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# PURIFICATION OF RADIOACTIVE WASTES BY LOW TEMPERATURE EVAPORATION (MEMBRANE DISTILLATION)

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## ABSTRACT

A method of radioactive waste concentration by membrane distillation is presented. Water flow through a hydrophobic membrane results from the temperature gradient between membrane surfaces which are in contact with two waste streams, warm and cold. A transport of water from the warm to the cold stream occurs and radionuclides and other impurities are concentrated in the warm stream (retentate).

## INTRODUCTION

The purification of radioactive waste in solution can be accomplished by many methods including chemical precipitation, sedimentation, ion exchange, thermal evaporation, as well as membrane permeation.

In a previous paper [1] we demonstrated purification of model radioactive solutions and original low-level radioactive wastes (specific activity $< 10^4$ Bq/dm$^3$) by application of ultrafiltration preceded by complexation of ions: $^{51}Cr^{3+}$, $H^{51}CrO_4$, $^{60}Co^{2+}$, $^{137}Cs^+$, with high-molecular-weight ligands. Employing seeded ultrafiltration, the following activity reduction coefficients were obtained:

| | |
|---|---|
| $^{51}Cr^{3+}$: | 93-128, |
| $H^{51}CrO_4^-$: | 102-135, |
| $^{60}Co^{2+}$: | 56-75, |
| $^{137}Cs^+$: | 32-45. |

Thus the application of seeded ultrafiltration enables a good removal of radioactivity, but the activity is still higher than the authorized maximum limits for radioactive discharges into the environment. Further decontamination is necessary. Extensive feasibility studies and pilot plant operations showed some limitations in the use of pressure-driven membrane processes employed for this purpose [2,3]. The limitations are as follows:

- Membrane fouling and the need for regular cleaning operations, resulting in the interruption to processing. About 1% of secondary wastes is produced by cleaning solutions.
- The purification plant is rather complex and operates at increased pressure, involving pumps. A long time of operation is needed to assess the lifetime of individual plant components.
- The presence of complexants in waste streams may entail pretreatment before ultrafiltration or hyperfiltration.

This work has led to the use of membrane distillation (MD), which can be employed separately or in combination with existing methods of decontamination. Membrane distillation (MD) is a process of evaporation through a porous, hydrophobic membrane. The membrane separates two liquids at different temperatures, $T_{WARM}$ and $T_{COLD}$, where $T_{WARM}>T_{COLD}$ . The temperature gradient generates the partial vapor pressure difference and transport of the vapor from the warm to the cold side of the membrane.

We have previously shown that membrane distillation can be used for separation of isotopes [4,5], as well as for concentration of aqueous solutions of salts and acids

[6,7] and for purification of liquid wastes [8]. In the present paper, we propose the use of this process for purification of low-level liquid radioactive waste. Radioactive wastes that are a mixture of salts, colloids, and suspensions in water may be easily processed by applying this method.

## EXPERIMENTAL

### Apparatus

The laboratory tests were performed using the setup shown in Figure 1. It consists of two systems: the warm feed (A) and cold distillate (B) cycles, which are arranged in the direct contact membrane distillation (DCMD) configuration. The distillate passing the membrane condenses directly in the cold stream. Radioactive wastes are placed in the thermostatted vessel 2. They are circulated in the warm system and through the heat exchanger 4, which is pumped by peristaltic pump 3. The thermostatted reservoir 5 is filled with distilled water. The water circulates in the cold system through the pump 6 and the radiator 7. The temperatures of warm and cold streams are controlled by thermometers 8 and 9 and operating feed-back loops 10 and 11. The main part of the setup is a capillary module BFMF 06-30-33 (Euro-Sep, Polish-Scottish Ltd., Poland) permeation unit, with an effective area of 0.3 m$^2$. The module is equipped with Accurel® polypropylene capillary membranes, characterized by the following parameters:

| | |
|---|---|
| length of capillaries | 200 mm, |
| inside/outside diameter | 0.33/0.63 mm, |
| cut off | 0.6 μm |
| porosity | 30% |

