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II. Possible Applications to Nuclear Fuel Reprocessing**

by

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LASER-ENHANCED CHEMICAL REACTIONS AND THE LIQUID STATE.
II. POSSIBLE APPLICATIONS TO NUCLEAR FUEL REPROCESSING

by

C. I. DePoorter and C. K. Rofer-DePoorter

ABSTRACT

Laser photochemistry is surveyed as a possible improvement upon the PUREX process for reprocessing spent nuclear fuel. Most of the components of spent nuclear fuel are photochemically active, and lasers can be used to selectively excite individual chemical species. The great variety of chemical species present and the degree of separation that must be achieved present difficulties in reprocessing. Lasers may be able to improve the necessary separations by photochemical reaction or effects on rates and equilibria of reactions.

ABSTRACT
This report was prepared as an account of work sponsored by the United States Government under the Atomic Energy and the United States Energy Research and Development Administration, and one of those employees and one of those contractors, subcontractors, or other employees making any invention, process, or design, or computer program, or software, or any improvements, modifications, or variations of any apparatus, apparatus, product, or process described in reference thereto, or the results and drawings prepared thereon.

INTRODUCTION

The first report¹ in this series discussed some general considerations of energy transfer and reaction dynamics in liquid systems, particularly in regard to vibrational enhancement by laser radiation. Although vibrational enhancement seems to offer more selectivity in the potential excitation of one bond in a molecule or one isotopic species, electronic excitation in the near-infrared, visible, and ultraviolet regions of the spectrum is known to produce reactions in solutions. Reaction rates can be accelerated by electronic excitation, or reactions different from those in the ground state may take place.² Since conventional sources of irradiation are suitable for many of these photochemical reactions, a greater background of information is available than for selective vibrational excitation.

In this report, we will consider the application of laser photochemistry to an industrial process, the reprocessing of spent nuclear fuel. We will stress electronic excitation because potentially powerful dye lasers are available in the wavelength ranges of interest.³ Although conventional sources are also available in this range, lasers offer the advantages of monochromaticity for

selectivity and the high photon flux required for the particle densities of solutions. We do not intend to exclude, however, the use of conventional sources if they are adequate.

In present nuclear fuel reprocessing methods, large volumes of solvents, oxidizers, reducers, and other reagents must be added to separate the uranium and plutonium from the other actinides and fission products present in the fuel elements. Laser-chemical methods may alter chemical equilibria, or the light itself may act as an oxidizer or reducer, thereby improving separations or reducing volumes of reagents required. Current practice is to separate the uranium and plutonium from the remainder of the components of spent fuel and to store the remainder. Because of the long half-lives of the actinides, isolation from the biosphere is required for tens to hundreds of thousands of years. Separation of the actinides from the fission products would simplify the management of these components; some are of economic use, such as ²³⁷Np, which is used to produce ²³⁸Pu for cardiac pacemakers and other power sources,⁴ and useless actinides could be recycled through nuclear reactors to produce stable elements. Periodic separations of inert material from remaining radioactive material in storage could also

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benefit waste management.⁵ Laser-chemical processes may simplify these separations.

Since the Purex process is most widely used for nuclear fuel reprocessing, we will use it as the basis of this report. We will assume that the reader has a scientific background, but no special knowledge of nuclear fuel reprocessing or photo-chemistry, and can refer to the first report¹ in this series for basic ideas in laser chemistry and the properties of liquids. The Purex process and the chemical nature of the reprocessing streams will be described. Potential laser-chemical processes that are relevant will be discussed in terms of methods that can easily be added to existing plants, methods that follow the general Purex process but would require substantial changes in plant equipment, and methods that require changes in the process itself.

THE PUREX PROCESS

The Purex process is based on solvent extraction, the partitioning of a solute between two immiscible liquids. Tributyl phosphate (TBP) extracts uranium in the +6 oxidation state as the uranyl (UO_2^{2+}) ion and plutonium in the +4 oxidation state from aqueous solutions, while extracting the other components of spent nuclear fuel to a much lesser degree. Plutonium in the +3 oxidation state is more soluble in the aqueous phase. In practice, approximately a 30% solution of TBP in kerosene is used as the organic phase. By the addition of appropriate oxidizers, reducers, and salting-out reagents, the uranium and plutonium can be removed from the dissolved fuel elements and separated from each other.

