Correspondent; Dr. Masaki Ozawa, 4002 Narita, O-arai-machi, JAEA O-arai Research & Development Center, Ibaraki-ken, Post.311-1393, Japan

Topical Area; Transmutation and Fuel Cycle, or Nuclear Hydrogen Production

Advanced ORIENT Cycle for Strategic Separation, Transmutation and Utilization of Nuclides in the Nuclear Fuel Cycle,
Focusing on Electrochemical Separation and Utilization of RMFP

Masaki Ozawa[1]and Reiko Fujita[2]

*[1] *Japan Atomic Energy Agency*
*[2] *Toshiba Corporation*

Abstract

A novel trinitarian R&D scheme (Advanced ORIENT Cycle) on partitioning, transmutation and utilization of actinides and fission products in the spent nuclear fuel has been proposed to realize ultimate reducing long-term radio toxicity of the radioactive wastes. Actinides (Pu, Am, Cm, etc), MLFP (Sr, Cs) and RMFP (Ru, Rh, Pd, Tc, etc) shall be highly separated and purified to meet well with the forward treatments like nuclide transmutation and/or utilization. Toward the total utilization of RMFP, CEE (catalytic electrolytic extraction) method was innovated to separate them from high-level liquid wastes of the nuclear spent fuel. The CEE, utilizing catalytic effect of Pd^{2+} vs. $RuNO^{3+}$, and that of Rh^{3+} vs. $RuNO^{3+}$ and ReO_4^- ions, could effectively separate Ru, Re, Tc as well as Pd from the nitric acid solution. The CEE of Rh^{3+} and Pd^{2+} vs. TcO_4^- were also probably. The RMFP-deposited Pt electrodes showed highly catalytic properties for electrolytic hydrogen production, about twice higher than that of smooth Pt in alkaline and sea waters. The RMFP would be expected to be a “FP-catalyst” to circulate between nuclear and hydrogen / fuel cell energy systems, thereby contributing to save the precious metal resources.

1. Introduction (Nuclear Fission Reaction as RM Production System)

Towards minimizing radioactive wastes in nuclear fuel cycle, partitioning and transmutation of long-lived fission products (LLFP^{*1}) have been investigated. In this context, extended recycling of rare metal fission products (RMFP^{*2}) by utilizing their chemical and radiochemical properties can be visioned as an alternative fate to present disposal measure,

^{*1}LLFP ($\tau_{1/2}>10^4$years); ^{79}Se, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs
^{*2}RMFP (mainly VII-X group elements in 5th period); Ru, Rh, Pd, Tc, Te, Se, Ag, etc

where utilization of newly created nuclides by transmutation of LLFP can also be pictured. The symbolical example is an utilization of non-radioactive ruthenium ($^{100-102}$Ru) resulted from neutron capture reaction of technetium（^{99}Tc） in fast reactor (FR) or accelerator.

$$^{99}\mathrm{Tc}(n,\gamma)^{100}\mathrm{Tc}\rightarrow\beta^-\rightarrow{}^{100}\mathrm{Ru}$$

Typical amounts of RMFP estimated by Origen-II calculation are shown in Table 1, where Ru and Rh are categorized as SLFP (short-lived radioactive). The calculation indicates that generation amounts of RMFP are proportional to burn-ups, and thus highly irradiated fast reactor (FR) spent fuel (burn-up; 150,000MWd/t, cooling; 4 years) will contain more than 30kg of RMFP per metric ton of SF.

Table 1 Typical Amount of RMFP per ton of FR Spent Fuel

Rare metal	Ru	Rh	Pd	Tc	Te	Se	Note
Amount (kg/HMt)	12.5	3.6	11.1	3.3	2.7	0.2	FBR-SF;150,000MWd/t, Cooled 4 years.

Fig.1 emphasizes the enrichment of transient elements of the 5th period in the SF comparing with those in the earth crust 1). Enrichment factors of Tc(VII), Ru(VIII), Rh(IX), Pd(X) and Te(XVI) are especially high, >10^5.

