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Electrochemical recovery of fission platinoids (Ru, Rh, Pd) from simulated high-level liquid waste

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ABSTRACT

Electrochemical behavior of ruthenium(III), rhodium(III) and palladium(II) present in the simulated high-level liquid waste (SHLLW) was studied, at 298 K, to explore the feasibility of recovering these fission platinoids from high-level liquid waste (HLLW). The cyclic voltammogram of SHLLW at platinum electrode consisted of a surge in cathodic current occurring at a potential of –0.38 V (Vs. Pd), which resulted in a large cathodic wave at –0.55 V (Vs. Pd) was attributed to the reduction of platinoid ions into their metallic forms. At stainless steel electrode, the onset of reduction occurred at –0.43 V (Vs. Pd), which resulted in a cathodic wave at –0.7 V (Vs. Pd). Electrolysis of SHLLW was carried out at various cathodic potentials and the recovery was in the order Pd >> Rh ~ Ru. The total recovery of ruthenium, rhodium and palladium increased with increase of applied potential and about 42% was recovered at the applied potential of –1.0 V (Vs. Pd) in 4 h. X-ray diffraction indicated the presence of all the three metals in the deposit and EDS analysis indicated the presence of palladium to the extent of 80–85% in all deposits.

Keywords: Ruthenium; Rhodium; Palladium; Voltammetry; Electrodeposition

1. Introduction

PGMs or platinoids find several applications in various industries [1,2]. However, the natural availability of these metals in the earth crust is very low and they are being exhausted by the huge demand from various industries. Therefore, finding alternative resources would be very attractive. One such resource is the spent nuclear fuel arising from the nuclear reactor [3–5]. Significant quantities of platinoids namely, ruthenium, rhodium and palladium, are formed as fission products in a nuclear reactor. It is estimated that by the year 2030, the amounts of fission platinoids produced by the nuclear reactor operations all over the world would be comparable with the amounts of platinoids available at that instant in the earth crust [3]. Therefore, the recovery of platinoids from the spent nuclear fuel may provide appreciable incentives in view of the growing demand of PGMs in various industries.

PUREX (Plutonium and Uranium Recovery by Extraction) process is being adopted for the recovery of uranium and plutonium from spent nuclear fuel dissolver solution. The raffinate rejected after extraction is called as high-level liquid waste (HLLW), which contains nearly 70% of platinoids existing in the form of complex nitrates [4]. Among the fission platinoids, the solution chemistry of palladium(II) in HLLW is relatively simple and the electrochemistry is well understood. However, the coordination and redox chemistry of ruthenium(III) and rhodium(III) in nitric acid itself is very complex [6]. Excellent reviews

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by Kolarik and Renard and Pokhitonov et al. detail the methods reported so far for the separation and recovery of fission platinoids [7–9]. Among the various procedures, the electrochemical method for the recovery of platinoids is simple and viable for scaling-up operation. This method does not demand addition of external reagents for the recovery and thus does not generate any secondary waste. Koizumi et al. [10] studied the electrolytic recovery of platinoids from nitric acid solutions and reported the efficacy of the process in the presence of various interfering ions like uranium. Kobayashi et al. reported the separation of ruthenium from other fission products by electrodeposition of ruthenium from ruthenium chloride and ruthenium nitrosyl nitrate solution spiked with ^{106}Ru(III) [11]. Motojima exploited the volatile nature of RuO_4 to separate radioruthenium from nitric acid solution [12]. Ruthenium(III) present in 3 M nitric acid was oxidized to volatile ruthenium tetroxide and it was extracted into n-paraffin. Kirshin et al. studied the electrolytic recovery of palladium from nitric acid solutions and reported the efficiency of the process in the presence of HNO_3, $NaNO_3$, uranium and other admixtures [13].

