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A Photo-induced Dissolution of UO_2 Sintered Pellets in a Simulated Solution

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Abstract–The objective of this study is to improve the established dissolution technique of UO_2 target by using a photochemical reaction. Photo-dissolution tests of UO_2 sintered powder and pellets were carried out in a simulated nitric acid solution at about 50 °C under UV irradiation. The simulated solution consists of 2 M nitric acid containing elements such as Cs, Sr, Zr, Ru, Mo and Nd. The light source is a Hg-lamp emitting 254 nm wavelength. As results, in the dark reaction, UO_2 sintered pellets were hardly dissolved, whereas UO_2 was rapidly dissolved after 7 hours of dissolution time in the UV irradiation. The very low dissolution rate in the dark reaction was due to surface characteristics of sintered pellets: UO_2 sintered pellet is very dense and has extremely low specific surface area. However, the dissolution rate of UO_2 sintered pellet was considerably increased in the simulated solution under UV irradiation. This was attributed to the fact that ruthenium and molybdenum ions in the simulated solution could accelerate the dissolution of UO_2 under UV irradiation. Additionally, when the pulverized sintered UO_2 powder was used, the dissolution rate of UO_2 increased more rapidly than that of UO_2 sintered pellet.

Key words: Photochemical Reaction, Dissolution, Uranium Dioxide, Sintered Pellet, Molybdenum

INTRODUCTION

Technetium-99m, which has been used in medical diagnostics, can detect a site of cancer cells in the thyroid, brain, skeleton, kidneys and other organs [Kirk and Othmer, 1980]. Two typical methods have been used to produce ^{99}Mo, the precursor of ^{99m}Tc, i.e., either via the ^{98}Mo(n, γ) ^{99}Mo nuclear reaction or via the neutron-induced fission of ^{235}U according to ^{235}U(n, f) ^{99}Mo [Ali and Ache, 1987]. The detailed production procedures are shown in Fig. 1. Of these methods, ^{99m}Tc obtained by fission of ^{235}U has been used widely at present due to the high specific activity. In order to produce ^{99m}Tc from ^{235}U, several unit chemical processes are involved. Among them, the dissolution process of UO_2 is the starting process in these unit chemical processes. Hence, many studies on dissolution of UO_2 in nitric acid solution have been reported [Taylor et al., 1963; Shabbir et al., 1968; Nishimura et al., 1995; Ikeda et al., 1995]. Experimental results showed that UO_2 could be dissolved in boiling HNO_3 and in relatively high HNO_3 concentration. However, this condition has some problems as follows: a high evolution rate of NO_x gas during dissolution of UO_2 and an installation of heating source in the hot cell. In particular, from an environmental point of view, a large quantity of nitrate waste issued from dissolution is also one of the difficult problems in waste treatment and disposal. Accordingly, some attempts have been made recently to dissolve UO_2 under mild conditions in which relatively low nitric acid concentration and room temperature are applied. Asano et al. [1995] demonstrated that, in HNO_3 solution containing 0.1 M $Ce(NO_3)_3$ bubbled with O_3 gas, UO_2 could be easily dissolved at low nitric acid concentration and even at room temperature. Wada et al. [1996] reported that UO_2 could be dissolved by using photo-chemistry. They could easily dissolve UO_2 powder at 3 M HNO_3 and room temperature. Kim et al. [1998] presented the experimental result on a dissolution of UO_2 sintered pellet under UV irradiation. Unlike UO_2 powder, it was very difficult to dissolve UO_2 sintered pellet because of its extremely low surface area caused by sintering. Accordingly, they recommended two methods to improve the dissolution of UO_2 sintered pellet in the presence of UV irradiation. One is an increase of oxidant concentration ($^*NO_3^-$, NO_2^-, etc.). This can be achieved either by increasing irradiation power (energy flux) or by increasing nitric acid concentration [Kim et al., 1998]. The other is an increase of surface area of UO_2 pellet that oxidants can easily attack. This method can also be solved either by pulverizing UO_2 sintered pellet or by etching the surface of those to increase surface area. Oxidants such as hydrogen peroxide can be used for a surface etching of UO_2 sintered pellet and subsequently dissolution rate of UO_2 sintered pellet could be considerably improved [Kim et al., 1998].

