BASIC STUDY OF PHOTOCHEMISTRY FOR APPLICATION TO NUCLEAR FUEL CYCLE TECHNOLOGY

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Abstract

In this study, we have accomplished for the first time the photochemical valence adjustment of Pu and Np for the separation and coextraction of these elements in a nitric acid solution using UV light irradiation. Also, the separation and coextraction of Pu and Np were substantiated in principle by the photochemical and solvent extraction operations. The separation and coextraction of Pu and Np by solvent extraction using 30% TBP/n-dodecane were carried out during and after the photochemical valence adjustment. By only one photochemical separation operation, about 86% of Pu and about 99% of Np were distributed into the organic phase and the aqueous phase, respectively, and then by only one photochemical coextraction operation, about 86% of Pu was distributed together with about 99% of Np into the same organic phase. Based on these experimental data, we determined that the photochemical oxidation reaction was due to the photoexcited nitric acid species, $*NO_3^-$. Using the strong oxidative ability of this species, the photochemical dissolution of UO_2 powder in a nitric acid solution by UV light irradiation was also accomplished for the first time at room temperature(20 ℃). Photochemical dissolution tests of UO_2 powder ranging 1 mg to 100mg suspended in 2 ml of 1-6M HNO_3 solutions were carried out at room temperature using a Hg lamp. From the results of the tests, 10mg of UO_2 powder was completely dissolved in 2ml of a 3M HNO_3 solution at 20℃ under an irradiation rate of 1.3W/cm^2 for 40min.

1. Introduction

Most nuclear fuel reprocessing plants have been adopting the PUREX process technologies. Uranium(U) and plutonium(Pu) in spent nuclear fuel are recovered and refined using these technologies with a high recovery efficiency.

Neptunium(Np), however, is distributed on both sides of the nuclear fuel production and also in highly radioactive aqueous waste. This phenomenon is caused because of the difficulty in valence adjustment of Np using various chemical reagents in nitric acid solution[(1)-(3)].

It is generally supposed that photochemical techniques offer a potential for selectivity in systems where chemical methods offer little selectivity. From that point of view, photochemical studies of U, Pu and neptunium(Np) have been carried out for separation and reprocessing techniques mainly in the USA. These studies can be divided into several categories which are the studies for the photochemical behavior of nuclear fuel[(4)-(8)], Np[(9)-(12)] and photochemical reprocessing technologies[(13)-(15)]. These studies, however, only describe the fundamental photochemical behavior of these elements' valences and did not carry out quantitative valence adjustment for the separation and coextraction of Np with experimental data. They did not then discuss the mechanism of the photochemical redox reaction such as our suggestion involving a photoexcited nitric acid species[(16)]. we report the results of the quantitative photochemical separation and coextraction experiments of Pu and Np and then we have considered that the photoexcited nitric acid species, $*NO_3^-$, contributed most effectively to the oxidation reactions of Pu and Np. These reactions are caused by a higher redox electrode potential of the photoexcited species than that of the ground state species, NO_3^- [(17)-(19)]. Based on the results, we have also attempted to use the strong oxidative ability of $*NO_3^-$ for the dissolution reaction of UO_2 powder at room temperature[(20)].

2. Experimental

2.1 Apparatus and analysis

As the light source, a super high-pressure Hg lamp (WACOM Co., Ltd. BMO-250DI) was used in the wavelength range of 250 nm to 600 nm. The maximum output intensity was 1.5 W/cm^2. The homogeneity and temperature of the test solution were kept constant using an electric temperature stabilizer and a magnetic stirrer during the tests.

The valences of Pu and Np in nitric acid solutions were analyzed using a spectrophotometer (Shimazu UV-1200).

2.2 Preparation of test solution and UO_2

The Pu stock solution was previously refined using an anion exchange column americium(Am) was removed from the solution. The concentration of Pu in the solution was calculated using its specific α-radioactivity obtained by mass spectrometric analysis and the data obtained by the α-ray counting method. The analyzed isotopic composition is shown in Table 1.

The α-radioactive purity of Np-237 in the Np stock solution was 100.0% and the concentration of Np in the solution was also determined by the α-counting method.

The test solutions of Pu and Np mixed solution containing additional reagents such as hydroxylamine nitrate(HAN) and hydrazine(HDZ) or urea, which were all reagent grade, were prepared by mixing their stock solution and additional reagents for about 10 mins. before the start of the irradiation test.

The specific properties of the UO_2 powder used for the tests are shown in Table 2.

Table 1 Isotopic composition of Pu used in test

Nuclide	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242
Abundance (Wt%)*	0.148	75.79	21.51	1.855	0.697

* : Analyzed on Feb. 10, 1993

Table 2 Specific properties of UO_2 Powder used in tests

U content (%)	O / U	Ave. par. size(μ m)	Density (g/cm^3)	Spec. surf. area(m^2/g)
87.73	2.06	0.68	1.96	4.28*

* : BET method

2.3 Experimental procedure

The photochemical valence adjustment and solvent extraction test experiments were carried out as follows.

(1) Photochemical valence adjustment

For Pu and Np in a nitric acid solution, the extractable valences are Pu(IV and VI) and Np(IV and VI), while the inextractable valences are Pu(III) and Np(V) with 30 % TBP/n-dodecane [21]. It is the purpose of this study to determine whether the photochemical technique can adjust the valences of Pu and Np to suitable valences for their separation or coextraction.

For the separation experiments, the initial valences in the test solutions of Pu and Np were previously adjusted to Pu(III) and Np(V) using HAN and HDZ before the light irradiation. It was then evaluated whether Pu(III) could be photooxidized to Pu(IV) and Pu(VI)(extractable valences) by the irradiation, and Np(V)(inextractable valence) remained at the same valence during the light irradiation. On the other hand, during the coextraction experiments, the initial valences in the test solutions containing urea were Pu(IV,VI) and Np(V). It was then evaluated whether the light irradiation could completely adjust them to Pu(IV,VI) and Np(VI)(all of these valences being extractable). Furthermore, their valence behavior was also examined under no light irradiation(dark reaction) for the comparison to that under the light irradiation.

Two ml of the test solution was placed in a 1cm square quartz cell generally used for photospectrometry. The cell was then irradiated using the Hg lamp for an appropriate time. The changes in the Pu and Np valences were measured by the photospectrometer at specified intervals using the quartz cell containing the test solution. In these tests, the experimental variables included the irradiation rate (0, 0.05, 0.15 and 1.45 W/cm^2) and the concentration of HNO_3 (0.4, 1, 2 and 3 M).

(2) Solvent extraction

First, for the separation of Np from the Pu and Np mixed solution, 1 ml of the 2M HNO_3 solution containing Pu ($1.0x10^{-3}$ M), Np ($1.0x10^{-3}$ M) and HAN+HDZ ($8.0x10^{-2}$ M each), and 1 ml of 30 % TBP/n-dodecane were placed in the quartz cell. The cell was set into the cell holder which contained the temperature stabilizer and stirrer, and the light irradiation and the solvent extraction were then started simultaneously.

In the case of the coextraction operation, 1 ml of the 3 M HNO_3 solution containing Pu ($1.0x10^{-3}$ M), Np ($1x10^{-3}$ M) and urea ($8.0x10^{-2}$ M), and 1 ml of 30 % TBP/n-dodecane were used. In one case, the light irradiation and the solvent extraction were simultaneously carried out. In the other case, the solvent extraction operation was done after the photochemical valence adjustment.

After specified intervals of the solvent extraction operation, aliquots of both phases were taken out of the other cell and analyzed using the spectrophotometer.

(3) Photochemical dissolution

1-100mg of UO_2 powder are weighed precisely and are placed in a quartz cell, normally used in photospectrometry, containing 2ml of a nitric acid solution. The solution is then irradiated using the Hg lamp, and the absorption spectrum of the solution is measured at the appropriate irradiation time.

The photochemical dissolution fraction of the UO_2 powder is calculated by the ratio between the absorbances Ai and At of UO_2^{2+} at 425nm and an arbitrary time i and t, which is the complete dissolution time at t, as follows.

$$\text{Dissolution fraction(\%)} = \frac{Ai}{At} \times 100 \qquad (1)$$

Ai : Absorbance at time i.
At : Absorbance at time t of the complete dissolution time.

The concentration of nitrous acid, HNO_2, a by-product of the UO_2 dissolution reaction, is also determined by the absorbance of the test solution at 370nm and a calibration curve which is obtained by analysis of standard concentrations of HNO_2 from $1.0X10^{-3}$ to $5.0X10^{-2}$ M.

The temperature and the homogeneity of the solution are kept constant with a temperature stabilizer and a magnetic stirrer during an irradiation test.

The experimental variables are the irradiation rate whose levels are 0, 0.7 and $1.3W/cm^{-2}$, the concentration of HNO_3 whose levels are 1, 3 and 6M and the weight of the UO_2 powder whose levels are 1, 10 and 100mg.

3.Results and discussion

3.1 Photochemical valence adjustment

For the photoreaction tests, three kinds of experimental conditions for the Pu and Np mixed solution were adopted

① the examination of the photochemical behavior of Pu and Np valences in the nitric acid solution without the addition reagent,
② the valence adjustment for the separation of Np from Pu, and
③ the valence adjustment for the coextraction of Np with Pu.

(1) Photochemical reaction of Pu and Np without addition reagent

Figure 1 shows the results of the photochemical reaction of Pu and Np in 3 M HNO_3 solution containing no addition reagent under the conditions of 1.40 W/cm^2 irradiation rate and 20 ℃.