Specific radio toxicities (Hazard Index: HI) of RMFP correspond to the spent fuel in the Table 1 are shown in Fig. 2 1). The HI is calculated as follows;

$$\mathrm{HI} = \Sigma\ (\text{Decay Constant of Nuclides}) \cdot (\text{Number of Nuclides}) / \mathrm{ALI}^{*3} \quad \text{-------}\ (1)$$

*3Annual Limitation Intake (ICRP Pub.61)

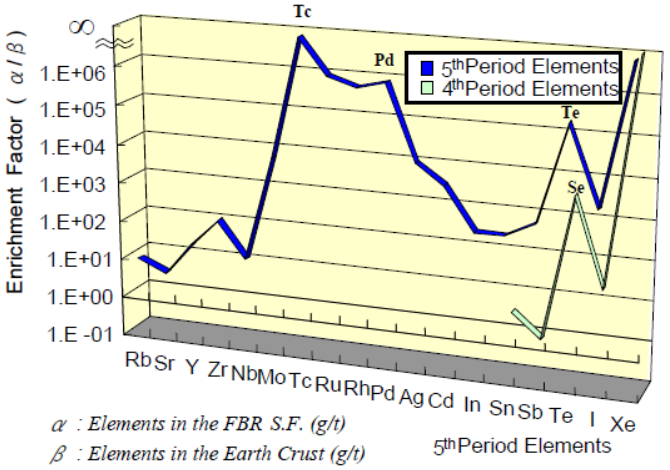

Fig. 1 Enrichment of RMFP in the FR Spent Fuel as "Artificial Ore"

Notably, Pd is LLFP due to the presence of ^{107}Pd (β^-, $\tau_{1/2}$: 7×10^6y, ^{107}Pd / ^{total}Pd: ca.16%), but its (and Te's) specific radio toxicity is very low, far less than that of uranium. Although the initial specific radio toxicities of Ru and Rh are high, yet they would significantly decrease to a negligible level within tri-decades owing to short-lived properties ($\tau_{1/2}$: ca.1 year, ^{106}Ru/^{total}Ru: only ca.0.4%). Tc and Se are long-lived owing to ^{99}Tc (^{99}Tc / ^{total}Tc: ca.100%, β^-, $\tau_{1/2}$: 2×10^5 year) and ^{79}Se (^{79}Se / ^{total}Se: ca.10%, β^-, $\tau_{1/2}$: 6×10^4year). However, light radiation shielding is enough because of their β^- radio activities.

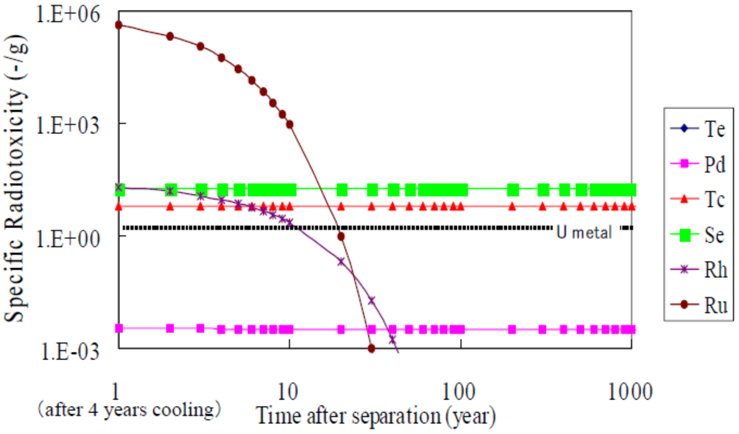

Fig. 2 Specific Radio Toxicity (Hazard Index) of RMFP in FR Spent Fuel after 4 years cooling. ^{106}Ru decay; ^{106}Rh→^{106}Pd (stable)

Changes of chemical impurities of each RMFP are illustrated in Fig.3. During 10^2 years storage, ^{99}Ru (stable) will be generated, but less than 10^3 ppm in Tc, and ^{106}Pd (stable) generated less than 10^4ppm in Ru, respectively. As for Rh and Pd, those impurities will be especially very low as ca.1 ppm of ^{102}Ru (stable) in Rh and ca.1ppm of ^{107}Ag (stable) in Pd. Once RMFP are highly purified, chemical