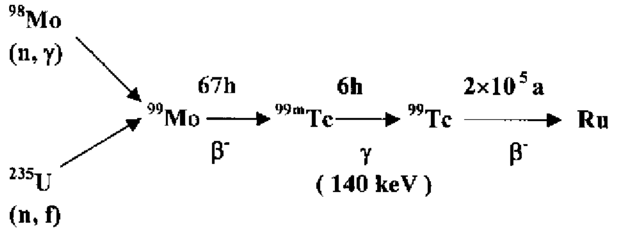

Fig. 1. Two different approaches for the production of Mo-99 the precursor of Tc-99m.

This work is also focused on dissolution of UO_2 sintered pellets at a relatively low concentration of nitric acid, so called mild condition, using a low-pressure mercury lamp. And ultimately, this study is related to dissolution of irradiated UO_2 fuel issued

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from a research reactor at which ^{235}U in the matrix of UO_2 was broken by neutrons and thereby ^{99}Mo as fission product is obtained for production of ^{99m}Tc for medical diagnostics as mentioned above. In general, an irradiated UO_2 fuel contains many fission products such as rare earth, transition, alkali and alkaline earth metals. Among them, some elements have an oxidation power to oxidize UO_2. Thus, the purpose of this study is to examine a photo-dissolution behavior of UO_2 sintered pellet containing various elements. Instead of a real irradiated UO_2 target, non-irradiated UO_2 sintered pellets were used in this work in order to investigate the effect of elements on dissolution behavior of UO_2. A simulated solution was prepared to match the composition of the real system. The solution consisted of the representative elements, which were selected from elements expected to be in an irradiated UO_2 target for production of ^{99m}Tc. The dissolution result obtained from this solution was compared with that from the solution without including elements. Based on this result, the effect of elements on dissolution of UO_2 sintered pellet was examined and the possibility of the application of this technique to a dissolution process was discussed.

EXPERIMENTAL

UO_2 sintered pellets used in this study were obtained from the facility for AUC (ammonium uranylcarbonate) process at KAERI (Korea Atomic Energy Research Institute). The physical properties and the detailed preparation method of UO_2 sintered pellet are available elsewhere [Brandau and Doerr, 1979; Assman et al., 1983]. UO_2 pellets were used as pieces, which were prepared by cutting the original pellet into six pieces having a similar shape and size: half-disk type (12.16 mm in diameter and about 5 mm in height). The physical properties of UO_2 used are listed in Table 1. In order to investigate the effect of the specific surface area of UO_2 on a dissolution rate, UO_2 sintered particles, which were prepared by crushing UO_2 sintered pellet, were used in this work. Reagent grade nitric acid was used as dissolution solvent and diluted with distilled water to the concentration of 2 M. The influence of elements on dissolution rate of UO_2 sintered pellet was investigated from the prepared simulated solution; the composition of elements included in this solution is listed in Table 2. The composition of elements in an irradiated UO_2 target was estimated from OREGON2 code. The specific data was obtained on the base that 93%-^{235}U of 60.002 g was charged into HANARO (Hi-flux Advanced Neutron Application Reactor) as a form UO_2 and burned up under flux of $3\times10^{+14}$ N/cm^2·sec to 9.49611 $\times10^{-1}$ MWD for 100 hours. As seen in Table 2, Li, Ag, Zn, Cd, etc. were not included in the simulated solution because the concentrations were very low and the presence of these elements was considered not to affect UO_2 dissolution. Accordingly, the representative elements in the simulated solution were as follows: Nd as a representative element for lanthanides; Cs and Sr for alkali and alkaline earth metals; Zr, Ru and Mo for transition metal. In particular, Mo is a main fission product for production of ^{99m}Tc. Ruthenium solution was supplied from Johnson Matthey Materials Technology (UK) as a chemical form of $Ru(NO)(NO_3)_3$ and composed of high nitric acid medium of around 8 N. Molybdenum consists of ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot4H_2O$] and supplied as solid form from Aldrich Chemical Co. (USA). Other metal salts such as Cs, Sr, Zr and Nd were also supplied from Aldrich Co. (USA) and as a nitrate form.

