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Recovery of uranium(VI) from acidic wastes using tri-*n*-octylphosphine oxide and sodium carbonate based liquid membranes

P.S. Kulkarni*

Dr. K.S. Krishnan Research Associate, Chemical Engineering Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

Abstract

Acidic wastes containing low concentrations of uranium are generated during uranium purification and processing. This study has been initiated to develop a suitable emulsion liquid membrane (ELM) technique for selective separation and recovery of uranium from such wastes using tri-*n*-octylphosphine oxide (TOPO) in paraffin as a carrier and sodium carbonate as a stripping agent. The waste, having a composition of nearly 600 ppm U(VI), 360 ppm Fe(III), 325 ppm Ca(II), 390 ppm Mg(II) at an acidity of 1.2 M HNO_3, was used as the feed phase. A comparison of ELM extraction was done between synthetically prepared uranyl feed solution and acidic wastes. Various factors that affect the emulsion stability as well as percentage extraction of uranium have been optimized in order to obtain maximum concentration of uranium from acidic wastes. An attempt was made to recover uranium without making any substantial changes to the wastes composition. In presence of various metal ions, selective permeation of uranyl ions through liquid membrane was observed to be more than 70%. Batch type extractions of U(VI) by the ELM method were performed to simulate a two-stage counter extraction and the experimental findings suggest that the U(VI) concentration in the final raffinate can be lowered to below 50 ppm. Potential of the method for the selective separation of U(VI) from acidic wastes is, thus, established.

Keywords: Aqueous acidic waste; Uranium(VI) recovery; Liquid membrane; Tri-*n*-octylphosphine oxide (TOPO); Sodium carbonate

1. Introduction

In recent years, efficient separation of radioactive metal ions has been studied actively in connection with the development of new, advanced processes with superior properties [1]. One such process-an emulsion liquid membrane (ELM) process-an advanced extraction technique for the recovery of metal ions has received considerable attention in the past three decades due to characteristics, such as ease of operation, low cost factors, high selectivity, low concentration of carrier, larger area for mass transfer, and higher fluxes [2–5]. The recent commercial applications of ELM on industrial scale include the removal of zinc at a textile plant in Austria, cyanide removal from waste liquors in gold processing plant in China and removal of phenol from wastewater [6].

The ELMs can be either W\O\W or O\W\O type. The liquid membrane phase is that which separates the encapsulated drops in the emulsion from the external continuous phase. ELM provides a potentially powerful technique for effecting a diverse separation operation, while simultaneously allowing the external solute to be concentrated strongly in the receiving phase.

Selective transport of uranium(VI) from a secondary source containing the metal ion at low concentration level has attracted the attention of nuclear scientists. Recovery of uranium from aqueous wastes is of specific interest in this study. Acidic wastes generated in uranium processing plant contains uranium along with other base metals. The selective separation and recovery of valuable uranium from the wastes is one of the major tasks to accomplish, since it is always desirable to recover uranium from such wastes not only for the strategic value of uranium as a fuel for nuclear reactors, but also to meet stringent discharge standards.

Preliminary results for the separation and recovery of uranium with ELMs have been reported in the literature [7–10]; however, very little is mentioned concerning the application of ELM technique on actual uranium wastes. This manuscript focuses on the studies carried out to concentrate uranium from such a waste stream, using ELM technique to facilitate recovery of uranium.

2. Experimental

2.1. Chemicals

TOPO (99% purity; Loba Chemie Pvt. Ltd., Mumbai), D2EHPA (97% purity; BARC make) and TBP (98.5%

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* Tel.: +91-22-5592660; fax: +91-22-5505151.
E-mail address: ps_kulkarni@rediffmail.com (P.S. Kulkarni).

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purity; S.D. Fine Chemicals Ltd., Mumbai) were used as such without further purification. Surfactant sorbitan monooleate (Span 80) was obtained from Mohini Organics (P) Ltd. Mumbai. Diluent paraffin ($\mu = 1.28\,\mathrm{mPa\,s}$, $\rho = 0.83\,\mathrm{g/ml}$) and heavy paraffin (HP) ($\mu = 5.76\,\mathrm{mPa\,s}$, $\rho = 0.89\,\mathrm{g/ml}$) were used in the membrane preparation. A typical batch of uranium matrix having waste composition nearly U(VI) = 600 ppm, Fe(III) = 360 ppm, Ca(II) = 325 ppm, Mg(II) = 390 ppm and free acidity 1.2 M HNO_3 was directly used as the feed phase. All other chemical reagents were of analytical grade and used as received.

