Advanced Hydrometallurgical Separation of Actinides and Rare Metals in Nuclear Fuel Cycle

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(Received March 16, 2010; Accepted March 30, 2010)

A hydrometallurgical separation technologies by novel solvent extraction (SX), ion exchange chromatography (IXC) and electrolytic extraction techniques are reviewed as separation tools for light PGM (Ru, Rh, Pd), Tc and f-elements in high level liquid wastes of the nuclear fuel cycle. The SX process using N,N-dialkylamide can isolate U(VI) from fission products without Pu(IV) valence control, and extractants with soft-hard hybrid donors (PTA and PDA) and those containing six soft donors (TPEN) show good separation of actinides (III) from lanthanides (III). The IXC process utilizing a tertiary pyridine resin (TPR) provides a very high degree of separation of the f-elements in spent nuclear fuel and the recovery of pure Am and Cm products. The catalytic electrolytic extraction (CEE) process utilizing Pd\text{adatom} or Rh\text{adatom} can effectively separate platinum group metals (PGM), Tc and Re by means of controlled under potential deposition (UPD). Some of the basic work on the hydrometallurgical separation of the elements of interest has been carried out through the strategic Advanced (Adv.-) ORIENT Cycle research in Japan. The Adv.-ORIENT Cycle process cannot only improve the radioactive waste problem, but can also provide useful rare metals to leading industries as from this secondary resource.

1. Introduction

Resources of natural energy (oil, gas, 235U) and most of rare metals will run out within 200 years. In particular at fiscal year 2004, the R (resource) / P (production) ratio (year) for oil was 41 years, 67 years for natural gas, 192 years for coal for and 85 years for uranium. Despite the rather long R/P ratio of ca.150 years for the platinum group metals (PGM), the current price increases for Ru, Rh, and Pd in the market have been significant, and it should be noted that the production of PGM is limited to mainly those two countries namely South Africa (75 %) and Russia (17 %) in the year 2008[1]. On the other hand, the R/P ratio for rare earths is not so limiting, but 93 % of rare earth production is monopolized by one country,
China. In this context, nuclear fission is said to be able to counter such a natural energy crisis issue if $^{238}\text{U}$ ($^{239}\text{Pu}$) can be utilized in fast breeder reactors (FBR) in future.

Fission reaction of $^{235}\text{U}$ and $^{239}\text{Pu}$ currently is creating more than 40 elements and 400 nuclides as fission products (FP) in the spent fuel, while generating enormous amounts of energy, approximately two million times greater than that from chemical reaction per gram of fuel. Among them, 31 elements are categorized as rare metals, and particularly Zr, Mo, Ru, Pd, Cs, Ce, Nd are highly enriched in FBR spent fuel. Because of their individual radiochemical properties, these should be recognized as not only the radioactive wastes but a second source of nuclear rare metals (NRM). Separation and utilization (stock-pile) technologies should be at once developed for the next generation, and hence in the nuclear fuel cycle, a policy change such as a Copernican Revolution is necessarily. This paper will review the state of the art of the hydrometallurgical, e.g., solvent extraction (SX), ion exchange chromatography (IXC) and electrolytic extraction (EE), technologies for the separation and recovery of NRM as well as actinides present in the radioactive wastes.

2. Nuclear Rare Metals, a New Product from a Copernican Revolution of the Nuclear Fuel Cycle

Typical yields for Pd, Ru, Rh (light PGMs) and Tc will reach to around 11kg, 13kg, 4kg and 3kg, respectively per metric ton of the reference FBR spent fuel (150 GWd/t, cooled for 5 years). The quantity of NRM is shown in Figure 1. Since such yields are proportional to the degree of burn-up, those in common light water reactors (LWR) will be approximately one third of FBR. It is notable that, Mo and some heavy lanthanides (Ln) (Dy, Er, Yb) are already non-radioactive and non-exothermic on reprocessing after 5 years cooling. Also, Nd and La are no longer radioactive beyond the natural one’s level. Furthermore, after cooling for more than 50 years in a stock-pile, the specific radioactivity of Ru, In, some of Ln like Pr, Gd and Tb will be less than 0.1 Bq/g. The quality (isotopic composition) of some of NRM is shown in Figure 2. The radiochemical properties are summarized as follows [2],

