separations

Review

Research Progress in Tritium Processing Technologies: A Review

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Abstract: Recent advancements in tritium separation technologies have significantly improved efficiency, particularly through the integration of vapor phase catalytic exchange (VPCE), liquid phase catalytic exchange (LPCE), and combined electrolysis catalytic exchange (CECE) methods. Combining these techniques overcomes individual limitations, enhancing separation efficiency and reducing energy consumption. The CECE process, which integrates electrolysis with catalytic exchange, offers high separation factors, making it effective for high-concentration tritiated water treatment. Solid polymer electrolyte (SPE) technology has also gained prominence for its higher efficiency, smaller equipment size, and longer lifespan compared to traditional alkaline electrolysis. While electrolysis offers high separation factors, its high energy demand limits its cost-effectiveness for large-scale operations. As a result, electrolysis is often combined with other methods like CECE to optimize both energy consumption and separation efficiency. Future research will focus on improving the energy efficiency of electrolysis for large-scale, low-cost tritiated water treatment.

Keywords: tritium separation; electrolysis; catalytic exchange; deuterium-tritium water treatment

Academic Editor: Dimosthenis Giokas

Received: 22 December 2024
Revised: 24 January 2025
Accepted: 26 January 2025
Published: 27 January 2025

Citation: Zhao, Z.; Sun, Y.; Chen, Q.; Li, T.; Liu, F.; Yan, T.; Zheng, W. Research Progress in Tritium Processing Technologies: A Review. *Separations* **2025**, *12*, 33. https://doi.org/10.3390/separations12020033

1. Introduction

Tritium is a naturally occurring radioactive isotope and one of the common radioactive byproducts in nuclear power plants, with a half-life of 12.3 years [1].

Approximately 99.78% of tritium in nature is found in the hydrosphere [2]. It exists in various forms, including tritiated water (HTO), tritiated hydrogen (HT), tritiated methane (CH_3T), and organically bound tritium (OBT). Over 99% of environmental tritium is present as tritiated water (HTO) [3], which shares almost identical properties with water, including strong diffusion, permeability, and adsorption abilities. Tritium can enter the human body through multiple pathways, such as inhalation, skin absorption (both liquid and vapor), or ingestion of contaminated water or food. It can also combine with certain cellular chemicals to form organic tritium. The biological half-life of tritium in the body is approximately 8 to 10 days, but some of it is difficult to eliminate and may remain in certain tissues for several years [4]. According to the International Commission on Radiological Protection (ICRP) Report No. 119 and China's current standard "Basic Standards for Radiation Protection and Safety of Radiation Sources" (GB18871-2002), tritium is classified as a low-toxicity radioactive nuclide. However, numerous studies suggest that as a radioactive isotope of hydrogen—a fundamental element of life—tritium participates in DNA synthesis and causes damage. Its radiological effects may be underestimated. While the relative biological effectiveness (RBE) of beta radiation is typically considered to be 1, many studies indicate that the RBE of tritium is greater than 1 despite its beta emissions [2].

HTO presents various radiation hazards to the body, including acute radiation damage, reproductive effects, carcinogenic effects, and impacts on the growth and development of offspring, among other non-stochastic effects. Research on the carcinogenic, genetic, and reproductive effects of tritium has shown that its radiation weighting factor ranges from 1.7 to 2.4. The International Commission on Radiological Protection (ICRP) has established the dose conversion factor for HT in biological organisms at 2.0×10^{-15} Sv/Bq, for HTO at 2.0×10^{-11} Sv/Bq, and for OBT at 4.2×10^{-11} Sv/Bq [5].

Moreover, in the context of public opinion, the release of tritiated wastewater following the Fukushima nuclear accident has heightened concerns about radiological risks. The public remains highly vigilant and sensitive to nuclear-energy-related accidents, with particular focus on radioactive substances that could affect health and the environment.

Due to tritium’s high mobility, it spreads extensively and persists in the environment for prolonged periods. In the event of a nuclear accident, its wide-ranging and enduring impact raises concerns that tritium leakage could affect larger areas and populations. In the absence of clear assessments and predictions, the public tends to adopt a cautious stance toward potential risks, leading to calls for stricter control measures on tritium. Therefore, managing tritium is also a response to public expectations and concerns about radiological safety.

In conclusion, for the nuclear power industry, controlling and managing tritium release is critical. By minimizing tritium emissions during nuclear facility operations, enhancing radiation protection for nuclear power plant workers to reduce their exposure to tritium, and establishing a comprehensive monitoring and assessment system, we can not only reduce environmental and health risks but also boost public confidence in the nuclear power sector. This will contribute to the safe and sustainable development of nuclear energy.

Earlier research on tritium separation technologies primarily focused on the physicochemical property differences between tritium, deuterium, and hydrogen, which arise from the hydrogen isotope effect. In the 1920s, German chemist F.H.A. Kehne first discovered the hydrogen isotope effect in the laboratory. However, it was not until the 1950s that American chemist Hammond conducted more detailed studies and found that atoms of the same element can have different numbers of neutrons, thus forming different hydrogen isotopes, such as hydrogen, deuterium, and tritium [6]. While atoms of different isotopes share the same electron configuration, they differ in mass. During chemical reactions, the mass of heavier atoms affects their movement, resulting in different reaction rates. This difference in reaction rates between isotopes is the fundamental basis for separating tritium from water. Various separation methods take advantage of these isotopic differences, as shown in Figure 1 [7,8].

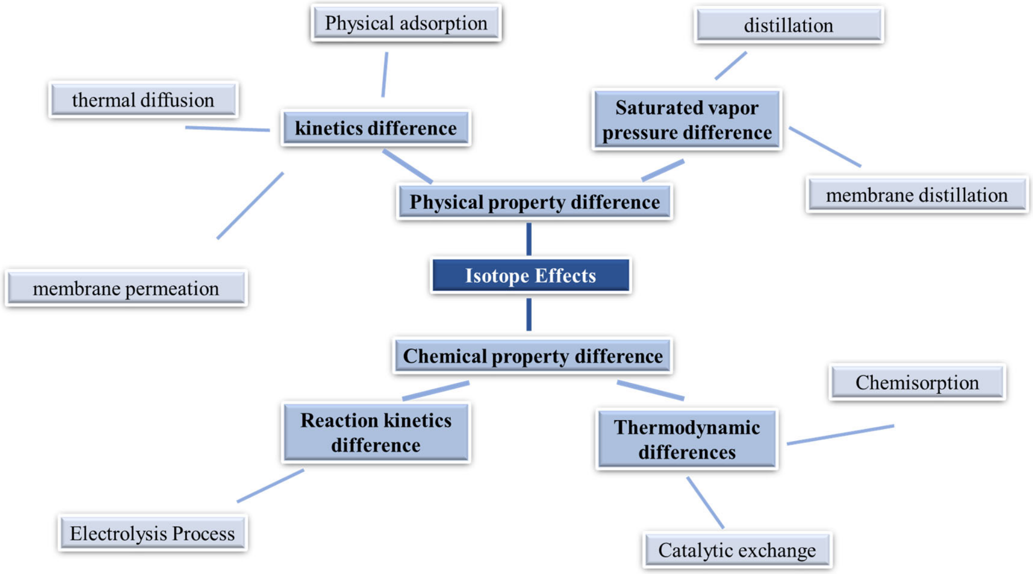

Figure 1. Mechanism of hydrogen isotope separation in water.