Table 1. The physical properties of UO_2 sintered pellets

Density (g/ml)	10.65
Specific surface area (m^2/g)	5.6×10^{-5}
% T.D.[a]	97
O/U ratio	2.001
Pellet dimension (OD/Height, mm)	12.16/15.57

[a] Theoretical density of UO_2: 10.96 g/ml

Table 2. Chemical composition of estimated UO_2 target and simulated solution

Element	Concentration (g/*l*)		Element	Concentration (g/*l*)	
	Discharged	Simulated		Discharged	Simulated
H	1.389×10^{-6}	-	Cd	2.862×10^{-4}	-
Li	1.256×10^{-8}	-	In	2.411×10^{-5}	-
Be	4.356×10^{-9}	-	Sn	9.549×10^{-4}	-
C	7.661×10^{-10}	-	Sb	1.095×10^{-3}	-
Zn	6.051×10^{-8}	-	Te	2.768×10^{-2}	-
Ga	5.764×10^{-8}	-	I	3.059×10^{-2}	-
Ge	1.752×10^{-5}	-	Xe	1.451×10^{-1}	-
As	1.898×10^{-5}	-	Cs	4.219×10^{-2}	4.2×10^{-2}
Se	1.825×10^{-3}	-	Ba	7.333×10^{-2}	-
Br	8.112×10^{-4}	-	La	4.235×10^{-2}	-
Kr	1.465×10^{-2}	-	Pr	2.281×10^{-2}	-
Rb	1.282×10^{-2}	-	Nd	6.906×10^{-2}	2.64×10^{-1}
Sr	5.671×10^{-2}	1.3×10^{-1}	Pm	6.297×10^{-3}	↓
Y	2.495×10^{-2}	-	Sm	7.527×10^{-3}	
Zr	1.243×10^{-1}	1.24×10^{-1}	Eu	8.178×10^{-4}	
Nb	9.740×10^{-4}	-	Gd	7.332×10^{-5}	
Mo	8.418×10^{-2}	8×10^{-2}	Tb	6.257×10^{-6}	
Tc	9.781×10^{-3}	-	Dy	5.449×10^{-7}	
Ru	6.268×10^{-2}	7.8×10^{-2}	Ho	1.758×10^{-8}	
Rh	1.976×10^{-3}	-	Er	5.228×10^{-9}	
Pd	4.101×10^{-3}	-	Ce	1.156×10^{-1}	
Ag	2.194×10^{-4}	-			

Equipment used for photo-dissolution of UO_2 was supplied from Rayonet (Model: R.P.R-208). This consists of Hg-lamps with 120 W, emitting 254 nm wavelength. A schematic diagram of the experiment is shown in Fig. 2. As shown in Fig. 1, the photo-reactor is a cylindrical type (40 cm in diameter and 60 cm in height). Eight mercury lamps were located at the circumference of reactor from which UV light travels in the direction of the core of reactor. Material of reaction tube was made of quarts and its capacity is 15 ml. As seen in Fig. 2, reaction tubes were located on the circumference of circular-type horizontal supporter, which was made of acrylic resin and designed so that eight reaction tubes could simultaneously be run. The amount of working volume used in every experiment was 10 ml. Sample of ranges of 10 to 100 μl was taken out at appropriate time intervals to determine the uranium and the nitrite ion concentrations in the solution during photolysis. The photo-dissolution fraction of UO_2

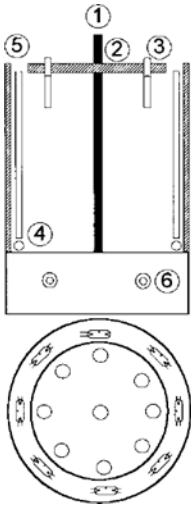

Fig. 2. Schematic diagram of the photoreactor.

