Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 185, No. 2 (1994) 331–346

ELECTROCHEMICAL PROCEDURES IN THE TREATMENT OF SPENT NUCLEAR FUEL

C. A. L. G. DE O. FORBICINI, B. F. DE ARAÚJO

Comissão Nacional de Energia Nuclear-SP,
Instituto de Pesquisas Energéticas e Nucleares,
Caixa Postal 11049-Pinheiros, 05499 – São Paulo (Brasil)

(Received August 1, 1994)

The use of an electrochemical process for U/Pu partitioning has demonstrated a good performance and is a safe alternative for nuclear facilities. Its great advantages are the lack of introduction of foreign ions into the process and, especially, the minimization of the waste volume generated. For the introduction of electrochemical U/Pu partitioning in the 2nd Pu purification cycle, preliminary studies were carried out with a single mixer-settler unit. Based on the results, an 8-stage electrolytic mixer-settler (M-S MIRELE) was designed. Titanium was MIRELE's housing material (cathode) and platinum the anode, insulated with PTFE. The Pu recovery was higher than 99%, indicating the efficiency of this equipment.

In the PUREX process, the main process for spent nuclear fuel treatment, U/Pu partitioning is performed by repeated changes of the Pu oxidation state, made by addition of reducing and oxidizing agents. Because of the several disadvantages presented by these chemicals, electrochemical techniques appeared to improve the process.

Besides being a clean process, the minimization of the generated waste is one of its main advantages.

Several studies about U/Pu partitioning using an electrolytic mixer-settler are reported.[1,2,4,6–8] Based on these studies, the main goal of this work is the development of a compact electrolytic M–S. The tests were begun with a single M–S unit, and the results were the basis for the final equipment design.

The use of this equipment was verified in U/Pu partitioning at the 2nd plutonium purification cycle and is a suggested one-cycle process for MOX [$(U–Pu)O_2$] fuel fabrication.

The resulting aqueous products were oxidized in an electrolytic cell (CELOX), to bring Pu back to + 4 valence and to destroy hydrazine, making possible the final product concentration.

Finally, two flowsheets, one for the 2nd plutonium cycle and the other for a one-cycle process, both with electrolytic equipment, are proposed.

Elsevier Science S. A., Lausanne
Akadémiai Kiadó, Budapest

Electrochemical process

The U/Pu partitioning by electrolysis consists of a liquid–liquid extraction process, using 30% TBP-diluent as an organic phase, loaded with uranium and plutonium, the plutonium being reduced to practically non-extractable Pu(III). The electrolyte solution (aqueous phase) is composed of HNO_3 and N_2H_4 (hydrazine), the latest used to stabilize Pu(III) by its reaction with the NO_2^- formed.

WEISHAUPT[11] and HAUSBERGER[5] have studied U/Pu partitioning by electrolysis, presenting the following equations for the oxidation–reduction reactions:

(1) Chemical reduction of Pu(IV) by U(IV):

$$U^{4+} + 2Pu^{4+} + 2H_2O \Leftrightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+ \qquad +0.58V$$

(2) Cathodic reduction of Pu(IV), HNO_3 and U(VI):

$$Pu^{4+} + e^- \Leftrightarrow Pu^{3+} \qquad +0.92V$$

$$UO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow U^{4+} + 2H_2O \qquad +0.33V$$

$$NO_3^- + 3H^+ + 2e^+ \Leftrightarrow HNO_2 + H_2O \qquad +0.94V$$

(3) Chemical oxidation with NO_2 and NH_3:

$$4NO_2 + 2H_2O \Leftrightarrow 2HNO_2 + 2HNO_3$$

$$2HNO_2 + N_2H_5^+ \Leftrightarrow N_2 + N_2O + 2H_2O + H_3O$$

$$HNO_2 + N_2H_5^+ \Leftrightarrow HN_3 + 2H_2O + H^+$$

$$Pu^{3+} + HNO_2 + H^+ \Leftrightarrow Pu^{4+} + NO + H_2O \qquad +0.08V$$

$$2Pu^{3+} + HN_3 + 3H^+ \Leftrightarrow 2Pu^{4+} + NH_4^+ + N_2 \qquad +1.04V$$

$$HN_3 + Pu^{4+} \Leftrightarrow 3/2N_2 + Pu^{3+} + H^+ \qquad +4.02V$$

(4) Anodic oxidation of Pu(III) and hydrazine:

$$Pu^{3+} - e^- \Leftrightarrow Pu^{4+}$$

$$N_2H_5^+ - 4e^- \Leftrightarrow N_2 + 5H^+$$

Other reactions to be considered:

$$HNO_2 + HN_3 + H_2O \rightleftharpoons NH_4NO_3 + N_2 \qquad +1.02V$$

$$HNO_2 + HN_3 \rightleftharpoons NO + 3/2N_2 + H_2O \qquad +4.10V$$

$$2HN_3 + HNO_3 \rightleftharpoons HNO_2 + 3N_2 + H_2O \qquad +4.04V$$

$$U^{4+} + 2HNO_2 \rightleftharpoons UO_2^{2+} + 2NO + 2H^+ \qquad +0.66V$$

$$UO_2^{2+} + 0.5N_2H_5^+ + 1.5H^+ \rightleftharpoons U^{4+} + 0.5N_2 + 2H_2O$$

$$N_2H_5^+ + H_2 + H^+ \rightleftharpoons 2NH_4^+$$

$$2Pu^{4+} + 2N_2H_5^+ \rightleftharpoons 2Pu^{3+} + 2NH_4 + N_2 + 2H^+$$

All these reactions occur at the same time in the electrolytic M–S, making the process very complex.