Previously, we reported the recovery of palladium from nitric acid and simulated HLLW (SHLLW) solutions and ruthenium and rhodium from nitric acid using stainless steel as working electrode [14–16]. These studies indicated that the recovery of palladium was quantitative from nitric acid and the recovery was lowered to <40% from simulated HLLW due to several complications [14,15]. The recovery of ruthenium and rhodium from nitric acid medium was <20% [16]. The electrochemical behavior of ruthenium, rhodium and palladium in nitric acid was also studied [16]. The total recovery of PGMs was limited to 20% at –0.5 V, which increased to 40% at –1.0 V. However, the electrochemical behavior and the recovery of all the three platinoids present in the simulated HLLW were not studied. Such a study is necessary to establish the recovery of all platinoids and the effects from other metal ions present in actual HLLW on the recovery. Therefore, the aim of the present paper is to report the electrochemical behavior of platinoids (ruthenium(III), rhodium(III) and palladium(II)) in SHLLW at stainless steel and platinum working electrodes, to explore the feasibility of recovering them from high-level liquid waste. The electrolysis of SHLLW was studied at various potentials and the results on the recovery and characterization of the deposit are presented in this paper.

2. Experimental

2.1. Material

All the chemicals used in the study were of analytical AR grade. All the studies were performed at 298 K. Rhodium(III) nitrate in nitric acid solution (10% w/v) and palladium(II) nitrate solution (10% w/v) were procured from Arora Matthey, India and ruthenium nitrosyl nitrate (1.5% w/v) was procured from Acros, India. Nitric acid was procured from S.D. Fine chemicals, Mumbai, India and was diluted to appropriate concentrations. The composition of SHLLW corresponds to the HLLW arising from reprocessing of fast reactor fuel (burn-up: 80,000 MWd/Te) is shown in Table 1 [17]. The SHLLW was prepared by dissolving the standard solution of their nitrate salt in nitric acid medium.

Table 1
Elemental compositions of simulated high-level liquid waste (HLLW) arising from reprocessing of fast reactor fuel (Burn-up: 80,000 MWd/Te) [17]

Element	FBR (80,000 MWd/Te) Elements present g/l
Antimony	0.01
Barium	0.41
Cadmium	0.04
Cerium	0.69
Cesium	1.12
Chromium	0.1
Dysprosium	0.005
Europium	0.31
Gadolinium	0.07
Iron	0.5
Lanthanum*	0.48
Molybdenum	1.09
Neodymium	1.131
Nickel	0.1
Palladium	0.6
Promethium	0.34
Promethium	0.05
Rhodium	0.26
Rubidium	0.06
Ruthenium	0.81
Samarium	0.05
Selenium	0.01
Silver	0.13
Sodium	3
Strontium	0.14
Technetium	0.26
Tellurium	0.16
Terbium	0.01
Tin	0.02
Uranium	2.64
Yttrium	0.08
Zirconium	0.89
Acidity (M)	4.0 M

La* – added for Y, Pm, Te, Dy.

Tc, Mo – not added.

Co – added for Ni.

2.2. Voltammetry

In voltammetric studies, platinum or stainless steel wire electrode (Surface area = 0.11 cm^2) acted as working electrode and platinum acted as counter electrode. Since, the standard reference electrodes are not compatible with ~4 M nitric acid medium, the potentials were recorded against the quasi-reference palladium wire electrode. All the voltammetric data were obtained after IR compensation. Electrolysis experiments were performed using stainless steel plates (Surface area = 6 cm^2) with platinum plate as counter electrode and palladium as quasi-reference electrode. Stainless steel was chosen as cathode due to its inexpensiveness and easy availability. A two-compartment electrolytic cell was used for all electrolysis experiments and the design of the cell is reported elsewhere [15].

2.3. Instrumentation

All electrochemical studies were performed using Autolab (PGSTAT-030) equipped with an IF 030 interface. A Philips field effect scanning electron microscope (SEM), model XL 30, with energy-dispersive spectrometer (EDS) working at 30 kV was used to examine the surface morphology and elemental composition of the deposit. X-ray diffraction pattern of the deposited samples were obtained using Philips 1011 X-ray diffractometer with Cu K_α radiation. The amount of platinoid deposited on the electrode was determined from the increase in weight of working electrode as well as by estimating platinoids present in the solution before and after the electrolysis using ICP-OES. Faradaic efficiency was calculated from the ratio of platinoid deposited to the platinoid deposit expected from the quantity of coulombs passed into the solution.

