

ISSUES ASSOCIATED WITH THE DETRITIATION OF LOW LEVEL AQUEOUS RADIOACTIVE WASTE

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Management of aqueous tritium-containing waste is viewed as a relevant challenge for many countries of the world. At present time, nuclear reactors designed for various purposes and spent nuclear fuel reprocessing plants are considered as key man-made sources of tritium waste. Tritium can be removed from water streams solely via physicochemical methods providing the separation of hydrogen isotopes. Two methods are considered as most promising in this respect, namely, water rectification under vacuum and chemical isotope exchange between hydrogen and water. The paper evaluates engineering and environmental aspects associated with the proposed methods providing light and heavy water detritiation.

Keywords: radioactive waste, tritium-containing water waste, detritiation, vacuum rectification of water, isotope exchange in the water-hydrogen system.

Trapping of tritium generated during the operation of nuclear power units of various types is considered of a great ecological importance. Light-water tritium-containing waste are generated both at nuclear power plants with their amount depending directly on the type and power level of relevant reactor and at spent nuclear fuel reprocessing plants [1], [2]. In particular, management of tritium-containing aqueous waste is currently seen as a most relevant challenge for Japan, where LRW are continuously generated due the Fukushima accident of 2011: the waste after being treated from all radionuclides except for tritium is stored in special containers at the NPP site. According to available data, by mid- 2019 the amount of such LRW with tritium concentrations of $(2-22) \cdot 10^5$ Bq/kg somewhat ranging from container to container exceeded

$1.1 \cdot 10^6$ m³ with a growth in the amount of such waste to $1.3 \cdot 10^6$ m³ forecasted by the end of 2020 [3], [4].

In most countries of the world, the concept providing for the reduction of technogenic tritium impact on the environment envisages the use of detritiation systems for water and gas flows providing a decrease in the volume of tritium-containing waste subject to further storage or disposal [1], [2], [5].

Treatment of aqueous process streams from tritium with its simultaneous concentration can be implemented based on hydrogen isotope separation methods solely, the most promising of which is the chemical isotope exchange (CIE) of hydrogen with water and vacuum distillation of water.

CIE separation of hydrogen isotopes between hydrogen and water is believed to be a most advantageous method due to high separation factor

achieved (for example, at $T=333\text{ K}$ for an isotope mixture $H-T$ $\alpha=5.18$, and for $D-T$ $\alpha=1.54$), non-toxicity of working substances and the process itself running at atmospheric pressure. Thanks to the hydrophobic catalysts developed in a number of countries around the world [6]–[9], including Russia, this method could be implemented in isotope exchange columns with an electrolyzer applied as a bottom flow reversal unit (BFRU). Due to the hydrophobic properties of the catalyst, the CIE columns have a low throughput (usually the linear velocity of hydrogen does not exceed 30 cm/s), while their diameter is usually not more than 100 mm . Typical height of the equivalent theoretical separation stage (HETS) for active catalysts in columns being up to 10 cm in their diameter at temperatures ranging between $333\text{--}345\text{ K}$ lies in the range of $20\text{--}30\text{ cm}$ [2], [10]–[11]. Figure 1 shows the basic process CIE flowcharts designed to address the de-tritiation challenge.

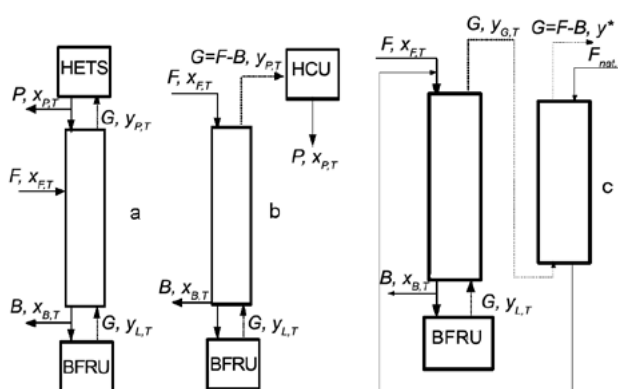


Figure 1. Schematic diagrams of separation units for de-tritiation by the CIE method in the water-hydrogen system: a – with an upper flow reversal unit, b – with a hydrogen combustion unit, c – with an additional CIE column

