Electrochemical processes for nuclear fuel reprocessing

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Abstract

The development of electroredox equipment, scaled up from laboratory apparatus to industrial application for the reprocessing of spent nuclear fuel, which is carried out worldwide by the Purex process, is presented. The design of the different electroredox equipment is described and operational results achieved in experimental facilities in laboratory and bench-scale equipment, as well as in an industrial reprocessing plant (Wiederaufarbeitungsanlage Karlsruhe, WAK), are described. The separation efficiency of plutonium from uranium is essentially increased by integration of electroreduction of tetravalent plutonium into liquid/liquid extractors. Electrooxidation of trivalent plutonium and of hydrazine lead to compact apparatus and simple and reliable process steps avoiding radioactive contaminated waste. The experimental work was connected with the development of a mathematical model (VISCO) finally allowing the simulation of the whole separation process. This enabled a drastic simplification of the whole Purex process demonstrated in the miniature reprocessing plant (MILLI) in the late 1980s.

1. Introduction

Oxide fuel light water reactors are dominant for nuclear electricity production worldwide. For this type of fuel an aqueous medium process to recover the fissionable material is well established. The chemical separation of the fission products and of uranium and plutonium is done in a counter-current extraction process using *n*-tributylphosphate (TBP) diluted with kerosene. This process, the Purex process, was first developed and industrially used in the USA in the early 1950s. A description of the process including extraction alternatives as well as research and development needs for commercial use was published by Baumgärtner [1, 2].

Determined by the demand of the following processes for reenrichment and fuel fabrication to minimize shielding and to facilitate the handling of the refabricated fuel elements, it is a particular requirement for the reprocessing process to guarantee an extreme product purity and to keep the radioactive contaminants as low as possible. The permissible contamination limit for the long lived fission product caesium, after reprocessing, is, for example, about 3 ppb (by weight) and the residual content for plutonium is limited to about 15 ppb in the uranium product. Furthermore, the process calls for a high product yield of 99%. For the extraction process about 99.5% is achievable in a modern plant. On average, this corresponds to a content of about 1 ppm plutonium in the extraction raffinates.

Another requirement of commercial reprocessing is minimization of the radioactive waste volume in order to reduce costs. The costs of radioactive waste treatment and storage are incomparably higher than the actual costs for conventional chemical wastes. The major part, more than 50% of reprocessing costs are capital costs. This is the reason why current R&D activities are directed to a cost reduction by a simplification of the process.

Figure 1 shows a scheme of the main part of a conventional Purex. Five extraction cycles are used to meet the product specifications. In the first high-active cycle the major portion of fission products is separated from uranium and plutonium. A radioactivity portion of about 10^{-5} of the 'nonproblematic' fission products and actinides (alkali elements, alkaline earths, rare earths, transplutonium elements etc.) leave this cycle with the products uranium and plutonium. The products are separated later in this cycle by reducing the tetravalent plutonium to Pu(III) which has a very low distribution coefficient and is backextracted into an aqueous phase. Between each cycle plutonium has to be reoxidized and hydrazine, which is necessary to stabilize plutonium in the trivalent state, must be destroyed.

One reason for incomplete separation is the degradation of the solvent by radiolysis and hydrolysis [3]. Some fission products and plutonium form complexes with the TBP degradation products. Thus the degradation products must be removed by an alkaline wash.

