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Extraction of Uranium from Wet Process Phosphoric Acid by Liquid Membranes

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Abstract

The liquid membrane process can effectively separate and concentrate uranium from wet process phosphoric acid and is economically superior to solvent extraction systems. The paper describes the process, compares it to other extraction schemes, and shows how it can be used for uranium recovery. A mathematical model useful for design purposes is presented and the effect of important variables is discussed.

INTRODUCTION

General Description of Liquid Membranes (LM)

The liquid membrane process utilizes emulsion technology to extract, concentrate, and recover, if desired, components of dilute solutions (*1–13*). It involves the dispersion of globules of oil and water emulsion into a third phase containing the material to be recovered. This is shown in Fig. 1. The upper left-hand corner shows the internal droplets of emulsion; these are typically quite small—on the order of 1–10 μm in diameter. The lower left-hand panel shows globules of emulsion dispersed into the third phase. Each of these globules contains many of the small internal droplets. For

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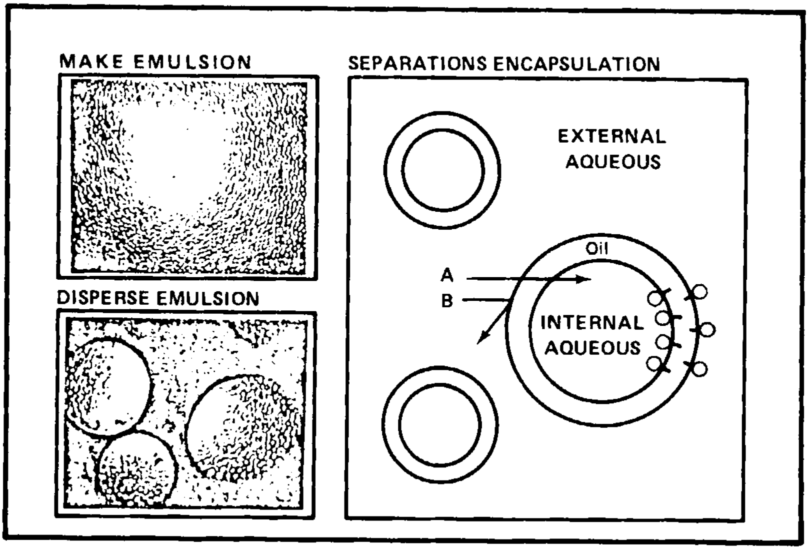

FIG. 1. Liquid membrane system.

illustration purposes however, globules are often shown as though they contain only one large internal droplet; the right-hand side of Fig. 1 is drawn in this fashion. This type of schematic is helpful in illustrating the transfer of species and chemical reactions.

For metals extraction the emulsion is normally oil external since feed streams are usually aqueous. Metal ions or complexes can be extracted through the oil "membrane" into the internal aqueous droplets of the emulsion as shown in the diagram. Individual chemical species can be trapped and concentrated in the internal phase for later disposal or recovery. The liquid membrane concept can also be used for encapsulation and controlled release if so desired.

Liquid membranes are stabilized by surfactant molecules which line up at the interfaces between the membrane and the aqueous phases. A reagent can be encapsulated in the internal phase either for controlled release or for reacting with the permeates. For a specific application the liquid membrane system would be tailor-made with suitable surfactants and reagents.

Facilitated Transfer Mechanisms

There are two facilitated transport mechanisms involved in liquid membrane systems. One is based on reaction in the internal phase, and the

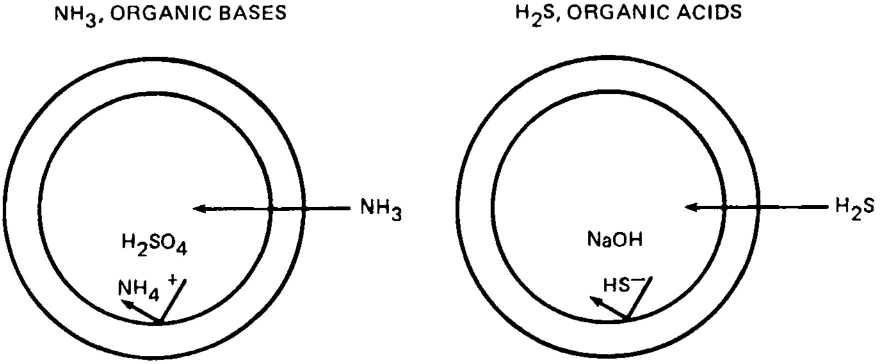

FIG. 2. LM extraction with reaction in internal phase.

other is based on reaction in both the membrane and the internal phase. By the first transport mechanism, liquid membranes can remove organic bases and compounds like NH_3 from their aqueous solutions. These compounds permeate from the external phase to the internal phase because of their appreciable solubility in the membrane phase (Fig. 2). Once in the internal phase, they will react with the encapsulated chemical reagents to form products that are not soluble in the membrane and therefore are held inside. For example, ammonia in the un-ionized form is soluble in the oil membrane and hence will permeate into the internal phase. There it reacts with encapsulated sulfuric acid to form ammonium ion, NH_4^+, which has no solubility in the membrane phase and is therefore held inside. H_2SO_4 at high concentration can be encapsulated in the internal phase in order to build up a high concentration of NH_3 in this phase. In a similar fashion, organic acids and compounds like H_2S can be removed because of their solubility in the membrane phase. A base such as NaOH can be encapsulated in the internal phase to neutralize the acidic permeates and trap them inside.

The second transport mechanism, the one involving reactions in both the membrane and internal phases, is used to remove ionic species which are not by themselves very soluble in the membrane phase (Fig. 3). This is the mechanism used to recover uranium ions from phosphoric acid solutions (wet process phosphoric acid, WPPA). Ionic compounds can react with specially chosen reagents in the membrane phase to form a membrane-soluble complex. A second reaction, this one at the internal phase boundary, decomplexes the product of the first reaction and deposits it in the internal phase. For example, a cation carrier in the membrane phase complexes with copper ions and moves them across the membrane to the interior side. There, the complex is decomposed because of an ion-exchange reaction with

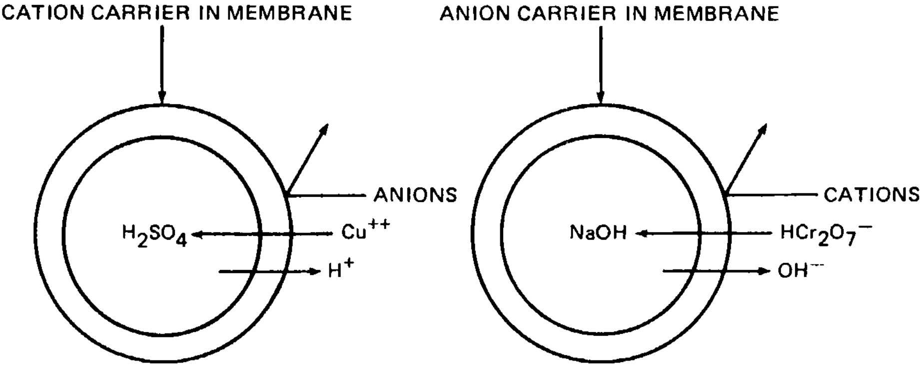

FIG. 3. LM extraction with reaction in both membrane and internal phase.

sulfuric acid. The complex will release copper and carry hydrogen ions back to the external side where the hydrogen ions will be replaced by copper ions and the whole cycle of ion-exchange reactions will start again. For anions, such as chromates, a specific anion carrier is needed in the membrane and a stripping reagent in the internal phase. The basic principle is the same as that for cation transfer.

It should be emphasized that liquid membranes simultaneously extract at the external interface and strip at the internal interface. The process of simultaneous extraction and stripping results in fast separation and requires only a small amount of extracting agent in the membrane phase.