(a) After 40 years in a FP stock-pile the radioactivity of Ru will decrease to be below the exemption level (BSS*) of $^{106}\text{Ru}$. Its isotopic abundance will become to stable Ru ($^{99}\text{Ru}$, $^{101}\text{Ru}$, $^{102}\text{Ru}$, $^{104}\text{Ru}$) and $^{106}\text{Pd}$ only. *Note BSS; International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources, Safety Series No.115, IAEA, Vienna (1996).
(b) After 80 years in a FP stockpile the radioactivity of Rh will decrease to below the exemption level (NRPB*) of $^{102}$Rh. Its isotopic abundance will become stable at $^{103}$Rh and $^{102}$Ru. *Note NRPB; National Radiological Protection Board-R306 (1999).

(c) Only $^{107}$Pd only is radioactive (long-lived) in isotopic abundance in FP Pd. Its ratio is ca.16 wt %, and $^{107}$Ag will be gradually generated. The radio toxicity of FP Pd is very low, just ca. 30 times as high as $^{107}$Pd’s BSS level (10$^5$ Bq/g).

(d) $^{99}$Tc is the only major radioactive (long-lived) nuclide in isotopic abundance of FP Tc. Stable $^{99}$Ru will be gradually generated.

From close investigation, a possible "exit strategy" can be drawn up for individual NRM with regard to utilization. Namely, (i) Material/Chemical use; Ru, Rh, Pd, Mo, Ln (La, Nd, Dy, etc) and Tc. It is particularly noted that the isotopic abundance of Mo in stable FP will be composed of mainly higher order nuclides like $^{97}$Mo (22.1 wt %) and $^{98}$Mo (26.8 wt %). Such abundances might be advantageous for the production of $^{99}$Mo and $^{99m}$Tc. (ii) Radiochemical use; $^{137}$Cs (e.g., radiation source as an alternative to $^{60}$Co), $^{90}$Sr, $^{238}$Pu, $^{241}$Am and $^{242,244}$Cm, (iii) Additional nuclear fuel; $^{237}$Np, $^{241}$Am and Cm (as $^{238,240}$Pu, by α decay of $^{242,244}$Cm), (iv) Sale of stable isotopes on the market; $^{99}$Ru, $^{102}$Ru, $^{103}$Rh, $^{106}$Pd and $^{107}$Ag. These stable nuclides will be obtained after long-term stock-piling of FP Ru, Rh, Pd and Tc. $^{100}$Ru can be also
obtained as a transmutation product of $^{99}$Tc. The exit strategy for PGM will depend on the ability to cool for several decades.

Prior to the industrial utilization of NRM, a radiochemically precise separation of them and the actinides in the spent fuel is required. Such separation technologies should be integrated to be well compatible with each other in the fuel cycle where the reprocessing function must also be changed to meet environment-friendly requirements.

3. Advanced Reprocessing

Spent nuclear fuel reprocessing recovers more than 95.5% uranium and plutonium from irradiated nuclear fuels in nuclear power plants. Solvent extraction technique is used in current spent nuclear fuel reprocessing for the separation of uranium and plutonium efficiently from the fission products. This reprocessing process is called the PUREX process, and tri butyl phosphate (TBP) used as the extractant.

Around 1950, new extractant design for reprocessing was developed energetically, and TBP was developed through methyl isobutyl ketone and di-butyl carbitol (Figure 3). Uranium and plutonium, which are the separation targets in the PUREX process, are strong acids as defined by the HSAB principle. Furthermore, uranium and plutonium are hard donor atoms, and thus uranium and plutonium have affinities for hard oxygen elements. Therefore, ketones, ethers, and phosphates containing oxygen atoms have been tried as an extractants for the separation of uranium or plutonium.