SCHMIEDER[7–9] has operated a small laboratory 16-stage electrolytic M–S, which was the basis for a 12-stage unit design used in the 2nd plutonium cycle at WAK plant. In both cases, the high efficiency in partitioning has proved the viability of reducing the number of stages.

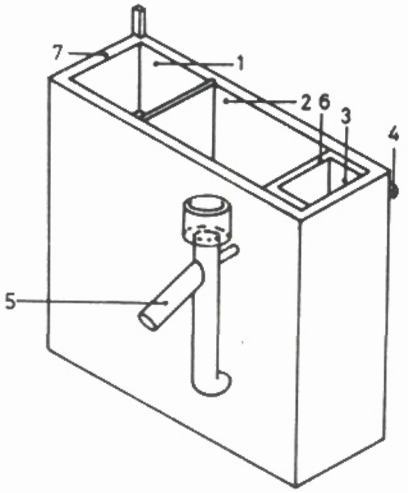


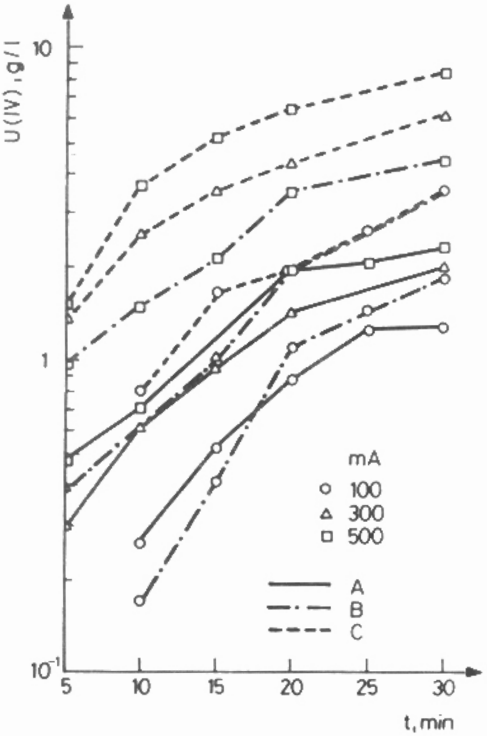
Fig. 1. Electrolytic single mixer-settler unit; 1 – mixing chamber, 2 – settling chamber, 3 – electrode chamber, 4 – organic phase outlet, 5 – aqueous phase outlet, 6 – insulator, 7 – titanium (cathode). Cathode surface (aqueous phase) = 54 cm^2, anode surface = 8 cm^2, aqueous phase volume = = 49.0 cm^3, organic phase volume = 54.9 cm^3

Experimental

Studies with a single M–S unit

The single M–S unit is described in Fig. 1. It is composed of three compartments: one mixing chamber, one settling chamber and one insulated chamber for the anode. The unit housing material, titanium, is the cathode and platinum is the anode.

Two different studies were made: (1) with a stationary aqueous phase loaded with uranyl nitrate and hydrazine; (2) with an organic phase loaded with uranyl nitrate and an aqueous phase composed of 0.2M HNO_3 /0.2M N_2H_4, in continuous flow. The U(IV) yield was the main parameter for the process evaluation.



Curve	U, g/l	H^+, M	N_2H_4, M
A	10.36	1.01	0.20
B	22.79	0.98	0.19
C	67.25	0.99	0.20

Fig. 2. Electrolytic U(IV) formation as a function of current strength, residence time and initital uranium concentration

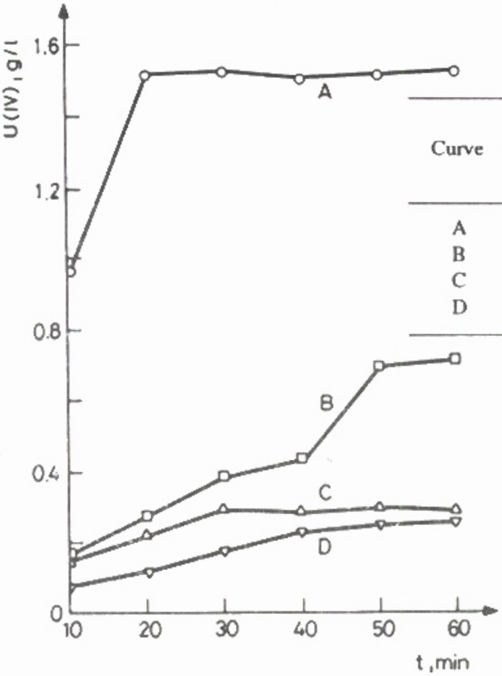
Figure 2 shows the conditions employed and the results of the studies on the influence of electrolysis time, applied current and uranium concentration over the U(IV) formation, using a stationary phase. It was verified that the three factors enhanced the U(IV) concentration. But the U(IV)/U ratio shows that the higher the uranium concentration in the initial aqueous solution, the lower is U(IV) formation.

