AVAILABILITY OF SEMIPERMEABLE MEMBRANES SEPARATION TECHNIQUES FOR THE TREATMENT OF LIQUID RADIOACTIVE WASTE

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Rezumat. *Tehnicile de separare prin membrane semipermeabile (ca: microfiltrarea, ultrafiltrarea şi osmoza inversă) se aplică unui domeniu larg de deşeuri radioactive, inclusiv unor soluţii care în mod obişnuit pun probleme serioase în timpul operaţiilor de tratare. Un exemplu relevant este oferit de deşeurile rezultate din operaţiile de decontaminare care au un conţinut ridicat de detergenţi şi agenţi de complexare. Lucrarea prezintă câteva teste experimentale cu tehnici membranare realizate pe un dispozitiv pilot, la Institutul de Cercetări Nucleare Piteşti. Scopul studiului experimental a fost elaborarea şi evaluarea unei tehnologii adecvate pentru tratarea deşeurilor radioactive lichide cu conţinut scăzut de săruri utilizând membrane semipermeabile indigene.*

Abstract. *The semipermeable membranes separation techniques (like: microfiltration, ultrafiltration and reverse osmosis) concern a wide range of radwastes that includes solutions, which are usually putting serious problems during treatment operations. A relevant example is given by the wastes issued from the decontamination operations which contain large quantities of detergents and complexant agents. The paper presents several experimental tests by membrane techniques carried out on a pilot scale device at Institute for Nuclear Research Piteşti. The purpose of the experimental study was to elaborate and evaluate an adequate technology for treatment of low salt content liquid radioactive waste, by using indigenous semipermeable membrane.*

Keywords: semipermeable membranes, decontamination, radioactive waste

1. Introduction

The nuclear industry generates a broad spectrum of low and intermediate level liquid radioactive wastes (LRWs). These liquid wastes may be produced continuously or in batches and may vary considerably in volume, radioactivity and chemical composition. A wide range of treatment methods has been used throughout the industry to treat these wastes. In recent decades various membrane separation processes have been developed and utilized in the field of potable

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water purification and more recently in the treatment of various process and waste liquors. Some of the membrane processes are capable of removing both dissolved and particulate contaminants. The best known and most utilized processes in the field of water and wastewater treatment are those utilizing pressure gradient as the process driving force. These processes include reverse osmosis, nanofiltration, ultrafiltration and microfiltration [1]. The pressure driven separation processes have been preferred by the nuclear industry.

2. General Overview of Membrane Separation Technology

2.1. Membrane Materials

It can be difficult to select the right membrane and membrane material for a given process, and some general information about the process environment must be available to make a proper selection. The first step is to determine the preferred process (RO, NF, UF or MF) and look at the membrane materials available. Based on the process environment the best suited membrane material can then be selected:

Cellulose acetate (CA). The material has a number of limitations, mostly with respect to pH and temperature.

Polysulfone (PSO). The main advantage is its exceptional temperature and pH resistance.

Polyvinylidenedifluoride (PVDF). Its main advantage is its high resistance to hydrocarbons and oxidizing environments.

Thin-film composite membranes (TFC). The main advantage is the combination of relatively high flux and very high salt rejection.

Except for established applications, the choice of membrane material may be difficult, and more than one membrane material often comes into question. As a general rule, only well planned and well performed pilot tests will provide good answers to membrane selection questions for given processes [2].

2.2. Membrane Module/Element Design

The spiral wound element type design was originally made exclusively for water desalination, but the very compact design and the low price made it attractive to other industries.

Tubular membranes can tolerate suspended solids, and most notoriously fibers, to a very high extent. All tubular membranes suffer from several disadvantages: require a lot of space, change of membranes may be quite difficult, large internal volume makes flushing and CIP costly.

Plate-and-frame (flat sheet) systems offer a very robust and compact design, but for a price. Modern flat sheet systems are built to tolerate very high pressure, in excess of 100 bar.

Fiber systems are similar to tubular systems. Only the ID of the fiber is small, typically <2 mm. The biggest difference from large diameter tubular membranes is that fiber systems are always unsupported.

Ceramic systems are very, very expensive. Theoretically, ceramic systems can be very effective for MF.

Hollow Fine Fibers was pioneer by DuPont for seawater desalination. They demand extremely good prefiltration [2].

2.3. Feedwater Pretreatment Requirements

Each membrane system will require some sort of feedwater pretreatment, either to protect the membrane integrity or to optimize its performance.

All good principles for pretreatment of the feed to membrane filtration equipment can be condensed into three rules [2]:

- Remove harmful suspended solids
- Remove oxidizers
- Prevent precipitation in the plant.