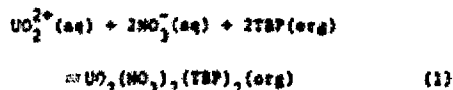
Figure 1 is a simplified flow chart of the Purex process.⁶ The fuel elements are first chopped into 2- to 3-cm pieces, which are treated with concentrated nitric acid. The metallic cladding does not dissolve and is mechanically removed from the mixture. Before the extraction of uranium and plutonium (Stage I), $NaNO_2$ is added to the feed to ensure that the plutonium is in the +6 oxidation state. In Stage I, most of the uranium and plutonium are separated from most of the other actinides and fission products. The uranium and plutonium are separated from each other (Stage II) by the reduction of plutonium to the +3 oxidation state and extracting it into an aqueous strip. This

separation is not complete, and a small amount of plutonium is carried on to Stages III and IV. In Stage III, the uranium and traces of plutonium and fission products are stripped from the TBP into water, which is then evaporated to the desired concentration, and the acidity is adjusted. The uranium is next separated from the remaining plutonium and fission products by reduction of the plutonium to Pu^{3+} and extraction of the uranyl ion into TBP. The uranium is again stripped from the TBP (Stage V) and purified by ion exchange to $UO_2(NO_3)_2$ product. The aqueous stream from Stage II contains most of the plutonium and a trace of the fission products. The plutonium is reoxidized to the +4 state and extracted into TBP (Stage VI), after which it is again reduced to Pu^{3+} , stripped from the TBP, and purified by ion exchange to the $Pu(NO_3)_3$ product.

For a more complete description of the Purex process, the reader should consult the book by Benedict and Pigford⁶ or the article by Siddall.⁷

Partitioning by solvent extraction is limited by the thermodynamic equilibrium distribution of an ion between the two solvent phases. The stringent requirements for separation imposed by the radioactivity of the components of spent nuclear fuel make necessary many extractions within each stage and the use of salting-out reagents. In present processes, 0.1 to 0.3% of the uranium and plutonium remain with the fission products, and the uranium and plutonium products must be purified of fission products by a final ion exchange step.

For the extraction of uranium, the partitioning involves the uranyl ion in the aqueous nitric acid phase and the complex $UO_2(NO_3)_2(TBP)_2$ in the organic phase. The uranyl ion is not by itself soluble in the organic phase, just as the complex $UO_2(NO_3)_2(TBP)_2$ is not by itself soluble in the aqueous phase. At the interface between the two solvents, the chemical reaction



takes place. The quantitative relationships between the chemical species in Eq. (1) are fixed by the thermodynamic equilibrium constant for the reaction,