Both laboratory and industrial experiences with the conventionally designed high-active first Purex cycle show that the product purity specifications can not be met, even for the 'nonproblematic' fission products [4].
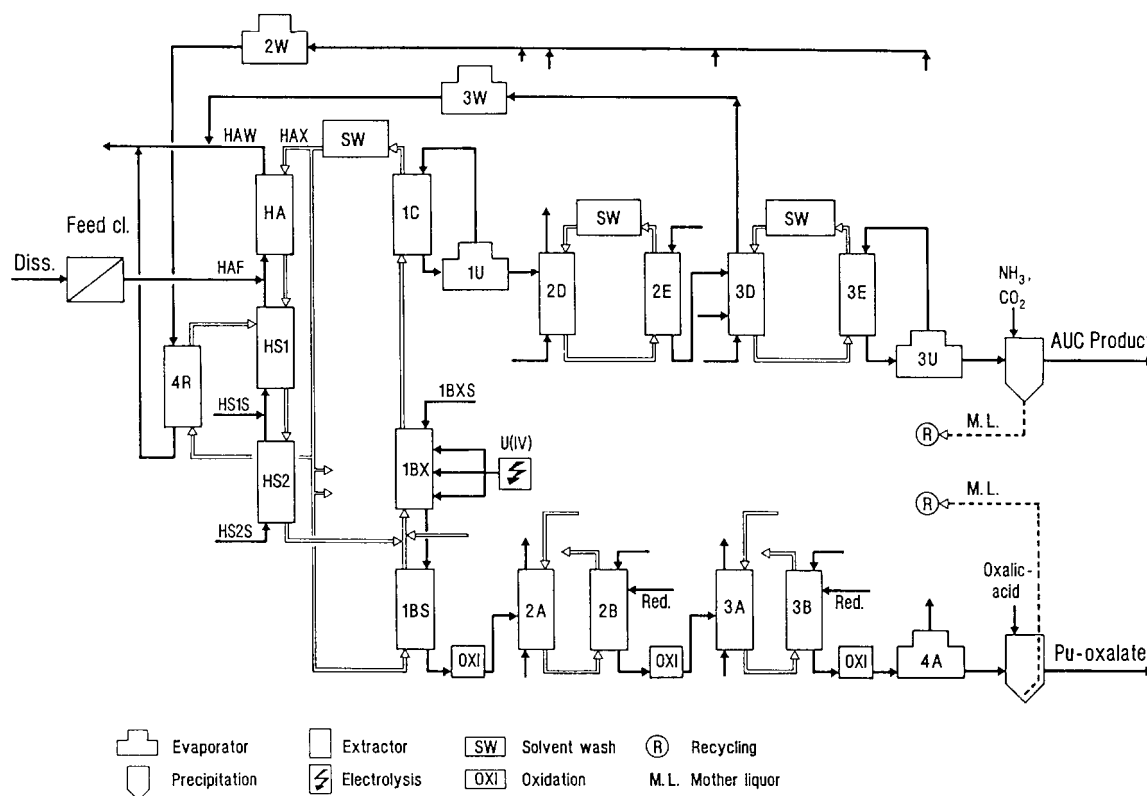
Fig. 1. Conventional Purex process. Historical flowsheet nomenclature is by combination of the following letters: A = U/Pu coextraction; B = Pu strip; C = U strip; D = U extraction; E = U strip; F = feed; H = high active cycle; S = scrub or scrub solution; U = U concentration; W = raffinate concentration or raffinate; X = extraction or extractant; leading 1–3 = cycle number, trailing 1–2 = partial unit number. Other abbreviations: 4R = raffinate recycling extractor, 4A = Pu concentration; AUC = U precipitation; Red = reductant; Feed cl. = feed clarification; Diss = dissolver, UNH = uranyl nitrate hexahydrate.

Therefore, two additional refining cycles are used for each product, uranium and plutonium, as shown in Figure 1.

2. Electroredox equipment for the Purex-process

For the separation of Pu from U four processes have been developed to technical maturity with the following four reductants: iron(II) sulfamate [5], uranium(IV) nitrate [6], hydroxyl-ammonium nitrate [7], electrore-duction within the extractor [8]. The external feed U(IV) process is usually applied in current industrial repro-cessing. U(IV) has at least two drawbacks: (i) demand for a high U(IV) excess, and (ii) occasionally failure of the process caused by the autocatalytic reoxidation of Pu(III) and U(IV) starting in the organic phase.

These facts initiated activities in different countries to develop the *in situ* electroreduction process [9–12]. A comparison of the chemical process with the electro-chemical process was made in an earlier publication and resulted in a preference for the electroreduction process [13]. According to our experience this process shows all the advantages of the U(IV)-process but avoids its drawbacks.

Since the first electroreduction experiments [5] per-formed at our institute, our efforts to design simple, compact and reliable electroredox equipment for indus-trial applications led to the following three design criteria [8]: (i) no diaphragm, (ii) casing of apparatus used as cathode, and (iii) current or voltage constant operation.