### Experimental procedure

1. Preliminary experiments were performed using the permeation cell with the flat-sheet membrane described in [5]. The Accurel® polypropylene membrane used

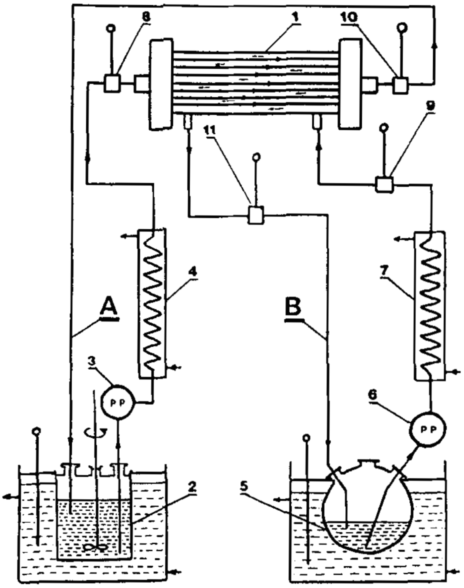

FIGURE 1. Experimental setup. A—warm system; B—cold system; 1—permeation module; 2—warm liquid reservoir; 3 and 6—peristaltic pumps; 4 and 7—heat exchangers; 5—cold liquid reservoir; 8, 9, 10, and 11—thermometers.

had a nominal pore size of 0.2 μm and an area of $15.2 \times 10^{-4}$ m$^2$. The radioactive model solution, with a specific radioactivity of $1.24 \times 10^4$ Bq/dm$^3$, was placed in the warm liquid reservoir, and the cold liquid reservoir was filled with distillate water. Membrane distillation was followed with $T_{WARM} = 60°C$ and $T_{COLD} = 23$ °C. The flow rates in the warm and cold systems were both $4 \times 10^{-3}$ m$^3$/h. Periodically, samples of distillate and retentate were drawn for analysis. The specific activity and conductivity of the samples were controlled.

Measurement of specific activity and total radioactivity was conducted using a standard probe equipped with a NaI/Tl scintillation crystal or an 800-channel analyzer DIDAC with the spectrometric probe SCINTILBLOC (Intertechnique, France). The measurements were conducted relative to standards with specific activity known

($^{51}$Cr, $^{60}$Co, $^{137}$Cs). The total concentration of Cr, Co, and Cs in the solutions was determined using an atomic absorption spectrometer (Perkin-Elmer 5000).

Conductivity measurements determined the total concentration of the salts in retentate samples on the basis of calibration curves.

2. Further experiments were conducted employing the capillary module, BFMF 06-30-33. To avoid the sorption of radionuclides in the system, the membrane surface was pretreated before the experiment with non-radioactive solutions containing the same compounds.

The warm stream (radioactive waste) was introduced into the capillaries, and the cold stream (water) in counterflow outside the capillaries. The temperatures of both streams were kept stable—warm stream inlet temperature - 50°C and cold stream inlet temperature - 30°C. The flow rates of warm stream and the cold stream were 8.3 x $10^{-3}$ $m^3/h$ and 12.4 x $10^{-3}$ $m^3/h$, respectively. Periodically, samples of distillate and retentate were drawn and specific radioactivity and conductivity were measured.

## Radioactive solutions

Experiments were performed using the model solutions and two original radioactive waste samples characterized by initial specific radioactivity $A_o$ and concentration of non-radioactive solute $c_S$ (Table 1).

## RESULTS AND DISCUSSION

The results of preliminary experiments conducted with flat-sheet membranes showed that membrane distillation produces an acceptably pure distillate and a more concentrated retentate solution. Further investigations with a capillary module confirmed that the membrane distillation can be usefully employed for the concentration of radioactive solution.