2. Research Progress on Tritium Separation Technologies

2.1. Water Distillation

The principle of water distillation (WD) is based on the hydrogen isotope exchange reaction that occurs between the vapor and liquid phases during the distillation process. In water distillation, water is evaporated into water vapor, which then undergoes a gas–liquid exchange reaction with the condensed liquid water. During the countercurrent contact between the gas and liquid phases, heat and mass transfer occur across the phases. The transfer of hydrogen and its isotopes between the two phases differs, with the relatively heavier tritium being redistributed in the process.

This process can be described by the following reaction:

$$\mathrm{H_2O(l) + HTO(v) \leftrightarrow H_2O(v) + HTO(l)} \quad (1)$$

In the tritiated water distillation process, α represents the ratio of tritium molar concentrations in the liquid and vapor phases. The separation factor for water distillation is relatively small (with α close to 1), requiring a large number of theoretical trays and a high liquid flow rate. Consequently, the equipment volume must be substantial, and energy consumption is high [9,10]. However, this method offers several advantages, including a simple device structure, ease of operation, no strong corrosion, and no need for catalysts [11]; compared with other technologies, water distillation is a “passive” method, which is much safer than other technologies such as CECE.

Sugiyama et al.[12] developed a simulation model for the H_2O-HTO separation performance during the water distillation process in a wetted-wall column. The results showed that under high mass transfer conditions, calculations using constant molar fraction boundaries tend to overestimate separation efficiency. At $P = 101.3$ kPa, $T = 373$ K, $R = 0.8$ cm, $H = 100$ cm, $K(v.A) = 1.0 \times 10^4$ cm/s, and Re-v = 600, the HETP value for the constant molar fraction boundary differed by -19% from the value predicted by the model.

While distillation columns are based on a simple principle and industrial attempts to build them have been carried out, they still face issues such as low separation efficiency and large equipment size. Some reports indicate that traditional water distillation columns can reach up to 58 m in height [9]. To address these challenges, many researchers have explored adding packing materials to distillation columns to enhance the separation efficiency of tritium and water and reduce the column height. The primary goal of these improvements is to shorten the distillation column. During the research process, Height Equivalent to a Theoretical Plate (HETP) has become a key metric for evaluating the performance of packing materials. As early as 1979, Stringle and others began investigating the relationship between packing materials and HETP in distillation columns [12–14]. Adding packing materials alters the contact between the gas and liquid phases, and some packing materials, with different affinities for tritium and water, can further improve the separation factor [15–18].

In the past century, materials like porcelain and Dixon rings have been tested as packing materials for distillation columns. In 1989, Yamamoto and others [19] added SUS Dixon rings to a simulated distillation column and found that the separation efficiency was mainly influenced by the gas flow rate. The HETP distribution ranged from 2 to 10 cm. Fukada et al. [20–22] discovered that silica gel has a higher affinity for HTO than H_2O, and therefore used it as a selective adsorbent in distillation columns. Experimental results showed that the separation factor (α) for the silica-gel-packed column was about four-times greater than that of an unpacked column and about twice that of Dixon rings. The adsorption effect not only improved the HETP but also enhanced the overall isotope separation factor in the water distillation column. Their analysis indicated that the material balance equation, assuming additional steam and liquid flow rates, accurately fits the transient behavior of tritium concentration. Miho et al. [23] conducted experiments using Sulzer packing with adsorption capabilities and Raschig rings coated with zeolite adsorbent as packing materials in distillation columns. The results demonstrated that, under steady-state operation, the adsorption process increased the apparent volatilization ratio of H_2O to HTO, effectively enhancing the tritium separation performance in the column. Analysis using the Danckwerts surface renewal model showed that the type of adsorbent and the liquid–gas flow conditions were the key factors influencing the separation efficiency.

Cryogenic distillation (CD) combines cryogenic and distillation technologies. Under the influence of a cryogenic cooling source, liquid hydrogen flows from the top to the bottom of the distillation column and into the reboiler. Under the heat source, gaseous hydrogen flows from the bottom to the top of the column and into the condenser. During this process, the heavier hydrogen isotopes transition from the vapor to the liquid phase, while the lighter components transition from the liquid to the vapor phase. As a result, the lighter hydrogen isotopes accumulate at the top of the distillation column, while the heavier isotopes accumulate at the bottom.

Cryogenic distillation is currently the only industrial-scale method for obtaining high concentrations of tritium. Although it has been applied in industry for separating tritium and water, several challenges remain in device operation, such as uneven cooling in the distillation column and inefficient transfer of cooling power to the gas mixture [24–26]. These issues complicate the separation dynamics. Consequently, key parameters in system design and operation—such as the number of theoretical plates, inlet area, reflux flow rate, extraction flow rate, and operating pressure—are the main focus of both simulation and experimental research [27–30]. Xia's [31] study examined how operating conditions, such as the total number of plates, feed position, reflux ratio, and recovery rate, affect the separation performance of hydrogen isotopes in cryogenic distillation. The research found that moving the feed position toward the bottom and increasing the reflux ratio reduced the HD concentration in both the reboiler and condenser. Simultaneously, the recovery rate at the top increased, and the HD concentration in the reboiler significantly rose.

As the impact of various process parameters became clearer, research on controlling and evaluating the entire distillation system gradually gained prominence. Niculescu et al. [32], using the Lewis–Matheson method and the tridiagonal matrix method, developed a mathematical model for the dynamic simulation of multi-component distillation columns for D-T separation. The model determined the time required for the entire distillation column to stabilize after process disturbances, such as changes in feed flow rate or concentration. Urm et al. [33,34]. evaluated the thermodynamic properties of cryogenic distillation columns for hydrogen isotope separation using the Peng–Robinson Twu equation of state. They examined the effects of parameters such as theoretical stages, feed position, diameter, distillate flow rate, and condenser load on tritium inventory, total pressure drop, and product quality. Subsequent studies also focused on the dynamic optimization of cryogenic distillation systems for hydrogen isotope separation. In the case of periodic fluctuations in feed flow rate, an optimal control problem was proposed to minimize tritium content under two product quality constraints. The optimal control strategy for distillate flow and reboiler heat load was developed.