2.2. Membrane preparation

Membranes were prepared by emulsifying an aqueous solution of strip phase with an organic phase (1:1 ratio). The organic phase consisted of surfactant Span 80 (v/v) and TOPO in diluent paraffin. The internal strip phase (sodium carbonate) was added dropwise to the stirred organic phase. The contents were stirred at 5000 rpm for 15 min with a four-blade turbine impeller of 40 mm diameter in a glass vessel of 90 mm diameter.

2.3. Separation of uranium from aqueous acidic wastes

The stable emulsion obtained was dispersed in the feed of acidic wastes stream from which uranium was to be recovered. The extraction runs were performed in a glass vessel having 80 mm internal diameter and a six flat bladed turbine impeller of 40 mm diameter rotating at 300 rpm. A treat ratio (emulsion to feed phase) of 1:5 was used for the extraction purpose. Samples of about 5 cm^3 were withdrawn from the extractor at different intervals of time and were filtered through a Whatman filter paper (no. 540) to separate emulsion from aqueous feed phase. The loaded emulsion was de-emulsified by thermal process for strip phase analysis [11]. Experiments on the liquid–liquid extraction equilibrium of uranium were carried out by mixing 25 cm^3 of organic phase and 25 cm^3 of aqueous phase and then shaking for 1 h. All experiments were carried out at ambient temperature (25 ± 2 °C).

2.4. Analytical

The concentrations of uranium in the aqueous feed and strip phases were spectrophotometrically determined using alkaline peroxide method [12] (model: CHEMITO 2000, TOSHNIWAL (P) LTD., India). The concentration of uranium in the organic phase was calculated by mass balance. The measurement of uranium extraction and stripping is described elsewhere [13]. Free acid present in the wastes was determined by titration with sodium hydroxide and the interference due to metals was suppressed by complexing with 3% sodium fluoride [14]. The concentrations of other metal ions (Fe, Ca, Mg) were determined using atomic absorption spectrophotometer (model: GBC, AVANTA-PM, Australia). Error in analysis of uranium was within ±4%.

3. Results and discussion

3.1. Extraction chemistry of uranium

The choice of extractant and strippant is vital for the success of ELM technology and this choice can be made on the basis of liquid–liquid extraction studies of the metal. An extensive literature is available on extractants and its application in uranium recovery. Some of the recently studied extractants are DHDECMP [15], PC-88A [16], HDBP [17], naphthenic acid [18], β di-ketones [19], etc.

Extractants, such as D2EHPA, TBP and TOPO have been frequently used in solvent extraction studies of uranium [20–22]. In the present investigation, these extractants were tried at their 0.1 M concentration in diluent and contacted with equal volumes of acidic wastes containing uranium(VI). The efficiency of the extraction system was measured in terms of distribution ratios (D), and selectivity of uranium over the other metals present in the wastes. Table 1 shows that extraction of uranium is higher in D2EHPA but the selectivity is very poor. On the contrary, selectivity of uranium(VI) is better for TOPO and the extraction is also reasonable. Thus, TOPO was found to be the most effective extractant for extraction of uranium from acidic wastes compared to the other extractants that were tried.

The extraction of uranium(VI) by TOPO [23] can be represented as:

$$UO_2(NO_3)_{2\,\mathrm{aq.}} + 2\mathrm{HR}_{\,\mathrm{org.}} \rightleftarrows UO_2(NO_3)_2\cdot 2\mathrm{HR}_{\mathrm{org.}} \qquad (1)$$

$$K_{\mathrm{ex}} = \frac{[UO_2(NO_3)_2\cdot 2\mathrm{HR}]_{\mathrm{org.}}}{[UO_2(NO_3)_2]_{\mathrm{aq.}}[\mathrm{HR}]^2_{\mathrm{org.}}} \qquad (2)$$

where K_{ex} is the stoichiometric equilibrium constant and HR represents TOPO. The distribution coefficient of uranium is defined as:

$$K_{\mathrm{D}} = \frac{[UO_2(NO_3)_2\cdot 2\mathrm{HR}]_{\mathrm{org.}}}{[UO_2(NO_3)_2]_{\mathrm{aq.}}} \qquad (3)$$

For the stripping of uranium from the loaded organic solvent several striping agents, such as HNO_3, H_2SO_4, sodium citrate and sodium carbonate were tested. It was found that sodium carbonate of 1 M stripped more than 90% of the extracted uranium, and less than 3% of the other metals. Hence,

Table 1
Distribution ratios for metals present in acidic wastes

Extractant (0.1 M)	Distribution ratios (D)			
	U(VI)	Fe(III)	Ca(II)	Mg(II)
D2EHPA	1.22	0.24	0.03	0.02
TBP	0.40	0.05	0.01	0.01
TOPO	1.14	0.02	0.01	0.00

sodium carbonate was found to be the promising stripping agent.

