

STRATEGIC SEPARATION OF TECHNETIUM AND RARE METAL FISSION-PRODUCTS IN SPENT NUCLEAR FUEL

- Solvent Extraction Behavior and Partitioning by Catalytic Electrolytic Extraction -

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Using state-of-the-art separation chemistry, extended recycling of Tc and other rare metal fission-products (RMFP; Ru, Rh, Pd, Se, Te, etc) from spent nuclear fuel is examined as a new strategy for reprocessing. Nuclear fission chain reactions produce several kilograms of RMFP in standard LWR spent fuel, which proportionally increases with burn-up. Dissolved ⁹⁹Tc (TcO₄⁻) and ¹⁰⁶Ru (RuNO₃⁺) used to dominate overall decontamination factors of reprocessing plants and Pd²⁺ would disturb solvent extraction (SX) steps in some minor actinides (MA) separation processes. Besides, Tc, Se and Pd are the “mother” FP elements of long-lived fission- products (LLFP; ⁹⁹Tc, ⁷⁹Se, ¹⁰⁷Pd, etc for possible future transmutation treatment. Notably, the specific radio toxicity (ARI) of FP Pd is extremely low, about 1/300 of that of natural uranium metal. Specific radio activities and toxicities of FP Ru and FP Rh are initially high, but rapidly decrease with the passing of time to become to far less significant after several decades when no specific radiation control is needed.

From observation at the semi-industrial LWR reprocessing plant TRP (Tokai-Reprocessing Plant) as indicated in Fig.1, 70% of dissolved Tc in the dissolver solution was extracted into the 1st cycle organic phase.

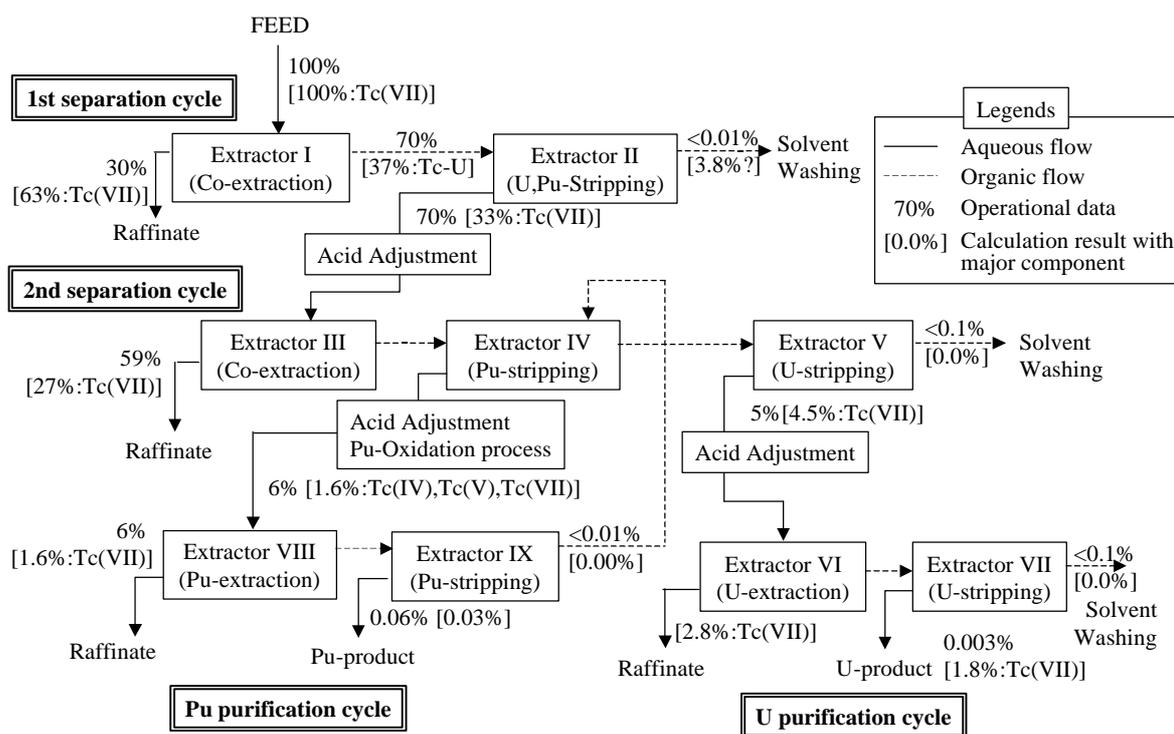


Fig.1 Behavior of Technetium in TRP Extraction Process

Most of extracted Tc was then rejected to the aqueous raffinate of the 2nd extraction cycle. The remainder was near equally distributed to the aqueous and organic phases in contact with the reductants U⁴⁺/hydrazine at the partitioning banks. By almost complete removal in the successive Pu and U purification cycles, Tc contamination to the products was kept to extremely low levels.

