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APPLICATION OF THE CMPO EXTRACTANT (SUPPORTED LIQUID MEMBRANE) FOR THE ALPHA DECONTAMINATION OF MARCOULE REPROCESSING CONCENTRATE

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APPLICATION OF THE CMPO EXTRACTANT (SUPPORTED LIQUID MEMBRANE)
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Reprocessing operations produce medium activity liquid wastes, in which the main components are sodium nitrate and nitric acid. These wastes are treated by evaporation, the distillate is discharged in the environment and all active and inactive salts are concentrated, leading to an important volume of wastes.

The overall objective of this work, carried out within the frame work of an CEC contract is to separate long life radionuclides (actinides and Cs - Sr) into a small volume from the large volume of the concentrate.

CHOICE OF EXTRACTANT

E.P.HORWITZ [1] and al, chose, among several neutral bifunctional compounds, octyl phenyl diisobutyl carbamoyl methyl phosphine oxide (C.M.P.O) the most suitable compound for removing the different actinides from acidic and high sodium content liquid waste.

The mixture, selected by P.DANESI [2], for the extraction of actinides is used :

CMPO (0.25 M) as extractant

TBP (0.75 M) as modifier of phase in order to avoid the appearance of a third phase.

Decalin (or decahydronaphtalene) as diluent.

SUPPORTED LIQUID MEMBRANE (S.L.M)

A supported liquid membrane is constituted by an organic liquid, absorbed into the pores of a microporous support, separating two aqueous solutions : the first one containing the permeating ions (feed solution), the second one free of these ions (receiving solutions).

For most of the laboratory experiments, a flat sheet membrane is used. (Fig.1)

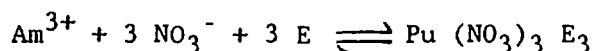
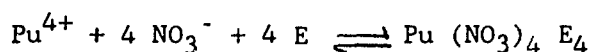
For industrial purposes, hollow fiber modules are used to provide high surface area/volume ratios. This ratio can approach $10,000 \text{ m}^2 \cdot \text{m}^{-3}$ for hollow fiber modules. Due to the small inventory associated with the membrane and to the non volatile nature of the organic phase used, small amounts of extractant are necessary, so expensive extractants such as CMPO can be used. (Fig.2)

The major drawback associated with the use of SLM'S is their stability : the organic phase must be very insoluble to avoid its slow dissolution in the aqueous solutions. With the CMPO/TBP/decalin, SLM's work for more than 300 hours without any problems.

The transport of ions through the membrane occurs when a chemical potential gradient is established between the two aqueous solutions. The chemical gradient is due to the difference of concentration of some chemical species : the nitrate ions.

To be transported through the membrane, the ion must possess a high distribution coefficient in the organic phase and on the contrary, a low distribution coefficient in the stripping solution. To improve this back-extraction, some complexing organic compounds can be added to the strip solution : formic acid, tartaric acid, sodium citrate....

The equations for the extraction of Pu and Am, from acidic nitrate solutions are respectively :



Nitric acid is transported by CMPO and TBP through the membrane, the build-up of nitrate ions in the strip solution decreases the driving force, the permeation of actinides slows down and even stops.

To avoid the build-up of nitrate, P. DANESI and al propose to remove the excess of nitrate by using a second S.L.M : nitric acid and actinides are transported through the first membrane and nitric acid only is transported in alkaline strip solution through the second membrane impregnated with a long chain primary amine (PRIMENE JMT).

EXPERIMENTAL SECTION

CMPO is produced by M and T Chemicals Co (Milwaukee)

The organic reagents are obtained from ALDRICH, except PRIMENE JMT from ROHM and HAAS, and inorganic reagents from PROLABO. All the reagents are analytical grade products, they were used without further purification.

Simulated wastes are prepared with 239Pu and 241Am from CEA stocks.

The genuine concentrate is obtained by evaporating in hot cell, at CEN Cadarache, liquid wastes from the COGEMA Marcoule reprocessing plant. (cf Table 1).

All the experiments were performed at 25±1°C with a membrane area of 35,2 cm². The volumes of feed and strip solutions were identical (600 ml for the simulated concentrate, 370 ml for the genuine concentrate) whatever the type of membrane used (flat sheet or hollow fiber modules).