1. Vertical supporter	4. Aeration port
2. Horizontal acrylic supporter	5. Hg-lamp
3. Sample tube	6. Power generator

was calculated by the method suggested by Wada et al. [1996]. The method measured the ratio between the absorbance A*t* and A∞ of UO_2^{+2} at 417 nm. Where, A*t* and A∞ represent the absorbances of an arbitrary time and the complete dissolution time, respectively. Accordingly, dissolution fraction of UO_2 is expressed by;

$$\text{Dissolution fraction (\%)} = At/A\infty \times 100.$$

During UV irradiation, temperature of the working solution is increased from room temperature (25±1 °C) to 50±1 °C within 30 min and then is kept stable all the time during photolysis. As it was not easy to cool down the photo-reactor used in this study to room temperature (25 °C), all the experiments were carried out at approximately 50 °C to be at a stable temperature. Thus, when temperature of the solution approached about 50 °C and became stable, UO_2 was placed into the solution. Instruments used in this study were UV spectrophotometer (Model: Shimadzu UV-160A) for measuring absorption bands of nitrate ion and uranium concentration, and a reflectometer (Reflectoquant, Merck) for measuring nitrite concentration.

RESULTS AND DISCUSSION

Fig. 3 shows results of photo-dissolution of UO_2 pellets in 2 M nitric acid solutions with and without UV irradiation. As seen in Fig. 3, the UO_2 pellets were hardly dissolved for seven hours of dissolution time irrespective of UV irradiation. However, in the presence of UV irradiation, UO_2 began to dissolve after 7 hours and then was rapidly dissolved. Wada et al. [1996] reported that UO_2 could be dissolved by UV irradiation as follows;

$$NO_3^- + hv = {}^*NO_3^- \qquad (1)$$

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

$$UO_2 + 2HNO_2 + 2H^+ = UO_2^{+2} + 2NO + 2H_2O \qquad (3)$$

From the above mechanisms it can be interpreted that UO_2 is first oxidized by ${}^*NO_3^-$ excited from nitrate ion under UV irradiation and subsequently dissolved into the aqueous solution. An ultra violet absorption spectrum of nitric acid solution is shown in Fig. 4. As seen from Fig. 4, it appears that nitrate ion absorbed the lights below 340 nm of wavelength. From this result we can confirm that 254 nm of wavelength emitted from the Hg-lamps may excite nitrate ions. And also, Fig. 5 shows that NO_2^- is produced during photodissolution of UO_2. This result supports the

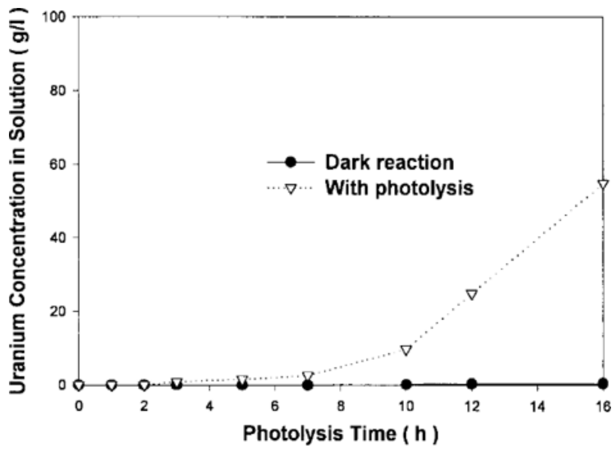

Fig. 3. Dissolution behavior of UO_2 sintered pellets at 2 M HNO_3.

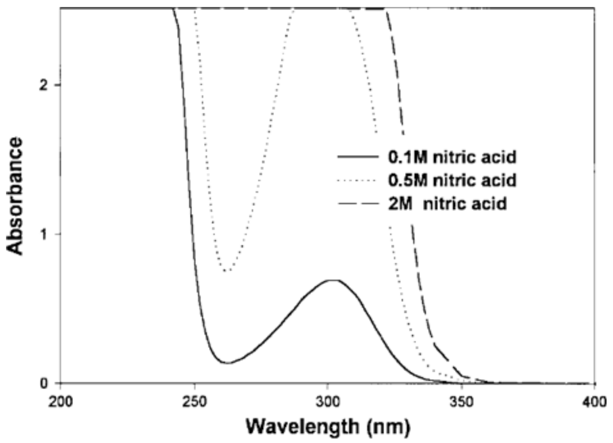

Fig. 4. UV spectrums of different nitric acid concentration.