The combination of TOPO and sodium carbonate was found to be the best during liquid–liquid extraction was used in ELM studies also. The ELM process involves the extraction and stripping in one-step.

3.2. *Extraction using liquid membranes*

In our earlier studies with synthetic solutions [13], it was observed that 3% (v/v) span 80, 0.05 M TOPO and 0.5 M concentration of Na_2CO_3 gave more than 90% extraction and 80% stripping of uranium at a pertraction time (where maximum extraction of uranium occurs in the membrane) of 15 min. In the present wastes system, in order to check the feasibility of the process same parametric composition was used and the results were correlated. The studies with actual acidic wastes show very low values of extraction (55%) and stripping (15%). It was also observed that the maximum extraction of uranium occurs at pertraction time of 6 min, which is very low compared to the synthetic solutions.

In order to achieve maximum extraction and stripping of uranium, it was decided to design a new membrane formulation for the recovery of uranium from acidic wastes.

3.2.1. *Extractant/carrier concentration*

Fig. 1 shows the effect of TOPO concentration on the ELM extraction of uranium. It was found that extraction increases with the increase in concentration of TOPO. This is because increase in carrier concentration will increase the mass transfer. The decrease in extraction after 6 min. is attributed to leakage of uranium from internal phase. It was also observed that change in concentration of TOPO did not affect the stability of emulsion.

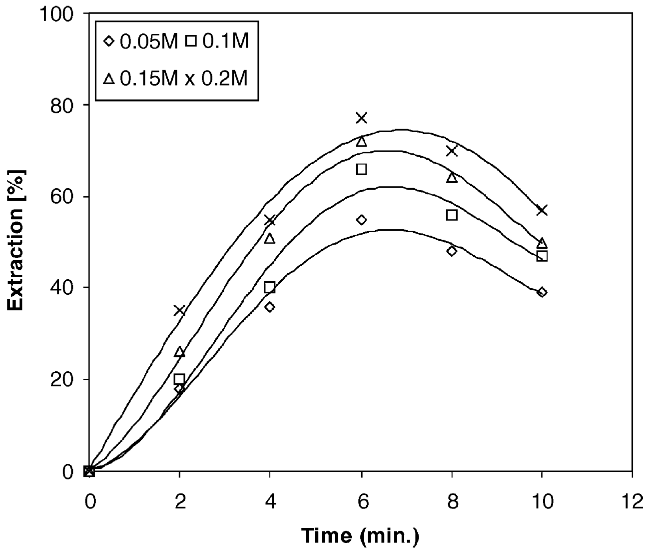

Fig. 1. Effect of carrier concentration on extraction of uranium.

3.2.2. *Feed phase acidity*

White and Ross [23], observed that increase in nitric acid concentration to a certain extent increases the extraction of uranium but with further increase in its concentration there is increased competition between uranyl ions and nitric acid for complexation with TOPO. In the present case, a highly acidic wastes is causing problems on the emulsion stability as well as on the extraction and stripping of uranium, hence, it was decided to neutralize some of the acid using caustic. Therefore, feed phase acidity was lowered from original 1.2–0.1 M, which is shown in Fig. 2. It was observed that decrease in acidity of the feed phase increases the extraction of uranium up to 0.3 M of the acidity. Further decrease in acidity of the feed phase resulted in a decrease of the extraction of uranium and also, the precipitation of Fe has started. Therefore, in the present ELM system in order to achieve maximum extraction of uranium from acidic wastes, it is very important to maintain the acidity at 0.3 M.

3.2.3. *Viscosity of the membrane*

The viscosity or thickness of the membrane determines the rate of transport of uranium and pertraction time. HP was added into the diluent to study the effect of viscosity on uranium extraction. It was found that increase in viscosity of membrane increases the stability and pertraction time of the emulsion and hence percentage extraction of uranium, which is shown in Fig. 3. But increase in viscosity beyond 30% HP was found to decrease extraction of uranium due to resistance of the emulsion to mass transfer.