2.4. Operational Aspects and Radiological Considerations

Scale control. Several methods are used to minimize or eliminate the formation of these scale deposits.

Chlorine content control. The presence of chlorine in the feedwater can result in chemical damage of reverse osmosis membranes.

Control of acidity/alkalinity. Excessive acidity or alkalinity of the waste feed is detrimental to most membrane material.

Prevention of fouling. The system design should integrate measures to control various types of fouling, such as colloidal, organic and/or biological.

Radiological Considerations. Among the factors need to be considered in terms of radiological are: containment of leaks, sufficient space for membrane removal, identification of potential hot spots and location of shielding [1].

3. Applicability of Membranes Techniques to LRWs

The membrane technology has been used for removal of radionuclides from low-level liquid wastes arisen at nuclear power plants. Because reverse osmosis rejects nearly all contaminants from a solution (dissolved gases and tritium being two exceptions), the high purity product water may be recycled within the power plant. The purified water is usually of such low activity (sometimes after ion exchange polishing) that it is suitable for discharge to the environment. In recent years reverse osmosis systems have been used to replace or augment existing evaporation and/or ion exchange technology. Reverse osmosis systems in the nuclear industry are usually a part of an overall liquid waste treatment system [1, 3].

Ultrafiltration is used in the treatment of fuel pond storage waters and of aqueous effluents from reprocessing plants. The use of complexing agents in combination with ultrafiltration has been seen as having the potential to yield high decontamination factors (DFs) for specific ions [3,4]. Inorganic ultrafilters based on zirconium/carbon and other matrices have shown potential in radioactive waste treatment [3,5]. Published information [3,6-8] indicates that DFs in the region of 1000 for α and 100 for β and γ species can be achieved, with an overall volume reduction of the order of 10^4 [1,3].

Microfiltration is used for particle separation in wastewaters generated by nuclear power plants and often provides a concentration factor (CF) of 100. The process can be used in conjunction with precipitation processes, provided the precipitated particles are suitably coarse. Organic as well as inorganic microfiltration membranes can be used, depending on the characteristics of the feedwater. Ceramic microfilters have been used in the nuclear industry for high activity wastewaters because of that material's radiation stability [1, 3].

In the nuclear industry, the major use of nanofiltration membranes has been in boric acid wastewater treatment. These have been used to reject radioactivity while allowing boric acid to pass through with the permeate, thus allowing the permeate to be recycled or discharged. Nanofiltration may also be used in fuel fabrication facilities to remove dissolved uranium ions from wash solutions, permitting their discharge with no further treatment [1, 3]

As each application of membrane technology in a nuclear plant or elsewhere is unique due to specific local conditions, different processing objectives and various other factors, the membrane systems used vary from application to application.

3.1. Experimental Tests

Using a filtration device at the pilot-scale, which have been entirely designed and manufactured at the Institute for Nuclear Research (INR) Pitesti – Romania, performed experimental determinations concerning the treatment of liquid radioactive waste on semipermeable membranes.

At the INR Pitesti the purpose of the experimental study was to elaborate and evaluate an adequate technology for treatment of low salt liquid radioactive waste, by using indigenous semipermeable membrane. The waste of concern are those produced during the POD, CAN-DECON, CAN-DEREM and AP decontamination processes and their treatment should assure: the effluents with activity concentration below the prescribed limits, radioactivity confinement in a volume as low as possible and an acceptable cost [3].

Each membrane system will require some sort of feedwater pretreatment, either to protect the membrane's integrity and/or to optimize its performance [8]. The sorption of radionuclides on natural inorganic sorbents (zeolites) is excellent pretreatment for membrane filtration.

The paper presents some experiments using simulated waste solutions like secondary waste from the decontamination process with modified CANDEREM (Canadian Decontamination and Remediation Process) solution and secondary waste from decontamination with modified CANDECON (Canadian Decontamination Process) solution. The CANDECON simulated wastes are diluted solutions containing oxalic acid, citric acid and Na4EDTA with concentrations of about the same order of magnitude (1 mol m^{-3}) and various radionuclide contents. The CANDECON process fell into disfavor in 1984 when 50 mm deep intergranular attack was noticed on Peach Bottom – 2 piping after decontamination. Lab testing suggested that oxalic acid was the reagent causing this base metal attack. The CANDEREM process was thus created by removing the oxalic acid, leaving citric and EDTA acids as the active ingredients [9,10].

To improve efficiency and economics of the process it was proposed to treat the waste by combining the sorption of radionuclides on volcanic tuff from the area of Marsid (Romania), converted to Na^+ form, with membrane filtration.

