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PHOTOCHEMICAL DESTRUCTION OF ORGANIC COMPOUNDS FORMED DURING DISSOLUTION OF URANIUM CARBIDE IN NITRIC ACID

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ABSTRACT

The dissolution of carbide fuels in nitric acid leads to the formation of a number of organic compounds which cause serious interference in the subsequent steps of reprocessing. In the present work, the optimum conditions for the photochemical destruction of these compounds by excited uranyl ion were established. The optimum concentration of uranium was found to be in the range 10 - 45 mg/mL. The destruction rate was found to decrease with increase in acidity. It was established that apart from oxalic and mellitic acids, some other unidentified compounds were also responsible for the interference in solvent extraction.

INTRODUCTION

Uranium-plutonium mixed carbides are known to be attractive candidates for use as Fast Reactor fuels. The Fast Breeder Test Reactor (FBTR) at Kalpakkam uses U-Pu mixed carbide (with Pu/U+Pu = 0.7) as the driver fuel.

One of the most challenging aspects of the carbide fuel cycle is the reprocessing of the fuel. A number of studies have been reported in the literature on the head-end treatment of carbide fuel for obtaining feed solutions compatible with the Purex process (1). Of the methods reported, oxidation in O_2 and CO_2 streams and pyrohydrolysis to convert the carbide to oxide have many disadvantages particularly in respect of carbide fuels with high-Pu content (1).

The direct dissolution of carbides in nitric acid is a comparatively convenient procedure. However, this step leads to the formation of a number of organic compounds (1,2). During the dissolution, less than 60% of carbon is removed as CO_2, the exact percentage depending on the conditions of dissolution (3).

The organic compounds formed during carbide dissolution cause emulsion formation in the solvent extraction steps of the Purex process. Further, they complex U(VI) and Pu(IV) resulting in the incomplete extraction of these ions. Retention of plutonium in the TBP phase during stripping has also been observed (1) when extraction is carried out from an aqueous phase containing these organic species.

Oxalic acid and mellitic acid have been identified as two of the many organic compounds formed (4,5). Choppin et al (6) concluded that oxalate alone is responsible for the aqueous complexing observed in the solutions obtained by dissolving the carbide in nitric acid. However, they did not examine the problem of stripping the plutonium. In any case, destruction of not only oxalic acid but also of the other compounds is desirable.

Destruction of the organic compounds by direct chemical oxidation has been attempted (1,7,8). However, this has the disadvantage of incomplete destruction of the compounds. Futher, the chemical destruction method involves the addition of oxidants which add to the solid waste generated. The electrochemical destruction of the organic compounds (9,10) also suffers from drawbacks such as incomplete destruction and increase in solid waste (if Ce(IV) is used). Corrosion of electrode materials is an additional unsolved problem.

Recently, Bokelund et al (11) have successfully demonstrated the feasibility of photochemical destruction of the organic compounds. The excited uranyl ion is known to be a highly reactive species which can oxidize organic compounds such as carboxylic acids, alcohols and carbohydrates (12). This is due to the relatively long life time and very high oxidation potential (2.6 V) of the excited state (13). Destruction of oxalate by excited uranyl ion has been well studied and is in fact used in chemical actinometry (14). The net reaction has been given (12) as :

$$H_2C_2O_4 \xrightarrow[UO_2^{2+}]{} CO_2 + HCOOH \qquad (1)$$

$$H_2C_2O_4 \xrightarrow[UO_2^{2+}]{} CO + CO_2 + H_2O \qquad (2)$$

The previous study by Bokelund did not examine the effect of uranium concentration. Further, the destruction was studied as a function of the concentration of nitric acid taken for dissolution and not the final acidity.

A detailed study of the direct dissolution of carbides in nitric acid as a head-end step for reprocessing has been initiated in our centre to support the need to reprocess the carbide fuel from FBTR. Studies are being carried out to establish the identity of the organic compounds formed but so far all of them have not been identified. This paper describes the result of the photochemical destruction of the organic species formed. In the present work, the destruction process was followed by monitoring the following parameters:

1. Absorbance of the solution at 400 nm.
2. Measurement of residual carbon content of the solution.
3. Measurement of the distribution coefficient for the extraction of Pu(IV) into Tri-n-butyl Phosphate (TBP).
4. Retention of plutonium in TBP during stripping.

