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A PHOTOCHEMICAL TECHNIQUE FOR REDUCTION OF
URANIUM AND SUBSEQUENTLY PLUTONIUM IN THE PUREX PROCESS

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ABSTRACT

A photochemical modification of the purex process is described in which a purified side stream of UO_2^{++} ion is reduced to U^{+4} outside the radioactive area of the reprocessing plant. The U^{+4} is then cycled back to step 2 of the purex process to reduce the Plutonium and effect separation within the partitioning column. This process is shown to be very energy efficient and compatible with existing conventional lamp technology. Preliminary cost estimates of the energy requirements for photon production are essentially negligible. Conceptual systems and photochemical reactor designs are presented. Potential benefits of this system are discussed.

INTRODUCTION

There have been numerous accounts of selective, quantitative photochemical reduction of U^{VI} (at concentrations as low as micromolar) to U^{IV} for solutions having large quantities of various contaminating ions.¹⁻⁴ Photoreduction of uranyl ions by various nonresidual reagents (a reductant that leaves no solids if the solution were evaporated to dryness) e.g., ethanol, formic acid, hydrazine, and H_2O_2 have been studied.³⁻⁸

The literature on uranium photochemistry is quite extensive, but the bulk of the data is 15 or more years old.⁶ There were numerous difficulties and contradictions in the data from the earlier studies. One source of difficulty was the failure to regulate the oxygen content of the solutions.³ Despite these limitations, there is sufficient evidence in several photoredox reaction systems to show that photochemistry has good potential for use in separating uranium from plutonium.

As early as the 1930's Ouellet⁽⁹⁾ demonstrated the reduction of $U(VI)$ by $HCOOH$ in the presence of nitrate ion. He measured the effects of various scavengers of the quantum yield and rate. He determined that nitrate inhibited the rate of reaction slightly using a polychromatic source. Under optimum conditions, he determined a quantum yield of approximately unity. Most recently Bell and co-workers⁽¹¹⁾ have performed some key experiments on uranium and plutonium photochemistry. These photochemical reduction experiments with $U(VI)$ in solution (approximately 1.0 molar nitric acid) indicate that high efficiency and reasonable rates can be expected in purex process type systems using either formic acid or hydrazine as reductants. Bell and co-workers avoided inhibiting effects from the nitrate decomposition by using filters on this light source, thus eliminating wavelengths which could produce nitrite ion.

Rofer-Depoorter and Depoorter⁽¹²⁾ determined that uranyl nitrate can be photochemically reduced in TBP solutions, with or without the presence of HNO_3 and water. Their work suggests that the formation of nitrite ion by UV photolysis of HNO_3 , slows the rate of reaction because the reduction takes place more readily with visible than ultraviolet light. It was the failure of early investigators to study the effects of wavelength on the photochemical reduction which has led to the confusion in the literature.^(13,14) regarding uranium reduction in nitric acid.

Bell, et al⁽¹¹⁾ have also shown that the reduction of plutonium can be selectively and quantitatively accomplished in 0.1 to 2.0 molar nitric acid using either hydrazine or formic acid as reductants.

Russian researchers⁽¹⁵⁾ have shown that plutonium can be oxidized from the plus three to the plus four state photochemically.

These systems display a large range of adjustable variables in the conditions for photoreduction. This flexibility is encouraging, considering the process restrictions that usually evolve in going from laboratory bench to industrial production. Detailed experiments are required to optimize rates and yields and to study the engineering parameters. However, the literature on the reduction of Uranium (VI) to Uranium (IV) indicates that sufficient spectral and wet chemistry data exist to allow design of an experimental program to test this photochemical process. Existing data indicate that certain photochemical redox reactions are very promising candidates for Purex type separations, because of the advantages gained by using nonresidual photochemical reagents.

Historically in the second step of the purex process, ferrous sulfamate was used to reduce plutonium (IV) to plutonium (III) in order to separate the plutonium from the uranium. Plutonium (III) is soluble in aqueous nitric phase

and uranium is soluble in the TBP phase, but ferrous sulfamate use leads to problems in subsequent processing.

The technique could be used in the purification of plutonium, e.g. the reaction

can replace the corresponding chemical oxidation used in the purex plant with absolutely zero substances added to the process stream.