For new extractant design for reprocessing, the requirements for the extractant are as follows, 1) extraction capacity for high-concentrated uranium, 2) high selectivity for uranium and plutonium, 3) high solubility in non-polar solvents, 4) high stability towards hydrolysis and radiolysis, 5) small influence of degradation products, 6) complete incineration, etc.

The difference in these requirements from non-radioactive solvent extraction is the stability against radiation. In the FBR under present development, the degree of burn-up is much higher than for LWR fuels, and thereby the demand for radiation stability is a very important factor. Moreover, the influence of degradation products must be evaluated and these degradation products also need to be removed.
The development of an \(N,N\)-dialkylamide as a new, more highly efficient extractant than TBP began in the 1960’s in the USA [3,4] and, up to the present, work is also reported from Italy [5,6], France [7-9], Russia [10,11], and India [12,13]. Also in the Japan Atomic Energy Agency (JAEA), development of new \(N,N\)-dialkyamides as alternative extractants to TBP began in 1992 [14,15]. \(N,N\)-dialkylamides have some advantages, namely, their complete incinerability (salt-free property) and high stability against hydrolysis and radiolysis. Their main degradation products are carboxylic acids and secondary amines which hardly affect the separation of U (VI) and Pu (IV) from FP. Further, the synthesis of \(N,N\)-dialkylamides is relatively easy, and various \(N,N\)-dialkylamides can be used for extraction. The most important advantage of solvent extraction technique using an extractant like TBP is the recovery of the objective metal cations by back-extraction. Therefore, it is difficult to develop a new extractant with moderate complexation capability between the extractant and the metal cations.

\(N,N\)-dialkylamides have been obtained by reacting an alkyl carboxylic chloride with a secondary amine, according to the reaction [1].

\[
\text{R}_1\text{COCl} + \text{HN}_2\text{R}_2\text{R}_3 \rightarrow \text{R}_1\text{CO}_{\text{NR}_2\text{R}_3} + \text{HCl} \quad [1]
\]

\(\text{R}_1, \text{R}_2, \text{R}_3\) in this reaction are alkyl radicals. Purification involves a distillation under low pressure (1 mm of Hg).

Typical extraction profiles for U (VI), Pu (IV), Np (IV, VI), and several types of simulated fission products from nitric acid media by \(N,N\)-dioctyl hexanamide (DOHA) are shown in Figure 4. From these results, U (VI), Pu (IV), Np (IV) and Np (VI) can be recovered by DOHA. These \(\text{R}_1, \text{R}_2, \text{R}_3\) substituents played an important role with regard to the coordination properties for the metal cation and the lipophilicity of the extractant. Furthermore, steric hindrance occurs with long alkyl chains and branched alkyl chains, which can be exploited in the separation of U (VI). Figure 5 shows extraction profiles for U (VI) and Pu (IV) which were obtained with the linear alkyl typed amide; DOHA and the branched alkyl type; \(N,N\)-di-(2-ethyl)hexyl-(2,2-dimethyl)propanamide (D2EHDMPA). Bulky \(N,N\)-dialkylamides like D2EHDMPA have selectivity only for U (VI). For this selectivity, branched \(N,N\)-dialkylamides are promising new extractants for reprocessing in the transition period from LWR to FBR (L-F transition periods). However, although D2EHDMPA was highly selective for U (VI), D2EHDMPA had a poor extraction capacity for highly concentrated U (VI). Therefore, a new amide compound in which only \(\text{R}_1\) was branched was developed. The new \(N,N\)-dialkylamide maintains the selectivity for U (VI) and has a
high loading performance for highly concentrated U (VI). On the other hand, a disadvantage of \( N,N \)-dialkylamides is the production of a secondary amine as the degradation product from hydrolysis and/or radiolysis. This secondary amine with a long alkyl chain exists in the organic phase, and cannot be removed by alkali scrubbing. Now, an evaluation of secondary amines in the reprocessing and removal techniques is being carried out.

