Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Two-Cycle Process for Enhanced Actinide Separation from Radioactive Liquid Wastes

A. Facchini[a]; L. Amato[b]; R. Nannicini[c]
[a] POLITECNICO DI MILANO, MILAN, ITALY [b] ENEA SALUGGIA, ITALY [c] ENEA-ERG/FISS/TASCO, ISPRA, ITALY

To cite this Article Facchini, A. , Amato, L. and Nannicini, R.(1996) 'A Two-Cycle Process for Enhanced Actinide Separation from Radioactive Liquid Wastes', Separation Science and Technology, 31: 16, 2245 — 2256
To link to this Article: DOI: 10.1080/01496399608001044
URL: http://dx.doi.org/10.1080/01496399608001044

SEPARATION SCIENCE AND TECHNOLOGY, **31**(16), pp. 2245–2256, 1996

A Two-Cycle Process for Enhanced Actinide Separation from Radioactive Liquid Wastes

A. FACCHINI
POLITECNICO DI MILANO
MILAN, ITALY

L. AMATO
ENEA
SALUGGIA, ITALY

R. NANNICINI
ENEA-ERG/FISS/TASCO
VIA E. FERMI, 21020-ISPRA, ITALY
FAX: 39-332-788207

ABSTRACT

A two-cycle process using OΦCMPO and HDEHP as extractants to achieve an alpha decontamination factor of HLLW greater than 10^3 together with a reduction of the lanthanides/americium weight ratio by a factor of about 200 is considered. Experimentally measured distribution ratios have been employed as input data of a suitable computer code to define operating conditions and M/S stage numbers of a process flow-sheet able to meet the above-mentioned objectives.

INTRODUCTION

In the frame of the closed nuclear fuel cycle operation (reprocessing and U, Pu recycle), the separation of long-lived radionuclides [LLR = minor actinides (MA) + long-lived fission products (LLFP)] from high level liquid wastes (HLLW) is desirable in view of their transmutation, specific use, or separate conditioning and disposal. LLR separation either by groups or by single elements may consequently be required.

High alpha-decontamination factors (e.g., $>10^3$) are required in the HLLW partitioning process to achieve an alpha contamination value of the conditioned wastes low enough for their ground disposal (e.g., <370 Bq/g). Moreover, when transmutation is foreseen, the LLR fraction to be transmuted must also be sufficiently free of other elements, specifically of fission product lanthanides (Ln) whose separation from trivalent actinides (Am and Cm) is notably difficult.

Therefore, the main objectives of the partitioning process examined in this paper are 1) an alpha-decontamination factor higher than 10^3 and 2) a reduction of the Ln/Am weight ratio to not less than 20, corresponding to an Ln content in the MA separated fraction lower than that of Am.

To satisfy these constraints, a process (Fig. 1) employing two extraction cycles has been considered. The first one involves the Truex process (1, 2) and makes use of a bifunctional extractant of the carbamoyl methyl phosphoryl type (CMPO) to separate MA and Tc from HLLW (2.5 M HNO_3) previously added with $NaNO_2$. The second cycle involves the Talspeak process (3, 4) and makes use of HDEHP (diethyl hexyl orthophosphoric acid) to separate trivalent Ln from trivalent transplutonium

