

Approach for Development of Tritium (^3H) Removal Technology from Contaminated Water Using Adsorption Methods

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1. Introduction

With the operation of nuclear power plants, the radionuclides that are emitted and affect the environment most are tritium (^3H , T) and ^{14}C . Depending on the characteristics of the reactor, ^3H is generated more in heavy water reactors and relatively less in light water reactors. However, due to the narrowness of the national territory, domestic nuclear reactors are being operated close to each other at power plant sites, and the emission management of these nuclides is receiving keen attention.

As ^3H is detected from groundwater around the Wolseong nuclear power plant, where heavy water reactors are in operation, social interest in ^3H removal technology is increasing rapidly, in addition to concerns about internal exposure of residents around the power plant.

More than 1.3 million tons of ^3H contaminated water (average ^3H concentration: 1,000 Bq/ml), which is still increasing due to the nuclear accident at the nearby Fukushima nuclear power plant in Japan, is being seriously considered for ocean discharge due to the excess of storage capacity and the lack of proper removal technology. ^3H is a beta-emitter with a half-life of 12.3 years, and it is very difficult to separate and remove ^3H from water because it exists in the form of tritiated water (HTO) with almost the same characteristics as H_2O in water. Therefore, all countries that operate nuclear power plants have been vigorously conducting various studies to remove ^3H from water [1-2].

To date, commercialized technologies for removing ^3H include LPCE (Liquid Phase Catalytic Exchange) technology used at Wolseong Nuclear Power Plant, for heavy water reactors in Korea, and CECE (Combined Electrolysis Exchange) technology used at Fukushima Nuclear Power Plant, Japan. These technologies use cryogenic catalytic exchange method and/or an electrolysis method, so there is a limitation in processing capacity and an economic problem with high operating cost. Therefore, the development of large-capacity ^3H removal technology is urgent.

To solve the above difficulties, this paper focuses on the development of a new high-capacity/high-efficiency technology for ^3H removal by modifying and fusing four previously reported lab-scale tritium removal technologies. After analyzing and identifying the characteristics of existing technologies, new technologies are being developed at four participating universities. In addition, after grasping the characteristics of each technology, a semi-pilot scale device will be configured to develop a hybrid type ^3H removal system capable of large-capacity processing. In this work,

technologies under development will be briefly introduced, and strategies to develop a hybrid technology by combining these technologies will be described.

1.1 Objectives

This study aims to develop a 100 L/hr scale ^3H removal technology that is cheaper in construction and operation than the existing ^3H removal technologies. Until now, the characteristics of each technology have been identified for scale-up, and based on these technologies, lab-scale and semi-pilot scale processes have been being developed.

2. Method and Results

2.1 Technical Characteristics for Removing ^3H

Since one of the four reported ^3H removal techniques is not yet reportable, this paper selects and describes three techniques with high probability of success based on the results obtained so far. The first reported technology is to separate the vapor phase HTO through a vacuum-pressure process using a surface-modified inorganic porous material as a ^3H adsorbent. However, this technology is evaluated to have limitations in securing energy efficiency, economy, and process continuity when scaled up. So, we plan to apply an adsorption tower process capable of large-capacity treatment using a surface-modified inorganic porous material as an adsorbent to remove HTO from water rather than vapor phase.

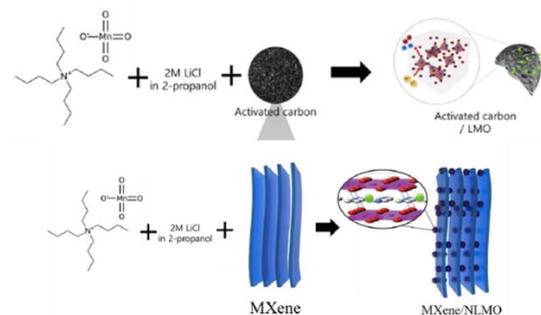


Fig. 1 Synthesis process of porous material supported LMO adsorbents for HTO

As a basic experiment for this, as shown in Fig. 1, adsorbents in which lithium manganese oxide (LiMn_2O_4 , LMO) with ^3H adsorption capability was supported on inorganic porous materials were developed. And the

ability to remove ^3H in water was evaluated through a batch-type adsorption experiment using these various adsorbents. The maximum removal rate of synthetic adsorbents was confirmed to be about 18% (Fig. 2). However, it is recognized that the maximum adsorption capacity of the developed adsorbent has not been confirmed because the content of ^3H is continuously decreasing over time. So, by controlling the amount of adsorbent, it is intended to improve the removal amount and removal rate.