3. Results and discussion

3.1. Cyclic voltammetry of platinoids at platinum electrode

Fig. 1 shows the cyclic voltammogram of Ru(III), Rh(III) and Pd(II) (20 mM each) present in SHLLW solution recorded at platinum working electrode at the scan rate of 10 mV/s, at 298 K. The cyclic voltammogram shows a gradual increase in cathodic current at –0.16 V (Vs. Pd) followed by a surge in cathodic current occurring at a potential of –0.38 V (Vs. Pd), which results in a large cathodic wave at –0.55 V (Vs. Pd). The prominent wave at –0.55 V could be attributed to the deposition of platinoids from SHLLW at the working electrode. The anodic side consists of a weak wave at –0.16 V (Vs. Pd) followed by a large anodic peak at 0.08 V. Nucleation loop is observed at –0.4 V (Vs. Pd). It is interesting to observe that the peak current and area of the anodic wave at 0.08 V (Vs. Pd) is much larger than cathodic peak area and peak current. This could be attributed to the predominant oxidation of Ru(III) to Ru(IV) in addition to the oxidation of PGMs deposits, which are usually irreversible [14]. When the electrode was removed after the first scan, the working electrode was covered with the black deposit of PGMs.

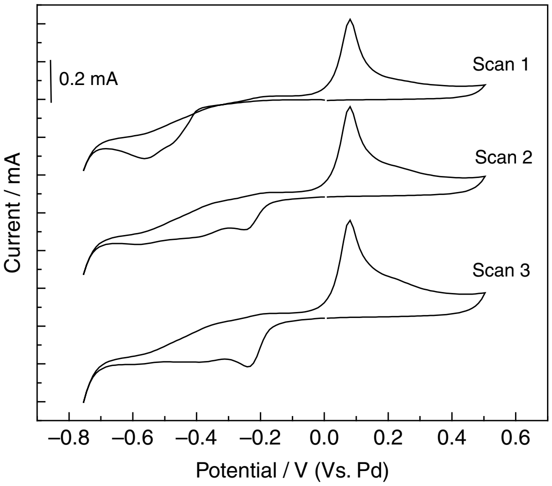

Fig. 1. Cyclic voltammograms of simulated high-level liquid waste containing 20 mM each of Ru(III), Rh(III) and Pd(II) recorded at platinum working electrode. Counter electrode: platinum wire. Reference electrode: palladium wire. Scan rate: 0.01 Vs^{-1} T: 298 K.

Fig. 1 also shows the second and third scans of SHLLW. A couple of additional cathodic waves are observed at –0.25 V (Vs. Pd), –0.39 V (Vs. Pd) in addition to the wave at –0.59 V (Vs. Pd). This indicates that the PGMs deposited on the working electrode in the first scan are not oxidized completely and they seem to favor the underpotential reductions of PGMs in the second scan. Moreover the peak current at –0.25 V increases from scans 2 to scan 3, confirming the underpotential reduction of PGMs by the deposit.

3.2. Cyclic voltammetry of platinoids at stainless steel electrode

Fig. 2 shows the cyclic voltammogram of SHLLW solution containing 20 mM each of Ru(III), Rh(III) and Pd(II) recorded at stainless steel working electrode at the scan rate of 100 mV/s, at 298 K. Cyclic voltammograms of blank-SHLLW (without platinoids) is also shown in the same figure for comparison. The onset of reduction occurs at –0.43 V (Vs. Pd), which leads to a prominent cathodic wave at –0.69 V (Vs. Pd). A nucleation loop is observed at –0.49 V (Vs. Pd). Controlled potential electrolysis at –0.5 V results in a deposition of PGMs at the working electrode. Based on these results electrolysis was carried out at potentials more cathodic to –0.5 V (Vs. Pd) at stainless steel working electrode.

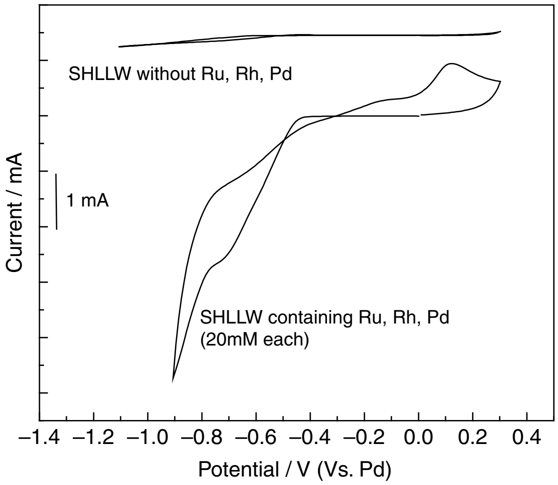

Fig. 2. Cyclic voltammograms of simulated high-level liquid waste in the presence and absence of platinoids recorded on a stainless steel electrode. Counter electrode: platinum wire. Reference electrode: palladium wire. Scan rate: 0.01 Vs^{-1} T: 298 K.