3.2.4. *Strip concentration*

The internal base solution always plays a critical role on the stability of emulsion and recovery of a metal. The increase in base concentration increases the permeation rate of solute, but, it also invites more water transfer and leads to instability of membrane [24]. Fig. 4 shows the effect of feed phase acidity on the strip concentration. It was found that final stripping of uranium increases as sodium carbonate concentration was increased from 0.1 to 0.75 M, thereafter, it starts decreasing. Further, it was very interesting to note that the osmotic balance of the ELM system was found to be good at feed phase acidity of 0.3 M and strip phase concentration of 0.75 M. This is because the highest recovery of uranium at this stage was discovered to be 70%. The final strip phase composition was found to be U = 1250 ppm, Fe = 14 ppm, Ca = 10 ppm and Mg = 4 ppm. These concentration values compared with the feed suggest that the process have a potential for selective separation and recovery of uranium from such wastes.

3.3. *Two-stage counter extraction by ELM process*

In order to achieve maximum lowering of uranyl ions in final raffinate a two-stage counter (batch type) extraction experiments with manual exchange of the settled phases between stages were conducted. Initially, the optimum

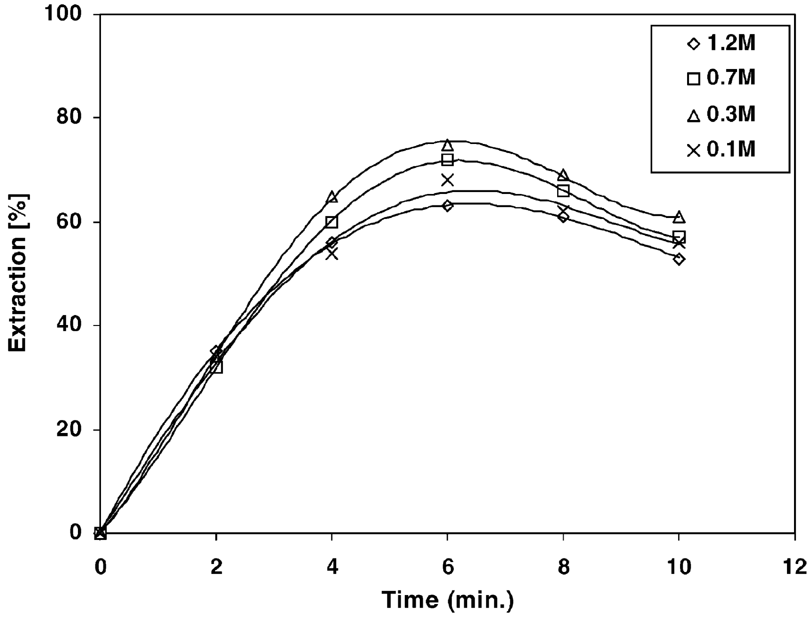

Fig. 2. Effect of feed phase acidity on extraction of uranium.

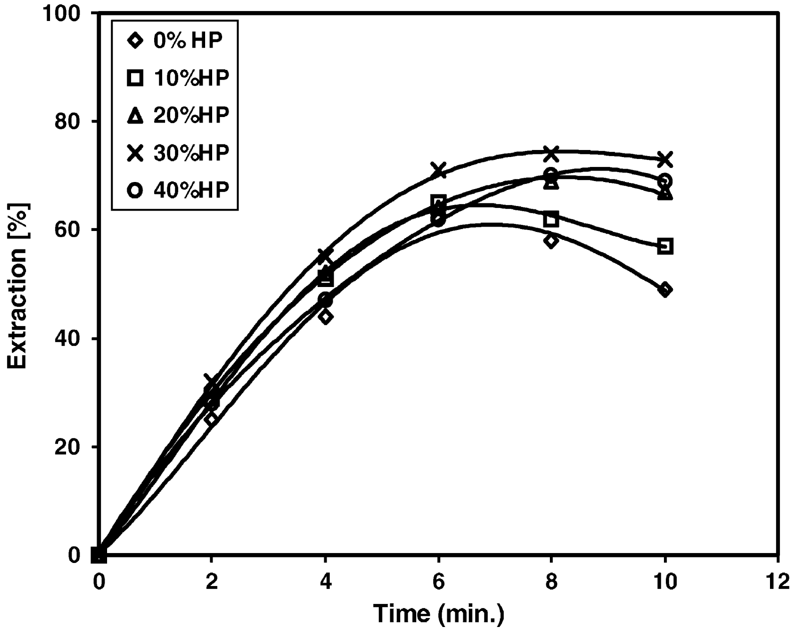

Fig. 3. Effect of viscosity of membrane phase on extraction of uranium.

conditions for ELM extraction of uranium from acidic wastes were determined based on values obtained for stability of emulsion and percentage of extraction. In this study, the most agreeable conditions were found to be 0.1 M TOPO with 3% Span 80 in 30% heavy paraffin (HP) in paraffin and 0.3 M acidity of the feed phase. Estimating from the preceding experiments, the emulsion is stable under these conditions for about 10 min and thus, the extraction time for each extraction was set at 8 min.

