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SYNTHESIS AND UTILIZATION OF NEW EXTRACTANTS FOR NUCLEAR HYDROMETALLURGY

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ABSTRACT

Recent progress in organic chemistry increases the possibility of controlling metal ions/organic molecules interaction. The use of macrocycles or polypodands (1) makes possible the creation of specific extractants for each metal ion. According to the actual needs in pollution elimination and precious metal recovery, this approach can lead to important renewals of extractants used in hydrometallurgy. In the present work, selective extraction of plutonium by dicyclohexano-18-crown-6 (DCH18C6) and paladium by thiapolypodands from high-level nuclear waste solutions is investigated, and the results are modeled and discussed.

INTRODUCTION

Since 1954, reprocessing plants of Savannah, Hanford, and Marcoule are using the PUREX process for the treatment of the spent nuclear fuel. The cycles of spent nuclear fuel reprocessing are illustrated in Figure 1.

Several investigators have outlined some modifications to increase the process efficiency. Nevertheless, after 35 years of technological developments, the

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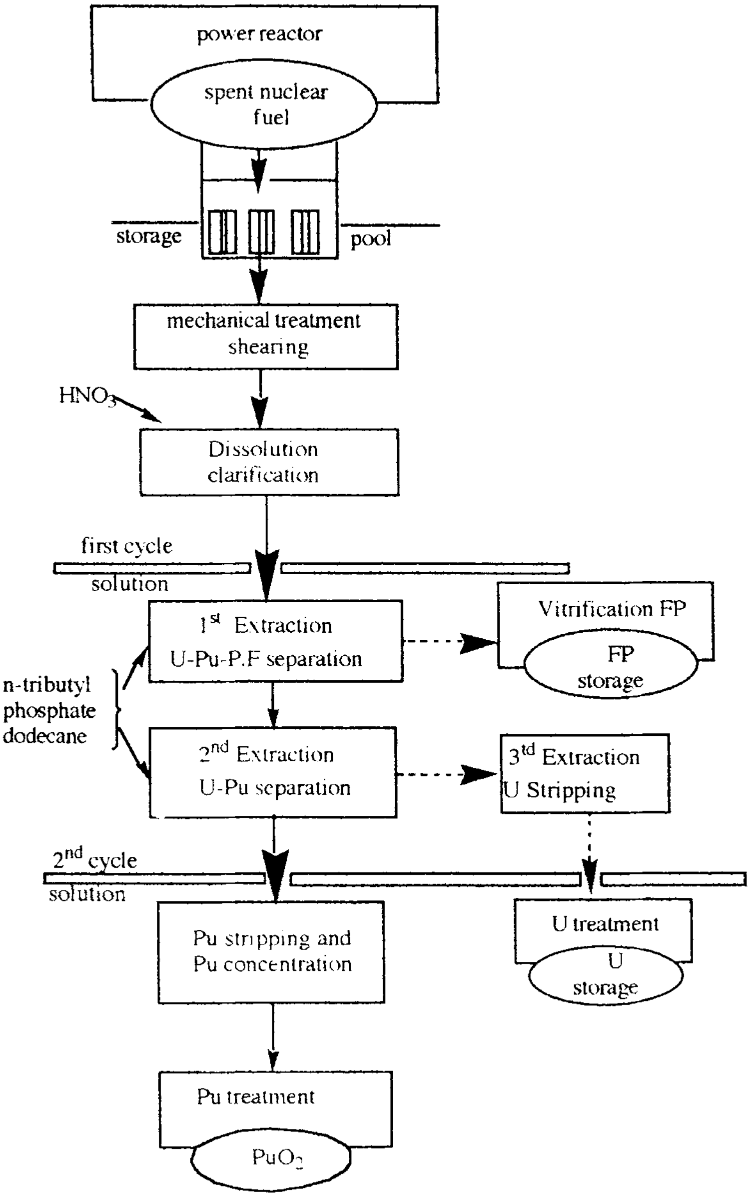


FIGURE 1. Spent nuclear fuel reprocessing cycles.

improvements of this process seem very limited. Indeed, irradiation and high concentration of fissile elements created many problems, especially in finding selective extractants that can tolerate the radiation fields (2). A new more efficient and stable extractant is a real need. Promising applications of macrocycles for the removal of highly active cations from concentrated fission-product solutions have been reported in patents and publications (3-5). Dicyclohexano-18-crown-6, a very stable crown ether (6), is particularly of great interest as it is reported to provide the direct separation of Pu(IV) from U(VI) (7).

In addition, irradiation of nuclear fuel in power reactors leads to the production of fission products including precious metals, among them palladium, which is of great commercial importance (electronic and catalysis uses). The extraction of palladium from high-level wastes has been recently reviewed (8), and various extractants have been suggested (9-10).

In the present work, selective extraction of plutonium by the DCH18C6 and of palladium by polythiapodands from high- or medium-level nuclear wastes is investigated, and the results are evaluated by modeling.