EXPERIMENTAL

Uranium carbide was obtained from BARC (prepared by carbothermic reduction of UO_2). The sintered pellets mainly consisted of uranium monocarbide (UC) phase with a small admixture of uranium sesquicarbide. The total carbon content of the pellets was about 4.5 wt %.

Approximately 100 g of uranium carbide was dissolved in 600 mL of 10M HNO_3 at room temperature (300 K). The resulting dark brown solution was then filtered. The uranium in the above solution was removed by contacting the solution twice with 30% TBP in Shellsol-T. The aqueous phase containing the organic species and some residual uranium was washed with an equal portion of benzene to remove any TBP. The washed aqueous phase containing the organic species was then reduced to a minimum volume, allowing all the nitric acid (and any trace level of benzene) to evaporate at 308 K using a rotary evaporator. The highly viscous residue was again dissolved in 4M HNO_3. This solution was diluted as follows for further experiments.

During the reprocessing of FBTR mixed carbide fuel, 75 g of carbide would be dissolved in one litre of nitric acid. It was found that when 7.5 g of uranium carbide is dissolved in 100 mL of nitric acid, 100 µL of this solution diluted to 10 mL gave an absorbance of 0.5 units at 400 nm. Therefore, while preparing the "carbide dissolver solution" in the present work, the concentrated solution referred to above, was diluted in such a way that 100 µL of the solution, diluted to 10 mL gave an absorbance of 0.5 at 400 nm. The uranium concentration in the solution was varied by adding different quantities of uranium at the dilution stage. This way, all the starting solutions had an equivalent concentration of the organic species, with varying uranium or nitric acid concentration. The wavelength of 400 nm was chosen for absorbance measurements to monitor the concentration of the organic species, because, at this wavelength, the organic species were found to

absorb strongly, while the absorption due to uranium was comparatively small.

A synthetic solution containing oxalic and mellitic acids was used in some of the experiments to examine the effect of irradiation on these compounds. This solution was prepared by dissolving 0.13 g of oxalic acid dihydrate and 0.033 g of mellitic acid in 65 mL of the solution. These concentrations (0.016 M and 0.0015 M respectively) correspond to 10% and 5% respectively of the carbide carbon which could be present in the form of these acids if 75 g of carbide was dissolved in one litre (2).

Irradiation experiments were carried out using an immersion well type annular reaction vessel of volume 65 mL. A 125 W medium pressure mercury vapour lamp either with a quartz or a glass immersion well was used. The light output of the lamp in the wave length region of 210 to 450 nm is 1.12 Einstein per hour. The emission characteristics of this lamp matches well with the absorption spectrum of uranyl ion. The temperature of the solution varied between 313 and 318 K during lamp operation.

All the absorbance measurements were performed using a Cary 17D model spectrophotometer. All the carbon analysis were performed by a wet chemical method developed in our laboratory (15).

A 30% solution of TBP in dodecane was used for the distribution coefficient measurements. A stock solution of 8.4×10^{-5} M Pu(IV) (20 μg/mL) was prepared by adjusting the oxidation state by the addition of nitrite (16). 50 μL of this stock solution was added to 2 mL of the carbide dissolver solution (acidity 4 M ; uranium concentration 21.2 mg/mL) or the synthetic solution. Equal volumes of this solution and TBP solution were equilibrated for about 5 minutes. The plutonium concentration in each phase was assayed by α- liquid scintillation counting.

In the stripping experiments, the extract obtained as above was equilibrated three times with an equal volume of 0.1 M HNO_3 solution, and the plutonium retained in the organic phase determined by liquid scintillation counting. Percent retention was calculated as

$$([Pu]_{as} / [Pu]_{bs}) \times 100$$

where $[Pu]_{as}$ refers to the plutonium concentration in TBP phase after stripping, and $[Pu]_{bs}$ refers to the concentration before stripping.