The average mass transfer coefficient (β_m) was calculated from the experiments by the expression:[9]

$$\beta_m = \ln \frac{[U(VI)]_i}{[I(VI)]_f} \cdot \frac{V_M}{S_c \cdot t_r} \qquad (a.1)$$

$$\beta_m = 0.006 \text{ cm/min}$$

where V_M – mixer volume (ml),
t_r – residence time (min),
S_c – cathode surface (cm^2),
$[\ ]_{i,f}$ – initial and final concentration (g/l), respectively.



Curve	Initial condition		R_a^o	R U(IV)/U
	U, g/l	H$^+$, M		
A	32.11	0.13	200/200	0.047
B	32.11	0.13	200/40	0.022
C	11.15	0.18	300/300	0.026
D	11.15	0.18	300/60	0.022

Fig. 3. Uranium(IV) formation as a function of phase ratio $R^C_A = 8.75$, $A = 500$ mA

The influence of cathode/anode surface ratio (R^C_A) was also studied. By experimental conditions, the best ratio lies between 6.5 and 9.8. This high ratio is a consequence of the absence of flow.

Finally, the influence of phase ratio (R^o_a) in continuous flow experiments was studied. Figure 3 shows that the best results were reached with a flow of 200 ml/h, $R^o_a = 1$, and a total residence time of 25 minutes (0.42 hours).

The M–S MIRELE

The design of the electrolytic M–S was based on the residence time obtained in the previous experiment with the one-stage M–S.

Considering 0.24 hour the total residence time (t_r) and assuming that the M–S has 8 stages, the mixing chamber volume (V_M) can be calculated by the following expression:

$$t_r = \frac{V_M}{v_a + v_o} \rightarrow V_M = 21.5 \text{ ml} \tag{b.1}$$

where v_a and v_o are the aqueous and organic flows (ml/h), respectively.

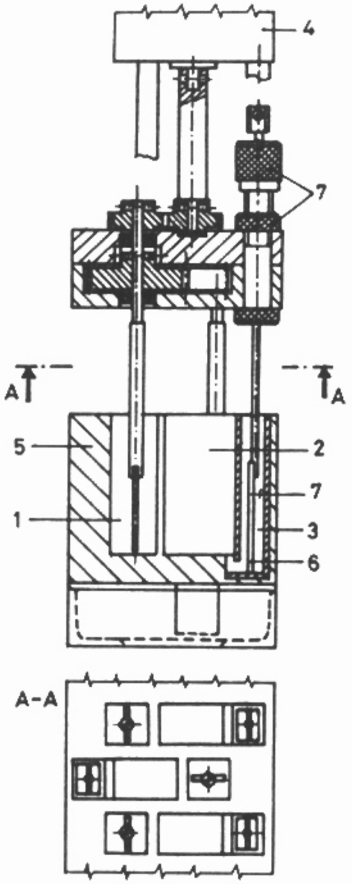
Keeping the same relations between the chambers of the single M–S unit, and using the calculation method of WILLIAMS et al.,[12] the M–S MIRELE was designed and is presented in Fig. 4.

Preliminary studies with M–S MIRELE: Running cold experiments, the M–S hydrodynamic behavior was verified, settling the interface control (using an external controller at the aqueous phase exit), the stirring velocity and the flows, in order to promote good stability during all the operations. An organic phase loaded with uranyl nitrate, and a 0.2M HNO_3 /0.2M N_2H_4 electrolyte solution as aqueous phase were used in the experiments.

Figure 5 shows the best results attained, whose conditions were used in the first experiment with Pu. The current distribution promoted higher U(IV) formation at the aqueous phase exit, which might ensure Pu(IV) reduction.

U/Pu partitioning in the 2nd plutonium cycle: The electrolytic plutonium reduction was determined using pure plutonium solution and employing the conditions settled in the previous experiment. The mass transfer coefficient calculated by Eq. (a.1) was 0.13 cm/min, which agrees with the literature.[8,9] The results in Fig. 6 show that the applied current was not suitable and plutonium losses have occurred.

In the next experiment (Fig. 7), using U–Pu solution, plutonium losses were observed even in the presence of U(IV).