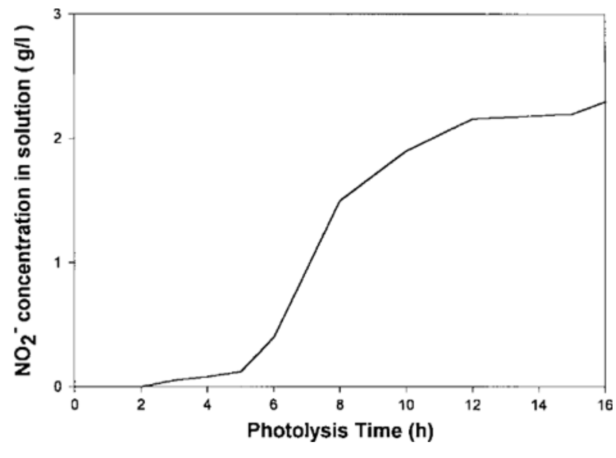

Fig. 5. Variation of NO_2^- ion during photodissolution of UO_2 sintered pellets at 2 M HNO_3.

dissolution mechanisms suggested by Wada et al. [1996]. In this regard, similar results have been also described elsewhere [Daniels et al., 1968; Sarakla et al., 1993]. Thus, the rapid dissolution of UO_2 in the presence of UV radiation can be considered to be the influence of $^*NO_3^-$, but further confirmation is needed because NO_2^- and OH radical besides $^*NO_3^-$ were produced as oxidizing agents in the solution during photolysis of NO_3^- [Sarakla et al., 1993].

As seen in Fig. 3, we could know that UO_2 was never dissolved at the beginning of dissolution although UV was irradiated. This was attributed to the fact that UO_2 sintered pellet was very dense. As it were, this means that since the UO_2 sintered pellets have an extremely low surface area as seen in Table 1, it is very difficult to dissolve UO_2 sintered pellets even in the solution with the excited $^*NO_3^-$ species [Kim et al., 1998]. Fig. 6 shows the results of dissolution of UO_2 pellets in the simulated solution and 2 M nitric acid solution. Surprisingly, UO_2 was dissolved far faster in the simulated solution than in 2 M nitric acid solution. This result indicates that metal ions in the simulated solution may accelerate the dissolution of UO_2 pellets. Thus, it was examined which element affected the dissolution of UO_2 pellet under UV irradiation. The result is shown in Fig. 7. Both molybdenum (VI) and ruthenium (IV) affected the dissolution rate of UO_2, whereas elements such as Cs, Sr, Zr, and Nd did not affect the dissolution rate of UO_2 pellet at all. Redox reactions of the elements used in this work with UO_2 are shown in Table 3. From Table 3, we can know that only both Mo(VI) and Ru(IV) can oxidize UO_2. This result indicates that UO_2 can be oxidized even by chemical reaction in absence of UV irradiation. Accordingly, in order to confirm this fact, experiments on UO_2 dissolution were carried out in the solution containing Mo(VI) ion without UV irradiation. The result is given in Fig. 8. We can find that UO_2 was hardly dissolved in the solution without UV irradiation. From this result we can conclude that when UV is not irradiated, Mo(VI) ion dose not largely affect dissolution rate of UO_2 in kinetic aspect although UO_2 can be easily dissolved in the thermodynamic aspect as shown in Table 3. Accordingly, we can suggest that Mo(VI) ion is excited into *Mo(VI) ion by absorbing the light, which can oxidize UO_2. As it were, this means that only the activated Mo(VI) ion, *Mo(VI), can easily oxidize UO_2, and subsequently dissolve UO_2. Fig. 9 shows the result of dissolution of UO_2 sintered pellet in the solution containing various amounts of molybdenum ions. This result shows that the degree of acceleration is not dependent on the molybdenum content. Probably, the present beam energy power seems to be insufficient for exciting large amounts of Mo(VI)

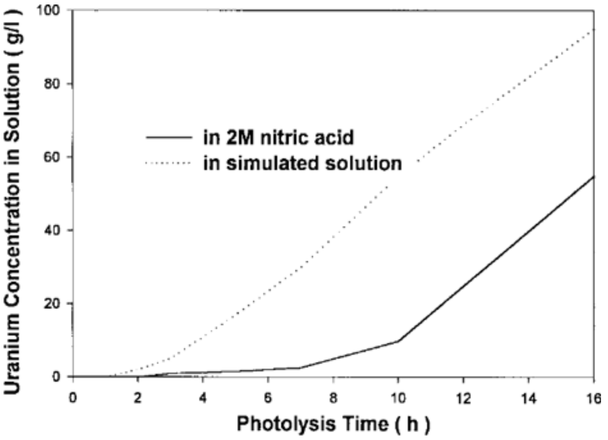

Fig. 6. Photo-dissolution behavior of UO_2 sintered pellets in nitric acid and simulated solution.

