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An Assessment of Photochemical Applications to Specific Stages in Savannah River Plant Actinide Reprocessing Streams

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Chemical Technology Division

AN ASSESSMENT OF PHOTOCHEMICAL APPLICATIONS TO SPECIFIC STAGES IN SAVANNAH RIVER PLANT ACTINIDE REPROCESSING STREAMS

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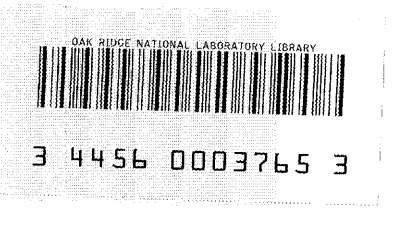

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ABSTRACT

The application of photochemical redox methods has been evaluated as a means of separating actinides in Purex reprocessing streams. This chemistry promises to eliminate many of the chemical reagents which are otherwise necessary to effect valence control of such actinides as plutonium and neptunium. The most promising processing stages of the Savannah River Plant reprocessing facility for feasibility testing of the photochemical method appear to be those in which the concentrations of the actinides in question are the lowest, thus minimizing the required amount of absorbed light. Although neptunium valence control appears to be feasible through the photochemical generation of nitrite ion, the urgency for its control is secondary to that of plutonium. Therefore, the Purex "2nd-U-cycle feed" stage has been selected as the top priority for testing the photochemical technique. The chemistry initially involves the photoreduction of U(VI) to U(IV), which in turn reduces Pu(IV) to Pu(III).

The results of preliminary experiments on nitrate ion and uranyl ion photoreduction are also given. With less than 100 W of absorbed power, the rates of NO_2^- and U^{4+} generation, respectively, appear ample to handle process requirements.

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1. INTRODUCTION

During recent years, we have given much attention to fundamental investigations of photochemistry as a means of actinide valence adjustment within Purex-related systems. Of the several reasons for desiring such an alternative means of valence control, perhaps the most compelling is the need to reduce the amount of waste solution generated in comparison to that when the customary chemical redox agents (i.e., ferrous sulfamate and sodium nitrite) are used.

The photochemistry of uranium, plutonium, and neptunium in aqueous nitric acid solution has been investigated, and many of the results have been described in the open literature.[1-4] In addition, several patents relating to specific processes, whereby these actinides may be photochemically separated from each other, have been either granted or filed.[5-7] The most attractive of these patents describes a means of separating neptunium from uranium and plutonium ions in aqueous nitric acid solution by first generating NO_2^- (photochemically from the NO_3^- ion) and utilizing the nitrite ion as the chemical reductant for Np(VI) to Np(V) conversion. Furthermore, it has been shown[8] that the nitrite ion reduction of Np(VI) is even greater if large amounts of uranyl ion, UO_2^{2+}, are present since the uranyl ion forms a complex with the Np(V) product, NpO_2^+, and thus shifts the equilibrium of Eq. (1) to the right:

$$2NpO_2^{2+} + NO_2^- + H_2O = 2NpO_2^+ + NO_3^- + 2H^+ . \qquad (1)$$

In addition, we have shown that it is possible to photochemically reduce Pu(IV) to Pu(III) using otherwise unsatisfactory reductants or by generating another reductant in solution (e.g., U(IV) present as U^{4+}), which in turn can reduce the Pu(IV) species.[5,9]

These photochemical reactions have received little attention as practical alternatives until recently when the Savannah River Laboratory (SRL) personnel became interested in incorporating them with system renovations that were being implemented at the Savannah River Plant (SRP). The current program at the Oak Ridge National Laboratory (ORNL) represents an effort to determine where the photochemical alternatives could be utilized at SRP and then, with further laboratory testing, to establish some of the scaleup parameters that would be necessary prior to testing under plant conditions.

This report describes an evaluation of various process areas (identified by the SRL staff) which would benefit most from the application of the photochemical alternative. In addition, some results on NO_3^- and UO_2^{2+} photolysis — which form the basis for Np(VI) and Pu(IV) reduction, respectively — are described.

2. GENERAL GUIDELINES

If a photochemical process is to be of practical value, it is necessary that certain criteria be met:

1. The solution must be transparent to the exciting photons except for the "target" species.
2. The target (i.e., the photochemically active entity) must have a quantum efficiency of sufficient value to effect adequate generation product.
3. The effective lamp power must be adequate for the application.

The ideal combination of these criteria will result in a rate of product generation that reaches the desired concentrations in an acceptable amount of time. In the case of a continuously flowing process, the rate of product generation should match the mass flows in question; as a result, it is important in any practical consideration to consider the mass flows that must be employed.

The number of photons per min per W of light varies with wave length, as indicated in Table 1. Also given in the table are the mol per min per W of product, providing the quantum efficiency or quantum yield (QY) of the process is unity. The table demonstrates that it would take approximately 8 W of absorbed 254-nm radiation to achieve a mmol/min

Table 1. Photons/min equivalency of a watt of power and the corresponding rate of product conversion if the quantum efficiency is unity

Wavelength (nm)	Irradiation rate (10^{19} photons/min)	Rate of product conversion (10^{-4} mol/min)
200	6.05	1.00
254	7.68	1.28
300	9.07	1.51
350	10.6	1.76
400	12.1	2.01

mass flow if the quantum efficiency for the photochemical process were unity. If the quantum efficiency were 0.1, however, as it would probably be for ions in some of these processes, then the absorbed wattage would have to be proportionately higher in order to maintain the same mass flow rate of product.

