ELECTROCHEMICAL SEPARATION OF RARE METAL FISSION PRODUCTS FROM HIGH-LEVEL LIQUID WASTE OF SPENT NUCLEAR FUEL

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Abstract

An electrolytic extraction was studied to separate rare metal fission product (RMFP) Pd, Ru, Rh, Tc, Te and Se from other FP in high level liquid waste. Some of them are long-lived radioactive (LLFP) but potentially strategic elements. Cyclic reaction of metallic cations such as Pd(II) or Fe(II), which originate in the solutions, may act as promoters (i.e., Pd_{adatom}) or mediators, thereby accelerates electrochemical deposition of RuNO(III), Rh(III) and Re(VII) (simulator Tc(VII)). Owing to the phenomena, recovery ratio of more than 99% became possible for RuNO(III) as well as for Pd(II). Based on the state-of-the-art separation chemistry, extended recycling of RMFP is proposed as a new strategy on reprocessing. The separation not only offers alternative material resources to meet expanding demands for catalysts in fuel cell/hydrogen energy systems but is also the first step for transmutation or other selective strategies for radioactive waste management containing LLFP. This paper suggested separating and utilising RMFP/LLFP generated by nuclear fission in a novel vision.

Introduction

An energy complex based on nuclear fission associated with soft energy systems is a candidate option for the present century, where a limited number of fast breeder reactors (FBR) may generate fuel, e.g. hydrogen, as well as large electrical outputs, whilst numerous fuel cells (FC) act as secondary dispersed or mobile power generators. The both are essentially sustainable and carbon-free, and thus the system would allow fossil fuels to be conserved or used for non-combustion purposes. Significant amounts of rare metal fission products (RMFP), such as platinum group metals [ruthenium (Ru), rhodium (Rh), palladium (Pd)] and others [technetium (Tc), selenium (Se) and tellurium (Te)], are generated in highly irradiated nuclear fuel. Some of those are long-lived but potentially useful, thereby likely to be applied as efficient catalysts for instance in FC systems. If this scenario is realised, RMFP can be the tertiary target substances to be recovered subsequently to uranium (U) and transuranium elements in the future nuclear fuel cycle.

Amongst the RMFP, Pd, Tc and Se are "mother" elements of the long-lived nuclides ^{107}Pd, ^{99}Tc and ^{79}Se, and the necessity of the separation will arise when transmutation or industrial utilisation is considered. If ionic ^{106}RuNO(III) and ^{99}Tc(VII) can be removed from the early stages of the PUREX process, this contributes considerably to improving its solvent extraction performances and the successive minor actinide separation processes, because ^{106}Ru and ^{99}Tc are both important contributors to the overall decontamination factor. Also, elimination of Pd, Mo and Zr would allow improving vitrification performance.
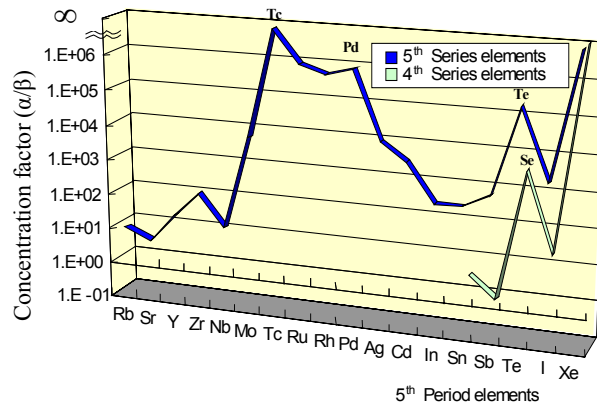
Rare metal fission products in spent fuel

In the case of FBR spent fuel irradiated to 150 000 MWd/t(HM), the total amount of RMFP becomes more than 30 kg/t(HM). When comparing the amounts of elements in FBR spent fuel (α) with those in earth's crust (β), as shown in Figure 1, the concentration ratio (α/β) is particularly high for Tc, Pd and Te in the 5th series elements and for Se in the 4th series elements. Hence, spent fuel may be regarded as a reservoir, a kind of "artificial raw ore" for such elements.