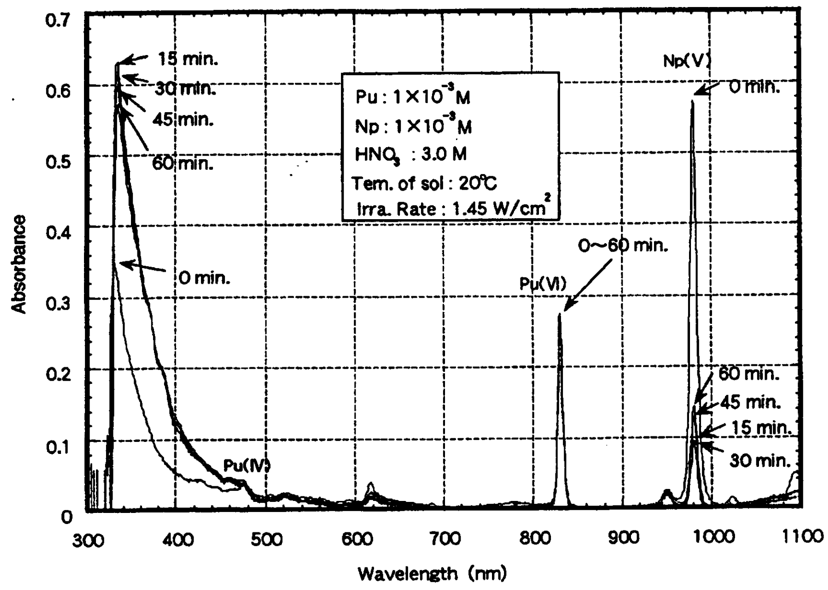


Fig.1 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO_3 solution containing no additional reagent vs. irradiation time

As seen in this figure, around 85 % of Np(V) decreased and was photooxidized to Np(VI) within 15 mins. After that, the reverse reaction of Np(VI)→Np(V) progressed predominantly, and then Np(V) gradually increased. This phenomenon is caused by the relationship between the oxidation reaction of the photoexcited nitric acid species(16), $^*NO_3^-$, and the redox reaction by nitrous acid(22), (23) of the photolysis product as follows.

- The oxidation reaction of Np(V)→Np(VI) by $^*NO_3^-$

$$^*NO_3^- + 3H^+ + 2e \rightarrow HNO_2 + H_2O,$$
$$NpO_2^{2+} + e \leftarrow NpO_2^+,$$
$$\downarrow$$
$$^*k_{5\rightarrow6}$$
$$^*NO_3^- + 2NpO_2^+ + 3H^+ \longrightarrow 2NpO_2^{2+} + HNO_2 + H_2O \text{ ---- (2)}$$

where $^*k_{5\rightarrow6}$: photochemical reaction rate constant.

- The reduction reaction of Np(VI)→Np(V) by HNO_2

$$NpO_2^{2+} + e \rightarrow NpO_2^+,$$
$$NO_3^- + 3H^+ + 2e \leftarrow HNO_2 + H_2O,$$
$$\downarrow$$
$$k_{6\rightarrow5}$$
$$2NpO_2^{2+} + HNO_2 + H_2O \longrightarrow 2NpO_2^+ + NO_3^- + 3H^+ \text{ ---------- (3)}$$

where $k_{6\rightarrow5}$: reaction rate constant.

Pu(IV) is also photooxidized to Pu(VI) by the photoexcited nitric acid species and a part of the Pu(VI) is reduced to Pu(IV) by nitrous acid(22).

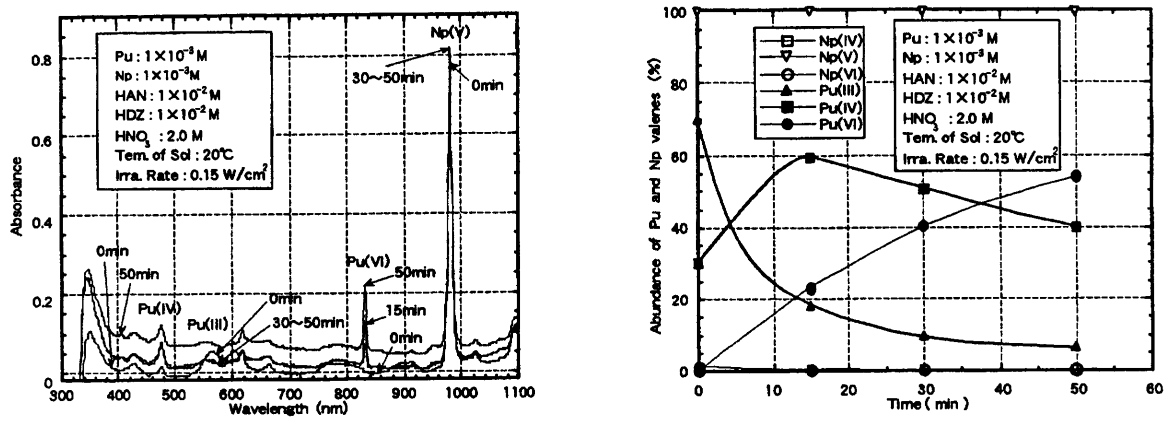
As seen in Figure 1, if the decomposition reagents such as HDZ(24) or urea(25) were not contained in the Pu and Np mixed solution, the complete valence adjustment for their separation or coextraction would not be attained using the Hg lamp irradiation.

(2) Photochemical valence adjustment for separation

1. Effect of concentration of HNO_3

Mixed solutions of 1×10^{-3} M Pu and Np containing reductants, 1×10^{-2} M of HAN and HDZ, were prepared by changing the HNO_3 concentration to 0.4 M, 1 M, 2 M and 3 M. These solutions were then examined at the irradiation rate of 0.15 W/cm^2. Figures 2 and 3 show the results of the irradiation tests at concentrations of 2 M and 3 M HNO_3, respectively. All of the results under the condition of each acidity are shown in Table 3. These data are calculated as the average reaction rate as follows.

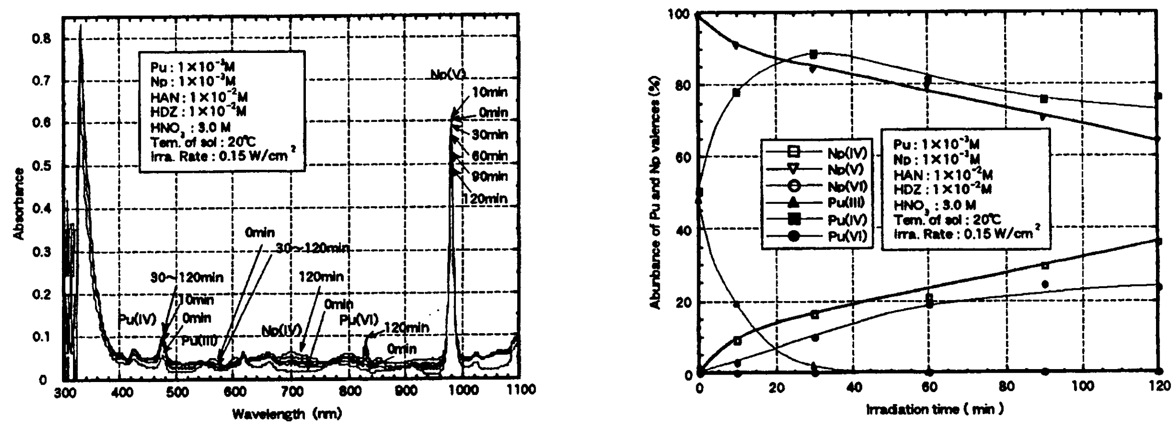
$$\text{Average photochemical reaction rate(M/min)} = \frac{\text{Variation value(mol)}}{\text{Reaction time(min)}} \text{ ------------(4)}$$



(a)Change in absorption spectra

(b) Change in abundance of valences

Fig.2 Change in Pu and Np valences by photochemical reaction in 2M HNO_3 containing HAN and HDZ vs. irradiation time



(a) Change in absorption speactra

(b) Change in abundance of valences

Fig.3 Change in Pu and Np valences by photochemical reaction in 3M HNO_3 solution containing HAN and HDZ vs. irrsdiation time

Table 3 Change in photochemical reaction rate according to increase in acidity

Acidity(HNO_3)	Average photochemical reaction rate (mol / min)*			
(M)	Pu(III)→Pu(IV)	Pu(IV)→Pu(VI)	Np(V)→Np(IV)	Np(V)→Np(VI)
0.4	1.07×10^{-6}	6.76×10^{-7}	-	-
1	5.78×10^{-6}	6.10×10^{-6}	-	-
2	1.27×10^{-5}	1.07×10^{-6}	-	-
3	1.29×10^{-5}	1.87×10^{-6}	2.06×10^{-6}	-

* : Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time.
[Pu] and [Np] = 1×10^{-3} mol/dm³, [HAN] and [HDZ] = 1×10^{-2} M, Irra. rate = 0.15 W/cm².
- : Can not be observed.

As shown in this table, the higher the acidity, the faster the photochemical reaction rate except only for the data of Pu(IV)→Pu(VI) at 3 M HNO_3.

In the case of Np, all of the results at lower than 2 M HNO_3 did not change at all in both cases of the oxidation and reduction reaction of Np(V). This is because an exception occurred due to the strong reducing ability of HAN and HDZ only at the highest acidity of 3 M HNO_3 even though the test solution was irradiated at the rate of 0.15 W/cm^2. On the other hand, Np(V) was continuously reduced to Np(IV) even after Pu(III) had completely disappeared after 40 mins. irradiation as shown Fig. 3-(b). This phenomenon indicates that Np(V) was not reduced by Pu(III) only, which is different from the results reported by Koltunov et al. [26]. After about 40 mins. irradiation, the reductants are only HAN and HDZ. Therefore, it can be considered that these reductants reduced Np(V) to Np(IV). However, we do not understand why Np(V) was not reduced to Np(IV) under the same condition of only Np(V) 3 M nitric acid solution as previously mentioned. This reason has to be clarified by future experiments.