There are 150 gallons of HLLW per ton of fuel reprocessed which contains 54.4 kg of solids requiring calcination and subsequent glassification. The ferrous sulfamate would increase these quantities of solids by approximately 27 kg per ton of fuel or about 50 percent. In addition, subsequent waste handling and processing would be required. Also complications in solvent cleanup and in transfer of solids would be introduced.

The use of uranium (IV) as a reductant either manufacture in situ or outside the system overcomes most of these difficulties. An electrolytic technique for producing the U^{IV} in situ has been adopted at the AGNS Plant in Barnwell, SC. This electrolytic technique requires a precise control system to maintain proper conditions for reduction of the uranyl ion. Two electrodes are in physical contact with the solution; however, there is generally a membrane used to separate the cathode from the other section of this cell. This electrolytic system has not been demonstrated commercially; therefore a need for a back up system exists! In case of a failure in the present electrolytic system maintenance would be difficult. Therefore uranium (IV) manufactured outside the system

is being considered by AGNS as a logical backup to their in situ electrolytic system. There are a number of techniques that could be used for the production of uranium (IV) outside the system i.e. thermal chemical, electrolytic, or photochemical.

There are several thermal chemical methods capable of manufacturing uranium IV from uranium VI, most of these involve a series of two or three thermochemical reactions. A good deal of process development work on thermochemical systems was conducted at BNL 10-15 years ago.¹⁴ The BNL process involved a precipitation reaction followed by digestion of the precipitate and then purification.

In the thermochemical uranium (IV) processes there is a need for preparation of large quantities of chemical solution under precise conditions as starting materials. Different isotopic compositions of starting material would be required to process different fuels so as not to change isotopic composition of PWR and BWR fuel materials. These thermal chemical techniques are quite slow, require removal of spent chemicals, and in most cases involve the handling of solids.

In 1968 the Indian workers¹⁶ developed an electrolytic uranium reduction system that is designed to operate outside the radiation environment of a reprocessing plant. This technique is an alternative to the in situ electrolytic system being installed at Barnwell; however, it is not the best choice for a backup system because if the electrolytic system that was developed by AGNS fails, the secondary electrolytic system may fail for the same reason, since they operate on the same principles and contain similar components. Thus a greater level of confidence can be obtained in the overall operation of the reprocessing plant

by choosing a backup system that is independent of the primary system. The photochemical process is such a system.

Photochemistry of the Uranyl Ion

In aqueous solutions U^{VI} is found primarily as the uranyl ion, UO_2^{++} , which is quite stable under a variety of conditions. The photochemistry of the uranyl ion will not be discussed in detail here because the topic has been the subject of several recent review articles.^{3,6,12} The mechanism proposed for the photochemical reduction of U^{VI} to U^{IV} in most studies involves a U^V intermediate, i.e., the uranyl ion absorbs a photon which promotes it to an excited state

then the excited uranyl ion will come in contact (collide) with a reductant species

and is reduced to the plus five oxidation state which later disproportionates

to the plus four and six oxidation states. This mechanism explains the 0.5 quantum yield which has been observed for solutions containing low concentrations of reductants.

The photochemistry of a number of uranyl systems with high concentrations of reductant have exhibited quantum yield approaching unity. The aqueous UO_2^{++}

and formic acid system is such an example. The high quantum yield can be explained by the fact that the formate ligand complexes with the uranyl ion forming a uranyl formate complex which absorbs a photon and then decomposes by an electron transfer mechanism. Other factors which lead to this conclusion are that the observed effects of inhibiting scavenger are minimized in high concentration of formic acid and that the uranyl complex is observed to increase and broaden the absorption band of the uranyl ion.

Understanding the basic nature of the uranyl photochemistry enables design of a bench level process experiment with a very high confidence level for successful performance.

Photochemical Reduction for the Purex Process

One of the parameters that will be varied in this test unit or module will be the reductant. Because of the nature of the photochemistry, several non-residual reductants will reduce the excited uranyl ion but not the unexcited species. Some of these nonresidual reductants are listed in Table 1. It is pointed out that the nonresidual reductants are generally oxidized to water and a gas or volatile liquid; e.g., formic acid forms water and carbon dioxide while hydrazine forms water and nitrogen.