EXPERIMENTAL

Plutonium Extraction

Chemicals and reagents. The mixture of DCH18C6 isomers was supplied by Fluka, and the DCH18C6 isomers were separated according to the procedure reported previously (11-12). The synthetic solutions from the second cycle of the Purex process were prepared by dissolving salts of uranyl and plutonium nitrates in nitric acid. The required volumes of spent nuclear fuel solutions were added to obtain fission-product activities of 110 MBq L^{-1}. The resulting solutions contained plutonium and uranium in Pu(IV) and U(VI) forms. The fission products are the chemical elements created by the fission of uranium and plutonium. Indeed, the irradiation of nuclear fuel in power reactors leads to the production of atoms of a wide range of fission products, ranging in atomic mass from 70 to 160 (13).

Extraction procedure. The extractions were carried out by shaking 20 mL (V) of a synthetic second-cycle solution ($[HNO_3] = 4.5$ mol L^{-1}) with 20 mL (V) of

DCH18C6 dissolved in benzonitrile. The organic solution was washed with 40 mL of 4.5 mol L^{-1} HNO_3 to eliminate the greater part of fission products. The scrubbing of the organic layer with 40 mL of 1 mol L^{-1} HNO_3 allowed the separation of Pu(IV) from both fission products and U(VI). The plutonium was stripped by using 40 mL of 2 mol L^{-1} H_2SO_4. Extractions were done according to the procedure shown in Figure 2.

Palladium Extraction

Chemicals and reagents. The thioethers were performed with commercially available products (JANSSEN Chimica).

Synthesis of the thioethers. Synthesis of alkylthioethers was performed by alkylation of commercially available dithiols supplied by JANSSEN Chimica (Figure 3).

Product	2	3	4	5	6
(A)	$(CH_2)_2$	$(CH_2)_3$	$(CH_2)_3$	$(CH_2)_4$	$(CH_2)_2S(CH_2)_2$

Synthesis of thiamacrocycles was performed according to the template effect technique (14) (Figure 4).

Product	7	8
A	$(CH_2)_2SCH_2CHC_8H_{17}$	$(CH_2)_3SCH_2CHC_8H_{17}CH_2S(CH_2)_3$
B	$(CH_2)_2$	$(CH_2)_3$

Extraction procedure in inactive medium. The palladium extractions with the thioethers were carried out by shaking for 24 h in equal volumes of nitric solution (2 mol L^{-1}) containing $Pd(NO_3)_2$ (1 mmol L^{-1}) with a chloroform solution containing a stoichiometric amount of ligand. The concentrations of palladium in the aqueous phase before and after extraction were measured to determine by difference the concentration of palladium complexed in the organic phase.

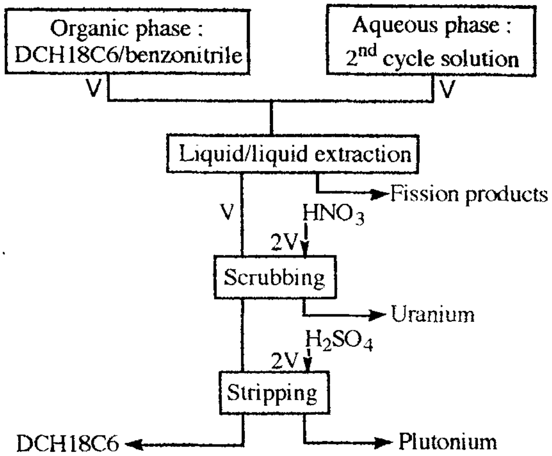


FIGURE 2. Extraction process of Pu from irradiated nuclear fuel solutions using DCH18C6/benzonitrile as extraction system.

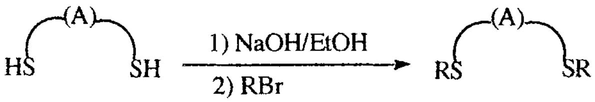


FIGURE 3. Alkylthioether synthesis.

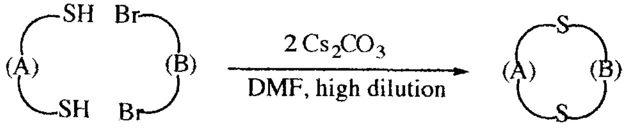


FIGURE 4. Thiamacrocycles synthesis.

Extraction procedure in active medium. The extractions were carried out by shaking for 3 h 20 mL of a 0.9 mol L^{-1} high-level waste solution containing a known concentration of palladium with 20 mL of compound **6** dissolved in chloroform (0.034 mol L^{-1}). The organic phase was washed with 20 mL of 3 mol L^{-1} HNO_3 to eliminate the great majority of uranium and plutonium. The palladium was reextracted by stripping the organic phase with 200 mL of water.

Analytical Section

Analysis procedure in inactive medium. Palladium concentrations were determined by atomic absorption and using the M 1100 system from PERKIN ELMER or/and by using the PAR method (15).

Analytical Procedure in Radioactive Medium

Measurements of the acidity. The acidities were measured on a METTLER DL 40 pH meter (16).