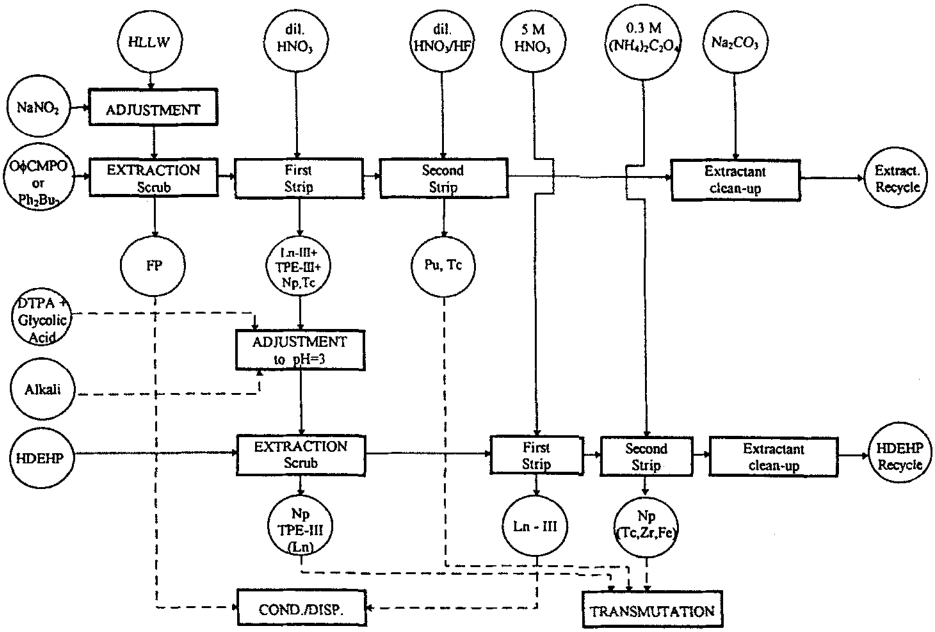


FIG. 1 Flow sheet of the two-cycle process for partitioning minor actinides (MA = Np, Pu, trivalent transplutonium elements), Tc, and lanthanides (Ln) from high level liquid wastes (HLLW).

TABLE 1
Composition of the Synthetic Solution Simulating the Reference HLLW
(4 m^3/t U; [HNO_3] = 2.5 M)[a]

Fission products		Corrosion products and additives		Actinides	
Element	mg/L	Element	mg/L	Element	mg/L
Rb	63	Ni	145	U	280
Sr	133	Co	154	Np	66
Y	74	Fe	908	Pu	96
Zr	737	Na	1471	Am	56
Mo	534	P	55		
Tc	90				
Ru	168				
Rh	47				
Pd	137				
Cs	576				
Ba	257				
Ln	1515				

[a] Total FP = 0.0265 mol/L; total Ln = 0.011 mol/L; total An = 0.0014 mol/L. The reported actinide amounts refer to the radionuclide added as tracer; U has been added to cover the difference to 0.0014 mol/L An.

elements (Am, Cm) and from Np and part of Tc, which are stripped together from the loaded solvent of the first extraction cycle.

A synthetic waste solution (Table 1) has been employed in the experimental work, simulating a HLLW (UP3 type) arising during processing of a high burn-up UO_2 spent fuel by the Purex process.

Two extractants have been examined for the first cycle of the partitioning process: 0.2 M octyl phenyl diisobutyl CMPO (simply called OΦCMPO) in *n*-dodecane 1.4 M TBP, and 0.2 M diphenyl diisobutyl CMPO (simply called Ph_2Bu_2) in *o*-xylene 1.4 M TBP. A solution of 0.3 M HDEHP (properly purified) in diisopropyl benzene has been used as extractant for the second cycle.

The problem of combining the two above-mentioned cycles has been solved through the selection of suitable conditions.

EXTRACTANTS AND ANALYTICAL METHODS

OΦCMPO is an SX-grade product (92–95% pure) whose content of octylphenyl phosphinic acid is less than 0.02%. Ph_2Bu_2 is 90–95% pure and its impurities have not been determined. HDEHP has been obtained by purifying it through the precipitation of its salt $Cu(DEHP)_2$ (5). Diluents and all nitrate salts required to prepare the synthetic waste solution were reagent-grade products.

Inductively coupled plasma/atomic emission spectroscopy (ICP/AES) was used to measure the stable istope and uranium content in the aqueous and organic phases (after quantitative backextraction). Standard radiometric essay and counting procedures (gamma spectrometry, LSC, and alpha counting) were used to measure the content of Tc, ^{152}Eu, Np, Pu, and Am in solutions spiked with them. Duplicate essays of each phase were routinely performed, and the material balance of each element was found to be satisfied within ±10%.

DISTRIBUTION RATIOS

Batch distribution ratios of key constituents of the reference waste solution were measured (at room temperature, 20°C) with solutions of OΦCMPO or Ph_2Bu_2 prepared as mentioned before and preequilibrated with 2.5 M HNO_3.

