NEW MEMBRANE CONTACT DEVICES FOR AQUEOUS TRITIUM-CONTAINING WASTE DETRITIATION

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Article received on November 24, 2021

The article presents new membrane contact devices with a Nafion-type membrane designed for tritium-containing aqueous waste detritiation via isotope exchange method in a water-hydrogen system. The designs of such contact devices open up relevant prospects for the development of mobile units providing aqueous radioactive waste treatment from tritium while reducing the waste inventory intended for storage.

Keywords: *radioactive waste, tritium-containing aqueous waste, detritiation, membrane contact devices, Nafion membrane.*

Tritium (T, ^{3}H), i.e., radioactive isotope of hydrogen, a soft β-emitter with a half-life of 12.35 years, deserves particular attention when it comes to the problems associated with the management of technogenic radionuclides. This topic was selected specifically as a separate focus area due to the specific features of tritium, primarily since tritium coming from ambient environment and constituting to almost any hydrogen-containing substance, mainly water, can produce damaging and mutagenic effect on the human body. Technogenic tritium results from the operation of commercial and defense nuclear facilities, is generated at enterprises producing nuclear weapons and reprocessing spent nuclear fuel, as well as in various scientific centers conducting research in radiochemistry. To reduce the radiation exposure of personnel and to minimize the environmental damage, liquid radioactive waste should be treated from tritium by special physic-chemical methods for hydrogen isotope separation, in particular, by chemical isotope exchange (ChIE) in the water-hydrogen system.

In the presence of a heterogeneous catalyst, isotope exchange in this system occurs in two stages, the first of which is the catalytic isotope exchange (ChIE) and the second one is the phase isotope exchange (PhIE) of water:

$$H_2O_{(v)} + HX_{(g)} \overset{Cat}{\leftrightarrow} HXO_{(v)} + H_{2(g)} \quad \text{(ChIE)} \qquad (1)$$

$$HXO_{(v)} + H_2O_{(l)} \leftrightarrow H_2O_{(v)} + HXO_{(l)} \quad \text{(PhIE)} \qquad (2)$$

$$H_2O_{(l)} + HX_{(g)} \leftrightarrow HXO_{(l)} + H_{2(g)} \quad \text{(ChIE)} \qquad (3)$$

where X is a heavy isotope of hydrogen: deuterium (D) or tritium (T).

Common packed-type contact devices used in countercurrent separation plants for isotope exchange in the water-hydrogen system involve a layer-by-layer loading or a uniform mixture of a hydrophobic catalyst and a hydrophilic packing. To implement this process, some countries (Canada, Japan, Russia, Belgium, Romania, etc.) have developed platinized hydrophobic catalysts that do not lose their activity upon their contact with liquid water [1—4]. It should be noted that due to the hydrophobic properties of catalyst particles, such contact devices have low throughput, which limits

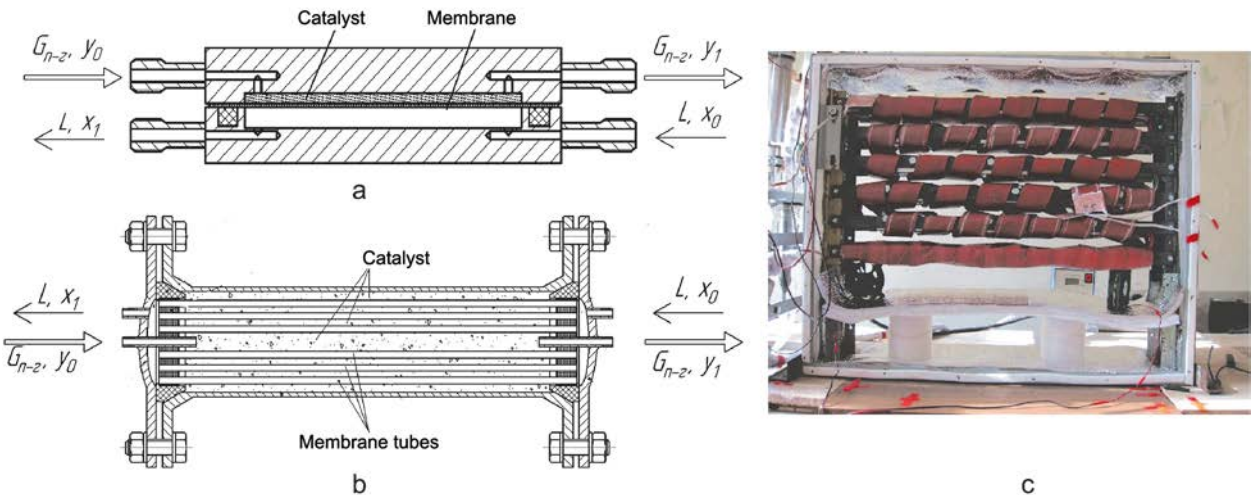

Figure 1. Membrane-type contact device:
a – with a flat membrane; b – with a tubular membrane; c – counterflow separating module with MCD

the use of PhIE method to relatively small-scale tasks of hydrogen isotope separation and also requires vertical orientation of separation columns being about 10 meters high [1, 4].

