

RECOVERY OF URANIUM FROM WET PROCESS PHOSPHORIC ACID BY SOLVENT EXTRACTION*

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Phosphate rock, which is a prime source of phosphate used in fertilizer manufacture in the United States, contains uranium. In general the uranium content of the rock rises with the phosphate content and most high-grade phosphate deposits ($>30\% \text{ P}_2\text{O}_5$) contain $>0.01\%$ uranium. The large tonnages of rock being mined represent a significant potential source of uranium that lends itself to recovery as a by-product of the wet-process phosphate industry. For example, in 1953, the U. S. Geological Survey estimated that recoverable phosphate reserves in the U. S. totaled about 5 billion tons and contained 600,000 tons of uranium.¹ This estimate did not include any rock from North Carolina which has since been estimated at about 2 billion tons. For the most part, the known, economically mineable U. S. reserves - estimated at about 7 billion tons - are concentrated in a few areas; 43% in the western states of Idaho, Montana, Utah and Wyoming; 28% in each of Florida and North Carolina and less than 1% in Tennessee. In the past Florida has supplied about 80% of the total U. S. production, practically all of which is land pebble phosphate. All forecasts indicate increased production rates from North Carolina and the western states.

In past years, only about 25% of the phosphate processed was converted to wet-process phosphoric acid, an intermediate step in the production of high analysis fertilizers. Much of the rock was applied directly to the

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soil or was simply wet with sulfuric acid and cured to produce superphosphate. A large fraction, particularly lower grade rock, was processed in an electric furnace. The uranium in these products is not presently recoverable. In addition, significant amounts of phosphate are discarded during beneficiation of the rock.

In recent years, the technology of phosphate fertilizer production has undergone a substantial change and more rock is being processed by the wet-process route. It is this production rate rather than total rock reserves or total rock processed that is of most importance relative to the amount of uranium available from this source. The latest by-product uranium production capability from wet-process phosphoric acid in the U. S. has been estimated by Frank McGinley,² Assistant Director, Ore Reserves and Production Division, ERDA. A portion of his data are summarized in Fig. 1. McGinley has estimated that about 20,000 tons of U_3O_8 could be produced from wet-process phosphoric at a cost of \$10 or less per pound through 1986 and about 70,000 tons of U_3O_8 through the year 2000. McGinley also points out that these estimates are sensitive to the predicted rate of growth of the industry and if one assumes a 7 percent annual growth rate, rather than the 5 percent for the projections shown in slide 1, the corresponding figures would be about 25,000 tons U_3O_8 through 1986 and about 110,000 tons U_3O_8 through 2000. The annual growth rate between 1960 and 1970 was greater than 10 percent. For comparison, ERDA has estimated uranium ore reserves, as of Jan. 1, 1975, recoverable at a cost of \$10 or less per pound, at 315,000 tons U_3O_8 .

Over the past 25 years, extensive research on recovering uranium from wet-process phosphoric acid has been carried out by the USAEC and by private

companies, many under contract to the AEC. Because of the strong complexing action of the phosphate for the uranium in the concentrated 5 to 6 M phosphoric acid solution and the low concentration of uranium present, the ordinary uranium extractants that have been used successfully in recovering uranium from sulfate solutions in the western uranium mills cannot be used because they do not have enough extraction power in this system. During the past 7 years, two potential solvent extraction processes have been developed at the Oak Ridge National Laboratory for recovering uranium from wet-process phosphoric acid. Both processes consist of two cycles. In each case, the first cycle is mainly a concentration step, in which the uranium is concentrated from about 1.5 lb per 1000 gal to over 100 lb per 1000 gal. This is accomplished by taking advantage of the oxidation state of the uranium. The first process³ uses the synergistic extractant combination of di(2-ethylhexyl) phosphoric acid and trioctylphosphine oxide (DEPA-TOPO) which extracts hexavalent uranium and the second process⁴ uses a commercial mixture of mono- and dioctylphenylphosphoric acid (OPPA) which extracts tetravalent uranium. The concentrated uranium phosphate solution produced in the first cycle of each of these processes is highly amenable to processing in a second cycle which is the same for both processes and uses the DEPA-TOPO extractant. Both processes have been successfully demonstrated in continuous bench scale mixer-settler tests at ORNL and the DEPA-TOPO process has been successfully demonstrated on a pilot-plant scale with fresh acid at several phosphate plants by four companies. Unfortunately, most of the information gained in these pilot-plant operations is proprietary.

PHOSPHORIC ACID SAMPLES

We obtained samples (Table 1) of wet-process acid from four commercial plants (identified as Companies A to D) that process Florida rock, one from a plant (Company E) that processes North Carolina rock and one from a plant (Company F) that processes western rock. Four of the companies (C to F) calcine their rock prior to the dissolution step. The so-called "green" acid produced from calcined rock is much easier to process than the "black" acid produced from uncalcined rock. The humus present in "black" acid is the major cause of phase separation problems which can lead to excessive solvent losses. In addition, the humus concentration can build up irreversibly in the solvent phase and decrease its extraction power for uranium.