The choice of these extractants has been made for the following reasons: 1) their widely proved capability in binding actinides because of the formation of stable cyclic complexes; 2) the opportunity to verify the influence of two phenyl groups in the molecule on the extractant properties through a possible AAS effect (anomalous aryl strengthening effect). As is known (6), directly P-bound aromatic rings in bifunctional extractants should allow formation of particularly stable americium complexes, contrary to what happens with monofunctional phosphoryl-type extractants. No clear results of this effect were found within the accuracy limits of analysis, whereas the addition of $H_2C_2O_4$ to the reference solution was necessary, when working with Ph_2Bu_2, in order to prevent precipitation of insoluble complexes. This was not the case with OΦCMPO.

Results are reported in Table 2 for nonradioactive constituents analyzed by ICP/AES and in Table 3 for elements traced with radioisotopes. It appears that all examined elements are more extracted at $[HNO_3] = 2.5$ M by OΦCMPO than by Ph_2Bu_2 except La, which has to be considered as one of the less extractable lanthanides with OΦCMPO. Moreover, distribution ratios of fission product elements with OΦCMPO are more remarkably reduced than those with Ph_2Bu_2 by $H_2C_2O_4$; thus, its addition to the aqueous phase would be advisable to improve actinide separation, particularly from Mo and Zr. Nevertheless, rare earth oxalate precipitation may occur in this case, and Pu is not negligibly stripped from the loaded OΦCMPO when stripping is performed at a low HNO_3 concentration. For the above reasons, $H_2C_2O_4$ has been abandoned and the use of

TABLE 2
Mo, Zr, La, and U Distribution Ratios at $[HNO_3] = 2.5$ M with OΦCMPO (columns a) and with Ph_2Bu_2 (columns b) as a Function of $H_2C_2O_4$ Concentration[a]

	Mo		Zr		La		U	
$H_2C_2O_4$ (M)	a	b	a	b	a	b	a	b
0.0	2.44	1.14	7.20	2.49	4.46	6.22	83	10
0.05	0.78	n.m.	0.08	n.m.	3.80	n.m.	44	n.m.
0.10	0.18	1.01	0.01	1.48	2.92	5.71	36	11.5
0.15	0.10	n.m.	0.004	n.m.	2.60	n.m.	37	n.m.

[a] Phases have been analyzed by ICP/AES. n.m. = not measured.

OΦCMPO as extractant of the first cycle has been employed. Mo and Zr separation with OΦCMPO can be reasonably improved by appropriate process parameters, taking into account the decrease of their distribution ratios to 1.1 and 0.7, respectively, at $[HNO_3] = 1$ M without $H_2C_2O_4$.

La, Eu, and Am distribution ratios are reported in Fig. 2 as a function of $[HNO_3]$, whereas those of Np and Tc have been measured as a function of the amount of $NaNO_2$ added to the referen-ce waste solution and the time elapsed after addition. It can seen from Table 4 that 1) a nonsignificant role is played by the time elapsed 2 hours after $NaNO_2$ addition; 2) at $[HNO_3] = 0.5$ M, only Np(V) is present in the aqueous phase at any $NaNO_2$ concentration (as supported by its low distribution ratio), whereas it is partially disproportioned at $[HNO_3] = 2.5$ M; 3) in the 0.5–2.5 M $[HNO_3]$ range, $NaNO_2$ addition plays an opposite role on Tc and Np distribution ratios; and 4) the high Tc distribution ratios are probably due

TABLE 3
Tc, Eu, Np, Pu, and Am Distribution Ratios at $[HNO_3] = 2.5$ M and $[H_2C_2O_4] = 0$ or 0.1 M with OΦCMPO (columns a) and with Ph_2Bu_2 (columns b)[a]

	Tc[b]		Eu		Np[b]		Pu		Am	
$H_2C_2O_4$ (M)	a	b	a	b	a	b	a	b	a	b
0	2.26	4.5	7.8	2.6	7.6	3.6	>1000	220	12	4.8
0.1	n.m.	n.m.	7.7	2.5	n.m.	n.m.	215	<10	11.4	3.4

[a] Phases have been analyzed by alpha counting, standard gamma spectrometry, and/or by LSC. n.m. = not measured.

[b] Feed has been added with $NaNO_2$ at $NaNO_2$/Np molar ratio = 100.

