

Photochemistry of the Actinides*

L. M. Toth, J. T. Bell, and H. A. Friedman
 Chemistry Division
 Oak Ridge National Laboratory
 Oak Ridge, TN 37830

MASTER

NOTICE
 This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prior to the advent of the laser, photo-induced reactions sat, for the most part, in the chemical background. Photochemists of that time typically gave little thought to actinide elements other than uranium which was known for years to be a very excellent chemical actinometer when present as the uranyl ion. The expertise and specialized equipment required in the handling of the other actinides, coupled with their very limited supply served to discourage photochemists from fundamental investigations of these elements. As a result, no report of actinide photochemistry (save that of uranium) is to be found in the open literature prior to 1969.

With no supporting fundamental data, reactor technologists concerned with the chemistry of reactor fuels could merely speculate on the behavior of the actinide solutions should they be exposed to electromagnetic radiation. Then as fuel reprocessing became a topic of much interest during the past decade, the concern of possible photo-chemical activity began to occupy the thoughts of some researchers.

The first attention given to actinide photochemistry was for the purpose of identifying any photochemical activity which might alter the efficiency of the extraction or exchange processes. Subsequently, the identification of photochemically active species of uranium and plutonium gave some indication that the photo-reactions could be turned to a useful end and, perhaps, offer a cleaner way to separate actinides from each other and from the other elements accompanying them in nuclear fuel elements.

Since that time, laser photochemistry has become a popular subject and with it have come the laser photochemists looking for a photon 'target'. Obviously, the first laser photons would be

* Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

aimed toward isotope separations which required the narrow bandwidths which the laser so uniquely provided; but spin-off targets have since included the separations of reactor fuel components in reprocessing and/or waste isolation systems. Although much has been promised from the application of lasers to the reprocessing of nuclear fuels, there has been very little evidence that would suggest their usage is essential. Consequently, most of the pertinent photochemical work has been performed with conventional light sources.

A relatively small amount of energy is required to do the job in a typical reprocessing plant. We estimate, under the most ideal circumstances that 2000 Watts of adsorbed light for a typical 5 ton/day plant would be necessary. (This is based on the assumption that the dominant photo-reaction will be UO_2^{2+} reduction with a Quantum Yield, QY, = 0.5. The two-fold excess of U^{4+} is then used to reduce Pu^{4+} which is present as 1 percent of the spent LWR fuel (1). Neptunium, occurring as 0.05 percent of the spent fuel, has been neglected for this estimate.) This is indeed an attractive alternative to some chemical reagents, but presently, for want of more data, no photochemical process has been seriously considered even though several interesting suggestions have been offered and some patents have been obtained.

This report shall review the basic photochemistry of uranium, plutonium, and neptunium which has been studied during the past several years, shall suggest where a photochemical process might be most efficiently applied and then shall assess the general applicability of photochemistry to fuel reprocessing. We shall assume that the attractive features of photochemical separations are appreciated and that the reader is able to perform the simple conversion of Watts input power to moles of resulting product provided the quantum efficiencies of the photochemical reactions are known. Most elementary texts on physical chemistry (2) or photochemistry (3) provide ample background that need not be repeated here. The focus of this report will be on the photochemistry of the actinides themselves and the promise which this gives to the possibility of separating them.

Historically, the study of actinide photochemistry at both Oak Ridge and elsewhere has proceeded along the sequence shown in Table I, moving from a spectroscopic study of uranyl species to photochemical reduction thereof and ultimately to the photochemistry of the more radioactive actinides. The fundamental photochemistry of plutonium and neptunium has been probed only during the past ten years and by only two laboratories (9-14), due largely to the difficulty of handling and their limited supply. The Russian workers were truly first to investigate plutonium and neptunium, but their reports are brief and do not mention essential factors such as quantum efficiencies and wavelength effects on the photo-induced reactions. For these reasons, the research which followed at Oak Ridge was performed to answer some of the essential questions.