Recently, the Mendeleev University has developed a membrane-type contact device (MCD): it provides spatial separation of catalyst, which the vapor-gas flow passes through, from the liquid water flow by a membrane permeable to water molecules [5, 6]. In this case, the ChIE stage occurs in the vapor-gas space and the PhIE one — on the membrane surface. This design increases the contact device throughput and does not require their vertical orientation to arrange a countercurrent separation process.

Figure 1 shows the layouts of contact devices with flat (Figure 1a) and tubular (Figure 1b) membranes.

Table 1 presents comparative characteristics: the MCD volume (V_{MCD}) and the catalyst volume ($V_{cat.}$), the number of transfer units (TUN, N_y) and the mass transfer coefficient (K_{oy}) of contact devices with flat (MCD) and tubular (MCD TM) membranes [7—8] in the process of isotopic exchange at atmospheric pressure and a temperature of 60 °C. In this series of experiments, we used perfluorinated sulfocationite membranes MF-4SK and TF-4SK [9], which are domestic analogues of the Nafion membrane [10], as well as a Russian-made platinized hydrophobic catalyst RCTU-3SM.

Table 1. Parameters of contact devices with a flat and tubular membrane

Parameter	V_{MCD}, cm^3	$V_{cat.}$, cm^3	N_y	$K_{oy}\cdot10^3$, m^3/(m^2·s)
MCD, MF-4SK membrane: δ=250 μm, S_M=42 cm^2	20.5	10	0.52	4.3±0.2
MCD-TM, TF-4SK membrane: δ=150 μm, S_M=34 cm^2	10.8	9	1.47	15.0±0.3

As can be seen from the table, MCD-TM design with tubular membranes allows to increase the mass transfer coefficient by a factor of 3.5 compared to MCD with a flat membrane design, while halving the volume of the contact device.

Figure 1c presents the appearance of a countercurrent separating module assembly fitted with MCD as part of an experimental water detritiation unit with concentrating (6 MCD) and exhaustive (12 MCD) elements and an electrolyzer acting as the lower flow circulation unit.

The column was fed with tritium- labeled water supplied to its middle part, whereas water of natural isotopic composition was supplied to irrigate the exhaustive part. Table 2 shows the separation degree (K), the number of theoretical separation stages (NTSS, N), TUN and the mass transfer coefficient for typical experiments in which the maximum vapor-hydrogen flow rate in the catalyst reached 2.0 m/s.

Based on the data obtained, the dimensions of a mobile installation suitable for the detritiation of small aqueous RW volumes with a tritium content of $3.7\cdot10^6$ Bq/kg, given a water treatment capacity of 18.4 m^3/year, treatment and concentration levels of 100 were calculated. After such treatment, the amount of liquid RW would not exceed 1 % of the processed flow. It was demonstrated that 14 m^2 of the MF-4SK membrane and 20 dm^3 of the RCTU-3SM catalyst is required to set a single separation module with MCD, whereas the entire separation complex, taking into account the electrolysis unit based on an alkaline electrolyzer with a capacity of 5 m^3/h (n. a.) (weight of 2 tons, 1800 × 1100 × 2300 mm) performing the functions of a lower flow circulation unit, can be placed on a car platform with a carrying capacity of not more than 5 tons.

Table 2. Characteristics of the detritiation process in the experimental unit with MCD at P = 0.1 MPa; T = 60 °C

G_{H2}, dm³/h (n. a.)	Concentrating part			Exhaustive part			K_{tot}	$K_{oy}\cdot10^3$, m/s
	K_{conc}	N_{conc}	$N_{y,conc}$	K_{ex}	N_{ex}	$N_{y,ex}$		
60	1.51	0.62	1.24	24.10	9.49	10.81	36.40	4.05
100	1.25	0.33	0.68	13.05	7.69	8.76	10.95	5.13
150	1.05	0.07	0.15	7.95	6.18	7.04	7.36	6.08

In conclusion, it should be noted that this detritiation module is also able to process LRW as part of the Eco-type mobile complex available at FSUE Radon [11] that treats liquid waste with a low salt content from various radionuclides with the exception of tritium. Therefore, the challenge can be addressed in a comprehensive manner and tritium releases into the environment can be avoided during the discharges of water treated from other radionuclides.

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Bibliographic description

Rastunova I. L., Chebotov A. Yu. New New Membrane Contact Devices for Aqueous Tritium-Containing Waste Detritiation. *Radioactive Waste,* 2022, no. 1 (18), pp. 38—42. DOI: 10.25283/2587-9707-2022-1-38-42. (In Russian).