The permeation of metal ions through the membrane is measured by periodic sampling. The actinides measurements are carried out using liquid scintillation counting or α spectrometry, γ emitters are measured by γ spectrometry (GeLi detectors).

The membranes (flat sheet or hollow fiber modules) used for the experiments are produced by HOECHST CELANESE Charlotte N.C. The main characteristics of the membranes are summarized in Table 2.

Simulated concentrates

Constituent	Concentrate (Na)	Concentrate (Mg)	Concentrate (Al)
HNO ₃	1	1	1
NaNO ₃	3,8	3,4	3,5
Al(NO ₃) ₃			0,41
Ca(NO ₃) ₂	0,03	0,015	0,015
Fe(NO ₃) ₂	0,015	0,0032	0,0032
NaCl	0,0032	0,012	0,012
NaF	0,076	0,017	0,017
Na ₂ SiO ₂	0,023	0,001	0,001
Na ₃ PO ₄	0,14	0,021	0,021
Na ₂ SO ₄	0,165	0,021	0,021
NH ₄ NO ₃		0,1	1,1
Genuine concentrate			
H ⁺	1,27	⁵⁴ Mn	800
Cl ⁻	< 2,2 10 ⁻²	⁶⁰ Co	1800
NO ₃ ⁻	4,52	⁶⁵ Zn	760
SO ₄ ²⁻	8,3 10 ⁻³	⁸⁹⁺⁹⁰ Sr	150000
PO ₄ ³⁻	2 10 ⁻³	¹⁰⁶ Ru+ ¹⁰⁶ Rh	160000
Na	2,52	¹³⁴ Cs	9000
Mg	0,56	¹³⁷ Cs	50000
Al	4,4 10 ⁻²	¹⁴⁴ Ce+ ¹⁴⁴ Pr	130000
K	1,9 10 ⁻²	¹⁵⁵ Eu	2600
Ca	0,15	²³⁸ Pu	360
Cr	5,8 10 ⁻²	²³⁹ Pu+ ²⁴⁰ Pu	740
Mn	5,8 10 ⁻³	²⁴¹ Am	1600
Fe	2,7 10 ⁻²	²⁴² Cm	1100
Cu	7,5 10 ⁻⁴	²⁴³ Cm+ ²⁴⁴ Cm	340
Zn	6,1 10 ⁻³		

Table 1 : Composition of concentrates
Concentration (M) Activity (KBq.l⁻¹)

	Flat membrane	Hollow fiber modules
Fiber wall thickness	25 μm	30 μm
Effective pore size	0,04 μm	0,05 μm
Porosity	45 %	30 %
Fiber diameter		400 μm
Number of fibers		900
Effective fiber length		20,3 cm
Effective surface area		0,2 m ²

Table 2 : Characteristics of the membranes

CHOICE OF THE STRIP SOLUTION

The distribution coefficients were obtained by equilibrating equal volumes of aqueous and organic phases (10 ml). After a one hour shaking period, an aliquot of each phase was withdrawn for measurements by α spectrometry.

The distribution coefficients of actinides between various extractants and the different concentrates are shown in table 3. The tested extractants are :

- CMPO (0.25 M) - TBP (0.75 M) in decalin
- DHDECMP (0.75 M) - TBP (1 M) in dodecane
- D2EHPA in dodecane
- TOPO (0.85 M) in cyclohexane.

Tested concentrate	Extractant	D _{UO₂2+}	D _{Pu⁴⁺}	D _{Am³⁺}	D _{Cm³⁺}
Simulated concentrate Na ⁺	CMPO/TBP	400	1000	14	
Simulated concentrate Mg ²⁺	CMPO/TBP	500	1000	35	
Simulated concentrate Al ³⁺	CMPO/TBP	550	1000	55	
Genuine concentrate	CMPO/TBP		1000	180	240
Genuine concentrate	DHDECMP		50	30	35
Genuine concentrate	D2EHPA		2	<0,5	1
Genuine concentrate	TOPO		50	<0,5	0,4

Table 3 : Distribution coefficients $D = \frac{[M^{n+}]_{org}}{[M^{n+}]_{aq}}$

CMPO extracts the actinides more strongly from the genuine concentrate than does DHDECMP. TOPO, as expected, extracts only Pu(IV) and D2EHPA is not effective for removal of actinides. The distribution coefficients of the CMPO are the same for the simulated or the genuine concentrate concerning plutonium and higher for the real concentrate in the case of americium.