4. Electrolytic mixer-settler MIRELE; 1– mixing chamber, 2 – settling chamber, 3 – anode chamber, 4 – stirring system, 5 – cathode (titanium), 6 – anode (platinum), 7 – insulator (PTFE)

The current in the three last stages was then enhanced to 150 mA (total current = 1.3A). Varying the concentration relations between uranium and plutonium (R = U/Pu = 690, 25 and 7), plutonium losses were below 0.1%. Figure 8 shows the resulting concentration profile and the best conditions for the M–S MIRELE operation.

A proposed flowsheet for the 2nd plutonium purification cycle is presented in Fig. 9.

Decomposition of hydrazine during the electrochemical process: Hydrazine may decompose by its reaction with nitrous acid, H_2 (formed in the reaction between Pu(III) and nitrous acid), U(IV), Pu(IV) and by direct oxidation at the anode.

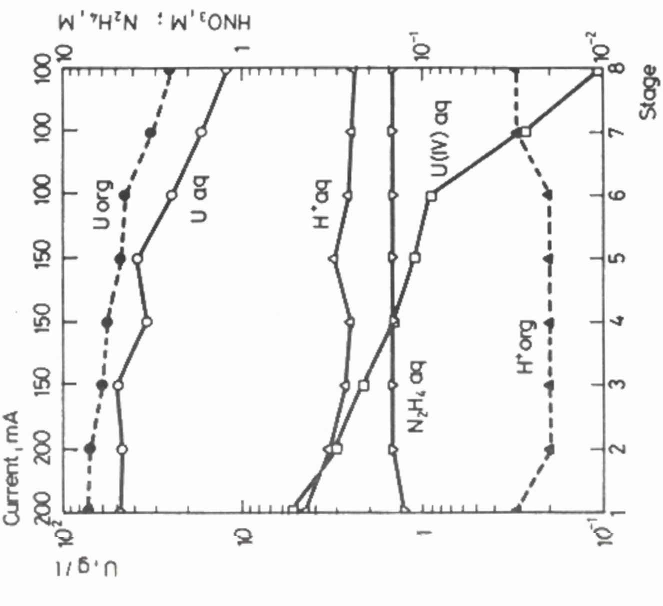


Fig. 5. Mixer-settler MIRELE concentration profile. Organic feed: 74.77 gU/l, 0.25M HNO_3, electrolyte: 0.2M HNO_3, 0.2M N_2H_4, organic and aqueous flows: 200 ml/h, $R_a^o = 1$

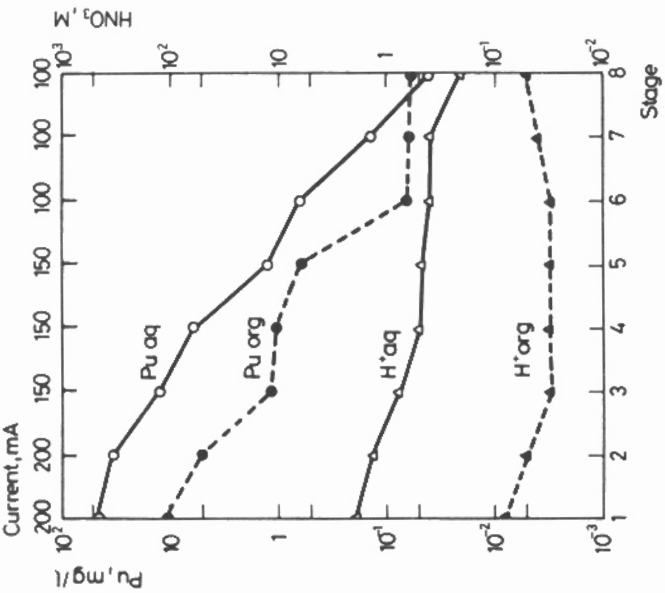


Fig. 6. Mixer-settler MIRELE concentration profile in absence of uranium. Organic feed: 60 mg Pu/l, 0.26M HNO_3, electrolyte: 0.2M HNO_3, 0.2M N_2H_4, organic and aqueous flows: 200 ml/h, $R_a^o = 1$

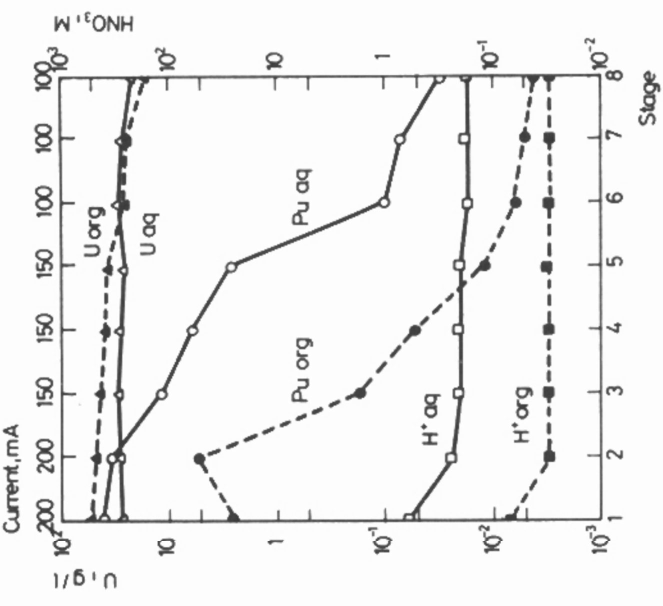


Fig. 7. Mixer-settler MIRELE concentration profile with *R* U/Pu = 690. Organic feed: 65.08 mg Pu/l, 45 g U/l, 0.21M HNO_3, electrolyte: 0.2M HNO_3, 0.2M N_2H_4, organic and aqueous flows: 200 ml/h, $R_a^o = 1$