RESULTS

During the dissolution of uranium carbide in 10 M HNO_3, only 40% of the total carbide carbon was evolved as CO_2 gas. The

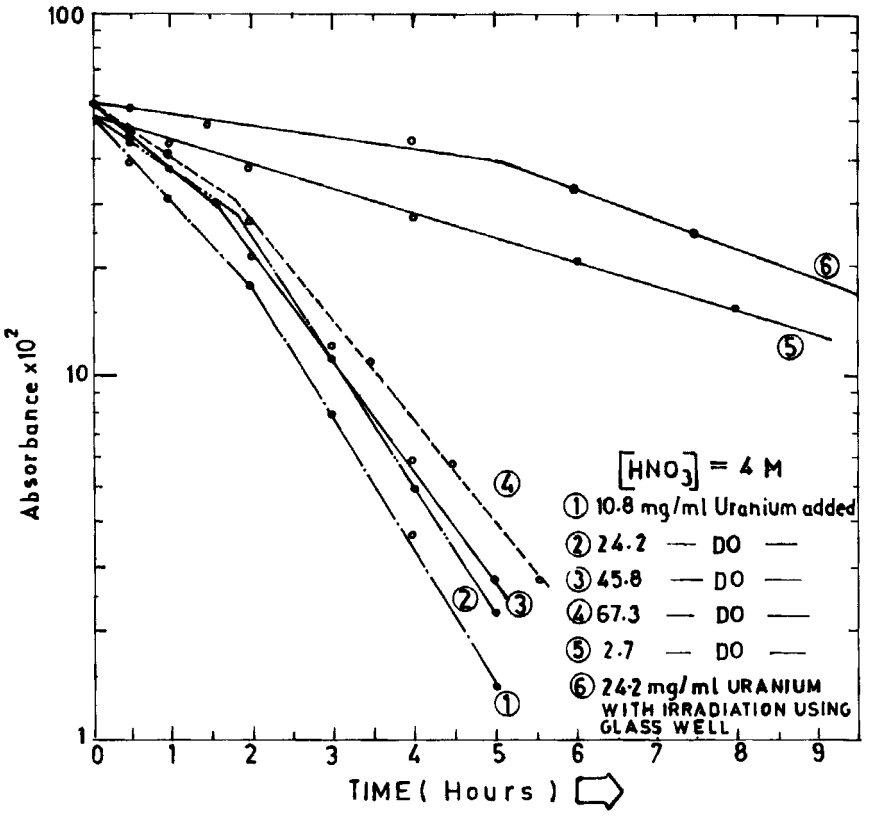

Fig.1. Photo-destruction of organic species as a function of time, with varying uranium concentration. Absorbance measured at 400 nm (path length 10 mm). $[HNO_3]$ = 4 M.

remaining 60% was transformed into carbonaceous by-products giving a dark red-brown solution.

During the extraction of uranium by 30% TBP/Shellsol-T little or no extraction of organic species was observed. This is in accordance with the observations of Ferris and Bradley (2).

The destruction of organic species as a function of time for various levels of uranium concentration was monitored by absorbance measurements at 400 nm. As stated earlier, the absorbance of the solution at this wavelength could be taken to indicate the concentration of the organic species. The results of the absorbance measurements are shown in fig.1. In this figure, curve no.6

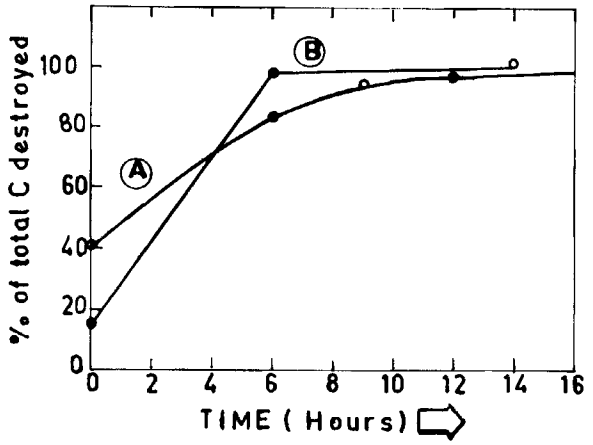

Fig.2. Residual carbon content of the irradiated solution as a function of time.
A: Carbide Dissolver Solution;
B: Synthetic solution containing oxalic and mellitic acids. $[HNO_3]$ = 4 M ; [U(VI)] = 21.2 mg/mL.

represents the results with glass well and the rest represent the results with quartz well. The semi-logarithmic plots clearly depict the bi-exponential nature of the destruction rate of the organic species. The rate of oxidation depends on uranium concentration. However, the optimum concentration of uranium appears to be around 10 - 45 mg/mL. Very high concentration of uranium may cause self-quenching of the uranyl excited state (17) and therefore may not be beneficial from the rate point of view. For the same uranium concentration the quartz immersion well showed a drastic enhancement in the rate of oxidation of organic species. However, even using the quartz well it took almost 6 hours to get a clear yellow solution of minimum absorbance (equivalent to the absorbance of corresponding uranyl concentration at 400 nm).