Measurements of the activity by γ-ray spectrometry (17). The INTERTECHNIQUE equipment was composed of a high-purity semiconductor Ge detector type, a preamplifier, an amplifier, a coder, an analyzer, and computer treatment.

Measurements of the activity by α spectrometry (18). Alpha activity measurements required actinide separation and were used to determine plutonium concentrations less than 0.5 mg L^{-1}. The NUMELEC equipment type ENU 15 B was composed of an argon-methane ionization chamber, a preamplifier, a high-voltage drawer, and a CANBERRA multichannel analyzer. The efficiency analysis line standardization and the energy adjustment were effected from standard solutions.

Measurements of the activity by β counting (19). The NUMELEC ENU 16 equipment was composed of an argon-methane ionization chamber, a preamplifier, a high-voltage drawer, and a counter.

ICP-AES measurements (20). The concentrations of uranium and palladium were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a JOBIN & YVON JY 38 spectrometer. The measurements were based on the internal standardization method.

Molecular absorption spectrometry measurements (21). These measurements were used to determine plutonium concentrations greater than $0.5 mg L^{-1}$. The equipment was a BECKMAN spectrophotometer UV 5260 provided with a tungsten lamp.

RESULTS AND DISCUSSION

Parameters Optimization in Plutonium Stripping

Extraction of actinides with crown ethers has been reported to be fast (22), particularly the DCH18C6 in $CHCl_3$, which permits the separation of U^{VI} and Pu^{IV} without the need of valence exchange as required in the Purex process (7). The commercially available DCH18C6 is a mixture of cis-syn-cis and cis-anti-cis isomers, and the selectivity of the plutonium extraction is higher when using the cis-syn-cis DCH18C6 isomer (23). The use of the cis-anti-cis DCH18C6 isomer improves the process by avoiding the coronate precipitation for high plutonium concentrations (24-25). The cis-anti-cis DCH18C6 isomer was used in the present study.

The parameters of extractant concentration, nitric acid concentration, sulfuric acid concentrations, and volume ratios were studied in view of plutonium stripping.

The metals were extracted according to the following extraction reaction :

$$m\overline{L} + M^{n+} + nNO_3^- \rightleftharpoons \overline{L_mM(NO_3)_n}$$

where $[\overline{L}]$ and $[\overline{L_mM(NO_3)_n}]$ indicates the concentrations in organic solutions and $[M^{n+}]$ and $[NO_3^-]$ indicates the concentrations in aqueous solutions. The definition of the extraction constant (K_{ex}) and distribution ratio (D) of cation (M^{n+}) by a specific extractant (L) with a stoichiometry L/M^{n+} of m were expressed by :

$$K_{ex} = \frac{\left[\overline{L_m M(NO_3)_n}\right]}{\left[\overline{L}\right]^m \left[M^{n+}\right]\left[NO_3^-\right]^n}$$

$$D = \frac{\left[\overline{L_m M(NO_3)_n}\right]}{\left[M^{n+}\right]} = K_{ex}\left[\overline{L}\right]^m \left[NO_3\right]^n$$

The nature of the diluent (25) and its various radiolysis products are shown to affect an extraction process. Generally, the extraction possibilities increase with the increasing diluent polarity; often to the detriment of the selectivity. Some experiments have been performed with a nonchlorinated polar diluent, such as the benzonitrile. It has been demonstrated that the DCH18C6 dissolved in benzonitrile permits the plutonium extraction with a high selectivity (26). In addition, the benzonitrile radiolysis products have been shown to be large (27) with a low global radiochemical yield of 0.15 (28). Because of the corrosive products generated by radiolysis of $CHCl_3$, experiments were carried out with the cis-anti-cis DCH18C6 isomer dissolved in benzonitrile.

Extraction Step

In order to separate plutonium and uranium from the greater part of the fission products, we have studied both the influence of the nitric acid concentration of the reprocessing solution and the DCH18C6 concentration.

Dependence of plutonium, uranium/fission products separation on nitric acid concentration. The distribution ratio variations as a function of the nitric acid concentration are given in Table 1.

Very high distribution ratios are observed for Pu(IV), and significant distribution ratios are observed for U(VI). An increasing acidity enhances both uranium extraction and selectivity in relation to the fission products without changing plutonium extraction.

Dependence of plutonium, uranium/fission products separation on DCH18C6 concentration. The distribution ratio variations as a function of the DCH18C6 concentration are summarized in Table 2.