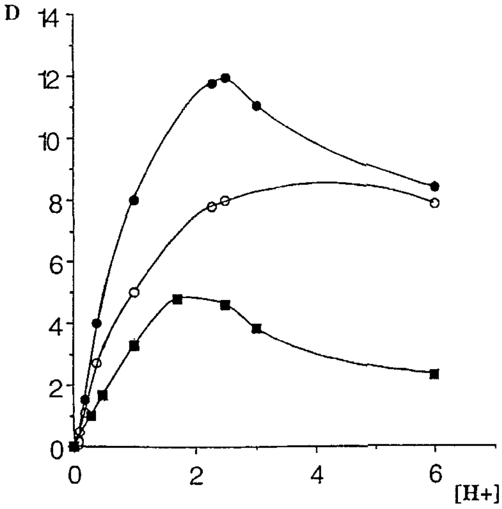


FIG. 2 Am (●), Eu (○), and La (■) distribution ratios as a function of HNO_3 concentration (organic phase: 0.2 M OΦCMPO, 1.4 M TBP in *n*-dodecane as extractant; aqueous phase: synthetic solution of Table 1).

TABLE 4
Np and Tc Distribution Ratios with OΦCMPO as a Function of HNO_3 Concentration, $NaNO_2$/Np Molar Ratio, and Time Elapsed after $NaNO_2$ Addition[a]

	$NaNO_{2m.r.}$/Np								
	0.5 M HNO_3			1 M HNO_3			2.5 M HNO_3		
D^0_a of Np, Tc	0 h	2 h	24 h	0 h	2 h	24 h	0 h	2 h	24 h
0 Np	0.35			1.06			3.22		
Tc	44.37			14.06			2.79		
10 Np		0.34	0.35		1.01	0.96		4.79	4.76
Tc		29.07	28.15		12.06	13.39		2.59	2.73
50 Np		0.36	0.35		1.22	1.05		4.72	5.05
Tc		24.33	25.00		9.34	11.74		2.46	2.39
100 Np	0.34[b]	0.37	0.35	1.51[b]	1.30	0.99	1.49[b]	7.04	7.66
Tc		18.53	21.45		9.12	10.29		2.27	2.26

[a] Reference waste solution at [HNO_3] = 0.5, 1, and 2.5 M has been traced with ^{237}Np solution 0.7 M [HNO_3] to give a final Np concentration of 66 mg/L and with standard ^{99}Tc solution; 24 hours later $NaNO_2$ was added.

[b] Extraction performed 3 minutes after $NaNO_2$ addition.

TABLE 5
Tc, Eu, and Np Distribution Ratios and HNO_3 Concentration Measured in Three Subsequent Strips with 0.001 M HNO_3 from Loaded OΦCMPO (columns a) and from Loaded Ph_2Bu_2 (columns b)[a]

Strip number	H^+ (M)		Tc		Eu		Np	
	a	b	a	b	a	b	a	b
1	0.95	0.93	13.63	7.1	2.24	0.60	0.98	0.46
2	0.40	0.44	16.20	8.5	0.84	0.44	0.49	0.25
3	0.12	0.15	9.55	7.4	0.30	0.58	n.m.	0.96

[a] Column a = OϕCMPO; column b = Ph_2Bu_2. Extractant previously equilibrated (O/A = 1) with the adjusted feed has been stripped (O/A = 2) three times with 0.001 M HNO_3 and H^+ molarity has been measured in the strip products. n.m. = not measured.

to nitrate group replacement by pertechnetate ions in the lanthanide–organic complexes.

Stripping tests of the loaded extractant with diluted HNO_3 (0.001 M) have been performed to obtaining distribution ratios (Table 5) which fit well with the values found by the extraction tests. A strip product of low HNO_3 concentration was required as feed to the second cycle. Actually, it was adjusted to 1 M glycolic acid, 0.05 M DTPA (diethylenetriaminepentaacetic acid), and to pH values around 3 in order to complex trivalent transplutonium elements. Distribution ratios of Eu, Np, Am, and HNO_3 obtained with 0.3 M HDEHP in diisopropylbenzene are reported in Table 6. A separation factor for Am/Eu of about 80 was obtained with purified HDEHP (but not higher than 10 with HDEHP), whereas a low separation factor Eu/Np (about 4.5) requires appropriate strip conditions for a satisfactory separation of Np from lanthanides. This can be achieved by a second strip employing 5 M HNO_3 which gives an Eu distribution ratio less

TABLE 6
Eu, Np, and Am Distribution Ratios with HDEHP 0.3 M in Diisopropylbenzene at Various pH Values (aqueous phase = first strip of the first cycle 1 M glycolic acid, 0.05 M DTPA)[a]

pH	Eu	Np	Am	HNO_3
2.22	3.52	n.m.	0.05	0.67
3.02	1.61	n.m.	0.02	0.06
3.10	2.20	0.49	n.m.	n.m.