For all solution except S-1, the distillate flow rate was in the range 0.159–161 $dm^3/h$. As the concentration increased, the flow rate fell to a value 0.157–0.128

TABLE 1. RADIOACTIVE SOLUTIONS

| Notation | Composition | $A_o$ [Bq/dm$^3$] | $c_S$ [g/dm$^3$] |
|---|---|---|---|
| model solution | | | |
| S-1: | $^{51}CrCl_3$ + Na $NO_3$ | 1.6x10$^4$ | 55 |
| S-2 | $^{60}CoCl_2$+ NaCl | 1.25x10$^4$ | 0.8 |
| S-3 | $^{137}CsCl$ +$Na_2SO_4$ | 1.1x10$^4$ | 1.7 |
| S-4 | $^{60}CoCl_2$+$^{137}CsCl$+ $Na_2SO_4$ | 1.9x10$^4$ | 2.2 |
| S-5 | $^{51}CrCl_3$+ $^{60}CoCl_2$+$^{137}CsCl$ + $NaNO_3$ | 1.5x10$^4$ | 1.35 |
| original waste | | | |
| W-1 | $^{51}$Cr(12%), $^{60}$Co(47%), $^{134+137}$Cs(20%), other γ and β emitters (21%) | 2x10$^3$ | 0.25 |
| W-2 | $^{51}$Cr(32%), $^{60}$Co(18%), $^{134+137}$Cs(39%), other γ and β emitters (11%) | 4.7x10$^4$ | 1.2 |

dm$^3$/h, according to the duration of experiment. The flow rate was strongly dependent on the initial concentration of the feed solution, which in our case was non-radioactive mixtures of $NaNO_3$, $Na_2SO_4$ or NaCl. Table 2 presents the permeate flow measurements results, where $Q_{po}$ represents initial distillate flow rate and $Q_{pl}$ represents the flow rate at the end of the experiment. The dependence of distillate flux on the concentration of solute is shown in Figure 2.

During long-time experiments with the capillary module, the specific radioactivity in the distillate was held at a fixed level of 32 ± 5 mBq/dm$^3$. Conductivity was also stable at 1.6–2.1 μS. The effect of raising the concentration of radioactive solution is presented in Figure 3, where the variation of radioactivity with the increase of volume reduction coefficient $(VRC) = V_o/V_R$, defined below, is shown.

TABLE 2. PERMEATE FLOW RATE FOR RADIOACTIVE SOLUTIONS TESTED

| Solution | Duration of the experiment [h] | $Q_{po}$ [dm$^3$/h] | $Q_{p1}$ [dm$^3$/h] |
|---|---|---|---|
| S-1 | 14 | 0.077 | 0.027 |
| S-2 | 11.5 | 0.161 | 0.154 |
| S-3 | 12 | 0.16 | 0.137 |
| S-4 | 13 | 0.159 | 0.128 |
| S-5 | 12 | 0.16 | 0.147 |
| W-1 | 11.5 | 0.161 | 0.157 |
| W-2 | 12 | 0.16 | 0.146 |

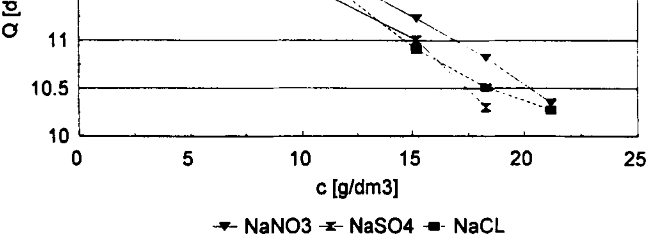

FIGURE 2. Distillate flux versus solute concentration .

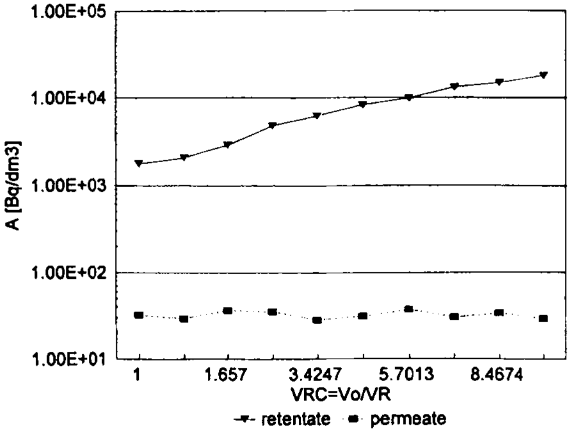

FIGURE 3. Raising the concentration of radionuclides via membrane distillation.