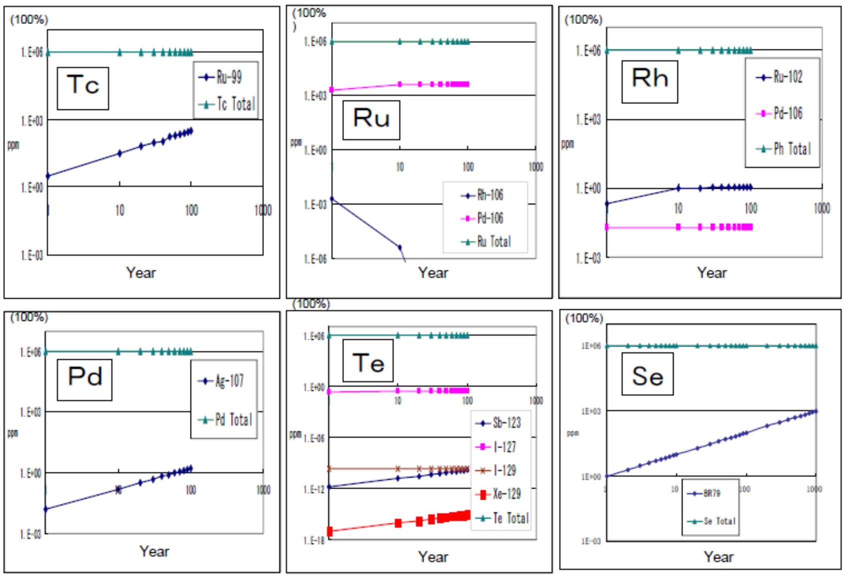

Fig. 3 Changes of Isotopic Composition of RMFP

purities can be kept in very low level on Rh and Pd for a long period.

If RMFP can be separated and utilized, the nuclear fission reaction system will be recognized as rare metal element production system.

2. Separation and Utilization of RMFP in Advanced ORIENT Cycle

2.1 Advanced ORIENT Cycle

In the course of spent fuel reprocessing by hydrometallurgical PUREX method, almost 70-80% of RMFP in the spent fuel were dissolved with actinides in boiling concentrated nitric acid. Ionic state of them are estimated to be $RuNO^{3+}$, Rh^{3+}, Pd^{2+}, TcO_4^-, Te^{4+} and Se^{4+}, respectively in 3-5 mol/dm^3 HNO_3 media, where redox potentials of those (except for Ru) are nobler than 0.7V (vs. SHE). Dissolved RMFP are distributed to aqueous raffinates and solvent phases in solvent extraction (SX) cycles, and finally more than 99% of FP concentrated in high level liquid waste (HLLW). However, some portion of Ru, Tc and Sb tend to diffuse in the whole PUREX plant. Thus, it seems to be rational to separate RMFP preferably from dissolved solution prior to the SX process.

Trinitarian research by separation, transmutation and utilization of radioactive wastes is its fundamental philosophy of advanced ORIENT cycle to achieve ultimate reduction of environmental burden by nuclear fuel cycle [2,3]. Concept of advanced ORIENT cycle is shown in Fig.4, where renovative reprocessing flow sheet by functional, soft-donor tertiary pyridine resin is adopted as main separation tool enabling to recover pure Cm and Am separately with minimum number of reprocessing steps. The recent experiments revealed that strong adsorption of ^{106}Ru, ^{125}Sb and very trace of ^{241}Am in this resin were observed under the diluted HCl medium, thereby ^{241}Am, ^{125}Sb-traced RMFP fraction and ^{106}Ru-free feed dissolver solution would be obtained at the IXC filter step [2]. The electrochemical separation step, CEE in Fig.4, will follow this IXC step for further purification and fabrication of RMFP