Table I. Actinide Photochemistry and Related Spectroscopy

(I) URANIUM

- | | |
|-----------------------------------|---|
| (A) Spectroscopy | Bell and Biggers [1965-68] (4)
Bell, Friedman, Billings [1974] (5) |
| (B) Photoreduction of UO_2^{2+} | Nemodruk et al. [1967] (6)
Bell et al. [1974-75] (7) |

(II) PLUTONIUM

- | | |
|----------------------------|--|
| (A) Photoredox | Palei, Nemodruk, Bezrogova [1969] (8) |
| (B) Polymer degradation | } Bell and Friedman [1976] (9)
Friedman, Toth, Bell [1977] (10) |
| (C) Equilibrium photoshift | |

(III) NEPTUNIUM

- | | |
|---|---|
| (A) Photoredox in $HClO_4$,
HCl , HNO_3 , H_2SO_4 | Nemodruk et al. [1972-73] (11,12,13,14) |
| (B) Photoredox in $HClO_4$,
HNO_3 | Friedman and Toth [1979] (15,16) |

(IV) REPROCESSING

- | | |
|------------------------------------|--|
| (A) Pu(IV) reduction with
U(IV) | Carroll, Burns, Warren [1961] (17)
Wilson [1971] (18)
Friedman, Toth, Bell [1977] (19)
Goldstein et al. [1977] (20)
Depoorter, Rofer-Depoorter [1978] (21) |
|------------------------------------|--|

Ultimately, a number of photochemistry groups turned their interests to reprocessing using the fundamental information thus far gathered and the realization of the benefits which photochemical processes had to offer. All of these investigators followed a similar path — that of photo-reducing uranyl to U(IV) and using the resulting uranium as the chemical reductant for Pu(IV) in order to achieve the reductive extraction of plutonium. The first known report of such work was by Carroll and coworkers (17) at Hanford in 1961 followed by a patent by Wilson (18) in 1971 from the same laboratory suggesting the organic phase reduction of UO_2^{2+} using tributyl phosphite and phosphoric acid.

Later, an aqueous phase photochemical process which would produce reductive extraction of plutonium from a TBP organic phase containing both uranium and plutonium was patented (19) at Oak Ridge. Goldstein and coworkers (20), although they could do no experimental work were quick to see the merits of uranyl reduction using photochemistry and have written several reports suggesting its usage as a means of separating plutonium from uranium. Since that time the group at Los Alamos has performed some experiments on organic phase reductions of uranyl ion (21) similar to that of the Hanford work in 1971; but instead of using tributyl phosphite and phosphoric acid as the reductants for uranium, they proposed the usage of the TBP itself. This has already been treated in a previous report (22) and the details shall not be discussed any further here.

It may seem strange at first that all of the groups involved in the reprocessing chemistry chose to look at the same basic idea — uranyl photochemical reduction to U(IV). However, realizing that the early workers were not aware of the plutonium and neptunium photochemistry and that they knew U(IV) was an acceptable chemical reductant for Pu(IV), the common course of action is not so difficult to understand. The later groups had the advantage of knowing that the quantum efficiency for direct reduction of Pu(IV) to Pu(III) was much less than that for photoreduction of uranyl to U(IV). In addition, there was the realization that uranyl could be photolyzed with light of wavelengths (7) well out in the visible while plutonium required the usage of ultraviolet radiation (<350 nm).

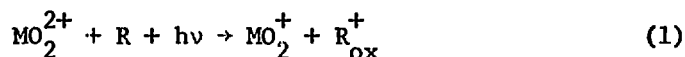
All of the photochemistry presented here will be with respect to aqueous solutions. Although others have considered photochemical reactions in organic media, the accompanying photo-degradation of organic molecules such as TBP (or oxidation of the organic molecules as a result of participation in photo-redox reactions) makes the organic phase an unattractive region for practical photochemical reprocessing.

Photochemical reactions of the actinides (and fission products) in the very radioactive dissolver solution have not been considered because the radioactive and otherwise-complex nature of the solution is such that controlled photo-reactions would be most

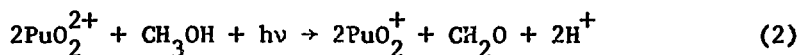
difficult therein. Downstream, however, in the aqueous stripping solution, conditions are much more amenable to the level of development presently achieved.