In laboratory dissolution tests with boiling 4 nitric acid, it was found that RMFP (including Se and Te) generally have a high solubility (>80%) in the standard dissolution mode. In the case of Ru however, a significant portion dissolved but some re-distributed to the off-gas stream so that the material balance sometime showed discrepancy between calculated and measured. The dissolved portions of RMFP are eventually gathered in HLLW. The elemental concentrations of target RMFP in HLLW are, as shown in Figure 2, almost above 1g/l, which is a satisfactory level for the radiochemical separation process.
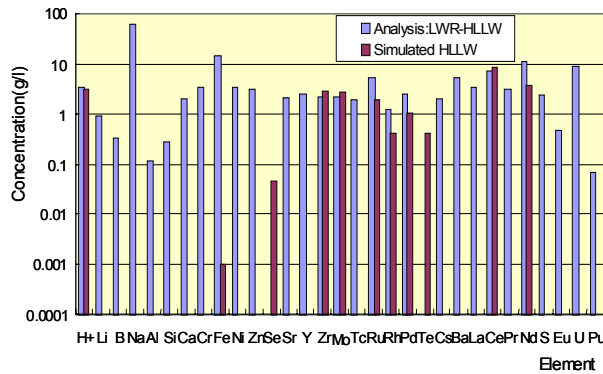
In typical FBR irradiated fuel cooled for 4 years, the abundance of radionuclides of RMFP are small except for Tc: i.e., Ru: 0.3%, Rh: 0.004%, Pd: 17.2%, Te: 0.04%, Se: 13.9%, Tc: 100%. Regarding the time dependency of their specific radioactivities (Bq/g), Tc, Se, Pd and Te are effectively constant due to the contribution of ultra long half-life radionuclides. Nevertheless, the high activity of Ru and Rh decline sufficiently to much less than 10^{-1} Bq/g by waiting just several decades.

Figure 1. **5th and 4th (Se) series elements in FBR spent fuel**
α: elements in the FBR-S.F (g/t), β: elements in the earth crust (g/t)

The specific radioactive toxicity of an isotope is obtained by dividing the specific activity by the annual limitation of intake (ARI) for workers by ingestion as recommended by the ICRP. In the time dependency of the specific radioactive toxicities, that of Pd (and Te) is constant and extremely low, those of Se and Tc are also constant but exceed that of natural U metal. Within several decades, the initially high level of Ru (and Rh) becomes less than that of Pd. Although any common index on specific radioactive toxicity is not established presently, fission platinum group elements become the same as or lesser level than U metal after several decades.

Figure 2. **Typical component composition of genuine LWR-HLL wand and simulated-HLLW**
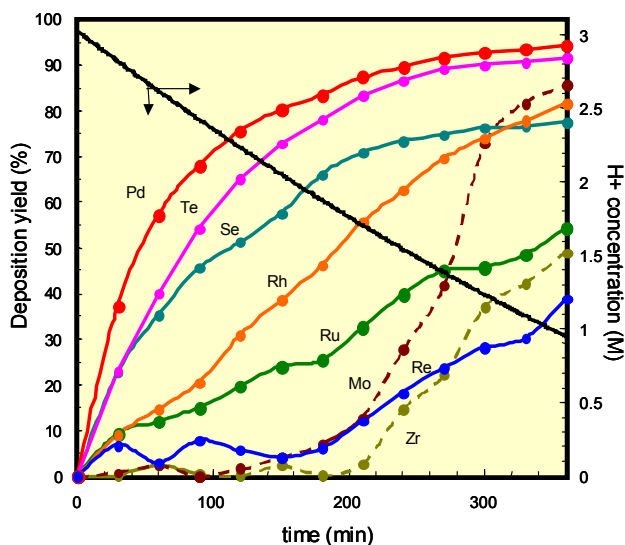(H+: mol/l)

Measurement and discussion of electrochemical extraction

For radiochemical separation process, the salt-free method, consistent with the principles of *green chemistry*, has been applied to the core part of the FBR PUREX reprocessing. [1] *In situ* electrochemistry is essentially salt-free, and thus has been proposed and demonstrated as an alternative tool to conventional chemical reactions and/or waste destruction methods throughout the PUREX process. Electrolytic extraction (EE) is generally carried out under low temperature conditions and provides a remotely controlled system utilising electrons to effect specific redox reactions. Crucially, it avoids generation of secondary saline wastes. If mediation or promotion can be applied to the electrochemical separation, process efficiency is expected to be improved significantly. Namely, EE is recognised as a simple, safe, and superior method for the recovery of RMFP whose redox potentials are favourably noble in acidic solutions.