Therefore, the simplest test of the photochemical process would probably be under conditions in which the mass flow was very small so that a minimal amount of photochemically generated product would be required. Secondly, the photochemical reaction with the highest possible quantum efficiency should be sought; and finally, the system should be at a stage where there are few, if any, interfering absorptions.

An examination of the process flowsheets should give an indication of where mass flows have reasonable values to match typically available lamp powers. Details will be considered in Sect. 3.

Quantum efficiencies for various related photochemical processes have been previously reported[9] and are reproduced in Table 2. The generation of U(IV) from uranyl ion is the most efficient of the pertinent processes with a quantum efficiency of 0.5. The reduction of NpO_2^{2+} is perhaps the next most efficient process, based on the quantum efficiencies of 0.04 to 0.07 using 254-nm radiation. It occurs through a two-step process initially involving the photochemical generation of NO_2^-, which then reduces NpO_2^{2+} (see Sect. 6.2). Although not used at the time the data of Table 2 were generated, it is now known[10] that the addition of certain radical-gettering agents such as alcohols, hydrogen peroxide, and benzene will increase the yield of NO_2^- by limiting the back reaction of Eq. (2):

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O\bullet \qquad (2)$$

Table 2. Quantum efficiencies for the redox reactions of the actinides shown as a function of acid concentration, when known

Reaction	Wavelength (nm)	Redox agent[a]	Medium	Quantum efficiencies for acid concentration (M)			
				0.1	0.5	1.0	4.0
U(VI) → U(IV)	250-600	C_2H_5OH	H_2SO_4,HNO_3	0.5	0.5	0.5	0.5
Pu(VI) → Pu(IV)	<350	C_2H_5OH	$HClO_4$,HNO_3			0.01	
Pu(IV) → Pu(III)	<350	C_2H_5OH,N_2H_4	N_2H_4			0.03	
Np(VI) → Np(V)	254	C_2H_5OH	$HClO_4$	0.07	0.068	0.068	0.040
	300	C_2H_5OH	$HClO_4$			0.068	
	254	$*NO_2^-$	HNO_3	0.04		0.03	0.002
	300	$*NO_2^-$	HNO_3	0.001		0.002	
Np(V) → Np(IV)	254	C_2H_5OH	$HClO_4$	0.006	0.006	0.008	0.011
	300	C_2H_5OH	$HClO_4$			0.004	
Np(IV) → Np(III)	254	C_2H_5OH	$HClO_4$	0.03	0.02	0.02	0.02
	300	C_2H_5OH	$HClO_4$			0.01	
Np(IV) → NP(V)	254	$*ClO_4^-$	$HClO_4$	0.02	0.011	0.010	0.005
Np(V) → Np(VI)	254	$*ClO_4^-$	$HClO_4$	0.004	0.005	0.010	>0.010

[a]Redox agents marked with * are associated directly with the solvent medium.

3. FLOWSHEET ANALYSIS

Along with the general guidelines, it is then necessary to consider the process flowsheets and determine what stages would be most promising for application of photochemical processing. The major parameter of importance in this consideration, if a particular photochemical reaction is to be technically feasible, is the mass flow rate. It is desirable to find a step in the process which has the lowest possible flow rates in order to minimize the lamp requirements. In addition, photochemistry related to neptunium redox changes was more attractive than other reactions because previous experience demonstrated how simply it could be achieved.

The information in Table 3 was provided[11] for the flowsheet analysis considerations. Using half-lives of 24,400, 86, and 2.14×10^6 years for ^{239}Pu, ^{238}Pu, ^{237}Np, respectively, the following conversion factors were calculated:

$$10^8 \text{ dpm/mL} = 0.734 \text{ g/L } ^{239}Pu$$

$$10^{10} \text{ dpm/mL} = 0.277 \text{ g/L } ^{238}Pu$$

$$10^6 \text{ dpm/mL} = 0.656 \text{ g/L } ^{237}Np \text{ .}$$

These factors were used to convert the reported count rates to concentrations. The plutonium was always assumed to be ^{239}Pu unless specified otherwise. With this assumption, the plutonium concentration was maximized and, therefore, the lamp power requirements would always be adequate.