High degrees of separation and concentration can be achieved with liquid membranes. For example, the concentration of chromate in wastewater was reduced in a continuous run from 100 to 1 ppm. This extraction was accomplished with a small amount of liquid membrane emulsion, which was recycled and reused continuously for 31 h. After that time, the internal phase had a chromate concentration of 182,000 ppm. Therefore, the concentration ratio between internal phase and external phase in this case was as high as 182,000 to 1 (*3*).

Comparison of Liquid Membrane with Other Processes

Liquid membranes appear to offer major technical advantages over other technologies in the separation field, and these advantages could in turn lead to major economic incentives for metals recovery and wastewater applications. The technical advantages have been confirmed in pilot operations on real feed streams (*6–8*).

A brief qualitative comparison of the technical differences between liquid membranes and three other extraction technologies—biological treatment, ion exchange, and solvent extraction (SX)—is given below. Comparisons with the first two for a wide range of possible applications are given next. Since the third technology, solvent extraction, is used commercially for uranium recovery from WPPA, it is compared to liquid membranes in a later section of the paper that deals with uranium from WPPA.

LM vs Biological Treatment

Biological treatment does not appear to be an effective way of recovering uranium, but a comparison of it with liquid membrane technology is given here to help position and define the characteristics of a liquid membrane process.

There are a number of differences between liquid membranes and biological treatment. Liquid membranes are less sensitive to upsets or changes in pollutant concentration or flow rate. Even the absence of pollutant can cause problems for biological treatment schemes by depriving the bacteria of nutrient. Because they are less sensitive to upsets, liquid membrane processes may be easier to control. Also, they are not limited to a narrow temperature range as biological schemes are. Biological processes typically operate somewhere between 20 and 40°C, while liquid membranes function well over a much wider range. Liquid membranes do not require as much land area or space as a biological plant. This can be significant where land costs are high. Liquid membrane processs do not produce sludges, whereas many biological schemes do. Sludges can pose difficult handling and disposal problems. In some cases the pollutant being removed is a useful material. Liquid membranes can recover the pollutant as a potentially valuable by-product, whereas biological treatment destroys it. For example, there could be a value in recovering phenol from coke oven waste streams rather than destroying it. Liquid membranes can be tailored to remove either a broad class of pollutants or only one specific pollutant. In general, biological processes remove an even broader range of material than liquid membranes. Whether or not selectivity is an advantage depends on the particular application. Finally, because liquid membranes involve contacting the aqueous feed stream with an oil membrane, they may leave a small amount of the oil membrane in the raffinate. This will be a disadvantage for LM processes; however, the amount of organic left can be minimized through the selection of paraffinic rather than aromatic oils for the membrane phase and through proper filtration and flotation of the raffinate phase. In some cases the liquid membrane process is followed by biological treatment as was the case in the ammonia removal process described in a separate publication (*15*).

LM vs Ion Exchange

Liquid membranes are not as easily fouled or plugged as ion-exchange resins. For example, organic brighteners in plating-shop waste tend to foul resins. Liquid membranes are less sensitive to suspended solids than fixed-bed ion exchange units but more sensitive than continuous fluidized ion-exchange beds. Because of capacity limitations, ion exchange is in general economically best suited to treat solutions containing less than 1000 ppm dissolved solids. Liquid membranes are less capacity limited and can treat more concentrated solutions. Ion exchange is normally a cyclic process (an ion-exchange bed has to go through an adsorption–regeneration cycle) while liquid membrane processes are not. Noncyclic processes frequently require less capital expenditure than cyclic processes. Because the process is not cyclic and can achieve large concentration increases, liquid membranes require less of the chemical complexing materials than ion exchange. In other words, ion exchange may require a sustantial amount of resin to achieve the same separation that a small amount of membranes can accomplish. In general, liquid membranes tend to be more selective than ion exchange for specific pollutants or valuable metals. Also, as mentioned before, liquid membranes may leave some organic in the raffinate where ion exchange will not.

Extraction Chemistry in Liquid Membrane System

A key requirement of any liquid membrane application is a chemistry that will extract, transfer, strip, and store the desired chemical species. This chemistry may differ from application to application. However, a suitable chemistry is frequently available. For example, if solvent extraction is currently being practiced for the same application, chances are that the chemistry employed could be utilized by the liquid membrane process. In this case, chemistry development would be minimized. If the chemistry is not available for a particular application, it might be possible to pattern it after an existing liquid membrane process.

LM EXTRACTION OF URANIUM FROM WPPA

Because uranium extraction from phosphoric acid is commercially practiced by using SX techniques, a brief description of the SX process will be given and the LM process compared against the current practice. This will be followed by discussion of a mathematical model for LM extraction and experimental results showing the effects of operating parameters. Finally, an economic comparison between SX and LM and the corresponding design basis will be discussed.

Uranium Extraction System

Extraction Chemistry

For both SX and LM technology the uranium in phosphate rock has to be solubilized before extraction can take place. In the manufacture of WPPA, both the P and U values in phosphate rock are solubilized. In the WPPA process, phosphate rock is contacted in an attack tank with sulfuric acid to produce gypsum and phosphoric acid. The acid so produced from the dihydrate process is normally about 30% P_2O_5, containing about 0.14 to 0.18 g/L of uranium, depending on the uranium content in the rock. 0.17 g/L corresponds to about a 1 lb U_3O_8 per ton of P_2O_5 and is representative of most of the currently mined Florida rock. In most phosphoric acid plants, this 30% acid is further concentrated to produce higher strength acid. Because of viscosity and equilibrium considerations, all of the uranium extraction plants currently in operation in the United States operate on the 30% acid stream. Basically, the 30% acid stream is diverted to the uranium extraction plant from its normal course. This would also apply for LM. The raffinate from the uranium extraction plant, appropriately treated to keep any organic carryover from the extraction operation to a minimum, is returned to the acid plant for further concentration via evaporation.

The extraction chemistry for the LM technology is essentially the same as that employed in SX. Details for LM are shown in Fig. 4.

Uranyl ion in the feed or WPPA phase is complexed by the complexing agents (CA), di-2-ethylhexyl phosphoric acid (DEHPA), and trioctyl phosphine oxide (TOPO), predissolved in the membrane. The resultant complex is transported across the membrane to the internal phase (IP). Since DEHPA-TOPO does not effectively complex the U(IV) ion, a reductant is used in the internal phase to strip the uranyl complex from the membrane and

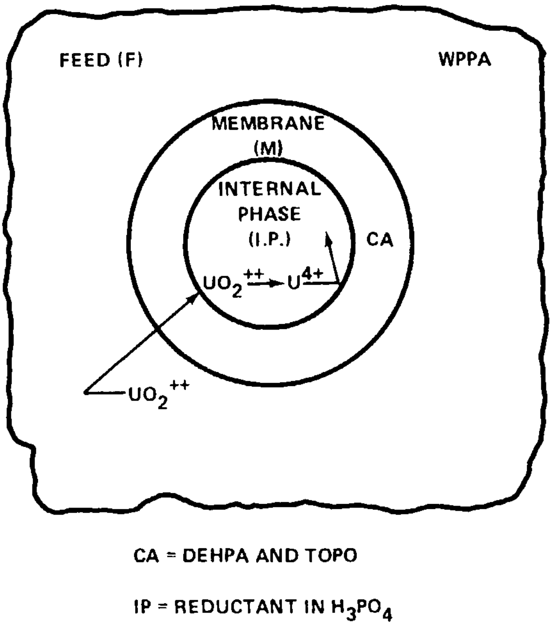

FIG. 4. Extraction of uranium from oxidized WPPA.

form the acid soluble U(IV) species, which is efficiently trapped and concentrated in the internal phase.

An alternative chemistry, studied by Oak Ridge National Laboratory, removed uranium from reduced WPPA by utilizing octylphenyl phosphoric acid (OPPA) to complex U(IV) ion. This chemistry was also explored in the LM system as shown in Fig. 5. The complexing agent in the membrane phase was OPPA. The internal phase of the emulsion employed an oxidant in phosphoric acid to convert the stripped U(IV) species to uranyl ion. Since OPPA preferentially complexed with U(IV) ion, conversion to uranyl ion in the internal phase provided both the driving force and trapping mechanism for uranyl ion.