Moreover, with the advancement of fusion technology, many researchers have begun exploring the combination of cryogenic distillation and catalytic exchange technologies to further purify separated tritium and achieve higher purity levels.

2.2. Thermal Diffusion

Thermal diffusion (TD) is the simplest method for producing high-concentration tritium. Due to the thermal diffusion effect, lighter molecules move toward the hot wire, entering the upward convection near the wire, and are carried upward by the airflow in the column. Heavier molecules, on the other hand, move toward the cold wall and are carried downward to the bottom of the column by the descending convection. This establishes a concentration gradient within the column, with heavier molecules concentrating at the bottom. When concentration diffusion causes the molecules to remix along the tube, equilibrium is reached, and convection acts as the separation effect of thermal diffusion [35,36].

There are two types of thermal diffusion columns: concentric tube type and hot-wire type. To achieve the required degree of separation, the gas volume used in the hot-wire type column is smaller than that in the concentric tube type column. The required separation can be achieved within a few hours. Hot-wire columns are relatively easy to manufacture, and the hot wire itself acts as a catalyst, accelerating the hydrogen isotope exchange process, converting hydrogen molecules in the forms of HD, HT, and DT into H_2, D_2, and T_2. The entire separation process operates at low pressure and low density in a three-component system [37].

Kobayashi et al. [38]. measured the pressure dependence of the separation factor for H_2-HT mixtures. Under 80 kPa, the maximum separation factor for H_2-HT was 12.7. A separation column with an outer tube radius of 9.53 mm and an inner tube radius of 14.2 mm, heated with hot water, achieved a separation factor of 64.4 at 144 kPa, with the separation factor increasing as the pressure increased. Arita [39] et al. experimented with different heaters and feed conditions. When the feed flow rate was 10 cm^3/min, the separation factor for the H-T system using tungsten wire at 1273 K was 55. The separation factor decreased with decreasing heater diameter, and the optimal pressure increased with increasing heater diameter. In the H-T system, when using a sleeve heater (11 mm) at a feed flow rate of 10 cm^3/min, the maximum separation factor reached 2660 even at 763 K. Shimizu [40] proposed a new tritium extraction system, which combined a hydrophobic platinum (Pt) catalyst with a SPE-water-lyser (EXEL-process) droplet bed hydrogen/water isotope exchange column and a thermal diffusion column cascade. This system was designed to remove tritium from irradiated heavy water in heavy-water-moderated reactors (HMR), where the volume of heavy water was 140 m^3, and the average neutron flux was 5×10^{13} n/cm^2·s. Numerical studies of tritium extraction from heavy water, where the tritium concentration was below 2.5 Ci/l (HW), were conducted to determine the system's dimensions.

The Canadian Chalk River Laboratory constructed a hot-wire type thermal diffusion column, which was tested in four experimental runs and two production runs with tritium gas at 20% atomic concentration. Over 400 mL of tritiated gas, reaching 86% (atomic) tritium content, was obtained in these runs. The U.S. Savannah River Site built a hot-wire type diffusion column mainly for further concentrating hydrogen–tritium systems with tritium concentrations ranging from 45% to 85% up to 95% to 99% [37].

2.3. Membrane Technology

In the tritium separation process, membrane separation technology is primarily divided into two methods: membrane permeation evaporation and membrane distillation. Both methods involve a phase change from liquid to vapor, but the key distinction lies in the role of the membrane. In permeation evaporation, the membrane is hydrophilic, and the driving force comes from the chemical potential difference between the feed liquid and the permeated vapor. In membrane distillation, the membrane serves solely as the interface between the gas and liquid phases and is hydrophobic. The driving force in this case originates from the vapor pressure difference between the components [7,35,36].

Permeation evaporation is particularly useful for separating mixtures with similar boiling points. The feed liquid mixture is heated while a vapor pressure difference is applied on the other side. The process involves the feed liquid being adsorbed by the membrane, diffusing through it, and evaporating on the other side [36].

The solubility and diffusion rates of hydrogen in palladium exhibit an inverse isotope effect, where the light isotopes have the highest solubility and the lowest diffusion rates. The permeation rates of hydrogen, deuterium, and tritium in palladium is the significant difference. When diffusion is the rate-determining step, tritium is the least permeable isotope through palladium alloy membranes. Therefore, many researchers use palladium-based materials as research objects for the separation of hydrogen isotopes by pervaporation [41–43].

Glugla et al. [41] set up a mathematical model, validated through experiments, to calculate the net isotope effect in permeation and discharge flow for different hydrogen isotope mixtures under varying feed and permeation pressures. These studies demonstrate the feasibility of using palladium-based materials as permeation membranes for isotope separation. Luo et al. [42] investigated the effects of temperature and gas composition on the hydrogen isotope separation factors of palladium alloy membranes with a reflux ratio of 0.9998. At various temperatures, the separation factor for H-D mixtures with different palladium alloy membranes ranged from 1.31 to 1.42, while for H-D-T mixtures with Pd8.6%Y alloy membranes, the separation factor ranged from 1.2 to 2.0. These results highlight the advantages of operating at higher temperatures, where increased permeation rates and separation factors significantly reduce the required membrane area for separation stages and units.

Currently, several methods exist for separating hydrogen isotopes (in elemental form), including cryogenic distillation, thermal diffusion, and gas-phase chromatography. However, these methods are often hindered by high complexity, substantial energy consumption, and elevated costs. Given these limitations, separation methods based on solid metal membranes offer advantages such as low energy consumption and reduced complexity, making them a promising alternative. These methods exploit differences in isotopic properties such as solubility, diffusivity, and permeability.

Bulubasa et al. [43,44]. integrated a membrane permeation-based isotope separation module into the exhaust pipe of an experimental facility currently in use at ICSi to recover and store hydrogen isotopes. We obtained experimental results showing that the maximum separation coefficient for the lowest concentration of deuterium (0.05 atomic fraction) in the hydrogen isotope mixture is 5.66. The results show that the palladium/silver membrane can achieve hydrogen isotope separation.

Lu et al. [45] observed that prolonged continuous operation leads to the accumulation of helium in the alloy, resulting in a tritium aging effect. At temperatures between 573 K and 723 K, the permeation rate of aged membranes significantly decreases, while the separation factor for H-D mixtures increases. Experimental measurements of the palladium/silver membrane's operational performance were conducted to study its use for hydrogen–helium isotope separation. Tests were carried out at temperatures ranging from 100 °C to 350 °C, with varying hydrogen partial pressures in the upstream membrane, within the range of 150 to 300 kPa.