In nuclear fuel reprocessing, the development of the isolation technology for U (VI) is a research objective. As seen from an industrial point of view, the next step in \( N,N \)-dialkylamides development should be tests with real spent fuels.

4. Separation of Minor Actinides

In the past three decades, partitioning and transmutation (P&T) of long-lived nuclides has been studied world-wide with the objective of creating an environmentally friendly nuclear fuel cycle. In this context, the TRUEX (TRansUranium EXtraction) solvent extraction process, using a bifunctional extractant \( O\text{O}D[\text{IB}]\text{CMPO} \) (n-octyl(phenyl)- \( N,N \)-diisobutylcarbamoylmethylphosphine oxide) with TBP in n-dodecane as the solvent, was successfully found to be a vital method for recycling trivalent actinides (An(III)) from high level liquid wastes (HLW) of spent fuel reprocessing [16]. The separation of trivalent actinides and lanthanides from HLW was investigated by not only CMPO but also malonamide in the European framework projects [17]. These extractants are in the development stage for practical use. The process flow-sheets using these extractants have been successfully tested. One of the technological issues was inter-group separation of trivalent Ln (III)) from An(III) for efficient actinide recycling into the FBR. As these are reviewed in other papers [18], the most topical two technologies for minor actinide (MA) / Ln separation and americium (Am) / curium (Cm) separation by P&T are reviewed in this section.

4.1 Separation of Minor Actinides from Lanthanides

As mentioned above, tri-valent An (III) existing in spent nuclear fuels, have been treated as high level wastes in the nuclear cycle. At present, transmutation of MA like An (III) by fast neutrons with an Accelerator Driven System (ADS) and/or a FBR has been studied. These transmutation technologies use a neutron source. Therefore, if a burnable poison like Ln is present in this target, the transmutation efficiency of Am (III) and Cm (III) is decreased. In order to achieve a high transmutation efficiency of Am (III) and Cm (III), separation of An (III) from Ln (III) is very important. On the other hand, the \( 5f \)-electrons on An (III) are of a largely relativistic, itinerant nature, providing a degree of covalency, which makes the behavior of An (III) ions slightly softer than Ln (III) ions. Consequently, most separations of An (III) from
Ln (III) were achieved with ligands using soft donors like sulfur (S) or nitrogen (N) atoms. For this purpose, new MA/Ln separation ligands were developed in several countries. These ligand structures are shown in Figure 6.

Figure 6  Structure of sulfur and nitrogen donor ligands.
The purified bis(2,4,4-trimethylpentyl) di-thio phosphinic acid (CYANEX 301) gave a high separation factor; \( \text{SF} [\text{Am} (\text{III}) / \text{Eu} (\text{III})] = 4900 \) [19,20]. Process flowsheets were developed and tested in China with real HLW and the radiolysis of CYANEX 301 was also investigated [21]. In the EUROPART project for international cooperation in Europe, many types of new N-donors have been synthesized and tested for the separation of An (III) from Ln (III). Typical N-donors are 2-pyridinecarboxyamide (picolinamides) [22], 2,4,6-tri-(2-pyridyl)-1,3,5-triazines (TPTZ) [23], bis-triazinyl-1,2,4-pyridines (BTP) [24,25], and 6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines (C5-BTBP) [26-28]. 2,6-bis-(5,6-di-n-propyl-1,2,4-triazin-3-yl)pyridine (nPr-BTP) exhibited good selectivity, with a SF[Am (III) / Eu (III)] of > 100. This high SF was obtained from 1.0 M (mol dm\(^{-3}\)) HNO\(_3\) acid solution with 0.04 M nPr-BTP in TPH / n-octanol (70/30 vol %). However degradation of nPr-BTP by radiolysis was very fast. In the ACSEPT (Actinide reCycling by SEParation and Transmutation) project in EU (which runs from 2008 to 2012), the development of a new BTBP and a new N-donor is under way.