Membrane Formulation

A typical liquid membrane for uranium extraction contains DEHPA, TOPO, a surfactant, which can be a pipsapolyamine manufactured by Exxon Chemical Co. (*7, 13, 15, 16*), and a hydrocarbon solvent, which can be LOPS manufactured by Exxon Chemical Co. LOPS is a mixture of

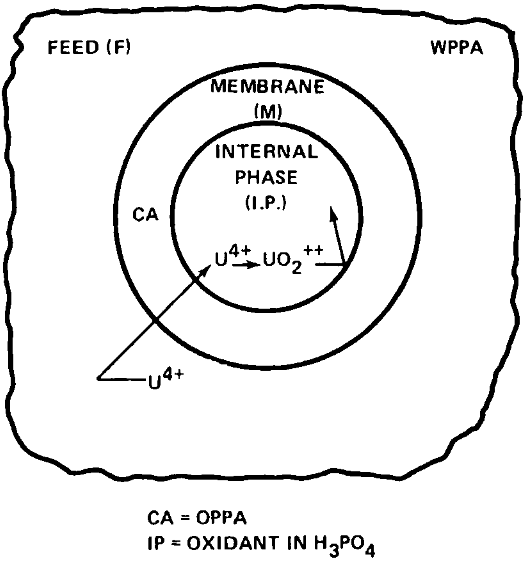

FIG. 5. Extraction of uranium from reduced WPPA.

hydrocarbons (about 52% paraffins, 45% naphthenes, and 3% aromatics) having a specific gravity at 60°F of 0.796, a viscosity of 2.15 cst, and a flash point of 152°F.

Commercial SX Technology

Uranium recovery from WPPA is, unfortunately, a somewhat complex operation. The SX process can be broken into three sequences consisting of acid pretreatment, primary extraction, and secondary recovery.

The pretreatment step (Fig. 6), as a minimum, will involve some means of solids removal and oxidation of the uranium to U^{6+} if the producers utilize DEHPA/TOPO, which requires the uranium in the hexavalent state to permit extraction. Some producers will cool the incoming acid from approximately 140°F to as low as 100°F, while others will go to extensive humic acid removal, such as treatment with activated carbon. One can characterize the current producers into two groups—those using minimal pretreatment consisting of solids removal and oxidation as shown in solid lines; and those practicing maximum pretreatment which, in addition to the

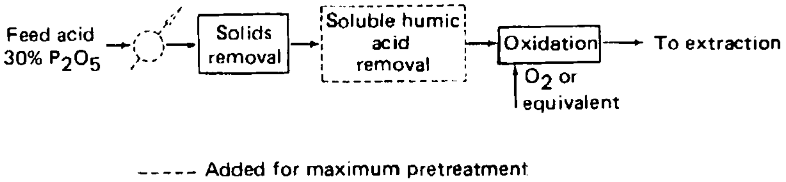

FIG. 6. Feed acid pretreatment SX.

foregoing steps, involves cooling, and soluble organics removal as well, shown by dashed lines. Some producers fall between these extremes; namely, they cool but do not remove soluble organics.

The pretreated feed is then contacted with a kerosene-type solvent containing DEHPA/TOPO—usually in 4–5 countercurrent mixer-settler stages labeled M/S 1 to 4 in Fig. 7. This will transfer in excess of 90% of the hexavalent uranium from the feed acid to the organic phase. The humic acids contained in the phos acid feed will normally form an interfacial crud in the settlers which has to be removed. Economics dictate that valuable components in this crud (such as uranium, DEHPA/TOPO, and solvent) have to be recovered. This is normally a separate operation, distinct from the extraction step. The uranium-rich organic from the first settler is then reductively stripped in a separate stripping operation with 3–4 countercurrent mixer–settler stages labeled M/S 5 to 8. The loaded organic is contacted with lean strip acid having sufficient ferrous ions content to reduce the hexavalent uranium in the organic to the U^{4+} state and, thereby, shifting the distribution coefficient in favor of solution of the six molar strip acid.

The U^{4+} loaded, rich strip acid goes to a secondary solvent extraction step where the uranium is further concentrated, purified, and yellow cake eventually produced. Because the secondary solvent extraction and subsequent yellow cake-production steps are identical to both the SX and LM schemes, these steps will not be described further.

The LM Process

For LM, the pretreatment of the 30% P_2O_5 acid consists of solids removal and oxidation; no soluble organics are removed nor is the acid cooled.

In the LM process (Fig. 8), the pretreated feed was contacted with a lean LM emulsion in a mixer–settler train. The oil continuous emulsion was prepared by contacting the typical membrane formulation described previously with the uranium lean aqueous reductive stripping solution in an

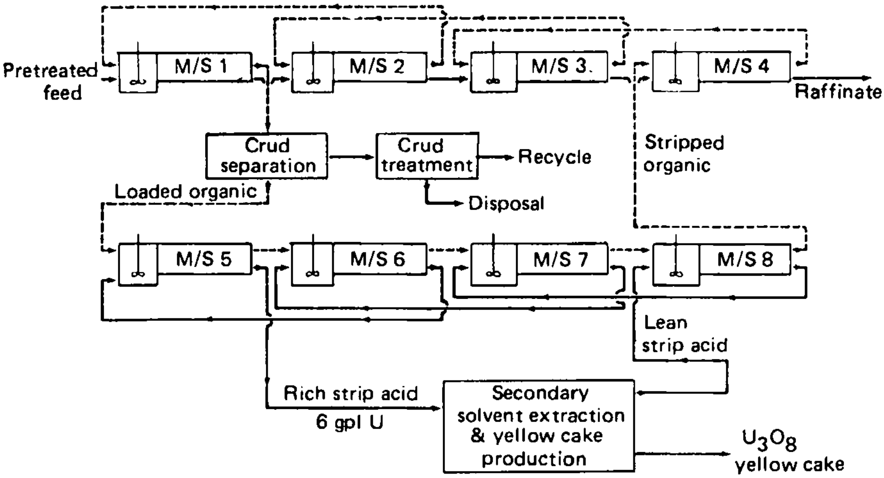

FIG. 7. Uranium recovery via solvent extraction.

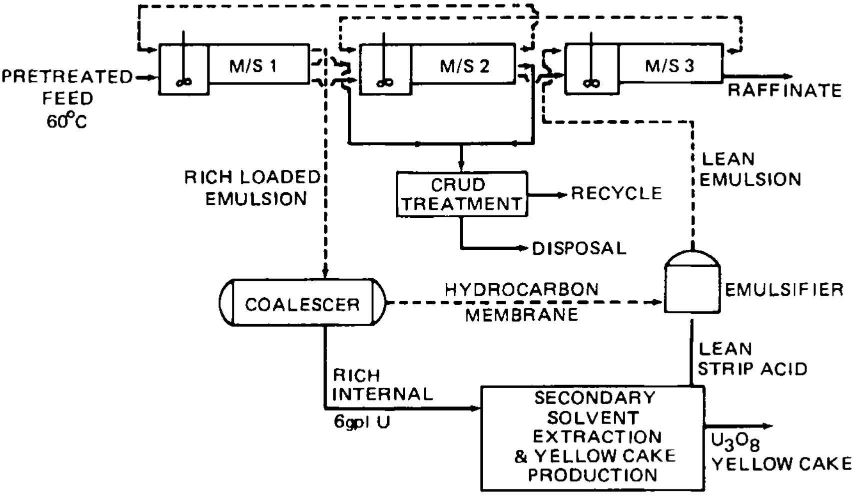

FIG. 8. Uranium recovery via liquid membranes.

emulsifier. The internal phase of the emulsion was therefore an aqueous stripping solution of phosphoric acid containing a reducing agent capable of reducing U^{6+} to U^{4+}. Contact of the feed with this emulsion resulted in extraction of 90+% of the uranium content in the feed which was accomplished in two or three mixer–settler extraction stages, depending on feed temperature. At 70°C, two stages were sufficient; at 60°C, three stages were required, shown as M/S 1 to 3.

