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Research Committee on Ruthenium and Technetium Chemistry in PUREX System, Organized by the Atomic Energy Society of Japan[1, 2]

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Abstract—The paper summarizes the activity of the committee "Ruthenium and Technetium Chemistry in the PUREX System," with a focus on basic information on technetium behavior in the PUREX process, the principles of plant design, and the behavior during the final waste treatment.

ACTIVITIES OF RESEARCH COMMITTEE

In advancement of the PUREX reprocessing system, improving the economy with ensuring the safety, becomes an urgent issue. In the initial developing stage of the reprocessing technology, major studies were aimed to attain high recovery ratios and purities of uranium and plutonium products. Some data bases were generated during these studies. Further, as separation of long-lived minor actinides also became a current topic, much attention was given to the chemical behavior of minor actinides, not only in the PUREX process but also in novel extraction processes. However, the behavior of fission products was studied insufficiently as compared to actinides. Actually, the chemical properties and extraction behavior of the fission products in the PUREX process are still insufficiently understood.

Among the fission products, ruthenium and technetium show a particular tendency to form extractable species with TBP and other organic extractants. Therefore, they are distributed throughout the reprocessing flowsheet and get into the environment. In the modern reprocessing plants, these two nuclides (^{106}Ru and ^{99}Tc) are the dominant nuclides determining the overall decontamination factors of the uranium and plutonium products. In other words, removal of these two nuclides will determine the design of the main separation process. Furthermore, ^{99}Tc is long-lived ($T_{1/2} = 2.12 \times 10^5$ years), and it will be a possible target nuclide for future transmutation using a fast reactor or accelerator [$^{99}\text{Tc} + n \rightarrow {}^{100}\text{Ru}$ (stable)]. On the other hand, ruthenium is one of the rare metal fission products to be potentially utilized in future, because ^{106}Ru has a short half-life ($T_{1/2}$ = 368 days), and its specific radioactivity will be negligible after cooling down for several decades.

Members of the Atomic Energy Society of Japan have organized a scientific committee on this problem in October 1999. The committee, entitled "Ruthenium and Technetium Chemistry in the PUREX System," consists of more than 30 members. At present, the committee's activities are aimed at deeper understanding of the PUREX-type LWR and FBR reprocessing systems with respect to the design, construction, operation, and safety evaluation.

The scope of the work of the committee includes the following major topics: (1) basic solution and solid-state chemistry; (2) basic solution and solid-state chemistry of minor actinides (in particular, Np); (3) partitioning chemistry in the PUREX system and environmental behavior of the components; (4) processes of recovery, purification, and utilization of rare metal fission products; (5) field data on plant design, operation, decontamination, and decommissioning; (6) numerical process simulations and process control technology; (7) compilation of a data base for process chemistry and plant engineering.

Tc CHEMISTRY IN PUREX SYSTEM

In the step of spent fuel dissolution in the PUREX process, some part of Tc does not pass into solution.

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[1] This article was submitted by the authors in English.
[2] Reported at the Third Russian–Japanese Seminar on Technetium (Dubna, June 23–July 1, 2002).

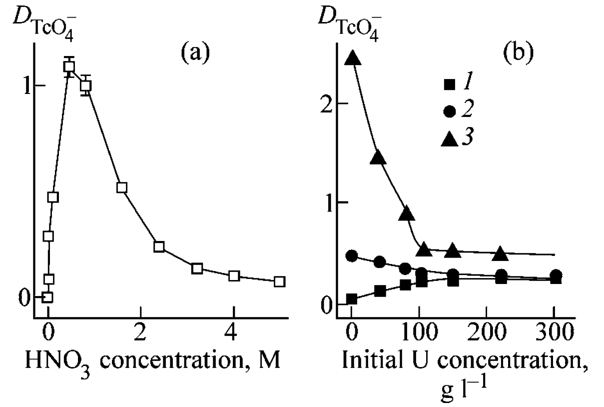

Fig. 1. Tc distribution ratio $D_{TcO_4^-}$: (a) in the absence of U and Pu, as a function of the HNO_3 concentration, and (b) in the presence of U and Pu, as a function of the initial U concentration, at Pu concentration, g l^{-1}: (*1*) 0.5, (*2*) 20, and (*3*) 50.