The information in Table 3 was converted to mass flow rates using the calculated concentrations (from the above factors) and the solution flow rates shown in column 3. These mass flow rates are presented in

Table 3. Savannah River processes requiring redox adjustment via oxidants or reductants

Process stream/step	Typical composition	Flow rate (L/min.)	Current procedure	Desired amount
Purex 1st-cycle (1B-bank)	80 g/L U 0.1 g/L Pu organic feed (1AP)	112	FS[a] and HAN[b] in 1BX reduction in bank	Pu(IV) → Pu(III)
Purex 2nd-U-cycle feed	400 g/L U 1 M acid Pu 10^3-10^4 dpm/mL	15	Add FS to feed	Pu(IV) → Pu(III)
Purex 2nd-Pu-cycle feed	<0.5 g/L Pu 3.5 M acid	20	Add nitrite to feed tank	Pu(III) → Pu(IV)
Purex 2nd-Pu-cycle strip	<0.1 M acid 0.1 M HAN Pu 3 g/L	4	Reduction occurs in bank operations	Pu(IV) → Pu(III)
Pu anion exchange	High nitrate, Al, Ca, Mg, F, and SS comp. 30 g/L Pu, 7.5 M HNO_3 2 g/L Pu in high salt soln.	 3 0.3	Reduction with FS, followed by $NaNO_2$	Pu(VI) → Pu(IV)
Pu(III) oxalate pptn. feed adjustment	3 M acid, 0.2 M sulfamate, 35 g/L Pu, 0.05 M HAN	1	Ascorbic acid added to help	Maintain Pu(III) and Pu(IV) → Pu(III)

Table 3. (continued)

Process stream/step	Typical composition	Flow rate (L/min.)	Current procedure	Desired amount
HM 1st-cycle feed (high enrichment)	<5 g/L U, 2 M acid, scrub is 4 M acid, Pu-238 10^8 dpm/mL	9	Scrub contains FS in situ reduction	Pu(IV) → Pu(III)
HM 1st-cycle feed (low enrichment)	<100 g/L U, 4.5 M acid, Np 10^3 dpm/mL	13	Nitrite added two steps: FS and NO_2^-	Np(IV,VI) → Np(V)
HM 2nd-Np-cycle feed (recycle of conc.)	5 g/L Np, 4.2 M acid, 0.06 M FS Pu 10^6 dpm/mL	17	FS added as reductant	Np(V,VI) → Np(IV) Pu(IV) → Pu(III)
HM 2nd-U-cycle feed	<6 g/L U, 4 M acid Pu 10^2 dpm/mL, Np 10^3 dpm/mL	14	Scrub contains FS to reject Pu and Np	Pu(IV) → Pu(III) Np(IV,VI) → Np(V)
Np anion exchange feed (agitated bed)	5-10 g/L Np, 8 M acid	1	FS co-fed to column	Assure Np(IV) anionic complex
Np oxalate pptn feed (B-Line anion exchange)	Butted to 3M acid; eluted with hydrazine, Np 30 g/L	1-2	Two steps: FS and NO_2^- valence adjustment	Assure low Np loss

[a]FS = Ferrous sulfamate.
[b]HAN = Hydroxylamine nitrate.

column 5 of Table 4, which is a reworked version of Table 3 with our numerical calculations added. Table 4 also shows a priority list (column 1) giving the most promising stages where a photochemical process might be applied.

The greatest potential (priority 1) for a photochemical process has been identified as the Purex 2nd-U-cycle feed. This stage of the process requires the reductive separation, Pu(IV)-Pu(III), of plutonium from a 400 g/L uranyl solution. Since the [Pu] is 10^7 to 10^8 times less than that of the $[UO_2^{2+}]$ and the potentially efficient reduction of $UO_2^{2+} \longrightarrow U^{4+}$ (QY = 0.5) can be utilized to provide the necessary reductant for Pu(IV) via

$$2H_2O + 2Pu^{4+} + U^{4+} \longrightarrow 2Pu^{3+} + UO_2^{2+} + 4H^+ \quad ,$$

very few photons would be required for the process.

The second priority that has been selected is the "HM 2nd-U-cycle feed," primarily because the concentrations of plutonium and neptunium are sufficiently small. Nevertheless, some added reductant (e.g., hydrazine or alcohol) would be required in order to effect the photoreduction of Pu(IV); and since we already recommend a small amount of methanol in the system, it would probably serve as the reductant for the Pu(IV) as well.

The third priority, involving an organic stream, would require either photoreduction in the organic phase or in an aqueous phase in contact with it. The former of these possibilities has been attempted previously[7] but suffers from the accompanying photolysis of the TBP extractant; the latter procedure would require the development of some hardware to permit a sidestream of recycle stream reduction.

Table 4. Savannah River processes requiring redox adjustments via oxidants or reductants

Priority	Process stream/step	Typical composition	Concentration[a]	Flow rate (L/min)	Mass flow (mol/min)
3	Purex 1st cycle (1B-bank)	80 g/L U 0.1 g/L Pu Organic feed (1AP)	0.336 M U $4.18\ 10^{-4}$ M Pu	112	37.6 U 0.0468 Pu
1	Purex 2nd-U-cycle feed	400 g/L U 1 M acid Pu 10^3-10^4 dpm/mL	1.70 M U $3.18\ 10^{-8}$ to $3.1\ 10^{-7}$ M Pu	15	25.5 U $4.7\ 10^{-7}$ to $4.7\ 10^{-6}$ Pu
	Purex 2nd-Pu-cycle feed	<0.5 g/L Pu 3.5 M acid	$2.092\ 10^{-3}$ M Pu	20	0.0418 Pu
	Purex 2nd-Pu-cycle strip	<0.1 M acid 0.1 M HAN[b] Pu 3 g/L	0.01255 M Pu	4	0.0502 Pu
	Pu anion exchange	High nitrate, Al, Ca, Mg, F, and SS comp. 30 g/L Pu, 7.5 M HNO_3 2 g/L Pu in high salt soln.	0.1255 M Pu 0.00837 M Pu	3 0.3	0.377 Pu 0.0025 Pu
	Pu(III) oxalate pptn.	3 M acid, 0.2 M sulfamate 35 g/L Pu 0.05 M HAN	0.1464 M Pu	1	0.146 Pu