Basic chemical investigations and corrosion tests of different materials showed that these criteria can be fulfilled for both the electroreduction extractors and the electrooxidation cell [8, 14]. Diaphragms are not neces-sary because of the irreversible character of the U(VI)-electroreduction in the used electrolyte [15] and of the hydrazine-electrooxidation. Titanium was found to be well suited as the container and cathode material, having corrosion rates of less than 50 μm per year under process conditions. Experiments with constant current or voltage operation showed that side-reactions such as hydrogen formation and nitrate reduction can be suppressed to a tolerable level, so that reference electrodes are not required for constant voltage operation.

Figure 2 shows schematically the construction of the electroredox equipment developed in Karlsruhe. The mixer–settler for electroreduction is made of titanium and the containment acts as cathode. The anodes are installed in the settler chambers where the electroreduc-tion takes place. The most stable anode material is platinum with corrosion rates of a few μm per year. For industrial electroredox equipment, platinized Ta, Ti or other materials are used.
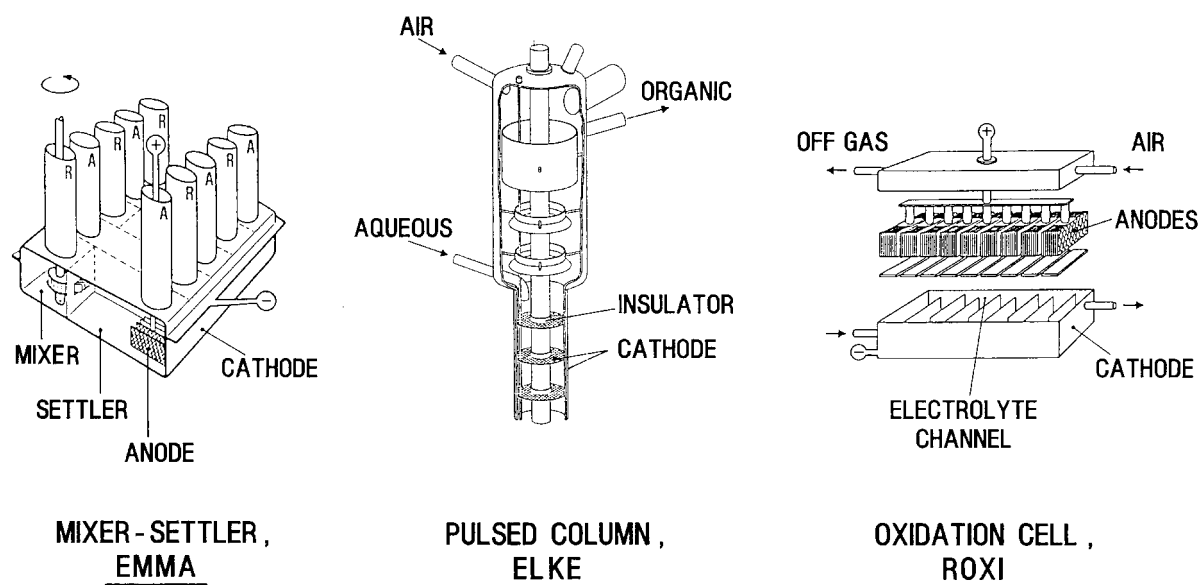
Fig. 2. Design principles for electroredox equipment.

The pulsed column is constructed in a similar way. The column and the sieve plates, made of titanium, function as the cathode, while the platinized central rod is the anode. In the top decanter of the column, separator shields are installed to promote the separation of electrolytic gas from the organic liquid. The ratio of cathode to anode areas is made as large as possible to reduce anodic reoxidation of Pu(III).

To eliminate any risk of a hydrogen explosion, the gas volume of the mixer–settler and of the top decanter of the pulsed column are sparged with air to dilute the hydrogen below the explosive limit. The hydrogen current yield can be kept below 10% under typical conditions.

The electrooxidation cell is a typical electrochemical flow reactor designed to minimise axial mixing. The electrolytic gas leaves the cell diluted with sparging air. The containment (cathode) is again made of titanium. The anode stacks are made of platinized metal sheets. The major advantage of electrooxidation compared to chemical oxidation with nitrogen oxides is the compactness of the apparatus. The chemical process requires one absorption column for the complete oxidation of hydrazine and Pu(III) and one additional column to desorb the excess of nitrogen oxides [16].