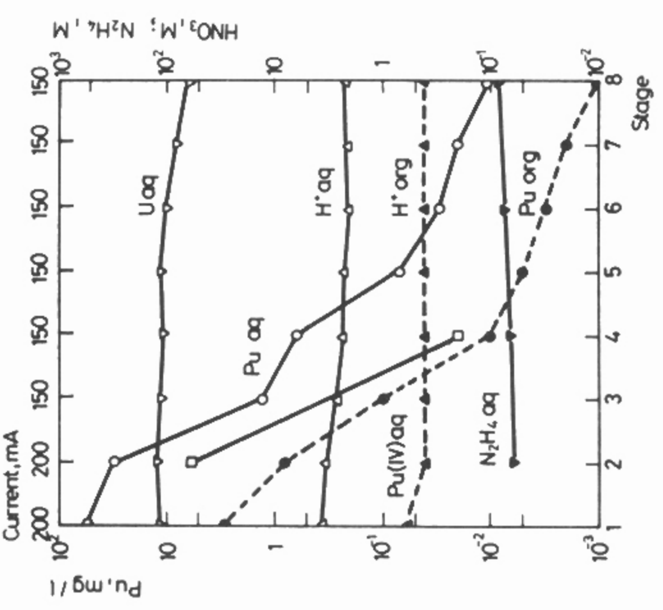


Fig. 8. Mixer-settler MIRELE concentration profile with *R* U/Pu = 25. Organic feed: 78.77 mg Pu/l, 2.0 g U/l, 0.19M HNO_3, electrolyte: 0.2M HNO_3, 0.2M N_2H_4, organic and aqueous flows: 200 ml/h, $R_a^o = 1$

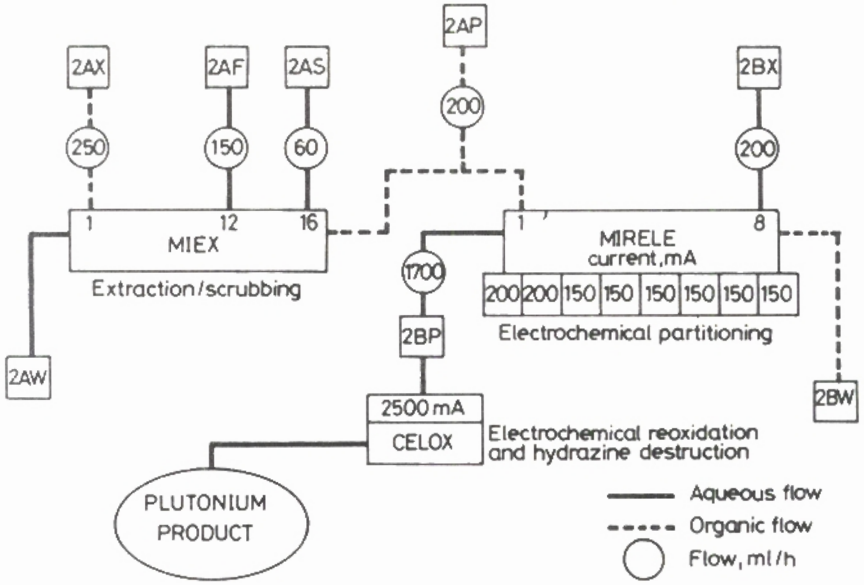


Fig. 9. Proposed flowsheet for the 2nd plutonium purification cycle with electrochemical partitioning

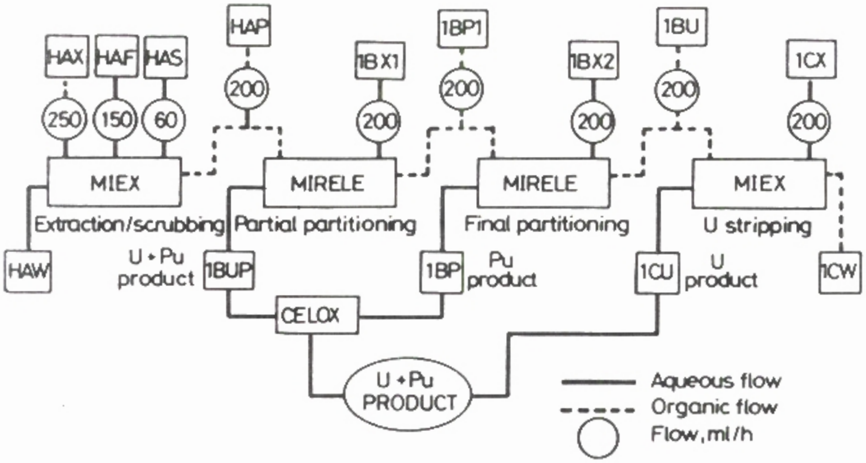


Fig. 10. Proposed flowsheet for the one-cycle spent fuel treatment employing electrochemical partitioning

In experiments using pure uranyl nitrate solutions, the decomposition rate of hydrazine was about 0.008M/Ah. Using U–Pu solutions, the hydrazine decomposition was enhanced to 0.02M/Ah, due to the reaction with Pu(IV).