The samples ranged from 5 to 6 M in phosphate and contained 0.06 to 0.19 g of uranium per liter. It has been reported⁵ that up to 30% of the uranium is undissolved and lost to the gypsum residues when calcined rock is digested; this could account for the lower concentration of uranium in the "green" acid. The phosphate rock of Carolina and the western states has a lower concentration of uranium than does Florida rock.

For maximum efficiency in extraction, all of the uranium should be in the hexavalent state when using the DEPA-TOPO process and in the tetravalent state when using the OPFA process. The U(IV)/U(VI) ratio is dependent on the Fe(II)/Fe(III) ratio and our tests have indicated that essentially all the uranium is tetravalent at Fe(II) concentrations of about 0.5 g/liter or greater. As shown here, the concentration of ferrous iron varies over a rather wide range, from 0.2 to 3.5 g/liter. However, most of these samples were several weeks old when received, and some of the ferrous iron initially present had oxidized as the acid aged. We believe that the ferrous iron concentration

in fresh acid will be greater than 0.5 g per liter and that no reduction of the acid will be necessary for the OPPA process. In the event that reduction is needed, it probably could be accomplished easily by completely reducing a small volume of acid and blending the resulting product with the main acid stream.

Oxidation of uranium to the hexavalent state for extraction with DEPA-TOPO was accomplished easily in the laboratory by adding one-sixth mole of NaClO_3 per mole of ferrous iron to the aged acid liquor or by bubbling air or oxygen through the liquor at 60 to 70°C. However, in later tests with fresh "black" acid at a plant site, sodium chlorate requirements were two to three times higher due to reaction with organic matter in the acid. Most processors fear that the larger amounts of chlorate needed for oxidation will lead to excessive corrosion from the chloride produced in the oxidation and prefer other oxidants. Hydrogen peroxide appears to be a suitable alternate.

In addition to iron, major impurities in the acid in g/liter were: 3-6 aluminum, 2-4 calcium, 19-33 sulfate, and 21-30 fluoride. With respect to a solvent extraction process, the major impurity in "black" acid is the organic matter or humus. Much of this material is colloidal and cannot be removed by filtration. However, it is readily coagulated by the extractant with which it forms a crud that tends to collect at the organic/aqueous interface.

Wet-process H_3PO_4 is supersaturated with gypsum. As the acid ages the gypsum precipitates slowly and continuously, carrying with it organic matter and other inorganic impurities. Also, some of the organic matter is removed or made inert by oxidation. Thus, the older the acid the more easily it becomes to process. All of our laboratory tests were made with aged acid (at least 2-3 weeks old) and for this reason needed confirmation at a plant site using fresh acid.

Many of the companies interested in uranium recovery have developed methods for cleaning up the acid. Although most of this information is proprietary, I can safely say that the methods involve two approaches: (1) coagulation with surfactants followed by filtration and (2) oxidation. In either case, a relatively clean acid can be produced.

DEPA-TOPO PROCESS

The DEPA-TOPO process (Fig. 2) consists of two cycles. In the first cycle, the oxidized acid is cooled to 40-45°C and the uranium is extracted in four stages with 0.5 M DEPA--0.125 M TOPO in an aliphatic diluent. Uranium is recovered from the solvent in 2 to 3 stages operated at 50°C, by contacting it with a phosphoric acid solution that contains ferrous iron. The ferrous iron reduces the uranium to the less-extractable tetravalent state and effects its transfer to the aqueous phase. It is convenient (and inexpensive) to borrow a small volume of raffinate from the extraction system for this purpose. Raffinate makes an ideal strip solution since it is suitably concentrated in H_3PO_4 and, after reduction with iron metal, contains a suitable concentration of Fe(II). Moreover, fluoride present in the acid catalyzes the reduction rate. Strip solutions containing about 12 g of uranium per liter are readily obtained. These solutions which are about a factor of 70 richer in uranium than the original acid are highly amenable to treatment in a second cycle using the same extractant.

In the second cycle, the uranium in the product solution is oxidized with oxygen or $NaClO_3$ to the hexavalent state and then extracted in three stages with 0.3 M DEPA--0.075 M TOPO. The extract is scrubbed in two to three stages with an ammonium carbonate solution. The solubility of uranium is inversely dependent on the ammonium salt concentration of the solution. Operation of

the system with a relatively concentrated (2 to 3 M) ammonium carbonate solution results in direct precipitation of ammonium uranyl tricarbonate (AUT) in the stripping system. The AUT settles rapidly in the aqueous phase and is continuously removed by filtration. The filtrate is recycled for further stripping. The AUT is calcined to U_3O_8 .