3. Results and discussion

3.1. Electroreduction mixer–settler

Table 1 summarizes the results of counter current experiments with the electroreduction mixer–settlers, called EMMA [8, 17, 18]. The 16-stages MILLI-EMMA was used for U/Pu split, as well as for Pu purification, but without a U scrub in the latter case. Because of the miniature size of the apparatus, the extraction stage efficiency was low, especially in experiments with a high organic to aqueous flow ratio. The major parameter variations were: (i) TBP concentration, (ii) Pu content, (iii) current density, (iv) HNO$_3$ concentration in the aqueous strip solution, (v) HDBP concentration in the organic solvent, (vi) flow ratios, and (vii) total volume flow rate (residence time).

Table 1. Results of test runs with electroreduction mixer–settlers

	Purpose of test	Flow ratio org./aq.	Pu product concentration /g l^{-1}	Separation		Voltage /V
				Pu–DF	U–DF	
MILLI–EMMA	U/Pu split FBR model fuel*	5–6.7	≤22	≤4500[†]	~3000[†]	2.8–8.0
	U/Pu split LWR model fuel	7.1–9.3	≤4.8	≤2000[†]	~3800[†]	2.8–8.0
	Pu purification cycle	2.0–3.5	≤46	≤20 000[‡]	–	≤6.0
WAK–2B-EMMA	Pu purification cycle	2.0–3.0	≤36	≤100 000[§]	–	2.0–8.0

* 20 Vol-% TBP, 30 Vol-% for all other experiments
[†] 9 practical stages for Pu strip, 7 for U scrub
[‡] 16 practical stages used for Pu strip, without U scrub
[§] 12 practical stages used for Pu strip, without U scrub

The most significant effect on the U/Pu separation was due to variations of the total volume flow rate, as expected. All other parameters, when varied within reasonable limits, had a smaller effect. A decrease in the total volume flow rate causes complex interactions in the counter-current extractor due to the increase in residence times for both phases. In the case of the miniature mixer–settler, the increase in extraction stage efficiency seems to be the dominant factor for separation improvement. In the Pu purification experiments an upper limit for the organic to aqueous flow ratio of 3:1 was found at Pu product concentrations of about 40 g l^{-1}.

The first industrial application was performed in the Pu purification cycle of the Wiederaufarbeitungsanlage Karlsruhe, WAK. The plant was equipped with an electroreduction mixer–settler (WAK-2B-EMMA, 12 stages) and an electrooxidation cell (WAK-2B-ROXI) in 1980 [18, 19]. In addition, in 1984, the first highly active cycle of WAK was equipped with an electroreduction mixer–settler.

In the WAK-2B-EMMA the flow ratio could not be raised above 3:1, corresponding to a Pu product concentration of about 36 g l^{-1}, although this apparatus has a significantly higher stage efficiency. One reason for the limitation of the Pu–DF to a maximum of 105 are the very long residence times (volume flow limitations for technical reasons) [18, 19]. To obtain a better understanding of the complex reductive Pu separation process we developed a mathematical model VISCO [13, 20].

Process simulations were made with Visco to determine the sensitivity of the individual parameters for Pu separation in multistage extractors. The results confirmed the importance of stage efficiency for an extraction cascade. Stage efficiencies below 75% result in reoxidation starting in the organic phase caused by a depletion of the hydrazine stabilizer. The importance of the organic to aqueous flow ratio and of the Pu product concentration limit (40 g l^{-1}) were also confirmed. The limitation by the Pu product concentration can be explained by the strong salting effect of Pu(III) for U(VI), Pu(IV) and HNO$_3$ [21]. The transfer of U(VI) and Pu(IV) to the aqueous phase is inhibited under these conditions and nitric acid accumulates in the strip part of the mixer–settler resulting in an insufficient aqueous concentration of U(IV) and a decrease in the Pu–DF.

3.2. Electroreduction pulsed column

The extractor type preferred today for industrial reprocessing plants are pulsed sieve plate columns. The main reason for this is the less complicated design of a critically safe pulsed column in comparison to a mixer–settler bank, at least for the U/Pu separation step.