The membranes used are of acetate cellulose type, Membrafil® and Membrasep®, provided by the Research Center for Macromolecular Materials and Membranes Bucharest. The nominal porosity, the average pore diameter and the distillated water flux of the microfiltration membranes were 75-85 %, 0.1-0.45 mm and 4.1×10^{-4} - 5.6×10^{-4} $m^3m^{-2}s^{-1}$, respectively.

For the ultrafiltration membranes used, the nominal porosity, the molecular weight cutoff (MWCO) and the distillated water flux were 80-85%, 10-20 kDa and 0.4×10^{-4}-1.4×10^{-4} $m^3m^{-2}s^{-1}$, respectivelly. For the reverse osmosis membranes used, the salt rejection and the permeate flux were 90-92% and 26-40 $lm^{-2}h^{-1}$, respectively [10].

3.2. Removal of $^{134,137}Cs$ and ^{60}Co from Simulated Radioactive Waste in tests at pilot-scale

The method developed was tested in the experiments with CANDECON, CANDEREM respectively, simulated radioactive liquid waste, on 20 dm^3 batch scale and with liquid radioactive waste without decontamination compounds.

The radioactive compositions of simulated waste solutions used are summarized in Table 1.

Table 1. Radioactive compositions of simulated waste solutions used for the experimental tests

Studied solutions	*Conductivity, [μS/cm]*	*pH*	*Radioactivity Concentration, [kBq/l]*		
			^{60}Co	^{134}Cs	^{137}Cs
CANDEREM simulated radioactive waste	1102	3-3.5	3.0±0.05	0.14±0.01	25.5±0.05
CANDECON simulated radioactive waste	655	3.5	2.4±0.08	0.07±0.01	22.7±1.0
Radioactive waste(DR1) (without decontamination compounds)	145.3	5.5	0.8±0.02	N/A	14.8±0.2
Radioactive waste(DR2) (without decontamination compounds)	187.9	5.5	0.8±0.02	N/A	15.8±0.2

For the pretreatment, 200 g of the zeolite in Na^+ form (0.5-1mm) was added to a 20 dm^3 CANDECON or CANDEREM simulated radioactive liquid waste. After mixing and 7 days of standing, phase separation was performed by microfiltration, ultrafiltration and reverse osmosis. Another test was done with the pretreatment by the addition of the following coagulant recipe: $[Fe(CN)_6]^{4-}/Al^{3+}/Fe^{2+}$= [100/100/100]mg/l waste. After settling phase separation was performed by microfiltration, ultrafiltration and reverse osmosis. For the separation, pH of samples was adjusted to 8.0–8.5 [10].

Pretreatment, such as pH adjustment, is used to maximize soluble contaminant precipitation. The microfiltration removal efficiency of gross β/γ of the combined radioactive waste from the Decontamination Center and Chemical drain system increases between pH 6 to 9, and remains invariant at about 90% thereafter [11]. The ultrafiltration rejection rates of Co and Cs increase as pH increases [12].

The experimental conditions of the microfiltration system were:

- Dead end filtration
- Constant feed pressure: 0.1 MPa
- Recovery factor: 100%
- Membrane surface: 0.5 m^2
- Membrane configuration: cartridge with plane membrane.

The experimental conditions of the ultrafiltration system were:

- Batch operation mode
- Cross-flow filtration

- Constant feed pressure: 1 MPa
- Recovery factor: 85%
- Membrane surface: 3 m^2
- Membrane configuration: spirally wound.

The experimental conditions of the reverse osmosis system were:

- Batch operation mode
- Cross-flow filtration
- Feed pressure: 1.6-2.8 MPa
- Recovery factor: 80%
- Membrane surface: 3 m^2
- Membrane configuration: spirally wound.

After each of the stages, the activity concentration of the solution was measured. The results of this treatment process are summarised in table 2.

Table 2. The global retentions for pilot scale experiments

	GLOBAL RETENTION, %					
Waste	*CANDECON*		*CANDEREM*		*DR1*	*DR2*
Pretreatment	*Sorption*	*Coprecipitation*	*Sorption*	*Coprecipitation*	*Sorption*	-
Retention ^{60}Co	60.1	58.6	47.3	42.3	83.0	87.2
Retention ^{134}Cs	>68.8	>36.9	>62.9	>11.4	N/A	N/A
Retention ^{137}Cs	92.1	56.8	92.0	52.5	91.5	99.9
DF *	8.92	2.3	8.17	2.06	11.20	136.66

* - decontamination factor

Conclusions

The membrane based separation systems provide an improved treatment technique for the liquid radioactive waste.

The ^{137}Cs retentions obtained for the pilot test were 92% and 99.9% for simulated solutions without decontamination compounds.

The decontamination compounds were decreasing the retention by semipermeable membranes, especially for cobalt.

R E F E R E N C E S

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