2. Effect of light irradiation rate

The results of the irradiation tests using the Pu and Np mixed 3 M HNO_3 solution containing 1×10^{-2} M of HAN and HDZ and changing the irradiation rates to 0.05, 0.15, and 1.45 W/cm^2 are shown in Table 4. These results are shown as the values of the average photochemical reaction rate. As seen in this table, the increase in the irradiation rate hastened the reaction rate of the photochemical oxidation of Pu and Np.

The reducing reaction of Np(V)→Np(IV) and the oxidation reaction of Np(V)→Np(VI) are shown in Eqs.(5), (6) and (7), respectively.

Table 4 Change in photochemical reaction rate according to increase in irradiation rate

Irradiation rate	Average photochemical reaction rate (mol / min)*			
(W/cm^2)	Pu(III)→Pu(VI)	Pu(IV)→Pu(VI)	Np(V)→Np(IV)	Np(V)→Np(VI)
0.05	7.33×10^{-6}	9.99×10^{-7}	9.13×10^{-7}	-
0.15	1.29×10^{-5}	1.87×10^{-6}	2.06×10^{-6}	-
1.45	5.52×10^{-5}	7.55×10^{-6}	-	3.80×10^{-6}

* : Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time.
[Pu] and [Np] = 1×10^{-3} mol/dm³, [HAN] and [HDZ] = 1×10^{-2} M, Irra. rate = 0.15 W/cm².
- : Can not be observed.

• Reducing reaction of Np(V) by reductants

$$4NpO_2^+ + 10H^+ + 2NH_3OH^+ \longrightarrow 4Np^{4+} + H_2N_2O_2 + 8H_2O \text{ ------ } (5)$$

$$4NpO_2^+ + 11H^+ + N_2H_5^+ \longrightarrow 4Np^{4+} + N_2 + 8H_2O \text{ ------ } (6)$$

• Oxidation reaction of Np(V) by the photoexcited nitric acid species, $*NO_3^-$.

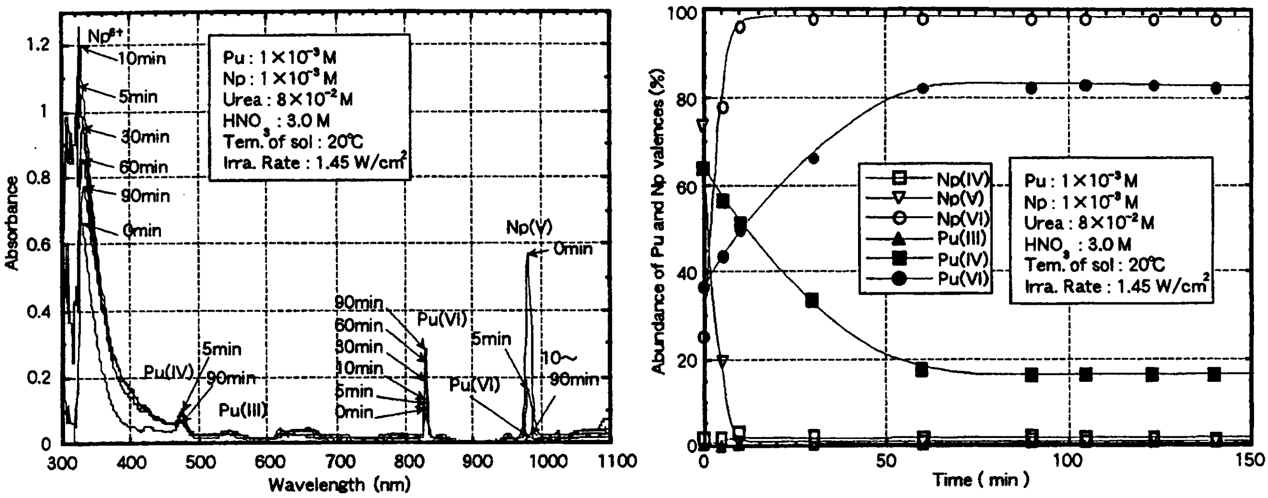
$$*NO_3^- + 2Np^{4+} + 3H_2O \longrightarrow 2NpO_2^+ + HNO_2 + 5H^+ \text{ ------ } (7)$$

From the comparison among each variable level in Table 4, it was found that the photooxidation rates of Pu(III)→Pu(IV) and Pu(IV)→Pu(VI) became faster, and then the reducing reaction of Np(V) → Np(IV) based on Eqs. (5) and (6) became inferior compared to the photooxidation reaction of Np(V)→ Np(VI) based on Eq. (7) according to the increase in the irradiation rate.

As shown in these results, the most suitable irradiation rate condition was 0.15 W/cm^2 for the separation of Np from Pu in the 2 M HNO_3 solution, which contains $1x10^{-3}$ M Pu and Np and also contains $1x10^{-2}$ M HAN and HDZ.

(3) Photochemical valence adjustment for coextraction

The experiments on the photochemical valence adjustment for the coextraction of Pu and Np were carried out using the Pu, Np mixed solution containing the additional reagent of $8x10^{-2}$ M urea and $1x10^{-3}$ M of Pu and Np in 3 M HNO_3. The irradiation rate was 1.45 W/cm^2. The results are shown in Figs. 4-(a) and (b). As seen in Fig. 4-(a), the absorption spectrum of Np(V) at 980 nm disappeared up to10 mins. irradiation, and only the minor absorption spectrum of Pu(VI) at 980 nm remained. Np(V) was completely photochemically oxidized to Np(VI). Pu(IV) was also photochemically oxidized to Pu(VI) and decreased according to the irradiation time. These results indicate that all valences of Pu and Np were photochemically adjusted to the coextractable valences for 30 % TBP/n-dodecane under the experimental conditions shown in this study.



(a) Change in absorption spectra

(b) Change in abundance of valences

Fig.4 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO_3 solution containing urea vs. irradiation time

(4) Dark reaction after valence adjustment

In general, there is at least an interval of several hours between the valence adjustment and the solvent extraction operation during an actual process. If the adjusted valences change during this interval, the efficiency of the separation or coextraction becomes low. Therefore, it is important to determine the stabilities of the adjusted valences in a nitric acid solution.

Figure 5 shows the results of the dark reaction, the stabilities of the adjusted valences after stopping the light irradiation of the Pu and Np mixed solution containing HAN and HDZ in 3 M HNO_3. As seen in this figure, Pu(VI) was rapidly reduced to Pu(IV), and then part of the Pu(IV) was further reduced to Pu(III) after stopping the light irradiation. Np(V) was also rapidly reduced to Np(IV). As shown by these results, the adjusted valences of Pu and Np in the 3 M HNO_3 solution containing HAN and HDZ were not stable. Therefore, in the case of the separation, the solvent extraction has to be immediately carried out after the operation of the photochemical valence adjustment or be simultaneously carried out during the light irradiation.

Figure 6 shows the results of the dark reaction after stopping the light irradiation of the Pu and Np mixed solution containing urea in the 3 M HNO_3. As seen in this figure, all of the photochemically adjusted valences were entirely stable after stopping the light irradiation for more than 4 hours. Based on these results, there is no problem for the solvent extraction operation even several hours after the valence adjustment in the case of coextraction.

3.2 Solvent extraction for separation and coextraction of Np from/with Pu

During or after the light irradiation, the solvent extraction operation was examined using 30 % TBP/n-dodecane to confirm whether Pu and Np can be separated or coextracted.

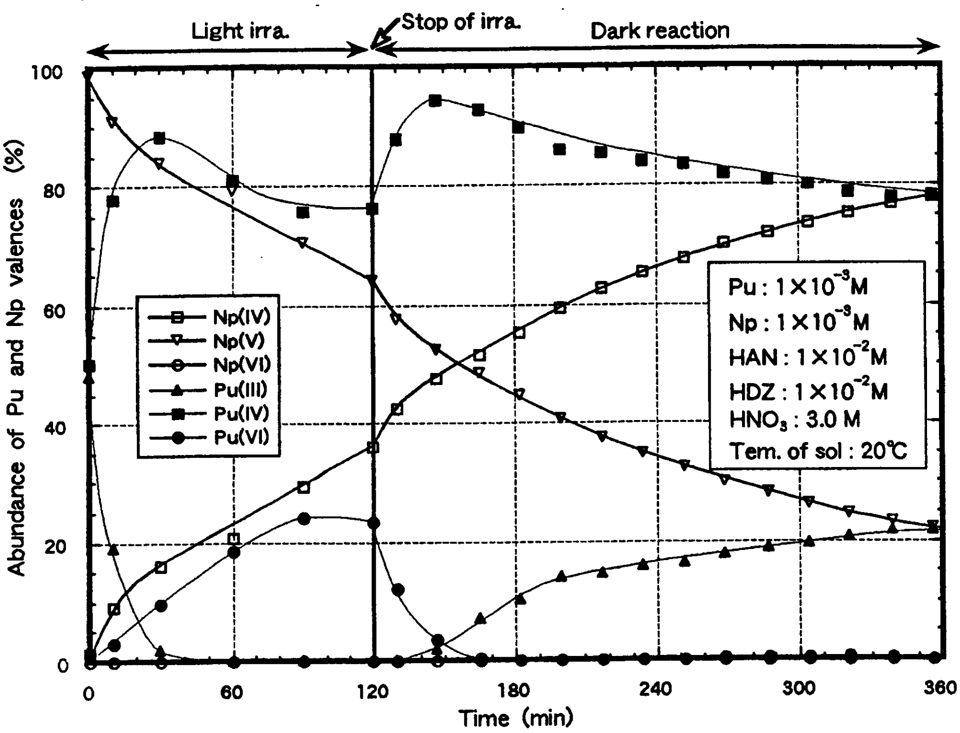


Fig.5 Stability of valences of Pu and Np in 3M HNO_3 solution containing HAN and HDZ after stopping light irradiation

