

RECOVERY OF URANIUM FROM THE I. M. I.
HYDROLYTIC ACID PROCESS

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IA-1268

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Israel Atomic Energy Commission

November, 1972

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ABSTRACT

The distribution of uranium in the various stages of the I.M.I. solvent extraction process for producing phosphoric acid was found to be highly dependent on the calcium chloride concentration in the aqueous streams. Utilizing this fact, a small aqueous stream with a relatively high amount of uranium can be obtained along the route of the phosphoric acid process. The uranium can easily be recovered from this stream by solvent extraction. Thus the cost of producing uranium as a by-product of phosphoric acid production can be considerably reduced, due to lower solvent losses in the aqueous solutions and smaller equipment size.

INTRODUCTION

The problem of recovery of uranium as a by-product of phosphoric acid production has aroused widespread interest. The processes developed so far were usually based on direct extraction of the uranium from the "wet-process" phosphoric acid with dialkyl esters of the pyrophosphoric acid^(1,2),

Recently a new process for the production of phosphoric acid has been developed in Israel⁽³⁾. This process, the I.M.I. process, uses hydrochloric acid for acidulation of the phosphate rock, and a liquid-liquid contact system for separating the phosphoric acid from the crude acidulate. Since the known methods for extracting the uranium directly

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from the rock decomposition liquor are impractical in this case, due to increased volume of the aqueous solution and low uranium concentration; a new method for recovering the uranium along the route of the process was sought.

It was found that when phosphate rock is decomposed with hydrochloric acid under reducing conditions, most of the uranium remains in the undissolved residue. A process for the recovery of the uranium, based on this phenomenon, was proposed by Ketzinel et al. (5). On the other hand, when phosphate rock is acidulated under normal or oxidizing conditions, most of the uranium is dissolved. The solution obtained contains about 40-50 milligrams of uranium per liter.

It is the purpose of this work to show how the I.M.I. process can be utilized as a basis for an economical method of recovering uranium.

THE I.M.I. PROCESS

A short outline of the I.M.I. process, based on the detailed description given by its inventors (3), is presented below.

Raw phosphate rock is dissolved in excess hydrochloric acid, the clear dissolution liquor is separated from the undissolved residue and fed to the solvent extraction section. The latter aims at separating the acids (phosphoric and hydrochloric) and purifying the phosphoric acid from the large amounts of calcium and minor quantities of other impurities (eg. Fe, F, Si) present in the aqueous dissolution liquor.

The solvent extraction section consists of four steps, as shown in Fig.1:

1. Extraction. This step is fed by the dissolution liquor. Most of the acids are transferred to the solvent while the bulk of the calcium remains in the aqueous phase.
2. Purification. The solvent extract is washed with a reflux stream taken from the aqueous exit of the next stage (back-extraction).

This removes minor quantities of impurities, coextracted in the previous step.

3. Back-Extraction. The acids are recovered from the purified solvent extract by washing it with water.
4. Stripping. The washed solvent leaving the back-extraction stage recovers the remaining acids from the raffinate leaving the

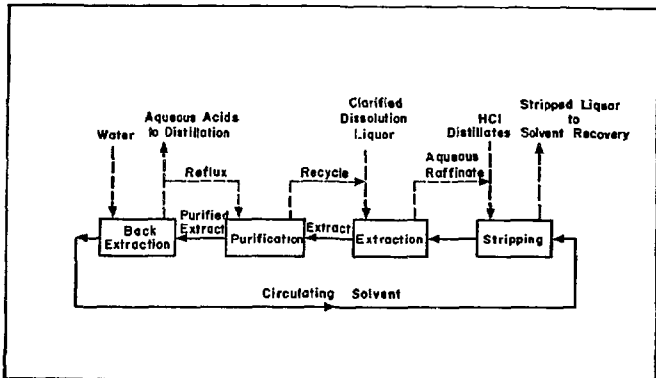


Fig. 1

Solvent extraction section of the I.M.I. process

The back-extracted aqueous acids are distilled, and the phosphoric acid is thus separated from the hydrochloric acid and from solvent traces dissolved in the aqueous phase. Further evaporation yields phosphoric acid of the desired concentration.

According to the practical flow charts of the I.M.I. process, a side stream of recovered HCl distillates is introduced into the aqueous stream between the extraction and the stripping sections.

The solvents suitable for these operations are primary aliphatic alcohols; usually butanol and iso-amyl-alcohol.