Uranium and Plutonium Reactions

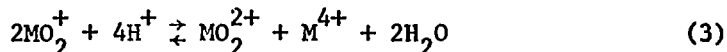
The photochemical reduction of the VI oxidation state:



(where M can be either uranium or plutonium) has been found to occur (8,9,10) using a variety of reductants, R, such as alcohols, aldehydes, hydrazine and hydroxylamine. The product of the reaction is the pentavalent actinide ion and the oxidized form of the reductant, R_{ox}^+ . For example:

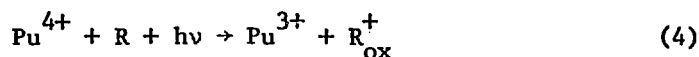


The MO_2^+ species of uranium and plutonium is ordinarily unstable and undergoes rapid disproportionation via:

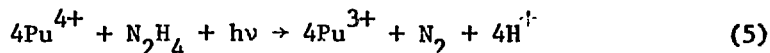


with the resulting formation of tetra- and hexa-valent actinide ions. A comparison of the quantum efficiencies for these reactions, listed in Table II, reveals one reason why the photo-reprocessing proposals rely so heavily on the uranyl photoreduction; it is simply a matter of higher efficiency.

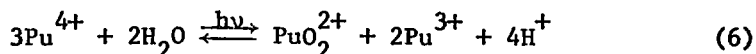
Other reactions observed for plutonium have been (1) the direct photochemical reduction of Pu(IV) using reductants such as formic acid, ethanol and hydrazine (8,9,10) in perchloric acid:



For example:



where quantum efficiencies as shown in Table II have been measured. (2) Photo-equilibrium shift of the Pu(IV) disproportionation reaction (9,10):



which, in reality, is a two-step equilibrium that involves the PuO_2^+ intermediate; and (3) Photo-assisted depolymerization of Pu(IV) hydrous polymers. (9,10) None of these will be further discussed because they have already been presented in detail and

Table II. Quantum efficiencies for the redox reactions of the actinides shown as a function of acid concentration, when known. Redox agents marked with * are associated directly with the solvent medium.

Reaction	Wavelength	Redox agent	Medium	Quantum efficiencies for Acid concentration (mole/liter)			
				0.1	0.5	1.0	4.0
U(VI) → U(IV)	250-600 nm	C ₂ H ₅ OH	H ₂ SO ₄ , HNO ₃	0.5	.5	.5	.5
Pu(VI) → Pu(IV)	<350nm	C ₂ H ₅ OH	HClO ₄ , HNO ₃			0.01	
Pu(IV) → Pu(III)	<350	C ₂ H ₅ OH, N ₂ H ₄	HClO ₄ , HNO ₃			0.03	
Np(VI) → Np(V)	254	C ₂ H ₅ OH	HClO ₄	.07	.068	.068	.040
	300	"	"			.068	
	254	*NO ₂ ⁻	HNO ₃	.04		.03	.002
	300	"	"	.001		.002	
Np(V) → Np(IV)	254	C ₂ H ₅ OH	HClO ₄	.006	.006	.008	.011
	300	"	"			.004	
Np(IV) → Np(III)	254	"	"	.03	.02	.02	.02
	300	"	"			.01	
Np(IV) → Np(V)	254	*ClO ₄ ⁻	HClO ₄	.02	.011	.010	.005
Np(V) → Np(VI)	254	"	"	.004	.005	.010	.010

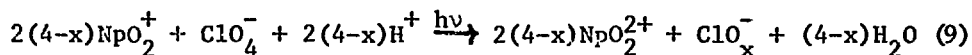
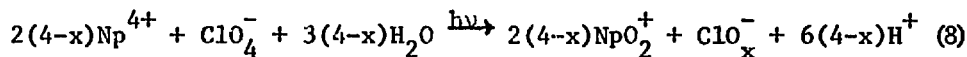
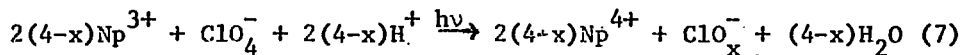
space here is limited. Instead, attention shall be focused on photo-reprocessing related chemistry and, in particular, neptunium which has not been previously considered.

Neptunium Reactions

Neptunium, like its plutonium neighbor, can exist in oxidation states that vary from +3 to +6 (disregarding the +7 state which is not pertinent to reprocessing-related solutions). In contrast to its uranium and plutonium analogs, neptunium has a very stable +5 oxidation state which tends to dominate the chemistry of inorganic acid solutions. Nemodruk and coworkers were the first to study the photo-redox reactions of Np and they looked separately at perchloric acid (11), hydrochloric acid (12), nitric acid (13) and sulfuric acid (14) media. However, noticeably absent in their work was any consideration of quantum efficiencies and wavelength effects for the various photoredox reactions.