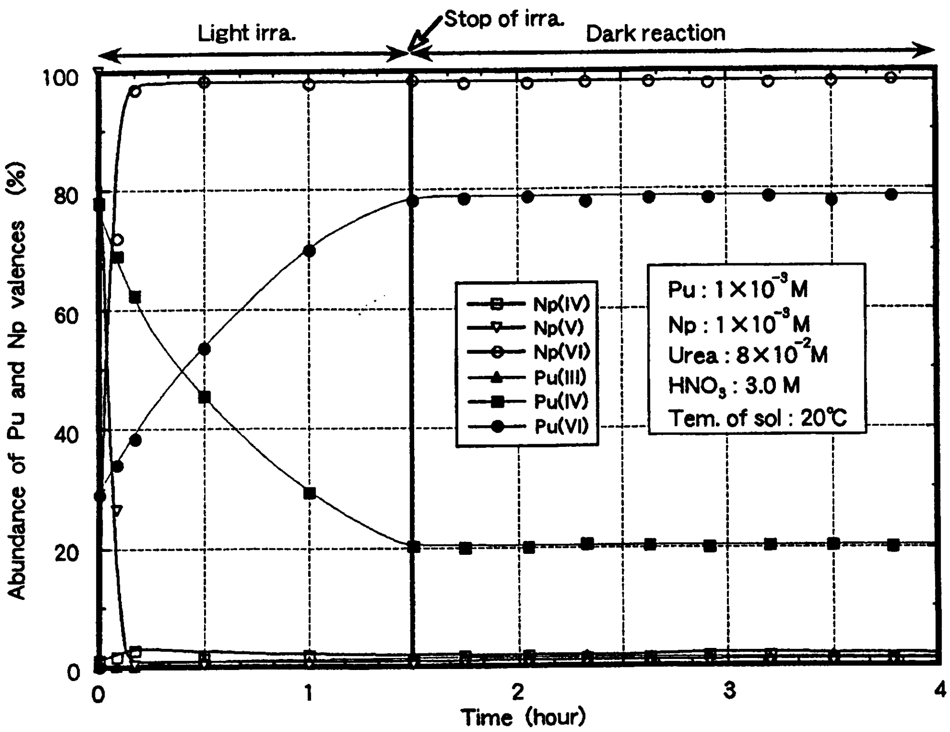


Fig.6 Stability of valences of Pu and Np in 3M HNO_3 solution containing urea after stopping light irradiation

(1) Separation

The results of the separation by the simultaneous operations of irradiation and solvent extraction are shown in Table 5. As seen in this Table, Pu(III) in the aqueous phase completely disappeared after 15 mins. operation. Pu(III) was photochemically oxidized to Pu(IV) and Pu(VI) like the results when only the operation of the valence adjustment was carried out, and Pu having these valences was then simultaneously extracted into the organic phase. In the case of Np, most of the initial Np(V) in the aqueous phase did not change and remained in the aqueous phase depending upon its specific distribution coefficient in the solvent. About 98 % of the initial Pu(III) was photooxidized to Pu(IV) or Pu(VI) and 86.2 % of Pu was extracted into the organic phase during 30 mins. During the irradiation and extraction, Pu(IV) in the organic phase gradually decreased, and Pu(VI) inversely increased. This oxidation reaction of Pu(IV) to Pu(VI) in the organic phase may be due to the photoexcited nitric acid species in the aqueous phase being in contact with both phases. The clear reason for this phenomenon must be defined by detailed data obtained in the future.

Consequently, 87.1% of Pu was extracted into the organic phase and 99.8% of Np remained in the aqueous phase only using one operation of the simultaneous irradiation and extraction.

Table 5 Results of simultaneous operation of irradiation and solvent extraction for separation of Np from Pu

(a) Abundances of Pu valences in both phases vs. operation time

	Valence	Abundance (%) Just before operation	Time of simultaneous ope. of irra. and ext. 15min	30min	50min
Aq.	Pu(III)	70.4	3.4	1.5	0.4
	Pu(IV)	29.6	8.1	4.7	3.0
	Pu(VI)	<0.1	4.7	7.7	9.6
Org.	Pu(III)		<0.1	<0.1	<0.1
	Pu(IV)	–	71.5	45.8	26.9
	Pu(VI)		12.2	40.4	60.2
Gross Pu in Org.		<0.1	83.7	86.2	87.1
in Aq.		100.0	16.3	13.9	13.0
Org. / Aq.		–	5.13	6.10	6.70

Pu : 1.0×10^{-3} M
Np : 1.0×10^{-3} M
HAN : 1.0×10^{-2} M
HDZ : 1.0×10^{-2} M

HNO_3 : 2.0M
Temp. : 20℃
Irra. rate : 0.15 W/cm^2

(b) Abundances of Np valences in both phases vs. operation time

	Valence	Abundance (%) Just before operation	Time of simultaneous ope. of irra. and ext. 15min	30min	50min
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1
	Np(V)	100.0	99.1	98.5	99.8
	Np(VI)	<0.1	<0.1	<0.1	<0.1
Org.	Np(IV)		<0.1	<0.1	<0.1
	Np(V)	–	0.9	1.52	0.2
	Np(VI)		<0.1	<0.1	<0.1
Gross Np in Org.		<0.1	0.9	1.52	0.2
in Aq.		100.0	99.1	98.5	99.8
Org. / Aq.		–	0.009	0.015	0.002

(2) Coextraction

1. Solvent extraction operation after photochemical valence adjustment

As shown in chapter 3.3, Np(VI), Pu(IV) and Pu(VI), which were photochemically adjusted in 3 M HNO_3 solution containing urea, were very stable for more than 4 hours even though the light irradiation stopped. The solvent extraction test was then carried out after the valence adjustment with the irradiation rate at 1.45 W/cm^2, using the 1×10^{-3} M of Pu and Np mixed solution containing 8×10^{-2} M of urea in 3 M HNO_3 and 30 % TBP/n-dodecane. The results are shown in Table 6. This table shows the changes in the abundance(%) of each valence in both the aqueous and organic phases at the appropriate operation time of the light irradiation and of the solvent extraction without light irradiation.

Table 6 Results of extraction operation after photochemical valence adjustment for coextration of Pu and Np

(a) Abundances of Pu valences in both phases vs. operation time

		Abundance(%)					
	Valence	Photochemical val. adj. time				Solv. ext. time	
		0 min	10 min	15 min	20 min	10 min	20 min
Aq.	Pu(III)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Pu(IV)	82.3	65.3	58.9	53.2	3.5	3.6
	Pu(VI)	17.7	34.7	41.1	46.8	7.9	8.1
Org.	Pu(III)					<0.1	<0.1
	Pu(IV)			–		36.1	36.8
	Pu(VI)					52.5	51.5
Gross Pu in Org.				–		88.6	88.3
in Aq.						11.4	11.7
Org. / Aq.				–		7.77	7.55

(b) Abundances of Np valences in both phases vs. operation time

		Abundance(%)					
	Valence	Photochemical val. adj. time				Solv. ext. time	
		0 mn	10 min	15 min	20 min	10 min	20 min
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Np(V)	100.0	7.0	0.3	<0.1	7.7	7.7
	Np(VI)	<0.1	93.0	99.7	100.0	<0.1	<0.1
Org.	Np(IV)					<0.1	<0.1
	Np(V)			–		<0.1	<0.1
	Np(VI)					92.3	92.3
Gross Np in Org.				–		92.3	92.3
in Aq.						7.7	7.7
Org. / Aq.				–		12.0	12.0

Pu : 1.0×10^{-3} M
Np : 1.0×10^{-3} M
Urea : 1.0×10^{-2} M

HNO_3 : 3.0M
Temp. : 20℃
Irra. rate : 1.45 W/cm^2

As seen in this table, Pu(IV) was gradually photooxidized to Pu(VI) and nearly 100 % of the Np(V) was photooxidized to Np(VI) after 20 mins. On the other hand, during the extraction operation, 92.3 % of Np was extracted in the organic phase, and 7.7 % of Np remained in the aqueous phase after 10 mins. The Np valence remaining in the aqueous phase was Np(V), in spite of the complete adjustment to 100 % of Np(VI) being achieved. This indicates that part(about 8 %) of Np photooxidized to about 100 % of Np(VI) was reduced to Np(V) during the mixing operation with 30 % TBP/n-dodecane. The remaining Np(V) in the aqueous phase would be completely extracted into the organic phase by the recycling operation of the photochemical oxidation and the extraction.

Based on these data, it was shown that Pu and Np in a nitric acid solution were efficiently coextracted in 30 % TBP/n-dodecane using this photochemical technique.

2. Simultaneous operation for coextraction

A simultaneous operation test of light irradiation and solvent extraction for the coextraction of Pu and Np was carried out using a Pu and Np mixed solution containing urea. The results of this test are shown in Table 7.

