Aspects Concerning the Emulsion Membranes for the Radioactive Metal Separation from Contaminated Wastewater

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Development of an emulsion membrane (ELM) was carried out, in view to separate the radioactive metals (cobalt and uranium ions) from the contaminated waters. For this purpose, we have studied by their specific properties, Span 80 (Fluka) as emulsifier, Aliquat 336 (tricapril-methyl-ammonium chloride) and an alkyl phosphoric ester, as carriers. Tests with emulsion membranes on wastewater containing uranium and cobalt radio nuclides were performed.

Keywords: ELM, surfactants, radioactive metal removal

The emulsion type liquid membranes exhibit two of the requirements unsolved in the classical separations by solvent extractions, namely: very large mass transfer area and minimum amount of membrane solvents.

However, in the actual development stage of the separation methods, the percentage of the separations by means of the emulsion membranes is not so high, caused by two important problems: obtaining of stable primary emulsions and the difficulty to breakdown double emulsions (after the separation of the required compound).

The wasted waters resulted from nuclear activities or other industrial processes are contaminated with radio nuclides, extremely dangerous to the human health and the environment. Over the last decades, there are increasing concerns about radioactive wastes management, due to the problem of environmental pollution. One of the challenging problems in the wastes management is to clean aqueous wastes from hazardous elements before reusing or discharging them to the environment.

A relatively new separation technique used to remove the radioactive metals from wasted waters is pertraction or liquid membranes technique [1-10].

Our work has as main goal the study of the possibilities of retention of natural uranium and ^{60}Co from wasted waters by the emulsion liquid membranes technique (ELM). The uranium is provided from the nuclear fuel fabrication process for the nuclear power station, and the cobalt from the decontamination process of the ion exchangers' filters of TRIGA experimental reactor - RAAN-SCN.

The separation process by emulsion membranes implies a three steps process (fig. 1,2):

- preparation of water / oil type primary emulsion, where the aqueous phase is the receiving phase and the oil phase is the membrane phase, outer the micelles. The emulsion is performed with an HLB<4 emulsifier [11-15]. The carrier, as it is known from literature, is solubilized in the membrane phase;
- the dispersion of the primary emulsion in the source phase (the aqueous waste), forming a water / oil / water double emulsion. A radionuclide – carrier complex is formed, which is transported through the membrane inside the micelles of the primary emulsion, which contains the receiving phase. An exchange reaction is taking place, the carrier is released, and the radionuclide remains within the receiving solution, immobilized as an ionic product;
- separation and destruction of the double emulsion, with the recovery of the primary emulsion and the aqueous solution from which we extracted the transported permeate.

The study regarding the retaining of the radio nuclides by the ELM technique had as main purpose the set up of the following parameters:

- choice of the receiving aqueous phase, depending on the nature of the radionuclide and the *p*H of the source phase. Alkaline and acid receiving phases of various concentrations were studied, in order to set up the optimum;

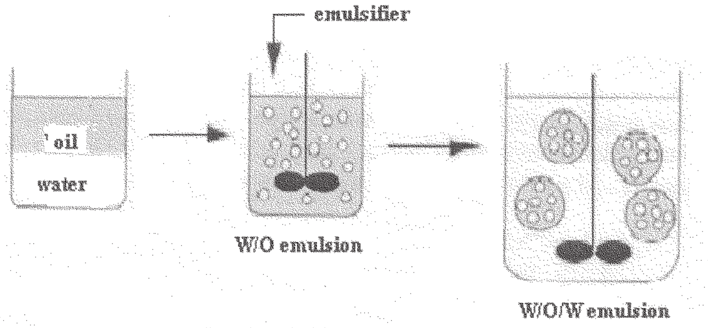

Fig 1. Forming of the W/O/W emulsion

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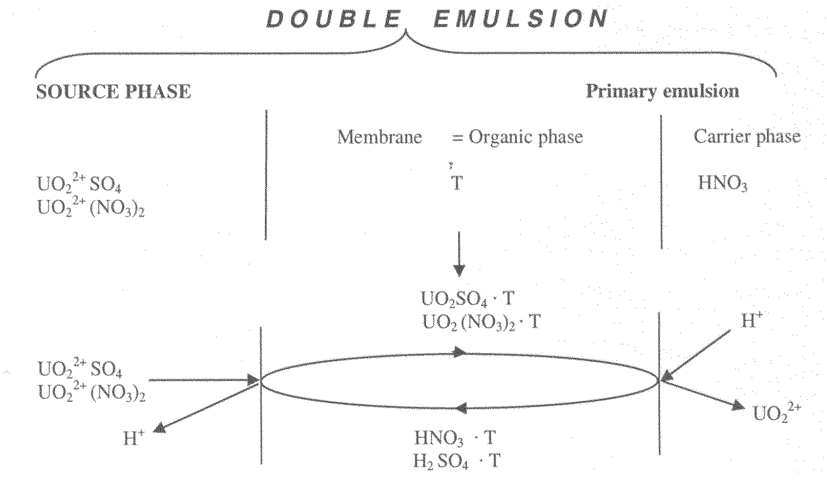

Fig 2. Principle of uranium retention from the waste by the emulsion type liquid membranes technique

- selection of the emulsifier (oil-soluble) needed to the obtaining of a primary emulsion and the set up of the optimal concentration;
- selection of the carrier and its concentration in the organic phase;
- setting of the optimal ratio organic phase / receiving phase;
- setting of the optimal parameters in order to obtain a stable primary emulsion: time, stirring speed, temperature.
- setting the optimal ratio wastewater / primary emulsion;
- setting of the optimal parameters in order to obtain a waste water : primary emulsion double emulsion: time, stirring speed, temperature;
- evaluation of the extraction yield of the radionuclide from the waste water.