This fraction, estimated at 10 to 20% of the total Tc for a UO_2 fuel, accompanies the "insoluble residues" essentially consisting of noble metals (Ru, Rh, Pd). These insoluble residues are incorporated in the vitrified wastes [1]).

In nitric acid medium in the absence of reducing agent, the dissolved Tc is in its highest valence (VII), which is the most stable. It occurs in the form of pertechnetate ion, TcO_4^-. This species can be coextracted with a metal cation by substitution of the pertechnetate group for the nitrate group in the neutral complex extractable with TBP.

Technetium is coextracted with the main metallic cations extracted by TBP, and particularly with the ZrO^{2+} cation, which is present in large amounts in the solution fed to the extraction cycle. This extraction of Tc seriously interferes with the U/Pu partitioning. Correspondingly, the PUREX process should be adapted to limit the extraction of Tc.

Tc FUNDAMENTAL CHEMISTRY

In spent fuel, Tc is mainly in the metal form. In the dissolution step, Tc is in the state of pertechnetate ion. Some of Tc is not dissolved in nitric acid and occurs in white inclusions, in the mixed alloy form.

Tc in the pertechnetate form is extracted with TBP by the following equations [2]:

$$H^+ + TcO_4^- + 3TBP \rightarrow HTcO_4 \cdot 3TBP, \quad (1)$$

$$UO_2^{2+} + NO_3^- + TcO_4^- + 2TBP \rightarrow UO_2(NO_3)(TcO_4) \cdot 2TBP, \quad (2)$$

$$Pu^{4+} + 3NO_3^- + TcO_4^- + TBP \rightarrow Pu(NO_3)_3(TcO_4) \cdot TBP, \quad (3)$$

$$Zr^{4+} + 3NO_3^- + TcO_4^- + TBP \rightarrow Zr(NO_3)_3(TcO_4) \cdot TBP. \quad (4)$$

In the absence of U, Pu and Zr, at low HNO_3 concentration, Tc is extracted with TBP in the form of $HTcO_4 \cdot 3TBP$ according to Eq. (1). In the presence of these elements, Tc is coextracted as mixed complexes $UO_2(NO_3)_2(TcO_4) \cdot 2TBP$, $Pu(NO_3)_3(TcO_4) \cdot TBP$, and $Zr(NO_3)_3(TcO_4) \cdot TBP$ according to Eqs. (2)–(4).

The Tc distribution ratio increases with an increase in the nitric acid concentration in the range of low $[HNO_3]$. At higher nitric acid concentrations, the pertechnetate ion in mixed complexes is substituted by nitric acid and displaced into the aqueous phase, and the Tc distribution ratio decreases with an increase in $[HNO_3]$. The extraction reactions proceed according to the following equations (from the right side to the left):

$$TcO_4^- + UO_2(NO_3)_2 \cdot 2TBP \leftarrow UO_2(NO_3)(TcO_4) \cdot 2TBP + NO_3^-, \quad (5)$$

$$TcO_4^- + Pu(NO_3)_4 \cdot TBP \leftarrow Pu(NO_3)_3(TcO_4) \cdot TBP + NO_3^-, \quad (6)$$

$$TcO_4^- + Zr(NO_3)_4 \cdot TBP \leftarrow Zr(NO_3)_3(TcO_4) \cdot TBP + NO_3^-. \quad (7)$$

Figure 1a shows the experimental data on the distribution ratio for equilibrium HNO_3 concentration in the aqueous phase of 0 to 5 M. In Fig. 1b, the Tc distribution ratio is plotted vs. initial uranium concentration in the aqueous phase in the system containing Pu and U. At 0.5 g l^{-1} Pu and traces of U, the Tc distribution ratio is similar to that in the system with straight nitric acid. As the U concentration in the system is increased, the Tc distribution ratio grows, reaching a plateau. This is in line with the formation of an extractable uranium nitrate–pertechnetate species.

At a high Pu concentration, the Tc extraction is greatly enhanced. Pu(IV) nitrate forms an extractable species with Tc, similar to Zr(IV) nitrate. Like the $Pu(NO_3)_4 \cdot 2TBP$ species, pertechnetate-containing adducts salted-out by the preferential extraction of uranium nitrate and uranium pertechnetate species are possibly formed. This is illustrated clearly by the results for 20 g l^{-1} Pu.