Table 7 Results of simultaneous operation of irradiation and solvent extraction for coextraction of Pu and Np

(a) Abundances of Pu valences in both phases vs. operation time

	Valence	Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Pu(III)	<0.1	<0.1	<0.1	<0.1
	Pu(IV)	83.0	1.7	0.9	0.2
	Pu(VI)	17.0	9.1	9.7	10.0
Org.	Pu(III)	–	<0.1	<0.1	<0.1
	Pu(IV)		33.0	17.1	10.7
	Pu(VI)		56.2	72.3	79.1
Gross Pu	in Org.	<0.1	89.2	89.4	89.8
	in Aq.	100.0	10.8	10.6	10.2
Org./Aq.		–	8.26	8.43	8.86

Pu : 1.0×10^{-3} M
Np : 1.0×10^{-3} M
Urea : 1.0×10^{-2} M

HNO_3 : 2.0M
Temp. : 20℃
Irra. rate : 1.45 W/cm^2

(a) Abundances of Np valences in both phases vs. operation time

	valence	Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1
	Np(V)	100	97.2	99.3	100.0
	Np(VI)	<0.1	<0.1	<0.1	<0.1
Org.	Np(IV)	–	<0.1	<0.1	<0.1
	Np(V)		0.9	0.7	<0.1
	Np(VI)		1.9	<0.1	<0.1
Gross Np	in Org.	<0.1	2.8	0.7	<0.1
	in Aq.	100.0	97.2	99.3	100.0
Org./Aq.		–	0.03	0.007	<0.001

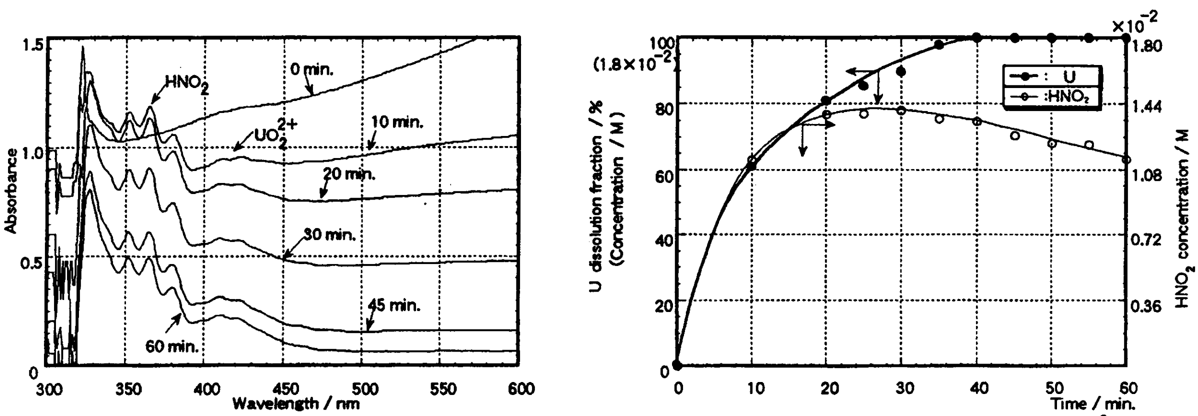
As seen in this table, the initial valences, Pu(IV) and Pu(VI), were extracted into the organic phase depending upon their specific distribution coefficients, and Pu(IV) in the organic phase decreased as Pu(VI) increased according to the irradiation time similar to the data shown in Tables 5-(a) and 7-(a). On the other hand, regarding Np, part of the Np(V) was photooxidized and was extracted into the organic phase. However, the extracted Np(VI) was gradually reduced to Np(V) and was then reversely extracted into the aqueous phase despite light irradiation. Therefore, Np(V) in the aqueous phase gradually increased. This result indicates that Np(V) was not photochemically oxidized to Np(VI) at all in the case of the simultaneous operation. It is quite different from the result shown in Table 6-(b) despite the same light irradiation.

This phenomenon also indicates that Pu and Np can be mutually separated using the Pu and Np mixed nitric acid solution containing not only HAN and HDZ but also urea in 3 M HNO_3 by the simultaneous operation of light irradiation and solvent extraction. This simultaneous operation is, however, not suitable for the purpose of the coextraction of Pu and Np with 30 % TBP/n-dodecane.

3.3 Photochemical dissolution

(1) Dissolution curve

Ten mg of UO_2 powder was placed in a quartz cell containing 2ml of a 3M HNO_3 solution. The solution was then irradiated using the Hg lamp at an irradiation rate of 1.3W/cm^2 while maintaining both the temperature of the solution (at 20 ± 1 ℃) and the homogeneity. Figure 7-(a) shows the results of the changes in the absorption spectrum of the solution according to the irradiation time. As shown in this figure, the absorption bands of UO_2^{2+} from 410 to 430nm and those of HNO_2 as a by-product of the UO_2 dissolution reaction from 360 to 390nm appeared after only 10 minutes of irradiation. These increases in the absorbances at these absorption bands show the increase in the dissolution fraction of UO_2 powder. Figure 7-(b) shows the changes in the UO_2 dissolution fractions which are calculated by Eq. (1) based on the data of Fig. 7-(a). The changes in the concentrations of HNO_2 according to the irradiation times are also shown in Fig.7-(b).



Vol.: 2ml, UO_2 powder: 10mg, Irra. rate (Hg lamp): 1.3W/cm^2
(a) Absorption spectrum

Vol.: 2ml, UO_2 powder: 10mg, Irra. rate (Hg lamp): 1.3W/cm^2
(b) Plots of dissolution fractions and HNO_2 concentration vs. time

Fig.7 Photochemical dissolution of UO_2 powder in 3M HNO_3 solution at 20℃

As shown in this figure, the UO_2 powders were completely dissolved after 40 mins. of irradiation even at 20℃, with the same amount of HNO_2 as compared to that of the dissolved UO_2 powder which was produced after15 mins. of irradiation. Then, after 30 mins. of irradiation, the amount gradually decreased.

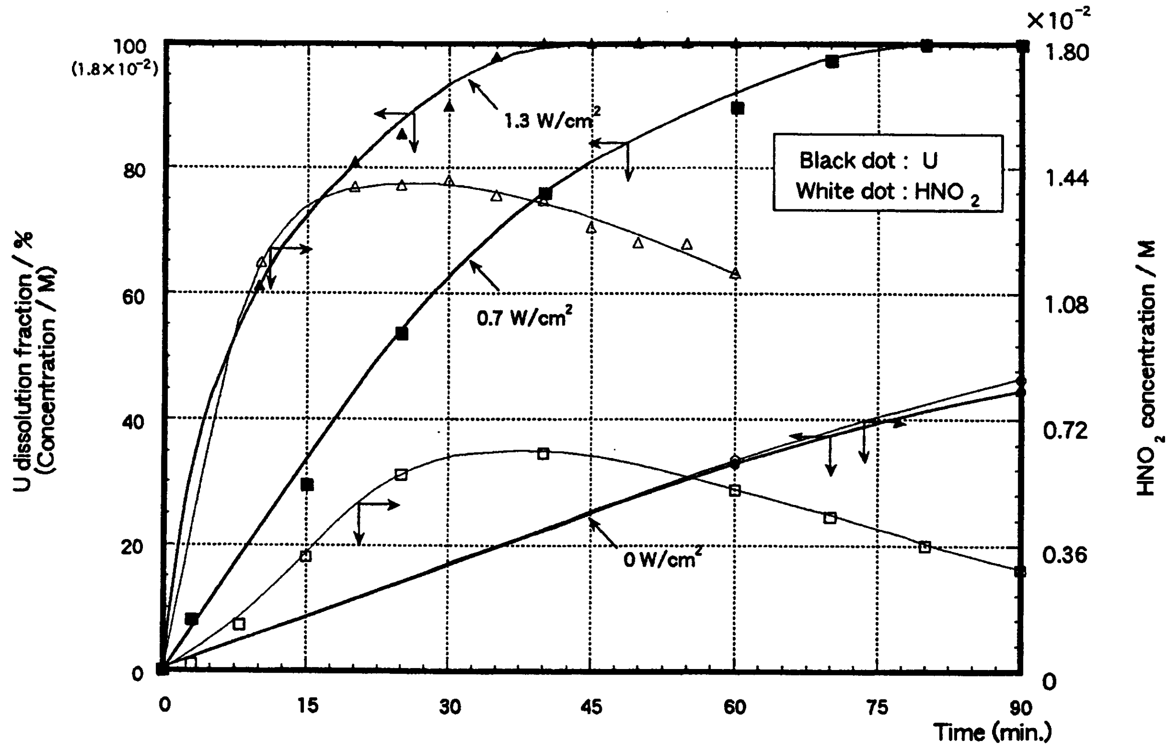
Figure 8 shows the difference in the dissolution curves, the relationship between the UO_2 dissolution fraction and the irradiation time, for the different irradiation rates 0(dark reaction), 0.7 and 1.3W/cm^2. As shown in this figure, the photochemical dissolution reaction of 10 mg UO_2 powder at 20℃ was completed at about 40 mins. and 80 mins. under the irradiation rates of 1.3 and 0.7W/cm^2, respectively. Under the dark condition, the dissolution fraction was 45% after 90 mins. of irradiation.

Judging from these data, the irradiation rate significantly affects the photochemical dissolution reaction.

Figure 9 shows the results of the dissolution reaction of 10 mg UO_2 which were obtained with a 0.7W/cm^2 irradiation rate at 20℃ while varying the concentration of HNO_3 to 1, 3 and 6M.

The photochemical dissolution reaction in the 6M HNO_3 solution was completed after only 14 mins. at a 0.7W/cm^2 irradiation rate. The complete dissolution time is about 1/5 of that in 3M HNO_3 solution. As for the 1M solution, the photochemical dissolution reaction hardly progressed, and the fraction being only 2-3% even after 90 mins. of irradiation.