Experimental part

Materials and methods

Source phase contains the uranium, cobalt ions respectively, which are to be separated.

The uranium aqueous waste used in our researches has a natural uranium content ranging between 0.38 – 164.8 mg U/L, and a *p*H value ranging between 1.5 – 7.

The uranium content was spectrophotometrically determined with a method based on the uranium (VI) extraction from the aqueous waste water with tri-n-phenylphosphinoxide in toluene, followed by acidulation , reduction of U(VI) to U(IV) and forming of a coloured complex with arsenazo III. The color intensity was determined with of a Hach DR/ 3000 spectrophotometer at 665 nm.

The cobalt aqueous waste has an initial activity of 9333 ± 208Bq/l and *p*H = 3.5.

The cobalt content was determined with of a multichannel γ spectrometer with a hyperpure Ge detector.

The organic phase – carrier and emulsifier - kerosene solution .

The kerosene we have used has a refractive index of 1.4551 at 20°C de, an inflammability point of 48^0C, and a distillation range between 215-370 C.

The emulsifier used in emulsion forming is: Span 80 (Fluka) – table 1.

The studied carriers were: Aliquat 336 (tricapril-methyl-ammonium chloride - Fluka) and the alkylphosphoric ester – table 2.

The receiving phase – we have studied the following receiving phases :

- solution 0,1% $NaHCO_3$
- solution 5% HNO_3
- solution 10% HNO_3
- solution 5% NaOH
- solution 0.05M Na_2CO_3 +0.005M NaOH

The primary emulsion was prepared by dissolving the emulsifier and the carrier into kerosene, and then by adding a volume of the receiving phase followed by emulsification by help of a Heidolph stirrer, at a stirring speed of 1700 rot/ min for one hour.

The aqueous phase / organic phase ratio is 1:1, whose value was kept at a constant level during the experiments. In order to obtain the optimal composition of the primary emulsion various concentrations of emulsifier, carrier and

Table 1

CHARACTERISTICS OF THE EMULSIFIER

Commercial name	Chemical name	HLB	Viscosity Pa.s(20^0C)	Soluble in
SPAN 80	Sorbitan monooleate	4.3	1000	Organic solvents

Table 2

CHARACTERISTICS OF THE ALIQUAT 336 AND ALKYLPHOSPHORIC ESTER CARRIERS

Carrier	Refractive index (n_D^{20})	Density (d^{20}) g/cm^3	Inflammability point	Solubility in water (20^0C) g/L	Boiling point ^{0}C	Melting point^{0}C
Aliquat 336	1.4665	0.884	> 110^0C	10		
Alkylphosphoric ester (TBP)	1.4240	0.9709	-	-	180-183	-79

receiving phase were considered. The stability of the primary emulsion was supervised, and only the systems with a stability of at least 20 min. were selected.

The double emulsion was performed by dispersing the primary emulsion into the contaminated waste water. Various waste : primary emulsion ratios and waste passes through the emulsion were taken into consideration. The dispersing was carried out with a magnetic stirrer at 450 rot/min, during 20 min. We have selected only the systems with an instantaneous separation after stopping the stirring and with a transparent aqueous layer.

The uranium activity concentrations in the unpurified waste (c_1) and the purified waste (c_2) were spectrophotometrically determined.

The purification yield (η_U) of the wastes containing uranium was calculated according to formula 1:

$$\eta_U = \frac{c_1 - c_2}{c_1} \cdot 100 \qquad (1)$$

The cobalt activity concentrations in the unpurified waste (AC_1) and purified waste (AC_2) were spectrometrically determined by means of a multichannel γ spectrometer with hyper pure Ge detector.

The purification yield (η_{Co}) of the wastes containing cobalt was calculated according to formula 2:

$$\eta_{Co} = \frac{AC_1 - AC_2}{AC_1} \cdot 100 \qquad (2)$$

Results and discussions

The composition and stability of the tested primary emulsions are given in table 3.

All the emulsions accomplished the compulsory stability conditions and have been tested in order to establish the Co and U radionuclids retention capacity (tables 4 and 5).

The primary emulsion A is efficient in cobalt retention. Even at the first pass the yield is 88.07%, and after three consecutive passes the yield is 95.48%.