In the photochemical method of generating U^{IV} , the only chemical addition to the system need be a nonresidual reagent. One of several of the nonresidual reagents that can be used to photochemically reduce the uranium VI is formic acid; e.g.,

Table 1. Nonresidual Reductants and the Gas Generated by Reaction with the Excited Uranyl Ion

<u>Reagent</u>	<u>Gas Evolved</u>
H_2NNH_2	N_2
H_2NOH	NH_3
HCOOH	CO_2
$\text{CH}_3\text{CH}_2\text{OH}$	CH_3CHO
$\text{H}_2\text{C}_2\text{O}_4$	CO_2
CH_3COOH	CO_2, CH_4

The carbon dioxide can be vented, leaving no residuals in solution. Thus a pure solution of U(IV) can be added to the purex process without complex chemical purification techniques.

Advantages of the Photochemical System

Benefits from using the photochemical method, rather than the thermochemical or the electrolytic methods as backup systems, could accrue because of increased flexibility in solution conditions required for controlling the reaction and because of the increased speed of photochemical reaction rates. The flexibility condition means a minimal control system will be required to monitor and meter the photochemical U(IV) generator, and the simpler the system the less likely it is to need repair. The fast reaction rate could enable a very short holdup time for the U(VI) to U(IV) system. Economically this could be significant if fuels of different uranium enrichment factors are to be reprocessed, i.e., switching from PWR to BWR spent fuel.

A key advantage of the photochemical uranium IV technique as a back up system is that no significant radioactivity is involved. Therefore no shielding is required and no interfering radiation effects are present.

In addition, the subsequent waste-handling problems and subsequent processing should be simplified with the photochemical system because the volume of waste has been reduced and complications of additional solids have been avoided. This photochemical technique can be expanded in a modular fashion since modular construction can be used; therefore any expansion of the plant would require only a simple increase in the number of modules.

There will be very little downside risks in the development of the photochemical backup system since the photochemical reactions that reduce uranium are very well documented under conditions which are virtually identical to those expected in the commercial system. Therefore, a minimal effort will be required to demonstrate this technique on a process level and there will be a very small effort needed to go from the process level to a commercial size. This is partly because we can expand in a modular fashion. A single module would only require roughly a 10 kw lamp, thus allowing use of commercially available visible lamps to perform the photochemistry. This permits inexpensive photochemical reactor construction and design. These lamps are both inexpensive, sturdy, and reliable. The operating replacement cost will be very low. The energy costs have been calculated to be virtually negligible.

This photochemical modification of the Purex process can be accomplished in the organic solution (TBP and Kerosene) or in the aqueous solution. Preferably, some purified uranium can be recycled and reduced before adding it to step 2 of the process stream as is depicted in Figure 1.

The reductant employed in the plutonium partitioning portion of the Purex process, regardless of what reductant is employed, is customarily supplied in a several-fold excess of the stoichiometric quantity calculated to affect the desired reduction of Pu^{IV} to Pu^{III} . For the estimates presented here, we have used four times as much U^{IV} as would be needed stoichiometrically to reduce the plutonium.

Figure 1 indicates the simple modifications to an existing Purex process plant that would be necessary to incorporate the photochemical technique suggested here. A small fraction (~4%) of a relatively pure aqueous uranium stream is withdrawn. (Since the photochemical reduction of U^{VI} to U^{IV} can be accomplished in either the organic solution (TBP and Vicrosene) or in the aqueous solution, the exact point for this withdrawal is subject to technical and economic analysis which now has to be deferred until some later date and subjected to photochemical reduction before recycling it to the plutonium partitioning column. By working with a stream of relatively pure uranium, the photochemical process efficiency does not suffer parasitic losses in extraneous ions, such as would be the case if relatively high concentrations of certain fission products and certain other actinides were present; also, a relatively broadband light source may be used, rather than a narrow spectrum which would be required if interfering ions were present. Furthermore, since the radioactivity level of the recycle stream is either low or at background, operational safety and maintenance are greatly simplified.