Figure 3. **Time dependency of deposition yields on rare metal fission products by electronic extraction in simulated HLLW**
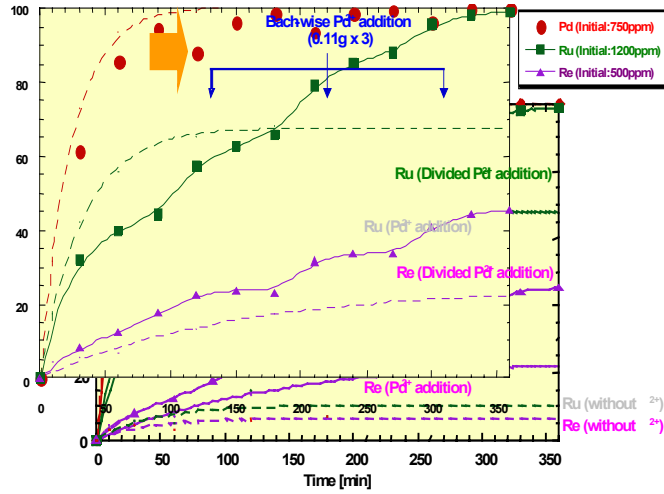
cathode current density: 500 mA/cm^2, elapse time: 6hr-

The electrochemical behaviour of some RMFP has been investigated in concentrated nitric acid solution, simulated dissolver solution and simulated high level liquid waste (sHLLW; see Figure 2). [3] Different time dependencies are observed for deposition of each RMFP from sHLLW (H^+_{init}:3.0 M) in galvanostatic electrolysis. Individual electrolysis conditions and apparatus were described in the reference. [3] The deposit was determined by the decrease of ionic concentration of metals in solution using ICP measurements. As shown in Figure 3, the deposition rates of Pd, Te, Se and Rh seemed to be independent of changing H^+ concentration, whilst H^+ greatly affected those of Mo, Zr, Ru, and Re (Tc simulator element). H^+ concentration in the catholyte decreased along with the generation of H_2 gas at the cathode, and finally reached ca. 1 M at the end of electrolysis. The deposition yield of Pd (and Te) was high, but those of Mo and Zr seemed the smallest at higher H^+ concentration. This observation implies that Mo and Zr never electro-deposit on the cathode, but precipitate as insoluble complexes at lower H^+ concentration.

The acceleration effect on the deposition yields of RMFP in 2.5 $\underline{M}$ HNO$_3$-sHLLW during 6hr electrolysis were evaluated under the conditions where Pd(II) or Fe(II) ion were continuously added at the rate of ca. 0.04 g/h. [4,5] As shown in Figure 4, [6] deposition ratio of Ru increased twice to more than 99% when added amount of Pd(II) became over equivalent to initial Ru (Pd$_{total}$/Ru$_{initial}$=1.6(wt. ratio)). In the case of Re, its deposition ratio became ca. 45%, triple, when Pd$_{total}$/Re$_{initial}$ was 3.75. These significant accelerations were observed just in the case of "divided addition" mode. A series of experiments confirmed, that the deposition yield of RMFP generally low with high H^+ concentration, but that those of Ru, Rh and Re were significantly improved by the addition of Pd(II) or Fe(II) cation even in high H^+ conditions. This suggests that, if this phenomenon can be utilised high recoveries of these elements become possible even from higher acidity solutions at good electrical efficiency.