The recent photochemistry interests at Oak Ridge have been turned to an examination of these aspects for neptunium in perchloric (15) and nitric acid (16) solutions. A perchloric acid medium provides a much simpler starting point because the ClO_4^- ion is not subject to photolysis as is the NO_3^- ion when exposed to light of 250-360 nm wavelength. Nevertheless, nitric acid media were ultimately examined because of their obvious practical importance.

In perchloric acid, solutions of Np(III), (IV), and (V) are oxidized after the absorption of 254 or 300 nm radiation in a stepwise fashion according to the following general reactions (15):

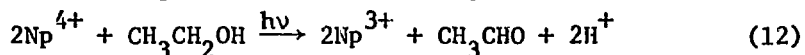
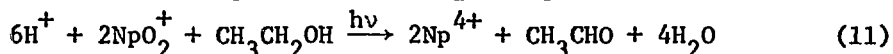
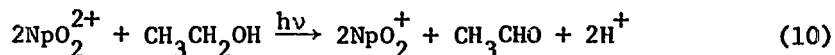


where the by-product ion is suspected to be either ClO_2^- or ClO^- . The change in species concentration for Np(IV) photo-oxidation is shown in Fig. 1 while that for Np(V) photo-oxidation is shown in Fig. 2. Quantum efficiencies for these and other reactions are given in Table II. The complex changes which occur when Np(IV) is photo-oxidized (cf., Fig. 1) demonstrate that several phenomena take place simultaneously. These include: (1) the retarding effects from the product ion ClO_x^- as seen at 250 minutes for the Np(V) species in 0.1 N H^+ ; (2) the acceleration of the Np(V) formation rate in 4.0 N acid as Np(V) accumulates and is, in turn, photo-oxidized at a higher quantum efficiency to Np(VI) which then combines rapidly with the residual Np(IV) to form Np(V); and (3) the build-up of Np(VI) in the low acid media prior to complete conversion of Np(IV) to Np(V), which is in contrast to the

observation of the previous workers (11).

The photo-oxidation of Np(V) is more straight-forward since there are only two species possible. Figure 2 shows the effect of acid as expected from the reaction given in Eq. 9.

The photo-chemical reduction of neptunium in aqueous perchloric acid is complicated because it must compete at times with the oxidation processes caused by the HClO_4 . In contrast to the previous study (11), the current results show that even the Np(III) state can be photochemically generated. The overall photoreduction reactions using ethanol have been identified as:



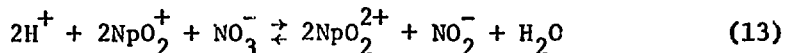
and the quantum efficiencies are given in Table II for each of these reactions. For more detail on this chemistry, the reader is referred to an earlier publication (15).

The photo-redox reactions of neptunium in nitric acid are, as stated earlier, complicated by the NO_3^- photo-reduction which prevents the complete photo-oxidation of neptunium to the (VI) state. At first this might seem to pose a dilemma which ought to be avoided, but recent results have shown how this apparent complication is essential to a photo-separation process. Two photo-chemical reactions working together will be shown to be necessary in order to reach what we have accepted as a practical result.

Photochemistry of Pure Solutions. In the absence of any added reductants, nitric acid solutions of Np(VI) and Np(IV) are converted to Np(V). The photochemistry of Np in nitric acid differs from that in HClO_4 solutions since in the former, reduction of Np(VI) \rightarrow Np(V) occurs, while in the latter, oxidation of Np(V) \rightarrow Np(VI) is observed (cf., Fig. 2 and Eq. 9). The difference is obviously due to the presence of photochemically produced NO_2^- which serves as the reductant for Np(VI). The quantum efficiencies for Np in Table II show that the reactions occur best when irradiated with 254 rather than 300 nm light in agreement with the increased QY for NO_3^- photo-reduction at shorter wavelengths (23) but in opposition to the difference in NO_3^- light absorption as shown in Fig. 3. The Np(VI) reduction probably involves an excited state of Np, but the evidence in support of this is not conclusive. Although the quantum efficiency for Np(VI) reduction is not as great as that for the reduction of UO_2^{2+} with ethanol or hydrazine, it is not so prohibitively low that it cannot be useful.