Table 4. (continued)

Priority	Process stream/step	Typical composition	Concentration[a]	Flow rate (L/min)	Mass flow (mol/min)
	HM 1st cycle feed (high enrichment)	<5 g/L U 2 M acid Scrub is 4 M acid Pu-238 10^8 dpm/mL 3×10^{-2} g/L Np	<0.021 M U 1.164×10^{-5} M Pu	9	<0.189 U 0.000105 Pu 0.0011 Np
	HM 1st cycle feed (low enrichment)	<100 g/L U 4.5 M acid Np 10^3 dpm/mL 1.5×10^{-2} g/L Pu	<.42 M U 2.77×10^{-6} M Np	13	<5.46 U 0.00003601 Np 0.00082 Pu
	HM 2nd-Np-cycle feed (recycle of conc.)	5 g/L Np 4.2 M acid 0.06 M FS[c] Pu 10^6 dpm/L	0.021 M Np 3.072×10^{-5} M Pu	17	0.357 Np 0.000522 Pu
2	HM 2nd-U-cycle feed (high enrichment)	<6 g/L U 4 M acid Pu 10^2 dpm/mL Np 10^3 dpm/mL	<0.025 M U 3.05×10^{-9} M Pu 2.77×10^{-6} M Np	14	<0.35 U 4.27×10^{-8} Pu 3.87×10^{-5} Np
	Np anion exchange feed	5-10 g/L Np	0.021-0.042 M Np	1	0.021-0.042
	Np oxalate pptn fed (B-line anion exchange)	Butted to 3 M acid; eluted with hydrazine Np 30 g/L	0.1266 M Np	1-2	0.1266-0.2532

[a] Pu-239 has been assumed in all cases where ^{238}Pu is not indicated. Otherwise, the [Pu] would be 265 times lower.
[b] HAN = hydroxylamine nitrate.
[c] FS = ferrous sulfamate.

The other process steps shown in Table 4 could be assigned priority levels also, but the limited opportunity for photochemical applications in reprocessing operations would make the listing meaningless at this time. We believe than the effort to apply photochemical techniques should be focused on no more than these three priorities, with special emphasis on the first at this particular time.

4. OTHER APPLICATIONS TO PUREX SYSTEM

Practical experience at ORNL has demonstrated that the reoxidation of Pu(III) to Pu(IV) occurs during the reductive stripping of Pu(IV) in mixer-settler contactors, with the Pu(IV) appearing in the organic phase. This reoxidation apparently sets up a cyclic oxidation/reduction process that consumes large quantities of hydroxylamine. If such a process is also found to occur in the SRL system, some U(IV) could be photochemically generated and transferred to the organic phase where it might serve to prevent the reoxidation of Pu(III).

Furthermore, the use of hydroxylamine for plutonium reduction is not as effective as when hydrazine is used as a holding agent since the former is much slower in reducing NO_2^-. [The presence of NO_2^- is known to promote the oxidation of Pu(III) to Pu(IV).] It might be possible to increase these kinetics through the application of a photochemical step. However, both of these processes would require much laboratory development prior to a more extensive consideration of an application to a working process. Before such laboratory work is initiated, it would be necessary to determine if there is any merit in these ideas with respect to the SRL operation.

5. SURVEY CONCLUSIONS

A review of the literature and study of the SRL flowsheet information reveals that photochemical processes could probably work very well as alternative means of actinide valence adjustment. The most promising stage appears to be in the Purex 2nd-U-cycle feed where Pu(IV) must be converted to Pu(III) in the presence of 400 g/L UO_2^{2+}. The low mass flow rate of plutonium, 4.7×10^{-7} to 4.7×10^{-6} mol/min requires only a minimal amount of absorbed radiation. The more efficient photoreduction of the UO_2^{2+} ion, which in turn reduces the Pu(IV) reduces the amount of required radiation even further --- to less than 100 W of absorbed power. Finally, the radiation need only be visible light since the UO_2^{2+} is effectively photolyzed at wavelengths >350 nm.

6. LABORATORY STUDIES

6.1 EXPERIMENTAL PROCEDURE

The photolysis of nitric acid solutions was performed in two systems. The first is shown in Fig. 1 and consisted of a small compact silica cell surrounded by a low-pressure Hg-arc coil emitting 254-nm radiation. The growth of the nitrite species produced was monitored during the photolysis by passing the spectrophotometer light beam down the horizontal aluminum support tubes that were attached to the ends of the cell.