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Figure 4. **Change of Ru and Re disposition rates with addition of Pd^{2+} Ion to 2.5 HNO$_3$ Pd/Ru mixture or Pd/Re mixture solutions**

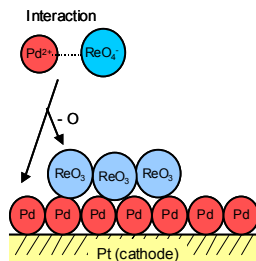electrolysis condition; H+: 2.5M, Temp.: 50Å, CD: 500mA/cm^2

The proposed electro-deposition models, as shown in Figure 5, are based on the assumption that Pd(II) participates as a promoter Pd$_{adatom}$ for RuNO(III), etc., but just an ionic interaction with Re(VII) anion. Structural parameters for electro co-deposited Pd-Ru were calculated by fitting the EXAFS curve with consideration of bonding between the Pd and Ru atoms in the cubic-closest-packed (ccp) structure. The EXAFS and other measurement suggest that Pd and Ru metal form a solid solution by breaking the Ru-NO bond at the electrode surface, while ReO$_3$ deposits by de-oxidation of Re(VII) as an "island state" on the Pd atom layer. The Pd-Ru deposit was electrochemically very stable at nobler electrode potential. In the case of Fe(II), while the same acceleration effect was observed, it never deposits. So, Fe(II) might act as a reductant mediator. This electrochemical process is hence regard as a catalytic electrolytic extraction (CEE) process. [5]

Figure 5. **Proposed models on Ru and Re deposition on the cathode by presence of Pd(II) in catalytic electrolytic extraction**
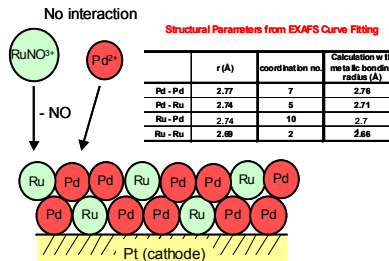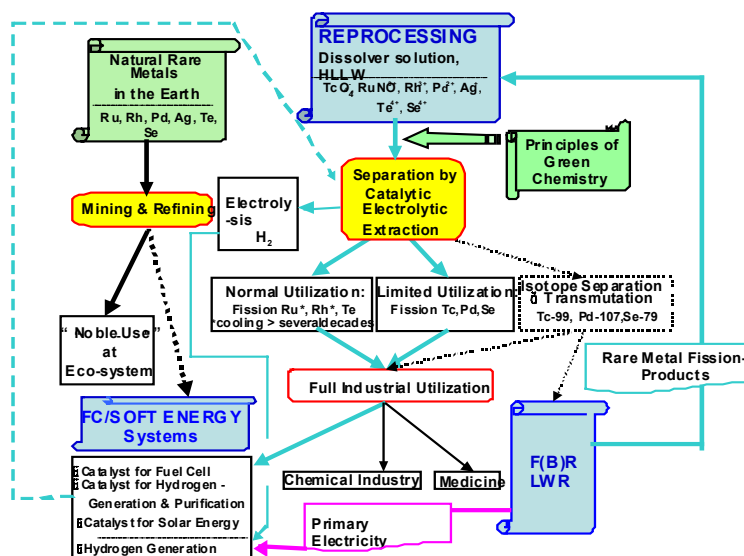
To confirm the CEE process in the real radiochemical condition, new three years collaborations were started in this year with Khlopin Radium Institute (KRI) and Japan Atomic Energy Institute (JAERI), respectively. Fundamental electrochemical behaviour of Tc(VII) and RuNO(III), and Pd_{adatom} effect on their deposition will be examined using real HLLW and/or dissolver solution.

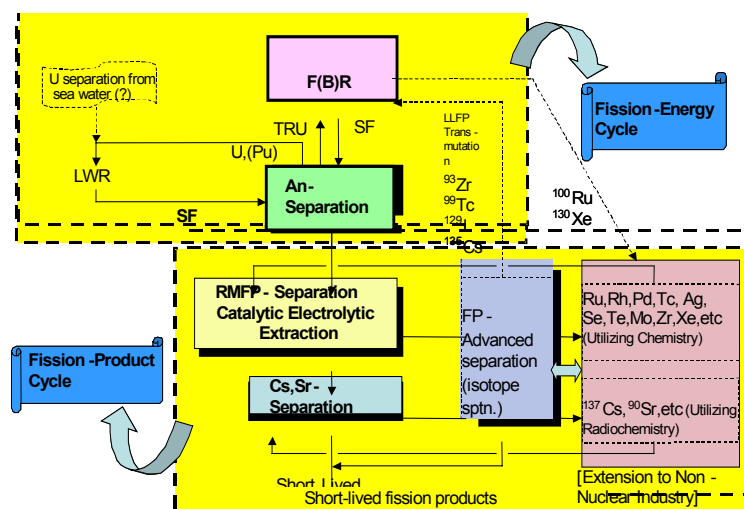**Potential application of RMFP in the forefront fields**

