

Study on Electrolytic Reduction of Pertechnetate in Nitric Acid Solution for Electrolytic Extraction of Rare Metals for Future Reprocessing

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Electrolytic reduction of Tc(VII) in a nitric acid solution was examined to recover Tc as well as rare metals (Pd, Ru, and Rh) by an electrolytic extraction method, i.e. electro-reductive deposition, from a spent fuel solution for future nuclear fuel reprocessing. An absorption peak at 482 nm observed after electrolytic reduction of Tc(VII) in 3 M HNO₃ at -0.3 and -1.0V vs SSE (standard silver electrode) suggests the reduction of Tc(VII) to Tc(IV). When Pd is present together with Tc in 1 M HNO₃, the concentration of Tc decreased to 85% of the initial concentration by electrolysis at ±0.0 V vs. SSE for 60 min, suggesting acceleration of Tc deposition by Pd (promoter effect). The Tc concentration, however, increased returning to the initial value after further electrolysis. The Pd deposit from Tc-Pd-Ru-Rh solution redissolved more easily than that from Pd-Ru-Rh, as a consequence of a change in the oxidation-reduction property of the Pd deposit due to the presence of Tc in the solution.

1. Introduction

In nuclear fuel reprocessing, many potentially useful rare metals, such as Pd, Ru, Rh, Tc, Te and Se, are vitrified as high-level waste. If it is possible to recover and utilize these elements, spent fuel reprocessing will be much more attractive. In the future, it will be strongly demanded to minimize the volume of radioactive waste arising from reprocessing. In an electrolytic extraction (EE) method,^{1,2} i.e. electrolytic reductive deposition, little secondary radioactive waste is produced because no extra chemical reagent is needed in the EE method. Therefore, the EE method is considered to be promising for recovering those precious elements. In the present work, we examined electrolytic reduction of Tc in a nitric acid solution to recover Tc together with rare metals (Pd, Ru, and Rh), whereas Re was used as a simulant for Tc in the previous work.^{1,2}

2. Experimental

To prepare Tc(VII) stock solution, 185 MBq of NH₄⁹⁹TcO₄ powder purchased from Du Pont Co. was used. The powder showed a black color suggesting the existence of Tc oxide (probably TcO₂·xH₂O), and was pre-treated to obtain pure NH₄TcO₄. In 30 mL of 0.1 M NH₃ solution, the powder was mildly heated with stirring and 10 M H₂O₂ solution was added dropwise. The powder was completely dissolved in 5 min, and then the solution was evaporated to dryness. The obtained white solid of NH₄TcO₄ was dissolved in 10 mL of water (stock solution). The concentration of Tc in the stock solution was determined to be 0.144 M by induction coupled plasma-atomic emission spectroscopy (ICP-AES).

Constant potential electrolytic experiments were performed with a BAS CV-660A voltammetric analyzer by a three-electrode technique. Carbon plates of 0.2 mm in thickness were cut into 1.0 cm squares, and three plates were used as a working electrode giving a surface area of 6 cm². A Pt wire of 0.6 mm in diameter was used as a counter electrode, and a standard sil-

ver electrode (SSE, Ag/AgCl in 3 M KCl) was used as a reference electrode. All of these electrodes were dipped in an electrolyte solution. The electrolyte solution was prepared from the Tc stock solution described above by adding aqueous solution of HNO₃ with desired concentration. Aqueous solution of Pd(NO₃)₂ was also added to the electrolyte if necessary. The concentration of Tc and Pd in the electrolyte solution was determined by ICP-AES. Photo-absorption spectra of the Tc (only) solutions were measured during electrolysis. The electrolysis was tentatively stopped after prescribed time and a part of an electrolyte solution (2 mL) was transferred to a 1 cm quartz cell. The spectrum of the solution was measured with a Shimadzu U-4100 spectrophotometer.