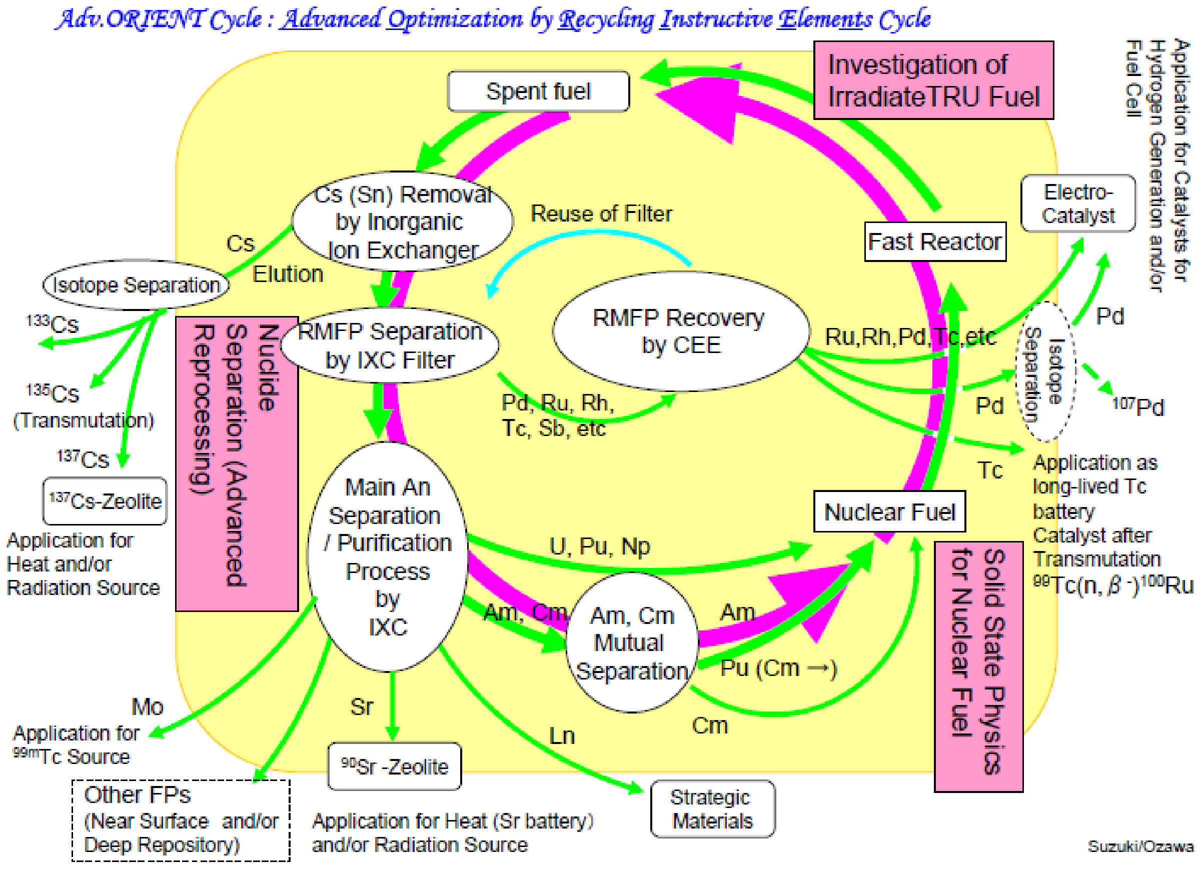

Fig. 4 Concept of Advanced ORIENT Cycle

electrode toward its wide utilization.

2.2 Electrochemical Separation of RMFP by CEE process

Electrolytic extraction method has been widely employed in the chemical industries to fabricate transient element, especially VIII to XI group materials. In its application to the nuclear fuel cycle however, nitric acid should be considered in the view point of forming nitrato, nitrosyl species for Ru and being rather oxidative media for Tc and Re. In a typical galvanostatic electrolysis condition by smooth Pt cathode in pure 0.5 mol/dm^3 HNO_3 solution, maximum electroreduction ratios of Pd and Rh were attained more than 99% however, just 14% for Ru, 16% for Re and 1.7% for Tc, respectively [4,5].

To prevent from those disturbances, it was also already reported elsewhere that Pd^{2+} cation itself would not only be easily (>99%) deposited from various nitric acid solutions, but enhanced the deposition of co-existing $RuNO^{3+}$ and ReO_4^- by acting as a catalyst (as Pd_{adatom}) [6,7]. Such a catalytic electrolytic extraction (CEE) was also valid in the case of $^{99}TcO_4^-$ deposition [8]. The deposit accelation ratio (*i.e,* CEE effect) in the nitric acid media is summarized in Fig.5. Rh^{3+} as well as Pd^{2+} significantly accelerated deposition of $RuNO^{3+}$. Rh^{3+} also accelerated ReO_4^-'s deposition. On the contrary, $RuNO^{3+}$ and ReO_4^- had not only no positive effect on the others, but also made negative effect on Rh^{3+}'s deposition. Deposition of Pd^{2+} was however constantly high, and was never affected by the other co-existing ion. These tendencies were correctly reflected to the deposition behaviors in the mixture case. In this case (soln. composition ; Pd / Ru / Rh / Re(Tc) = 1 / 1 / 1 / 1(0.5)) resulted deposition ratios of Pd, Ru, Rh, Re and Tc were 86.3-95.7%, 41.1-46%, 13.4-14.5%, 19% and 26.5%, respectively. Higher acceleration on Tc would thus be attributed to mainly Rh^{3+}'s mediator effect as was observed for ReO_4^-. At the Pt cathode CEE by Pd_{adatom} on Tc [8] proceeded involving H_{adatom} like,