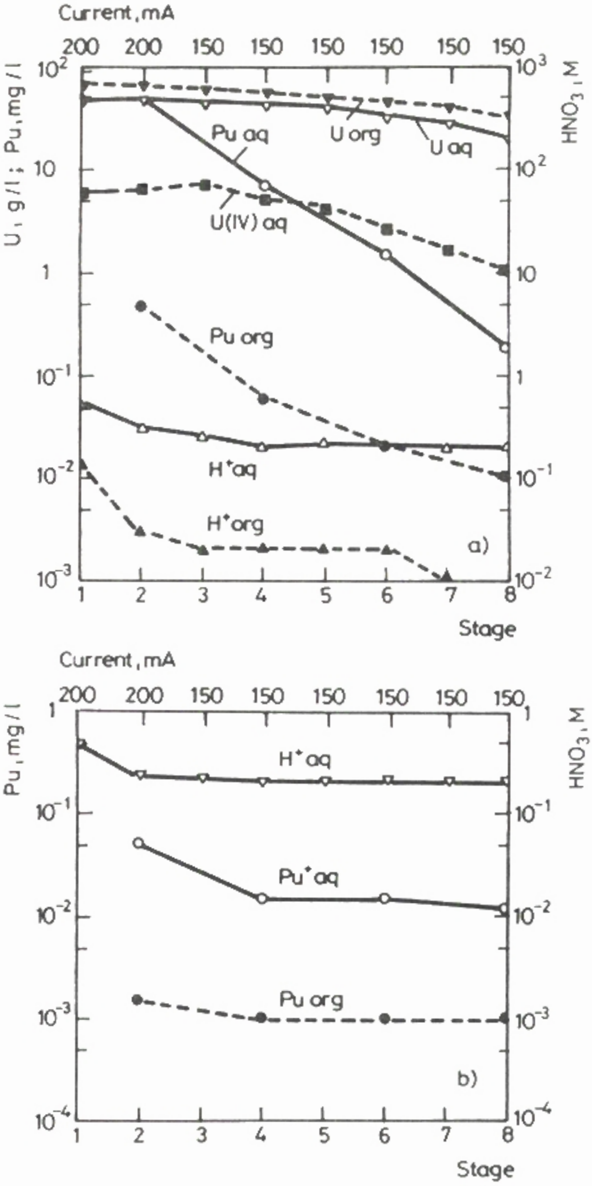


Fig. 11. Electrolytic mixer-settler MIRELE concentration profile in the partial and final partitioning of one-cycle spent fuel treatment; (a) partial partitioning, organic feed = 47.95 mg Pu/l; 72.6 g U/l; 0.18M HNO_3, electrolyte = 0.2M HNO_3; 0.2M N_2H_4, aqueous and organic flows = 200 ml/h; $R_a^o = 1$; (b) final partitioning, organic feed = 0.01 mg Pu/l; 18.99 g U/l; 0.02M HNO_3, electrolyte = 0.2M HNO_3; 0.2M N_2H_4, aqueous and organic flows = 200 ml/h; $R_a^o = 1$

U/Pu partitioning in absence of hydrazine: According to SCHMIEDER,[9] U/Pu partitioning may occur in absence of hydrazine and at nitric acid concentrations below 0.1M, which causes lower nitrous acid formation, the main cause responsible for Pu(III) reoxidation.

Two runs using 0.1 and 0.05M HNO_3 as electrolyte solution have demonstrated that nitrous acid, even at concentrations of the order of 10^{-5}M, oxidizes Pu(III). In both cases plutonium losses were higher than 0.1%. After 5.5 hours, no HNO_2 was detected and the concentration of Pu(IV) had increased.

Use of M–S MIRELE in one-cycle spent fuel treatment: Several studies have been made on the way of one-cycle treatment for irradiated nuclear fuels.[3,10] Based on the flowsheet proposed by ZABUNOGLU,[13] for the treatment of long-cooled light water reactor (LWR) fuel, a flowsheet was proposed using the M–S MIRELE in two steps involving U/Pu partitioning, called partial and final partitioning.

The conditions used and the concentration profiles of M–S MIRELE in the partitioning steps are shown in Fig. 10. In partial partitioning complete Pu stripping to the aqueous phase was almost reached. The Pu/U relation has increased from 1 to 2.2, a reliable condition for MOX fuel fabrication. In the final partitioning, a good purification of U was also reached, with Pu losses for the organic phase below 0.1%.

