

## TRITIUM EXTRACTION FROM WATER

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Tritiated water production is ubiquitous in facilities that handle tritium gas. Sources range from decontamination efforts, to the deliberate conversion of elemental tritium to tritiated water in processes that strive to reduce emissions to the environment, to gaseous effluents to the environment. At low concentrations, ranging from a few  $\mu\text{Ci/L}$  to  $\text{mCi/L}$ , high throughputs are required to process the high-volume, low-activity water. Combined Electrolysis Catalytic Exchange (CECE) shows promise by offering high throughput, reliability, economic viability, and facile coupling to isotopic separation systems if necessary. This paper will discuss the features of two production-scale CECE facilities: a  $7\text{-m}^3/\text{h}$  throughput system that uses an alkaline electrolysis cell and a  $21\text{-m}^3/\text{h}$  throughput system that uses a proton exchange membrane (PEM) electrolysis cell. The former is in service and has been modified to improve reliability; the latter is in the initial stages of commissioning.

**Keywords:** water detritiation, Combine Electrolysis Catalytic Exchange, liquid phase catalytic exchange, heavy water

## I. MOTIVATION

As of 2018 there are 451 nuclear reactors operating in 31 countries with an additional 59 reactors currently under construction. All of these nuclear power stations have chronic releases of tritium that can be measured in the surrounding groundwater. For example, in the United States, concentrations between 20 nCi/L and 0.1  $\mu$ Ci/L have been observed. The dose to an individual drinking 4.4 L of 1  $\mu$ Ci/L of water every day for a year is equivalent to only 30% of the annual dose received from natural background radiation. While the scientific community understands that the chronic release of tritium to the groundwater is not dose relevant, the public is far more sensitive to the issue. Even in locations where the groundwater activity is below the EPA maximum contaminant level of 4 mrem per year, land owners have successfully sued nuclear power stations over the contamination. Therefore, chronic tritium release to the groundwater remains an imminent concern for any nuclear power station operator. Newly constructed fission or fusion plants require robust strategies to mitigate the release of tritium to the environment to help alleviate public backlash and limit legal liabilities.

This paper will detail the combined electrolysis and catalytic exchange (CECE) method for removing tritium from water to either recover tritium from waste streams before discharge or to reduce the volume of radioactive water for long-term storage. It is important to provide a tritium recovery system as close to the source of contamination as possible to minimize the size of the system and the effort to extract the tritium. Unlike a fission plant, fusion plants will have a large variety of sources such as oxidation of HT/DT effluents from process loops, regeneration of glovebox cleanup system getter beds, decontamination of surfaces, and vacuum effluents. Rather than dilution and disposal of these waste streams, it will be far more effective to collect and volume reduce the water for long-term storage or recycling.

## II. LIGHT WATER OPERATIONS

CECE technology has been under development for several years in national laboratories [1–6] but has seen limited commercial deployment. The process provides an elegant, compact, and powerful option to concentrate tritium activities in water. The system comprises a Liquid-Phase Catalytic Exchange (LPCE) column integrated with an electrolysis cell. A schematic of the system is provided in Fig. 1. The electrolysis cell provides a constant supply of elemental tritiated gas to the bottom of the LPCE column. As the gas is directed up the column a counter flow of clean water is added to the top of the column. The isotopic exchange of the tritium from the rising elemental gas to the descending water has the effect of “washing” the tritium to the bottom of the column. Clean hydrogen gas is emitted from the top of the column while the majority of the tritium is contained in the water at the bottom. The tritiated feed stock water can be combined with the tritiated water leaving the column to collect in a tank. This water is used to feed the electrolysis cell to create more elemental gas. If the molar feed rate of the clean water at the top of the column plus the tritiated feed stock water at the bottom of the column are equal to the molar rate of release of clean hydrogen from the top of the column the system will remain in balance with all of the tritium concentrating in the water in the bottom tank.

The isotopic exchange from the gas phase to the water phase occurs in the LPCE column, which can have either a random or structured packing. In both cases the packing has two components: a catalyst on an inert substrate that is used to promote isotopic exchange between the elemental hydrogen and the water vapor along with some inert media that are used to promote vapor condensation of the tritiated water vapor. In a random packed column, the two components are equally mixed across the entire height of the column. In a structured packed column, the components are layered in an alternating manner across the height of the column.