After the extraction was accomplished, the loaded emulsion from M/S 1 was broken in an electrostatic coalescer into its components—namely, a rich internal phase and the hydrocarbon membrane phase. The rich internal phase, containing on the order of 6 g/L of uranium, was treated in an identical manner to the strip acid from solvent extraction. The uranium-depleted lean strip acid from the secondary solvent extraction step was recirculated back to the emulsifier after the reducing agent was replenished. At the emulsifier, this replenished strip acid was contacted with the hydrocarbon membrane phase which had been separated in the coalescer, and in this fashion fresh lean liquid membrane emulsion was prepared for contact with the feed in M/S 3.

The main differences between liquid membranes and solvent extraction are shown in Fig. 9 and in Table 1. In pretreatment, LM requires no soluble organics removal or cooling, while SX may require some of these steps. In extraction, we have a maximum of three LM stages versus eight SX stages for extraction and stripping. LM, however, requires a separate coalescer and emulsifier—offsetting to some extent the capital cost savings associated with the elimination of the stripping stages. The secondary solvent extraction step is identical for both processes.

In addition to the equipment-related advantages, there are additional advantages to using the LM technology. They lie primarily in the amount of crud that is formed and organic losses associated with extraction and crud formation. Because the DEHPA/TOPO concentrations in the LM organic phase is 1/5th the concentration normally employed in SX, the amount of crud formed is only 1/4th to 1/5th that normally experienced in SX with equivalent feed pretreatment. Finally because simultaneous extraction and stripping takes place in LM, the organic phase never is the bulk carrier of the uranium. Therefore, the organic circulation rate can be reduced to as low as a feed-to-organic ratio of 18:1 compared to the 1:1 normally found in SX plants. Because of these characteristics of LM, hydrocarbon circulation losses are cut by at least a factor of 10 and chemical make-up costs are considerably lower. Not only is less organic lost in the crud, but the cost of the organic phase is materially less than that employed in solvent extraction because of the lower DEHPA/TOPO concentration.

The LM process is based on an extensive experimental program which

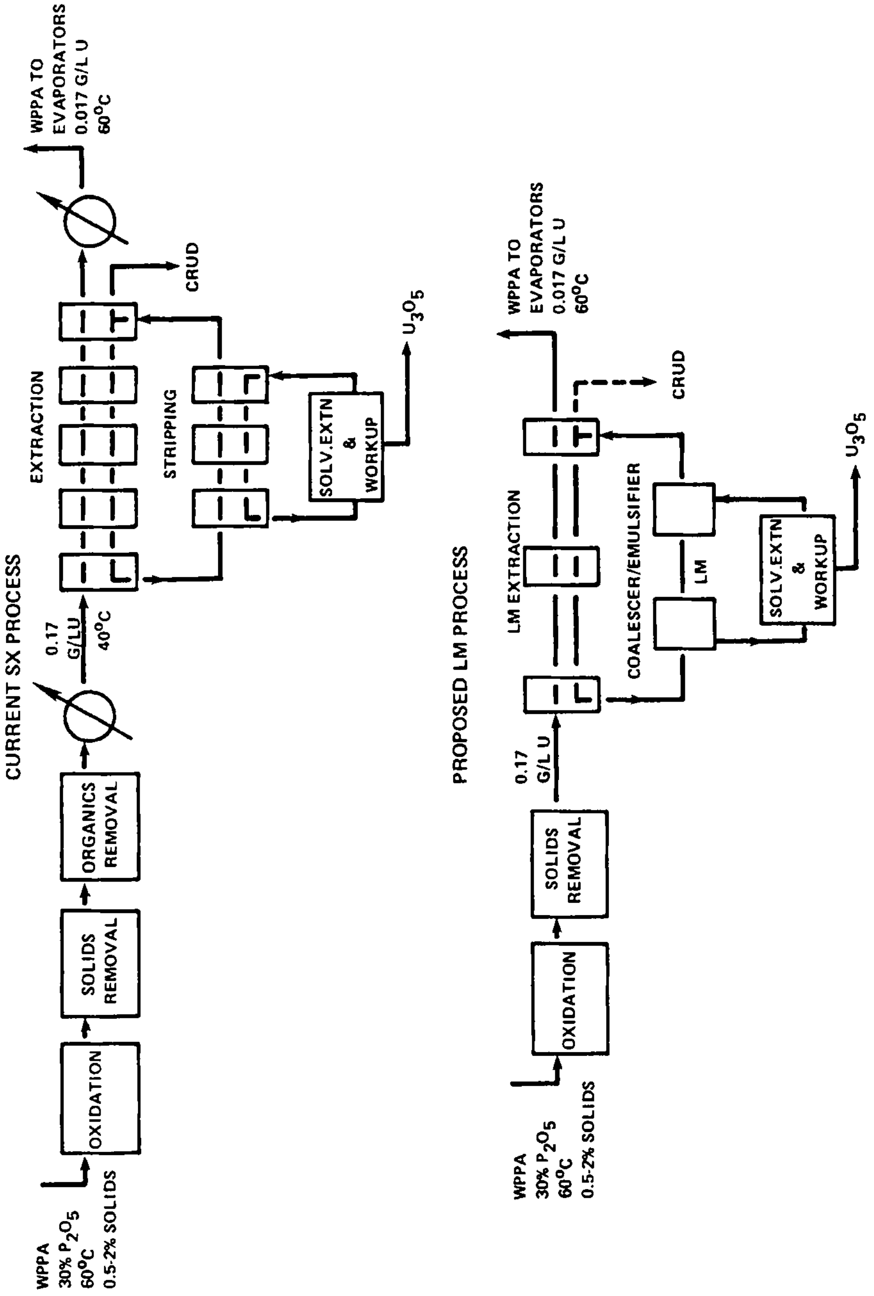

FIG. 9. Comparison of the LM and SX processes for uranium recovery from WPPA.

TABLE 1
Differences between LM and Solvent Extraction

	LM	SX
Feed pretreatment	Oxidation Solids removal	Oxidation Solids removal Cooling Soluble organics Removal
Extraction/stripping	Max. three stages Coalescer Emulsifier	Eight stages
Secondary extraction	Identifical for both	
DEHPA/TOPO		
Concentration	1/5	1
Crude make	1/4–1/5	1
Feed/organic ratio	18:1	1:1

culminated in the operation of a 1 L/min continuous pilot plant at Agrico's WPPA plant in South Pierce, Florida (*11*). This unit provided the underlying data for the process design and confirmed many of the assumptions inherent in the economic analysis. In addition to the continuous pilot plant operation, batch laboratory experiments were also conducted to determine how operating parameters affect the uranium extraction rate. Generally, the extraction rate is expressed in terms of mass transfer coefficients. In order to obtain mass transfer coefficients, a mathematical model had to be developed for the description of the mass transfer rate. In the following section the mathematical model and extraction results showing the effects of operating parameters on the uranium extraction are discussed.