The distribution coefficients of actinides between the organic phase and different complexing aqueous solutions are shown in table 4.

Solutions	D _{UO₂2+}	D _{Pu⁴⁺}	D _{Am³⁺}
Formic acid (1 M)	1.9	2 10 ⁻²	2.6 10 ⁻²
Sodium citrate (0.5 M)	10 ⁻²	3 10 ⁻³	9 10 ⁻⁴
Tartaric acid (1 M)	0.38	4 10 ⁻²	0.19
Ammonium acetate	5 10 ⁻²	1.1	0.5 10 ⁻²
Demineralsed water	6.2	0.7	0.7

Table 4 : Distribution coefficients $D = \frac{[M^{n+}]_{org}}{[M^{n+}]_{aq}}$

The distribution coefficient measurements show that two solutions are interesting : sodium citrate which is the most effective strip solution due to its buffering capacity and demineralised water, which makes it possible to achieve the highest concentration factors.

The double membrane device was investigated, but it leads to a high transport of nitrate through the membrane, thus provoking an excessive deacidification of the feed solution and a precipitation of some cations inside the pores of the membrane.

EXPERIMENTS WITH FLAT SHEET S.L.M. (F.S.S.L.M.)

Experiments were carried out with simulated concentrate (Mg) as feed solution and different strip solutions : demineralised water and sodium citrate solution at different concentrations (0.5 M - 0.05 M).

When sodium citrate (0.5 M) is used as a strip solution, the pH remains high after 173 hours running ; at the beginning, the extraction of actinides is fast (80 % of activity removed after 24 hours), then it slows down, but 99 % of the actinides are transferred to the strip solution. It should be noticed that although the concentration of U is much higher than that of the two other actinides, the rates of transfer of the three elements are almost identical. It can be observed, in spite of much higher distribution coefficients of Pu, that this element is transported with the same effectiveness as Am. (Fig.3)

With a lower concentration of sodium citrate (0.05 M) for the first hours, pH is kept high, it decreases at 0.85 after 24 hours. The low pH of the strip solution leads to a progressive decline of the transfer of actinides and , in particular of Am : only 90 % of the activity is transported through the S.L.M.(Fig. 4)

When demineralised water is used as a strip solution, the pH decreases sharply for the first hours, in these conditions only 85 % of the actinides are removed from the concentrate.(Fig.5)

These experiments show that complete removal of actinides is only possible if pH remains high in the strip solution. Sodium citrate presents two advantages : a complexing power towards actinides and a buffering effect which makes it possible to overcome the drawback due to the high transport of acidity.

EXPERIMENT WITH HOLLOW FIBER S.L.A (H.F.S.L.M)

The experiment with sodium citrate (0.5 M) was performed this time, in conditions similar to those previously mentioned (same volume of aqueous solutions : 600 ml) but with a hollow fiber module possessing a much higher membrane area (0.2 m² versus 35.2 cm² for the flat sheet) in a recycling mode.

For the first hours, the transfer of actinides in the organic phase is fast especially plutonium, but the stripping is much slower. After 3 hours working, 93 % of Pu is extracted but only 22 % is back-extracted and after 6 hours, 98 % of gross activity is removed from the concentrate, 64 % of the activity is stripped. 24 hours are required for the stripping of 90 % of the actinides, a prolongation of the experiment (up to 56 hours) does not lead to a measurable increase of the stripping of α emitters. (Fig.6)

EXPERIMENT WITH THE GENUINE CONCENTRATE

The experiment was first performed with a flat sheet membrane. Its area is the same as that used with the simulated concentrates. The volumes of feed and strip solutions are identical but lower (370 ml instead of 600 ml) than previously mentioned.