It can be shown that the height of a packed column depends on the isotopic separation factor in the electrolyzer ( $\alpha_{el}$ ), the isotopic separation factor ( $\alpha_{col}$ ) in the column, the concentration at the top of the column ( $y_t$ ), the ratio  $\lambda$  of the molar gas flow up the column (G) to the molar flow rate of water down the column (L) ( $\lambda = G/L$ ), and the height-equivalent theoretical plate (HETP) for the catalyst according to the relation [7]:

$$h = \text{HETP} * \frac{\ln\left(\frac{x_{el} * \alpha_{col} - \lambda}{\alpha_{el} * y_t * \alpha_{col} - 1}\right)}{\ln\left(\frac{\alpha_{col}}{\lambda}\right)}. \quad (1)$$

The quantities  $\alpha_{el}$ ,  $\alpha_{col}$ , and HETP are fixed when operating at a fixed temperature with a particular catalyst. For a given gas-to-liquid molar ratio, the height of a column is determined by two parameters: the concentration of the electrolyte,  $x_{el}$  and the concentration of the effluent at the top of the column,  $y_t$ . Both parameters are at the discretion of the end user. Figure 2 illustrates the column height's dependence on those two parameters for fixed  $\lambda$ .

It is more economical to operate at a higher  $\lambda$  because there will be less counter-flowing water that needs to be electrolyzed back into elemental gas. For a chosen column height, the trade-off will be to operate at the highest possible  $\lambda$  within a prescribed emission discharge limit at the column top.

If the CECE system is being used to concentrate tritiated water for either long-term storage or to reduce volume as the first step in tritium recovery, the column height is selected for the maximum decontamination factor. Assuming the activity at the top of the column approaches zero, in steady state, tritium balance requires that the amount of tritium introduced to the system ( $L_f * x_f$ )

must equal the amount drawn as concentrate ( $L_c * x_c$ ), where  $L_f$  is the molar feed rate into the electrolysis system at a concentration of  $x_f$  and  $L_c$  is the rate at which the concentrate is extracted from the system at a concentration of  $x_c$ . It follows that the rate of concentrate draw is inversely proportional to the ratio of the feed activity to the concentrate activity:

$$L_c = \frac{x_f}{x_c} * L_f. \quad (2)$$

As an example, assume a feed concentration of 100  $\mu\text{Ci/kg}$  is delivered to the system operating at 90% efficiency, at a gas-to-liquid molar ratio of 2 ( $\lambda = 2$ ) and driven by a 21- $\text{m}^3/\text{h}$  electrolyzer. In steady state, this system will accept 418 U.S. barrels per year (66,480 L) and produce 3.3 L of concentrate at 2 Ci/L for a volume reduction of  $\sim 20,000$ . In this example, a column height of 3.9 m would result in an emission of 0.17 Ci per year and a net activity collection efficiency of 98%. Increasing the column height by an additional 0.7 m would reduce the effluent activity by a factor of 10.

### III. SYSTEM DETAILS

Many considerations must be addressed when designing and building a tritium-compatible CECE system. The electrolyzer will have the greatest tritium concentration in both the water and gas phases and must therefore be fully tritium hardened to reduce component failure and tritium release. Commercially available electrolyzers are not designed for tritium operations. They are not built with the correct materials for tritium service and do not have the required leak tightness ( $<10^{-9}$  scc/s helium) to prevent tritium leakage when the gas activity approaches 1 Ci/ $\text{m}^3$ . For

example, PVC piping, tygon tubing, and national pipe thread (NPT) fittings are not appropriate for a tritium system.

A tritium-hardened electrolyzer should contain only stainless-steel tubing with metal seals. All effluent streams like gas purges, oxygen discharge, and feed-water rejection systems must be monitored and, where necessary, treated to eliminate chronic tritium losses from the system. Figure 3 illustrates a tritium-compatible electrolyzer design that has been successfully implemented. This alkaline electrolyzer uses 33 wt% potassium hydroxide (KOH) as the electrolyte to help in the electrolysis of the water. The alkaline system has proven to be very robust and is able to continuously handle both low water quality and high tritium activities. Over time any contaminants in the feed stock will concentrate in and precipitate out in the cell. However, these impurities can be filtered out of the electrolyte without damage to the electrolyzer cell.