PROCESS VARIABLES

1. The choice of diluent for the extractant can significantly affect extraction performance and phase separation characteristics. Best results are obtained with aliphatic diluents. Although ordinary kerosene is a suitable diluent for process application, we have recommended the use of refined high-flash-point aliphatic diluents such as Amsco Odorless 450 which was used in most of our tests, or Napoleum 470 (Phillips Petroleum) which appears equally suitable. Uranium extraction coefficients obtained with aromatic diluents were significantly lower than those obtained with the aliphatic diluents.
2. The maximum uranium extraction occurs when the TOPO:DEPA mole ratio is approximately 1:4 and we have used this ratio in most of our tests (Fig. 3). However, since our program first started in late 1967 the cost of TOPO has gone from \$2.50 to \$10.00/lb while the cost of DEPA has remained relatively constant. For this reason, one might consider decreasing the ratio to 1:6 since our data shows that this could be done with little loss in coefficient.
3. The uranium extraction coefficient decreased by a factor of over two as the H_3PO_4 concentration was increased from 5 to 6 M, the typical concentration range of wet-process acid (Fig. 4).
4. Without cooling, the temperature of wet-process acid feed to a solvent extraction plant would be about 60°C. By cooling the acid to about 40°C, which phosphate producers say can be done economically, the uranium extraction coefficient is increased by a factor of about 2 (Fig. 5).

Cooling below 40°C does not appear advantageous due to higher cooling costs plus the added disadvantage of poorer phase separation at lower temperatures.

5. The dependence of the uranium extraction coefficient on the DEPA concentration (with a constant TOPO:DEPA ratio) is about 1.5 in this system (Fig. 6). Consequently, the extraction efficiency can be increased by increasing the extractant concentration. This is done, however, at the expense of higher solvent costs. In most of our test work, the DEPA concentration has been in the range of 0.2 to 0.5 molar, which appears to be suitable for process use. The optimum concentration could vary from plant to plant, depending on the temperature and the phosphoric acid concentration of the liquor.
6. In the reductive stripping system, intrastage recycle of the aqueous phase from the settler to the mixer was provided to give an aqueous/organic phase ratio of about 2 in the mixer. This provision and operation at ~50°C ensured that a sufficient amount of U(VI) was transferred to the aqueous phase and made available for reaction with Fe(II) to give suitably rapid kinetics for continuous operation. Pilot plant studies indicated that it is very important to maintain a relatively high concentration of ferrous iron (preferably 20-25 g/liter) and to exclude air from the system with an inert gas (N_2 or CO_2) blanket to minimize reoxidation.

PROCESS DEMONSTRATION

Figure 7 shows the extraction of uranium with 0.5 M DEPA--0.125 M TOPO from Company A and Company B acids at about 40°C. The data for the two experiments were essentially equivalent and are plotted as a single isotherm. McCabe-Thiel diagrams indicate that about 96% of the uranium could be recovered in four ideal extraction stages when operating with an aqueous/organic flow

ratio of 2/1. Assuming a uranium concentration of 0.17 g per liter in the feed liquor, loading of the solvent extractant would be about 0.33 g of uranium per liter.

We have made continuous demonstrations of the first-cycle process in a small mixer-settler test array, using 0.5 M DEPA--0.125 M TOPO--Amsco 450 to recover uranium from samples of acid from Companies A and B. No change in performance was detected for periods of operation equivalent to about 40 complete cycles of the solvent through the extraction-stripping system.

Figure 8 shows typical stage data. As predicted uranium recovery from Company A acid at 40°C was about 96% in four extraction stages with an aqueous to organic flow ratio of 2:1. The extract, which contained about 0.32 g of uranium per liter, was stripped with a small volume of raffinate that had been reduced with iron metal. About 95% of the uranium was stripped in two stages at 50°C, yielding a product solution that analyzed 11.8 g of uranium per liter. Although results were satisfactory in these tests, the use of two stripping stages is marginal. Addition of a third stage appears desirable, in order to decrease the amount of uranium recycled in the solvent to the extractor and to allow preparation of more concentrated strip product solutions.

The first-cycle product solution was oxidized with oxygen at 70°C on a batch basis and then the uranium was recovered in a second cycle at 25°C with 0.3 M DEPA--0.075 M TOPO (Fig. 9). More than 99% of the uranium was extracted in three stages, producing an extract that contained more than 9 g of uranium per liter. In addition to uranium, the extract contained 1.8 g of phosphate and 0.13 g of iron per liter. Three water scrub stages, operated at an organic to aqueous ratio of 5:1, removed more than 98% of the phosphate but very little iron; most of the iron precipitates in the stripping unit and contaminates the AUT product.

Almost all of the uranium was removed from the extract with ammonium carbonate solution in the first of two stripping stages. The first stripping unit was designed to facilitate continuous precipitation and discharge of the AUT precipitate. Intrastage recycle of the slurry from the settler through a filter and back to the mixer was provided for continuous removal of AUT. Makeup ammonia and carbon dioxide were bubbled directly into the aqueous phase of the first-stage settler in order to maintain the ammonium carbonate concentration at about 2 M. The recycle solution contained about 4 g of uranium per liter. Dilute (0.5 M) ammonium carbonate solution was fed at a very low flow rate to the second stripping stage, the function of this stage being primarily to scrub entrained uranium from the solvent stream. The flow rate of this solution was set to balance the loss of water from the stripping system which occurs on conversion of the DEPA to its ammonium salt which is hydrated. No precipitation occurred in the second stage.