The results of carbon analysis as a function of irradiation time are shown in fig.2. Curve A shows that the residual carbon content reaches a stable minimum value after about twelve hours. Curve B shows the residual carbon content as a function of irradiation time for the synthetic solution. It can be seen that within 6 hrs almost all the oxalic and mellitic acids have been destroyed .

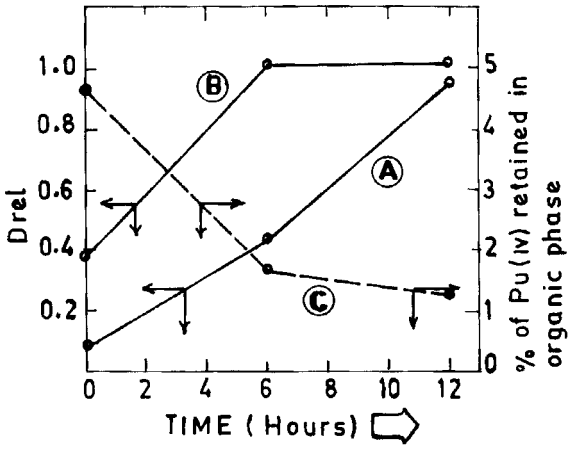

Fig.3. Variation of relative distribution coefficient (D_{rel}) for extraction of Pu(IV) into 30 % TBP/n-Dodecane as a function of irradiation time.
A: D_{rel} for extraction from carbide dissolver solution;
B: D_{rel} for extraction from synthetic solution;
C: Percentage retention of Pu(IV) in TBP phase for carbide dissolver solution, after three stages of stripping.

The extraction of tracer Pu (IV),added to the carbide solution, into 30% TBP and its subsequent stripping from the TBP phase was studied as a function of irradiation time. The results are shown in fig.3. In this figure, the values of D_{rel} refer to the ratio:

$$D_{rel} = D_t / D_{std}$$

where D_t is the distribution coefficient obtained when the carbonaceous compounds are present and D_{std} is the distribution coefficient for a system without these compounds. For the carbide solution (curve A), the D_{rel} reaches a maximum value only after 12 hrs of irradiation. However, for the solution containing only oxalic and mellitic acids (curve B) this occured within 6 hrs.

The results of stripping studies are also shown in fig.3 (curve C). Original retention of 4.6% decreased to 1.25% in the course of irradiation. With the synthetic solution no retention of Pu(IV) in TBP phase was observed at any time although it showed a lower D_{rel} value initially.

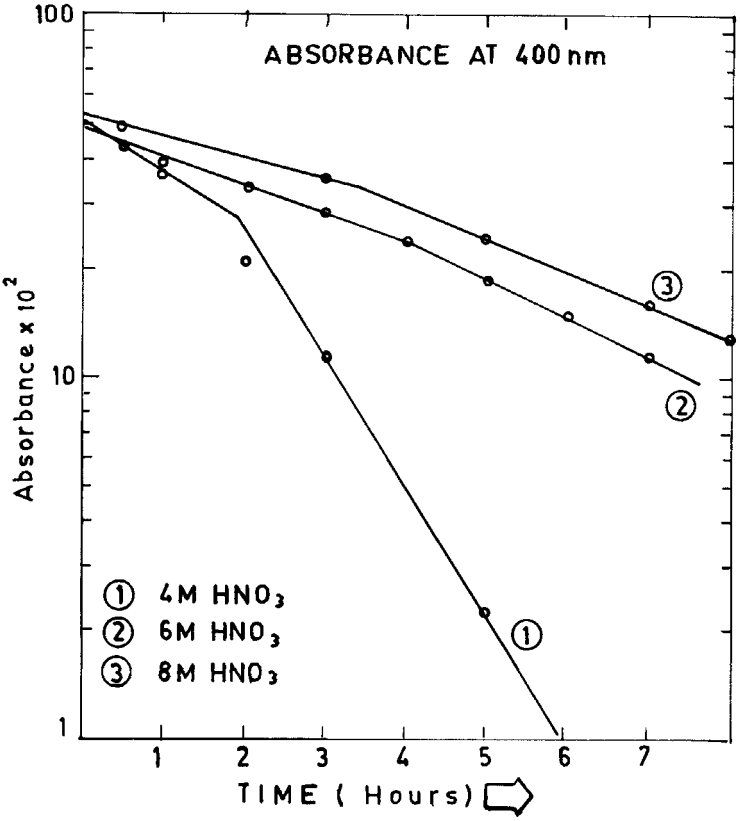

Fig.4. Photo-destruction of organic species in carbide dissolver solution as a function of time, for varying nitric acid concentration. [U(VI)] ▫ 21.2 mg/mL.