3.3. Electrolysis of SHLLW: effect of cathodic potential

Electrolysis of SHLLW containing Ru(III), Rh(III) and Pd(II) (60 mg each) was carried out at three cathodic overpotentials varied from –0.5 V (Vs. Pd), where the onset of cathodic current occurs and –1.0 V (Vs. Pd), where the onset of hydrogen evolution occurs. The electrolysis is carried out for 4 h. Table 2 shows the variation in the recovery of platinoids at three different potentials. The recovery is only 26% at –0.5 V (Vs. Pd) and increases to 33% and 42% when the potential is increased to –0.7 V (Vs. Pd) and –1.0 V (Vs. Pd), respectively. However, the current efficiency decreases from 41% to 5% when the applied potential increases from –0.5 V (Vs. Pd) and –1.0 V (Vs. Pd). This could be attributed to the competitive redox reaction such as hydrogen evolution, reductions of other metal ions such a Fe(III), Ag(I), U(VI), NO_3^- that are present in SHLLW [14].

Table 2
Recovery of platinoids from simulated high-level liquid waste at various cathodic potentials. Working electrode: Stainless steel. T: 298 K, Time: 4 h, $[\text{Metal}]_{ini}$ = 60 mg of each platinoid (Ru, Rh and Pd)

Potential, V (Vs. Pd)	Recovery of			Total recovery		Faradaic efficiency
	Pd %	Rh %	Ru %	%	mg	%
–0.5	86.2	1.7	9.3	26.0	46.8	40.8
–0.7	85.9	5.2	7.7	32.7	58.9	10.9
–1.0	77.2	8.7	12	42.2	76.0	4.8

*Around 2–2.5% (1.5 mg) of silver was found as co-deposit in all cases.

Evolution of RuO_4 was reported during the electrolysis of Ru(III) from nitric acid medium [16] and the evolution aggravated in the presence of palladium and rhodium in nitric acid medium. In contrast to this observation, no such evolution of RuO_4 was observed in the present study.

3.4. Characterization and surface morphology

The deposit obtained at the cathode was characterized by X-ray diffraction, which is shown in Fig. 3. It indicates the presence of all the three platinoids. The deposits obtained at various potentials were also characterized by scanning electron microscopy (SEM). The SEM images are shown in Fig. 4. All the images indicate the formation of sub-micron spheres on the electrode. The density of the microspheres increases with increase of applied potential. When the applied potential was –1.0 V, the deposit is very dense (Fig. 4E) and in some places dendrites are observed. EDS analysis of the deposit indicates that it is composed predominantly of palladium in all cases (80%) with ~8% of rhodium and ~12% ruthenium. Among other metal ions present in SHLLW, silver was co-deposited to an extent of 2–2.5 % in all the cases.

3.5. Rate of deposition

The rate of electrodeposition of platinoids from SHLLW was studied at a cathodic overpotential of –1.0 (Vs. Pd). The initial concentration of each platinoid was 60 mg/ml. At various intervals of time, an aliquot was drawn from the electrolytic medium and the PGMs present in SHLLW was determined by ICP-OES. The

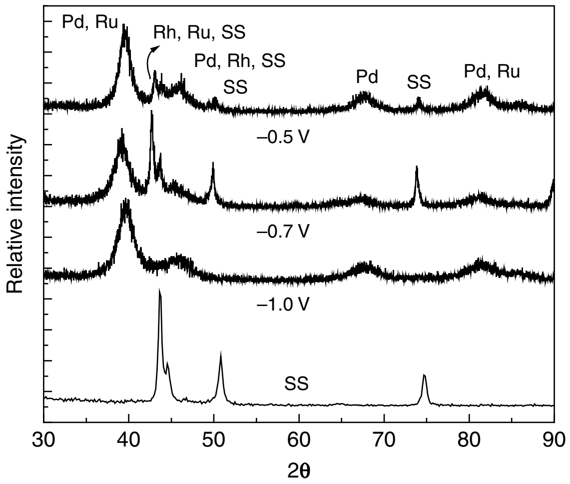

Fig. 3. Comparison of X-ray diffraction pattern of the deposits obtained by electrolysis of simulated high-level liquid waste containing platinoids.