The platinum group metals are well known to have extraordinary chemical capabilities, and industrial applications are diverse including auto exhaust catalysts (Pd, Rh), chemical catalysts (Pd, Rh), electrical (Pd, Rh, Ru), electrochemical (Ru), dental (Pd), jewellery (Pd) and glass (Rh), etc. The properties of Tc are not fully researched presently since is extremely rare in nature (except for ^{99m}Tc, very short-lived γ- active, as used in medical science), but its use is foreseen due to similar properties to rhenium. Very little information is available on the application of Te and Se except for semi-conductor alloys. Presently, very promising applicability is expected for Ru and Pd as electrode catalysts for the fuel cell and hydrogen production/purification in the most growing fields of soft energy industry; for example, the Pt-Ru catalyst is promising as an anode material with hydrogen fuel due to its CO poisoning resistant characteristics. Among the platinum group metals, the highest demand has been recorded for Pd with a rapid increase in auto catalyst application since around 1994 (e.g., in 1998, 254 t). Due to its sensitive characteristics against hydrogen, the demand for Pd will increase further for purification of hydrogen fuel. With expanding needs for FC catalysts, demand for Pd, Ru and Rh are likely to increase 5-10 folds in the near future. [7]

Figure 6. **Overall concept on FBR/FC energy complex centred on rare metal fission products**

Accordingly, the RMFP in spent nuclear fuel should strategically cover a worthwhile part of industrial demand in the future. As such a new vision on energy system, a concept is proposed based on a fast breeder reactor and fuel cell energy complex bridged by the recycling of the RMFP. [8] In the scheme in Figure 6, separated RMFP by the CEE process should be utilised according to their radiochemical characteristics while allowing natural rare metals to be preferentially conserved or used where environmentally or economically more attractive.

Figure 7. **Strategic fuel cycle concept by two reprocessing systems: fission-energy cycle and fission-product cycle**

In this context, nuclear fuel cycle should also be changed to be new one consisting of two different separation cycles. [6] The upper, as shown in Figure 7, is the "fission-energy cycle" based on burning of low-decontaminated actinides and transmutation of ^{99}Tc and other LLFP from the lower cycle. Bifunctional neutral phospho-organic compounds (BNPC) dissolved in fluorinated polar diluents (fluoropols) is one candidate for the recovery of all the actinide by single cycle flowsheet using a mono-extractant system. [9] The lower is the "fission-product cycle" based on fine separation of elements and isotopes of RMFP/LLFP/ML (middle-lived) FP for the chemical/radiochemical utilisation in deep combination with non-nuclear industries.

There are few R&D programmes aiming at utilising real RMFP up to now, [10] except for Tc [11] in the past in Russia. As one trial to evaluate applicability of RMFP to the soft energy field, new precedent experiments will move in this year in the field of hydrogen production by γ-ray assisted electrolysis of alkali water/seawater using electro-deposited Ru/Rh/Pd/Re.

Conclusions

An electrolytic extraction was studied to separate rare metal fission product Pd, Ru, Rh, Tc, Te and Se from other FP in high level liquid waste. Cyclic reaction of metallic cations such as Pd(II) or Fe(II), which originate in the solutions, may act as promoters (i.e., Pd_{adatom}) or mediators, thereby accelerates electrochemical deposition of RuNO(III), Rh(III) and Re(VII) (simulator Tc(VII)). Owing to the phenomena, recovery ratio of more than 99% became possible for RuNO(III) as well as for Pd(II). Based on the state-of-the-art separation chemistry, extended recycling of such rare metal FP is proposed as a new strategy on reprocessing.

The separation not only offers alternative material resources to meet expanding demands for catalysts in fuel cell/hydrogen energy systems but is also the first step for transmutation or other selective strategies for radioactive waste management containing long-lived FP. Enhanced radioactive waste fractionation is in accordance with the general trend of progress in partitioning and recycling of wastes toward zero-emission.

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