[a] n.m. = not measured.

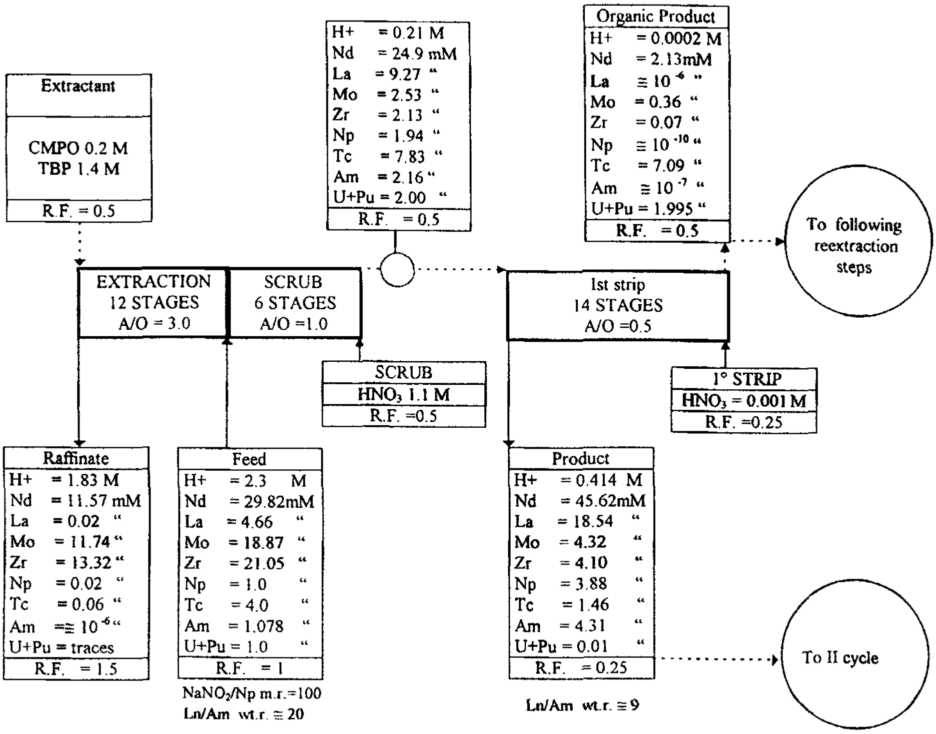
than 10^{-2} and a Np distribution ratio of 4.9. Np can be finally recovered by 0.3 M $(NH_4)_2C_2O_4$ because its distribution ratio has been found to be 0.5.

Solvent clean-up operations by means of Na_2CO_3 solution are necessary for both extraction cycles to prevent accumulation of elements (e.g., U, Am, Fe) and of solvent degradation products (e.g., dibutylphosphoric acid) (7, 8).

COLD TESTS WITH MIXER/SETTLER BATTERIES AND CODE CALCULATIONS

Tests with bench-scale mixer/settler batteries have been performed using the OΦCMPO solution mentioned before as extractant and the synthetic waste solution reported in Table 1 as the aqueous feed. U was used to replace the expected content of all actinides.

The number of battery stages was 6 for extraction, 3 for scrubbing, and 9 for the first strip of the first cycle of the process flow sheet. The aqueous/



organic phase ratios were 3, 1, and 0.5, respectively. HNO_3 1.1 M was used as the scrub solution and HNO_3 0.001 M for the stripping solution. Samples were taken and analyzed each hour (corresponding to about each of the three residence times of the organic phase).