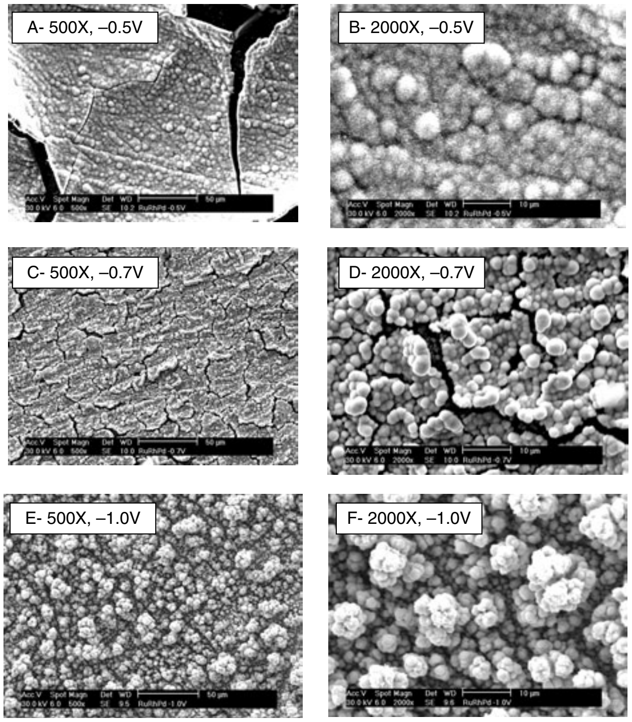

Fig. 4. SEM images of ruthenium-rhodium-palladium deposits obtained from SHLLW solutions at various applied potentials. Working electrode: stainless steel. Counter electrode: Pt plate. Quasi-reference electrode: Pd wire. T: 268 K, Duration: 4 h, The cathodic potentials and magnifications are given therein.

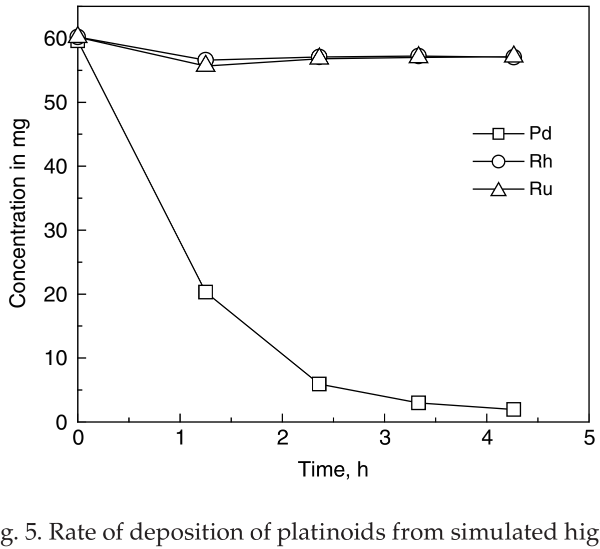

Fig. 5. Rate of deposition of platinoids from simulated high-level liquid waste solutions at a applied cathodic potential of –1.0 V. Working electrode: Stainless steel. Counter electrode: platinum. Quasi-reference: palladium wire. T: 298 K. $[\text{Metal}]_{\text{initial}}$ = 60 mg/25 ml.

results are shown in Fig. 5. It is observed that the concentration of palladium in SHLLW decreases rapidly with time and in about 4 h the palladium present in SHLLW is negligible. This indicates the recovery of palladium from SHLLW at –1.0 V is quantitative. However, the recovery of ruthenium and rhodium was only ~10% and 8% respectively, in 4 h of electrolysis and these results compares well with the EDS analysis of the deposit.