Mathematical Model and Extraction Results

Mathematical Model

A detailed mathematical model containing overall mass transfer coefficients for extraction into membrane droplets and leakage out of membrane droplets has been developed (*14*). A version of this model describing uranium extraction is shown schematically in Fig. 10. Solute A, in this case uranyl ion U(VI), diffuses from the external feed phase to the surface of an internal phase droplet. The mass transfer coefficient associated with this diffusion is called K_A. At the surface of the droplet the solute, U(VI), reacts

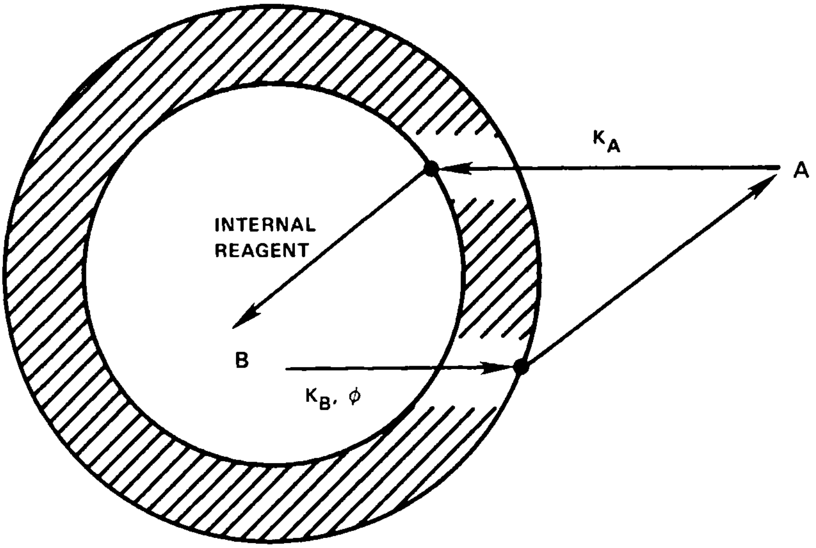

FIG. 10. Schematic of the mass transfer model.

with a reducing reagent, Fe^{2+}, in the internal phase to become Solute B, U(IV). B can "leak" or transfer from the internal phase to the external phase via the diffusion mechanism associated with the mass transfer coefficient K_B and the breakage mechanism associated with the coefficient ϕ. When it arrives at the external phase, B is oxidized and converted into A. In this case, A exists only in the external phase whereas B exists only in the internal phase.

The equation describing this model in a batch extraction operation is as follows:

$$\frac{d(V_e C_{eA})}{dt} = -K_A^\circ C_{eA} + (K_B^\circ + \phi V_i)C_{iB} \tag{1}$$

where

$$K_A^\circ = K_A(V_m + V_i) \tag{2}$$

$$K_B^\circ = K_B(V_m + V_i) \tag{3}$$

K_A and K_B are the overall mass transfer coefficients for A and B, respectively. ϕ is the breakage coefficient and C_{eA} and C_{iB} are the concentrations of A in the external phase and B in the internal phase respectively, V_m is the membrane phase volume, V_i is the total volume of the internal phase, and V_e is the external phase volume. The initial conditions for Eq. (1) are given in Eqs. (4) and (5):

$$C_{eA} = C_{eA,0}, \qquad t = 0 \tag{4}$$

$$C_{iB} = C_{iB,0}, \qquad t = 0 \tag{5}$$

For small breakage, i.e., $\phi = 0$ or $\phi \leq 0.001\ \text{min}^{-1}$, the solution for Eq. (1) can be expressed by Eq. (6) (*14*):

$$C_{eA} = \frac{(V_e C_{eA,0} + V_i C_{iB,0})}{V_e} \frac{(K_{B\phi}/V_i)}{(K_A/V_e + K_{B\phi}/V_i)} \left[1 + \frac{1}{K_{B\phi}/V_i)} \left(\frac{K_A C_{eA,0} - K_{B\phi} C_{iB,0}}{V_e C_{eA,0} + V_i C_{iB,0}}\right) e^{-\left(\frac{K_A}{V_e} + \frac{K_{B\phi}}{V_i}\right)(V_m + V_i)t}\right] \tag{6}$$

where

$$K_{B\phi} = K_B + \phi \left(\frac{V_i}{V_m + V_i}\right) \tag{7}$$

For large breakage, the solution for Eq. (1) can be shown by Eq. (8) (*14*):

$$C_{eA} = \frac{(V_{e,0} C_{eA,0} + V_{i,0} C_{iB,0})}{V_0} + \frac{V_{i,0}(C_{eA,0} - C_{iB,0})}{V_0} \left(\frac{V_0 - V_{i,0}}{V_0 e^{\phi t} - V_{i,0}}\right)^{\left(1 + \frac{K_A}{\phi V_0}\right)} e^{-\frac{K_B}{\phi V_{i,0}}(e^{\phi t} - 1)}$$

$$- \frac{E(K_A^\circ - K_B^\circ)(V_{e,0} C_{eA,0} + V_{i,0} C_{iB,0})}{\phi V_0 (V_0 - V_{i,0})} \left(\frac{V_0 - V_{i,0}}{V_0 e^{\phi t} - V_{i,0}}\right)^{\left(1 + \frac{K_A}{\phi V_0}\right)} \times e^{-\frac{K_B}{\phi V_{i,0}} e^{\phi t}} \tag{8}$$

where

$$E = \int_{1}^{e^{\phi t}} \left(\frac{V_0 X - V_{i,0}}{dX} \right)^{\frac{\overset{\circ}{\kappa_A}}{\phi V_0}} e^{\frac{\overset{\circ}{\kappa_B}}{\phi V_{i,0}} X} \tag{9}$$

$$V_0 - V_{i,0}$$

$$V_0 = V_{e,0} + V_{i,0}$$

$V_{e,0}$ and $V_{i,0}$ are the initial volumes for the external phase and the internal phase, respectively.

Separation Results from Batch Extraction

Batch extraction of uranium from WPPA was achieved in the lab with the standard beaker and stirrer set-up (*2, 3, 7, 15*). The runs were usually conducted at 60°C, the temperature of the feed stream for WPPA plants. Figure 11 presents the results of a typical batch run—90% extraction was achieved in about 13 min (*5*). This figure shows good agreement between the model and experimental data.

Mass Transfer Coefficient

The mass transfer coefficients used in the above equations are overall mass transfer coefficients. To better understand the transfer mechanism, the transfer sequence needs to be examined in more detail. There are actually five steps involved, and each step has a specific mass transfer coefficient.

If the transfer is from the external phase to the internal phase (Fig. 12), the first step is the mass transfer from the external phase to the interface between the external and membrane phases. This is represented by the mass transfer coefficient k_e. The second step is the transfer across this interface, which can be represented by the mass transfer coefficient k_{me}. The third step is diffusion through the membrane phase, represented by the mass transfer coefficient k_m. The fourth step is the transfer across the interface between the membrane and the internal phase, represented by the mass transfer coefficient k_{im}. The last step is the diffusion into the internal phase, represented by the mass transfer coefficient k_i. In general, the membrane phase and its two interfaces offer higher mass transfer resistance than the two aqueous phases; this means that the mass transfer coefficients k_m, k_{me}, and k_{im} would be controlling parameters in the overall permeating process.

There are a number of important factors that affect the mass transfer coefficients k_m, k_{me}, k_{im}, and the mass transfer area. Those that affect mass