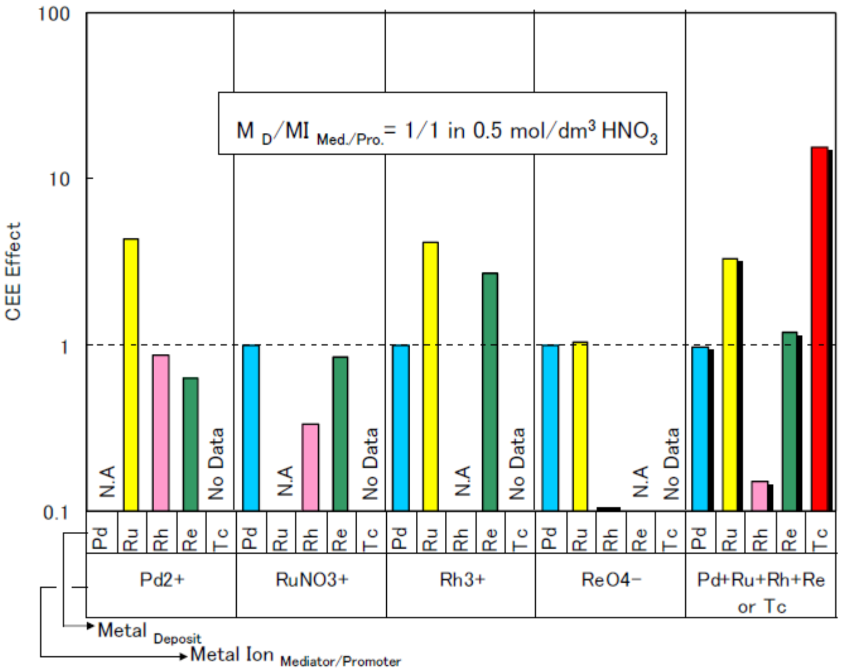

Fig.5 Typical CEE Effect in Metal Concentration Ratio as Metal $_{Deposit}$ / Metal Ion $_{Mediator/Promoter}$ =1*/1 in 0.5 mol/dm^3 HNO_3

$$TcO_4^- + 3H_{ad} + H^+ \rightarrow TcO_2 \cdot 2H_2O \quad E^0 = 0.738V \text{ (V vs. SHE)} \qquad \text{--------(2)}$$

the same H_{adatom} mechanism was probable for the electrodeposition of ReO_4^-,

$$ReO_4^- + 2H_{ad} \rightarrow ReO_3 \cdot H_2O \quad E^0 = 0.768V \text{ (V vs. SHE)} \qquad \text{-------(3)}$$

$$\text{and/or } ReO_4^- + 3H_{ad} + H^+ \rightarrow ReO_2 \cdot 2H_2O^{\,9)} \quad E^0 = 0.51V \text{ (V vs. SHE)} \qquad \text{--------(4)}$$

By the EDS(EPMA) analysis, Re deposit was estimated to be ReO_3, thus the reaction (3) is probably true for this case. As ReO_3 was readily re-dissolved in 0.5 mol/dm^3 HNO_3, thus the deposition ratio of Re was limited to be low. The deposition of Tc was easier than Re in the RMFP mixuture solution.

Taking above into the consideration, the composition of FR spent fuel as Pd/Ru/Rh/Tc=3.5/4/1/1 seems to be suitable, and addition of Pd^{2+} and/or Rh^{3+} will cause further improvement on the recovery of Ru and Tc. If one wants to recover pure Rh from the spent fuel, it will be possible after the completion of the deposition of Pd, Ru and Tc. A dramatic increase in recovery can be expected for all RMFP in the reducing media of HCl. This prospect will be discussed in another paper.

2.3 Electrochemical Utilization of RMFP as Hydrogen Production Catalyst

Addition of Pd^{2+} caused either to change the dendritic deposition form or to improve electrochemical property of deposits in the HNO_3 media. The RMFP deposit, especially quaternary-, Pd-Ru-Rh-Re, deposits on the Pt electrode became rather spherical in shape and stable, seemed to be electrochemically agglomerated by nano-micro particles. The deposits showed electrochemically nobler at initial hydrogen evolution potential ($\varphi_{Hint.}$), and in the given potential of -1.25V (vs. Ag/AgCl) the highest cathodic current corresponding to the hydrogen generation reaction was obtained for the deposit from the solution with a composition of Pd/Ru/Rh/Re=3.5/4/1/1, as shown in Fig.6. Namely, that catalytic activity for hydrogen production was <u>*ca.*</u> twice superior to that of the Pt electrode in alkaline solution 10,11). We recently confirmed that the reactivity of Pt-black electrode, whose actual surface area was <u>*ca.*</u>37 times higher than that of smooth Pt estimated by Q_{Hd} corresponding to the desorption reaction,

$$H_{ad} \rightarrow H^+ + e^- \quad \text{--------(5)}$$

with the hypothesis that atomic ratio of H_{adatom} vs. Pt_{atom} was 1, was intermediate between those of smooth Pt electrode and quaternary deposit RMFP-Pt electrode from the solution with the composition of Pd/Ru/Rh/Re=3.5/4/1/1.