An ELM extraction was performed by contacting a fresh emulsion with waste solutions of uranium concentration, which are supposed to be the uranium concentration in the raffinate of the first stage. The uranium concentrations in external solutions before and after the extraction are shown in Table 2 (Part I). The uranium concentration after the extraction corresponds to that of the raffinate of the second stage. The results suggest that if the uranium concentration in the feed solution of the second stage, which is the raffinate of

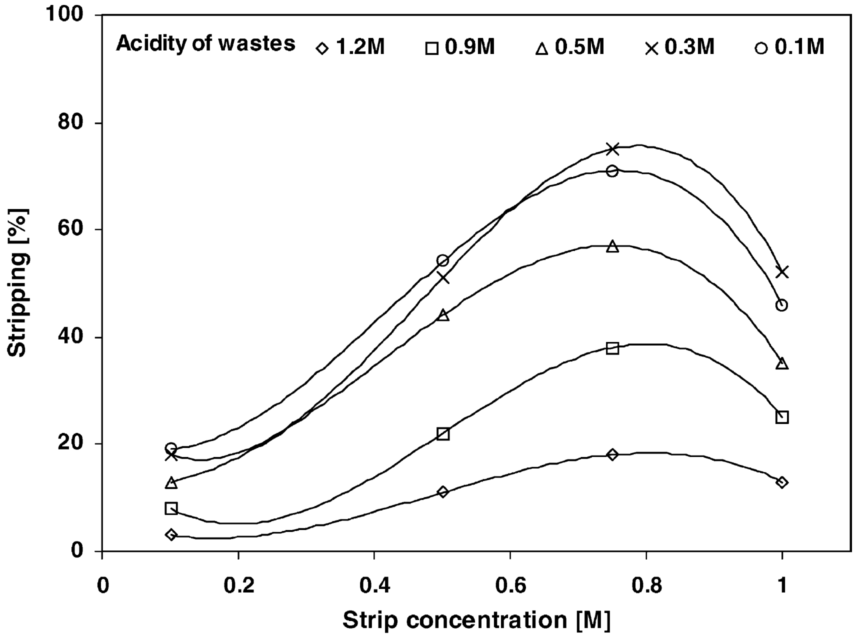

Fig. 4. Effect of strip phase concentration on uranium recovery.

Table 2
ELM experimental results for simulation of two-stage counter extraction of uranium

Experiments	Uranium concentration in external feed phase (ppm)	
	Initial	Final
Part I	180	48
	175	45
Part II	600	224
	600	226

Part I: fresh emulsion; Part II: loaded emulsion.

the first stage, is below 180 ppm, the uranium concentration in the raffinate of the second stage can be lowered to below 50 ppm.

The loaded emulsions of the first part was manually separated from the external solutions and further used for extraction experiment. Table 2 (Part II) shows the results of the extraction experiments using the loaded emulsions and initial acidic waste. Further, the strip phase analysis of loaded emulsion shows 1700 ppm of uranium and less than 3% of the other metal ions. But unlike Hirato et al. [25] the uranium concentration in the raffinate after extraction doesn't exactly correspond to that of the first stage extraction in two-stage counter extraction, which may be due to the difference between a real waste stream and a synthetic solution. Thus, final uranium concentration was lowered to less than 50 ppm by two-stage counter extraction.

4. Conclusions

An ELM process using TOPO and sodium carbonate to concentrate dilute uranyl ions from aqueous acidic waste is investigated. A comparison in ELM extraction between waste stream and synthetic uranyl solution shows a lot of difference in emulsion stability, pertraction time and percentage of extraction and stripping of uranium. Hence, various factors, including the concentrations of TOPO, viscosity of the diluent, feed phase acidity and stripping concentration, were examined in order to get maximum recovery of uranium from acidic wastes. It was found that higher recovery of uranium from acidic wastes was obtained when the internal phase concentration of sodium carbonate is 0.75 M and feed phase acidity is 0.3 M. Selective permeation of uranium from various cationic impurities suggests potential application of this method in nuclear industries. More than twice enriched uranium was obtained in the strip phase using these parameters. The stability and reproducibility of the membrane with the increase in viscosity were found to be excellent in impregnation mode. This is advantageous for the application of the ELM system to treat actual waste stream for recovery of uranium. To simulate a two-stage counter extraction, batch type extractions of acidic waste by ELM method were performed. The experimental findings suggest that the uranium concentration in the final raffinate can be lowered to below 50 ppm when the feed containing 600 ppm is treated by two-stage extraction.

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