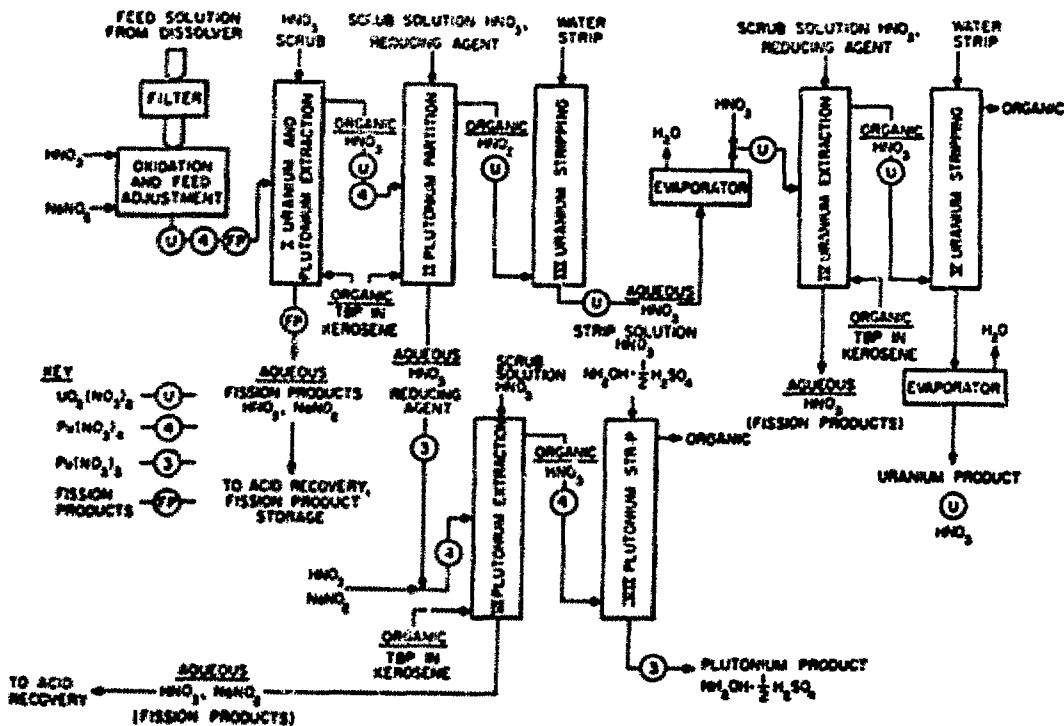


Fig. 1. Flow chart of PUREX process.

$$K_{eq} = \frac{a_{UO_2(NO_3)_2(TBP)_2(org)}}{(a_{UO_2^{2+}(aq)})(a_{NO_3^-(aq)})^2(a_{TBP(org)})^2} \quad (2)$$

In Eq. (2) the a 's are the activities of the components in the aqueous and organic phases. To simplify this discussion, the activity will be assumed equal to the concentration. This is an oversimplification, but it gives an accurate outline of the principles involved.

Expressing Eq. (2) in terms of concentrations gives

$$K_{eq} = \frac{[UO_2(NO_3)_2(TBP)_2(org)]}{[UO_2^{2+}(aq)][NO_3^-(aq)]^2[TBP(org)]^2} \quad (3)$$

where the brackets denote concentration. Since K_{eq} depends only on temperature and pressure, the basis of solvent extraction can now be seen. Consider a nitric acid solution containing uranyl ion which is placed in contact with a TBP-kerosene solution. At the interface, a nonequilibrium situation exists. To reach equilibrium, the forward chemical reaction

of Eq. (1) takes place until the concentrations of the components are in the ratio given in Eq. (3) by K_{eq} . Thus, uranium is removed from the aqueous phase and transferred to the organic phase. Similarly, if the organic phase containing $UO_2(NO_3)_2(TBP)_2$ is placed in contact with nitric acid, a nonequilibrium condition will exist at the interface. To reach equilibrium, the reverse reaction of Eq. (1) will occur until the concentrations of the components are in the ratio given by K_{eq} . Therefore, the nitric acid strips the uranium out of the organic phase.

Because the equilibrium constant is a ratio of concentrations in the aqueous and organic phases, the contacting between the aqueous solution and fresh organic solution must be done several times to remove the desired amount of uranium. Similarly, successive extractions with clean nitric acid must be done for stripping.

Although the numerical value for K_{eq} is fixed, concentrations of the components can be varied to make each stage more efficient. For example, if an

excess of nitrate ion over that required to make $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{TBP})_2$ is used, Eq. (3) implies that the ratio $[\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{TBP})_2(\text{org})]/[\text{UO}_2^{2+}(\text{aq})]$ will increase if the TBP concentration remains constant. More of the uranium enters the organic phase than if the stoichiometric amount of nitrate ion were used. However, when considering the effects of salting agents such as the nitrate ion, the full expression for activity coefficients must be used for accurate predictions. In addition, an excess of one component may affect the extractability of other components. For a complete understanding, equations like Eq. (1) must be written for the extraction of every component in the solution. From the chemical equations, equilibrium constant expressions must be written with activity coefficients. Only when the complete set of equations is examined can the effects of adding components be determined.

The thermodynamic equilibrium constant, K_{eq} , gives the activity ratio at equilibrium. However, thermodynamics cannot be used to predict how long it will take to reach equilibrium. Therefore, the partitioning calculated from the equilibrium constants will be the upper limit on what can be expected.

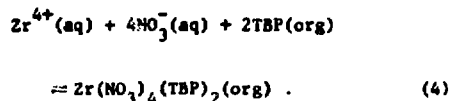
CHEMICAL NATURE OF THE REPROCESSING STREAMS

In order to consider photochemical processes for nuclear fuel reprocessing, the elements present in the reprocessing streams, their valence states, and their photochemical properties must be known. In this section, a brief survey of these properties will be given.