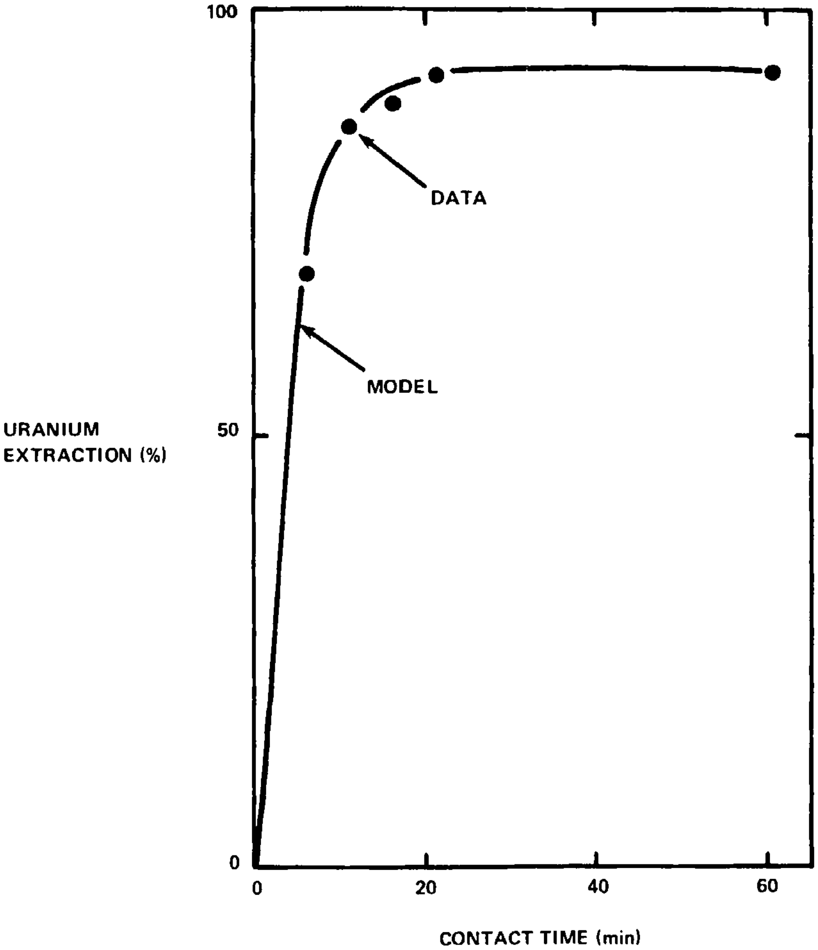

FIG. 11. Comparison of the model and experimental data for the typical batch LM extraction of uranium.

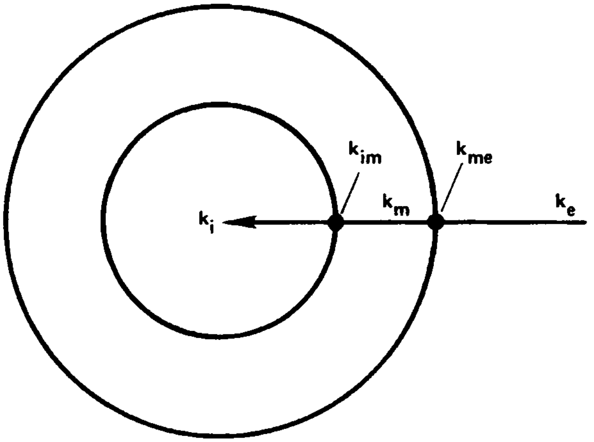

FIG. 12. Schematic of mass transfer sequence in LM extraction.

transfer at the membrane interfaces are (a) surfactant type and concentration, (b) surfactant molecular packing at the interface, (c) the reaction rates for extraction and stripping at the interfaces, and (d) temperature. The factors that affect the mass transfer in the membrane phase are viscosity, diffusivity, thickness (which is related to the membrane-to-external-phase ratio), and temperature. Mass transfer area is affected by globule size (which is related to the mixing rate), the internal phase droplet size, the membrane-to-internal-phase ratio, and the feed-to-emulsion ratio.

Effects of Mixing Rate and Temperature

Figure 13 shows the effect of mixing rate on the overall mass transfer coefficient in uranium extraction. The effect is very dramatic—when the mixing rate was increased 2.4-fold, i.e., from 250 to 600 rpm, roughly a 4-fold increase in mass transfer coefficient was achieved.

Figure 14 shows the effect of temperature on mass transfer. The effect is also quite pronounced—when the temperature was increased from 50 to 90°C, the mass transfer coefficient was roughly tripled.

It is interesting to note that the complexation of uranium by DEHPA-TOPO is favored by low temperature, whereas decomplexation or stripping is favored by high temperature. A solvent extraction process can involve

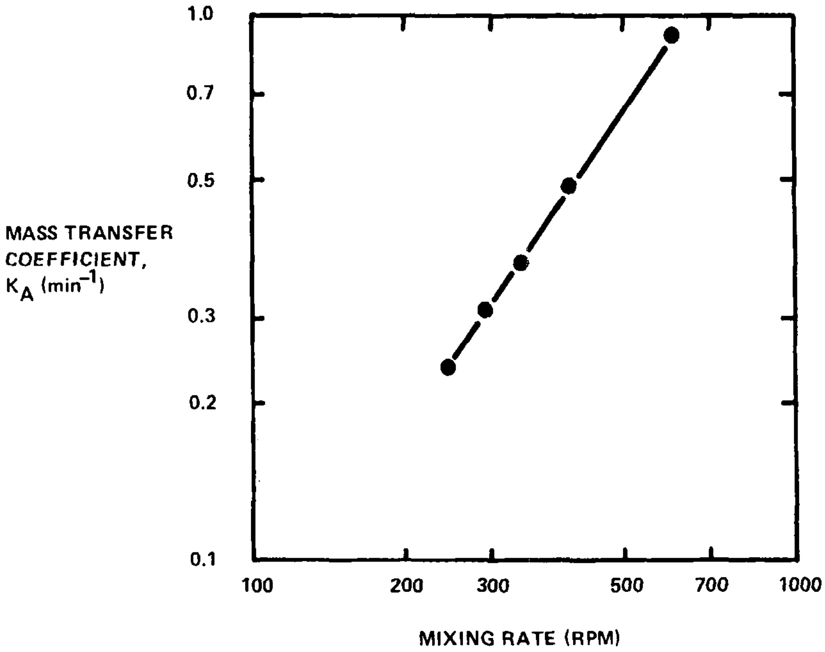

FIG. 13. Effect of mixing rate on mass transfer.

cooling of the acid feed from 60 to 40°C for the extraction part and heating back to 60°C for the stripping part. A liquid membrane process can do extraction and stripping simultaneously and effectively at 60°C. This implies that diffusion of the uranyl complex through the membrane and stripping are the rate-controlling steps.

Effect of Complexing Agent Concentration

Because of liquid membrane's ability to simultaneously extract and strip, the concentration of complexing agent required is much less than that in solvent extraction for any given separation. Also, the change of concentration has much less effect on extraction rate (*7*, *8*). As a matter of fact, in the concentration range of DEHPA from 0.07 to 0.14 *M* with DEHPA to TOPO molal ratio varying from 4 to 23, there was no observable effect on the extraction rate of uranium (*9*).

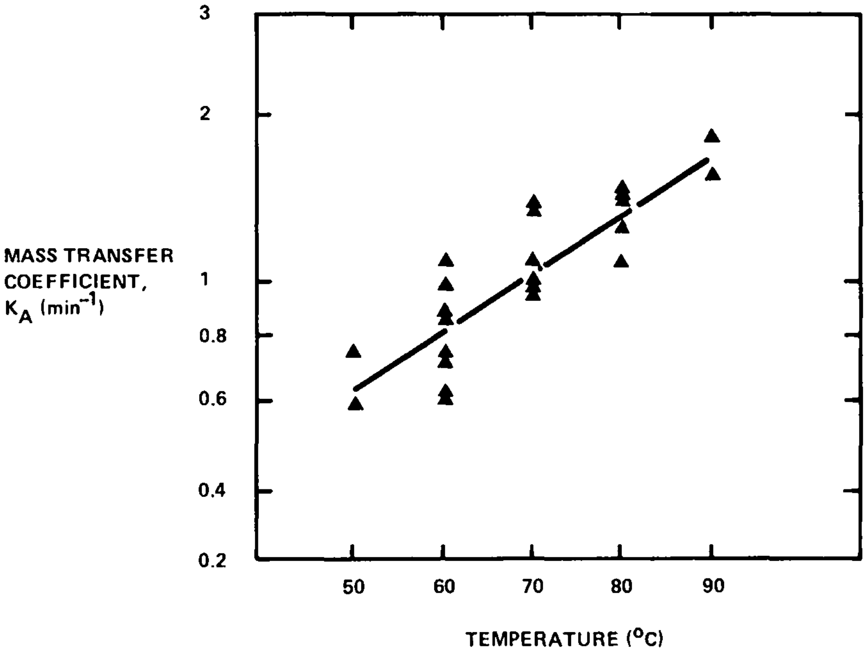

FIG. 14. Effect of temperature on mass transfer.