The AUT precipitate was washed and calcined for 2 hr at 600°C. The product from our bench scale tests analyzed 97.5% U_3O_8 , 0.5% Fe, 0.06% PO_4 , and 0.5% CO_3 , 25 ppm Ti, 40 ppm V, and 0.7 ppm Mo. Calcined product from one of the pilot plant tests analyzed 98.53% U_3O_8 , 0.73% Fe, 0.14% PO_4 , 20 ppm Ti, and 10 ppm Mo. This product would be a highly suitable feed for uranium refineries that produce UF_6 .

PHASE SEPARATION

Phase separation in all systems of both cycles was satisfactory in both bench scale and pilot plant tests. In the first-cycle extraction system, separation of the phases was rapid and clean, provided mixing was done in the organic continuous mode - i.e., dispersion of aqueous droplets in the organic phase. When "black" acid was treated, solids accumulated at the aqueous-organic interface but did not interfere with the operation. Although the band of solids

appeared soon after start-up, the thickness of the band reached a certain level and then increased only slowly with extended operation. For commercial operations some provision would be needed for periodic removal of solids and recovery of solvent from the solids. Although the tests indicated that the system could be operated with solids present, it was established that removal of organic and solids from the acid prior to extraction is essential to minimize interfacial crud in the settlers and optimize operating conditions.

The amount of organic phase entrained in the aqueous raffinate leaving the bench-scale extractor usually ranged from 0.2 to 0.3 gal per 1000 gal of acid. Passing the raffinate through a 0.5-hr holdup tank reduced this loss to less than 0.10 gal per 1000 gal of acid. In pilot plant operation, solvent losses were somewhat higher, averaging 0.5 gal/1000 gal of relatively clean pretreated acid. It is essential that most of the entrained solvent be removed from the acid prior to evaporation of the acid in the next production step in order to prevent damage of the rubber lined evaporators.

CHEMICAL REAGENT COSTS

At the completion of our bench scale tests in early 1970, total reagent costs for the process were estimated to be less than \$1.00 per lb of U_3O_8 and the prices being quoted for U_3O_8 were \$6.25-6.50/lb. Our data showed that the economic success of the process depended heavily on controlling losses of the relatively expensive solvent and the measurement of these losses needed confirmation at the pilot plant level with fresh acid.

Now, the picture has changed. Prices being quoted for U_3O_8 are over \$30/lb with projections to \$50/lb by 1980. During this period our estimated reagent costs have also increased; our present estimates range from about \$2 per lb U_3O_8 for clean "green" acid to \$5 per lb for "black" acid that requires

extensive pretreatment (Table 2). The major increase in costs, excluding the pretreatment which could range from \$2-3/lb, is due to the price of TOPO which has increased from our earliest quote of \$2.50/lb to the range of \$10/lb. At present, General Mills appears to be the only potential supplier.

In addition to the increase in the cost of TOPO, the assumed loss of solvent by entrainment has been increased from 0.3 to 0.5 gal per 1000 gal of acid based on pilot plant tests. Also, the diluent cost was increased from \$0.28 to \$0.36 per gal.

THE OPPA PROCESS

The proposed OPPA process (Fig. 10) also consists of two-cycles. In the first-cycle the acid is cooled to 40-45°C, and the uranium is extracted in four stages with 0.3 to 0.4 M OPPA in an aliphatic diluent. Uranium is recovered from the solvent in three stages operated at 30°C, by contacting it with a 10 M H_3FO_4 solution that contains NaClO_3 ; the chlorate oxidizes the uranium to the less-extractable hexavalent state and effects its transfer to the aqueous phase. A convenient source of strip solution is the 45 to 55% P_2O_5 product acid from the evaporators. The strip solution can be loaded with uranium to 15 to 20 g per liter and after dilution to 6 M H_3FO_4 , can be fed directly to the second cycle of the DEPA-TOPO process.

SOLVENT PREPARATION

The octylphenylphosphoric acid extractant (Fig. 11) is available commercially (Mobil Chemical Company) as an approximately equimolar mixture of the mono- and diacids. This extractant is prepared by reacting 3 moles of octylphenol with 1 mole of P_2O_5 and contains a number of impurities in addition to the mono- and diacids. The nonhomogeneous-looking dark brown to light tan solid mixture, as received, was heated to about 65°C in order to liquefy and homogenize it

for sampling. Equal volumes of the sample and 6 M HCl were then stirred under reflux at 60°C for 16 hr in order to hydrolyze any pyro acids present. Thorough elimination of the pyro acids would not be required prior to process use of the octylphenylphosphoric acid but was necessary for experimental studies since the pyro acids are extremely powerful, although unstable, uranium extractants and their presence could produce misleading extraction results. After hydrolysis, the viscous mixture was diluted with three volumes of Amsco-450 diluent to aid in separation of the phases and then the solvent phase was filtered. This filtrate, after titration with NaOH solution to determine the concentrations of the mono- and diacids, was used as a stock solution.