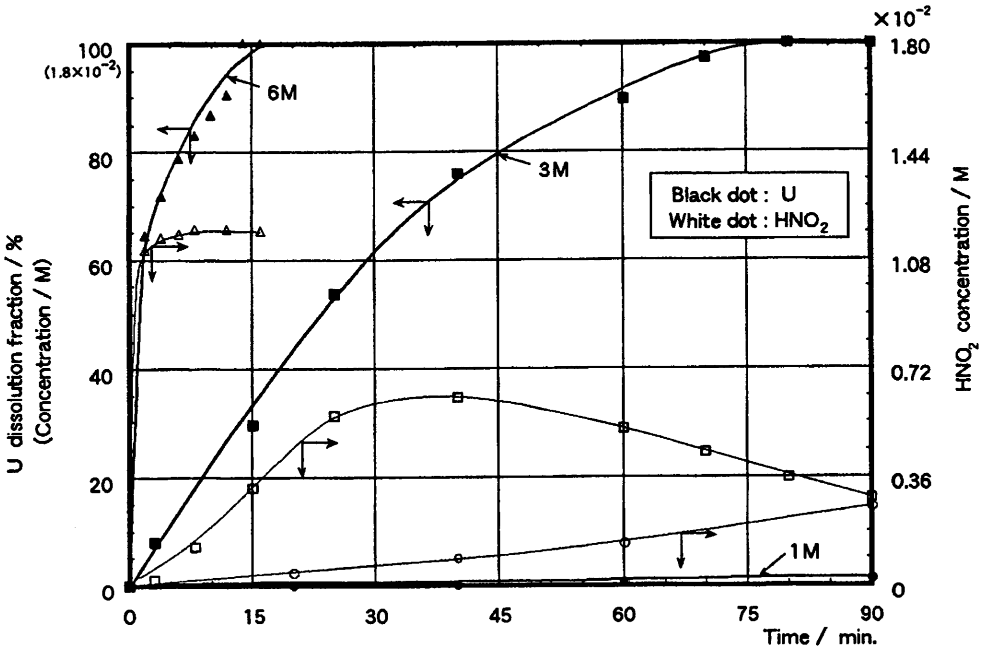
The concentration of HNO_3 significantly affects the photochemical dissolution rate of UO_2 powder as seen above.



Irra.rate(Hg lamp): 0W/cm^2 ; ● and ○, 0.7W/cm^2 ; ■ and □, 1.3W/cm^2 ; ▲ and △,
Weight of UO_2 : 10mg, Vol. of sol. : 2ml

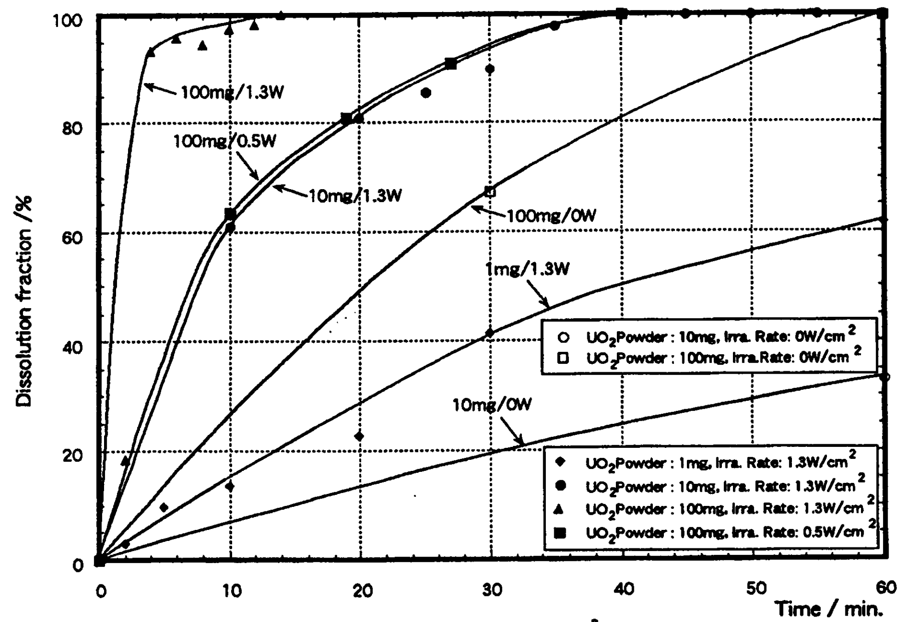
Fig.8 Photochemical dissolution of UO_2 powder in 3M HNO_3 solution at 20℃ under various irradiation rates

Figure 10 shows the results of the photochemical dissolution reaction obtained by changing the weight of the dissolved UO_2 powder from 1, 10 and 100mg. As shown in this figure, the dissolution rate become faster in the order of 100, 10 and 1 mg, and the complete dissolution time become shorter in the same order



Conc. of HNO : ▲ and △ ; 6M, ■ and □ ; 3M, ● and ○ : 1M, Vol. of sol. : 2ml
Irra. rate (Hg lamp) : 0.7W/cm^2, Weight of UO_2 : 10mg

Fig.9 Photochemical dissolution of UO_2 powder in various concentration of HNO_3 at 20℃



Irra. rate (Hg lamp) : 1.3 and 0.5W/cm^2, Temp. of sol. : 20℃

Fig.10 Photochemical dissolution of UO_2 powder 1mg, 10mg and 100mg in 2ml of 3M HNO_3 solution

(2) Photochemical dissolution reaction of UO_2 powder

The dissolution reaction mechanism of UO_2 powder in nitric acid solution has been studied by Y. IKEDA and H. TOMIYASU et al.(27) using a UO_2 powder enriched with ^{17}O. Additionally, X. MACHURON-MANDARD and C. MADIC(28) studied the dissolution reaction mechanism of PuO_2 powder using ^{18}O-enriched water. In these studies, they concluded that the UO_2 and PuO_2 powders were dissolved through a one or two electron transfer reaction based on the data from NMR analysis. These experiments indicate thst the dissolution mechanism is by the redox reaction of electron transfer between a solvent such as nitric acid and UO_2 or PuO_2 powder.

Therefore, the standard electrode potentials are important in evaluating the dissolution reaction. The standard redox electrode potentials of nitric acid, nitrous acid, UO_2, PuO_2 and related ion species based on several references(29),(30),(31) are shown in Fig.11.

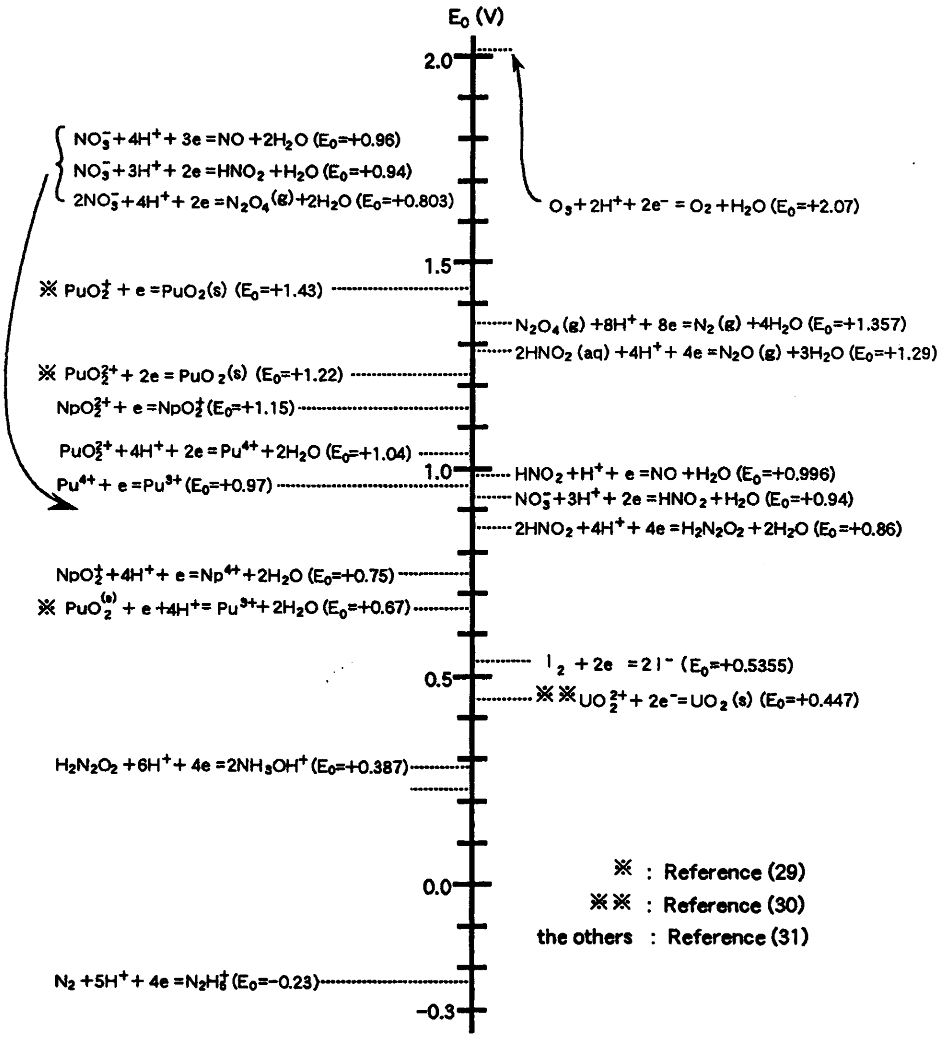


Fig.11 Standard redox electrode potentials of various reactions related to this study

