the CECE process.

In the plant the tritium product is immobilized as titanium tritide inside a stainless steel container that can be used either for long term storage or for transportation and recovery for subsequent use in fusion systems [7].

Deuterium gas is circulated in a loop between the LPCE column and the cryogenic distillation column by means of carbon vane positive displacement blowers. A magnetic coupling between the drive motor and the rotor eliminates potential leakage from the drive shaft and seals that would otherwise be required. These pumps were developed and supplied by Nova Magnetics Ltd. a former subsidiary of the Nova Scotia Research Foundation.

For assessing the operation of the process, on-line tritium process monitors measure the tritium concentration of some process streams. The ability to measure tritium as DT in D_2 in a wide range of concentrations was a requirement. Commercial instrumentation for this task does not exist and a program was undertaken at CRNL to develop a series of monitors to fulfill this function [8].

The recombiner-type wetproofed catalyst is also employed as part of the tritium emission monitoring system [9]. The release of tritium in the ventilation exhaust is determined for tritium in both the hydrogen and water forms by an analysis train, consisting of bubblers to remove the HTO fraction followed by a wetproofed catalyst recombiner to convert HT to HTO, which is subsequently removed in a second set of bubblers.

3.1.3. Safety

There are two main hazards associated with the process: radiological safety from the tritium, and explosion and fire hazard from the hydrogen (deuterium) inventory.

For radiological safety the philosophy used is to design, build and operate the plant to limit radiation exposures to both the public and the site personnel to within the prescribed limits and to as low as reasonably achievable for both normal and accident conditions. The actions taken to minimize dose uptake due to tritium exposure are:

- design and build the process system to minimize leaks, using appropriate approved design codes, quality controlled components and construction methods,
- concentrate the tritium only when it is in the hydrogen form,
- provide double containment when tritium is present in high concentrations,
- provide a high ventilation rate to minimize tritium concentrations in the building atmosphere, and,
- provide an extensive tritium monitoring and alarm warning and process shutdown system.

A system of automatic isolation valves is installed to isolate various sections of the process system in the event of a tritium leak or other hazardous situation. The code selection for the process systems was based on the Canadian Standards Association "General Requirements for Pressure Retaining Systems and Components in CANDU Nuclear Power Plants" CAN3-N285.0-M81. Piping system design was done to the ANSI B31.3 Chemical Plant and Petroleum Refinery Piping code. Electrical equipment in the process was designed to the Canadian Electrical Code and the buildings to the National Building Code, the National Fire Protection Association and the Ontario Health and Safety Act and Regulations for Industrial Establishments. The process components are all of high integrity, with welded joints wherever possible. Bellows sealed valves are used throughout the process gas system. Where tritiated water must be handled, the equipment is designed to prevent splashing hazards and to collect any spillage. The tritium in the feed water is transferred to the DT form prior to concentration, to minimize the hazard. Tritium is separated from deuterium and concentrated to T_2 by cryogenic distillation. Tritiated hydrogen is a factor of about 10000 less toxic than tritiated water [10]. Cryogenic operation requires the distillation columns be contained within an evacuated cold box to provide insulation. This cold box also provides a volume to contain tritium should a leak in the process system occur. In this plant the cold box is not designed to provide full secondary containment but will prevent release of tritiated gas until 200 kPa is reached in the cold box and then discharge it directly to base of the exhaust stack and thereby prevent contamination of the building air. Because the columns contain liquid deuterium, there are potentially high pressures when the refrigeration shuts down. The maximum pressure is limited to approximately 4 atmospheres, by providing large expansion tanks for both distillation columns. The expansion tank for the high tritium concentration column is contained within a nitrogen purged glove box. When the T_2 product is withdrawn from the distillation column it is doubly contained in a nitrogen purged glove box system where it is packaged for storage. After packaging it is stored outside the glove box as a solid titanium hydride in a storage package with double containment. Nitrogen is used as the glove box atmosphere to limit oxidation of escaped tritium to the more toxic water form. The ventilation system provides for 10 air changes per hour in the lower floors of the building and 30 changes per hour in the tower area. The tritium detection system continuously monitors the air at several locations in the plant. A lower alarm, set near normal operational levels, provides warning in the event of an increasing tritium concentration. At a second higher level setting, an alarm sounds to initiate evacuation of the building and shutting of the process isolation valves.