DETERMINATION OF URANIUM DISTRIBUTION COEFFICIENTS

The behaviour of uranium in the liquid-liquid contact systems of the I.M.I. process was studied by determining its distribution coefficients; i.e. its organic-to-aqueous phase concentration ratios. Extraction of uranium in alcohols is well known⁽⁶⁾, but the published data are not relevant to the problem under discussion.

The experiments were carried out on the system $H_3PO_4 - HCl - H_2O - CaCl_2$ - solvent, using synthetic solutions. The concentration ranges of interest were⁽³⁾:

$CaCl_2$: from 0 to 360 g/liter

HCl : from 0 to 3 N

H_3PO_4 : from 0 to 100 g P_2O_5 /liter

Because of its low concentration, uranium has no effect on the distribution of the various compounds. Its concentration was up to 50 mg/liter.

Most of the measurements were taken with hexavalent uranium (i.e. uranyl ion), because most of the dissolved uranium in the I.M.I. process is in the oxidized state. A few measurements were taken with tetravalent uranium.

The solvents tested were n-butyl alcohol, iso-amyl-alcohol and a mixture of the two.

Aqueous solutions were prepared by mixing appropriate amounts of concentrated phosphoric acid, hydrochloric acid, water and crystalline calcium chloride. Uranium was introduced into the aqueous solutions as uranyl-chloride crystals. Fresh solvent was used in each experiment. All the reagents were of analytical grade.

Results

Typical examples of the effect of the composition of the aqueous phase on the distribution of uranium in the system $H_3PO_4 - HCl - CaCl_2 - H_2O$ - alcohol (50% n-BuOH, 50% i-AmOH) are shown in Fig. 2. It is evident that high HCl concentration favours the transfer of uranium to the organic phase. A prominent phenomenon is the strong effect of the aqueous $CaCl_2$ concentration on the uranium distribution, as clearly illustrated in Figs. 2 and 3.

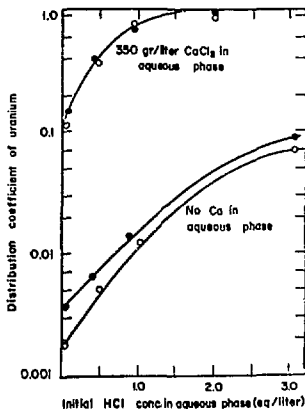


Fig. 2

Effect of aqueous phase composition on the extraction of uranium.

Solvent: 50% n-BuOH + 50% i-AmOH.

Initial phosphoric acid conc.: ● - 1.4 moles/liter, ○ - 0.7 moles/liter

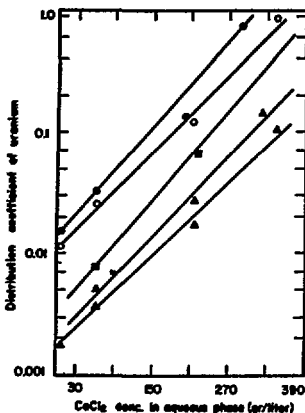


Fig. 3

Effect of CaCl_2 concentration on the extraction of uranium.

Solvent: 50% n-BuOH + 50% i-AmOH

Initial aqueous phase composition:

	HCl (M)	$\text{H}_3\text{PO}_4 \text{ (M)}$	CaCl_2
●	1.00	1.40	variable
○	1.00	0.70	"
▲	0.05	1.40	"
△	0.05	0.70	"
■	0.05	0.01	"

The effect of the alcohols on the extraction of uranium is demonstrated in Fig. 4. As the primary role of these alcohols is to extract phosphate, their ability to extract uranium is compared with reference to the extraction of phosphate. It can be concluded that when the CaCl_2 concentration is high, uranium is extracted approximately as well as phosphate, while low CaCl_2 concentrations decrease its distribution coefficient. Butanol is found to be a better solvent for uranium than i-AmOH under the conditions studied.

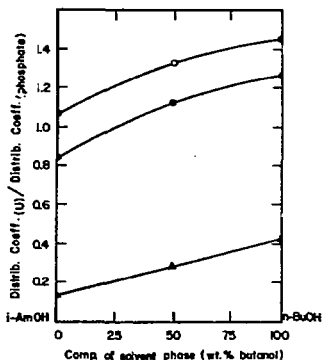


Fig. 4

Extraction of uranium by n-butanol and i-amyl-alcohol.