The first experiments with the electroreduction column ELKE done in the plutonium test facility PUTE under the conditions of a Pu purification cycle yielded decontamination factors of up to 106 depending on the residual U content, flow ratio, nitric acid concentration etc. [22]. The effective column length was about 8 m.

The following experiments were carried out to study the electroreduction feasibility in the first extraction cycle, that is, for U/Pu separation. Based on the results achieved in the purification cycle a comparable outcome was expected for separation. However, the experiments showed a surprisingly poor separation efficiency: decontamination factors of only 200 to 2000 were achieved [23]. Theoretical calculations with the computer model Visco excluded slow reaction kinetics in explaining this effect. Therefore, we suspected a fluid dynamic cause. By installation of an additional glass electroreduction column it was possible to directly observe the dispersion and the two-phase flow. It then was observed that in the middle region of the column unusually large organic drops appeared with diameters of up to 20 mm and with inclusions of aqueous phase. This latter effect explained the observed insufficient U/Pu separation by heterogeneous contamination, in this case aqueous drops.

The first way to reduce the amount of entrained aqueous phase transported with the organic drops is an increase in pulse energy. Table 2 shows the results for the glass column (the first row is for the titanium column) [24]. In a part of the experiments (last row) the lower section of the column was used to scrub uranium (BS section).

The results show a steep increase in the Pu–DF when increasing the pulse energy $A \times f$ (amplitude $\times$ frequency) from 90 to 180 cm min^{-1}. The visual observation show an improved dispersion quality within the column with increasing pulse energy. Applying a pulse energy of $A \times f = 180$ cm min^{-1} small organic drops form a homogeneous dispersion without any inclusions of aqueous phase and a maximum Pu–DF of about 12 000 was achieved with only 5 m for the reductive Pu strip (BX part). To meet the final product specification for U, a Pu–DF of about 500 000 is necessary, however. To further increase separation we therefore used two consecutive columns in order to extend the reductive strip height as well as to minimize the entrainment effect by the introduction of an intermediate decantation. The results are summarized in Table 3 [24]. Row 2 shows that the desired Pu–DF can be reached with a flow ratio of 7.25 (which is usual in this process step for LWR fuel)

Table 2. Results of U/Pu separation in one column as function of pulse energy $A \times f$ (amplitude $\times$ frequency)

Pulsation $A \times f$ /cm min^{-1}	Extraction height for Pu strip (BX) /m	[Pu] in raffinate /mg l^{-1}	Pu–DF
90	7.6	0.63	1350
90	6.0	2.75	268
140	6.0	1.30	692
180	5.0	0.06	11 900

Org. feed: 89 to 92 g U + Pu l^{-1}, [U]/[Pu] $\approx$ 100, [HNO$_3$] $\approx$ 0.2 M
Strip solution: [HNO$_3$] = 0.1 M, [N$_2$H$_5^+$] = 0.05 to 0.1 M
Volume flow ratio org./aq. in BX part: 5 to 6
Cathodic current density: 0.5 to 3 mA cm^{-2}

Table 3. Results of U/Pu separation with two electroreduction columns in series

Volume flow ratio org./aq. in BX part	Pulsation 1. Column /cm min⁻¹	A × f 2. Column /cm min⁻¹	[Pu] in raffinate /mg l⁻¹	Pu–DF	U–DF
6.00	135	180	≪0.01	≫73 000	143
7.25	135	180	0.0015	507 000	345
9.33	135	180	0.005	116 000	311

Org. feed: 88 to 90 g U + Pu l⁻¹, [U]/[Pu] ≈ 100, [HNO₃] ≈ 0.2 M
Strip solution: [HNO₃] = 0.1 M, [N₂H₅⁺] = 0.05 to 0.15 M
Extraction height: BX part: 6.6 m + 6 m
                 BS part: 1 m
Volume flow ratio in BS part: 1
Cathodic current density: 0.5 to 0.8 mA cm⁻²

by the use of two combined columns with 12.6 m total length.

Furthermore, it was also shown in the experiments, that in the case of a maloperation (interrupted hydrazine feed), no inadmissibly high Pu accumulation appears. The measured maximum concentration (first column) was always less than 20 g Pu l⁻¹ within 30 h after interruption in hydrazine supply.