The Tc distribution ratio is expressed in the absence of U, Pu and Zr and in the presence of U and Zr by empirical equations (8) and (9), respectively [3]. These equations are obtained by fitting a large body of experimental data.

$$D_{\mathrm{TcO_4^-}} = A\frac{aC^{b}_{\mathrm{NO_3^-,aq}}}{1 + cC^{d}_{\mathrm{NO_3^-,aq}} + eC^{f}_{\mathrm{NO_3^-,aq}}}, \qquad (8)$$

where $C^{b}_{\mathrm{NO_3^-,aq}}$ is the $\mathrm{NO_3^-}$ concentration in the aqueous phase (M); $A = 1$ (30 vol % TBP), $a = 2.324\exp(8070\tau)$, $b = 0.848\exp(230\tau)$, $c = 0.157 \times \exp(3240\tau)$, $d = 4.69\exp(410\tau)$, $e = 1.72\exp(3150\tau)$, $f = 1.95\exp(160\tau)$, $\tau = 1/(\theta + 273) - 1/298$ (θ is the temperature in °C);

$$D_{\mathrm{TcO_4^-}} = {}^{0}D_{\mathrm{TcO_4^-}} + K_{\mathrm{Tc,U}}C_{\mathrm{UO_2^{2+},org}}(1 + kC^{1.343}_{\mathrm{NO_3^-,aq}}) + K_{\mathrm{Tc,Zr}}(C_{\mathrm{Zr^{4+},org}} - C_{\mathrm{TcO_4^-,org}})C^{-0.707}_{\mathrm{NO_3^-,aq}}, \qquad (9)$$

where $D_{\mathrm{TcO_4^-}}$ is the $\mathrm{TcO_4^-}$ distribution ratio in the presence of $\mathrm{UO_2}^{2+}$, $\mathrm{Zr^{4+}}$; ${}^{0}D_{\mathrm{TcO_4^-}}$ is the Tc distribution ratio in the absence of $\mathrm{UO_2^{2+}}$, $\mathrm{Zr^{4+}}$; $C_{\mathrm{UO_2^{2+},org}}$ is the $\mathrm{UO_2^{2+}}$ concentration in the organic phase (M); $C_{\mathrm{NO_3^-,aq}}$ is the $\mathrm{NO_3^-}$ concentration in the aqueous phase; $C_{\mathrm{Zr^{4+},org}}$ is the $\mathrm{Zr^{4+}}$ concentration in the organic phase; $C_{\mathrm{TcO_4^-,org}}$ is the $\mathrm{TcO_4^-}$ concentration in the organic phase; $K_{\mathrm{Tc,U}} = 0.33\exp(-1060\tau)$; $k = 4.87\exp(980\tau)$; $K_{\mathrm{Tc,Zr}} = 1670\exp(2810\tau)$.

Equation (9) reflects the effect of U and Zr on the Tc distribution ratio, illustrated by Figs. 1a and 1b.

Equations (8) and (9) are included in the program simulating the extraction step. It can simulate the extraction behavior of U, Pu and nitric acid based on the Richardson calculation model.

Figure 2 shows the results of calculations using the ESCCAR program developed in JAERI and incorporating the above-given equations [3]. The calculation results agree well with the experimental data. The simulation program has been further developed to include more detailed data on chemical reactions in the PUREX system.

Figure 3 illustrates the reduction of Tc with hydrazine at room temperature [4]. The percentage of Tc(VII) is plotted against time. After 3 h of induction period, the percentage decreases and reaches a minimum at about 10 h. At this time, almost all Tc exists as Tc(IV). Then the percentage of Tc(VII) increases and reaches approximately the initial value. The reaction is generally explained as Tc(VII) reduction to Tc(IV) with hydrazine and reoxidation of Tc(IV) with nitrate. The mechanism, however, presumably includes intermediate species such as Tc(VI) and Tc(V) [5].