Exposure of Np(V) solutions to 254 nm radiation produces a

steady-state conversion of about 10 percent Np(V) \rightarrow Np(VI) which returns to Np(V) in the dark. These observations can be explained by the shift of the equilibrium:



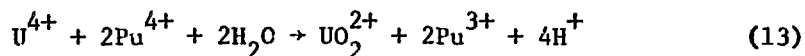
upon photo-excitation of NpO_2^+ .

Exposure of Np(IV) nitric acid solutions produces a simple photo-oxidation of Np(IV) \rightarrow Np(V) similar to the forward reaction of Eq. 13.

Photolysis with Added Reductants. The addition of hydrazine has little effect on the neptunium photo-reactions in nitric acid. There is some evidence that it serves as a reductant, but it is not enough to be significant. Experiments are still in progress which should further define the Np redox chemistry in the presence of added reductants; but the competition between the various redox reactions involving both solvent and added reagents limits the potential for application to process conditions.

Actinide Separation Processes

Taking the foregoing neptunium photochemistry into account, it would be useful to apply it to the development of a more complex photo-separation scheme than has been mentioned previously (19,24), one which includes Np, U and Pu. Since Np(VI) can be photochemically reduced in the absence of any intentionally added reductants, it might be possible to photolyze a nitric acid solution containing the three actinides, reducing the Np(VI) while leaving the Pu(IV) and U(VI) unchanged. After the Np(V) has been removed by an extraction process, hydrazine could then be added and the solution photolyzed to achieve the simultaneous reduction (as was described previously) of UO_2^{2+} to U^{4+} and Pu^{4+} to Pu^{3+} with the accompanying assistance of the reaction:



The separation of Np from U and Pu was actually accomplished in a 0.5 N HNO_3 starting solution containing approximately 0.005 M, each, of Np(VI), U(VI) and Pu(IV). Previously, it was demonstrated that Pu and Np could be individually separated from U (19,24). The results of these separation processes are shown in Table III, thus demonstrating photo-separations of these ions are feasible.

Summary

To summarize the promise of actinide photochemistry briefly, it has been found that all three major actinides have a useful

Table III. Effect of light on the reductive extraction of Np-Pu-U solutions.

Solutions (approx 10 cc) typically contained approx. 0.005 M of each actinide in question. Wavelength, exposure time, absorbed intensity, starting acidity, and final adjusted acidity were as follows: A, 254 nm, 20 min, 1W, 0.5 N, 2.0 N; B, 200 nm, 30 min, 1W, 1.4 N, 2.6 N (contained also 0.5 M hydrazine nitrate); C, 254 nm, 10 min, 1W, 0.5 N, 2.0 N. Acidification was followed by extraction into an equivalent volume of 30% TBP in dodecane. Part B taken from previous results (19,24).

	Dark Sample	Light Sample
A Separation of Neptunium from Np-U Mixture		
Aqueous Layer	14% Np 12.4% U	93.8% Np 12.3% U
TBP Layer	86% Np 87.6% U	6.2% Np 87.7% U
B Separation of Plutonium from Pu-U Mixture		
Aqueous Layer	33% Pu 3% U	90% Pu 3% U
TBP Layer	67% Pu 97% U	10% Pu 97% U
C		
Aqueous Layer	22% Np 18.1% U 16% Pu	82.3% Np 13% U 20% Pu
TBP Layer	78% Np 81.4% U 84% Pu	17.7% Np 86% U 80% Pu

variety of photochemical reactions which could be arranged in a sequence to achieve a separations process that requires fewer reagents, and, understandably, a reduced volume of waste solutions. Most of the impact of photochemistry on reprocessing is admittedly speculative since only the chemical feasibility has been demonstrated.