TABLE 1. INFLUENCE OF INITIAL NITRIC ACID CONCENTRATION ON DISTRIBUTION RATIOS, DCH18C6 0.537 mol L^{-1}

Initial HNO_3	Distribution Ratios			
(mol L^{-1})	D_U	D_{Pu}	D_{FP}	D_U/D_{FP}
3	2.53	≥100	0.19	13.4
4.5	5.00	≥100	0.15	26

TABLE 2. INFLUENCE OF DCH18C6 CONCENTRATION ON DISTRIBUTION RATIOS, INITIAL HNO_3 4.5 mol L^{-1}

DCH18C6	Distribution Ratios					
(mol L^{-1})	D_{Pu}	D_U	D_{Pu}/D_U	D_{Pu}/D_{FP}	D_{Pu}/D_{Ru}	D_{Pu}/D_{Sr}
0.034	6.2	0.4	15.5	1550	39	3.3
0.134	45	0.8	54	5020	141	6.8
0.268	98	2.4	40	4890	238	10.4
0.537	98	5.6	17.5	2450	123	9.6
0.604	106	5.9	17.9	1330	122	5.8
0.671	106	6.0	17.8	1520	111	7.0
0.738	102	6.1	16.6	1460	110	12.6
1.074	111	7.7	14.5	930	71	18.8

Required plutonium distribution ratios are observed from a DCH18C6 concentration of 0.268 mol L^{-1}, but a decrease of selectivity is observed for higher concentration values; uranium is coextracted. In view of those results, two processes can be carried into effect, coextraction uranium-plutonium with a DCH18C6 concentration of 0.537 mol L^{-1} or plutonium stripping with a DCH18C6 concentration of 0.268 mol L^{-1} in considering uranium as an impurity. On the other hand, with a DCH18C6 concentration of 0.268 mol L^{-1}, plutonium and uranium selectivities in relation to the fission products are enhanced; so, we worked at this concentration.

Scrubbing Step

We have studied the influence of scrubbing nitric acid concentration on both fission products and uranium stipping. Indeed, it is necessary to define a range of nitric acid concentration where the extent of uranium stripping is maximal and other conditions where the release of residual fission products is also maximal. In particular, during the scrubbing, cesium and ruthenium can be released in the aqueous phase as a function of the nitric acid concentration of the scrubbing solution. These two metals could be considered as tracers of fission-products, except for the strontium which is coextracted with plutonium. This last part is a limiting factor for the process; nevertheless, in a real effluent of second cycle, the concentration of strontium is very low and could be neglected.

Dependence of cesium and ruthenium release on scrubbing nitric acid concentration. Stripping of cesium and ruthenium as a function of the nitric acid concentration is represented on Figure 5.

At a concentration of 1 mol L^{-1} HNO_3, the major part of cesium and ruthenium remains in the organic phase; near 5 mol L^{-1} HNO_3, these elements are released in the aqueous phase. In conclusion, β, γ decontamination of the organic phase can be improved by scrubbing with high concentrated nitric acid.

Dependence of uranium stripping on scrubbing nitric acid concentration. Several nitric acid concentrations were examined for uranium and plutonium stripping. The results obtained are shown in Figure 6.

Uranium and plutonium distribution ratios are maximal for HNO_3 concentrations of 5.5 and 3 mol L^{-1}, respectively. Elimination of fission products and uranium from the organic solution of plutonium required two different scrubbing steps: (1) high concentration of nitric acid for fission products elimination and (2) medium nitric acid concentration for uranium recovery. To reach uranium-plutonium separation, the acidity must be restricted at a concentration of 1 mol L^{-1}. At this concentration, the uranium recovery is maximal although the plutonium distribution ratio remains superior to 100. In a nitric acid range of concentration of 1 mol L^{-1}, the cesium and ruthenium stripping is minimal.

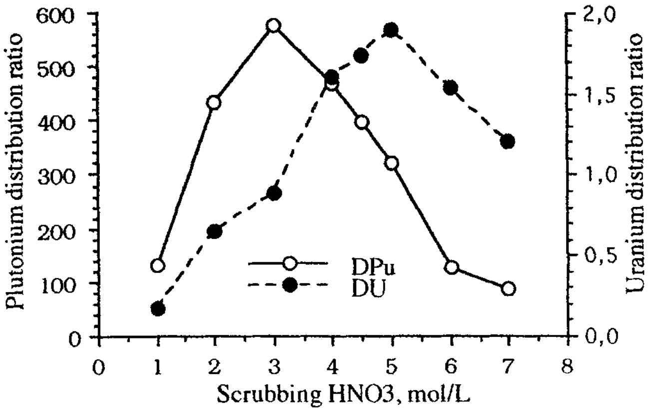


FIGURE 5. Dependance of ruthenium and cesium release on nitric acid concentration
DCH18C6, 0.268 mol L^{-1}.

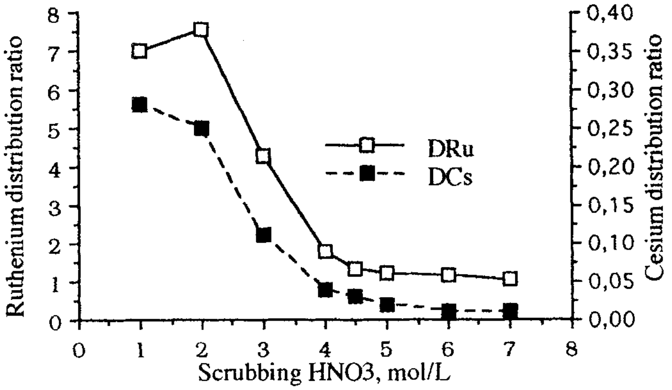


FIGURE 6. Uranium, plutonium recovery selectivity as a function of the acidity
DCH18C6, 0.268 mol L^{-1}.