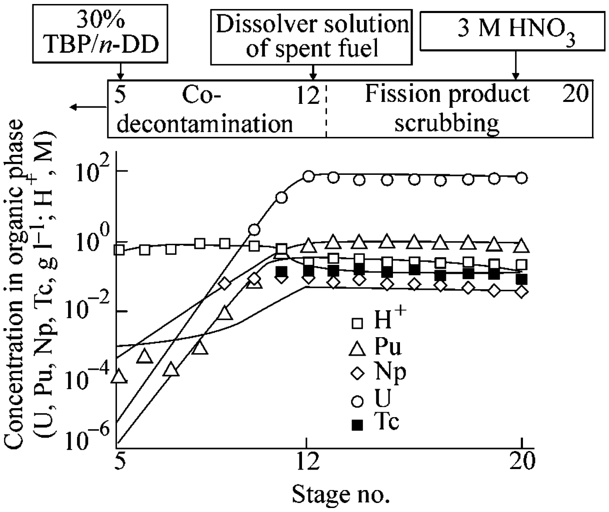

Fig. 2. Concentration profiles of U, Pu, Np, Tc, and nitric acid in the co-decontamination and fission product scrubbing steps in the PUREX system: (points) experiment and (lines) calculation.

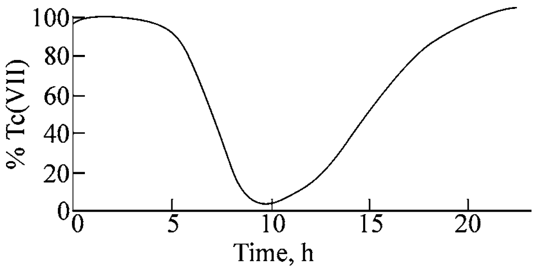

Fig. 3. Reduction of Tc with hydrazine at room temperature.

Tc BEHAVIOR IN INDUSTRIAL PROCESS

Figure 4 shows the distribution of Tc over the designed flowsheet of the Rokkasho Reprocessing Plant (RRP). In the first stage, fission products are separated, and then Pu is separated from U by reduction with U(IV) and hydrazine. In the second stage, U and Pu are purified. In the first stage, the organic phase from the extraction column is effectively scrubbed with 2 M HNO_3 in the first scrubbing column and by more concentrated HNO_3 in the second scrubbing column. The values of 95 and 33% in Fig. 4 are maximal for the process; therefore, their sum exceeds 100%.

Figure 5 shows the Tc distribution over the flowsheet of the Tokai Reprocessing Plant (TRP). The TRP flowsheet includes three solvent extraction

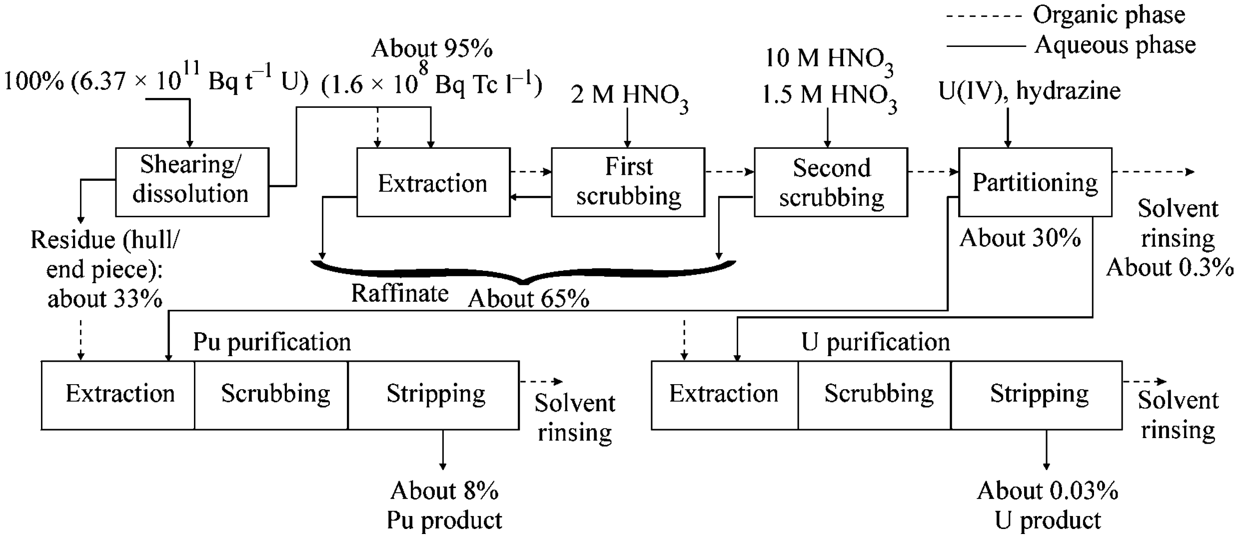

Fig. 4. Tc balance at Rokkasho Reprocessing Plant.