The commonly noted disadvantage of alkaline cells is the potential for potassium hydroxide migrating into and deactivating the catalyst in the LPCE column. Figure 3 shows how KOH transport to the LPCE column is reduced to trace levels. Hydrogen gas destined to the LPCE column is first passed through a rinser filled with stainless-steel wool to encourage KOH plate-out on the wool surface. Feedstock water is introduced to the electrolysis cell at the top of the rinser to redirect KOH transport back to the cell. This “washing” technique has been very effective: no KOH accumulation has been measured at the bottom of the LPCE column after thousands of operational hours. Downstream of the rinser, the hydrogen is passed through a catalyst to convert trace amounts of oxygen in the stream to water and then a condenser to reduce water vapor carryover from the cell to the column.

The oxygen gas stream leaving the electrolyzer also contains both tritiated water vapor and trace amounts of elemental tritium that must be removed before release. This is accomplished in a

similar manner to the hydrogen gas stream with a catalyst to convert the trace elemental into water and a condenser to cool out the majority of the water vapor. Molecular sieve driers polish the gas stream to reduce the relative humidity of the stream below  $-35^{\circ}\text{C}$  dew point. The effluent stream is passed through a tritium monitor to indicate when the drier approaches its loading capacity.

Important lessons were learned during several years of operation with the tritium-hardened electrolyzer illustrated in Fig. 3. Initially, the system operated very stably but after the first year of operation it became more difficult to operate at full capacity. The maximum attainable current decreased over time. Spurious overvoltage spikes across the cell routinely shut down cell operations. Precipitates in the electrolyte caused the cell to short circuit at high currents. The addition of an on-line filter did not resolve this issue. Removing the electrolyte from the cell and rinsing the cell with a small amount of water proved to be an effective solution. Periodic cell washes permit full-capacity operations with no issues.

One of the most labor- and cost-intensive maintenance issues centered on the stem tip replacement of bellows sealed valves in the oxygen drier circuit. Multiple types of stem tips have been tried but the warm ( $60^{\circ}\text{C}$ ), wet oxygen proved to be too corrosive for all but the VESPEL tips. Even these stem tips would last only a month before requiring replacement. Figure 4 illustrates an example of a failed VESPEL stem.

The remediation of this issue was to replace the catalyst/condenser/drier assembly in the oxygen side of the electrolyzer shown in Fig. 3 with a stand-alone small-diameter scrubber column. The column was packed with a wet-proof catalyst rinsed with a small counter flow of clean water in a manner similar to the LPCE. Elemental tritium and hydrogen in the oxygen stream were oxidized on the catalyst and then condensed in the inert packing and returned to the cell. To maintain a discharge emission at the  $\text{O}_2$  scrubber top below the target set on the hydrogen side,

the inactive water molar feed rate had to be matched to the molar hydrogen feed entrained in the oxygen stream. This additional inactive water feed was less than 5% of that introduced on the hydrogen side. The marginal reduction in throughput was offset by a significant increase in system uptime by removing a labor-intensive monthly maintenance requirement.

#### **IV. HEAVY-WATER TREATMENT**

The CECE system has also been used to concentrate tritium from heavy water. In this case the deuterium effluent gas from the top of the column would not be vented because it represents the first step in the final product. As well, the counter flow of heavy water introduced to the top of the column is derived from the  $D_2$  released from the column top. Figure 5 illustrates how the CECE system is configured to provide this functionality.

The heavy-water detritiation system is similar to a light-water detritiation system except a recombiner and condenser have been included at the top of the column to convert the deuterium gas into water. Some of this clean heavy water can then be used as the counterflow water while the rest is collected as product.