The effectiveness of the treatment is confirmed by this test performed with the genuine concentrate of which the initial acidity is 2M. The initial acidity is 2 M in order to maintain a sufficient acidity and make a further treatment with crown ethers possible in order to remove cesium and strontium. Although the membrane area is higher, the transfer of actinides is slower. 99 % of plutonium and 97 % of trivalent actinides (Am^{3+} , Cm^{3+}) are removed from the concentrate and transferred to the strip solution. Among the β, γ emitters present in concentrate, only cerium (92 %) and a low fraction of manganese and ruthenium are extracted, respectively 8 and 6 %. (Fig.7-8)

The actinides are recovered in a complexing solution containing sodium citrate and also sodium, calcium and iron nitrate transported through the membrane, so the concentration factor (C.F) is low. H_2O_2 , in destroying at 80°C sodium citrate, in presence of iron as a catalyst, makes possible a precipitation and a quantitative separation of actinides and iron from sodium solution. This sodium solution is used to partially neutralize the decontaminated concentrate before embedding (Cf flowsheet). Thus, concentration factors higher than 100 are achieved. It must be noticed that further treatment with crown ethers (DC 18 C 6) leads to an increase of the decontamination of the actinides, thus a total D.F. of 400 is achieved.

CONCLUSIONS

The work performed has confirmed, on a genuine concentrate, the findings of P.DANESI : S.L.M.s containing a mixture of CMPO and TBP, diluted in decalin, adsorbed on microporous supports can be used to selectively remove actinides from high sodium content acidic evaporator concentrates.

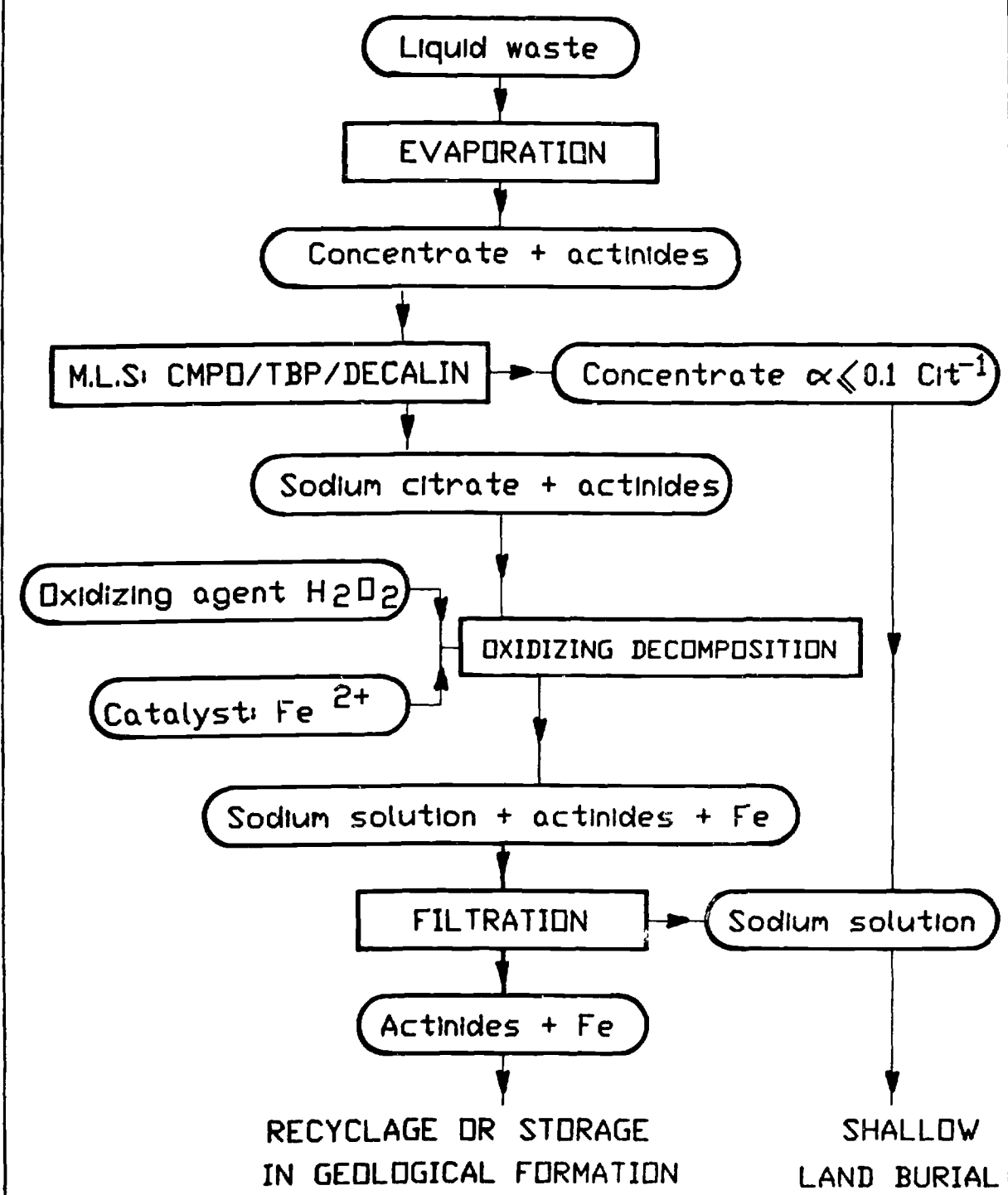
The S.L.M's show a satisfactory life-time, working for 300 hours without trouble. The main problem to overcome is the slowing down of the transfer of acidity through the membrane and maintaining a high pH in the strip solution in order to avoid a sharp decrease of transfer rate of the actinides.