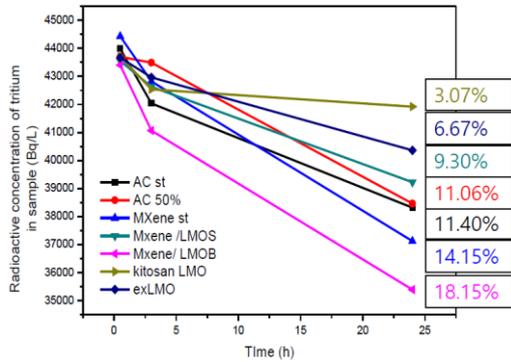


Fig. 2 ^3H adsorption performance of porous material supported adsorbents

The second technology removes HTO using an ion separation membrane coated with a spinel structure manganese oxide ($\lambda\text{-MnO}_2$) [3]. $\lambda\text{-MnO}_2$ (protonated manganese oxide) prepared by replacing Li^+ in the LMO lattice with H^+ ions through acid treatment is used as a ^3H adsorbent in this technology. It is known that $\lambda\text{-MnO}_2$ can remove ^3H by replacing H^+ in the lattice of $\lambda\text{-MnO}_2$ and T^+ of HTO. However, the reported process of this technology is difficult to scale up due to low throughput. To solve this problem an electrochemical ^3H removal module using a metal oxide adsorbent is being developed in this study (Fig. 3). This technology concentrates ^3H through an electrochemical module and applies $\lambda\text{-MnO}_2$ as an adsorbent in the concentration stage. To verify the capabilities of this module in a radiation-free way, using the property that the mechanism of adsorption of T^+ and Li^+ to $\lambda\text{-MnO}_2$ is almost the same, the concentration of Li^+ instead of ^3H was evaluated so far. It was confirmed that Li^+ was concentrated up to 6 times through this electrochemical module.

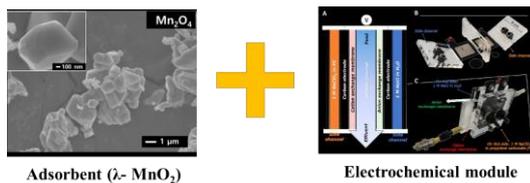


Figure 3 Development strategy for electrochemical ^3H removal module using metal oxide adsorbent

The last technology announced by DOE in the US is the ion exchange resin tower process filled with resin loaded with Al^{3+} . This process utilized the phenomenon that Al^{3+} holds HTO more strongly than H_2O . The overall process to be developed in this study will be designed to continuously adsorb, desorb, concentrate and store HTO, where resin will be supplied to continuous treatment processes including adsorption and regeneration (desorption). The resin was prepared with the recipe in Fig. 4, and an 80 cm ion exchange column was constructed to evaluate the removal capability of HTO.

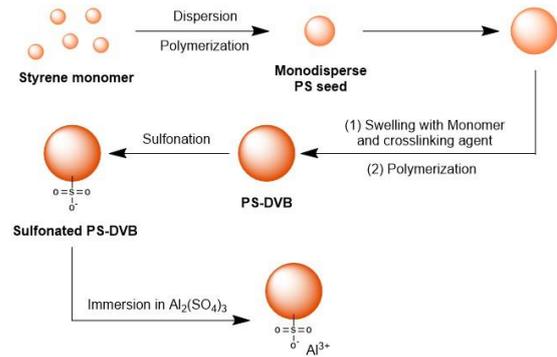


Fig. 4 Preparation of Al^{3+} loaded ion exchange resin

To evaluate the ^3H removal ability in each technology, a cocktail was prepared mixing 12 ml and 8 ml of a scintillation solution and HTO respectively, and the activity of ^3H was measured using a liquid scintillation counter (LSC, Hidex 300SL).

2.2 Strategy

Lab-scale device configuration and experiments for each of the aforementioned technologies have been conducted so far. In addition, research on ^3H removal technology using separation membrane technology is also being conducted. In future work, after grasping the characteristics of these four technologies, we plan to develop a hybrid-type process by selecting and integrating technologies applicable to the pilot scale. For more efficient ^3H removal, as shown in Fig. 5, a pretreatment process (removing impurity ions, particulates and suspended solids) based on desalination treatment to increase removal efficiency and a post-treatment process to treat the concentrated HTO will be added.

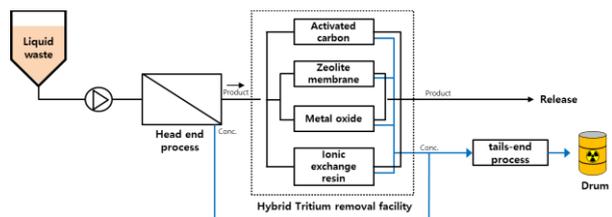


Fig. 5 Conceptual diagram of hybrid ^3H removal system

3. Summary

Various technologies will be developed through empirical experiments to separate and concentrate tritiated water (HTO) contained in contaminated water at nuclear power plants. The proposed four technologies will be carried out step by step from laboratory-scale research to semi-pilot-level research. Through this cooperative research in consortiums, we plan to develop a ^3H removal technology that can operate the concentration of HTO and regeneration of the adsorbent in a continuous process using ^3H adsorbents. Currently, the ^3H removal capacity of each technology is being evaluated. After grasping the characteristics and advantages of each technology, we intend to develop a hybrid type ^3H removal system in which each technology is combined. Since the research is still in early stages, this paper focuses on the introduction of each technology and the fundamental experiments on their ^3H removal ability. The progress of future development stages will be introduced through this journal.

4. Acknowledgments

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