The photo-oxidation of organic compounds was also studied as a function of nitric acid concentration for fixed uranium concentration . The results shown in Fig.4 suggest that higher acidity inhibits the process, as observed by Bokelund et al (11).

During the course of photo-oxidation, no change in uranium oxidation state, no precipitation and very little consumption of nitric acid was observed (change in nitric acid concentration was between 0.2 and 0.7 M).

DISCUSSION

The marked superiority of a quartz well over a glass well can be attributed to an overall increase in the steady state concen-

tration of excited uranyl ion. This increase is clearly due to the increase in transparency below 400 nm thus causing an overall increase in absorbed light. The molar absorptivity of uranyl ion is very high for wavelengths less than 330 nm (18). However, the presence of nitrate ion in very high concentrations will decrease the net energy absorbed by uranyl ion, as the nitrate ion has an absorption maximum around 300 nm (19).

A marked difference was found between our observations and that of Bokelund et al (11) in the correlation between absorbance measurements and carbon analysis. In the previous work, the results of determination of carbon left in the solution agreed with the measurement of decrease in absorbance at 400 nm. In the present work, it was observed that 14-18% of carbon still remained in solution even when the absorbance value at 400 nm reached a minimum. This observation suggests that some colourless organic species remained in the solution, which may pose problems in plutonium and uranium recovery. The D_{rel} value and the percentage retention value clearly support the above view point and indicate that some or all of these compounds are extracted into TBP and cause the retention of plutonium. As mentioned earlier, the distribution coefficient data (Fig.2,curve B) and the carbon analysis data for the synthetic solution indicate that oxalic and mellitic acids are destroyed within about 6 hrs of irradiation. However, the D_{rel} values and the carbon analysis results for the carbide solution indicate the presence of interfering organic compounds even after 6hrs of irradiation. It can therefore be inferred that not only the oxalic and mellitic acids but some other organic compounds are also responsible for complexation in aqueous phase as well as retention in organic phase. This is in contradiction with the observations of Choppin et al (6). Again, the observation that no retention in any case was found with the synthetic solution supports the above inference.

The percentage of retention of tracer Pu(IV) in organic phase was found to be quite high in our experiments (1.25% in 12 hrs). This value is likely to be much lower with the actual reprocessing solutions since the concentration of the organic compounds are expected to be much lower than that of plutonium and uranium.

The failure to detect any CO in the off gas by Bokelund et al (11) clearly rejects the reaction path way (equation 2) in the uranyl sensitized photo-oxidation. The following reaction has been suggested to account for the destruction of HCOOH (11).

$$HCOOH + NO_3^- \longrightarrow CO_2 + H_2O + NO_2^- \qquad (3)$$

It has been found by Bokelund et al (3) that during the dissolution in 4 M HNO_3, the percentage of carbon evolved as CO_2 (60%) is greater than during dissolution in 6 M or 8 M HNO_3. On the other hand, the work done by the same authors shows that less than 50% of carbon is evolved as CO_2 at 353 K (11). It is, there-

fore, very difficult to infer from their results whether the effect of acidity on photo-destruction is due to the acid concentration or due to variation in the nature and amount of carbonaceous by-products. Our data in Fig. 4 show the effect of nitric acid concentration alone on the rate of photo-destruction, since dissolution conditions were the same in all cases. Apart from the concentration of the hydrogen ion, which inhibits the decomposition of $H_2C_2O_4$ or similar acids by excited uranyl ion (20), the concentration of nitrate ion is also of significance since it is known to quench the excited uranyl ion (21).

In the absence of a thorough knowledge of the nature and amount of organic compounds formed during dissolution, it is difficult to determine the exact quantum efficiency of the photo-destruction process. However, it should be possible to measure roughly the quantum yield of the over all process, and this could lead to an assessment of the cost of the process vis-a-vis other processes for head-end treatment.

Some of the metal ions are known to quench the excited state of uranyl ion (13). Therefore, the presence of fission products could have a bearing on the use of the photochemical destruction method for the Purex process dissolver solutions.

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