Many of the steps taken to provide for tritium safety are also effective for hydrogen safety. In addition to these, the design of the plant is such that all of the hydrogen containing systems are located in the Process Building which is isolated from the rest of the plant. This building is designed for hydrogen service with explosion proof equipment installed wherever possible. Where explosion proof equipment is not available, special local ventilation is provided to prevent the build-up of an explosive mixture of deuterium in the air.

Because of conflicting requirements for monitoring tritium releases from the building which means directing the ventilation exhaust to one point, and the desirability of having a very open structure with many points of exhaust for hydrogen safety, a pressurized ventilation system was used. Air is supplied by a blower to the Service Building rather than being drawn through the plant by an exhaust unit at the top of the tower where the maximum concentration of hydrogen would occur.

To satisfy the internal safety review an outside industrial firm with experience in processes using low pressure hydrogen was contracted to provide an independent hydrogen safety audit of the plant.

3.1.4. Licensing

There are five steps in the licensing process [11]:
- a letter of notification,
- concept review and location approval,
- construction approval,
- licensing of commissioning and startup, and,
- submission of an updated final safety analysis report.

Three major documents are required. The Conceptual Safety Assessment Report is prepared to request approval of the concept and the proposed location for the plant. The Preliminary Safety Analysis Report includes the initial safety analysis, a detailed description of the plant, the proposed code selection, and it requests approval for construction. The Final Safety Analysis Report (FSAR) provides a complete detailed description of the plant and its proposed operation as well as the detailed safety analysis. Acceptance of the FSAR gives permission to commission and start up the plant. When commissioning is complete an updated FSAR containing results of the commissioning work must be submitted and this becomes part of the permanent licensing documentation for the plant. A number of other documents must be submitted and accepted before acceptance of the FSAR is obtained. These include the design manual, the overpressure protection report, completion assurance documentation, maintenance plan and procedures, an in-service inspection plan, operator training plan and commissioning and operating procedures.

3.2. Construction

3.2.1. History

Design and construction of the TEP was carried out primarily by laboratory personnel and because of resource limitations has been extended over a number of years. Approval to proceed with the project was received in November 1981. Detailed design began at that time. Construction of the buildings began in the middle of 1983 and was complete in about one year. Process design proceeded in parallel with procurement of equipment and construction of the larger process vessels. The cryogenic distillation columns and associated equipment were designed and supplied by Sulzer Bros. of Switzerland. The contract was let June 1984 and the partially assembled components were delivered to CRNL in June of 1986. The remainder of the process equipment installation took place over the following months with all the main process systems installed by mid-1988. Completion of auxiliary systems and documentation continued through the first half of 1989, when preliminary commissioning activities started. Some modifications that arose from the hydrogen safety audit will be completed in the last half of 1989 with the expected introduction of tritium in 1990.

3.2.2. Status

Construction is complete and cold commissioning in progress.

3.2.3. Scope

The approximate cost of the plant was in the range of $16–20M(Can.).

3.3. Detailed description

3.3.1. Equipment

The process equipment is described in more detail elsewhere [2]. A summary is included here.

LPCE column

The isotopic exchange reaction occurs in the liquid phase catalytic column. It is fabricated from 316L stainless steel pipe, 0.15 m diameter, with five flanged sections. The wetproofed catalyst mixed with inert packing material is randomly packed in the column in four separate beds with a water distributor between each section; the fifth section at the bottom of the column contains only inert packing to humidity the incoming D_2. The flanged sections are bolted together to form a column 17 m in height. Sample points at each catalyst section permit measurements to be made to determine the performance of each section of catalyst. Glass view ports are installed at each distributor to inspect their operation.