Initial aqueous phase composition:

	<u>HCl(M)</u>	<u>H₃PO₄(M)</u>	<u>CaCl₂ gr/liter</u>
○	2.0	1.4	350
●	2.0	0.7	350
△	3.0	1.4	0

The distribution coefficients of tetravalent uranium were found to be 50-80% of those of the hexavalent state.

URANIUM DISTRIBUTION IN THE I.M.I. PROCESS SOLVENT EXTRACTION SECTION

As described⁽³⁾, the various stages of the I.M.I. solvent extraction section can be classified into two groups according to the CaCl₂ concentration in the respective aqueous streams:

- a) The extraction and stripping stages, which have high CaCl₂ content.
- b) The purification and back-extraction stages, which contain negligible calcium concentrations. (The purification stage aqueous exit may contain an appreciable amount of CaCl₂ but the other streams contain but minor quantities).

An attempt to predict the distribution of the uranium in the various stages of the I.M.I. process, in view of its calcium-dependent behaviour, leads to the following conclusions.

Uranium is extracted along with the phosphoric and hydrochloric acids into the solvent extract as it passes through the extraction and stripping batteries (see Fig.1). On purification, an appreciable fraction of the uranium is stripped off the solvent and transferred to the aqueous recycle stream. Due to high water transfer from the aqueous reflux to the organic extract; the recycle stream is small compared with the aqueous feed and the solvent extract; therefore, the concentration of uranium in the recycle stream is high relative to that in other process streams. The unstripped part of the uranium is washed out of the solvent when the acids are back-extracted; and is finally found in the phosphoric acid product.

The uranium in the recycle stream is fed back to the extraction stage and is actually circulated between the extraction and the purification steps. The circulation is governed by the different calcium levels in these two stages.

Uranium, which is constantly fed to the system with the decomposition liquor, thus accumulates in the solvent extract and in the recycle. Its build-up continues until steady state is established. Then all the uranium that enters the system leaves with the product stream, while relatively high concentrations of uranium are maintained between extraction and purification, especially in the recycle.

If the uranium in the recycle is removed, no accumulation occurs, but its concentration in the recycle will still be higher than in the feed. Hence the conditions of the purification, which tend to concentrate uranium in the small-volume aqueous recycle stream, permit its simpler and cheaper recovery.

Quantitative calculations

A quantitative model of the phenomena described above can be obtained by considering a linked extraction-scrub system, as shown

schematically in Fig. 5. The scrub section corresponds to the purification stage of the I.M.I. process. For the purpose of the mathematical model it is assumed that ideal conditions of fixed flow rates and fixed distribution coefficients hold throughout each liquid-liquid contact section.

The concentrations in Fig. 5 refer to uranium. The flow rates are determined by the behaviour of the main component (i.e. phosphoric acid) and are not discussed here.

It can easily be shown that, when circulation exists, the concentration of the recycle is given by the formula:

$$\frac{x_o}{x_F} = \frac{F}{L} \frac{P_E P_S}{1 - P_E P_S} \quad (1)$$

Here:

P_E and P_S represent the distribution of the desired component in the extraction and scrub stages respectively, and are defined by the well known Kremser-Brown equation:

$$P_S = \frac{y_2 - y_3}{y_2} = \frac{R_S^{m+1} - R_S}{R_S^{m+1} - 1} \quad (2)$$

$$P_E = \frac{x_2 - x_1}{x_2} = \frac{R_E^{n+1} - R_E}{R_E^{n+1} - 1}$$

where:

$$R_S = \frac{L}{D_S S} \quad R_E = \frac{D_E S}{L + F}$$

and

D_E, D_S are the distribution coefficients in the extraction and scrub sections respectively,

F, L, S are flow rates as shown in Fig. 5,

n, m are the number of stages in extraction and stripping respectively.

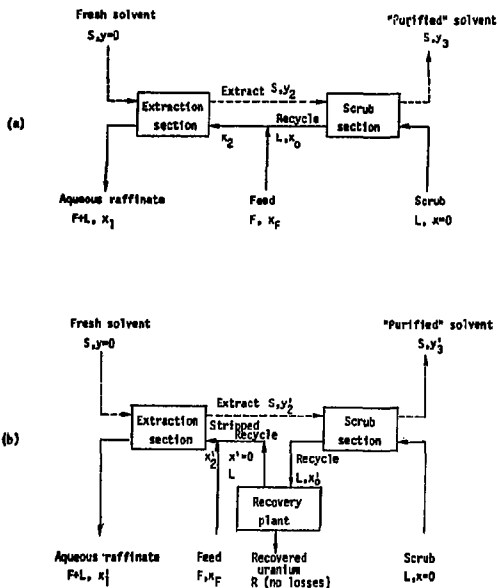


Fig. 5

Linked extraction-scrub system. Flow rates are expressed as volume per unit time. Concentrations are expressed as weight per unit volume. R is expressed as weight per unit time.