Membrane distillation is particularly suitable for cases where the feed composition is primarily water, such as in the separation of water isotopes. The process is driven by the vapor pressure difference between the heated feed liquid and the permeate. A hydrophobic membrane is used as the gas–liquid interface, preventing the liquid solution from entering the pores, a phenomenon known as pore wetting. This membrane provides a large surface area for contact between the water and permeate sides, acting as a physical barrier between the feed and counter-current phases.

In the field of membrane distillation, graphene-based and graphene oxide (GO)-based membrane distillation processes have demonstrated excellent performance in separating H_2O/D_2O recent years. As a laboratory-scale model for H_2O/HTO separation, ongoing research is focused on developing new membrane materials and structures to improve permeation flux or separation factors. This remains a key research direction in membrane distillation technology [46–49].

Lozada-Hidalgo [50] clearly demonstrated that there is an order-of-magnitude difference in the permeability of graphene-based membranes to protons and deuterons under environmental conditions. They further obtained graphene by chemical vapor deposition, and the proton–deuteron separation factor was approximately eight. Compared with existing technologies, it is expected that energy consumption will be reduced by several orders of magnitude. This technology is simple and efficient [51]. Poltavsky et al. [52] further proved that the magnetic conduction mechanism of this system changes from quantum tunneling of protons to quasi-classical transport of heavy isotopes. The quantum nuclear effect shows significant temperature and mass dependence, providing a new direction for controlling the ion transport mechanism in nanostructured separation membranes by manipulating the barrier shape and transport process conditions. Wang et al. [53] studied the radiation resistance of graphene in tritiated water. Six months of tritiated water immersion did not structurally damage the single-layer graphene samples on copper foil substrates at detectable levels. From the perspective of radiation damage resistance, this study initially indicates that the use of single-layer graphene for "P-T" separation in tritiated water has specific practical feasibility.

In 2015, Sevigny et al. [46] conducted the first separation experiment of hydrogen isotope water vapor using graphene oxide (GO) membranes. The experiment showed that the GO membrane achieved a separation factor for T/H in water of about 1.6, exhibiting strong molecular sieving performance, far surpassing the separation capabilities of traditional microporous polymer membranes. García-Arroyo et al. [47] found that the separation of hydrogen isotopes during their transport through GDY (Graphdiyne) membranes, enhanced by mass-dependent quantum effects, which are amplified by the confinement provided by their inherent sub-nanometer pores. Computational studies revealed that the selectivity for T_2/H_2 reached its maximum value of about 21 near 45 K. Li et al.'s [48]. research found that adjusting the intermembrane spacing and the physicochemical properties of the membrane can improve the performance of graphene oxide (GO)-based membrane distillation processes for hydrogen isotope separation. The resulting threedimensional layered GO-MWCNT composite membrane (G/M-1:3) exhibited the highest permeation flux, and its separation factor (1.045) was similar to that of the original GO membrane (1.046). Luo et al. [49]. successfully used GO/g-C_3N_4 composite membranes for the first time for hydrogen isotope separation in water. The H/D separation factor and permeation flux were both higher than those of GO membranes, offering promising potential for isotope handling.

In addition, researchers are actively exploring other membrane materials. Sun et al. [54,55] investigated boron nitride (BN) and molybdenum disulfide (MoS_2) as membrane materials within a PTFE (polytetrafluoroethylene) support membrane. The PTFE/BN membrane showed higher permeation flux than PTFE/MoS_2 and PTFE/GO membranes, with a higher separation factor than PTFE/GO membranes and better performance than PTFE/MoS_2 membranes. Further exploration of binary PTFE/BN/GO and PTFE/MoS_2/GO heterostructural composite membranes showed that the PTFE/BN/GO membrane had a higher permeation flux and separation factor compared to PTFE/MoS_2/GO and PTFE/GO/GO membranes. It is believed that other two-dimensional materials or heterostructural membranes may offer even better performance in hydrogen isotope separation. Koyanaka et al. [56,57] reported using a membrane containing deuterated manganese dioxide to separate tritium from tritiated heavy water at room temperature. This membrane is capable of continuously extracting tritium from light water. Compared to using protonated manganese dioxide powder alone, the method that employs a proton-conducting polymer membrane in an acidic aqueous solution, with protons supplied by the membrane, proved highly effective in maintaining continuous tritium extraction from light water. The extraction mechanism likely involves neutralization between H+/T and OH-/OT-, with pre-oxidation occurring at the interface between protonated manganese dioxide and water.

2.4. Adsorption Method

In recent years, the use of inorganic and organic porous materials for selective adsorption has been considered as a promising low-cost separation method. Zeolites, inorganic substances, possess a significant adsorption capacity for water and demonstrate rapid desorption characteristics, thereby rendering them the most extensively employed crystalline porous materials. They are renowned for their superior thermal and chemical stability, longevity, and reusability, which have positioned them as a focal point of research in the domain of tritium adsorption [58,59].

Sircar et al. [60] have conducted studies on a variety of adsorbents, including zeolites 3A, 4A, 5A, 13X, and activated carbon, under low-temperature conditions. Their findings reveal that hydrogen isotopes undergo reversible physical adsorption and monolayer adsorption on potential adsorbents, with hydrogen adsorption being more pronounced on 4A zeolite, deuterium adsorption on 13X zeolite, and activated carbon exhibiting no isotopic preference. Iwai et al. [61,62] studied the effects of cations on HTO/H_2O separation and dehydration characteristics of Y-type zeolites. It was found that the dehydration characteristics of HTO were affected by the accumulated purge volume, and the purge volume had little effect on the dehydration characteristics. The influence of temperature on HTO dehydration is also small, especially in the early stage of dehydration. Changing the pressure is an effective way to dehydrate HTO. Then, NaX and NaY zeolite were used to investigate the effects of SiO_2/Al_2O_3 on the adsorption and desorption of tritiated water in H_2O-HTO binary system in the range of 2.0~10.0. The skeleton SiO_2-Al_2O_3 ratio has little effect on the isotope separation factor. At room temperature, the water removal capacity of NaY10.0 is approximately four times that of NaA2.0. The weak interaction produces isotopic effects on desorption. There is a strong correlation between the HTO dehydration rate and the accumulation of purge volume. Dehydration is independent of the purge gas flow rate. In the Tritium Laboratory Karlsruhe (TLK), both NaA and MFI-ZSM5 were selected for tritium processes. Borisevich et al. discusses the results obtained for the separation of a binary mixture of water vapor and helium. The permeances were highly dependent on the temperature for high water contents, reaching values as low as 10^{-3} μmol $m^{-1}s^{-2}Pa^{-1}$ for the NaA membrane [63].