Radionuclides and other impurities present in the radioactive solution did not pass into the distillate stream. All the solute remained in the retentate, and this observation is confirmed by comparison of the three coefficients—*VRC*, $\chi$, $\phi$:

volume reduction coefficient (*VRC*):

$$VRC = \frac{Vo}{V_R},$$

where

$V_o$- initial volume of the feed,

$V_R$- final volume of the retentate.

concentration increase coefficient $\chi$:

$$\chi = \frac{CR}{Co},$$

where

$c_R$ - concentration of solute in the retentate,

$c_o$ - concentration of solute in the feed.

activity increase coefficient $\phi$:

$$\phi = \frac{A_R}{A_o},$$

where

$A_R$ - radioactivity of the retentate,

$A_o$ - radioactivity of the feed.

Coefficients *VRC*, $\chi$, $\phi$ calculated for all tested solutions are shown in Table 3. In every case we observe

$$\phi < \chi < VRC,$$

which suggests that there was sorption inside the apparatus: in the permeation module and in the pipes or joints in the experimental setup. The chemical pretreatment was not sufficient to prevent this difficulty. Sorption problems will have to be solved before further process development.

The experiments showed that membrane distillation can be considered as a method for radioactive waste concentration. The process of membrane distillation applied for radwastes treatment offers many advantages:

- Moderate process conditions: ambient pressure and moderate temperatures, close to the ambient temperatures. This enables the utilization of cheap, low-energy sources, such as waste heat from the cooling system of a nuclear reactor.
- High selectivity of the process produces concentrated solutions of radionuclides

TABLE 3. *VRC*, $\chi$, $\phi$ COEFFICIENTS CALCULATED FOR MODEL SOLUTIONS AND ORIGINAL RADWASTES

| Coefficient | S-1 | S-2 | S-3 | S-4 | S-5 | W-1 | W-2 |
|---|---|---|---|---|---|---|---|
| VRC | 1.638 | 9.302 | 10.152 | 9.622 | 8.621 | 10.152 | 9.756 |
| $\chi$ | 1.633 | 9.288 | 10.130 | 9.615 | 8.629 | 10.087 | 9.633 |
| $\phi$ | 1.598 | 9.210 | 9.621 | 9.378 | 8.478 | 9.889 | 9.349 |

(retentate) and high-purity water (distillate), higher than that from conventional evaporators.

- Moderate operational conditions permit the use of plastics instead of stainless steel in the apparatus, thereby minimizing capital costs and corrosion.
- Simple apparatus, without the movable parts existing in film-layer evaporators.
- Elimination of fouling and scaling phenomena on the hydrophobic surface of the membrane.
- The process can run at the high solute concentration.
- Small distance between evaporation and condensation surfaces makes the apparatus more compact.
- Low energy consumption and low operating costs. It was determined that the process is particularly profitable for medium-capacity plants [9]. In the purification plant for radioactive waste treatment, the volume of processed liquid effluents is not large. For conditions that exist in Poland, the plant capacity of 50 $dm^3/h$ seems to be sufficient.

Membrane distillation avoids various problems concomitant with normal evaporation such as corrosion, scaling or foaming, and drops entrainment. Lower operational temperature mitigates the corrosion of stainless steel, even at high nitric acid concentration. The entrainment of drops is avoided by a membrane which separates two streams.

Operation at low evaporation temperatures decreases the volatility of volatile nuclides such as tritium and some forms of iodine and ruthenium which are very often present in radioactive wastes.

It is important to note that when compared with other membrane methods, membrane distillation allows the complete purification of radioactive waste in one stage and does not require additional processes to ensure adequate purification of the water being discharged to the environment.

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