In the electroreduction process only small amounts of the byproducts hydrazoic acid and ammonium are formed thus reducing the hydrazine consumption. The values found in the presence of representative amounts of catalytically acting technetium (Table 4) are generally lower than in the organic continuous operating mode which was proposed by BNFL [25, 26] as a modification for the U/Pu separation. Electroreduction has the potential to be operated without the addition of hydrazine as was demonstrated in the PUTE facility [27, 28]. This requires the nitric acid concentration to be kept below 0.7 M within the whole extractor.

3.3. Electrooxidation

As mentioned previously, between each cycle of the Purex process, plutonium has to be reoxidized to the tetravalent state and hydrazine must be destroyed. For this purpose we have developed an electrooxidation cell, called Roxi. The anodic destruction of hydrazine is aided by the reactions of hydrazine with Pu(IV) formed by anodic oxidation and with HNO₂, which is cathodically produced with small yield.

The yield of the direct anodic oxidation of Pu(III) depends on the nitric acid concentration. Under typical conditions, the major part of the Pu(III) is oxidized autocatalytically by HNO₂. The accompanying U(IV) is consumed by reduction of Pu(IV).

The formation of Pu(VI) is suppressed at a HNO₃ concentration higher than 2 M. The formation of ammonium by cathodic reduction of HNO₃ depends on the electrolyte composition and was measured to be 0.03 to 0.46 mmol A⁻¹ h⁻¹ for an electrolyte without hydrazine [29].

The average values achieved with the two electrooxidation cells installed in the PUTE facility are given in Table 5. For typical feed compositions, current consumption of about 100 A h mol⁻¹ N₂H₅⁺ were measured in the Ti–ROXI. For the Hf–ROXI, a higher current demand was measured, which is probably caused by a smaller fraction of cathodic reaction supporting the hydrazine destruction. The ammonium formation is low but in some cases still higher than expected. This can be explained by the formation of ammonium in parallel to the electroreduction of HNO₃.

3.4. Corrosion

The corrosion of titanium under cathodic conditions depends on the electrolyte composition and on the current density. Average corrosion rates estimated by different methods are shown in Table 6. For the relevant and maximum HNO₃ concentration of 2.5 M, gravimetric experiments show a drastic decrease in corrosion in the presence of reducible cations (row 1, Table 6); no definite effects of current density are detected in this case.

Traces analysis in the product solutions confirm this effect for various pieces of equipment. Only a small increase in corrosion is observed at higher ROXI current densities (rows 2 and 3). Thickness measurements of the PUTE–ROXI channel sheets show, after an operation

Table 4. Hydrazine consumption and formation of ammonium and hydrazoic acid in BX/BS columns

	[N₂H₅⁺]$_{BXS}$/M	[Tc]$_{BSP}$/mg l⁻¹	$\frac{\Delta N_2H_5^+}{Pu}$	$\frac{\Delta HN_3}{Pu}$	$\frac{\Delta NH_4^+}{Pu}$	$\frac{\Delta HN_3}{\Delta N_2H_5^+}$	$\frac{\Delta NH_4^+}{\Delta N_2H_5^+}$
U(IV)–	0.2	465	15.8	4.2	5.9	0.27	0.37
Feed process	0.2	215	10.9	2.4	3.2	0.22	0.29
Org. continuous	0.2	0	2.0	<2	0.07	<1	0.04
U(IV)–	0.2	450	7.1	2.6	5.3	0.67	0.75
Feed process	0.2	280	4.9	2.0	4.4	0.41	0.90
Aq. Continuous	0.05	310	3.1	1.4	1.1	0.45	0.36
Electroreduction	0.2	290	5.0	2.0	1.8	0.41	0.37
Process	0.2	170	3.8	1.7	0.3	0.45	0.08
Aq. Continuous	0.2	0	2.1	<0.6	0.09	<0.3	0.04
	0.035	130	1.6	1.1	0.3	0.70	0.21
	0	80	–	<0.7	0.15	–	–

Table 5. Average results of electrooxidation cells in Pute

Apparatus	$N_2H_5^+$ current consumption /Ah mol^{-1}	Pu(VI) formation /% of Pu	NH_4^+ formation /mmol A^{-1} h^{-1}
Titanium-ROXI	≤100	≤2	~1
Hafnium-ROXI	≤170	≤2	0.1–2
Hafnium-ROXI	~150	<1	~0.6

period of 1950 h, comparably small corrosion rates of 23 μm a^{-1} (i.e., micrometre per year) even at current densities up to 135 mA cm^{-2} (last row). The corrosion rate of hafnium, estimated from traces analysis, amounts to 7.7 μm a^{-1} at current densities of 50 mA cm^{-2}.