Except zeolite, some researchers have also discussed the treatment effect of other adsorption materials for tritium separation. Tulenko et al. [64] evaluated several common organic and inorganic high surface area materials to assess their ability to selectively adsorb low concentrations of HTO. The experimental results show that cationic ion-exchange resins with cation functionalities, chitosan, sodium alginate, and several inorganic media modified with metal cations exhibited promising results. Biomaterials, such as chitosan and modified alginate, showed positive results.

Taguchi et al. [65] found that mesoporous silica (MCM-41) has a narrower pore size distribution and larger specific surface area than other adsorption materials. The tritium removal capacity and adsorption capacity are higher than those of mercerite (MOR) and Linde-type A (LTA). The separation factor for HTO was 1.26.

Vergari et al. [66] discussed the effects of irradiation, oxidation and fluoridation on the adsorption capacity, adsorption and desorption kinetics of graphite. It was found that these three phenomena increased the tritium adsorption capacity of graphite. It is expected that neutron irradiation and reaction with fluoride will decrease the tritium adsorption rate, while oxidation will increase the tritium adsorption rate. The effect is obvious when the tritium fraction is low.

Yeon et al. [67] systematically studied the effects of temperature, H_2O_2 and reuse times on the performance of purified and diluted tritium water activated carbon. It was found that the increase of temperature had a negative effect on the selective separation, but the addition of H_2O_2 had a positive effect. The reuse of activated carbon also had a negative effect, but the first three reuses did not have a significant impact on performance. In addition, Edao et al. [68] found that layered titanate could selectively inhibit the adsorption of tritiated water on the material. This provides a new angle for tritium separation materials.

Molecular sieve is the most commonly used porous adsorption material and its engineering applications are also being gradually explored [69–71]. Fu et al. [70] reported a tritiated heavy water distillation process with a metal–organic framework (MOF) modified surface. The interfacial contact between water droplets, steam and fillers can be improved by using a MOF with a microstructure, micropores and hydrophilic properties, to ensure superhydrophilic properties. Under optimized operating conditions, the separation efficiency is high, and the separation height is equivalent to 1.53 cm of the theoretical plate (HETP). A new idea has been proposed for the design of intrinsically safe tritiated heavy water distillation for industrial applications. The employment of molecular sieve beds at low temperatures for hydrogen adsorption has been chosen as the separation process for hydrogen isotopes in the tritium extraction system (TES) for the helium-cooled ceramic reflector (HCCR) experimental reactor system (TBS) in Korea. Park and colleagues [69] assessed the hydrogen adsorption efficacy of a large CMSB and examined the alterations in CMSB performance in relation to the inundation ratio, total pressure, and flow rate within the hydrogen partial pressure range of 100 to 700 Pa. Despite the hydrogen adsorption performance being slightly inferior to that observed in small-scale isothermal experiments, this discrepancy may be attributable to the scaling effect and the experimental results are satisfactory. This technology is feasible in terms of industrialization.

2.5. Catalytic Exchange

The vapor phase catalytic exchange (VPCE) process involves purifying tritiated heavy water to remove impurities, then heating it to 200 °C and mixing it with D_2 gas. The mixture is passed through a catalytic exchange column, where hydrogen isotope exchange takes place. In this process, liquid tritium (DTO) in the tritiated heavy water is converted into gaseous tritium (DT). When coupled with low-temperature distillation (CD) for hydrogen isotope separation, the gaseous tritium (DT) can be further separated to obtain high-purity tritium (T_2). The VPCE process primarily facilitates phase conversion, transferring tritium or hydrogen from the water vapor phase into the gas phase. The gaseous tritium and hydrogen are then separated and concentrated using hydrogen isotope separation technologies [37,72]. The transfer of protium and tritium from heavy water to deuterium gas proceeds as follows:

$$\mathrm{DTO} + \mathrm{D_2} \leftrightarrow \mathrm{D_2O} + \mathrm{DT} \tag{2}$$

$$\mathrm{HDO} + \mathrm{D_2} \leftrightarrow \mathrm{D_2O} + \mathrm{HD} \tag{3}$$

In the DTO process, tritium atoms are converted into DT and, with the aid of D_2 gas, enter the low-temperature distillation system. Due to the difference in boiling points between D_2 and DT, tritium is enriched at the bottom of the distillation column, while D_2 accumulates at the top. The de-tritiated heavy water collected from the VPCE column's top is condensed, collected, and returned to the reactor for reuse. Most of the D_2 from the distillation column is reintroduced into the VPCE column to continue its role as a carrier gas, maintaining the continuous operation of the de-tritiation process. The remaining D_2 undergoes a hydrogen–oxygen reaction to convert into heavy water, which is then returned to the reactor for further use.

The VPCE process employs hydrophilic catalysts and operates in a multi-stage serial configuration. Each stage requires high-temperature conditions, leading to high energy consumption and low separation efficiency, making the process complex both in terms of equipment and operation. While this method is mature and has been industrialized, its technological approach is now considered outdated and has been superseded by the LPCE process.

The core of the liquid phase catalytic exchange (LPCE) process is the hydrophobic catalyst. This catalyst, along with hydrophilic filler, is packed into a catalytic column. Tritiated water and exchange gases (H_2 or D_2) undergo gas–liquid countercurrent contact inside the column, where hydrogen isotope catalytic exchange reactions occur. The hydrogen–water exchange reaction is slow and requires the catalyst to quickly achieve equilibrium. Like VPCE, LPCE facilitates the phase conversion of hydrogen isotopes, but additional methods are needed for further concentration and separation of hydrogen isotopes.

The primary feature of the LPCE de-tritiation process is its use of a hydrophobic catalyst, eliminating the need for repeated vaporization and condensation. The exchange process is depicted in Figure 2.

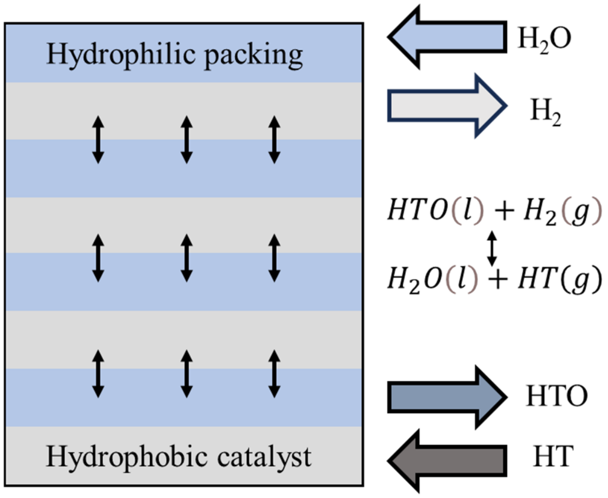

Figure 2. Process of LPCE catalytic exchange column detritiation.