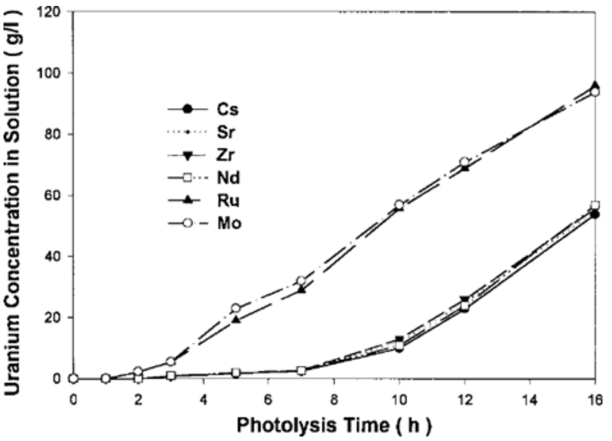

Fig. 7. Effect of elements on dissolution of UO_2 sintered pellets during photolysis.

Table 3. Redox potentials (V) of each element

Element	Redox couples	Volt, V
Ru	$UO_2+2Ru^{+4}=UO_2^{+2}+2Ru^{+3}$	+0.461
	$2Ru^{+3}+NO_3^-+3H^+=2Ru^{+4}+HNO_2+H_2O$	+0.032
	$Ru^{+3}+HNO_2+H^+=Ru^{+4}+NO+H_2O$	+0.075
	$3Ru^{+3}+NO_3^-+4H^+=3Ru^{+4}+NO+2H_2O$	
Mo	$UO_2+2Mo(VI)=UO_2^{+2}+2Mo(V)$	+0.083
	$2Mo(V)+NO_3^-+3H^+=2Mo(VI)+HNO_2+H_2O$	+0.41
	$Mo(V)+HNO_2+H^+=Mo(VI)+NO+H_2O$	+0.453
	$3Mo(V)+NO_3^-+4H^+=3Mo(VI)+NO+2H_2O$	
Cs	$UO_2+2Cs^+=UO_2^{+2}+2Cs$	−3.367
Sr	$UO_2+Sr^{+2}=UO_2^{+2}+Sr$	−3.337
Zr	$2UO_2+Zr^{+4}=2UO_2^{+2}+Zr$	−1.839
Nd	$3UO_2+2Nd^{+3}=3UO_2^{+2}+2Nd$	−2.817

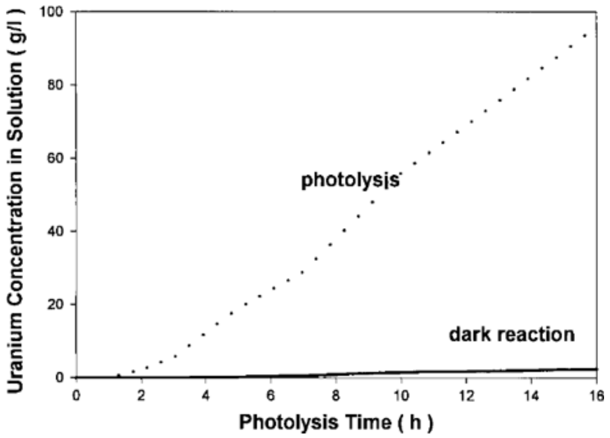

Fig. 8. Dissolution behavior of UO_2 sintered pellets in the solution containing ruthenium during photolysis and dark reaction (Mo=0.08 g/*l*).