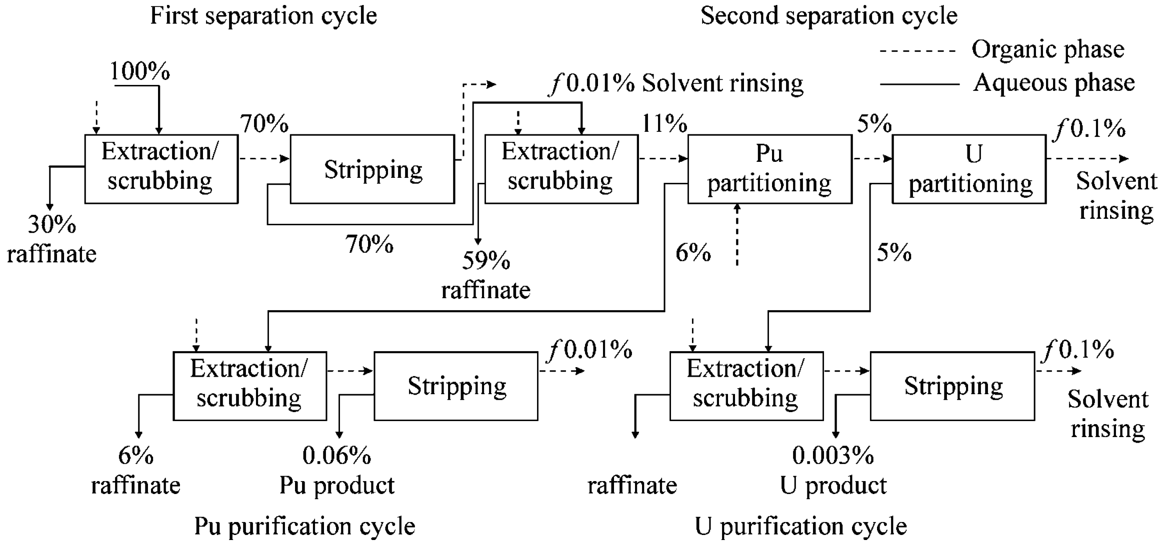

Fig. 5. Tc balance at Tokai Reprocessing Plant.

cycles. In the first cycle, 70% of Tc is extracted. In the second, most of Tc is stripped, and a small amount of extracted Tc goes in almost equal proportions to the U and Pu purification cycles. In both purification cycles, Tc is quantitatively separated. This Tc behavior is presumably due to coextraction with Zr, U, and Pu.

Tc BEHAVIOR IN RADIOACTIVE WASTE DISPOSAL

Radioactive wastes from nuclear power plants and reprocessing plants contain Tc. Tc is one of the most important radionuclides in the safety assessment of waste disposal.

The chemical forms, solubility, and sorption coefficient [K_d, ratio of the nuclide concentration in solid (Bq g^{-1}) to the nuclide concentration in liquid (Bq ml^{-1})] of Tc are given in Table 1. In shallow disposal, presumably under oxidizing conditions, the

Table 1. Tc behavior at waste disposal

Parameter	Shallow disposal	Deep disposal
Chemical species	TcO_4^-	TcO_2 or $TcO(OH)_2$
Solubility	Soluble	4×10^{-8} M
K_d, ml g^{-1}:		
cement	About 0–1	About 100–1000
soil, rock	About 0.5	About 1000

Table 2. Main research issues for Ru and Tc chemistry toward advancing PUREX system