Table 3 shows a comparison of the uranium extraction power of the OPPA mixture with that of the DEPA-TOPO solvent. Extraction coefficients with 0.32 M OPPA-Amsco 450 were a factor of 3-4 higher than with 0.5 M DEPA-0.125 M TOPO-Amsco 450.

In many respects, the effect of process variables, such as H_3PO_4 concentration, temperature, and reagent concentration dependence, is essentially the same for both processes. Ferric iron is much more strongly extracted by the OPPA and has an adverse effect on uranium extraction.

PROCESS DEMONSTRATION

A continuous demonstration of the first-cycle flow sheet shown in Fig. 10 was made in bench-scale mixer-settler units. The 0.32 M OPPA-Amsco 450 solvent was submitted to about 80 complete extraction-stripping cycles. Samples of solvent, which were removed from the system periodically, showed no appreciable loss of extraction power with cycling. Titration of the solvent showed that the sum of the concentration of the mono- and di-OPPA components remained relatively constant although the mono-OPPA/di-OPPA ratio decreased slightly.

Preferential loss of mono-OPPA would be expected since batch distribution measurements have shown that its distribution loss to the aqueous phase is about 25 parts per million parts of aqueous, whereas the distribution loss of the di-OPPA is negligible. Typical stage data is shown in Fig. 12. Uranium recovery from Company D "green" acid in four extraction stages was about 98% with an aqueous/organic flow ratio of 4/1. More than 98% of the uranium was stripped from the extract which contained 0.30 g U/liter in three stages at 30°C, to give a product solution that analyzed 16.4 g U/liter. This corresponds to a concentration factor across the extraction-stripping system of 225. The decontamination factor of uranium from iron was about 50. This is adequate since the DEPA-TOPO solvent efficiently separates the uranium from iron in the second cycle.

The minimum chlorate consumption achieved was about 0.8 lb per lb of uranium recovered, a factor of 5 to 6 higher than the stoichiometric requirement. We found that the major consumption of chlorate was not due to the oxidation of uranium but to a side reaction in which chlorate reacts with chloride in the acid to produce chlorine and/or chlorine dioxide. When these gaseous products were contained, by sealing the stripping units from the atmosphere, much more efficient utilization of the chlorate was achieved. Also, by operating the stripping units at 30°C and by adding most of the chlorate, in the form of an almost saturated water solution, to the first stripping stage (the balance was added to the third stage) more efficient utilization of the oxidant was obtained. The addition of sodium chlorate to the system caused precipitation of sodium silico fluoride, but this did not cause physical problems.

Since our tests showed that the mono component was preferentially lost from the solvent, it was apparent that a source of mono-OPPA would be needed to maintain the proper concentration range during continuous operation. For this reason, a method was developed to separate the mixture into relatively pure mono- and diacid fractions. When these fractions were tested alone and in various combinations, we found that the extraction power of the mixture was about 15 times greater than either component alone (Table 4). As shown here, the uranium extraction coefficient was about 30 in extractions with an equimolar mixture compared to about 2 with either component alone. Also, the coefficient remained approximately constant as the di-mono ratio was increased from 1/1 to 7/1. In the tests described here, some of the impurities (non-acidic components) in the original mixture were still present in the separated fractions and the mono- and diacids were soluble in Amsco 450. However, in later tests in which essentially all of the impurities had been removed, neither the mono- or diacid was soluble in the Amsco 450 diluent. It was obvious that some other component in the commercial mixture was affecting the solubility and possibly uranium extraction.

CHEMICAL REAGENT COSTS

Total chemical reagent costs for the process, based on the continuous bench-scale tests using "green" acid containing 0.12 g U_3O_8 /l were previously estimated to be \$0.71/lb U_3O_8 (Table 5). Thus, if planned stability and solubility tests confirm our previous data, the OPPA process should have a significant cost advantage over the DEPA-TOPO Process.

SUMMARY

The OPPA process offers three potential advantages over the DEPA-TOPO process. The OPPA extractant is much less expensive and has a higher extraction power for uranium than the DEPA-TOPO solvent. In addition it extracts U(IV),