3. Results and Discussion

Figure 1 shows a change of absorption spectra of the Tc solution by electrolysis at the potential of -0.3 V vs. SSE. The solution showed a reddish brown color. Three peaks at 368,

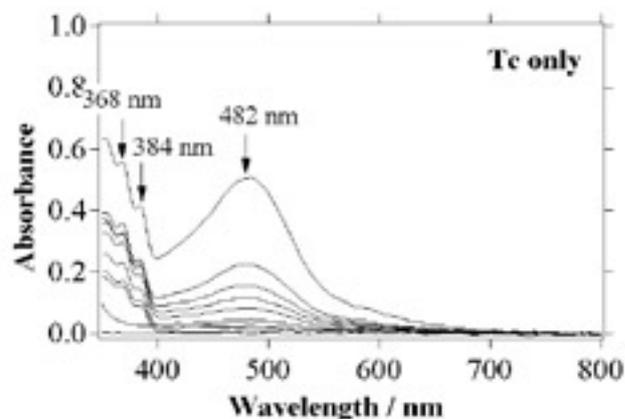


Figure 1. Absorption spectra of Tc solution of electrolysis. Electrolyte: 1.5 mM of initial Tc in 3 M HNO₃ aqueous solution. Electrolysis conditions: Potential of -0.3 V vs. SSE, current density of approximately 2 mA cm⁻². Line: a baseline, the spectrum of initial solution, the spectra of the solution electrolyzed for 10, 20, 30, 40, 50, 60, 90, and 210 min.

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384, and 482 nm are observed in the spectra. The spectra of the solution electrolyzed at -1.0 V vs. SSE were almost the same as Figure 1. The two peaks at 368 and 384 nm are specific to HNO_2 and imply evolution of HNO_2 during the electrolysis. From colorimetric measurements, the concentration of HNO_2 was determined to be 6 mM after 60 min of electrolysis. An additional absorption peak at 482 nm in the spectra is not attributed to HNO_2 . Boukis et al. reported the chemical reduction of Tc(VII) to Tc(IV) by hydrazine in a nitric acid solution and the formation of Tc(IV) complex with DBP.³ They found a weak shoulder of Tc(IV) at 470 nm. They also found a strong absorption peak of a Tc(IV) complex with DBP⁻ at 472 nm in pentane. Spitsyn et al. found an absorption peak at 500 nm after electrolytic reduction of KTcO_4 in H_2SO_4 solution and attributed the peak to the formation of a complex composed of Tc(IV) and SO_4^{2-} .⁴ The absorption peak at 482 nm observed in the present work suggests that Tc(VII) was reduced to Tc(VI). It is reasonable to consider that the significant absorption peak (483 nm) implies the formation of a Tc(IV) complex.

Figure 2 shows a change of absorption spectra of the Tc solution containing hydrazine, a well known HNO_2 scavenger, by electrolysis at -0.3 V vs. SSE. After electrolysis the solution became yellowish. In the spectra, only a peak at 430 nm was observed. There are no peaks at 368 and 384 nm arising from HNO_2 . The spectra of the solution electrolyzed at -1.0 V vs. SSE were almost the same as Figure 2. The wavelength of 430 nm for the absorption peak observed here is fairly shorter than that of Tc(IV).³ In literatures,^{5,6} an absorption band at 400–430 nm is reported for a yellowish complex of Tc with isothiocyanate. From the results of elemental and electrochemical analyses, the valence state of Tc in the complex is established to be Tc(III).⁵ The absorption peak (430 nm) observed here may suggest the formation of a Tc(III) complex by electrolytic reduction.

In Figure 3, a concentration change of Tc during electrolysis in 3 M HNO_3 aqueous solution without hydrazine is shown. At -0.3 V vs. SSE, the Tc concentration decreased to 95% of the initial value after 30 min of electrolysis. After 60 min, however, the concentration increased nearly to the initial value, and the concentration hardly changed until 120 min. At more noble potential of -1.0 V vs. SSE, the concentration hardly changed as shown in Figure 3. Maslenikov et al. reported that the Tc concentration decreased to 91% of the initial value after 2 h of electrolysis at -0.5 V vs. SCE (standard calomel electrode, the potential value against SCE being roughly the same to the value against SSE) with a graphite electrode in 4 M HNO_3 .⁷ This value is compatible to the present experiment at -0.3 V vs. SSE after 30 min. They also reported that the concentration decreased to 66% at -1.0 V vs. SCE. This result does not agree