The pH of the solution can then be adjusted, if necessary, and the resultant solution is fed into step 2 in the purex process, as illustrated in Fig. 2. It perhaps should be noted that the U^{IV} solutions are quite stable, if usual

and ordinary precautions to neutralize oxidizing agents are taken such as avoiding the use of UV light below 350nm which decomposes the nitrate ion to form the oxidant NO_2 .

Photochemical Reactor

Figure 3 depicts schematically a possible modular construction for the photochemical U(IV) generating systems. U(VI) and a suitable reductant are fed into a mixer and then the purex steam flow is divided into several photochemical reactors. In these reactors the reductant is decomposed to form a gas and water and the U(VI) is reduced to U(IV). A more pictorial illustration of the photochemical reactor concept is depicted in Figure 4. It shows the separation of the gas from the liquid and the annular construction of the lamp cooling system and filter about the centrally located mercury lamp. The uranium solution flows through the outer annulus of this reactor where the uranium reduction reactions (referred to as R_x in Figure 4) take place. In practice this reactor would be situated horizontally and the liquid level would be adjusted to cover the annular section or depicted in the figure.

Preliminary Cost Estimate

Using 9 kg Pu/metric ton of fuel reprocessed and four times the stoichiometric amount of U^{IV} , the theoretical minimum light energy requirement (at 3 ev/photon for 4150A° light and 1 photon per uranium atom reduced) is 0.504 kilowatts per metric ton of fuel reprocessed/day. Using a quantum efficiency of 0.5, which is often exceeded for uranium photochemical reactions, the minimum light energy requirement becomes 1.08 KW/(MT/day). If now parasitic and other losses are generously assumed to reduce the light utilization by a factor of 2, the light to be supplied becomes 2.16 KW/(MT/day). Using 10 per cent as the ef-

efficiency of converting electricity to useable light, the electrical power to be purchased becomes 21.6 KW/(MT/day); i.e., about 108 KW for a Barnwell-size reprocessing plant (1500 MT/year, nominally 5 MT/day).

Using 3¢/KWh_e as the cost of purchased electric power some years in the future, this corresponds to 0.161 ¢/gm Pu for the photochemical process light power cost, for the nominal 5 MT/day reprocessing rate. Since the worth of Pu is certainly in the dollars/gm range, the energy costs for photochemical partitioning of Pu by the suggested technique are virtually negligible. Consequently, the efficiencies for the processes assumed in the calculations above could be much less (even though they are not expected to be less) and still be economical.

Heat Effects

Most of the heat losses are associated with the inefficiency of converting electrical energy to useable light, but that heat does not have to influence the process solution temperatures, since the lamps may be independently cooled with air or with water or indeed with any other coolant for which some advantage might accrue.

However, the useable light must interact with the process solution. The heat effects of this interaction is what is of interest here. If a 1-molar solution of uranyl ions is chosen as a benchmark concentration, the energy corresponding to 1 photon at 3ev/photon for each uranium atom amounts to 18.07×10^{23} ev/liter. If all of this energy appeared as heat in the aqueous solution, the solution temperature would rise about 124°F (69°C), assuming a specific heat of unity for the solution. In an organic solution, the temperature rise would be greater, because of the generally smaller specific heats of organics in com-

parison with water. Since the actual heat effects are expected to be larger because of various inefficiencies, it is clear that the system design will have to provide for cooling of the process solution in one way or another.

Gas Generation

If formic acid is used as the reductant, one mole of CO_2 is formed per mole of U^{IV} produced. Each liter of solution will generate, if the solution contains 1 mole U/liter, 22.4 liters (at STP) of CO_2 gas! Accommodation of this fact will certainly influence the engineering design of any reactor and the use of reductants like formic acid which, generates a gas as one of the reaction products. (Other reductants, for example ethanol, allow photochemical reduction of U^{VI} to U^{IV} without gas generation, and it is conceivable that such systems may have other advantages. This is an area which deserves further investigation).

Window Fouling

Light must get to the process solution, if a photochemical effect is to be brought about. Sometimes the nature of the process solutions is such that fouling of the windows through which the light must pass to get to the solutions comes about by any one of a number of possible mechanisms: deposits on the window; pitting or corrosion of the window surface; growth of crystals or organisms on the window surface. Preliminary experimental and analytical results indicates that this will not be a serious problem for the systems under consideration here, but the question cannot be overlooked and should form a part of an experimental inquiry.