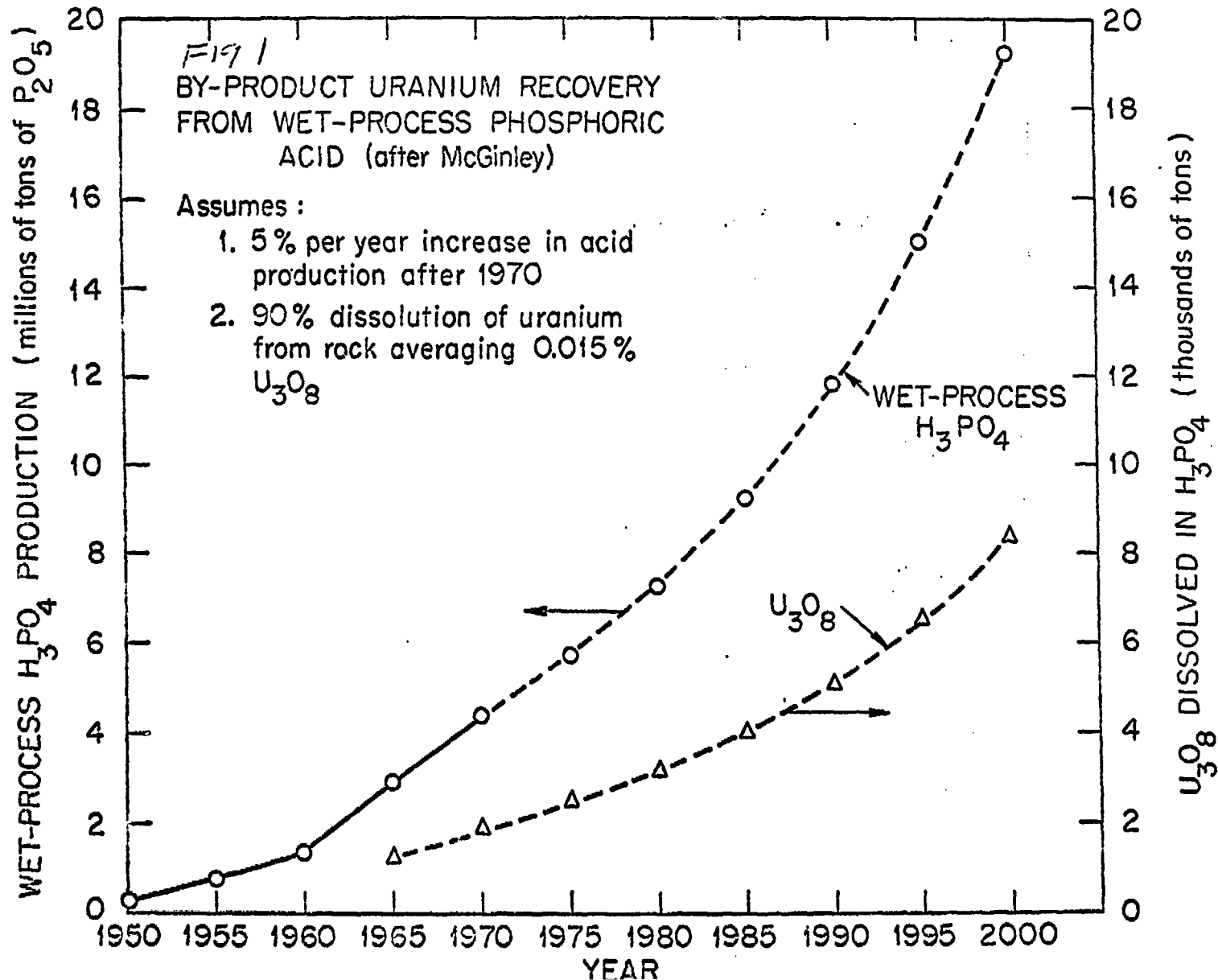
the prevailing oxidation state of uranium in wet-process phosphoric acid and this eliminates the liquor oxidation step required in the DEPA-TOPO process. However, the DEPA-TOPO solvent is known to be extremely stable and this process has been successfully demonstrated on a pilot-plant scale at phosphate plants. It is my understanding that several companies are planning to commercialize this process in the near future. On the other hand, the potentially more attractive OPPA process has not been proven in a pilot plant operation and some questions about the solubility and stability of the OPPA need to be answered.

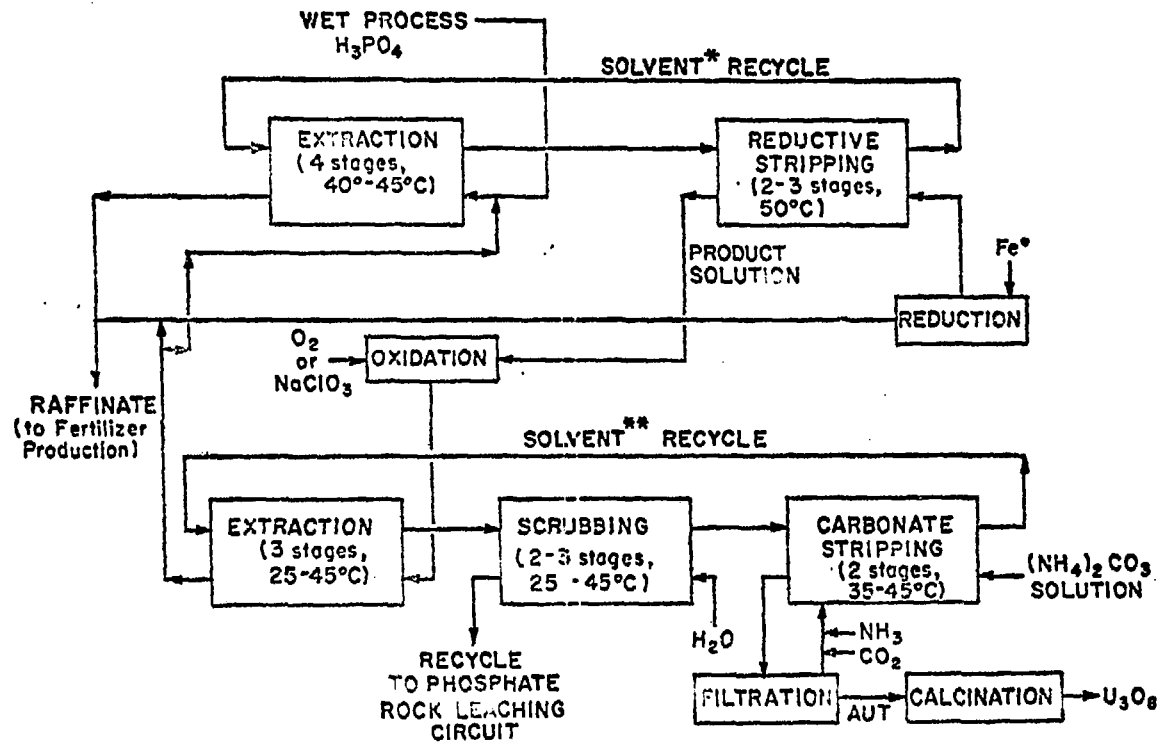
Because of the wide spread interest in this process, we have recently started a program in cooperation with Mobil and Allied Chemical companies to study this extractant. We hope to identify and isolate the material that solubilizes the mono- and diacids and to determine the optimum concentration and ratios for uranium extraction. In addition we plan to make a long term cyclic test to better define solubility losses and stability of the extractant. Consideration will also be given to improving the recovery of uranium lost to the gypsum during calcination.