The quantitative extraction of Tc peculiar to the 1st cycle HA bank is attributed to complex formation with some multi-valent FPs (*e.g.* Zr⁴⁺)^{1/1} and actinides (*e.g.*, Pu⁴⁺, U⁶⁺) as,



For instance, the concentration of Zr⁴⁺, having significant synergistic extraction property with TcO₄⁻, was sufficiently in excess as *ca.* five-fold versus that of TcO₄⁻ in the feed.

The observed Tc paths were complex, and seemed to be similar to those of Np. So Tc recovery should be considered mainly from dissolver solution or high level liquid waste, but the raffinate of the 2nd extraction cycle would be the next candidate since the concentration of the FPs or actinides are very limited in the "late split" system reprocessing plant.

As a separation methodology, the first priority was given to avoiding secondary rad-wastes arising with high separation efficiency. In this direction of research, *in-situ* electrochemical processing becomes a possible candidate. Aqueous electrolytic extraction was applied to high-level liquid waste (HLLW) since it contains around 80 % of RMFP in dissolved and concentrated form.

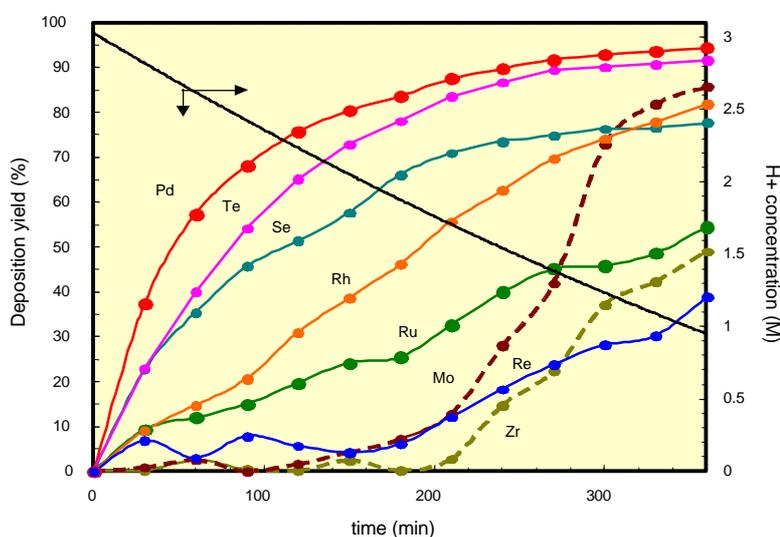


Fig. 2 Time Dependency of Deposition Yields on Rare Metal Fission-products by Electrolytic Extraction in Simulated HLLW
-Cathode Current Density : 500mA/cm², Elapse time : 6hr-

In the basic electrochemical experiments, metal ions whose $E^0 > 0.8\text{V}$ tended to deposit on the cathode by galvanostatic electrolysis even from high concentration nitric acid solution in accordance with the series of standard potential (Fig.2). In particular, deposition of Pd²⁺ was rapid and independent of other metal ions. Its yields were consistently high 90 *ca.* 100 % under wide electrolysis conditions (*e.g.*, H⁺ 0.5 – 4.5M, CD_{cathode} 10 – 700mA/cm²). By contrast, the deposition rate of Re (Tc simulator), Ru and Rh were low, but were accelerated with the addition of inorganic catalyst ions such as Pd²⁺ or Fe²⁺ despite the interference of nitric acid. Pd²⁺ acts as a promoter (Pd_{adatom}) on the surface of the cathode and Fe²⁺ as a reduction mediator in the bulk of the solution (CEE: catalytic electrolytic extraction).¹²⁾

By the CEE method, more than 99% of RuNO₃³⁺ was successfully deposited from 2.5M nitric acid solution. Based on EXAFS measurement (Fig.3), electrochemical deposition involved the dissociation of nitrosyl groups to form stable Pd (one or two atoms)-Ru (one atom) solid solution alloy metal when more than equimolar Pd²⁺ to RuNO₃³⁺ was added to the electrolyte. The electrochemical reduction of ReO₄⁻ proceeded with deoxygenation of one oxygen atom to deposit as

ReO₃ in so-called “island state” on the surface.