The second system used in the study of the HNO_3 photolysis consisted of a coil of silica tubing that surrounded a 1000-W, high-pressure, Hg-Xe arc and through which the nitric acid solution was pumped. The solution circuit also included a pass through a cooling coil for temperature

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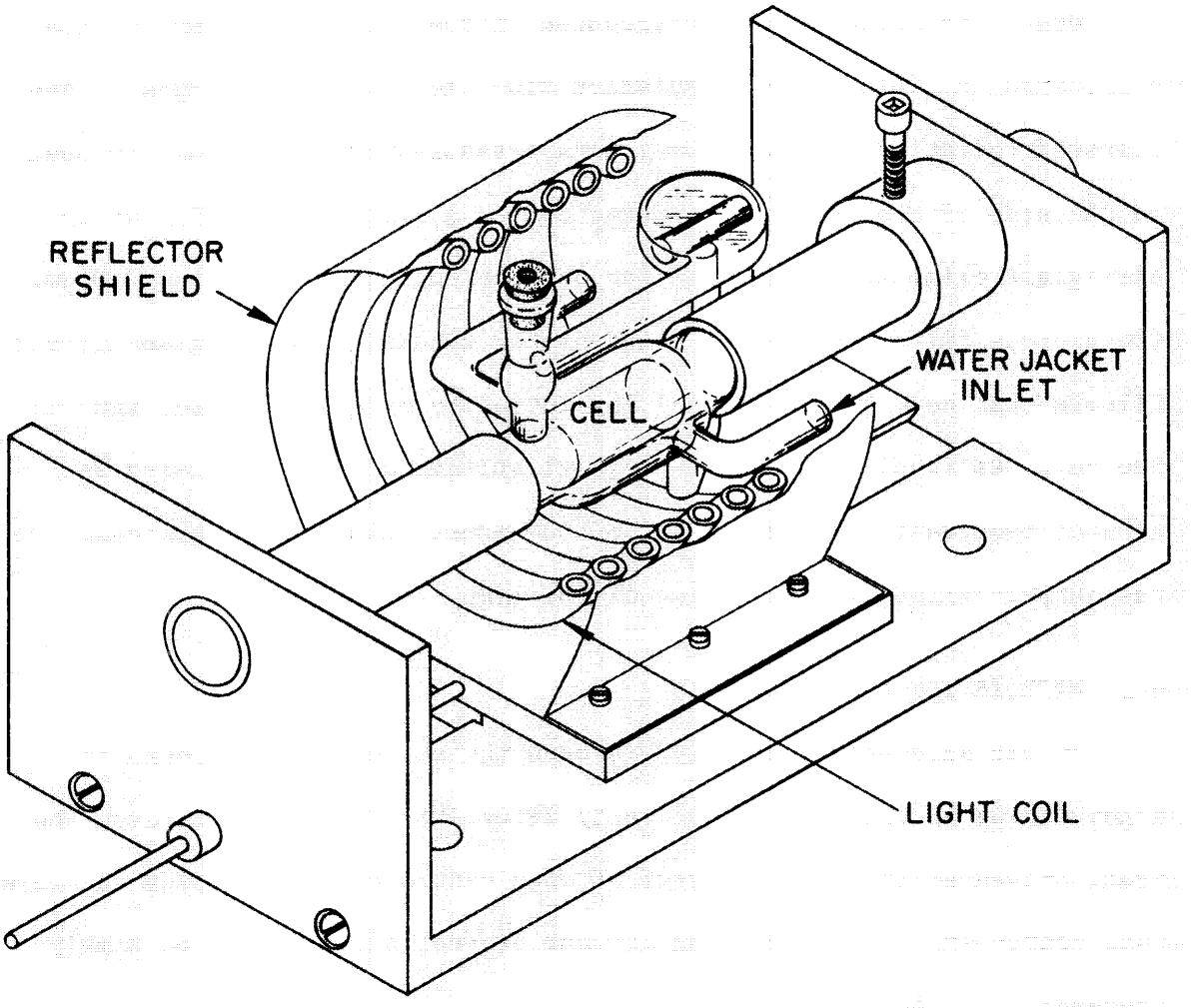

Fig. 1. Compact photochemical cell that permits in-line absorption spectrophotometric measurements.

control and from there to an in-line spectrophotometer cell where the progress of the photolysis was monitored.

Uranyl solutions were photoreduced in the cell arrangement of Fig. 1; but instead of using 254-nm radiation from the low pressure Hg arc, the filtered radiation from a 1000-W, high-pressure, Hg-Xe lamp was focused on the side of the spectrophotometer cell. A simple cutoff filter of plexiglass eliminated all radiation of wavelengths shorter than 350 nm. (This crude filter was used in lieu of the standard Corning glass cutoff filters that have been ordered.) The intensity of the absorbed light in the cell was found to be ~1 W by uranyl sulfate actinometry using an ethanol reductant; regular checks of the exact value were required since the output varied with the aging of the lamp.

6.2 NITRATE ION PHOTOLYSIS

Nitric acid photochemistry has been the subject of considerable study dating as far back as the early 1900s.[10,12-14] Nevertheless, the exact mechanism is still a matter of some controversy.[13] Hoping to avoid that controversy, the mechanism for our present purposes can be simply represented by Eq.(2).