The process through further treatment of the concentrate with crown ethers and destruction of the sodium citrate, makes it possible to achieve, for all the actinides (Pu, Am, Cm) a D.F. higher than 100 and a concentration factor of about 100.

REFERENCES

- [1] E.P.HORWITZ, K.A.MARTIN; H.DIAMOND, L.KAPLAN. Extraction of Am from nitric acid by carbamoyl-phosphoryl extractants : The influence of substituents on the selectivity of Am over Fe and selected fission products. Solvent extraction and ion exchange 4(3) 449-494(1986)
- [2] P.R.DANESI, R.CHIARIZIA, P.RICKERT, E.P.HORWITZ - Separation of actinides and lanthanides from acidic nuclear wastes by supported liquid membranes. Solvent extraction and ion exchange 3 (182) 111-147 (1985).

FLOW SHEET



RECYCLAGE OR STORAGE
IN GEOLOGICAL FORMATION

SHALLOW
LAND BURIAL

D.F. \approx 50-100 F.C. \approx >100

with crown ethers D.F. \approx 400

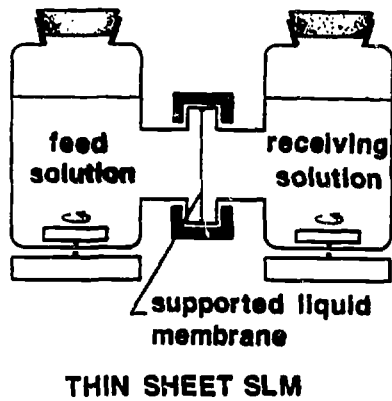


FIGURE 1

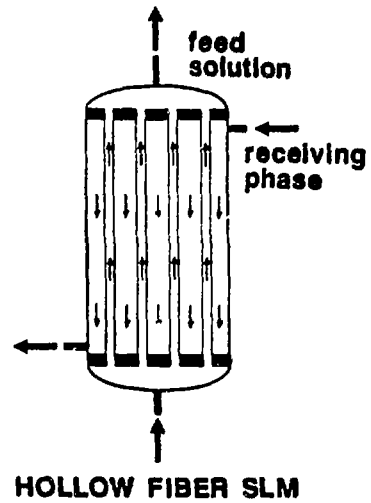


FIGURE 2

FLAT SHEET MEMBRANE : CELGARD 2500

LIQUID MEMBRANE : CMPO 0.25M / TPB 0.75M / DECALINE

FEED SOLUTION : simulated concentrate (Na) (²³⁸U, ²³⁹Pu, ²⁴¹Am)