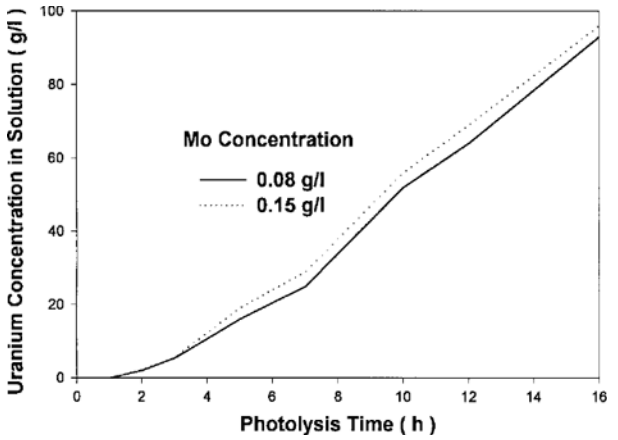

Fig. 9. Dissolution behavior of UO_2 sintered pellets according to molybdenum ion content at 2 M HNO_3 during photolysis.

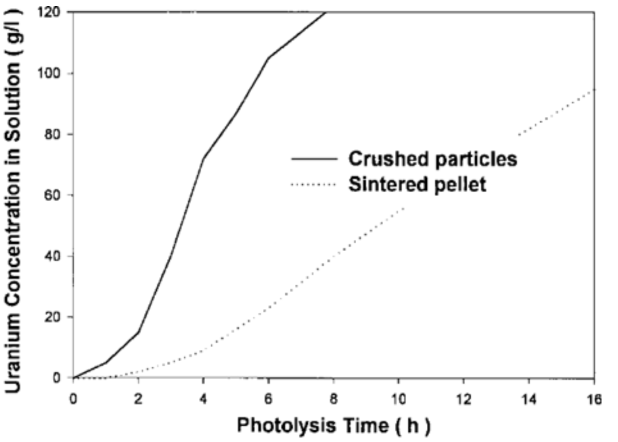

Fig. 10. Dissolution behavior of UO_2 sintered pellet and crushed UO_2 particles in the Mo containing nitric acid solution during photolysis.

ions. And, the reduced element Mo(V) can be re-oxidized in the nitric acid medium as bellow,

$$3Mo(V)+NO_3^-+4H^+ = 3Mo(VI)+NO+2H_2O \tag{4}$$

From this result, we can suggest that so many amounts of Mo(VI) ions may be not required for the dissolution of UO_2 at a given beam energy flux because molybdenum ions repeat the oxidation and reduction cycles continuously during UO_2 dissolution in nitric acid medium.

Fig. 10 shows the result of dissolution of UO_2 powder obtained by pulverizing UO_2 sintered pellets. The pulverized UO_2 powder was sieved into the range of 1,000 μm to 2,000 μm. As seen in Fig. 10, it appears that the dissolution rate of the pulverized UO_2 powder is more than three times faster than that of UO_2 pellet in 2 M nitric acid solution containing Mo(VI) ion under UV irradiation. In fact, a real UO_2 target for production of ^{99}Mo the precursor of ^{99m}Tc is tubular type: UO_2 is coated by an electrical deposition method inside zirconium tube of 22.4 mm in diameter and layer thickness of UO_2 of approximately 50 μm [Arino et al., 1973]. Therefore, if the real UO_2 target will be dissolved at the same condition as mentioned above, it is expected that dissolution rate of UO_2 will increase more rapidly than that of UO_2 obtained from this study.

CONCLUSION

In this study, the dissolution experiments of UO_2 sintered pellets and particles were carried out at 2 M HNO_3 solution and the simulated solution under UV irradiation using a Hg-lamp. Effects of metal ions on dissolution of UO_2 sintered pellets were investigated. The results are as follows:

1. In the dark reaction UO_2 sintered pellets were hardly dissolved, whereas in UV irradiation UO_2 sintered pellets were rapidly dissolved after 7 hours of photolysis time. However, at the beginning of UO_2 dissolution, UO_2 sintered pellets were not dissolved at all irrespective of UV irradiation. This was considered to be due to surface characteristics of UO_2 sintered pellets which have an extremely low surface area.
2. Dissolution rate of UO_2 sintered pellets in the simulated solution containing elements such as Cs, Sr, Zr, Mo, Ru and Nd increased more than two times than that of UO_2 sintered pellets in the solution without metal ions. This confirmed that Mo and Ru affect dissolution rate of UO_2 sintered pellets under UV irradiation.
3. In the simulated solution, the use of UO_2 sintered particles led to the increase of dissolution rate far faster than when UO_2 sintered pellets were used. This was interpreted to be due to an increase of surface area of UO_2 sintered pellets.

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