Steady-state concentration profiles in the battery stages were then drawn for each constituent and compared with those obtained with a computer code (9, 10) using the distribution ratios experimentally measured. The maximum difference percent found between calculated and experimental concentration profiles was ±5% for HNO_3 and ±20% for La and U. Differences up to 100% have been found for other elements (e.g., Mo and Zr) because they are less extracted than expected by the code. This is probably due to the high lanthanide concentration in the organic phase that reduces Mo and Zr extraction.

On the basis of the satisfactory agreement, distribution ratios experimentally measured or screened from available data (particularly for

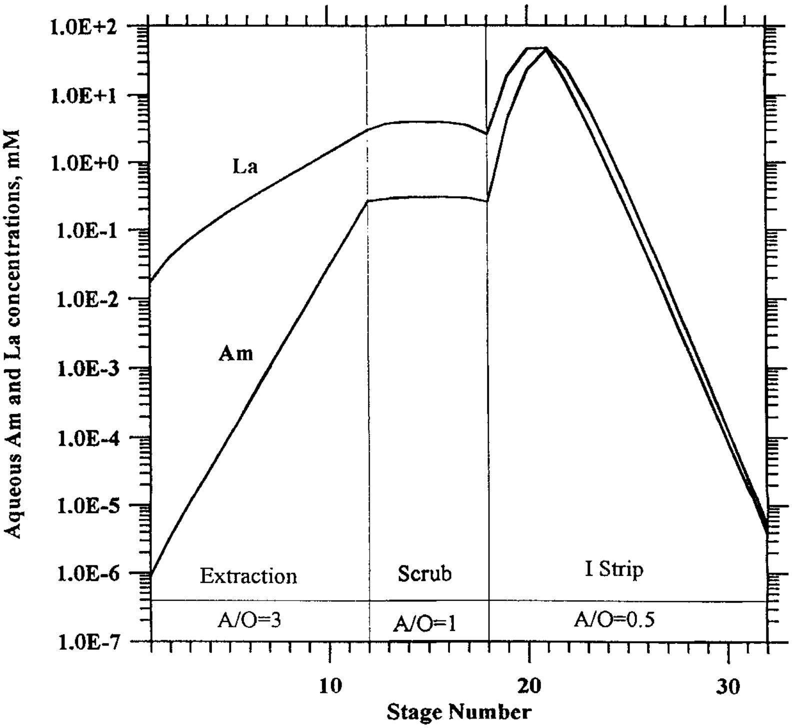


FIG. 4 Aqueous Am and La concentration profiles as a function of the first cycle stage number.

HNO_3, U, and Pu) have been used to define through the code the process operating conditions able to reach the above-mentioned objectives.

Figure 3 shows the first cycle flow sheet by which a satisfactory alpha decontamination of the HLLW feed can be achieved together with a reduction of the Ln/Am weight ratio by a factor of about 2. Actually, U, Pu, and Am contents are reduced to trace levels in the raffinate, whereas Np and Tc are reduced to a few percent of their content in the feed. The extracted Mo and Zr amounts are in the range of 5 to 10% of their contents in the feed, and they are almost completely recovered by the first strip. Nevertheless, Am and lanthanides are not sufficiently separated from each other, so that the second cycle of the process is required. Am and La concentration profiles in the aqueous phase are reported in Fig. 4 as a function of the first cycle stage number.

To the first strip product, after a suitable volume reduction, is added glycolic acid, DTPA, and ammonium hydroxide to reach pH 3, plus 1 M glycolic acid and 0.05 M DTPA at the same element concentration. This