The LPCE process enables multi-stage countercurrent gas–liquid phase exchange under ambient temperature and pressure. This process is straightforward, using simple equipment and easy system sealing. Additionally, during the process, the tritium concentration in the heavy water does not exceed the tritium concentration in the reactor's raw heavy water, making it safer and more suitable for tritium removal. A major challenge of the LPCE process is the use of hydrophobic catalysts, which can suffer from deactivation and poisoning after prolonged use in tritiated heavy water [73].

The hydrophobic catalyst is a key material in the LPCE process, and there are problems of deactivation and poisoning in long-term use of tritium-containing heavy water. Therefore, the exploration of catalysts in catalytic exchange fields has always been the focus of research. Lu et al. [74] modified mesoporous silica (SBA-15) by constructing a hydrophobic microscopic reaction environment to improve the catalytic activity of the LPCE reaction. By modifying the SBA-15 carrier and loading metal Pt with tetramethyldisilazane to prepare a superhydrophobic Pt@SBA-15-tetramethyldisilazane catalyst, the catalyst's catalytic performance was improved, and it had good catalytic activity. The catalyst still had high catalytic activity after being placed in tritium water environment for 30 days. Ionita et al. [75] tested two catalytic mixed packing materials based on a hydrophobic Pt-catalyst; with closed separation performances, catalysts were proposed for LPCE column. The effects of β radiation from tritium and impurities in the feed fluid on the performance and parameters of the catalytic mixed packings were tested. The results showed that the SCK-CEN packing had a stable structure after a 3-month durability test experiment. Li et al. [76] prepared a Pt-loaded cross-linked styrene-divinylbenzene copolymer (SDB) hydrophobic catalyst Pt/SDB by impregnation method, and studied the influence of residual double bond content on the loading of Pt and the catalytic activity and stability of Pt/SDB catalyst during the preparation process. It was found that as the residual double bond content increased, the loading of Pt increased accordingly. In addition, the Pt/SDB with higher residual double bond content had higher column efficiency and better stability. Fan et al. [77] used 1H, 1H, 2H, 2-Hydrofluorotrialkoxysilane (HFTMS) and 1H, 1H, 2H, 2-Perfluorotrialkoxysilane (PFOTMS) to modify the nanoscale Al_2O_3 with hydrophobicity, resulting in HFTMS-Al_2O_3 and PFOTMS-Al_2O_3. To improve the hydrophobicity and strength of the SDB carrier, the stability of the hydrophobicity was better than that of SDB. The modified SDB carrier had good hydrophobicity and compressive strength overall, and could be used for the treatment of tritiated wastewater. Ionita et al. [78] selected key elements of the LPCE process, mixed catalytic fillers, as their evaluation points and screened the mixed catalytic fillers. Considering that platinum is the most active and effective catalytic metal, TEFLON is the best hydrophobic carrier for moisture resistance. The content of platinum exceeding 2%, the properties of the platinum sol and the solvent have no significant influence on the catalytic activity and isotope separation performance. The ordered mixed catalytic filler with a maximum hydrophobic–hydrophilic ratio of 2.5 has better processing effects than the random filler.

As the LPCE process becomes increasingly mature, research on optimizing its operating conditions through experiments and modeling is becoming a new research hotspot. Stefan et al. [79] studied the isotope exchange reaction (IER) between HTO molecules in H_2O solution and atmospheric H_2O vapor. The study results show that increasing the amount of atmospheric H_2O vapor can significantly reduce the concentration of HTO in the solution. Sakharovski et al. [80] increased the efficiency of the separation tower by changing the operating temperature at the top of the isotope exchange tower. Li et al. [81] evaluated the tritium separation efficiency of highly hydrophobic carbon-supported platinum catalysts (Pt/C/PTFE). The experimental results showed that the separation efficiency was higher at the optimal reaction temperature of 60~80 °C and a molar feed ratio of G/L of 1.5~2.5. The inhibitory effect of the kinetic factor was obvious at 80 °C and a G/L of 1.5. Sohn et al. [82] studied the problem of irreversible uniform poisoning and permanent loss of catalyst due to high internal diffusion resistance in the case of the Wolsong tritium removal facility (WTRF) deuterium removal device using hydrophobic catalyst benzene-divinylbenzene copolymer (SDBC) loaded on a platinum catalyst and LPCE tower. They believed that impurity control was the factor affecting the life of the packing. If no serious poisoning of the catalyst by impurities occurred, the LPCE tower could operate for more than 10 years without the need for any regeneration of the catalyst.

The combined electrolysis catalytic exchange (CECE) process combines electrolysis and catalytic exchange methods, and its greatest advantage is that the direction of the reactive components being transferred from the liquid water phase to the liquid water phase during hydrogen–water catalytic exchange is the same as the direction of the reactive components being concentrated in the electrolyte during electrolysis, which makes the separation factor of CECE as high as several thousand [83]. The exchange process is shown in Figure 3.

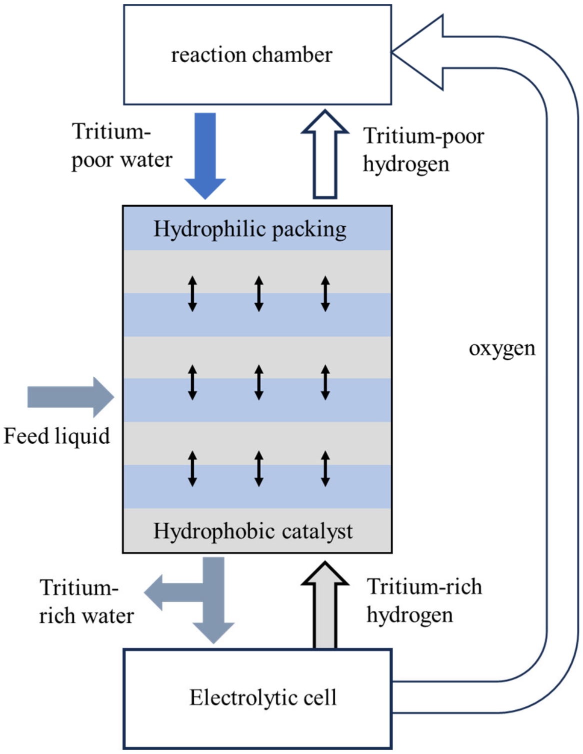

Figure 3. Process of CECE catalytic exchange column detritiation.