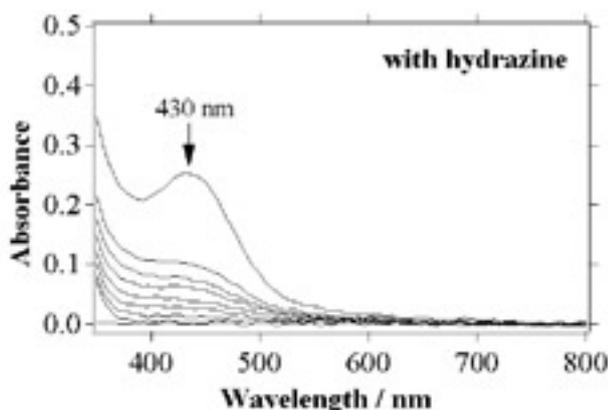


Figure 2. Time dependence of concentrations of Tc in electrolyte solution of constant potential electrolysis determined by ICP-AES. Electrolyte: 5 mM of initial Tc in 3 M HNO_3 aqueous solution. Electrolysis conditions: current density approximately 2 mA cm^{-2} for -0.3 V vs. SSE and 6 mA cm^{-2} for -1.0 V vs. SSE. Line: a baseline, the spectrum of initial solution, the spectra of the solution electrolyzed for 10, 20, 30, 40, 50, 60, 90, and 120 min.

with the present result for -1.0 V vs. SSE. One possible explanation for this discrepancy is a difference in the current density, which was not high in the present experiment as compared with their experiment. As shown in Figure 4, the Tc concentration decrease was not significant at -0.3 V vs. SSE with co-existing hydrazine. At -1.0 V vs. SSE, the concentration decreased during 90 min of electrolysis. Although the concentration was 90% at 90 min, the concentration increased again after 120 min. Remarkable deposit formation on the electrode was not observed in every case where the concentration decreased.

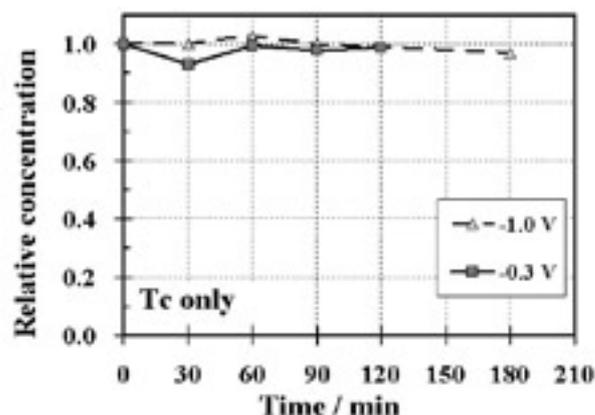


Figure 3. Absorption spectra of Tc solution of electrolysis. Electrolyte: 1.5 mM of initial Tc and 0.1 M of hydrazine in 3 M HNO_3 aqueous solution. Electrolysis conditions: Potential of -0.3 V vs. SSE, current density about 28 mA cm^{-2} .

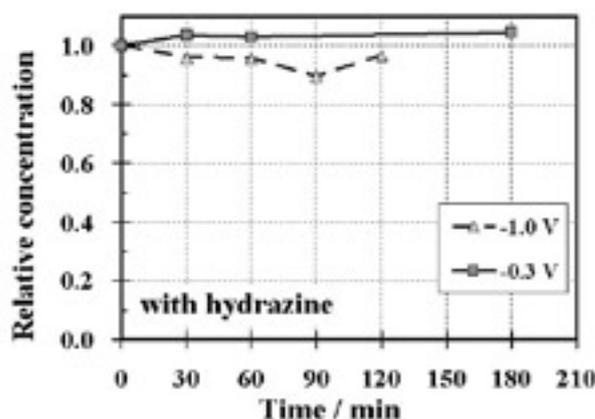


Figure 4. Time dependence of concentrations of Tc in electrolyte solution of constant potential electrolysis determined by ICP-AES. Electrolyte: 5 mM of initial Tc and 0.1 M of hydrazine in 3 M HNO_3 aqueous solution. Electrolysis conditions: current density approximately 14 mA cm^{-2} for -0.3 V vs. SSE and 28 mA cm^{-2} for -1.0 V vs. SSE.