This system requires longer columns for the same detritiation factor (DF) of a light-water column because  $\alpha_{el}$  decreases from 5 to 2 at 60°C, and  $\alpha_{col}$  decreases from 4.9 to 1.55 at the same temperature [6,8–10]. Additionally, one degree of freedom is lost because the inactive heavy-water feed is not independent of the water production rate in the recombiner. The graph in Fig. 6 compares the column heights for the two case. It should be noted that to attain similar activities at the top of the column, the column height must be increased significantly and the gas-to-liquid molar ratio must decrease to below 2 in the heavy-water case.



Performance of a 25-m column using the configuration illustrated in Fig. 5 is shown in Fig. 7. Initially the system was run in closed loop ( $G/L = 1$ ) to establish a profile across the column and to produce sufficiently inactive heavy water to provide water to wash down the column from the top. A DF of  $5 \times 10^7$  was achieved. The dependence of DF on the G/L was explored between 4 and 16 metric tons processed. At a G/L ratio of 1.05, a DF of  $3 \times 10^7$  was achieved. Under these operating conditions the activity of the product water was  $0.2 \mu\text{Ci/kg}$ . Increasing the G/L to 1.33 increased the throughput but decreased the DF by approximately a factor of 10. A system failure at 16 metric tons destroyed the column profile, which was reestablished in the following 3 metric tons.

The heavy-water detritiation system can also be operated at reduced DF with a focus on reducing the dose to operators that are handling heavy water rather than producing heavy water with ultralow activities. An example is provided in Fig. 8. Heavy water with an activity of 2 Ci/kg is passed through a 5-m column to decrease the activity by about a hundredfold to 0.2 Ci/kg. A throughput of the order of 30 bbl/year can be attained with a  $6\text{-m}^3/\text{h}$  electrolysis cell. In this example, throughput can be increased if additional column length is available without compromising the target DF. In this scenario, heavy-water research reactors can swap higher-activity water for lower-activity water to reduce worker dose, resulting from DTO vapors.

## V. ENHANCING PERFORMANCE

The current heavy-water detritiation system comprises a recombiner that is limited to  $4.5 \text{ m}^3/\text{h}$  and an alkaline electrolyzer that operates stably at  $6 \text{ m}^3/\text{h}$ . The existing 4-in.-diam LPCE columns are expected to operate optimally at molar flows up to  $13 \text{ m}^3/\text{h}$ . Augmenting the system with a  $21\text{-m}^3/\text{h}$  electrolyzer will permit one to explore the column performances at higher flow

rates than those achieved to date. Additionally, the existing 17-m column can be decoupled into two 8.5-m columns to operate in parallel to help increase throughput.

Finally, the recombiner, which is the limiting throughput component, can be replaced with a more-economical, robust, and compact fuel cell to increase the throughput from 4.5 m<sup>3</sup>/h to the full gas flow of the electrolyzer at 21 m<sup>3</sup>/h. Figure 9 shows an upgraded heavy-water treatment system using a higher throughput proton exchange membrane (PEM) electrolyzer and a fuel cell.

Using the more advanced components will allow the system throughput to increase fivefold and to explore the nuances of operating a PEM electrolysis-based [11] detritiation facility. For example, PEM cell technology is reputed to require very clean feed water, unlike the more robust alkaline cell suggesting that an *in-situ* feed water treatment system be required. The added cost of the water treatment should be offset by the much more compact design of the PEM cell and the greater throughput in a smaller footprint. Secondly PEM cells have more distributed water discharge streams compared to alkaline cells, which will require additional management. Finally, the long-term performance of PEM cells in a tritium environment is unknown.

## VI. CONCLUSIONS

The use of nuclear power will continue to grow in the world, driven by the need for carbon neutral energy systems. Whether the reactors are fission or fusion based, it will be incumbent on the operators to reduce tritium releases to appease the public perception. Combined electrolysis and catalytic exchange systems similar to ones described above provide economical and robust forms of tritium capture and sequestration. The experience developed in an industrial environment attests to the simplicity and efficacy of these systems. With options to recover tritium from both light water and heavy water over a broad range of activities and throughputs using the small

footprint of the CECE technology indicates that this technology will become an important effluent mitigation tool.