The important role of electrolysis in the CECE process is to provide phase transformation functions and complete the backflow phase reversal task at the bottom of the LPCE catalytic tower. At the same time, since the reactive components will be concentrated in the electrolyte during electrolysis, electrolysis can also increase CECE's ability to further preconcentrate deuterium or tritium. Compared with the VPCE and LPCE gas phase catalytic exchange processes, CECE has the function of concentration for tritium-containing gases, which can greatly reduce the amount of tritium-containing gases sent to subsequent processes and reduce the downstream energy consumption. Therefore, the application of the combined electrolysis catalytic exchange method is increasingly becoming apparent.

This technology was selected by the International Thermonuclear Experimental Reactor (ITER) as an important route for water deuterium removal. Canada, the United States, Japan, Russia, and China have all built CECE facilities of various scales.

The Saint Petersburg Nuclear Physics Institute has been operating an experimental industrial facility since 1995 to develop the electrolytic catalytic exchange (CECE) process for hydrogen isotope separation. The facility is also used to process tritium-contaminated heavy water; several tons of reactor-grade heavy water have been produced [84].

The experimental results of decontamination of heavy water by Alekseev's team [84] show that the decontamination factor is approximately 10^3. Up to 4.5 kg of heavy water with tritium content reduced to less than 10^5 Bq/kg can be extracted daily as the main product. The CECE process is suitable for high-flux PIK heavy water reactors decontamination facilities. The process can be applied in the ITER (International Thermonuclear Experimental Reactor) fusion facility. The domestic development of CECE-related processes is relatively late, with reports mainly from the China Academy of Engineering Physics and the China Institute of Atomic Energy Science. Wu Dong et al. [85] conducted technical research on deep purification and deuterium removal based on the joint electrolytic catalytic exchange process for the three tritium-contaminated water (light water) systems of inland nuclear power plants, ITER, and Fukushima nuclear power plant, and gave specific examples of process design. They proposed that a modular design scheme should be adopted when the feedwater containing tritium is large.

2.6. Electrolysis Process

The electrolysis process (EP) is a method used to concentrate tritiated water by exploiting the differences in the chemical bond energies of hydrogen isotopes. In this process, tritiated water is subjected to direct current. According to the two-phase distribution theory of isotopes, light isotopes (hydrogen and deuterium) are electrolyzed first, and tritium (T) is only electrolyzed once it reaches a certain concentration. As a result, the light isotopes concentrate in the gas phase, while the heavy isotopes concentrate in the liquid phase, thus achieving the separation of tritiated water [86,87].

In the 20th century, electrolysis in aqueous solutions has become an industrial method for obtaining heavy water. Early electrolysis separated hydrogen isotopes using alkaline solutions as the electrolyte. The traditional electrolysis method for processing high concentrations of tritium has the problem of self-radiation decomposition of the alkaline solution, which produces large amounts of secondary radioactive waste. The alkaline solution also causes strong corrosion to the pipe system, affecting the service life of the equipment [88,89]. Compared with traditional alkaline electrolysis, PEM has the advantages of small volume, high current density and electrolysis efficiency, long service life, and simple system process [90–94]. Research on PEM materials has received widespread attention. Zhou et al. [91] prepared graphene-Nafion and hBN-Nafion, two types of two-dimensional nanocarbon composite proton exchange membranes by solution casting method, and the ion exchange capacity, proton conductivity, and mechanical properties of the composite membranes were improved to varying degrees. In particular, when the mass fraction was 0.50%, the proton conductivity of graphene-Nafion and hBN-Nafion composite membranes was increased by 1.25-times and 1.14-times, respectively. When the initial tritium water activity was 3.51×10^{-7} Bq/L, the system could continuously electrolyze for more than 60 h, and the tritium–deuterium separation factors of the two composite membranes were 5.73 and 8.46, respectively, with tritium recovery rates of 78.53% and 85.35%, indicating that the hBN-Nafion composite membrane has better tritium–deuterium separation performance. Zabolockis et al. [92] developed a water phase tritium enrichment system based on a proton exchange membrane (PEM) electrolyzer and fuel cell. As the PEM, we used NafionTM and laboratory-synthesized sulfonated polyether ether ketone (SPEEK) membranes, and added a graphite layer to improve the tritium separation factor. The study confirmed the promoting effect of graphite on the separation efficiency.

However, studies have shown that PEMs generally experience a performance drop due to radiation exposure in practical applications [93,94]. The Canadian Nuclear Laboratories (CNL) conducted an exposure study that used various commercial and patented SPE materials and exposed them to highly tritiated water (similar to 1000 Ci/kg, 37 TBq/kg). Exposed at typical cell operating temperatures (60 °C), all types of commercial membranes were found to lose significant ion exchange capacity, show reduced water absorption, and show reduced stress until failure. Tensile tests showed that they were almost completely degraded even at low doses. Iwai et al. [95] tested the radiation resistance of Nafion 117 and Nafion 1110 membranes, finding that the membrane state would change accordingly in the case of a tritiated water activity of approximately 3.7×10^{13} Bq/kg. Therefore, researchers have also actively sought other membrane separation materials. Pushkarov et al. [96] evaluated the feasibility and efficiency of using bentonite, saponite, and kaolin as separation membranes for hydrogen isotope separation by electrodialysis. They found that tritium electrolyte solutions are filtered through weak permeation membranes by electrodialysis under the action of an electric field. The degree of proton conductivity of the membrane determines the strength of ion redistribution between dissociated HTO molecules at the cathode and anode chambers. Using kaolin in combination with bentonite increases the stability of the membrane. The largest isotopic effect was obtained in the montmorillonite–kaolin composite membrane, where the extraction factor α between the interlayer space was 1.16 and 1.12.

In PEM electrolysis, solid polymer electrolytes (SPE) function as proton conductors, separators of product gases, and insulators between electrodes. Therefore, research on solid polymers has also received widespread attention. Ogata [97] uses solid polymer electrolyte layers to electrolyze the separation of tritium from heavy water. The cathode is made of stainless steel or nickel. Electrolysis is conducted for 1 h at temperatures of 5 degrees, 10 degrees, 20 degrees, and 30 degrees. Palladium catalysts are used, and the generated hydrogen and oxygen are recombined and collected by a cold trap. The activity of the sample is measured using a liquid scintillation counter. The apparent separation factors of tritium in heavy water and light water at 20 °C are approximately 2 and 12, respectively. Wei [98], using density functional theory (DFT), investigated the influence of single-layer graphene (MLG) and single-layer hexagonal boron nitride (h-BN) on the permeability resistance and separation factor of hydrogen isotopes in SPE electrolytic environments. It was found that hydrogen isotopes could pass vertically through the geometric center of the two-dimensional crystal. It was believed that the existence of SW (55–77) defects in MLG and h-BN would significantly reduce their permeability barrier. Compared with traditional SPE electrolysis method (H+/D+ approximate value of 2, H+/T+ approximate value of 12), two-dimensional materials will significantly improve the separation factor of hydrogen isotopes. Wen et al. [99] developed a SPE solid electrolyte tritium water concentration device and conducted electrolysis concentration experiments on water containing about 1Bq/L of tritium, obtaining a concentration enrichment coefficient of 13.7 times. After one year of operation, the performance was stable.