Normal operating temperature of the column is 325 K and provisions is made to isolate the column from the process loop and regenerate the catalyst by purging with 425 K air.

Cold box components

The cold box is made of carbon steel, with stainless steel used for the columns and process piping. Aluminum plate-fin type heat exchangers are used to transfer heat between the refrigerant helium gas and the process gas. Two distillation columns are used to separate the deuterium and tritium. The larger column, 0.2 m diameter, is filled with Sulzer CY packing; the smaller column is a stacked column with two diameters, 50 mm and 12 mm, filled with random stainless steel wire coil packing. Insulation is achieved by wrapping components with aluminized mylar insulation and by operating the cold box at low pressure, ~ 0.1 Pa. Vacuum pumping of the cold box is provided by an oil diffusion pump and an oil-sealed, rotary vane mechanical pump. Equilibriation of D and T among D_2, DT, and T_2 is done in a warm catalyst bed, located on a side stream near the lower end of the small distillation column. Each of the distillation columns is connected to an external stainless steel expansion tank, to limit pressure rise during boil off of the liquid deuterium/tritium mixture.

Refrigeration system

The refrigeration gas is helium and the equipment in this circuit includes a two stage compressor, pulsation dampeners, water cooled heat exchangers and a gas bearing turbo-expander. Piping operating below 250 K is stainless steel; above 250 K carbon steel is used. The helium temperature in the distillation system varies from 15 to 30 K.

Packaging system

The packaging system handles pure T_2 in an all stainless steel system with no elastomer or plastic components. The T_2 is immobilized as a solid titanium hydride inside a stainless steel vessel. All valves are bellows sealed. The components include a vacuum line connecting titanium beds, a uranium bed, a metering tank, an ion chamber, and pressure and temperature instrumentation. The pumping system is a Normetex all-metal moving spiral pump backed by a Metal Bellows Corp. pump. Analysis of the T_2 isotopic purity is done by an on-line gas chromatograph.

Deuterium make-up system

Deuterium is supplied to the plant by the electrolysis of heavy water using KOD as the electrolyte. The electrolytic cell has a capacity of 3 m^3/h. The gases are separated in the cell by an asbestos diaphragm. Delivery pressure is atmospheric to a surge tank from which it is compressed to 500 kPa for injection into the process.

Off-gas system

Some deuterium streams from the process are recombined back to water in a catalytic recombiner. The recombiner is a 0.15 m diameter stainless steel vessel, 2 m long filled with a wetproofed catalyst/inerts mixture and cooled with water.

Control system

The process is very stable and is manually controlled where possible. Automatic control is provided by 28 commercial digital process controllers in a microprocessor-based system.

Tritium monitoring system

Five in-process monitors, seven area monitors, two discriminating bubblers and one discriminating HTO/HT analyzer cover the tritium monitoring functions in the plant [9,12]. All but the bubblers are ion chamber-based. The process ion chambers are constructed of stainless steel and meet the pressure rating of the plant piping system. They were designed and built at CRNL, as were the bubblers. The discriminating HTO/HT monitor was built at CRNL using Scintrex tritium instruments. The area monitors were manufactured by Overhoff and Associates.

3.3.2. Staff

The plant will be operated 24 hours a day, 7 days a week. A total operating staff of 14 operators with two professional staff is anticipated. Maintenance will be provided as required from the site maintenance group.

4. Summary

A plant scale tritium system has been designed and built to extract tritium from heavy water, concentrate the tritium to pure T_2 and package it in a manner that is safe for long term storage or for reuse in fusion fuel applications or in commercial applications such a stritium powered lights or labelled compounds. In the process of extracting tritium from heavy water, a number of new technologies will be demonstrated in an integrated system.

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