The major chemical elements present in the reprocessing streams are shown in Fig. 2. Although the relative amounts differ with the fuel used (^{235}U , ^{239}Pu , or ^{233}U), the reactor type, the cladding type, and the amount of burnup, the same chemical elements are present.

In the Purex process, yttrium and the lanthanides are easily separated from uranium and plutonium. However, zirconium, niobium, molybdenum, technetium, and ruthenium are more difficult to separate.

Most of the zirconium and niobium participate in a chemical equilibrium between the aqueous and organic phases similar to that for uranium:



However, a small amount interacts with an unidentified component of the reprocessing stream to form a species that remains in the organic phase and releases the zirconium and niobium into the aqueous phase slowly during stripping. As a result, appreciable amounts of zirconium and niobium remain in the organic phase with the uranium and plutonium.

Ruthenium is difficult to extract completely because it forms several species in acidic solution. The extractability varies for the different species. Ruthenium also differs from other fission products in that TBP displaces water molecules from the primary coordination sphere after, rather than during, extraction. Conversion among the various species is slow; equilibrium takes a long time to be reached.

The elements in the reprocessing streams that have been reported² to undergo photochemical reactions are indicated in Fig. 2. In addition to those indicated, it may be expected that the remaining lanthanides and actinides will be photochemically active.

BACKGROUND

Photochemistry by electronic excitation has been studied in detail for many of the transition metals, some lanthanides and actinides, and many other elements.^{2,8} Light has been found to induce chemical reactions that would otherwise not take place and to enhance rates of chemical reactions. In addition, for many metal-ion complexes, irradiation at one wavelength will produce oxidation or reduction, while irradiation at another wavelength will produce a rearrangement of the complex or exchange of a complexing molecule for a solvent molecule. All of these processes may be useful in nuclear fuel reprocessing.

A nonrigorous thermodynamic argument will be presented here to indicate the way in which light may affect some of the relevant chemical reactions. Rigorous thermodynamic arguments would be more extensive and might require the addition of non-equilibrium thermodynamics. The interaction of