STRIP SOLUTION : sodium citrate 0.5M

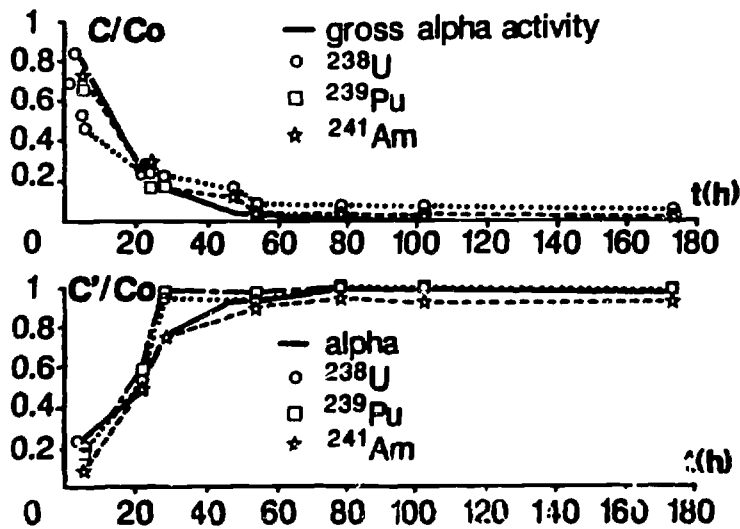


FIGURE 3

FLAT SHEET MEMBRANE : CELGARD 2500

LIQUID MEMBRANE : CMPO 0.25M / TPB 0.75M / DECALINE

FEED SOLUTION : simulated concentrate (Na) (^{238}U , ^{239}Pu , ^{241}Am)

STRIP SOLUTION : sodium citrate 0.05M

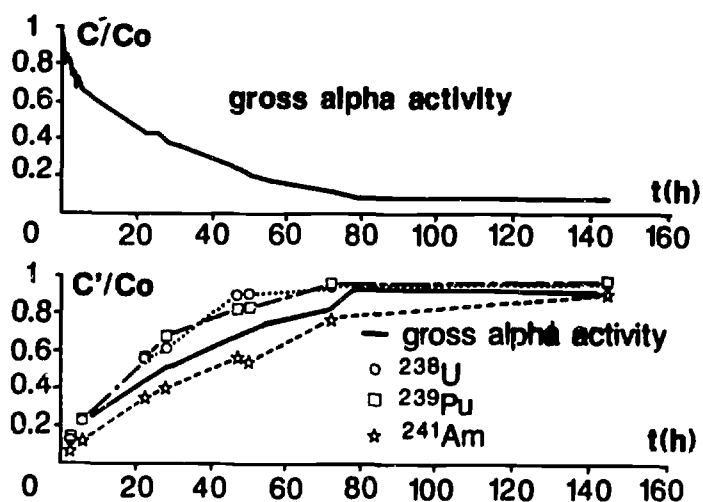


FIGURE 4

FLAT SHEET MEMBRANE : CELGARD 2500

LIQUID MEMBRANE : CMPO 0.25M / TBP 0.75M / DECALINE

FEED SOLUTION : MAR 400 (^{238}U , ^{239}Pu , ^{241}Am)

STRIP SOLUTION : demineralized water

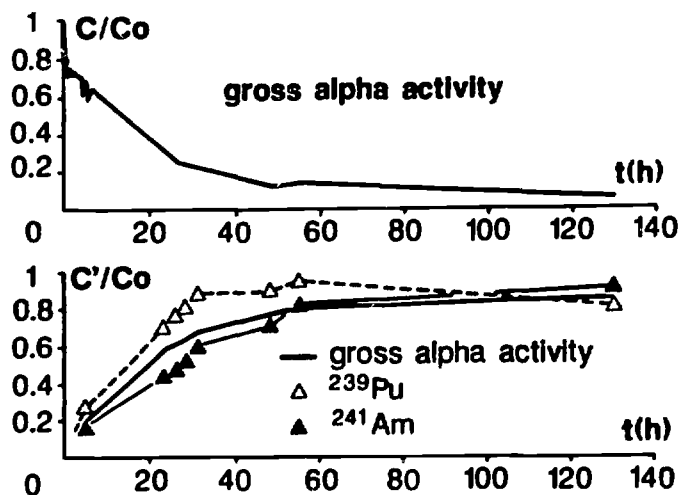


FIGURE 5

HOLLOW FIBER MODULE : CELGARD

LIQUID MEMBRANE : CMPO 0.25M / TBP 0.75M / DECALINE

FEED SOLUTION : MAR 400 (²³⁸U, ²³⁹Pu, ²⁴¹Am) vol=600ml

STRIP SOLUTION : sodium citrate 0.5M vol=600ml

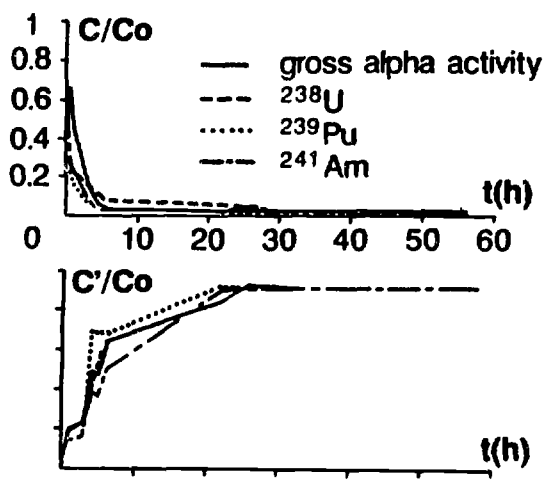


FIGURE 6

FLAT SHEET MEMBRANE : CELGARD 2500

LIQUID MEMBRANE : CMPO 0.25M / TBP 0.75M / DECALINE

FEED SOLUTION : genuine concentrate ($\text{H}^+ = 2\text{N}$)