In general, if the difference between two electrode potentials of a pair of half reactions, ΔE_o , is larger than 0.4V, the redox reaction between the pair might easily progress. For example, in the case of the dissolution reaction of UO_2 in a nitric acid solution, the difference, ΔE_o , between the two half redox reactions of NO_3^- and UO_2 is about 0.5V. Therefore, the reaction will easily progress. However, in the case of the dissolution reaction of PuO_2 in a nitric acid solution, the difference in the electrode potentials, ΔE_o , is a negative value between these half reactions, Eqs.(8) and (9).

$$NO_3^- + 3H^+ + 2e = HNO_2 + H_2O \ (E_o = +0.94) \text{ -------(8)}$$

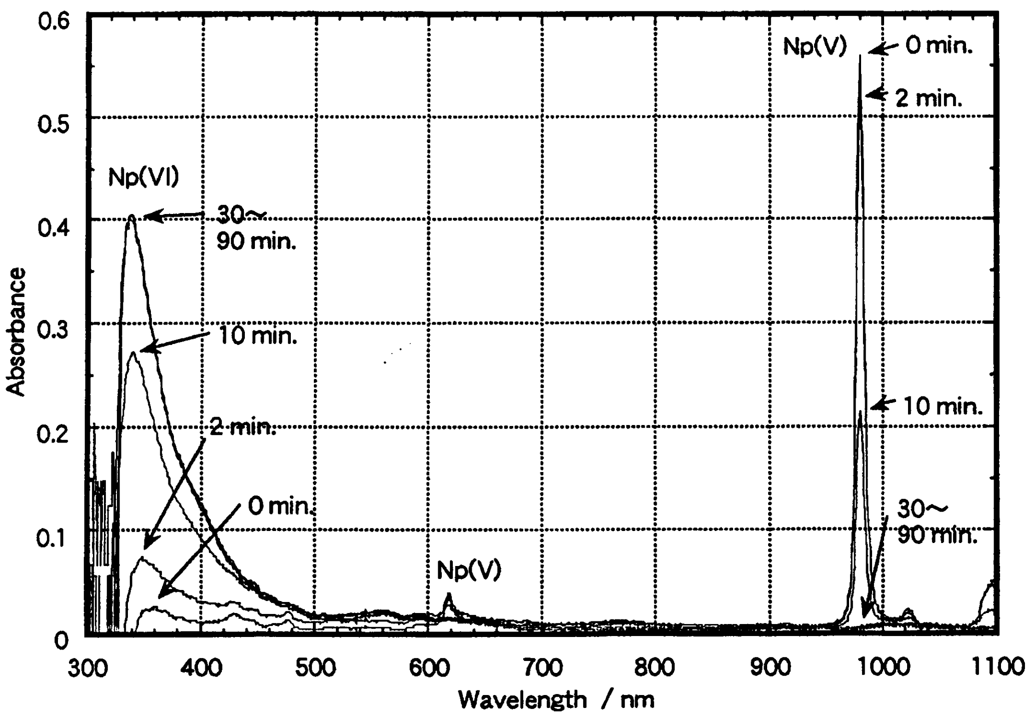
and

$$PuO_2^{2+} + 2e = PuO_2(s) \ (E_o = +1.22). \text{ ------------(9)}$$

Therefore, in general, we have to heat the nitric acid solution to activate the potential of Eq. (8).
On the other hand, in the case of the oxidation reaction of Np(V) to Np(VI) by nitric acid ion, the difference between two of the half reactions, Eqs. (8) and (10) is also a negative value.

$$NpO_2^{2+} + e = NpO_2^{+} \ (E_o = +1.15V) \text{ -----------------(10)}$$

Therefore, the oxidation reaction of Np(V) to Np(VI) hardly progresses at room temperature in nitric acid solution. However, Figure 12 obtained in our previous study indicates that the oxidation reaction of Np(V) using the photochemical technique easily progresses. This oxidation reaction is thought to be caused by the photoexcited nitric acid ion, $*NO_3^-$ (16), shown in Eq.(11) below.



Np : 1×10^{-3} M , Urea : 8×10^{-2}M , Acidity : 3.0M , Tem. of sol. : 20℃ , Irra. rate : 1.45W/cm^2 , Irra. light wavelength : 250~600nm

Fig.12 Oxidation reaction of Np(V) to Np(VI) by photoexcited nitric acid

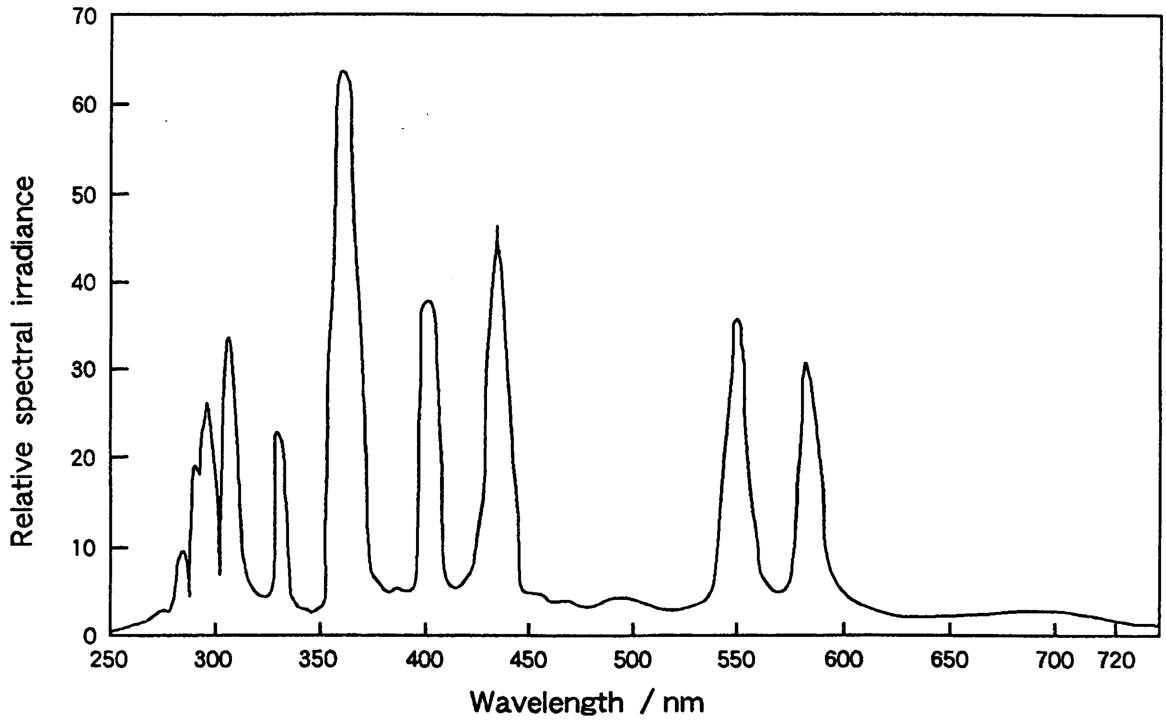


Fig.13 Relative spectral energy distribution curve of mercury lamp

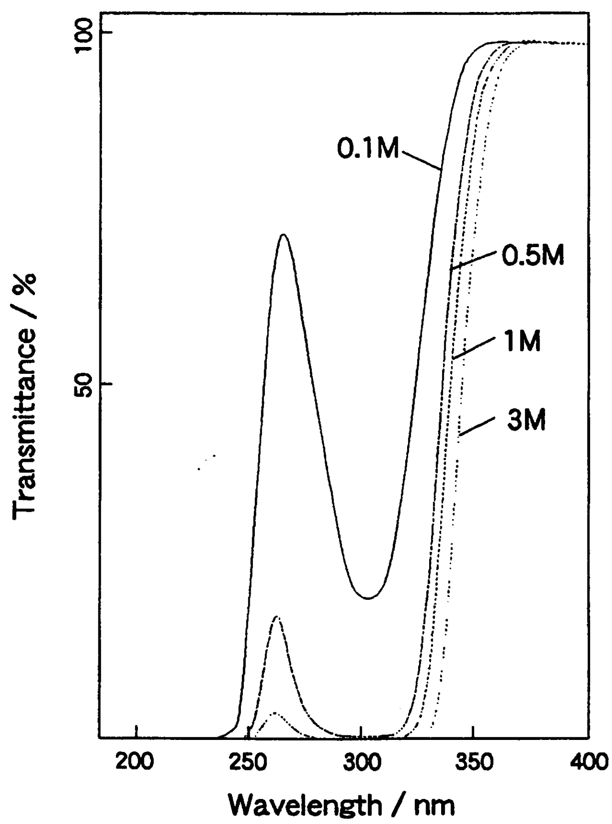


Fig.14 Absorption spectrum of HNO_3

$$*NO_3^- + 3H^+ + 2e \rightarrow HNO_2 + H_2O$$
$$NpO_2^{2+} + e \leftarrow NpO_2^+$$
$$\downarrow$$
$$*NO_3^- + 3H^+ + 2NpO_2^+ \rightarrow 2NpO_2^{2+} + HNO_2 + H_2O \text{ ---------------(11)}$$

In general, a photoexcited species formed by the absorption of photon energy is more active and has a short-lived redox potential in proportion to the photon energy absorbed by the species(32).