Plutonium Stripping

The excellent plutonium extraction selectivity by the DCH18C6 allows the separation of Pu(IV) from U(VI) without the need of valence exchange. Stripping of plutonium can be performed by using a very hydrophilic anion (29). Chloride or fluoride anions induce an important corrosion of the stripping installation; however, sulfate ion appears very adapted for plutonium stripping. We have studied the plutonium stripping as a function of the acidity of the scrubbing sulfuric acid concentration. Plutonium stripping was made with increasing volumes of 0.5 mol L^{-1} sulfuric acid. The results are shown in Table 3.

The maximum plutonium stripping was obtained with an aqueous phase/organic phase ratio of 0.6, but the selectivity was better with a ratio of 0.4. To increase the concentration factor of the plutonium, the same study has been made with different concentrations of H_2SO_4 and aqueous phase/organic phase ratios (Table 4).

The maximum enhancement in plutonium stripping and selectivity was obtained with 2 mol L^{-1} H_2SO_4 with an organic phase/aqueous phase ratio of 0.2. Thus, this process required 12 moles of sulfuric acid per mole of plutonium. Then, an additional concentration factor of 5 can be obtained during the plutonium stripping.

Conclusion on the Study of Optimization Parameters

An optimal DCH18C6 concentration of 0.268 mol L^{-1} permits a process for plutonium stripping consistent with restraints bound up with an industrial process. The elimination of the fission products at the first stage of the process needs an initial HNO_3 concentration of 4.5 mol L^{-1}. A scrubbing step with the same or higher acidity permits release of fission products coextracted. A second scrubbing step at weaker acidity (1 mol L^{-1} HNO_3) is necessary in view of eliminating the uranium stripping. Finally, the plutonium is stripped with a good selectivity by using a 2 mol L^{-1} H_2SO_4 solution and an aqueous phase/organic phase ratio of 0.2 or 0.6.

Plutonium Stripping Process Valuation at Pilot Scale

The number of theoretical extraction stages was calculated using the "Kremser formula." After readjusting the concentrations, the following plutonium

TABLE 3. DEPENDENCE OF PLUTONIUM STRIPPING ON 0.5 mol L^{-1} SULFURIC ACID VOLUME

$\frac{V\ H_2SO_4}{V\ org.}$	Pu stripped (%)	$\frac{\%\ Pu}{\%\ U}$	$\frac{\%\ Pu}{\%\ Ru}$
0.2	55.9	0.7	30.5
0.4	91.6	1	41.6
0.6	96.9	1	21.5
5	89.9	1.1	4.6

TABLE 4. INFLUENCE OF H_2SO_4 CONCENTRATION ON PLUTONIUM STRIPPING

[Pu] (g L^{-1})	[H_2SO_4] (mol L^{-1})	$\frac{VH_2SO_4}{V\ org.}$	Pu stripped (%)	$\frac{\%\ Pu}{\%\ U}$	$\frac{\%\ Pu}{\%\ Ru}$
2.87	0.5	0.6	96.9	1	21.5
2.88	1.5	0.2	91	0.9	49.7
3.78	2	0.2	92.5	1	54.1

stripping facility is proposed as a function of the dictated concentrations for second-cycle solutions of spent nuclear fuel reprocessing (Figure 7). The pilot installation requires an extraction reactor of 17 stages and a stripping reactor of 4 stages; with solvent decontamination going off in 1 stage (Figure 7).

A pH-adjusted second-cycle solution with a flow rate of 8 L h^{-1} was added at the fifth stage to the extraction solvent introduced at the first stage with a flow rate of 1 L h^{-1}. In five stages, the majority of the fission-products were separated from uranium and plutonium. At the fourteenth stage, 7.5 mol L^{-1} HNO_3 was added with a flow rate of 2 L h^{-1} to eliminate the residual fission products. At the seventeenth stage, 1 mol L^{-1} HNO_3 was added at a flow rate of 2 L h^{-1} to separate uranium from plutonium which was isolated in the organic phase with a concentration factor of 8. The plutonium was reextracted in 4 stages in introducing into the first stage 2 mol L^{-1} H_2SO_4 at a flow rate of 0.6 L h^{-1}. More than 99% of the plutonium was stripped with a concentration factor of 13. Solvent was decontaminated with 3 mol L^{-1} H_2SO_4. 85% of the strontium is recovered, but in a real liquid waste, the