Deposition of Re with Pd

- Interaction between ReO₄⁻ and Pd in the bulk solution
- Deposition of ReO₃ and Pd on the cathode
- No change of the deposition potential for Re from the mono ionic solution of Re

Deposition of Ru with Pd

- No interaction between RuNO₃³⁺ and Pd in the bulk solution
- Deposition of Ru-Pd alloy on the cathode
- Decrease of the deposition potential for Ru from the mono ionic solution of Ru

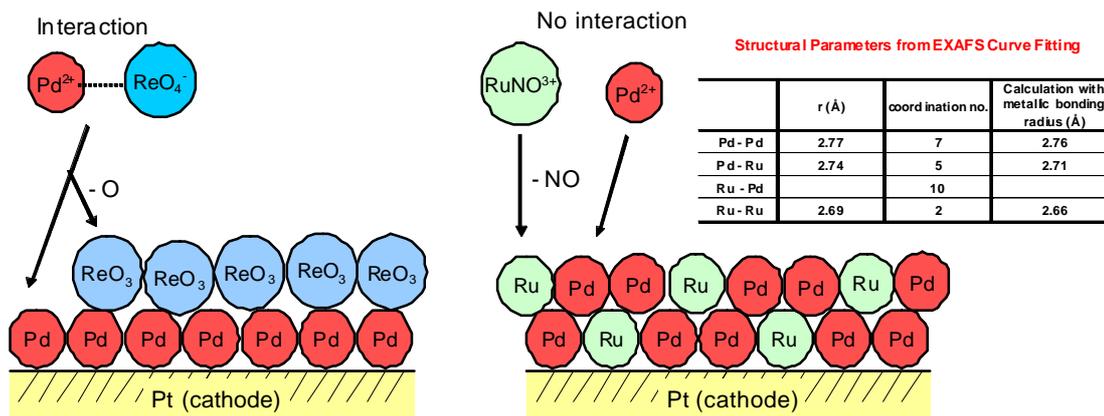


Fig. 3 Proposed Models of Ru and Re Deposition on Cathode by Catalytic Electrolytic Extraction

These observations were confirmed with the cyclic voltammograms for Pd-Ru and Pd-Re co-deposited on Pt electrodes in pure 0.5M nitric acid solution. In the case of the Pd-Re-Pt electrode, peculiar redox currents belonging to those of Pd, Pd(O), Pd(H) and ReO₃ were obtained, but no special current peaks, except for the currents of hydrogen and oxygen evolution, were observed for the Pd-Ru-Pt electrode.

The CEE method is advantageous because systematic partitioning can be achieved by just adjusting acidity, current density and adding inorganic catalysts like Fe²⁺ or Pd²⁺. The latter originates from the HLLW.

As natural platinum elements are presently very scarce and occur in limited regions of the world, RMFP (including Tc) will be treated as “strategic metals” in the near future. RMFP are likely to be utilized as industrial soft energy materials for fuel cell / solar batteries, hydrogen production and purification, et al. systems due to their high catalytic ability inherent to their *d*-metal nature. For instance, an FBR & FC energy complex can be proposed as new energy model using hydrogen and RMFP for the main flow materials. To realize this concept, a new back-end fuel cycle consisting of two different process cycles is proposed (Fig.4). The upper is the “fission-energy cycle” based on burning of actinides and transmutation of ⁹⁹Tc and other LLFP, and the lower is the “fission-product cycle” based on separation and chemical/ radiochemical utilization of purified RMFP & middle-lived FP in deep combination with non-nuclear industries. RMFP fractionation is in accordance with the international trend toward zero-emission of toxic materials, and not only offers alternative material resources to meet expanding demands for catalysts in Fuel Cell / Soft Energy

systems but is also the first step for transmutation or other selective strategies for waste management of LLFP.