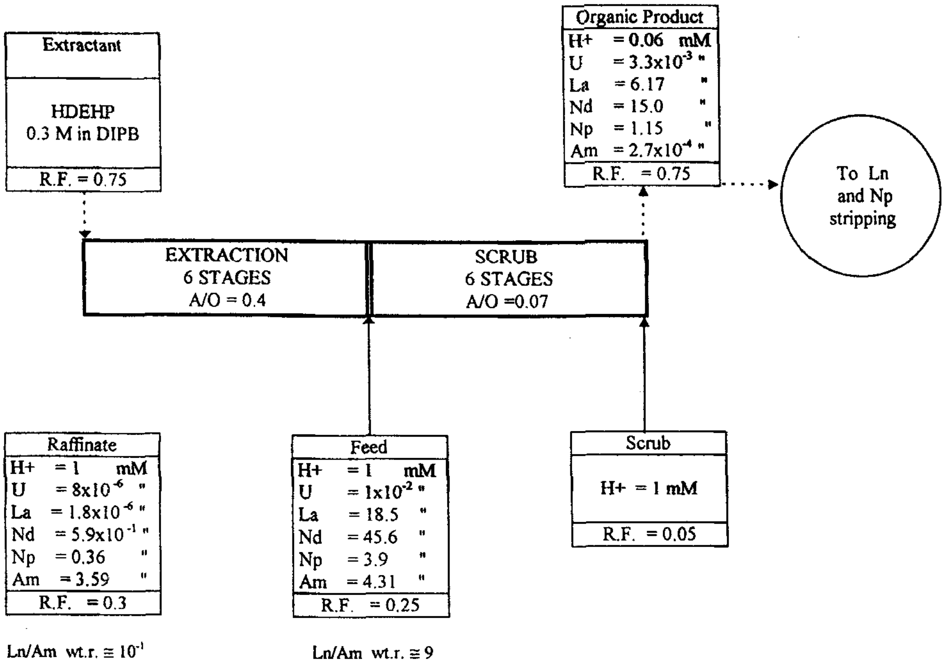


FIG. 5 Second cycle flow sheet elaborated by computer code.

solution is fed to the second cycle, whose flow sheet has been elaborated by computer code and is reported in Fig. 5. As shown, a reduction up to about 0.1 can be achieved for the Ln/Am weight ratio.

CONCLUSIONS

A process based on the two extraction cycles OΦCMPO/HDEHP allows alpha decontamination factors of HLLW greater than 10^3 to be achieved together with a reduction of the lanthanides/Am weight ratio by a factor of about 200. This has been obtained by defining the process operating conditions through a computer code making use of experimentally measured distribution ratios of the HLLW constituents.

Further investigations and battery tests with fully active liquid wastes are needed to obtain better knowledge of specific problems like that related to extractant stability, whose hydrolysis and radiolysis products can be responsible for accumulation of elements (e.g., U, Am, Fe) in the organic phase.

ACKNOWLEDGMENTS

This work was partially financed within ENEA/CEE Contract FI2W-CT90-0056 and performed under an ENEA/Politecnico contract.

REFERENCES

1. E. P. Horwitz, D. G. Kalina, et al., "The TRUEX Process. A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified Purex Solvent," *Solv. Extr. Ion Exch.*, *3*(1&2), 75–109 (1985).
2. Z. Kolarik *Separation of Actinides and Long-Lived Fission Products from High Level Radioactive Wastes* (*A Review*), KfK Report 4945, 1991.
3. B. Weaver and F. A. Kappelmann, *Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolylacetic Complex with a Monoacidic Organophosphate or Phosphonate*, ORNL Report 3559, 1964.
4. F. Mannone and H. Dworschak, *Chemical Separation of Actinides from High Activity Liquid Wastes*, CEE Report S.A./1.07.03.84.02, 1984.
5. J. A. Partridge and R. C. Jensen, "Purification of Di-(2-ethylhexyl)phosphoric Acid by Precipitation of Copper(II) Di-(2-ethylhexyl)phosphate," *J. Inorg. Nucl. Chem.*, *31*, 2587–2589 (1969).
6. A. M. Rozen et al., "Study and Selection of New Extractants for Actinide Extraction," *At. Energ.* (1985).
7. E. P. Horwitz et al., "Behaviour of Americium in the Strip Stages of the Truex Process," *Solv. Extr. Ion Exch.*, *6*(1), 93–110 (1988).
8. R. A. Leonard et al., *The Extraction and Recovery of Plutonium and Americium from*

Nitric Acid Waste Solutions by the Truex Process—Continuing Development Studies, ANL Report 85-45, September 1985.

9. W. C. Scotten, *Solvex. A Computer Program for Simulation of Solvent Extraction Processes*, Savannah River Laboratory Report 1391.
10. F. Ghisalberti, "Estrazione liquido-liquido di radionuclidi a lunga vita: indagine sperimentale e modellizzazione di uno schema di processo," Ph.D. Thesis, Politecnico di Milano, 1995.

Received by editor November 10, 1996