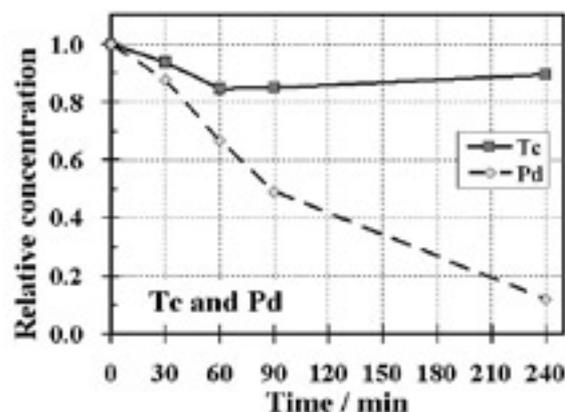


Figure 5. Time dependence of concentrations of Tc and Pd in electrolyte solution of constant potential electrolysis determined by ICP-AES. Electrolyte: 1.8 mM of initial Tc and 6.1 mM of initial Pd in 1 M HNO_3 aqueous solution. Electrolysis conditions: potential of ± 0.0 V vs. SSE, current density about 0.3 mA cm^{-2} .

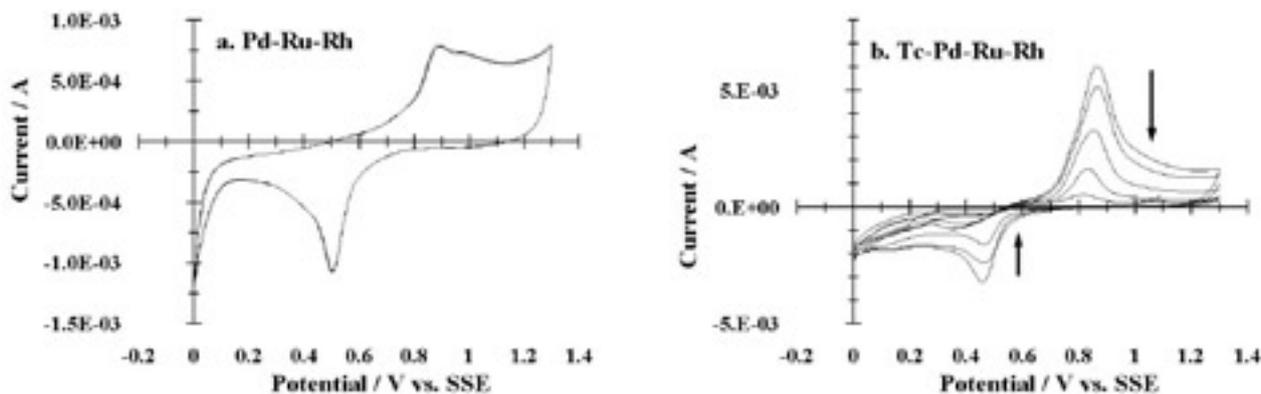


Figure 6. Cyclic voltammograms of the deposits under multiple potential scans up to the tenth cycle. Anodic current positive. Initial potential: 1.1 V vs. SSE. Initial scan direction: cathodic. Scan rate: 0.1 V s^{-1} . Potential range: ± 0 to 1.3 V vs. SSE. a) Deposit from Tc-Pd-Ru-Rh solution. Electrolyte: 4.7 mM of Pd, 5.4 mM of RuNO_3^+ and 5.6 mM of Rh^{3+} in 3 M HNO_3 aqueous solution. Quantity of electricity for deposition: 26.6 mC. The first and the tenth cycles. b) Deposit from Tc-Pd-Ru-Rh solution. Electrolyte: 5.4 mM of Tc, 7.4 mM of Pd, 5.4 mM of RuNO_3^+ and 4.7 mM of Rh^{3+} in 3 M HNO_3 aqueous solution. Quantity of electricity for deposition: 378 mC. The first, the second, the fourth, the sixth and the tenth cycles.

From previous results for Re,¹ it is expected that the co-existence of Pd^{2+} , depositing easily as Pd black, will accelerate the Tc deposition (promoter effect). Figure 5 shows concentration changes of Tc and Pd during the electrolysis in 1 M HNO_3 aqueous solution containing both Tc and Pd at the potential of $\pm 0.0 \text{ V}$ vs. SSE. In this case, the formation of a black deposit was observed and the Pd concentration decreased to 10% of the initial value after 240 min of electrolysis. It is supposed that the recovery of Pd by EE method is not interfered by co-existing Tc. The Tc concentration also decreased to 85% of the initial value after 60 min. The decrease is larger than that observed in the case of Tc only shown in Figures 3 and 4. The result suggests the promoter effect of Pd on Tc deposition. The Tc concentration, however, increased again in further electrolysis longer than 60 min. It might be supposed that once deposited Tc redissolved.