Recently, \( N,N′-\text{dialkyl-}N,N′-\text{diphenylpyridine-2,6-dicarboxyamide} \) (PDA) [29,30], \( N,N′-\text{dialkyl-1,10-phenanthroline-2-carboxyamide} \) (PTA) [31] and \( N,N,N′,N′-\text{tetrakis(2-pyridylmethyl)ethylene-diamine} \) (TPEN) [32-34] were synthesized and investigated for MA / Ln separation. These two ligands, PDA and PTA, have soft (N)-hard (O) hybrid donors. In particular PTA exhibited a SF [Am (III) / Eu (III)] value of ca. 20 at an aqueous concentration of 1.0 M HNO\(_3\). However, although PDA and PTA had good SF [An / Ln] values, the behavior of FPs with PDA and PTA was not clear. In Japan and in the ACSEPT project in the EU, the above separation of minor actinides from lanthanides is progressing and has a strong connection with national strategy (especially fuel fabrication).

TPEN is a hexadentate ligand with 6 nitrogen-donors and complexes with softer metal ions selectively. Trivalent MA ions, such as Am (III) and Cm (III), which are softer than lanthanide ions, are extracted to the organic phase containing TPEN selectively. A SF [Am (III) / Eu (III)] value of ca. 100 was observed in the pH range > 4 [32,33]. From the viewpoint of practical use, some hydrophobic TPEN analogs wherein long alkyloxy groups were introduced to four pyridine rings were synthesized and the effect of the introduction of the alkyloxy groups on the separation of Am (III) and Eu (III) was tested. In an acidic solution at pH 3, the extractability of TPEN was improved by the introduction of butoxy groups, and a SF [Am (III) / Eu (III)] value of ca. 90 was observed at pH 3 [33].

In the meantime, the simultaneous recovering of all of the actinides with one type of solvent, bifunctional organophosphorus extractants dissolved in highly polar fluorinated diluents, was studied. 0.4M OØD[iB]CMPO with 30% TBP dissolved in metanitrobenzotrifluoride (Fluoropole-732) was found to achieve simultaneous extraction of all of the \( f \)-elements from the dissolver solution of spent nuclear fuel without splitting a third phases [35]. This new solvent system was named the ORGA process.

![Figure 7 Tertiary Pyridine Resin (TPR)](image-url)
4.2 Mutual Separation ofAmericium andCurium

The properties of a tertiary pyridine resin (TPR), as shown in Figure 7, with a nitrogen atom in its six-membered ring, are characterized by simultaneously having two functions as a weakly basic anion-exchanger and a soft donor ligand. The TPR is synthesized by co-polymerization of 4-vinylpyridine and m/p-divinylbenzene on a high porous silica carrier (φ 60μm) at room temperature. The total exchange capacity is ca. 5 meq / g (dry) in the Cl⁻ form as an actual measurement value [37]. The TPR was hardly damaged by up to 3MGy irradiation from a ⁶⁰Co source, with an ensuing particularly high resistance to radiation (~10MGy) in HCl media. An original idea by T.Suzuki, et al. [38] of combining the use of conc.HCl and conc. HNO₃ media for inter- and intra-group separation of the f-elements was based on such facts, as shown in Figure 8, as the recognition of softer ions like Am (III) and Cm (III) (5f-elements) was particularly improved (e.g., higher distribution ratios) compared to Ln (III) (4f-elements) in HCl media, and, in HNO₃ media, the distribution ratios would depend not on the difference of the softness between 4f- and 5f-elements but just on the difference in ionic radius. The presence of a high conc. of methanol in acidic media, improved the separation of intra-group f-elements by enhancing the complexion of the dehydrated f-element ions with anions [39]. Using these facts, a HCl / HNO₃ hybrid scheme was demonstrated in the reprocessing of a trace amount of MOX spent fuel irradiated (143.8 GWd/t) in the fast experimental reactor “Joyo” [38]. Individual recoveries of pure Am (III) product (¹⁰⁶Ru, ¹²⁵Sb, ¹³⁷Cs, ¹⁴⁴Ce, ¹⁵⁵Eu, ²⁴³Cm) / ²⁴¹Am: < 10ppm) and Cm (III) product (²⁴¹Am / ²⁴³Cm: 0.78 %) were attained, respectively. These separations will satisfy any separation degrees set up for MA product such as Ln / MAproduct < 5 %mass. 