Nevertheless, the attractive characteristics of photochemical reactions will continue to be stated (and sometimes overstated) as laser-related research interests grow. During the past years, we have realized several features which merit enumerating in conclusion: (1) Laser photochemistry is not, at the moment, as uniquely important in fuel reprocessing as it is in isotopic enrichment. The photochemistry presently at hand can be successfully accomplished with conventional light sources. (2) The easiest place to apply photo-reprocessing is on the three actinides discussed here. The solutions are potentially cleaner and more amenable to photo-reactions. (3) Organic-phase photo-reactions are probably not worth much attention because of the troublesome solvent redox chemistry associated with the photochemical reaction. (4) Upstream process treatment on the raffinate (dissolver solution) may never be too attractive since the radiation intensity precludes the usage of many optical materials and the nature of the solution is such that light transmission into it might be totally impossible.

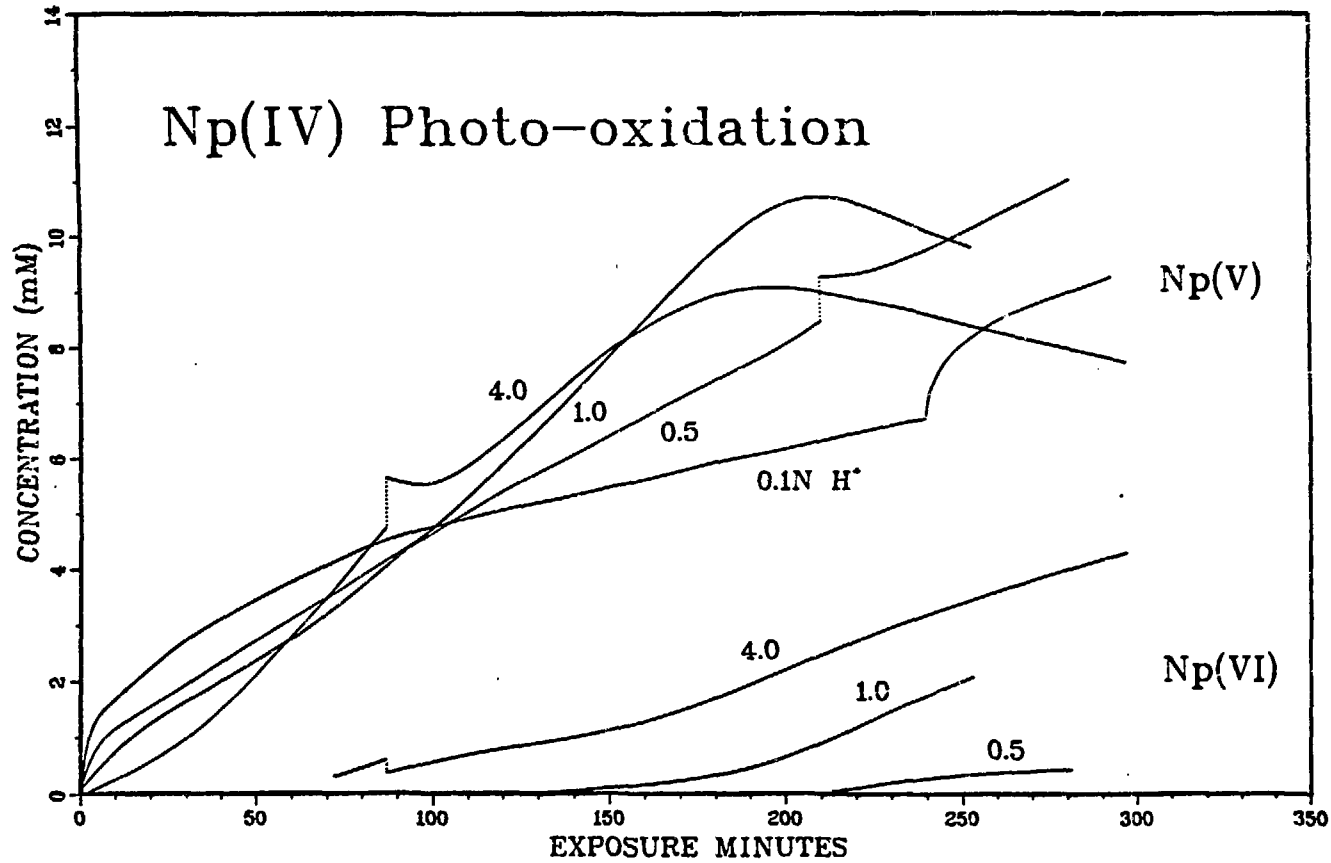
Literature Cited

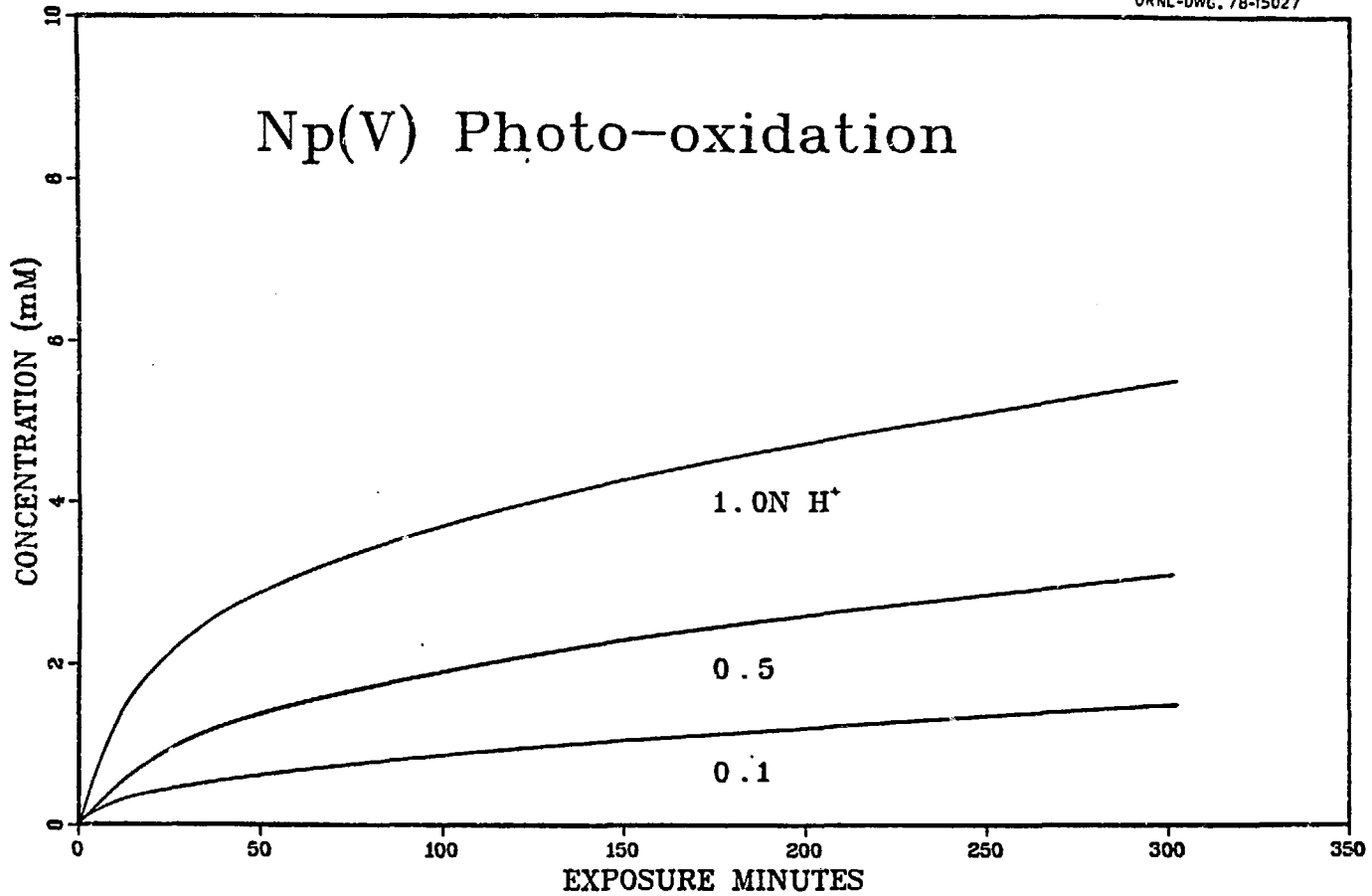
1. Croft, A. G.; Tedder, D. W.; Drago, J. P.; Blomeke, J. O.; Perona, J. J. "A Preliminary Assessment of Partitioning and Transmutation as a Radioactive Waste Management Concept"; ORNL/TM-5808, Sept. 1977.
2. See for example: Moore, W. J. "Physical Chemistry"; 4th ed., Prentice Hall Inc.; New Jersey, 1972; p. 792.
3. Calvert, J. G.; Pitts, J. N. Jr. "Photochemistry"; John Wiley & Sons Inc., New York, 1966.
4. Bell, J. T.; Biggers, R. E. J. Mol. Spectry., 1968, 25, 312.
5. Bell, J. T.; Friedman, H. A., Billings, M. R. J. Inorg. Nucl. Chem., 1974, 36, 2563.
6. Nemodruk, A. A.; Bezrogoва, E. V. Zh. Anal. Khim., 1968, 23, 388.
7. Bell, J. T.; Buxton, S. R. J. Inorg. Nucl. Chem., 1974, 36, 1575.
8. Palei, P. N.; Nemodruk, A. A.; Bezrogoва, E. V. Radiokhimiya, 1969, 11, 300.
9. Bell, J. T.; Friedman, H. A. J. Inorg. Nucl. Chem., 1976, 38, 831.
10. Friedman, H. A.; Toth, L. M.; Bell, J. T. J. Inorg. Nucl. Chem., 1977, 39, 123.
11. Nemodruk, A. A.; Bezrogoва, E. V.; Ivanova, S. A.; Novikov, Yu. P. Zh. Anal. Khim. 1972, 27, 73.