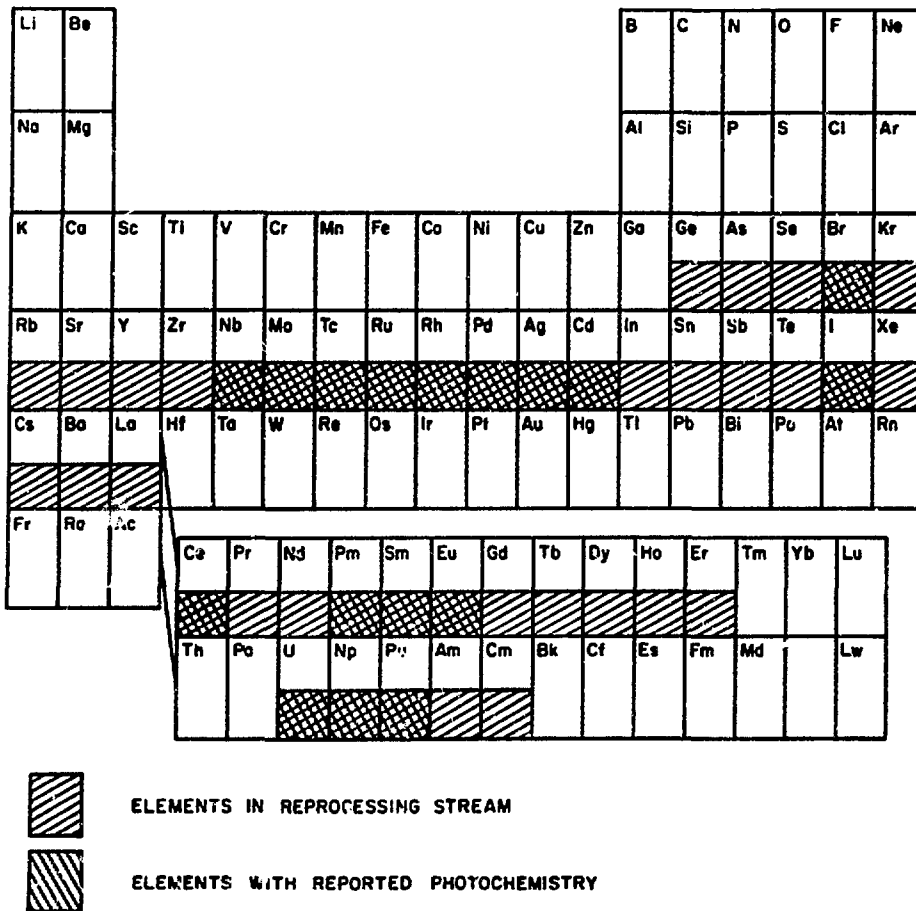


Fig. 2. Major elements in fission reactor fuel reprocessing stream.

light with chemical systems is one of the least explored aspects of thermodynamics, but interest is developing with the use of lasers in chemistry.^{9,10}

Enhancement of reaction rates in the Purex process may lead to better separations or the use of smaller amounts of reagents. Consider the chemical reaction



At equilibrium, the principle of microscopic reversibility requires that

$$k_f[A][B] = k_r[C] \quad (6)$$

where the brackets denote concentration and k_f and k_r are the rate constants for the forward and

reverse reactions. Rearranging Eq. (6) gives

$$\frac{k_f}{k_r} = \frac{[C]}{[A][B]} = K_{eq} \quad (7)$$

where K_{eq} is the equilibrium constant for Reaction (5). Assume that by irradiation of a system initially at equilibrium, component A only is placed in an excited electronic state and that electronic excitation increases the rate of the forward reaction so that k_f^* , the forward rate involving electronically excited A, is greater than k_f . If $[A_T]$ is the amount of A present at thermodynamic equilibrium and $[A^*]$ the amount of electronically excited A, the forward rate becomes

$$k_f^*([A_T] - [A^*])[B] + k_f[A^*][B] \quad (8)$$

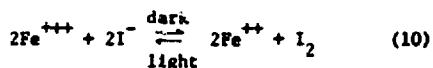
Rearranging Eq. (8) gives

$$(k_f^* - k_f)[A^*][B] + k_f[A_T][B]. \quad (9)$$

Comparing Eqs. (9) and (6) shows that in the presence of light the forward reaction rate is greater by $(k_f^* - k_f)[A^*][B]$ than is the forward rate at thermodynamic equilibrium. Of course, for this to be true, the excited state lifetime must be long enough to allow the chemical reaction to occur from the excited state.

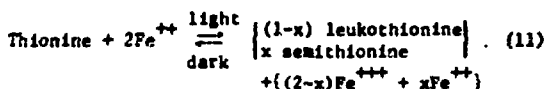
Another way to consider the effect of light in this example is in terms of the equilibrium of the system. In the same manner as a change in concentration of one of the reagents, the light has displaced the equilibrium to the right of the chemical reaction.

One of the earliest reports of a shift in equilibrium by the action of light deals with the ferrous-ferric:iodine-iodide equilibrium.^{11,12} The reaction is



where the I_2 is the photosensitive constituent. It was also shown that, under conditions of uniform illumination with light from an electric lamp, a photochemical equilibrium different from the dark equilibrium is attained.

Another example of a light-sensitive equilibrium is the thionine-iron system, which has been described in detail by Rabinowitz.^{13,14} The system is



In the dark, the equilibrium lies entirely on the left side of the equation. The photosensitive component of this system is thionine. This reaction system was used in a photogalvanic cell.

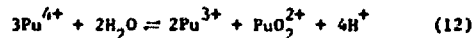
The effect of light on chemical equilibrium is also known in organic systems.¹⁵⁻¹⁸ Acidity constants of organic compounds, again an equilibrium property of the system, are a function of the electronic state of the molecules.