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<u>ORNL-DWG. No.</u>	<u>Fig. No.</u>	<u>Title</u>
75-17663	1	By-Product Uranium Recovery from Wet-Process Phosphoric Acid (after McGinley) Assumes: 1. 5% per year increase in acid production after 1970. 2. 90% dissolution of uranium from rock averaging 0.015% U_3O_8 .
71-161R2	2	DEPA-TOPO Process Flowsheet for Recovery of Uranium from Wet-Process Phosphoric Acid.
71-165	3	Effect of TOPO:DEPA Ratio on Uranium Extraction at 25°C. Conditions: organic and aqueous phases mixed 5 min at a ratio of 1:1 NND-n-dodecane.
71-166R1	4	Effect of H_3PO_4 Concentration on Uranium Extraction.
69-36-R2	5	Effect of Temperature on Uranium Extraction from Company A Acid with 0.2 M DEPA-0.05 M TOPO.
71-164	6	Effect of DEPA Concentration on Uranium Extraction. Conditions: organic and aqueous phases mixed 5 min at a phase ratio of 1:1. Ratio of TOPO:DEPA in the organic phase was constant at 1:4.
69-32	7	Isotherm for Extraction of Uranium from Wet-Process Phosphoric Acid with 0.5 M DEPA-0.125 M TOPO.
71-163R1	8	Demonstration of First-Cycle DEPA-TOPO Flowsheet. Numbers in blocks show concentration in grams per liter at steady state.
71-162R1	9	Demonstration of Second-Cycle Flowsheet. Numbers in blocks show concentration in grams per liter at steady state.
73-7733	10	OPPA Process Flowsheet for Recovery of Uranium from Wet-Process Phosphoric Acid.
73-8553	11	Octylphenenyl Phosphoric Acid (OPPA)
73-7734	12	Demonstration of First-Cycle OPPA Flowsheet. Numbers in blocks show concentration in grams per liter at steady state.





* 0.5 M D2EHPA--0.125 M TOPO--Amsco 450
 ** 0.3 M D2EHPA--0.075 M TOPO--Amsco 450

Fig. 2 Process Flowsheet for Recovery of Uranium from Wet-Process Phosphoric Acid.