From the absorption spectrum of Fig. 2, we see that the nitrate ion absorbs throughout the ultraviolet region. Photochemical activity as far out as 300 nm has been reported,[10] but the highest quantum efficiencies are typically found at the shorter wavelengths.[12] In spite of the smaller absorption coefficient at 254 nm, we have found it convenient to utilize a low-pressure mercury discharge lamp to generate the nitrite ion, because most (95%) of the lamp radiation is emitted at 254 nm with a minimal amount of heat.

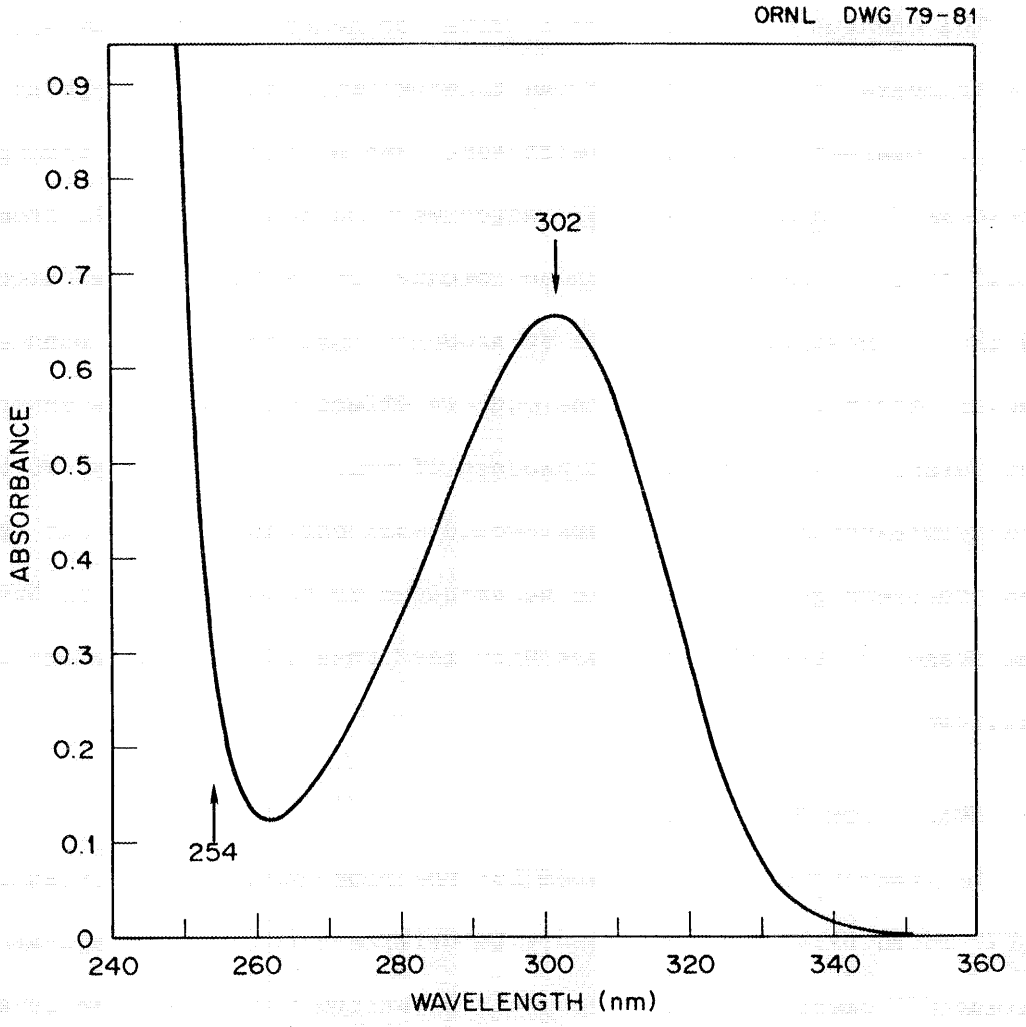

Fig. 2. Absorption spectrum of NO_3^-. Molar absorptivity at 302 nm = 7 $\underline{M}^{-1}$ cm^{-1}.

The quantum efficiency for nitrite ion generation is unusually low in acid media, as indicated by the quantum efficiency-versus-pH curves in Fig. 3. However, the quantum efficiency can be increased by adding as little as 0.05 M methyl alcohol, which we have found raises it from ~0.025 to 0.1. Methanol was chosen because it is the simplest alcohol and thus is most likely to give by-products that are easy to handle. However, ethanol was found to be equally effective; and it is expected that butanol, (a decomposition product of tributyl phosphate), which is already present in trace amounts, would work satisfactorily. It appears, then, that enough nitrite could be produced to reduce Np(VI) to Np(V) at some stages of the SRP processes with less than 100 W of absorbed 254-nm radiation.

6.3 URANYL ION PHOTOLYSIS

In order to develop a system for the photochemical reduction of Pu(IV) to Pu(III), it is necessary to utilize a reductant that has a maximum efficiency both with respect to quantum yield and kinetic speed. (The reason for separating these two apparently redundant characteristics will be obvious in the following discussion.) We have not found a reductant that satisfies those requirements directly, since the direct photochemical reduction of Pu(IV) has never been found to be very efficient. However, the dark reaction of U(IV) with Pu(IV) is so effective, and thus attractive, that a photochemical means of reducing U(VI) to U(IV) could provide a very satisfactory indirect photochemical reduction of Pu(IV).