(a) with uranium circulation, (b) without uranium circulation

When the uranium is recovered from the recycle, its concentration in this stream will be:

$$\frac{x_O'}{x_F} = \frac{F}{L} P_E P_S \quad (3)$$

and the recovered fraction of the uranium is:

$$\frac{R}{F x_F} = P_E P_S \quad (4)$$

Equations (3) and (4) apply provided no losses of uranium occur in the recovering plant.

It can be concluded from Eqs. (1), (3) and (4) that with suitable operating parameters concentration of the uranium occurs in the recycle stream. If L is small compared with F , and $P_E P_S$ (overall component recovery) is high enough, then the recovery of the uranium from the recycle instead of the feed stream may be considered feasible.

As stated above, this mathematical model holds only if fixed flow rates and distribution coefficients exist along the extraction and scrub batteries. If not, more sophisticated calculation methods are required. In the case of the I.M.I. process, only very rough estimates can be made using the above equations, and the mathematical model serves mainly as a means for a general study of the circulation process.

BENCH-SCALE PROCESS SIMULATION EXPERIMENTS

Experiments were carried out to verify the above conclusions. The various process stages were simulated on bench-scale equipment, and the effect of the operational variables on the behaviour of the uranium was studied. The experimental procedure and the main results are described below.

Dissolution

Dissolutions of phosphate rock were carried out in a 1 m^3 polypropylene vessel equipped with a variable speed agitator and foam-breaker; a vent-condenser and a live-steam heating system. A slurry of

raw rock with water was put into the vessel, heated, and dissolved with concentrated hydrochloric acid. The amount of acid was so adjusted that the free HCl concentration of the acidulate was about 1.0 mole/liter. A typical analysis of an acidulation experiment is shown in Table I. At the end of dissolution, the mixture was allowed to cool, the undissolved residue discarded and the clear solution collected and used for the solvent extraction experiments.

TABLE I
Typical analysis of the acidulation process components

	Raw phosphate rock	Decomposition liquor	Undissolved residue
Quantity	210 kg	550 liters	16 kg (dry)
Component			
P ₂ O ₅	28 w/o	106 g/liter	3.7 w/o
HCl	-	1.2 N	-
Ca	37.2 w/o	110 g/liter	11.0 w/o
Fe	0.1 w/o	0.40 g/liter	0.1 w/o
U	150 ppm	46 mg/liter	350 ppm
F	3.2 w/o	5.0 g/liter	19.3 w/o
SiO ₂	1.5 w/o	2.0 g/liter	4.5 w/o
MgO	0.3 w/o	1.3 g/liter	0.1 w/o
SO ₃	1.8 w/o		17.2 w/o
Al ₂ O ₃	0.3 w/o	0.6 g/liter	2.1 w/o
H ₂ O	2.0 w/o		-
CO ₂	13.2 w/o	-	-
O.M.	0.2 w/o	-	2.0 w/o

Liquid-Liquid Contacting

Solvent extraction experiments were carried out with banks of bench-scale mixer-settlers, equipped with "pump-mix" impellers. The effective volume of each mixing chamber was 150 cc. Each settler was 500 cc in volume and had a separation area of 90 cm². The streams were introduced into the successive mixing chambers with dosing pumps. The experimental equipment was arranged in accordance with the I.M.I. process flow scheme (Fig. 1), except that the uranium-bearing recycle stream obtained was not returned to extraction but was collected for further experiments.

A mixture of n-BuOH (50%) and i-AmOH (50%) was used as solvent.

The duration of every run was 60-100 hours. At the end of each run; when steady state was established, samples were taken from each phase in every stage. The flow rates of the entering and exit streams were measured continuously.

Results

A typical profile of the uranium concentrations in the various stages of the above experiment is shown in Fig. 6. It is seen that the behaviour of the uranium agrees with what was expected. The distribution coefficients in these experiments, however, differ from those observed with synthetic solutions, probably because of minor amounts of certain impurities (e.g. fluorine).