Figure 11 shows the proposed flowsheet for one-cycle spent fuel treatment.

Studies on hydrazine and plutonium oxidation

The aqueous product solution resulting from U/Pu partitioning contains Pu almost totally as Pu(III) due to the presence of hydrazine. To make possible product Pu concentration, the solution must be oxidized, to destroy hydrazine and bring plutonium back to +4 valence.

The electrolytic equipment used in those studies (CELOX) was designed as a simple flow cell (Fig. 12), where the aqueous phase in contact with the electrodes is oxidized. As the electrolytic M–S, the housing material, titanium, is the cathode. Therefore, in this case, the anode surface, platinized titanium, is higher than the cathode surface, to ensure anodic oxidation. Also here the insulator material is PTFE. The free space at the top of the cell must be purged with air for safety reasons in order to ensure the dilution of hydrogen (formed in the electrolytic reaction at the cathode) to levels below the explosive limit.

Figure 13 shows the results of studies on the influence of current in hydrazine decomposition. The highest decomposition rate occurred at 3000 mA, but due to the compromise between plutonium oxidation and current density, 2500 mA was chosen to avoid oxidation to PuO_2^{2+}.

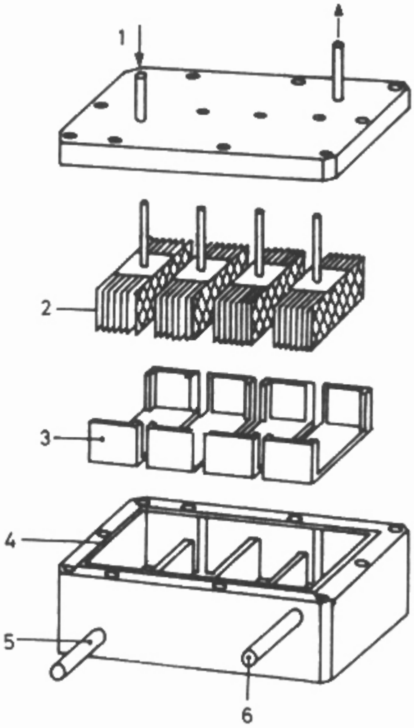


Fig. 12. Electrochemical oxidation cell CELOX; 1 – scavenging air, 2 – anode (platinized Ti), 3 – insulator (PTFE), 4 – cathode (Ti), 5 – solution inlet, 6 – solution outlet; volume: 250 ml, cathode surface: 100 cm^2, anode surface: 980 cm^2, specific anode surface: 3.92 cm^2/cm^3, $R_a^o \cong 10$

Nitric acid concentration caused no influence on the hydrazine decomposition rate.

Using the solutions from the partitioning process, complete hydrazine decomposition, with a rate of 0.008M/Ah, and total Pu oxidation were achieved (Fig. 14).

Conclusion

The evaluation of the results has demonstrated that the utilization of electrochemical techniques for the treatment of spent nuclear fuel is suitable for the purposes of this work.

The M–S MIRELE, developed for the studies on U/Pu partitioning, proved its efficiency and flexibility, being used even in the process of advanced fuel cycles, where uranium and plutonium are separated together from the other elements, for further fabrication of MOX fuel.

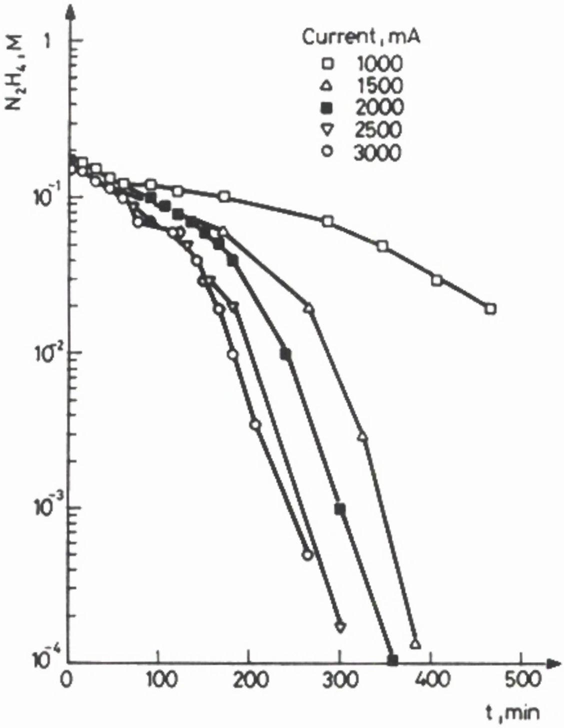


Fig. 13. Influence of applied current in hydrazine decomposition; $[HNO_3] = 0.4M$

In both studies, after the adjustment of the applied current, the plutonium losses were below 0.1%, indicating the high efficiency of the equipment.

U(IV) formed in the M–S MIRELE during the electrolysis, contributes favorably to the reduction and stripping of plutonium, which can be seen comparing experiments in the absence and in presence of uranium.