12. Nemodruk, A. A.; Bezrogova, E. V.; Ivanova, S. A.; Novikov, Yu. P. Zh. Anal. Khim. 1972, 27, 1270.
13. Nemodruk, A. A.; Bezrogova, E. V.; Ivanova, S. A.; Novikov, Yu. P. Zh. Anal. Khim. 1972, 27, 2414.
14. Nemodruk, A. A.; Bezrogova, E. V.; Ivanova, S. A.; Novikov, Yu. P. Zh. Anal. Khim. 1973, 28, 379.
15. Friedman, H. A.; Toth, L. M.; Osborne, M. M. J. Inorg. Nucl. Chem. 1979, in press.
16. Toth, L. M.; Friedman, H. A. (results to be published).
17. Carroll, J. L.; Burns, R. E.; Warren, H. D. "The Photo-activated Reduction of Uranium (VI) to Uranium (IV) Nitrate" HW-70543, 1961.
18. Wilson, A. S. "Organic Phase Reduction of Plutonium in a Purex-Type Process", U.S. Patent 3,620,687 (1971).
19. Friedman, H. A.; Toth, L. M.; Bell, J. T. "Method for Selectively Reducing Plutonium Values by a Photochemical Process", U.S. Patent 4,131,527 (12/26/78).
20. Goldstein, M.; Barker, J. J.; Gangwer, T. "A Photochemical Technique for Reduction of Uranium and Subsequently Plutonium in the Purex Process", BNL-22443 (1976).
21. Rofer-DePoorter, C.K.; DePoorter, G. L.; Hayter, S. W. "Photochemically Produced Uranium (IV) as a Reductant for Plutonium (IV) and Applications in LWR Fuel Reprocessing", LA-UR-78-383 (1978).
22. DePoorter, G. L.; Rofer-DePoorter, C. K. "Application of Photochemical Techniques to Actinide Separation Processes", Preceeding paper in this symposium.
23. Kistiakowsky, G. B. "Photochemical Processes", ACS Monograph Series, 1928, p. 225.
24. Toth, L. M.; Friedman, H. A.; Bell, J. T. "Photochemical Separation of Actinides in the Purex Process" CONF-770506-1 (1977).

Figure Titles

- Figure 1. Photo-oxidation of Np(IV) with 254 nm radiation at 22°C. Formation of Np(V) and Np(VI) products shown. Total [Np] = 12 mM for each solution photolyzed. Dotted portions on curves represent dark period interruptions during the photolysis run.
- Figure 2. Photo-oxidation of Np(V) with 254 nm radiation at 22°C. Total [Np] = 12 mM for each solution photolyzed. Np(VI) concentration as a function of time shown.
- Figure 3. Absorption spectrum of HNO₃. Concentration = 0.1 N, cell pathlength = 1.0 cm.





3

ORNL . DWG 79-81