Figure 13 shows the relative spectral energy distribution curve of the Hg lamp used in our study. Figure 14 shows the absorption spectrum of a HNO_3 solution from 0.1 to 3M HNO_3. Judging from both figures, it is acertained that the Hg lamp light below 350nm photoexcites a nitric acid ion species, NO_3^-. Based on the above-mentioned photoexcited nitric acid, $*NO_3^-$, the results of the photochemical dissolution reaction of the UO_2 powder in nitric acid solution can explained as follows. Ikeda, Y. et al(27) explained the UO_2 dissolution reaction with nitric acid as follows:

$$UO_2 + 2NO_3^- + 4H^+ = UO_2^{2+} + 2NO_2(aq) + 2H_2O \text{ -------------(12)}$$
$$2NO_2(aq) + H_2O = HNO_3 + HNO_2 \text{ -------------------(13)}$$

From Equations.(12) and (13), Eq.(14) is derived.

$$UO_2 + NO_3^- + 3H^+ = UO_2^{2+} + HNO_2 + H_2O \text{ ---------------(14)}$$

Equation (14) proves the production of UO_2^{2+} and HNO_2 as shown in Fig.1-(a).
This nitrous acid then dissolves UO_2(33).

$$UO_2 + 2HNO_2 + 2H^+ = UO_2^{2+} + 2NO + 2H_2O \text{ --------------(15)}$$

Under the Hg lamp irradiation, the irradiation rate and the concentration of nitric acid significantly affected for the dissolution rate. This is brought about by the increase in the concentration of the photoexcited nitric acid, [$*NO_3^-$] . The dissolution reaction of the photoexcited nitric acid is shown in Eq.(14)' as related to Eq.(14).

$$UO_2 + *NO_3^- + 3H^+ = UO_2^{2+} + HNO_2 + H_2O \text{ ---------------(14)'}$$

Nitrous acid is regenerated by the catalyzing reaction (33),(34) after the dissolution reaction according to Eqs.(9) and (10).

$$2NO + HNO_3 + H_2O = 3HNO_2 \text{ ----------------------(16)}$$

As shown in Figure 7-(b), the concentration of the dissolved UO_2 and the generated HNO_2 were equal up to 20 mins. of irradiation time. This is due to the relationship amoung Eqs.(14)',(15) and (16).

Results similar to those of Fig.7-(b) were reported by T. Fukasawa et al. [35]. After 20 mins. of irradiation time, the concentration of HNO_2 gradually decreases mainly due to the decomposition reaction of HNO_2 by the light as follows.

$$2HNO_2 \xrightarrow{\downarrow h\nu} NO + NO_2 + H_2O \quad \text{----------------(17)}$$

(3) Effect of irradiation rate on photochemical dissolution rate

Based on the results of Figures 8 and 10 obtained by the tests changing the variable level of the irradiation rate, the coefficient of the dissolution rates V($mol \cdot cm^{-2} \cdot min^{-1}$) for 10mg UO_2 and 100mg UO_2 were calculated by the following Eq. (18) and are shown in Tables 8-(a) and -(b), respectively.

Table 8 Change in photochemical Dissolution rate depending on irradiation rate

(a) Weight of UO_2 : 10mg

Irra. rate (W/cm^2)	Disso. rate coef. ($mol \cdot cm^{-2} \cdot min^{-1}$)	Ratio to dark rate coef.	Time for complete disso. (min)
1.3	3.50×10^{-6}	14.4	40
0.7	1.05×10^{-6}	4.3	78
0.0	2.43×10^{-7}	–	350

Acidity : 3M HNO_3, Temp. of sol. : 20℃

(a) Weight of UO_2 : 100mg

Irra. rate (W/cm^2)	Disso. rate coef. ($mol \cdot cm^{-2} \cdot min^{-1}$)	Ratio to dark rate coef.	Time for complete disso. (min)
1.3	9.35×10^{-6}	8.9	14
0.5	3.00×10^{-6}	2.9	40
0.0	1.05×10^{-6}	–	60

Acidity : 3M HNO_3, Temp of sol. : 20℃

$$V = \frac{\Delta D_0}{S_0 \times 10^4 \times w/1000} \qquad \text{-------------------- (18)}$$

where V : Coefficient of dissolution rate(mol・cm^{-2}・min^{-1})

ΔD_0 : Slope of dissolution curve obtained in tests at the beginning of dissolution reaction(mol・min^{-1})

S_0 : Specific surface area(m^2/g) of UO_2 powder used in test shown in table 2

w : Weight of UO_2 powder used(mg).

In the case of 10mg UO_2, the ratio of the coefficients of the dissolution rate, $V_{1.3}$ and V_0, and the complete dissolution times between the irradiation rates of 1.3W/cm^2 and 0W/cm^2(dark) was 14.4 and 8.75, respectively. The ratio of the rate coefficients between $V_{1.3}$ and $V_{0.7}$ under 1.3W/cm^2 and 0.7W/cm^2 was 3.3, though the ratio of the irradiation rate was 1.9. In the case of 100mg of UO_2, the ratio of the coefficients of the dissolution rate between $V_{1.3}$ and V_0 was 8.9. The ratio of the rate coefficients between $V_{1.3}$ and $V_{0.5}$ was 3.1 though the ratio of the irradiation rates was 2.6.

Thus, the increase in the irradiation rate of the Hg lamp significantly accelerated the photochemical dissolution rate of UO_2 powder in 2ml of a 3M HNO_3 solution at 20℃, although the effect of the difference in the irradiation rate for 100mg of UO_2 dissolution was smaller than that for 10mg.

(4) Effect of concentration of HNO_3 on photochemical dissolution rate.

Based on the results of Figure 9, obtained by the tests changing the level of the HNO_3 concentration from 6M, 3M to 1M under an irradiation rate of 0.7W/cm^2, the coefficients of the photochemical dissolution rate were calculated and are shown in Table 9.

Table 9 Change in photochemical Dissolution rate depending on concentration of HNO_3

Conc. of HNO_3 (M)	Disso. rate coef. (mol・cm^{-2}・min^{-1})	Ratio to dark rate coef.	Time for complete disso. (min)
6	4.20×10^{-5}	3.0	14
3	1.05×10^{-6}	4.3	75
1	1.17×10^{-8}	-	-

Weight of UO_2 : 10mg, Irra. rate : 0.7W/cm^2, Temp. of sol. : 20, - : No mea.

As shown in this table, the ratio of the rate efficients between 6M and 3M HNO_3 is 40.0 though the ratio of the acidity is only 2.0. The ratio of the rate coefficients between the photochemical dissolution reaction at 0.7W/cm^2 and the dark reaction under 6M HNO_3 is 3.0. The ratio of the coefficients of the photochemical dissolution rate at 6M and 1M HNO_3 is 3590. Thus, the effect of the concentration of HNO_3 on the photochemical dissolution reaction is clearly more significant than the effect of a change in the irradiation rate.

(5) Change in photochemical dissolution rate depending on weight of UO_2 dissolved

How much UO_2 powder can be photochemically dissolved in a definite volume of nitric acid solution is an important point for evaluating the applicability of this technology. Especially, as the penetration ability of the light is weak, and the transmittance of the Hg lamp light into the 1cm square spectrophotometeric quartz cell containing 100mg UO_2 powder in 3M HNO_3 solution is only 1%.

At the beginning of this study, we doubted whether a weight of as much as 100mg of UO_2 powders can be photochemically dissolved in an amount as small as 2ml of 3M HNO_3 was in fact possible.

We, therefore, examined the photochemical dissolving ability by changing the weight of the UO_2 powder. Figure 10 shows the results when 1, 10 and 100mg of the UO_2 powder were photochemically dissolved in 2ml of 3M HNO_3 solution under the conditions of an irradiation rate of 1.3W/cm^2 and a solution temperature of 20℃.

Based on the results of Figure 10, each coefficient of the dissolution rate, the time for complete dissolution and the ratio of the rate coefficient to the dark reaction are shown in Table 10. As shown in this table, the dissolution rate for 100mg UO_2 in 2ml of 3M HNO_3 solution, which is a suspension rather like a concentrated mud solution, is the fastest of the three variable levels. The ratio of the coefficient of the dissolution rate between 100mg and 10mg UO_2 is 2.7.

Furthermore, the ratio of the time for the complete dissolution of 100 and 10 mg of UO_2 is 0.35.

Table 10 Change in photochemical Dissolution rate depending on weight of UO_2 powder dissloved

Weight of UO_2 (mg)	Disso. rate coef. ($mol \cdot cm^{-2} \cdot min^{-1}$)	Ratio to dark rate coef.	Time for complete disso. (min)
100	9.35×10^{-6}	8.9	14
10	3.50×10^{-6}	14.4	40
1	6.78×10^{-7}	-	105

Irra. rate : 1.3W/cm^2, Acidity : 3M HNO_3, Temp. of sol. : 20, - : No mea.

Thus, in the range of 1 to 100 mg, it is concluded that the larger the amount of UO_2 powder, the faster the UO_2 powder dissolves. Although more detailed experiments and evaluations are required hereafter for more precise and quantitative estimations, the reasons for this phenomenon are considered nevertheless to be as follows:

- The larger the amount of UO_2 powder suspended in the nitric acid solution, the greater the probability of a collision between the photoexcited nitric acid species and the UO_2 powder is during the photoexciting state, the faster the UO_2 powder dissolves.
- The larger the amount of UO_2 powder suspended in the solution, the higher the concentration of nitrous acid generated due to the dissolution reaction is and also the faster the UO_2 is dissolved by the generated nitrous acid.
- The catalytic effect of UO_2^{2+} promotes the dissolution reaction of UO_2 powder(33), (36).

4. Conclusion

As advanced Purex technologies, separation and coextraction of Np from/with Pu in a mixed nitric acid solution and effective dissolution are needed in a new nuclear fuel cycle technology in the future.

The results of this study indicate that photochemical techniques for the separation and coextraction of Np from/with Pu, which involve the valence adjustment followed by solvent extraction, and the dissolution at room temperature have much potential for the above-mentioned purpose in principle.

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