From the quantum efficiencies in Table 2 for uranyl ion reduction, we see that a maximum value of 0.5 is feasible. Furthermore, it is possible to achieve this reduction with a variety of reductants and with light of relatively low photon energy (i.e., visible light).

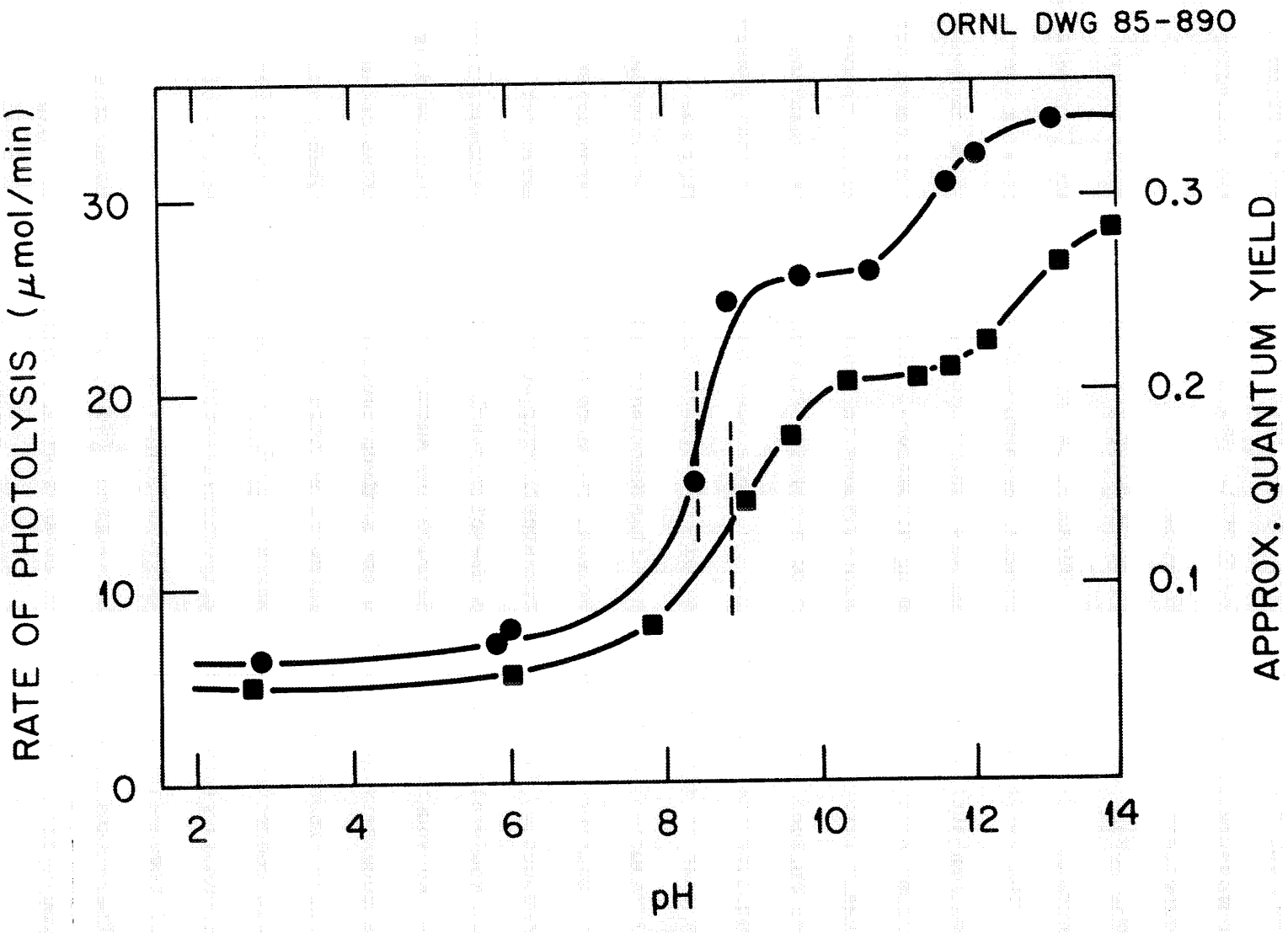

Fig. 3. Quantum yield for NO_2^- production from NO_3^- versus pH using 300-nm radiation. Taken from ref. 10. By using information in ref. 12, the value at 30 μM/min is equivalent to a QY of 0.3.

We sought to determine optimal conditions for uranyl ion reduction and then built a laboratory-scale system that utilized the U(IV) product in a demonstration reduction of Pu(IV). The uranyl photolysis optimization experiments are described below.