Another class of chemical reactions that is of interest is ligand transfer within metal-ion

complexes. This reaction takes place in the transfer of a metal ion from one phase to the other in solvent extraction. It has been studied in great detail for the transition metal ions,^{19,20} and is known to be accelerated by light in many cases.² Metal ions complex with several molecules, often of the solvent or anions that are present in solution. In the case of uranyl ion solvent extraction, the uranyl ion is complexed with six water molecules in the aqueous phase, and two nitrate anions and two TBP molecules in the organic phase. In going from one phase to the other, the liganda exchange, presumably accounting for the "resistance" noted in studies of the Purex process.²¹ Light is known to accelerate the rate of substitution of a solvent molecule for another ligand, but the particular reaction depends upon the metal ion, the solvent, and other conditions. Ligand-transfer reactions are poorly understood for the uranyl ion.²

Photochemical oxidation and reduction of metal ions has also been extensively studied. Oxidation is more commonly seen, but reduction can take place under the proper solvent conditions.² Often the solvent molecules in the primary coordination sphere serve as oxidants or reductants.

Information available for the various components of the nuclear fuel reprocessing streams ranges from extensive to almost nonexistent. The photochemistry of the uranyl ion has been studied for almost a hundred years.^{22,23} The available data are complex and sometimes conflicting. The photochemistry of plutonium and the other actinides has been studied much less. Recently, Bell and Friedman²⁴ have investigated the effect of ultraviolet light on plutonium solutions. They have shown that the equilibrium constant for the reaction

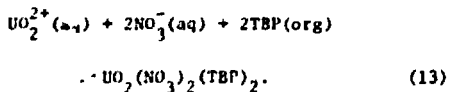


is increased by a factor of three by irradiation and that the rate of return to the dark equilibrium is slow. They have also shown that ultraviolet irradiation increases the rate and extent of depolymerization of Pu^{4+} hydrolysis polymer.

Photochemical data are available for many of the fission products. It should be noted that the alkali metals and alkaline earth metals, rubidium, strontium, cesium, and barium, are unlikely to

display significant photochemical reactions in solution.

Consider again the solvent extraction reaction for uranium,



The uranyl ion is photochemically active. Formation of $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ is slow. By exciting the uranyl ion electronically, the primary coordination sphere may be disrupted or ligand transfer may be enhanced to help form the TBP complex with the uranyl ion, enhancing the forward rate. However, it is also possible that electronic excitation would speed up water substitution for TBP in the primary coordination sphere, enhancing the reverse rate. Only experiment can determine whether the rate is enhanced, and, if so, in what direction.

If the multitude of chemical reactions involved in the solvent extraction systems are examined, many of these reactions may be found to be enhanced by light. Ligand transfer reactions and equilibrium displacements may improve solvent extraction of various components. Alteration of plutonium oxidation states has been demonstrated; extension of this principle to ruthenium would be useful. Light might be used as an oxidant or reductant instead of chemical reagents. As is the case for uranium, only experiment will give the answers.

A potential problem in the application of photochemistry to nuclear fuel reprocessing is the background α , β , and γ radiation level. This radiation promotes chemical reactions and excites molecules and ions. The energy will tend to degrade the selectivity of photochemical reactions. Whether it will preclude the use of photochemical techniques is not clear at this time; most likely it will affect them less than it does standard chemical techniques. One approach to determining the extent of its effect might be to work out a photochemical technique with nonradioactive isotopes, then test it under conditions similar to those of an actual reprocessing stream.

LASER ADD-ONS FOR CURRENT PUREX SYSTEM

In the following discussion, we shall refer to lasers as the illumination sources for photochemical