In addition to high separation factor and high activity, the stability of the anode electrocatalyst is increasingly in demand. The exploration of the anode material in electrolysis is also a research focus in the electrolysis field. Xue [100] used gold as the anode catalyst, with a separation factor of 7.47 for Au/C in proton exchange membrane water electrolysis, which is approximately twice that of Pt/C. Furthermore, the electrochemical performance of the full cell is comparable to that of the Pt/C cell. Zhao et al. [101] used MoS_2-RS with a rich edge site (MoS_2-RS) as a hydrogen isotope separation electrocatalyst. The MoS_2-RS anode has a low overpotential of 182.4 mV at a current density of 10 mA cm^{-2}, a small Tafel slope of 61 mV dec^{-1}, and a high hydrogen–deuterium separation factor (S-H/D) of 10.22, which is much higher than the S-H/D of commercial Pt/C catalysts (6.33) in acidic conditions. It also has good long-term stability in acidic conditions.

Some researchers found that adding additives to the system can enhance the separation effect of electrolysis technology. Ando and others [102] added carbon carbide powder and mineral (silica) powder as additives to radioactively contaminated water bodies and treated the polluted water bodies through stirring/circulation and electrolysis. During the electrolysis process, colloidal particles of HTO deposited on the two electrodes under the action of direct current voltage, effectively removing tritium. The addition of additives enhanced the system’s removal of tritium.

As a tritium separation technology that has been industrially applied, ongoing efforts are being made to optimize the process equipment and operating conditions for electrolytic tritium separation. Varlam et al. [103] modified the HOGEN H series industrial electrolyzer for characterization. The electrolyzer reached a stable state after running for 120 h, with a concentration factor approaching five. Zeng et al. [104] constructed a high-current-density, high-durability PEM electrolyzer for hydrogen isotope separation. With a high current density of 1 a /cm^2, the isotope separation performance was very stable, and the electrolysis of deuterium water exceeded 700 h, proving the practicality of large-scale hydrogen isotope separation. It was also found through a computational model that high current density could significantly promote the tritium enrichment process.

The advantage of electrolysis is that it can achieve a high separation factor, and it is one of the auxiliary methods currently being used at home and abroad for the effective separation of deuterium and tritium in water. However, the energy cost of electrolysis is high, and the operating costs are expensive. Using electrolysis as a standalone process for the large-scale deuteration of tritium-containing water is economically challenging, so the technology is often combined with catalytic exchange technology and is mainly used for further concentration treatment of high-concentration tritium-containing wastewater.

3. Conclusions

At present, there are numerous types of tritium separation technologies, and these technologies can be combined with each other to achieve different enrichment effects (Table 1). However, since tritium and hydrogen are isotopes with similar physical and chemical properties, compared with conventional pollutants, tritium water treatment consumes more energy and has a higher cost. From the perspective of sustainability, the composition of the source term and the expected treatment effect should be fully considered before tritium water treatment, and the possibility of the simultaneous removal of other pollutants and tritium should be explored, thereby indirectly reducing the cost of tritium water treatment.

Table 1. Key tritium separation techniques comparison.

Technology	Tritium Separation Factor	Operating Temperature (K)	Industrial Feasibility	Technical Challenge
VPCE	0.47 [105]	473 [105]	Industrialized	Have been replaced
LPCE	0.14 [105]	298 [105]	Industrialized	Catalyst optimization, process equipment optimization
CECE	150–250 [106]		Industrialized	Catalyst optimization, process equipment optimization
Water distillation	1.056 [107]	333 [107]	Industrialized	
Cryogenic distillation	1.82 [108]	21–24 [108]	Industrialized	The technology is complex and the security risk is high
Electrolysis process	10 [109]	353 [109]	Mainly used in laboratories	Low processing efficiency
Membrane permeation	H/D: 1.05–1.09 [110]		Have matured	High membrane cost

Due to the development of nuclear fusion technology, research on the preparation of tritiated water that meets these requirements has gradually attracted the attention of researchers, especially tritium separation. In the future, technologies with high tritium separation coefficients and large processing capacities, such as LPCE and CECE, will develop rapidly. Although LPCE and CECE technologies have already begun industrial applications, their operating costs are high, and there is a need to further develop more durable catalysts and more energy-efficient processes.

The following four key conclusions can be drawn from the research progress in tritium separation technologies:

1. Significant Advancements in Tritium Separation: Recent developments in tritium separation technologies have been substantial, particularly with the integration and optimization of vapor phase catalytic exchange (VPCE), liquid phase catalytic exchange (LPCE), and combined electrolysis catalytic exchange (CECE) methods. By combining complementary techniques, the limitations of individual methods can be overcome, significantly improving the efficiency of tritium separation. For instance,

the CECE process combines electrolysis and catalytic exchange, not only enhancing the separation factor of hydrogen isotopes but also reducing energy consumption in downstream processes, thereby offering a more efficient approach for handling high-concentration tritiated water.

2. Advantages of solid polymer electrolyte (SPE) technology: SPE technology has demonstrated clear advantages in tritium separation, particularly in terms of reducing energy consumption and improving electrolysis efficiency. Compared to traditional alkaline electrolysis, SPE offers smaller equipment size, higher current density, longer lifespan, and simpler system design. This technology has become one of the leading solutions for processing tritiated water. SPE is especially effective in the treatment of high-concentration tritiated water and wastewater concentration, providing an innovative solution for enhancing tritium enrichment efficiency.
3. Electrolyte operation with tritium generates safety concerns; the number of facilities for water detritiation is low, and characterization of packing materials is carried out at a relatively small scale.
4. Energy consumption challenges of electrolysis: While electrolysis methods offer high separation factors and the ability to concentrate tritium, their high energy consumption limits their economic viability when used alone for large-scale tritiated water processing. As a result, electrolysis is typically combined with other separation technologies, such as CECE, to fully utilize its separation efficiency while minimizing energy usage. Moving forward, further optimization of electrolysis energy efficiency will be crucial to achieving cost-effective, large-scale treatment of tritiated water.

Author Contributions: Conceptualization, Z.Z. and Y.S.; methodology, Y.S. and F.L.; validation, Q.C. and T.L.; data curation, Z.Z. and Q.C.; writing—original draft preparation, Z.Z.; writing—review and editing, T.L.; visualization, T.Y. and W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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