The extraction and stripping sections were only slightly affected by changing the operating conditions, provided no phosphate losses occurred. Increasing the number of extraction stages tended to favor the extraction of the uranium into the solvent, while the number of stripping stages had no significant effect. The purification stage, which serves as the uranium concentrator, was more sensitive to process variables, especially aqueous-to-solvent flow ratio. The higher the flow rate of the reflux stream, the higher the transfer of uranium to

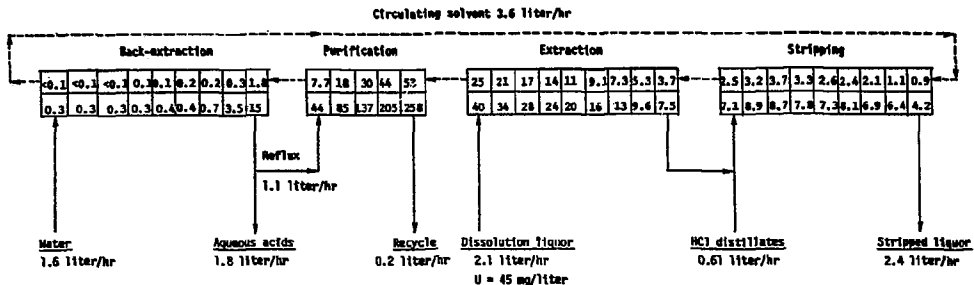


Fig. 6

Typical uranium profile in a continuous bench-scale experiment.
 ————— Solvent streams; ————— Aqueous streams.
 Each column represents one "mixer-settler" stage of a solvent extraction battery. The upper half of the column represents the solvent phase, and the lower half the aqueous phase.

the recycle stream. Quantitative examples of these observations are summarized in Table II.

TABLE II

Effect of process parameters on the recovery of uranium via the I.M.I. process

Step	Operating conditions			Uranium losses		
	Number of stages		Aqueous-to-solvent stream flow ratio	Source	Amount	
	Extraction	Stripping				
Extraction and stripping	6	12	0.6 ⁽¹⁾		Aqueous exit	23%
	9	9	0.6 ⁽¹⁾		from stripping	6%
	12	6	0.6 ⁽¹⁾			3%
Purification	5		0.28 ⁽¹⁾	0.03 ⁽²⁾	Purified solvent exit	50%
	5		0.33 ⁽¹⁾	0.052 ⁽²⁾		32%
	10		0.29 ⁽¹⁾	0.032 ⁽²⁾		40%

(1) based on inlet streams

(2) based on outlet streams

It was thought that the yield and concentration of uranium in the recycle stream could be increased by using water (instead of the reflux stream) for purification. Experiments confirmed this idea. Water balance in the process was not interfered with because less water was needed in this case for washing out the acids from the charged solvent.

Ferric ions were found to follow approximately the same route as the uranium. Experiments showed that under normal operating conditions, iron did not affect the behaviour of uranium.

RECOVERY OF URANIUM FROM THE RECYCLE STREAM

It was shown above that the I.M.I. phosphoric acid process can be utilized to concentrate uranium in a small aqueous stream, thus permitting economical extraction of the uranium.

The extraction may be performed by the octyl-pyro-phosphoric acid (OPPA) process^(1,2), in which the uranium is reduced to the tetravalent state, extracted with OPPA diluted in kerosene, and precipitated as a green cake of UF_4 by re-extracting the pregnant solvent with a mixture of sulfuric and hydrofluoric acids. Detailed descriptions of this process have been published^(1,2).

After recovery of the uranium, the recycle stream is returned to the I.M.I. extraction step and follows the normal process flowsheet.

Successful pilot-plant runs of this process were carried out, using the equipment described previously. Overall uranium recovery from the recycle stream was approximately 90%, and no special problems arose while operating the pilot-plant.

CONCLUSIONS

In the liquid-liquid contact system of the I.M.I. process the problem of extracting uranium from large aqueous volumes of crude phosphoric acid can be avoided. Thus expenses due to solvent losses and equipment costs can be considerably reduced, compared with known processes.

The mechanism of extraction has not yet been established, but it seems that $CaCl_2$ is the determining factor in the extractability of uranium. It is not known if the $CaCl_2$ acts as an effective salting out agent or as a complexing agent due to its considerable effect on the chloride content of the solution. Research on the more fundamental aspects of this extraction process is being carried out at present.

ACKNOWLEDGEMENT

The authors wish to thank Mrs. C. Shenberg and Mr. J. Nave for their help in directing the analytical work. Thanks are also due to Mr. Z. Maimon who was responsible for most of the experimental work.

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