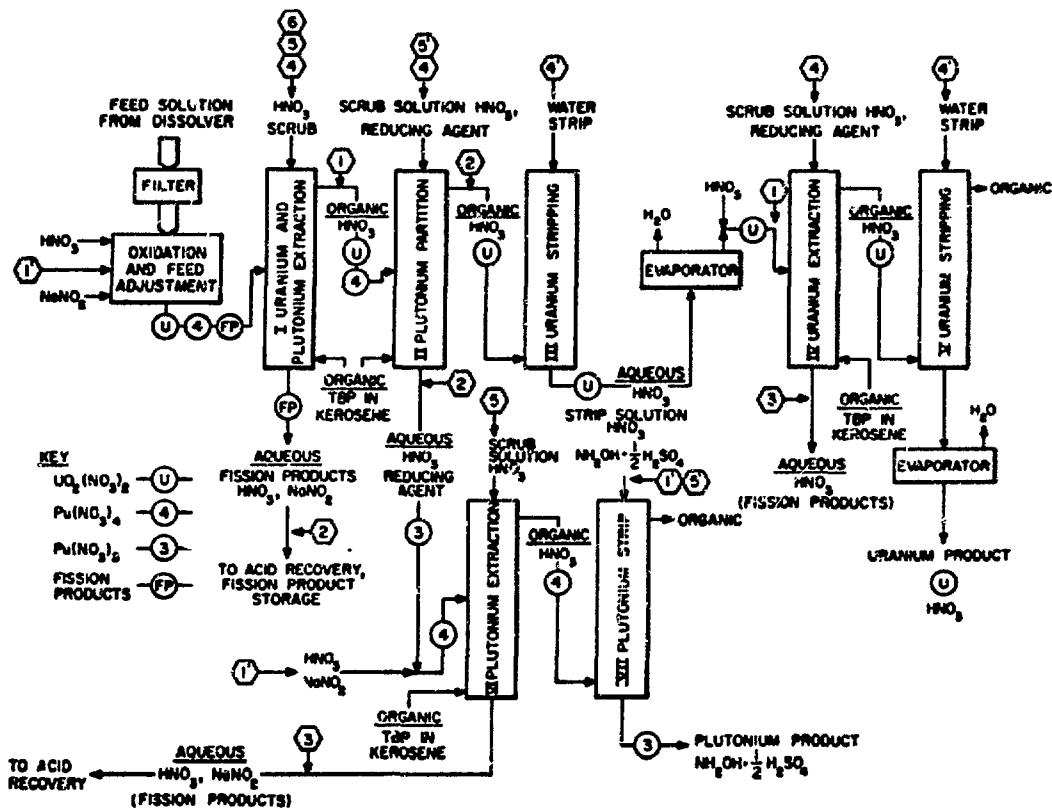
processes. Other light sources, however, may be suited to specific applications and more economical than lasers. For research in photochemistry, lasers provide a monochromatic source with a high photon flux, eliminating much of the ambiguity present with other sources. Monochromaticity allows one absorption band of one component of a mixture to be selected; a high photon flux is necessary for solution photochemistry because of the particle density. Once conditions have been obtained for a process, systems studies can evaluate whether the advantageous qualities of a laser balance its cost for use in a reprocessing plant.

Laser applications to the current Purex system that would require minimal modification of existing process equipment will be referred to as "laser add-ons." They involve additional processing on streams between various stages in the process. Three possible laser add-ons are (1) reduction of plutonium, (2) clean-up operations on the process streams, and (3) further separation of fission products.

In a 1961 report, Carroll, Burns, and Warren discuss using U^{4+} as a reducing agent for plutonium.²⁵ The U^{4+} was to be produced by photochemical reduction of the uranyl ion. Addition of a reducing agent contributes appreciably to the salt content of the waste. U^{4+} is a satisfactory plutonium reductant, and, under the proper operating conditions, can be completely recovered with the other uranium. Figure 3 shows potential add-ons and modifications to the Purex process. Photochemical reduction of uranium to serve as a reductant for plutonium could be added at the points marked with a 1 in a hexagon.

It may also be possible to directly reduce the plutonium photochemically, but this may be less desirable because plutonium quantum yields seem to be less than for uranium.²⁴ Photochemical oxidation of plutonium may also be possible. Direct oxidation or reduction of plutonium is indicated by 1'.

As mentioned earlier, the separation of the uranium and plutonium from the fission products is not complete. The aqueous stream from Stage I contains residual amounts of uranium and plutonium in addition to the fission products. The uranium-plutonium separation in Stage II is also not complete; there is a small amount of uranium in the aqueous stream from Stage II. Similarly, residual plutonium is present in the organic stream between



KEY

UO₂(NO₃)₂ (U)

Pu(NO₃)₄ (A)

Pu(NO₃)₆ (3)

FISSION PRODUCTS (FP)

EXPLANATION OF SYMBOLS

Number in Hexagon

- 1 Photochemical reduction of UO₂²⁺ for Pu reduction
- 1' Photochemical reduction or oxidation of Pu
- 2 Further removal or separation of U and Pu
- 3 Further treatment of process stream to remove selected components

Modifications

- 4 Enhance extractability of UO₂²⁺ into TBP
- 4' Enhance extractability of UO₂²⁺ into water
- 5 Enhance extractability of Pu⁴⁺ into TBP
- 5' Enhance extractability of Pu³⁺ into water
- 6 Oxidation state control of fission products

Fig. 3. Purex process flow chart showing photochemical applications.