5. Separation of Nuclear Rare Metals

In the PUREX process, SX technology was historically been developed for the separation of An (U, Pu) from FP while the recovery of valuable FP has been an issue in its nuclear application. Furthermore, since their valences are...
widely distributed from I to VII, group separation as for the f-elements seems to be impossible in the PUREX nitric acid system. Therefore non-SX methods, like IXC, solid adsorption and EE, have been studied for their individual separation.

5.1 Ion Exchange Chromatography of PGM and Tc

The acid dependency of the distribution coefficients of PGM and Tc on the TPR is shown in Figure 9. The distribution coefficients were evaluated by the batch experiments carried out at room temperature. The data suggest that all light PGM and TcO₄⁻ are strongly adsorbed by the TPR over a wide HCl concentration range. If no adsorption of actinides (U (VI), Pu (IV), Am (III)) occurs, separation of Pd²⁺ and TcO₄⁻ in highly dilute HCl conditions will be possible. These predictions have been definitely supported by the strong adsorption of ¹⁰⁶Ru and ¹²⁵Sb in the previous hot test results.

As Figure 9 shows, it will be necessary to develop viable, salt-free, complexing reagents for efficient elution of PGM and Tc from the resin as the next step.

On the separation of cesium and strontium, the selective separation of Cs⁺ by highly functional adsorbents (silica gel loaded with ammonium molybdophosphate (AMP-SG(D)) and Sr²⁺ by hybrid microcapsules containing D18C6 (D18C6-MC) are discussed in the other papers [40,41].

5.2 Catalytic Electrolytic Extraction of PGM and Tc

Catalytic electrolytic extraction (CEE) [42] can effectively separate Ru, Tc and Re (Tc simulator) from either HNO₃ or HCl solution under controlled potential deposition (UPD) with the formation of insoluble metal (Ru, Rh, Pd) / oxide (ReO₃, TcO₂) solid solutions in acidic media. In the case of Re oxide, an island type deposit was sometimes observed. In the UPD concept as shown in Figure 10, Pd or Rh may act as a promoter at the surface of the electrode (i.e., Pd_{adatom} Rh_{adatom}) and a mediator in the bulk solution (i.e., redox ion pair). The adatom, is a contraction of “adsorbed (single) atom”, lying on surfaces and surface roughness, will act as a deposition catalyst. Pd and Rh were easy to deposit from the both media. Characteristics of the deposits are also described in the

Figure 10 Concept on Mediator and Promoter in the Under Potential Deposition
figure. In dilute hydrochloric acid (HCl) media in particular, such CEE occurred more readily. For instance, the addition of Rh$^{3+}$ significantly accelerated the deposition of Tc and Re as shown in Figure 11. As typical deposition characteristics in the one to four NRM metal ion mixed solutions (corresponding to FBR spent fuel composition), the observed deposition yields (average) were typically high in the following order;

\[
Pd, \text{Rh (} > 99 \% \text{)} > \text{Re (91 \%)} > \text{Ru (85 \%)} > \text{Tc (69 \%)}
\]

where the CEE was galvanostatically carried out with typically changing cathode current density like 2.5 mA / cm$^2$ (1 hr) $\rightarrow$ 75 mA / cm$^2$ (2 hr) $\rightarrow$ 100 mA / cm$^2$ (4 hr) in 0.5M HCl at 50$^\circ$C. At the initial stage, setting a lower cathode current density with compulsory stirring was necessary to form Pd cores and the adatom layer. This procedure was essential to obtain higher amounts of co-deposits of Ru and Tc (Re) ions.