Operation	Solution, coordination, extraction chemistry	Solid chemistry	Analytical chemistry	Radio-, electro-, thermo-, catalytic chemistry
Dissolution, filtration	Undissolved residue; optimal dissolution; Ru accumulation; Ru/Tc precipitation; cocrystallization with U(VI); Ru deposits; colloid formation; nanofiltration; colloid separation		Quantitative analysis for Tc in multicomponent radioactive solutions	Electrochemical dissolution
Solvent extraction	Distribution ratios; Ru/Tc in third phase; Ru/Tc complexation; redox mechanism; oxoanions and ion pairs; control of decontamination factors; mathematical simulation; supercritical fluid extraction	Ru/Tc decontamination from actinides by crystallization and supercritical fluid extraction	Ru/Tc chemical species and their identification in PUREX solutions; polynuclear NMR for structural analysis; quantitative analysis for Tc	Electrochemical redox control for more efficient decontamination of Ru and Tc
Evaporation	Ru/Tc vaporization; efficient evaporation for LLW volume reduction; recycling of distillate	Ru deposition on equipment walls		Ru/Tc vaporization behavior in evaporator; Ru/Tc vaporization during thermal denitration of uranyl nitrate hydrate
Vitrification, disposal	Tc chemical forms in repositories; environmental diffusion; Ru solubility and sorption in environment; reaction thermodynamics and kinetics; reactivity toward natural organics (e.g., humus)	Materials for Tc immobilization, Tc encapsulation, Tc vaporization	Microanalysis methods to confirm redox reactions; pH changes	Vaporization of Ru and Tc in melter or incinerator
Decontamination, decomissioning	Separation of anions	Properties of precipitated Ru/Tc, efficient decontamination of precipitates	Microanalysis methods	Electrochemical decontamination (e.g., electrocleaning)
Recovery, purification, utilization	Development of novel separation processes based on coordination chemistry and ion exchange	Ru/Tc recovery from undissolved residues		Electrochemical recovery of Ru/Tc; industrial application of fission products; radiation effects; clearance level; shielding/storage; medical applications of Tc

chemical form of Tc is TcO_4^-, and K_d is low. On the other hand, in deep disposal, in which reductive conditions may be realized, the chemical form of Tc is TcO_2 or $TcO(OH)_2$, and K_d is high. More detailed studies on this problem are necessary.

MAIN RESEARCH ISSUES FOR Ru AND Tc CHEMISTRY TOWARD ADVANCING PUREX SYSTEM

Table 2 summarizes the main research issues on the Ru and Tc chemistry for either PUREX process or its surrounding processes, aimed to make them more efficient and economical. In this table, the rows are the fields of chemistry, and the columns are specific problems to be studied. These items were formulated by more than thirty members of the committee.

Also, a number of scientific and technical problems were formulated, reflecting the novel strategy on the PUREX system with consideration of peculiar properties of Ru and Tc among various fission products. The problems are related to separation of Ru and Tc in the ionic or solid/colloid state, decontamination conditions, solubility or mobility in repository, and recovering/purification technology for the future utilization.

(1) Basic scientific and technological aspects: identification of Ru and Tc chemical species in PUREX solutions and in radioactive waste repositories; complex formation of Ru and Tc with degraded extractants and diluents.

(2) Plant engineering and environmental aspects: Tc in the white inclusions, method for efficient dissolution of insoluble residues; distribution behavior in the multicomponent highly radioactive extraction systems (e.g., dissolver solution, HLLW); Tc synergistic extraction with coexisting actinides and fission product cations; optimization of the system from the viewpoint of decontamination from Tc.

(3) Common and future aspects: analytical methods for identifying chemical species, structure, quantities; recovering/purification methods as applied to transmutation or utilization of long-lived ^{99}Tc; accumulation of data on physicochemical and radiochemical properties.

Along with advancing the PUREX process, it is intended to study more extensively the environmental behavior and utilization of Tc as a long-lived fission product. In this context, it is quite necessary to gain profound knowledge on the separation and purification chemistry, materials science to fabricate ^{99}Tc target, and nuclear properties.

Thus, it is necessary to investigate and summarize the solid/liquid, coordination, and separation chemistry of Tc and Ru, and also the related chemical engineering data. These data will also be usfeul for ensuring safety operation of the Tokai and Rokkasho Reprocessing Plants. Furthermore, these data are required for minimizing generation of radioactive wastes during future decommissioning of the reprocessing plants.

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