Effect of Acid Strength

The effect of acid strength on extraction rate was also found to be much smaller than that in solvent extraction (*9, 17*). When the phosphoric acid concentration was increased from 5 to 8 *M*, the extraction rate was only reduced by a factor of about 20% (*9*). In some phosphoric acid plants this could be a very strong advantage for liquid membranes over solvent extraction, since flow rate, vessel size, chemical inventory, etc. are related to acid strength. The more concentrated the acid, the smaller the extraction plant for liquid membranes, at least for the concentrations investigated.

The foregoing advantages of LM over SX should result in improved capital and operating costs. Therefore, an economic comparison of the LM process versus the commercially practiced solvent extraction technology was made. The effect of operating parameters on extraction rate, coupled with the data from the continuous pilot plant unit, provided the basis for a process design for the LM extraction. For solvent extraction, process descriptions and data from the literature were used to develop comparable process

TABLE 2
Cost Estimate Design Basis: Uranium Extraction-Recovery

		SX	
	LM	Minimum pretreatment	Extensive pretreatment
Extraction mode	Countercurrent		
Extraction stages	3	4	4
Stripping stages	—	4	4
Emulsifier/coalescer	1/1	—	—
Crud treatment	Mechanical	Mechanical/chemical	—
Uranium recovery	Solvent extraction		
Raffinate treatment	Flotation cells		

designs. These were then used as the basis for developing comparative cost estimates for both technologies.

ECONOMIC COMPARISON OF LM AND SX

Design Basis

There are major differences in the phosphoric acid pretreatment among the designs. In LM, oxidation flocculation, clarification, and filtration are used for solids removal. For the SX design, two concepts were used—one employing a minimum pretreatment of the phosphoric acid feed, the other involving more extensive pretreatment. For minimum pretreatment, flocculation and clarification are used, followed by oxidation. The elimination of filters saves considerable capital, and some solvent extraction plants operate in this manner. For the more extensive pretreatment case, flocculation and clarification are followed by a fixed-bed activated carbon treatment to remove soluble humic acids before oxidation of the feed (Table 1).

The design basis for the uranium extraction and recovery is shown on Table 2. For LM, the extraction section would contain three countercurrent stages; for the two SX cases, four countercurrent stages would be required. With respect to the stripping operation, LM would not require this step, while the two SX cases would have four stages. Offsetting this, the LM process will require an emulsification and a coalescing step (*15, 18*). Crud treatment will be of a mechanial type in LM. It is usually a combination of mechanical and chemical type in solvent extraction with minimum feed pretreatment. With

TABLE 3

Capital Cost Estimates (Basis: 400,000 tons/year P_2O_5 acid capacity, central Florida location, second quarter 1979 construction costs)

	M dollars		
		SX	
	LM	Minimum pretreatment	Extensive pretreatment
On-site	14.0	15.4	19.4
Off-site	5.8	6.3	6.6
	19.8	21.7	26.0
Project contingency	4.8	5.4	6.5
Process allowance	2.7	—	—
	27.3	27.1	32.5
Solvent inventory	0.1	0.9	0.9
Total investment	27.4	28.0	33.4

more extensive feed pretreatment, it has been assumed that no crud would form because of the prior removal of all soluble organics. Uranium recovery, in all cases, would consist of a secondary solvent extraction step followed by production of yellow cake. Raffinate treatment for removal of suspended organic would also be identical for all cases.

Capital Costs (Table 3)

The capital cost estimate was based on grass roots facilities capable of extracting uranium from a 400,000 ton per year P_2O_5 plant in a central Florida location, constructed in the second quarter of 1979. The uranium production capability was estimated at 350,000 lb/yr, allowing for a 5% phase dislocation between operations of the uranium extraction plant and the phosphoric acid plant. All capital costs have an allowance for a 25% project contingency over and above the estimated installed equipment cost, and in the case of LM an additional process allowance of $2.7M has been added to compensate for some of the remaining uncertainties in the process design. LM facilities are estimated to cost $27.4M, including the associated off-sites and solvent inventory as compared to $28 and $33.4M for the two SX cases. It should be pointed out that these estimates are of a reseach guidance quality, but based on detailed equipment cost estimates. Further development activity on LM will probably permit the eliminaton of feed filtration and

TABLE 4

Operating Cost Estimates (Basis: 400,000 tons/year P_2O_5 acid capacity, 350,000 pounds/year U_3O_8 recovery, second quarter 1979 costs)

	Dollars per pound U_3O_8		
		SX	
	LM	Minimum pretreatment	Extensive pretreatment
Organic make-up:			
Circulation loss	0.1	3.9	3.9
Raffinate loss	0.1	0.2	0.2
Crud loss and treatment	1.0	2.9	0.0
Chemicals and supplies	1.4	0.9	1.6
Utilities	0.7	0.9	1.0
Labor, maintenance, taxes, and insurance	7.1	7.1	8.6
Depreciation	4.6	4.7	5.6
Total operating costs	15.0	20.6	20.9

one extraction stage, thereby reducing the estimated cost by \$4+M, to a possible \$23M.

Operating Costs

Table 4 shows the operating costs for the extraction facilities expressed in dollars per pound of uranium recovered. One of the major differences between the LM and SX costs are associated with organic make-up. A circulation loss of 1/10 of 1% of the organic circulation is assumed which amounts to 10¢/lb of uranium for the liquid membrane case as compared to \$3.90/lb for solvent extraction. The very low cost of LM is due to the fact that, compared to SX, only 1/18th the volume of organic is circulating in the LM process and that the cost of the organic membrane is only about 1/4 the unit cost of the solvent extraction hydrocarbon phase. This also accounts for the lower cost of the raffinate losses for LM.

The losses and costs associated with crud are estimated at about \$1/lb for the LM case as compared to \$2.90 for SX with minimum feed pretreatment. There are no costs associated with crud loss for the extensive feed pretreatment case. That, however, is offset by the higher chemical costs associated with the activated carbon that is employed for pretreatment. The LM chemicals and supplies cost of \$1.40/lb includes the 50¢/lb for filter aid

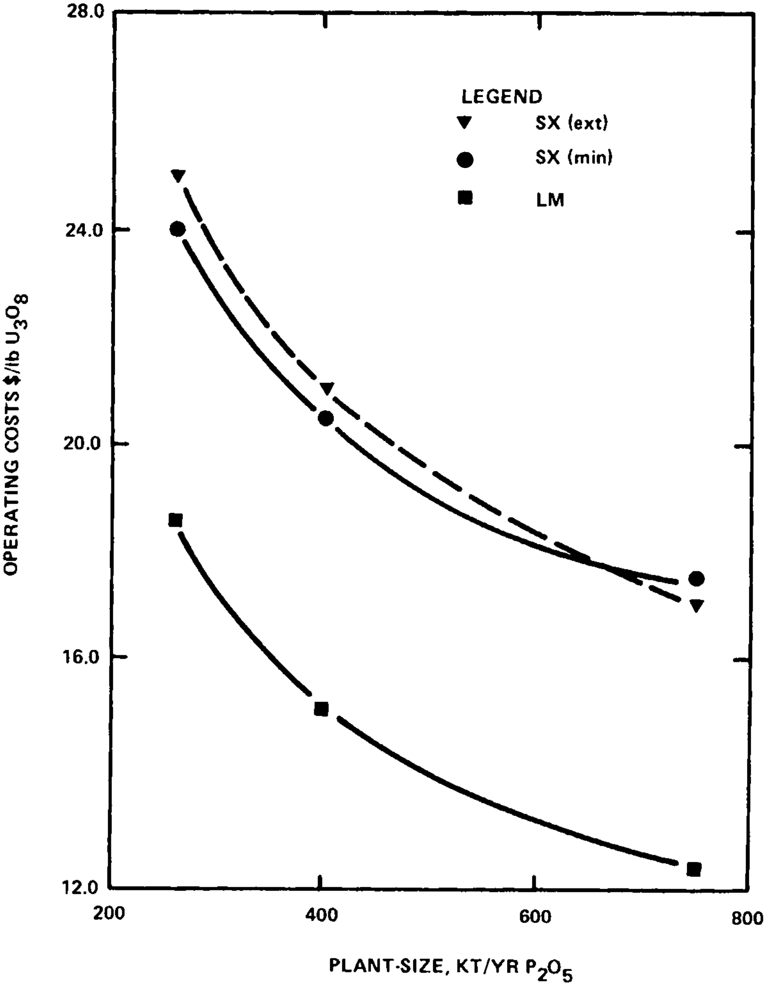

FIG. 15. SX and LM operating costs (2nd quarter, 1979, Central Florida location). 30% P_2O_5 acid.

which could be saved if filtration were eliminated in the pretreatment step. Utility costs for LM are somewhat lower than for SX.