During the CEE, the reduction process for Rh was similar to Pd, i.e., through direct reduction of Rh$^{3+}$ to Rh metal. However, reduction of Ru might proceed at least by two steps via following reactions,

\[
\begin{align*}
\text{Ru(NO}_3^+) + e & \rightarrow \text{Ru}^{2+} + \text{NO} & E^0 = 0.044V \text{ (vs. Ag/AgCl)} \\
\text{Ru}^{2+} + 2e & \rightarrow \text{Ru(s)} & E^0 = 0.255V \text{ (vs. Ag/AgCl)}
\end{align*}
\]

A H-type electrochemical cell, where a nafion-117 cation-exchange membrane separated the catholyte and the anolyte, was employed in both the CEE experiments and for hydrogen evolution by the NRM deposited electrodes after changing the catholyte.

Recently, preliminary experiment on EE using a simulated high level liquid waste (S-HLW; 0.5M HNO$_3$, containing 26 metal elements corresponding to real HLW by LWR-reprocessing) has been carried out [39]. The CEE deposits were apparently the same as shown in Figure 10 (right picture) with fine coagulated spherical particles as were observed in the case of the Pd$^{2+}$ involved deposits. The reduction ratio of Pd was as high as 89 % as expected, while other NRM as Ru, Re and Mo were limited to around 20 % and less than 10 % for Rh, Te and Se. Such lower deposition ratios were probably attributed to the significant consumption of the electricity by the large amount of the corrosion product iron contained in S-HLW through the reduction of Fe$^{3+}$ to Fe$^{2+}$. In addition, the PGM content itself was lower compared to
the previous experiments with FBR-HLW, and neither Pd$^{2+}$ nor Rh$^{3+}$ was added in this experiment. For higher deposition yields, the CEE utilizing UPD by Pd$_{adatom}$ or Rh$_{adatom}$ is highly recommended with prior separation of actinides and the other elements with nobler redox potentials by IXC. The reduction behaviors of Mo, etc., require to be investigated in details.

The CEE method is advantageous for radiochemical separation of NRM, because of minimal irradiation with no simultaneous deposition of actinides, but also because they are recovered in the solid state at an electrode surface. The sphere deposits were dense and mechanically more stable than dendritic deposits, while showing electrochemically high catalytic reactivity on electrolytic hydrogen production [43]. In particular, the catalytic reactivity of the quaternary, Pd-Ru-Rh-Re (3.5:4:1:1, corresponding to the composition of FBR spent fuel) deposit on a Pt electrode for electrolytic production of H$_2$ was the highest, exceeding that of a smooth Pt electrode by ca. twice both in alkaline solution and artificial seawater. Such higher reactivity will attribute to the higher numbers of adsorption sites on the surface of the deposit for protons.

Ru has been confirmed as the dominant element responsible for high reactivity, while Pd behaved as just a “starter” nucleus and a “binder” among the involved elements during the deposition. It is noticeable that Tc seems to have a higher or the same catalytic ability as Re. The high reactivity of Tc suggests that it may be a possible alternative to Re in the field of catalysts.