Table 3

COMPOSITION AND STABILITY OF THE PRIMARY EMULSIONS

Primary Emulsion	Carrier	Receiving phase	Remarks
A	0.5% ALIQUAT + 1%TBP	1 % $NaHCO_3$	Stable emulsion for 30min
E2.1	0.5%TBP	5% HNO_3	Stable emulsion for 20min.
E2.2	0.5%TBP	10% HNO_3	Stable emulsion for 20min.
E2.3	0.5% ALIQUAT +0.5%TBP	5% HNO_3	Stable emulsion for 30min..
E2.4	0.5% ALIQUAT +0.5%TBP	10% HNO_3	Stable emulsion for 30min..
E2.6	0.5% ALIQUAT +0.5%TBP	5% NaOH	Stable emulsion for 105min.
E2.7	0.5% ALIQUAT +0.5%TBP	1:1 solution 0.1M Na_2CO_3 +0.01M NaOH	Stable emulsion for 20min.

Table 4

RESULTS CONCERNING THE COBALT RETENTION AT PASSING THROUGH EMULSION A, WASTE: EMULSION RATIO A=10:1

No. exp.	Initial Co activity concentration in waste AC_1 (Bq/l)	Final Co activity concentration in the purified waste AC_2 (Bq/l)	Extracted Co activity concentration AC_1-AC_2 (Bq/l)	Purification yield (%)	Global yield (%)
1	9333	1113	8220	88.07	**95,48**
2	1113	528	585	52.56	
3	528	422	106	20.08	

Table 5

RESULTS REGARDING THE URANIUM RETENTION AT PASSING THROUGH THE E2.1-E2.7 EMULSIONS, WASTE: EMULSION RATIO =10:1

No. exp.	Tested emulsion	waste pH	U content in the unpurified waste, c_1 (mg/l)	U content in the purified waste, c_2 (mg/l)	Purification yield (%)
1	E2.1	7	0.38	0.036	90,53
2	E2.2	7	0.38	0.084	77.89
3	E2.3	7	0.38	0.042	88.95
4	E2.4	7	1.044	0.066	93.68
5	E2.6	7	1.044	0.124	88.12
6	E2.7	7	1.044	0.114	89.08

Table 6
RESULTS REGARDING THE RETENTION OF URANIUM PRESENT IN VARIABLE AMOUNTS
IN THE WASTE WATER, AFTER PASSING THROUGH THE E2.1 EMULSION, WASTE: EMULSION RATIO =10:1

No. exp.	Tested emulsion	waste pH	U content in the unpurified waste (mg/l)	U content in the purified waste (mg/l)	Purification yield (%)
4	E2.1	1.5	164.80	78.80	49.09
3	E2.1	2.0	107.68	57.88	46.25
2	E2.1	3.0	15.28	8.77	42.60
1	E2.1	7	0.38	0.036	90.53
5	E2.1	0,5	3990	3930	1,5

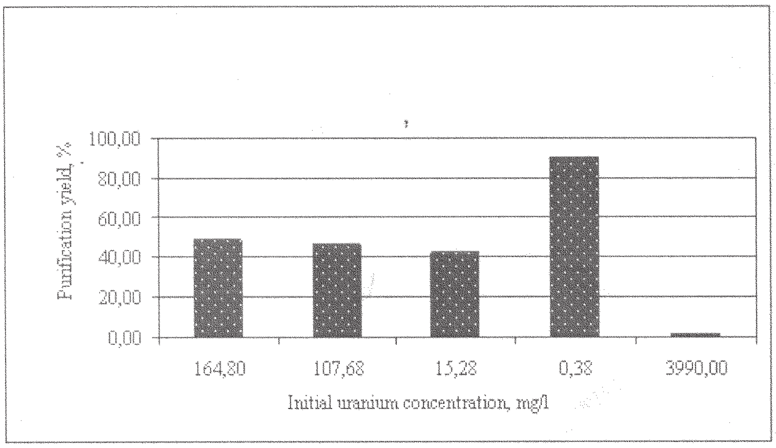

Fig. 3. Purification yield variation versus the initial uranium concentration

As a result of the tests carried on the E2.1-E2.7 emulsions, related to the retention of the uranium from the waste waters with an uranium content ranging between 0.38 – 1.044 % , the E2.1 emulsion was selected, which provides an yield of 90.53 %.

The variation of the yield depending on the initial uranium concentration in the unpurified waste was also pursued (table 6 and fig. 3).

The uranium retention yield by passing through the E2.1 emulsion diminishes as its concentration increases within the waste water (fig. 3), leading to the fact that the uranium retention procedure from wastes by means of the emulsion-like liquid membranes technique is efficient only for uranium concentrations below 1 ppm.

Conclusions

The cobalt retention might be performed with a yield of 95 % by its retaining in the A emulsion, having the couple Aliquat + TBP as carriers, and the receiving phase being a 1 % $NaHCO_3$ solution.

Uranium retention yields of 90 % were obtained for the E2.1 emulsion, at uranium concentrations below 1 ppm.

When the uranium content in the waste water is of the order of hundreds of ppm, the E2.1 emulsion leads to yields ranging between 40-50 % at a single passage. The yield might be enhanced by repeated passages – in cascade – of the waste through the emulsion.

The E2.1 emulsion we have selected for the retention of the uranium from waste waters with a concentration below 1 ppm, has the alkylphosphoric ester TBP as carrier, the receiving phase being a 5% HNO_3 solution.

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