The separation column in Figure 1a simultaneously treats the feed stream F from tritium and concentrates the radionuclide with the treatment and concentration rates depending only on the heights of the concentrating (from $x_{F,T}$ to $x_{B,T}$) and exhaustive (from $x_{F,T}$ to $x_{P,T}$) parts. The open circuit in Figure 1b is designed to concentrate the heavy isotope and the tritium concentration in the treated stream P running from the hydrogen combustion unit (HCU) cannot be less than $x_{F,T}/\alpha$. Due to the problems associated with the development of reliable and safe HCU, in recent years, the diagram shown in Figure 1c is becoming more and more widespread: in it, the second CIE column irrigated with natural water is used to extract tritium and to bring its concentration in the treated hydrogen stream G to levels corresponding to the discharge

standards [12]–[14]. In addition to the problem of hydrogen oxidation noted above, the use of an electrolyzer as BFRU also poses a number of problems associated with high energy costs, radiation resistance of structural materials and a high probability of electrolyte autoradiolysis [15], [16]. Despite this, the CIE process is mostly used for heavy water de-tritiation purposes [17]–[19].

Water distillation method is widely used to separate both hydrogen and oxygen isotopes [20]. Since the separation coefficients are almost equal to 1, extraction involving a single separation effect is negligible, which requires the processing of large flows and a significant number of theoretical separation stages. In this regard, the process is run under vacuum, usually at $0.02\text{--}0.03\text{ MPa}$. The main advantages of the method include absolute environmental safety of the process, absence of corrosion and the possibility of its application to address problems deferring in their capacity from several kilograms to tons per year [21]. Development of high-performance packed contact devices reduces the height of the columns in a significant way and provides the processing of much larger flows compared to the CIE method [20].

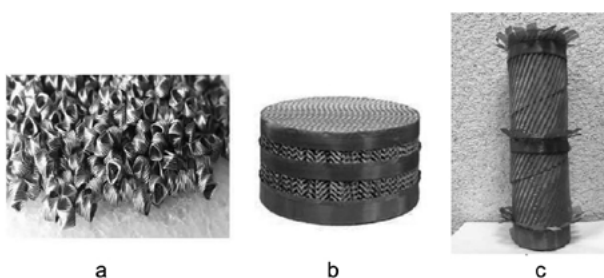


Figure 2. Some types of nozzles: a – irregular spiral prismatic nozzle (SPN), b – regular Sulzer CY nozzle, c – regular rolled tape-screw nozzle (RTSN)

As it comes to the water distillation process, stainless steel nozzles are applied most commonly: the most popular is the spiral prismatic nozzle (SPN) (Figure 2a). The paper [22] overviews a study of an SPN with element sizes ranging from 2 to 10 mm in columns with a diameter of 60 and 120 mm . The study showed that an increase in the size of the nozzle element by a factor of 5 could result in a proportional specific throughput increase from $L_{sp}^*=912\text{ kg/(h}\cdot\text{m}^2)$ to $L_{sp}^*=4,600\text{ kg/(h}\cdot\text{m}^2)$ at $P=0.02\text{ MPa}$ with a more than 7 -fold increase in the HETS (from 1.9 mm to 14.2 cm). In this case, an extremely weak dependence of HETS on the column diameter was noted.

Regular nozzles are characterized by an ordered structure, have a significantly higher throughput

and lower hydraulic resistance compared to the irregular ones. Sulzer Mellapak CY-type nozzle (Figure 2b) is widely used in the separation of mixtures with similar properties, including the isotope production area. The rolled tape-screw nozzle (RTSN) developed at the RKhtU named after D. I. Mendeleev should be noted as well: its distinguishing feature are the units that can have different height corresponding to the side of the column (Figure 2c), in contrast to the Sulzer nozzle, which is manufactured from standard-sized units. Comparison with the Sulzer Mellapak 750 CY nozzle at a pressure of 0.02 MPa showed that the HETS for RTSN turned out to be more than 2 times higher (16 and 8 cm, respectively), but its throughput being equal to $L_{sp}^* = 6,600 \text{ kg}/(\text{h}\cdot\text{m}^2)$ was about 1.5 times higher and unattainable for the Sulzer nozzle [23]. Based on the above, it can be concluded that, taking into account the higher throughput and almost no dependences between HETS and the flow and the diameter of the column, RTSN can be considered promising for its application for isotope separation purposes during vacuum-based water distillation.