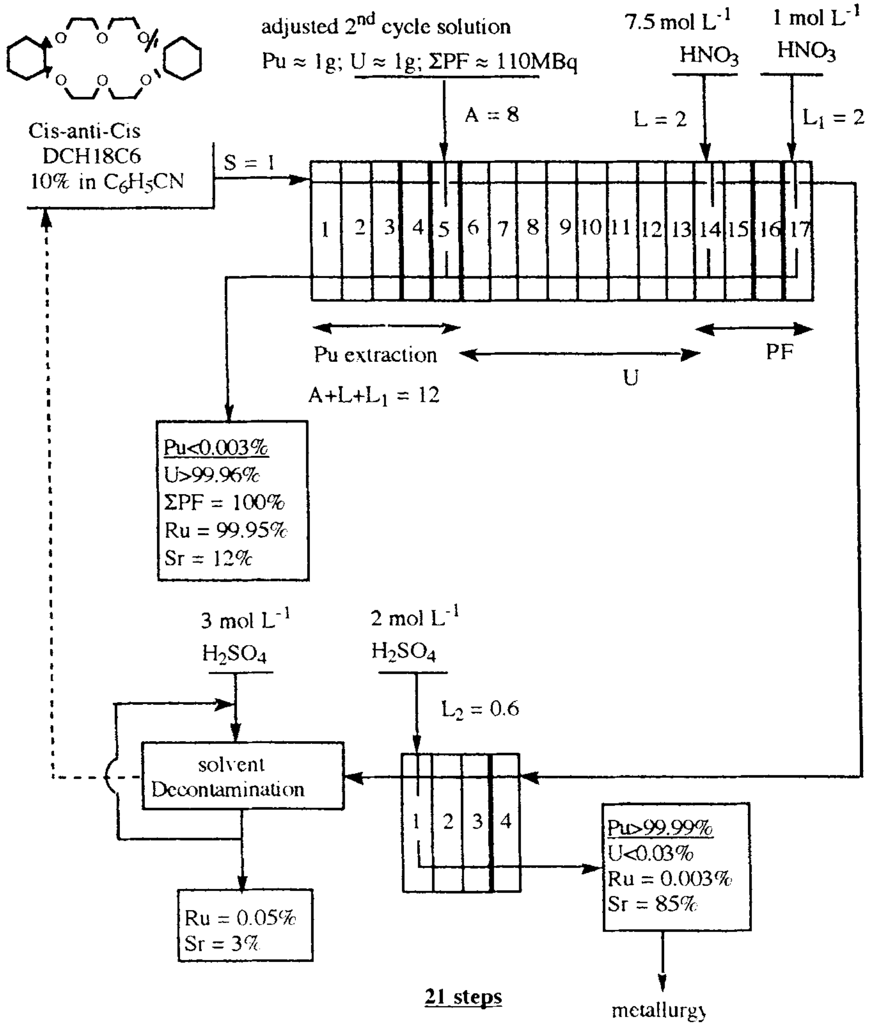


FIGURE 7. Plutonium stripping facility.
S : organic phase flow rate, **A** : adjusted 2nd cycle solution flow rate, **L** : fission products scrubbing HNO_3 flow rate, **L_1** : uranium scrubbing HNO_3 flow rate, **L_2** : plutonium stripping H_2SO_4 flow rate.

strontium concentration is negligible in relation to uranium and plutonium concentrations.

This installation, in 21 steps, produces plutonium released from uranium and fission-products in the same way as the plutonium stripped by the PUREX process but without valence exchange and with a selectivity toward fission products 4 times greater. Moreover the efficiency, in terms of decreasing the number of stages, is increased by 10, compared with the TBP/dodecane experimentations.

Palladium Recovery from High-Level Nuclear Waste

Although the soft β emission exhibited by the palladium-107 limits its use to industrial applications, the six stable palladium isotopes are industrially valorizable. On the other hand, palladium might be separated from nuclear wastes to improve the process by eliminating the potential formation of insoluble palladium residues.

Alkyl-di- and -tri- thioethers and cycle thioethers have been synthesized (11) to evaluate their extraction efficiency and selectivity toward the palladium. Considering the constraints imposed by the radioactive medium, tests were first run on inactive solutions and later on radioactive wastes.

Tests in Inactive Medium

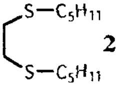
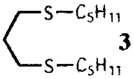
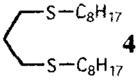
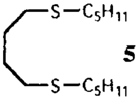
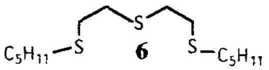
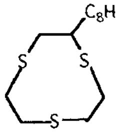
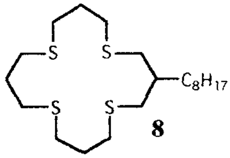
The palladium was extracted according to the following extraction reaction :

$$\overline{nL} + Pd^{2+} + 2NO_3^- \rightleftharpoons \overline{L_nPd(NO_3)_2}$$

where $[\overline{L_nPd(NO_3)_2}]$ was the concentration of palladium complexed in organic phase, and $[\overline{Pd^{2+}}]$ was the palladium concentration in aqueous phase.
The definition of the extraction constant (K_{ex}) and distribution ratio (D) by a thioether (L) with a stoichiometry L/Pd^{2+} of n were expressed by

$$K_{ex} = \frac{\left[\overline{L_nPd(NO_3)_2}\right]}{\left[\overline{L}\right]^n \left[Pd^{2+}\right]\left[NO_3^-\right]^2} \qquad D = \frac{\left[\overline{L_nPd(NO_3^-)}\right]}{\left[Pd^{2+}\right]}$$