The reductants that were considered for the uranyl photolysis were (1) methanol, (2) ethanol, (3) butanol, (4) hydroxylamine, and (5) hydrazine. The first two were considered because they are favorites in fundamental investigations and the last three because they are more common constituents in fuel reprocessing situations. Although most of these are comparably effective as reductants, shown in Table 5, we found it necessary to include a small amount of a holding reductant such as hydrazine, to stabilize the U(IV) product. [We have considered, however, the possibility that it might be unnecessary to hold U(IV) stable during the actual reduction of Pu(IV) since it might react before being reoxidized by any impurity ions. Nevertheless, the same stability concerns exist with respect to Pu(III), and the stabilizing agent that is added for Pu(III) would also probably be useful for U(IV).] In the development procedure, we sought mainly to minimize the amount of reductant and holding agents necessary and to obtain the maximum conversions and rates for a given light input (which was found to be about 0.7 W of absorbed power). The acid concentration was fixed at 1 M HNO_3 to be consistent with the conditions as given in the first priority of Table 4. The results of some of these experiments are given in Table 5.

These data demonstrate that butanol (BuOH) is the most effective reducing agent in comparison to those tested. Hydrazine (N_2H_4) was approximately ten times less effective and hydroxlyamine nitrate (HAN)

Table 5. Photochemical reduction of 1.25 M uranyl nitrate in 1 M HNO_3 using ~0.7 W of absorbed power from a 1000-W, Hg-Xe, high-pressure arc lamp.

(Radiation filtered to achieve a cutoff of all wavelengths below 350 nm; volume of the photochemical cell, 15 mL.)

Reductant	Photolysis time (min)	U(IV) production	
		Max. conc. (10^{-3} mol/L)	Rate (10^{-6} mol/min)
1 M N_2H_4	60	33	9.5
0.1 M N_2H_4	120	27	3.6
0.01 M N_2H_4	60	1.4	0.37
0.1 M HAN	40	0	0
0.05 M HAN/0.05 M N_2H_4	120	10	1.3
0.1 M BuOH	60	6.4	1.5
0.1 M BuOH/0.01 M N_2H_4	9	26	43
0.01 M BuOH/0.01 M N_2H_4	48	11	4.0
0.01 M BuOH/0.001 M N_2H_4	40	9.4	4.1
0.01 M BuOH/0.005 M N_2H_4	54	9.4	4.2
0.01 M BuOH/0.0001 M N_2H_4	36	9.6	4.1
0.01 M EtOH/0.01 M N_2H_4	56	7.5	2.4
0.001 M TBP	20	0	0

was found to be totally ineffective. In fact, BuOH was even more effective than a comparable concentration of ethanol (EtOH). An aqueous nitric acid solution saturated with 30% tributyl phosphate (TBP) in n-dodecane (i.e., ~1 mM TBP) was found to be ineffective in reducing any of the uranyl ion present in solution. In all cases, the U(IV) that was produced was unstable unless hydrazine was present. A concentration of 0.01 M N_2H_4 was required to hold the U(IV) produced for a period of 4 to 5 h, whereas 0.001 M was only effective in holding the U(IV) for a period of a few minutes.

These results demonstrate that an optimal starting system for the subsequent reduction of Pu(IV) would consist of 0.01 M BuOH/0.01 M N_2H_4 and would yield a U(IV) production rate of 4×10^{-6} mol/min. In our particular system of 0.015-L volume, this would net 11 mM U(IV) after 48 min of photolysis. This situation is considered to be adequate to reduce any Pu(IV) that might be present.

REFERENCES

1. J. T. Bell and H. A. Friedman, J. Inorg. Nucl. Chem. 38, 831 (1976).

2. H. A. Friedman, L. M. Toth, and J. T. Bell, J. Inorg. Nucl. Chem. 39, 123 (1977).

3. H. A. Friedman, L. M. Toth, and M. M. Osborne, J. Inorg. Nucl. Chem. 41, 1339 (1979).

4. L. M. Toth and H. A. Friedman, Radiochem. Acta 27, 173 (1980).

5. H. A. Friedman, L. M. Toth, and J. T. Bell, "Method for Selectively Reducing Plutonium Values by a Photochemical Process," U.S. Patent No. 4,131,527.

6. H. A. Friedman and L. M. Toth, "Method for Selectively Reducing Neptunium Values by a Photochemical Process," patent applied for May 12, 1983.

7. G. L. DePoorter and C. K. Rofer-DePoorter, "Method for Photochemical Reduction of Uranyl Nitrate by TBP and Application of this Method to Nuclear Fuel Reprocessing," U.S. Patent No. 4,080,273.

8. L. M. Toth and H. A. Friedman, J. Inorg. Nucl. Chem. 43, 1611 (1981).

9. L. M. Toth, J. T. Bell, and H. A. Friedman, "Photochemistry of the Actinides," in Actinide Separations, J. D. Navratil and W. W. Schulz, eds., American Chemical Society Symposium Series #117, ACS, Washington, DC, 1080.

10. M. Daniels, R. V. Meyers and E. V. Belardo, J. Phys. Chem. 72(2), 389 (1968).

11. Communication from J. R. Wiley, Savannah River Laboratory, November 16, 1984.

12. G. B. Kistiakowsky, Photochemical Processes, American Chemical Society Monograph Series, The Chemical Catalog Co., Inc., New York, 1928, pp. 224-227.

13. A. V. Dubovitskii, L. N. Leksina, and G. B. Manelis, Khimiqa Vysokikh Energii 15(4), 347-350 (19810.

14. I. Wagner, H. Strehlow, and G. Busse, Zeit. fur Phys. Chem. (Neue Folge) 123, 1 (1980).

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