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## REFERENCES

1. I. A. ALEKSEEV et al., "The CECE Experimental Industrial Plant for Reprocessing of Tritiated Water Wastes," *Fusion Sci. Technol.*, **41**, 3P2, 1097 (2002); <https://doi.org/10.13182/FST02-A22753>.
2. J. P. BUTLER et al., "Separation of Rate Processes for Isotopic Exchange Between Hydrogen and Liquid Water in Packed Columns 10," in *Proceedings of the Sixth International Congress On Catalysis*, edited by G. C. BOND, P. B. WELLS, and F. C. TOMPKINS (Imperial College, London, 1977), Vol. 2, p. 747.
3. J. P. BUTLER et al., "Catalytically Active Mass for the Exchange of Hydrogen Isotopes Between Streams of Gaseous Hydrogen and Liquid Water," U.S. Patent No. 4,228,034 (14 October 1980).
4. I. CRISTESCU et al., "Investigation of Separation Performances of Various Isotope Exchange Catalysts for the Deuterium-Hydrogen System," *Fusion Sci. Technol.*, **41**, 3P2, 1087 (2002); <https://doi.org/10.13182/FST02-A22751>.
5. L. GEENS et al., "Separation of Tritium from Aqueous Effluents," Commission of the European Communities (CEC), Luxembourg, Report EUR-11551 (1988).
6. A. PEREVEZENTSEV et al., "Difference in HETP and HTU for Isotopic Mixtures of Protium-Tritium and Protium Deuterium in Isotopic Exchange Between Water and Hydrogen on Hydrophobic Catalyst," *Fusion Sci. Technol.*, **41**, 3P2, 1107 (2002); <https://doi.org/10.13182/FST02-A22755>.
7. A. BRUGGEMAN et al., "Separation of Tritium from Reprocessing Effluents," in *Management of Gaseous Wastes from Nuclear Facilities*, IAEA-SM-245/52 (IAEA, Vienna, Austria, 1980), p. 157.

8. J. T. ENRIGHT and T. T. CHUANG, "Deuterium Exchange Between Hydrogen and Water in a Trickle Bed Reactor," *Can. J. Chem. Eng.*, **56**, 2, 246 (1978); <https://doi.org/10.1002/cjce.5450560213>.
9. K. M. KALYANAM and S. K. SOOD, "A Comparison of Process Characteristics for the Recovery of Tritium from Heavy Water and Light Water Systems," *Fusion Technol.*, **14**, 2P2A, 524 (1988); <https://doi.org/10.13182/FST88-A25186>.
10. J. H. ROLSTON, J. DEN HARTOG, and J. P. BUTLER, "The Deuterium Isotope Separation Factor Between Hydrogen and Liquid Water," *J. Phys. Chem.*, **80**, 10, 1064 (1976); <https://doi.org/10.1021/j100551a008>.
11. T. E. SPRINGER, T. A ZAWODZINSKI, and S. GOTTESFELD, "Polymer Electrolyte Fuel Cell Model," *J. Electrochem. Soc.*, **138**, 8, 2334 (1991); <http://jes.ecsdl.org/content/138/8/2334.abstract>.

## FIGURE CAPTIONS

Fig. 1: Schematic of the Combined Electrolysis Catalytic Exchange (CECE) system. Liquid-Phase Catalytic Exchange (LPCE) column and an electrolysis cell to process tritiated light water (HTO).

Fig. 2: Column height's dependence on the discharge concentration and the gas-to-liquid molar ratio.

Fig. 3: Schematic of an alkaline electrolysis system designed for tritium service with a take off point to an Isotope Separation System (ISS).

Fig. 4: Picture of a dissolved VESPEL stem tip of a valve removed from the oxygen circuit of an alkaline electrolysis cell.

Fig. 5: CECE configuration for detritiating heavy water (DTO).

Fig. 6: Comparison of the operational conditions needed for light- and heavy-water detritiation systems to achieve comparable activities at the column top.

Fig. 7: Performance of an alkaline-based heavy-water CECE system's dependence on the volume of processed heavy water.

Fig. 8: High through low DF heavy-water processing to reduce worker dose.

Fig. 9: Heavy-water detritiation system based on a proton exchange membrane (PEM) electrolyzer and a fuel cell.