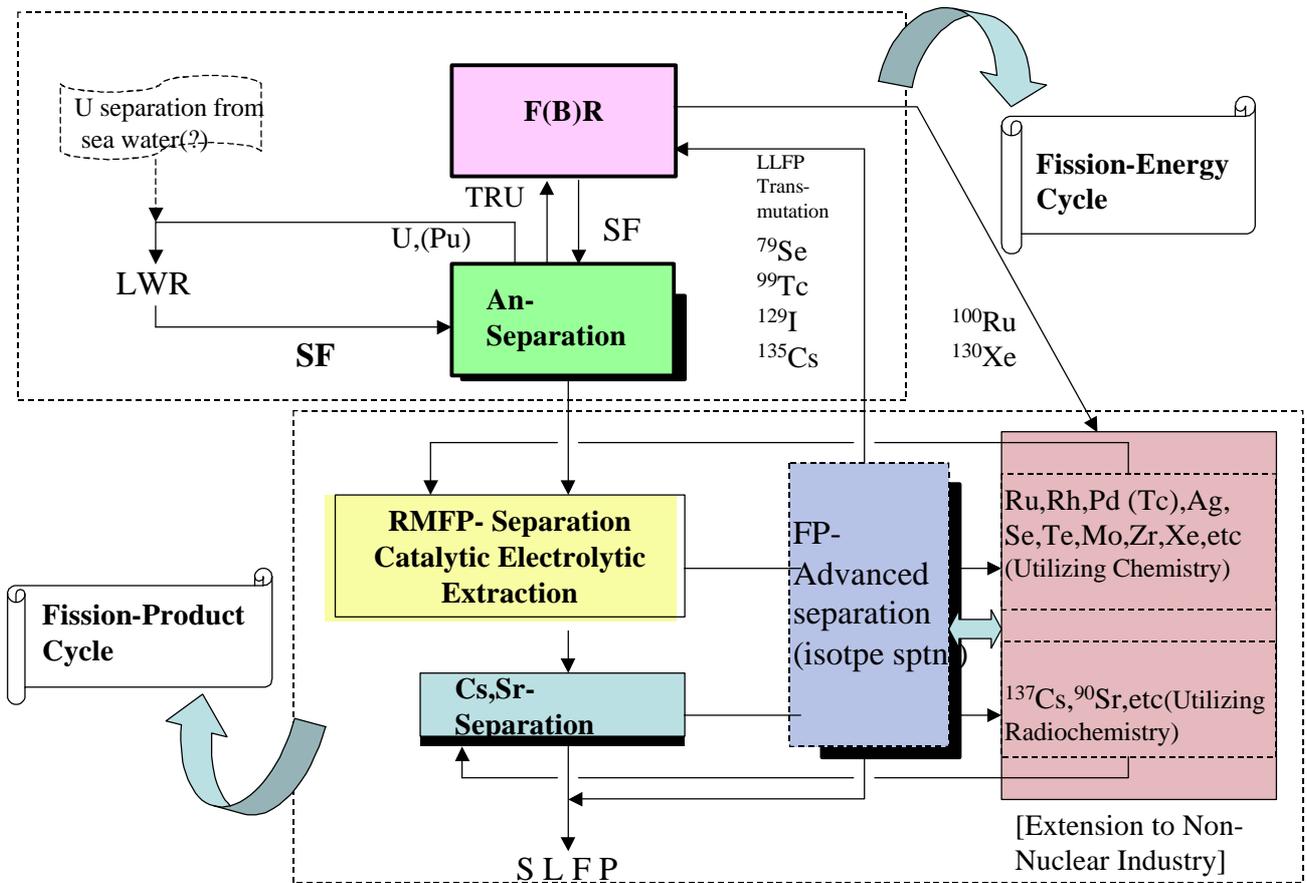


Fig. 4 Strategic Reprocessing Concept on Two recycle systems ; Fission-Energy cycle by Actinides and LLFP, and Fission-Product cycle by RMFP and MLFP

[References]

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- /2/ M. Ozawa, Y. Shinoda, Y. Sano, The Separation of Fission-Product Rare Elements Toward Bridging the Nuclear and Soft Energy Systems, *Progress in Nuclear Energy*, Elsevier Science, in printing, 2001.