TABLE 5. PALLADIUM DISTRIBUTION RATIOS USING DI-,TRI-THIOETHERS AND THIAMACROCYCLES

Product	[L] mmol L^{-1}	Stoichiometry L/Pd^{2+}	K_{ex}	D
$C_7H_{13}-S-C_7H_{13}$ **1**	2	2/1	21 683 405 $mol^{-4}\,L^4$	6.1
 **2**	1	1/1	25 080 $mol^{-3}\,L^3$	7.1
 **3**	1	1/1	234 153 $mol^{-3}\,L^3$	39
 **4**	1	1/1	158 461 $mol^{-3}\,L^3$	29.3
 **5**	1	1/1	235 002 $mol^{-3}\,L^3$	42
 **6**	0.5	1/2	12 $mol^{-1}\,L^1$	1.1
 **7**	2	2/1	81 996 944 $mol^{-4}\,L^4$	1.08
 **8**	1	1/1	14 439 $mol^{-3}\,L^3$	5.8

The stoichiometry of the extracted complexes was obtained in using the molar ratio method (30). Stoichiometries palladium/ligand of 1/1 for dithioethers and the thiamacrocycle **8**, of 1/2 for the heptyl thioether or the thiamacrocycle **7**, and of 2/1 in the case of the trithioether **6** were observed (Table 5). Dithioethers exhibit higher distribution ratios as compared to the mono or trithioethers. An increase of the carbon atom numbers between the two thioethers leads to an increase of the distribution ratios (Table 5, products **2**, **3**, **5**). Indeed, the formation of palladium

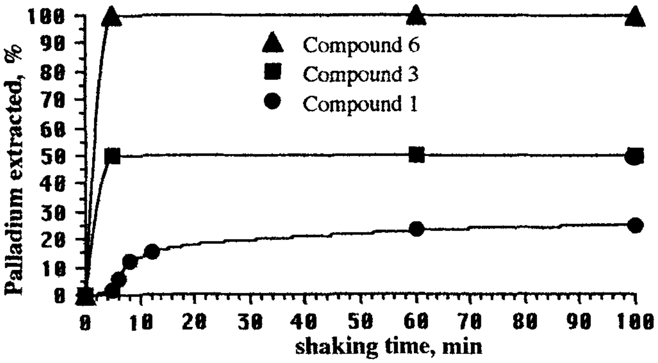


FIGURE 8. Percentage of palladium extracted as a function of the time.

complex requires three or four CH_2 between the two donor atoms (31). On the other hand, the increase of lipophilic chain length decreases the distribution ratios (Table 5, products **3**, **4**). This can be explained by the stereohindrance due to the octyl chains.

The use of cyclic thioethers ligands to stabilize bonding is linked to the thermodynamic macrocycle effect in which macrocyclic complexes are observed to be of greater stability than their open-chain analogues (32). The macrocyclic effect of the **7** and **8** thioether ligands (Table 5) is much diminished due to reorganizational energy considerations (32-33); and consequently, their distribution ratios are relatively low. The kinetics of extraction of palladium with the compounds **1**, **3**, and **6** are illlustrated in Figure 8. The palladium was rapidly extracted by the thioethers **3** and **6**. Indeed, the equilibrium was reached in 5 min, whereas in the same conditions, this equilibrium was not reached out of 2 h in the case of the compound **1** (Figure 8), which was already used as the selective extractant for palladium in a nonactive medium. The curves are in good agreement with the stoichiometries summarized in Table 5.

Tests in Active Medium

The thioether **6** exhibits a high specificity toward the palladium ions, permitting selective extraction of palladium traces contained in high-level first-cycle reprocessing solution and their stripping (Figure 9).

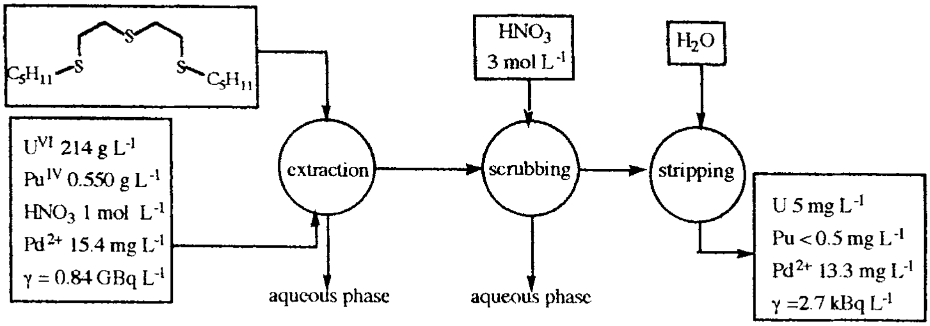


FIGURE. 9. Recovery of palladium traces from high-level nuclear waste.