To examine oxidation-reduction property of the deposit, cyclic voltammetry (CV) measurements was performed using 3 M HNO_3 solution containing HTcO_4 , Pd^{2+} , RuNO_3^+ and Rh^{3+} as an electrolyte solution. As a reference, an electrolyte solution without HTcO_4 was also used. Before CV measurements, a black deposit of Pd-black was formed on the Pt wire (0.6 mm in diameter) working electrode by polarizing it at +0.1 V vs. SSE for 5 min. The quantities of electricity for the deposition were 378 mC for Tc-Pd-Ru-Rh solution and 26.6 mC for Pd-Ru-Rh solution. After the deposition, the cyclic voltammetry measurement with ten continuous sweep cycles was performed in the same electrolyte solution using this Pt electrode with deposit. Figure 6a shows the CV curves observed for the deposit from Pd-Ru-Rh solution. The curves hardly changed as the sweep cycle proceeded. The cathodic peak current at +0.5 V vs. SSE was 1.08 mA and the anodic peak current at +0.89 V vs. SSE was 0.798 mA for the first cycle. As shown in Figure 6a, the curve drastically changed in the case of Tc-Pd-Ru-Rh. The observed current peaks decreased as the potential sweep cycle proceeded. The cathodic peak current at +0.46 V vs. SSE was 2.40 mA for the first cycle, and this peak almost disappeared in the tenth cycle. The anodic peak current at +0.87 V vs. SSE was 6.05 mA for the first cycle, and the current decreased to 0.511 mA with a slight shift of the peak potential to +0.81 V vs. SSE for the tenth cycle. After the tenth cycle of the measurement, the deposit disappeared from the electrode. The deposit may redissolve in the solution by oxidation occurring at the potential +1.3 V vs. SSE or lower. To remove the deposit from the electrode in the Pd-Ru-Rh case, a potential of +1.6 V vs. SSE or higher had to be applied. The Pd deposit from the Tc containing solution redissolved more easily than that from the solution containing no Tc.

4. Conclusion

The electrolytic reduction of Tc in nitric acid solution was performed to examine the possibility of Tc co-recovery by the EE method. A significant absorption peak at 482 nm observed as a consequence of the electrolytic reduction of Tc(VII) at -0.3 and -1.0 V vs. SSE suggests the reduction of Tc(VII) to Tc(IV) and a possibility of the formation of Tc(IV) complexes. On deposition of Tc by electrolysis, remarkable deposit formation on an electrode could not be observed in the cases of Tc only, despite the Tc concentration decrease to 93% (Tc only, in 3 M HNO_3 , at -0.3 V vs. SSE) and 90% (with hydrazine, in 3 M HNO_3 , at -1.0 V vs. SSE) of the initial concentration. In the case of Tc and Pd electrolyzed at $\pm 0.0 \text{ V}$ vs. SSE in 1 M HNO_3 , a black deposit of Pd was observed and the Tc concentration also decreased to 85% of the initial one. The co-existence of Pd and Tc in the solution might accelerate the deposition of Tc (promoter-effect). Quantitative deposition of Tc was not achieved, and further studies are needed to recover Tc by electrolysis. It was also found from cyclic voltammetry measurements that Tc affected the oxidation-reduction property of the Pd deposit in the course of its redissolution.

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References

- (1) M. Ozawa, Y. Sano, Ch. Ohara, and T. Kishi, Nucl. Technol. **130**, 196 (2000).
- (2) K. Koizumi, M. Ozawa, and T. Kawata, J. Nucl. Sci. Technol. **30**, 1195 (1993).
- (3) N. Boukis, The Chemistry of Technetium, Report KfK 4362 (1988).
- (4) V. I. Spitsyn, A. F. Kuzina, A. A. Oblova, M. I. Glinkina, and L. I. Stepovaya, J. Radioanal. Chem. **30**, 561 (1976).
- (5) C. E. Crouthamel, Anal. Chem. **29**, 1756 (1957); J. Garaway and P. D. Wilson, J. Less-Common Metals **97**, 191 (1984).
- (6) H. S. Trop, A. Davidson, A. G. Jones, M. A. Davis, D. J. Szalda, and S. J. Lippard, Inorg. Chem. **19**, 1105 (1980).
- (7) A. G. Maslenikov, O. Courson, V. F. Peretroukhine, F. David, and M. Masson, Radiochim. Acta **78**, 123 (1997).