There are only few examples of water distillation method application for detritiation purposes. The papers [24], [25] present calculations of heavy water deprotization and detritiation cascades using a mathematical model based on the stage-to-stage calculation method taking into account the hydrodynamic and other characteristics of the contact devices. [26] described a complex detritiation technology designed for various waste types generated during the production of tritium-labeled drugs by GE Healthcare (Cardiff) using water distillation to preconcentrate tritium from 3 to 2000 ppm.

[27] proposes a complex detritiation flowchart, which includes water distillation in combination with CIE in a water–hydrogen system. The paper [28] compares CIE and vacuum water distillation methods using the example of a detritiation unit

with a capacity of 100 kg/h of water. The study allowed to conclude that the capacity of the distillation unit is almost 50 times higher than the capacity of the required CIE column assuming comparable energy costs. It should be noted that, in our opinion, this comparison is not entirely correct, since the possibility of using cheap low-grade steam at nuclear power plants, as well as heat recovery operations [29] in case of water distillation will reduce the cost of energy consumption relative to CIE which requires electrical power for BFRU operation.

[30] considers the option of a vacuum water distillation column cascade providing the detritiation of low-level aqueous waste at a nuclear power plant. Figure 3 presents a schematic diagram of the process. The plant is designed to process 100 kg/h of water with a tritium content of $3.7 \cdot 10^6 \text{ Bq/kg}$ and provides a water treatment level of $7.6 \cdot 10^5 \text{ Bq/kg}$, which complies with Russian standards for waste water. The plant is designed as a cascade of distillation columns with exhaustion, which includes a concentrating (two-stage cascade with flow reduction) and an exhausting part.

In conclusion, it should be noted that various hydrogen isotope separation technologies have been developed to date: these can be used to address the challenge of treating aqueous process streams and aqueous tritium-containing RW from tritium. In this case, the choice of technology will be governed by a particular task and its specific aspects taking into account the required performance, reference to a specific facility and requirements concerning the weight and the size characteristics of separation equipment. According to the authors, to address the large-scale water detritiation problems, such as treatment of tritium-containing process streams from nuclear power plants or elimination of accumulated low-level water at the Fukushima-1 NPP, it seems most reasonable to apply vacuum water rectification method in large-diameter columns with a regular nozzle.

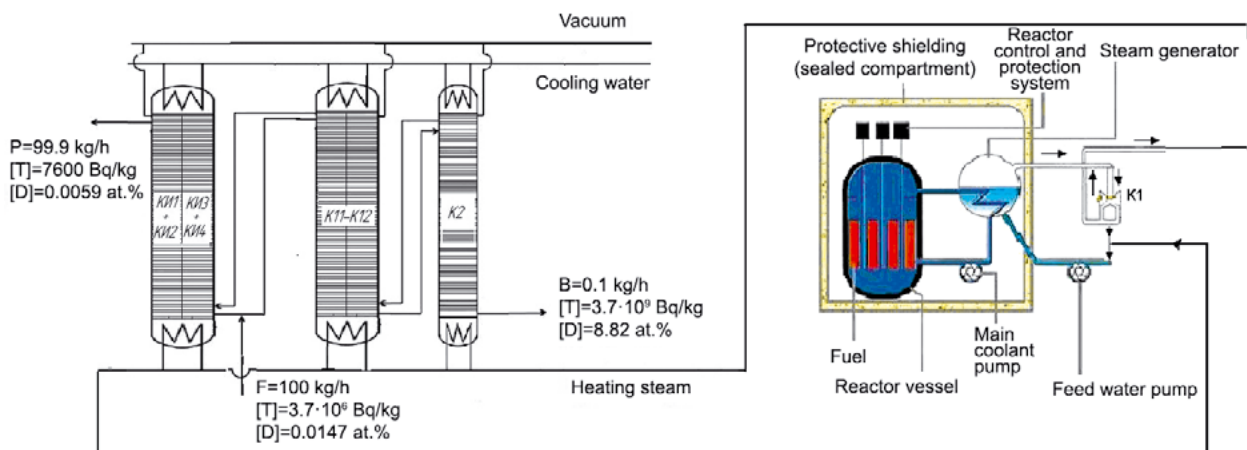


Figure 3. Schematic diagram of a detritiation unit for low-level tritium-containing aqueous waste based on a nuclear power plant

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