The anodic corrosion of platinum increases with decreasing nitric acid concentration and with increasing current density and temperature [30]. The corrosion rates obtained by gravimetric, trace and neutron activation analysis for typical electrolyte compositions and current densities amount to a few μm per year.

4. Conclusions

Compared with chemical separation processes for Pu, electroreduction is simpler from both engineering and operational points of view. The process has all the advantages of the externally fed U(IV) process but avoids its drawbacks. Because of its simplicity and compactness, electrooxidation has significant advantages when compared to the chemical oxidation process. Titanium, platinum, and hafnium show sufficiently low corrosion rates to guarantee a long life-time of the electroredox equipment.

Together with results for an improved fission product separation achieved in the MILLI plant [31–33] the improved U/Pu split by use of electroredox equipment confirm the potential to simplify significantly the separation in the first Purex cycle. By application of these methods, which we summarise by the term
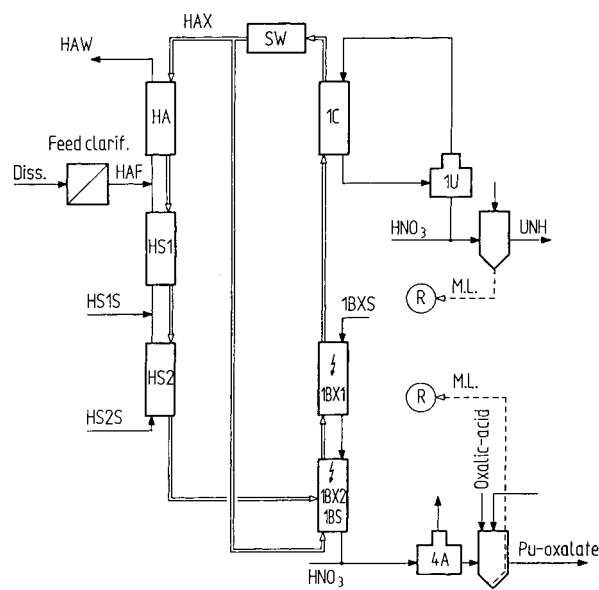

Fig. 3. Concept for an one-cycle Purex process. For the engineering symbols see Figure 1.

'Impurex', the final product specification was met for both products in the first cycle. By optimization of the discussed process it is likely that the high separation efficiency can also be achieved in an industrial reprocessing plant.

Furthermore, the following conditioning process steps of fuel refabrication should be included in the overall-consideration of the total separation achievable. This applies to the conventional plutonium oxalate precipitation, as well as for the newly proposed uranyl nitrate crystallisation [34]. The product yield of the whole process can be kept high by recycle of the precipitation and crystallization mother-liquors to the extraction.

Figure 3 summarizes the concept of the one-cycle process. In comparison with Figure 1 the simplifications are evident.

Table 6. Titanium corrosion rates of electroredox equipment, T ≈ 50 °C

Method	Electrolyte/M				Average current density /mA cm^{-2}	Estimated corrosion rate /mm a^{-1}	Remarks
	[HNO$_3$]	[N$_2$H$_5^+$]	[U]	[Pu]			
Gravimetric	2.5	0.2			5	0.34	Approx. 500 h
					50	0.67	
	2.5	0.2	0.1		5	0.022	
					15	0.088	
					50	0.018	
							2B-EMMA
Traces analysis of Pu product solution	≤0.5	≤0.5	≤0.01	≤0.1	≤5	≤0.009	Test operation
						<0.002	WAK operation
	≤0.7	≤0.3	≤0.04	≤0.16	3.0–7.3	≤0.002	PUTE–ELKE
	1.5–2.0	≤0.1	~0.002	≤0.15	25–94	<0.017	PUTE–ROXI
							PUTE–ROXI
Measurement of sheet thickness	0.6–2.5	<0.5	0–0.36	0–0.17	5–135	0.023	After 1950 h of operation

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