STRIP SOLUTION : sodium citrate (0.5M)

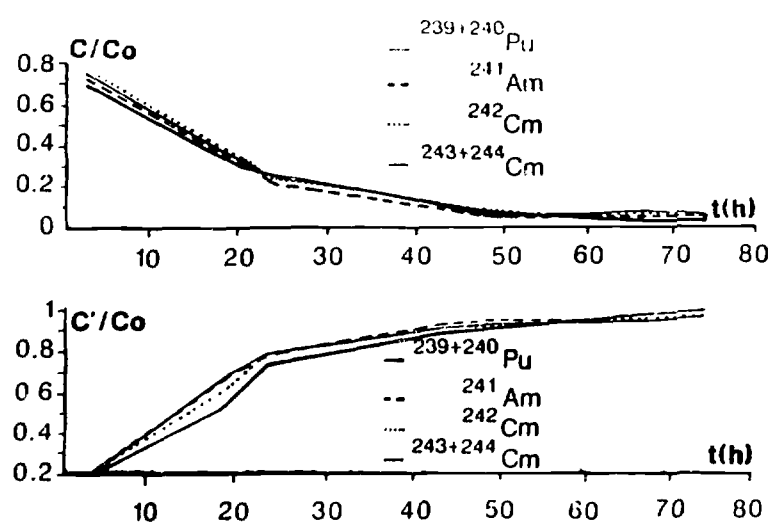


FIGURE 7

FLAT SHEET MEMBRANE : CELGARD 2500

LIQUID MEMBRANE : CMPO 0.25M / TBP 0.75M / DECALINE

FEED SOLUTION : genuine concentrate ($H^+ = 2N$)

STRIP SOLUTION : sodium citrate (0.5M)

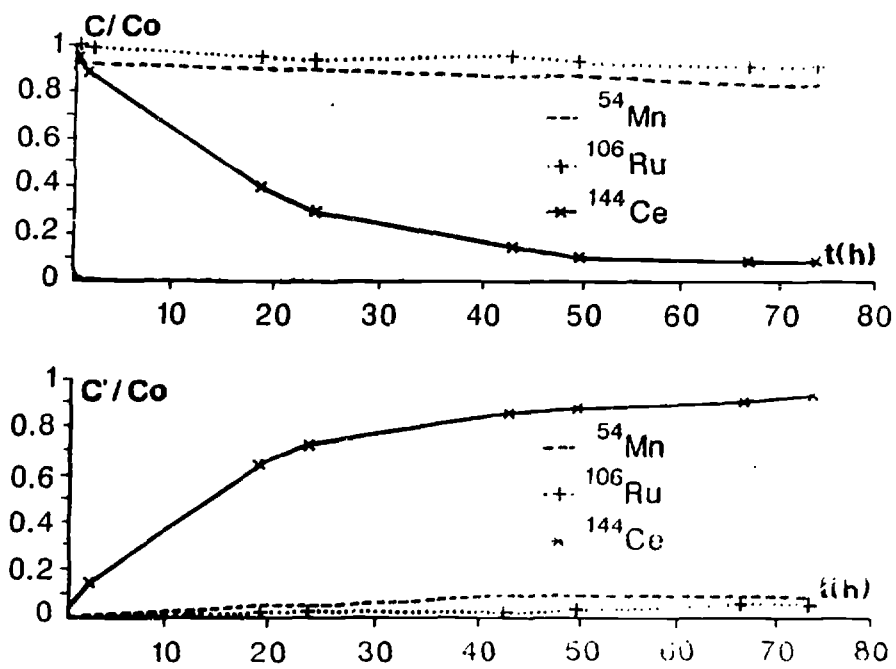


FIGURE 8