4. Conclusions

Voltammetric behavior of ruthenium(III), rhodium(III) and palladium(II) in SHLLW was studied at platinum and stainless steel electrodes to optimize the potentials needed for electrodeposition. Electrolysis of SHLLW was carried out at various cathodic potentials ranging from –0.5 V to –1.0 V (Vs. Pd). The total recovery of ruthenium, rhodium and palladium increased with increase of applied potential. The recovery of palladium was quantitative at the applied potential of –1.0 V (Vs. Pd) in 4 h; however, the recovery of rhodium and ruthenium was only ~10%. Studies with SHLLW indicated the feasibility of recovering palladium quantitatively from HLLW. Nevertheless, more studies are needed to understand the electrochemical behavior and recovery of palladium, rhodium and ruthenium from the real HLLW.

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References

[1] N.N. Greenwood and A. Earnshaw, Chemistry of Elements, 2nd Edition, Elsevier reprint, New Delhi, 2005.

[2] R.J. Seymour and J.I. O'Farrelly, Platinum group metals, In: Kirk-Othmer Encycl. Chem. Technol., John Wiley & Sons Inc, New York, 2001.

[3] G.A. Jensen, A.M. Platt, G.B. Mellinger and W.J. Bjorklund, Recovery of noble metals from fission products, Nucl. Technol., 65 (1984) 305–324.

[4] H.J. Ache, L.H. Baestle, R.P. Bush, A.F.Nechaev, V.P. Popik and Y.Ying, Feasibility of separation and utilization of ruthenium, rhodium and palladium from high level wastes, Technical report series - No. 308, IAEA, Vienna, 1989.

[5] Z. Kolarik and E.V. Renard, Potential applications of fission platinoids in industry, Platinum Met. Rev., 49 (2005) 79–90.

[6] E. Blasius and K. Muller, Ruthenium nitrosyl complexes in radioactive waste solutions of reprocessing plants. III. Behavior of ruthenium nitrosyl complexes during storage, concentration and calcination, Radiochim. Acta, 37 (1984) 217–222.

[7] Z. Kolarik and E.V. Renard, Recovery of valuable fission platinoids from spent fuel, Part I: General considerations and basic chemistry, Platinum Met. Rev., 47 (2003) 74–87.

[8] Z. Kolarik and E.V. Renard, Recovery of valuable fission platinoids from spent fuel. Part II: Seperation processes, Platinum Met. Rev., 47 (2003) 123–131.
[9] Yu.A. Pokhitonov and V.N. Romanovskii, Palladium in irradiated fuel. Are there any prospects for recovery and application? Radiochemistry, 47 (2005) 1–13.
[10] K. Koizumi, M., Ozawa and T. Kawata, Electrolytic extraction of platinum group metals from dissolver solution of Purex process, J. Nucl. Sci. Technol., 30 (1993) 1195–1197.
[11] Y. Kobayashi, H. Yamatera and H. Okuno, The electrodeposition of ruthenium from a ruthenium (III) and ruthenium (IV) solution and a fission products solution, Bull. Chem. Soc. Jap., 38 (1965) 1911–1915.
[12] K. Motojima, Removal of ruthenium from PUREX process, (II) - Fundamental research of electrolytic oxidation of ruthenium, J. Nucl. Sci. Tech., 27 (1990) 262–266.
[13] M. Yu. Kirshin and Yu. A. Pokhitonov, Recovery of Pd from spent Fuel: 1. Electrochemical recovery of palladium from nitric acid solutions, Radiochemistry, 47 (2005) 365–369.
[14] M. Jayakumar, K.A. Venkatesan, T.G. Srinivasan and P.R. Vasudeva Rao, Studies on the feasibility of electrochemical recovery of palladium from high-level liquid waste, Electrochim. Acta, 54 (2009) 1083–1088.
[15] M. Jayakumar, K.A. Venkatesan, T.G. Srinivasan and P.R. Vasudeva Rao, Electrolytic extraction of palladium from nitric acid, Desalin. Water. Treat., 12 (2009) 34–39.
[16] M. Jayakumar, K.A. Venkatesan, T.G. Srinivasan and P.R. Vasudeva Rao, Feasibility studies on the electrochemical recovery of fission platinoids from high-level liquid waste, J. Radioanal. Nucl. Chem., 284 (2010) 79–85.
[17] J.N. Mathur, M.S. Murali, M.V. Balarama Krishna, R.H. Iyer, R.R. Chitnis, P.K. Wattal, A.K. Bauri and A. Banerji, Recovery of neptunium from highly radioactive waste solutions of PUREX origin using CMPO, J. Radioanal. Nucl. Chem., 213 (1996) 419–429.