Stages II and III. Wherever plutonium or uranium is present in a small amount, the component present in small amount might be photochemically removed from the process stream. This is indicated by 2.

An area where add-ons could make a significant contribution is in further separation of fission products and actinides from the waste stream. Cesium-137, ⁹⁰Sr, and ²³⁷Np are removed in special cases,^{4,26,27} but most plans are for all components

to be stored together. Rupp⁵ has pointed out that storage could be simplified and volumes reduced if separations were initially made according to half-life and inert criteria/ subsequently removed from the material in storage. Separation also allows actinides to be transmuted in nuclear reactors. Possible commercial markets exist for many of the isotopes, such as rhodium and palladium.²⁸⁻³¹ Laser photochemical techniques may make these separations possible.

MODIFICATIONS TO CURRENT PUREX SYSTEM

In this section, we will consider laser techniques requiring more substantial changes in the process equipment. The greatest change would be in the design of solvent extractors to allow light to interact with the process streams during or just before solvent extraction. Reaction chambers can be designed for laser input.³²⁻³⁵ Investigation of window transparency in the presence of strong nuclear radiation may be required. On a laboratory scale, a rotary shaft extractor may be suitable. Design requirements for solvent extractors cannot be specified until more experimental data are available on the photochemical processes and systems data on the best light source. Nor can the stream compositions and other details of the flow chart be set.

In Fig. 3, the pairs of processes identified as 4, 4', 5, and 5' will only work in one direction; only one of each pair will be operative. As discussed before, the rate of solvent extraction of the uranyl ion may be increased by the presence of light, but the direction of the rate enhancement cannot be predicted; process 4 represents one direction, and 4' the other. The same is true for plutonium extraction. Enhancement in one direction improves extraction, and enhancement in the other direction improves stripping.

Process 6, oxidation state control of the fission products in the processing stream, could possibly be applied to ruthenium. Ruthenium is currently removed by increasing the TBP concentration. However, this causes less of the uranium to be extracted. Control of ruthenium oxidation states could make uranium extraction more efficient.

NEW REPROCESSING SYSTEMS

This discussion must be speculative; we indicate here only two possibilities. They may improve and simplify the Purex process, or they may grow into a new fuel reprocessing system.

Ruthenium is one of the most troublesome fission products in solvent extraction; it also forms dark compounds that absorb much of the light that might be used for photochemistry of other components. Therefore, it might be useful to remove the ruthenium at an early stage of the process, before the uranium and plutonium are separated from the other fission products. A possible method might be to alter the ruthenium equilibrium among oxidation states photochemically to put most of the ruthenium into one oxidation state that could be extracted either conventionally or through a liquid membrane containing a crown ether³⁶ that is selective for ruthenium in that oxidation state. (For a discussion of crown ethers, see Ref. 37.) Since uranium and plutonium are much larger ions than ruthenium, they would be unlikely to pass through the liquid membrane. Removal of the ruthenium would simplify both photochemical and conventional chemical separations at later stages.

Photochemical investigations of process stream chemistry may develop solvents more suited to photochemical methods than TBP. Other solvents also show selectivity for uranium and plutonium, and their photochemical properties may be more useful. For example, a solvent might be able to double as an oxidant or reductant, or its energies of solvation may be more favorable for the promotion of photochemical processes.

CONCLUSIONS

Photochemistry is worthy of consideration for nuclear fuel reprocessing because of its potential for reduction in volumes of reagents needed to separate the components of spent fuel. Lasers provide monochromaticity and high photon fluxes, which will be necessary for selectivity and adequate reaction in research studies for the application of photochemistry to reprocessing. In addition, lasers may be the most suitable light sources for production applications, although their costs are high.

A large volume of information is available on the photochemistry of many of the components of the reprocessing streams, but much is poorly understood. Systems studies can indicate the most useful light sources for production and the appropriate integration of photochemical techniques into a reprocessing scheme. Further research could lead to great improvements in nuclear fuel reprocessing.

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