Partitioning experiments in the absence of hydrazine have indicated that even at nitric acid concentrations below 0.1M, nitrous acid is formed, with high distribution in the organic phase, causing plutonium reoxidation and losses to the organic raffinate.

The oxidation cell CELOX was used to oxidize plutonium to +4 valence state and to destroy hydrazine, affording an aqueous solution in conditions favoring final products concentration.

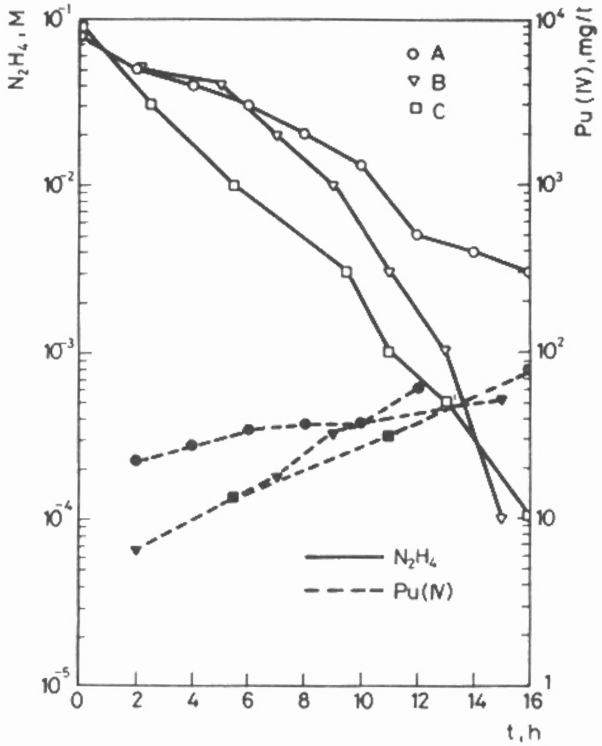


Fig. 14. Time required for Pu reoxidation and hydrazine decomposition in CELOX

Curve	U, g/l	Pu_{total}, mg/l	Pu(IV), mg/l	N_2H_4, M	HNO_3, M
A	35	67.20	20.00	0.08	0.21
B	50	64.00	8.97	0.13	0.21
C	10	79.61	12.62	0.08	0.23

References

1. F. BAUMGÄRTNER, Chemisch-Verfahrenstechnische Entwicklungen zum Wiederaufarbeitungsprozess von 1965 bis 1975 im Institut für Heisse Chemie, KfK–2285, Karlsruhe, Kernforschungszentrum, 1976.
2. F. BAUMGÄRTNER, H. SCHMIEDER, Radiochim. Acta, 25 (1978) 191.
3. H. J. BLEYEL, D. ERTEL, H. GOLDACKER, G. PETRICH, J. RÖMER, H. SCHMIEDER, Kerntechnik, 55 (1990) 21.
4. L. FINSTERWALDER, H. HAUSBERGER, H. GOLDACKER, H. SCHMIEDER, Trans. Am. Nucl. Soc., 31 (1979) 519.

5. H. HAUSBERGER, Ein Betrag zur reduktiven,. elektrolytischen Plutonium–Uranium-Trennung im Mischabsetzer, Ph.D. Thesis, Karlsruhe, GmbH, 1972.
6. G. PETRICH, U. GALLA, H. GOLDACKER, H. SCHMIEDER, Chem. Eng. Sci., 41 (1986) 981.
7. H. SCHMIEDER, F. BAUMGÄRTNER, H. GOLDACKER, H. HAUSBERGER, Electrolytic Techniques in the Purex process, ORNL-tr-2999, Oak Ridge, Tenn., Oak Ridge National Lab., 1975.
8. H. SCHMIEDER, H. GOLDACKER, M. HEILGEIST, M. KLUTH, H. HAUSBERGER, L. FINSTERWALDER, Electrolysemischabsetzer (2B-EMMA) und Electrooxidationzelle (ROXI) für den zweiten Pu-Zyclus der Wiederaufarbeitungsanlage Karlsruhe. II. Plutonium-Betrieb, KfK-2957, Karlsruhe, Kernforschungszentrum Oct. 1980.
9. H. SCHMIEDER, Mise au point et étude d'un mélangeur-décanteur à électroréduction pour la séparation du plutonium au cours du rétraitement des combustibles nucléaires. FRNS-TH-2873, Institut National Polytechnique de Grenoble, Grenoble, May 1985.
10. H. SCHMIEDER, G. PETRICH, Radiochim. Acta, 48 (1989) 181.
11. M. WEISHAUPT, H. HAUSBERGER, H. SCHMIEDER, KFK-Nachr. 18 (1986) No 2, 61.
12. J. A. WILLIAMS, L. LOWES, M. C. TANNER, Trans. Instn. Chem. Engrs., 36 (1958) 464.
13. O. H. ZABUNOGLU, B. I. SPINRAD, Nucl. Technol., 93 (1991) 376.