The sea water is an ultimate resource for hydrogen production in future. In the course of sea water electrolysis, though the heavy disturbance due to $Ca(OH)_2$ and $Mg(OH)_2$ precipitation was inevitable, the cathodic current of the quaternary deposit of RMFP was the highest as the same as to that of Pt electrode in the alkaline water. Though the hydrogen overpotential of Tc(metal) was reported essentially being the same or a little higher than that of Re(metal), the reverse tendency on $\varphi_{Hint.}$ for Tc-Pt and Re-Pt electrodes was unexpectedly observed as in Fig.6. To confirm the phenomena, electrochemical property of RMFP, especially Tc and Re, is under investigation with a special interest on Tc as an alternative element to Re.

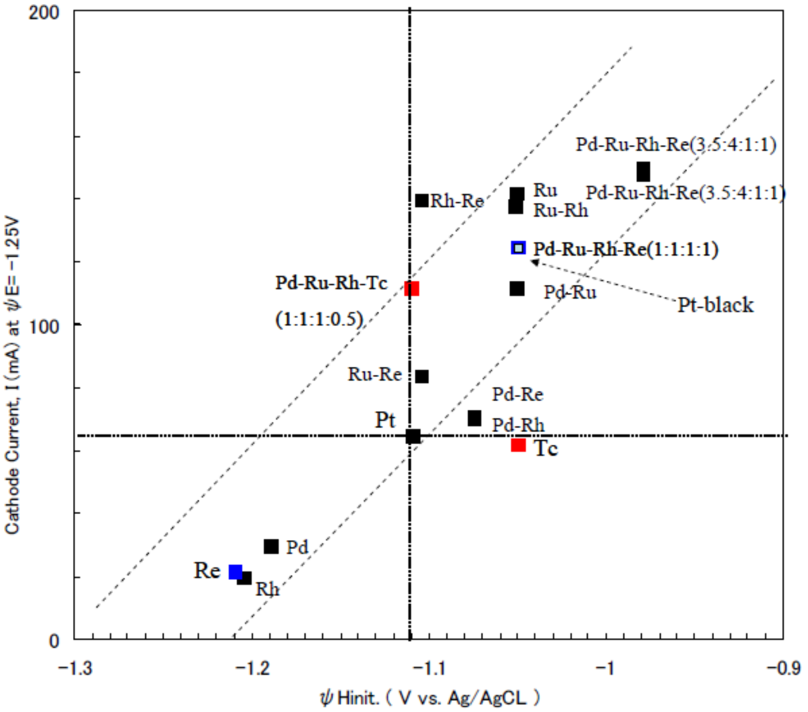

Fig.6 Relation between cathodic current corresponds to hydrogen evolution at –1.25V (vs. Ag/AgCl) and initial hydrogen evolution potential on each deposit electrode in 1 mol/dm^3 sodium hydroxide solution.

3. Conclusive Summary

A novel trinitarian R&D scheme (Advanced ORIENT Cycle) on partitioning, transmutation and utilization of actinides and fission products in the spent nuclear fuel has been proposed. As for the total utilization of RMFP (Rare Metal Fission Products; Ru, Rh, Pd, Tc, etc), CEE (Catalytic Electrolytic Extraction) method was a vital tool to separate and utilize them as deposited FP electrodes from the nuclear spent fuel.

The CEE effect is parametrically investigated. In a mixture solution with the composition of spent fuel, depositions of Ru and Tc were highly accelerated. Resulted RMFP-deposited Pt electrodes showed excellent catalytic properties for electrolytic hydrogen production, about twice higher than that of smooth Pt, and more superior to Pt-black electrodes in alkaline water. The RMFP would be expected to be a "FP-catalyst" to circulate between nuclear and hydrogen / fuel cell energy systems, thereby contributing to save the precious metal resources.

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