The extractant **6** (1% in chloroform) permits the separation of 86% of the palladium from a large amount of uranium and other metals contained in a solution of spent nuclear fuel, in one extraction and a single scrubbing step during which a decontamination factor of 3 x 10^5 (defined as the ratio of the initial gamma activity to final gamma activity) was observed. In regard to these results, it is industrially possible to recover precious metals contained in high-level wastes by using a lipophilic thioether.

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REFERENCES

1. T. E. Kron and E. N. Tsevtkov, Russ. Chem. Rev. 59 (3), 283 (1990).
2. M. Isaac, The use of Tri-n-Butyl Phophate in Plutonium Extraction Radiolysis and Recycle of the Solvent, CEA-2349, 1963.
3. E. Blasius, W. Klein and U. Schön, J. Radioanal. Nucl. Chem. 89, 389 (1985).
4. V.V. Yakshin et al., Radiokhimiya 31, 67 (1989).

5. E.P. Horwitz and M.L. Dietz, Process for the Recovery of Strontium from Acid Solutions, U.S. Patent 5,100,585 (1992).

6. M. Draye et al., J. Radioanal. Nucl. Chem. Lett. 175 (1), 55 (1985).

7. M. Lemaire, A. Guy, R. Chomel and J. Foos, J. Chem. Soc. Chem. Commun. 1152 (1991).

8. H.J. Ache et al., Feasibility of Separation and Utilization of Ruthenium, Rhodium and Palladium from High Level Wastes, IAEA Technical Report No. 308, Vienna, 1989.

9. J.O. Liljenzen, J. Rydberg and G. Skarnemark, Sep. Sci. and Technol. 15, 799 (1980).

10. J.A. Daoud, S.A. El Reefy and H.F. Aly, J. Radioanal. Nucl. Chem. Lett. 166, 5, 441 (1992).

11. V. Guyon et al., Chem. Lett. 723 (1992).

12. M. Lemaire et al., Procédé de séparation des isomères d'un éther couronne permettant de récupérer en particulier l'isomère cis-syn-cis du dicyclohexyl 18 couronne 6, F.P. 89 16637 (1989), U.S. Patent 5 082955 (1992).

13. R. P. Bush, Platinum Met. Rev. 35, 202 (1989).

14. J. Buter and R. M. Kellogg, J. Org. Chem. 46, 4481 (1981).

15. N.M. Sudaramurthi and V.M. Shinde, Bull. Chem. Soc. Jpn. 63, 1508 (1990).

16. COGEMA Marcoule 361-2-PR-43-03-Ind 0, 1984.

17. COGEMA Marcoule 361-2-MA-49-08, Indo, 1987.

18. COGEMA Marcoule 361-2-MA-49-04-Ind 0, 1984.

19. COGEMA Marcoule 361-2-MA-49-02-Ind 02, 1982.

20. G. Andrieu, Adaptation au milieu radioactif d'un ensemble de spectrométrie d'émission atomique avec une source de type plasma d'argon à couplage inductif, Mémoire CNAM Paris, 1988.

21. COGEMA Marcoule 361-2-MA-46-01-Ind B, 1988.

22. W. Wenji, C. Bozhong, J. Zhong-Kao and A. Ailing, J. Radioanal. Nucl. Chem. 76, 49 (1983).

23. J. Foos et al., Procédé de récupération au moyen d'un éther couronne du plutonium présent dans des solutions telles que les effluents aqueux, les solutions concentrées de produits de fission et les solutions concentrées de plutonium, F.P. 89 16639 (1989), U.S. Patent 07 625 550 (1990).

24. M. Lemaire et al., Procédé pour séparer au moyen d'éthers couronnes le plutonium de l'uranium et des produits de fission, dans les premiers stades de retraitement des combustibles nucléaires irradiés, F.P. 89 16636 (1992), U.S. Patent 5 085 834 (1992).

25. A. Dakshinamoorthy et al., J. Radioanal. Nucl. Chem. 162,1 , 155 (1992).

26. J.P. Shukla and K.V. Lohithakshan, Analusis 16, 147 (1988).

27. J. A. Knight, J. Chromatogr. 79, 325 (1973).

28. J. A. Knight, Jr., Radiation Chemistry of Mono-substituted Aromatic Compounds, USAEC Report, N. ORO-3519-12, 1973.

29. M. Germain, Le traitement des combustible irradiés. Les cycles de purification de l'uranium et du plutonium, INSTN, III.5, 5, 1987.

30. E. Sekido, H. Kawahara and T. Tsuji, Bull. Chem. Soc. Jpn. 63, 1508 (1990).

31. R. D. Hancock and A. E. Martell, Chem. Rev. 89, 1875 (1989).

32. R. D. Hancock and A. E. Martell, Comments Inorg. Chem. 6, 237 (1988).

33. D. W. Margerum and G. F. Smith, J. Chem. Soc., Chem. Comm., 807 (1975).