Advantages of Using a Recycle Stream

In addition to more efficient energy usage, easier maintenance and elimination of shielding requirements, which have been mentioned previously, using a recycle stream of relatively pure uranium will allow greater flexibility in design and operation and upgrading of the facility, and should result in minimizing capital expenditures.

Parasitic Losses in U^{IV}

The U^{IV} absorption spectrum partially overlaps (at the longer wavelengths) that of U^{VI} (as uranyl ions) in 3M H_2SO_4 solutions as shown in Figure 5. If the behavior in HNO_3 solutions is similar, this will have to be taken into account in the design of the system. There are at least two ways to circumvent this problem, if it turns out to be important.

One, the light used can be restricted to the shorter wavelength end of the U^{VI} band. This eliminates the U^{IV} absorption problem, but sacrifices light utilization efficiency, probably, since the longer wavelength light will be generated but has to be filtered out or otherwise excluded, unless a lamp with the unique requirements is available or can be procured.

Two, somewhat more U^{VI} can be recycled, even though only about 4 percent of the main stream flow needs to be converted to U^{IV} . This increases the probability of absorption by U^{VI} and overwhelms the absorption in U^{IV} . An excess of U^{VI} in the recycle stream is therefore desirable.

Obviously, there is room for engineering study of the economics of these alternatives.

Uranyl Photochemical Range

The U(VI) ion has absorption bands extending from $\sim 4800 \text{ \AA}$ on into the ultraviolet. However, essentially only the band in the 3600 to 4800 $\text{\AA}$ region is available for use in the photochemical excitation of the uranyl ion. As has been previously mentioned, the parasitic loss of light due to absorption by $\sim 2\text{--}3 \text{ M}$ nitric acid solutions becomes important for wavelengths below 3500 $\text{\AA}$. Thus the uranyl ultraviolet absorption bands are not accessible for photochemical processing with such solutions. Reduction of the nitric acid concentration by a factor of ~ 10 would be required before photochemical utilization of the uranyl bands below 3500 $\text{\AA}$ would be considered on the basis of light loss criteria. The photochemical decomposition of nitric acid yields reactive species such as the nitrous acid, hydroxyl radical, and pernitrite ion. The affect of the resultant chemistry undergone by these species on the uranous yields would have to be evaluated in considering use of light below 3500 $\text{\AA}$.

Just as consideration of the effects of absorption of light by nitric acid will determine the lower end of the photochemical light range, fixing of the upper end of the range will involve consideration of the effects of light absorption by uranous ion. The U(IV) ion has a number of bands which absorb from $\sim 4100 \text{ \AA}$ on through the visible. Thus a portion of the U(VI) spectral range is overlapped by the U(IV) ion as is illustrated in Figure 5. The integrals of the extinction coefficients for the uranyl and uranous absorption bands over the 3600 to 4800 $\text{\AA}$ region are approximately equal (i.e., for uniform light irradiation of solutions containing equal concentrations of U(VI) and U(IV) approximately 50% of the absorbed light will be absorbed by each ion). Therefore, the extent of parasitic light loss due to the overlap or uraneous ion absorption will be roughly equivalent to the U(IV)/U(VI) ratio. Thus the upper limit to

the U(VI) photochemical range will depend on the extent of conversion of the U(VI) to U(IV). For example, if 10% of the U(VI) is converted to U(IV), the light loss due to U(IV) absorption will be roughly 10%. The possibility of loss of U(IV) due to photochemical reactions involving excited U(IV) are considered very unlikely but thus must also be verified before the U(VI) photochemical range can be fixed.

Even with these possible restrictions it is clear that simple, sturdy, inexpensive and efficient lamps can be used in this application; these lamps are available from a variety of sources.

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Photochemical Modified Purex Process

Figure 1

Figure 3. Schematic of the Module Photochemical Generator

Figure 4. A Photochemical Reactor Concept for U(IV) Production

Fig. 5. Visible spectra of UO_2^{2+} and U^{4+} in 3 M H_2SO_4 .