Labor, maintenance, taxes, and insurance have been estimated as a percentage of capital cost for all cases and will vary from a low of \$7.10 for LM and the minimum SX pretreatment case to \$8.60 for extensive pretreatment. Straight line depreciation was taken over a 17-yr period. These operating cost components add up to estimated total of \$15 for LM as compared to about \$20–21/lb of U_3O_8 for SX.

The change of operating costs with varying acid plant capacity was investigated (Fig. 15). For a 250,000 ton per year P_2O_5 plant, operating costs will be about \$24–25/lb for a SX plant, depending on type of pretreatment, and about \$18.50 for LM extraction. This cost difference of roughly \$6.00/lb is maintained for all plant capacities studied. As an example, SX operating costs for a 750,000 ton per year P_2O_5 plant will be about \$17.50/lb of U_3O_8 recovered as compared to \$12/lb for liquid membranes.

Further improvement in LM economics can be accomplished if a 40–45% P_2O_5 acid stream is available for uranium extraction rather than a 30% stream (Fig. 16). The operating costs for extraction from 45% acid are represented by the lower curve, while the upper curve reflects extraction costs from 30% acid. At the lower end of capacity (namely 250,000 tons per year), use of higher concentration acid could provide an additional operating cost saving of \$2.50/lb to bring operating costs down to \$16.0/lb. The incentive to extract from higher concentration acid diminishes with increasing plant size, reducing to \$1.20/lb at 750,000 tons/year P_2O_5 plant capacity. In determining these costs, it was assumed (no laboratory confirmation) that the acid pretreatment for the 45% acid would be identical to the 30% acid.

Because of capital cost differences between the various cases, one should also examine the operating costs including return on investment. Figure 17 shows a plot of operating cost including a 15% discounted cash flow return on the investment, expressed as dollars per pound of U_3O_8 recovered against plant size of the phosphoric acid plant. The four curves represent solvent extraction with extensive and minimum pretreatment and LM for 30 and 45% acid strength as feed.

CONCLUSION

The LM technology appears to have sufficient return on capital at today's depressed uranium prices to warrant extraction from phosphoric acid plants. It is believed that additional improvements for LM can be achieved, such as

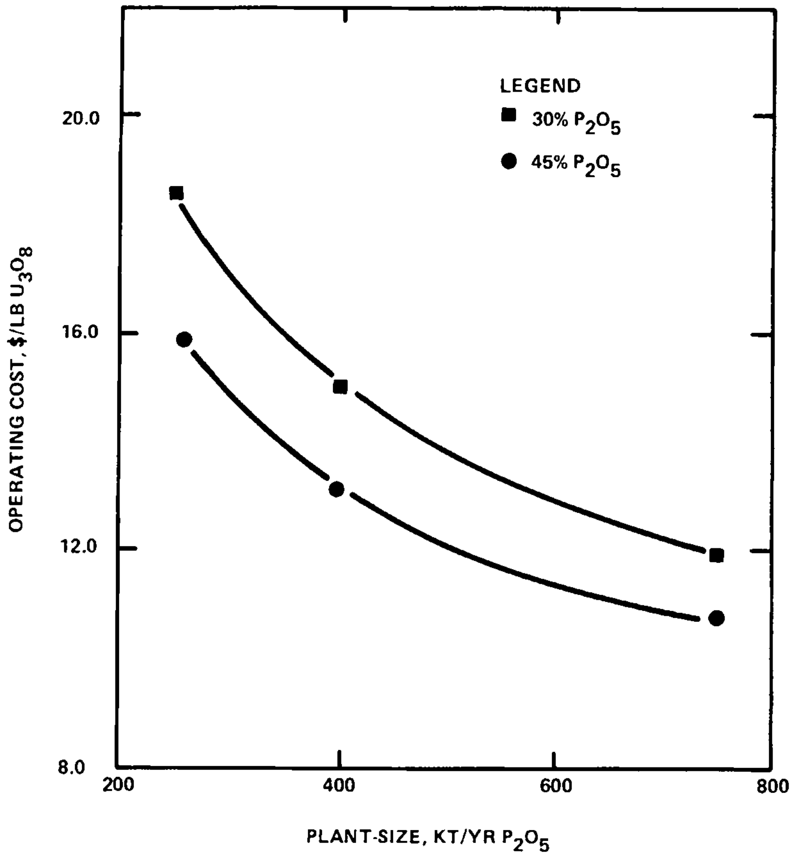

FIG. 16. LM operating costs for different acid strengths (2nd quarter, 1979, Central Florida location).

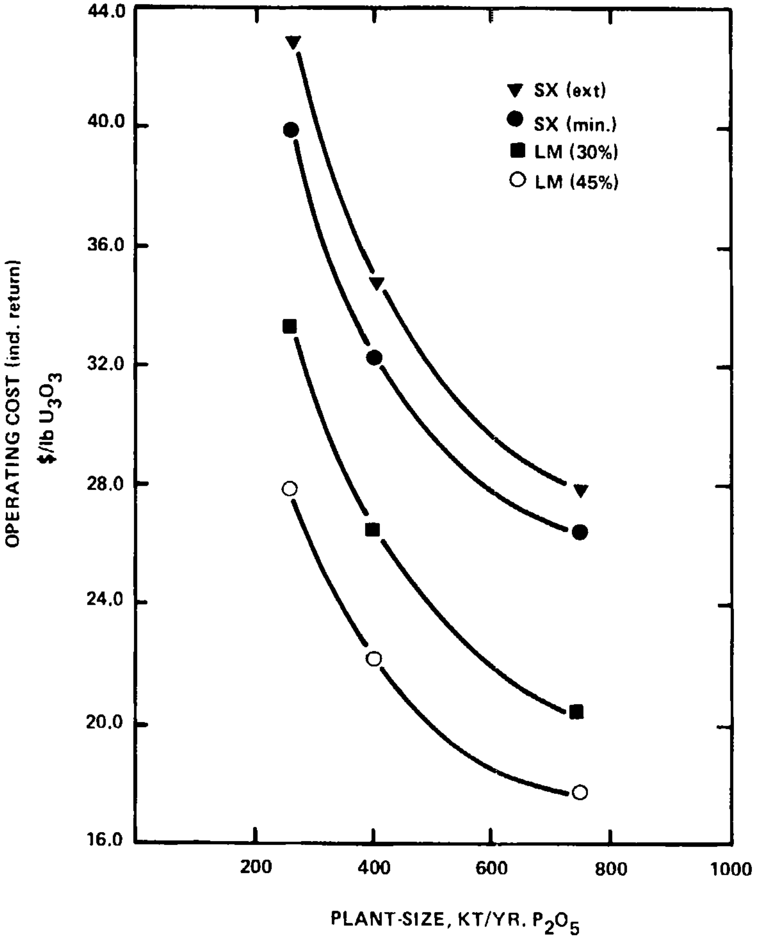

FIG. 17. SX and LM operating cost including return on investment (2nd quarter, 1979, Central Florida location).

the elimination of filtration in feed pretreatment and operation at 70°C, which would reduce extraction to two stages. This will improve the operating margin for LM uranium extraction even further, making LM potentially the lowest cost technology for the recovery of uranium from WPPA. For this reason, the LM process would be a strong candidate to be considered for new extraction plants when the demand for uranium is increased.

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