6. A New Back-end Strategy as Copernican Revolution

Aiming at simultaneous realization of the utilization of elements/nuclides and ultimate minimization of radioactive wastes, a new fuel cycle concept, *Adv.-ORIENT (Advanced Optimization by Recycling Instructive Elements) Cycle* [2, 41, 43, 44], is proposed under the following strategies as shown in Figure 12:

1/ Trinitarian research on separation, transmutation and utilization (S&T, U) of nuclides and elements, based on FBR fuel cycle.
2/ Significant reduction of radioactive wastes and eventual ecological risks: Within a few hundred years, achieve a radiotoxic inventory decrease to the level of natural U tons corresponding to one ton of vitrified HLW.
3/ Cascade separation of all actinides, NRM, Cs and Sr by a multi-functional and compact reprocessing process and plant.
4/ Challenge on isotope separation of long lived radio nuclide $^{135}$Cs from FP Cs for advanced transmutation.
5/ Accept and separate natural radioactive materials (U, Th) to burn, on demand of the RE industry.

The most important policy change is that NRM shall not be just the waste constituents but be the main product in the fuel cycle. Actinides will no longer be the products, but will just be the material burned in
the reactors. To realize this concept at both scientific and industrial levels, several separation tactics are proposed as follows;

1/ Higher purity of NRM for utilization, while lower decontaminated actinides are permitted for burning in FBR. Separation factors of 90-99.9 % will be chosen for the individual impact of radio nuclides.

2/ Adopt soft hydrometallurgical separation processes with salt-free reagents to reduce the secondary radioactive wastes. Ultimately, low greenhouse gas emission technology is required.

3/ A high degree of separation of all actinides into 3-4 groups, U, Pu/U/Np, Am and Cm, directly from the spent fuel by an IXC method.

4/ As non-SX methods, CEE and adsorptive separation methods for NRM are chosen to alleviate the radiation effect. Solid state will be preferable as the end product for utilization and/or stockpiling.

5/ HCl media is allowed in combination with HNO₃ media to improve the separability.

6/ Identification of anti-corrosive materials in both conc. HCl and HNO₃ are indispensable from an industrialization point of view. Verification of thermo- and radio-chemical stability of the novel IX resin is also required.

7/ Preliminary separation of actinides from the NRM is advantageous because Zr, Mo, Pd, ⁹⁹Tc, ¹⁰⁶Ru and ¹²⁵Sb, etc will disturb the operation of both reprocessing and vitrification of HLW.

**Adv.-ORIENT Cycle since 2006**

Figure 12  *Adv.-ORIENT Cycle Concept*
The time to reduce the radio-toxicity Sv (Sievert) of 1 ton of vitrified HLLW below the level of equivalent tons of natural raw uranium is one of the indexes for environmental impact. In the Adv.-ORIENT Cycle, by putting the separation factors at 99.9% for all actinides, 99% for $^{137}$Cs, $^{90}$Sr and the other NRM, and 90% for Ln, such a period can dramatically be reduced to around $10^2$ years.

7. Conclusion

The isotopic composition and radiochemical properties of nuclear rare metals have been reviewed. Hydrometallurgical separation technologies using solvent extraction (SX), ion exchange chromatography (IXC) and catalytic electrolytic extraction (CEE) techniques were developed as vital separation tools for light PGM (Ru, Rh, Pd), Tc and f-elements present in high level liquid wastes of the nuclear fuel cycle. The SX process using N,N-dialkylamide can isolate U(VI) from fission products without Pu(IV) valence control, and extractants utilizing soft-hard hybrid donors (PDA and PTA) and those containing six soft donor atoms (TPEN), which have been developed mainly in Japan, show good separation of An(III) from Ln(III). The IXC process utilizing a tertiary pyridine resin (TPR) gives a high separation of the f-elements in spent nuclear fuel and produce pure Am and Cm products. The CEE process utilizing Pd$_{adatom}$ or Rh$_{adatom}$ can effectively separate PGM, Tc and Re by utilizing under potential deposition (UPD) phenomena.

Some of the basic work on hydrometallurgical separation of concerned elements is being progressed in the flame of strategic Advanced (Adv.-) ORIENT Cycle research program in Japan. The Adv.-ORIENT Cycle process can not only improve the rad. waste problem, but also offer useful rare metals to leading industries from this secondary resource.

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