ORNL DWG 71-165

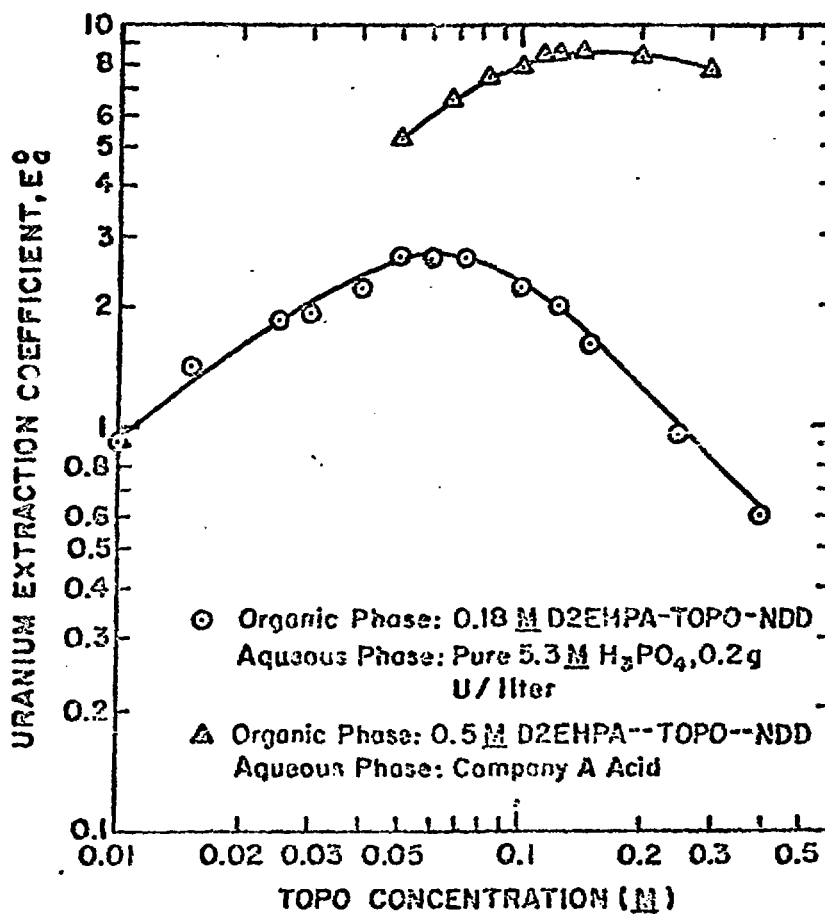
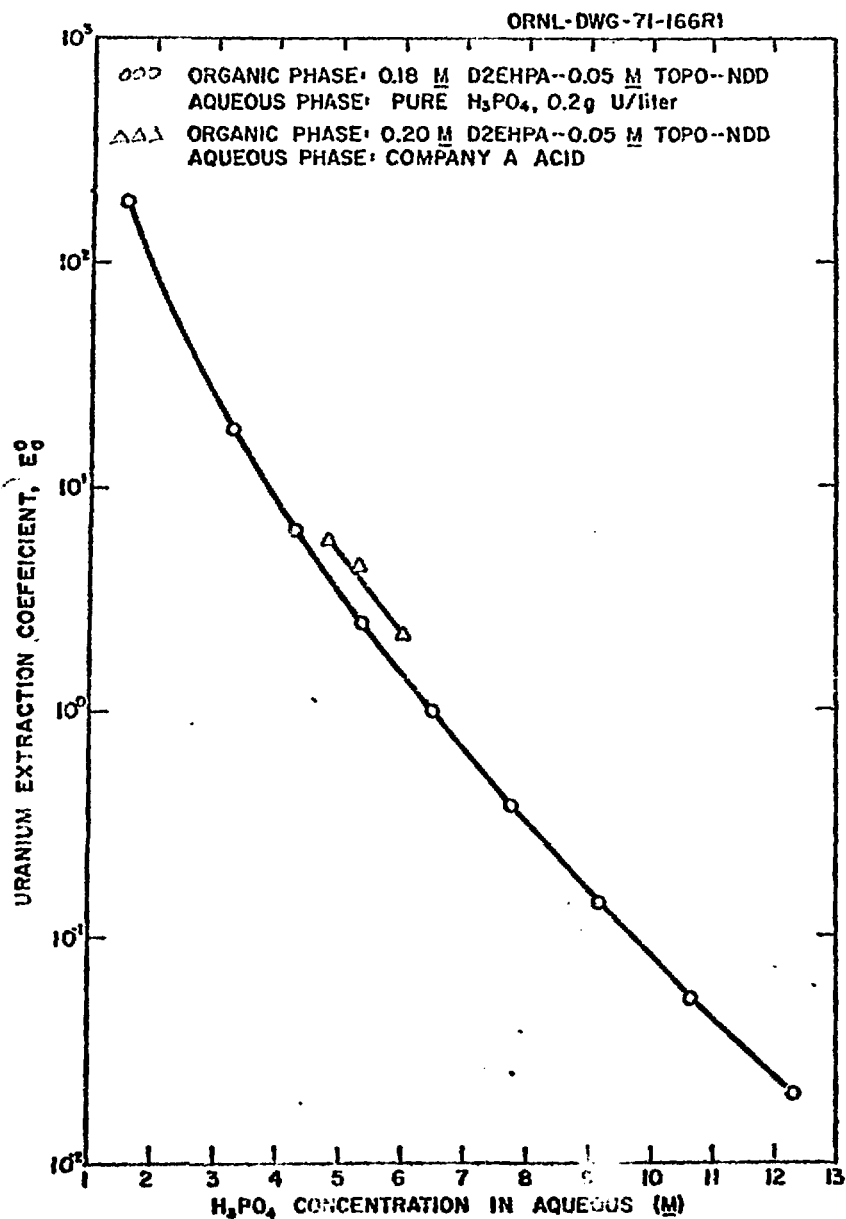


Fig. 3 Effect of TOPO:D2EHPA Ratio on Uranium Extraction at 25°C.

Conditions: Organic and aqueous phases mixed 5 min at a ratio of 1:1.



EFFECT OF H_3PO_4 CONCENTRATION ON URANIUM EXTRACTION

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Fig. 4. Effect of H_3PO_4 Concentration on Uranium Extraction.

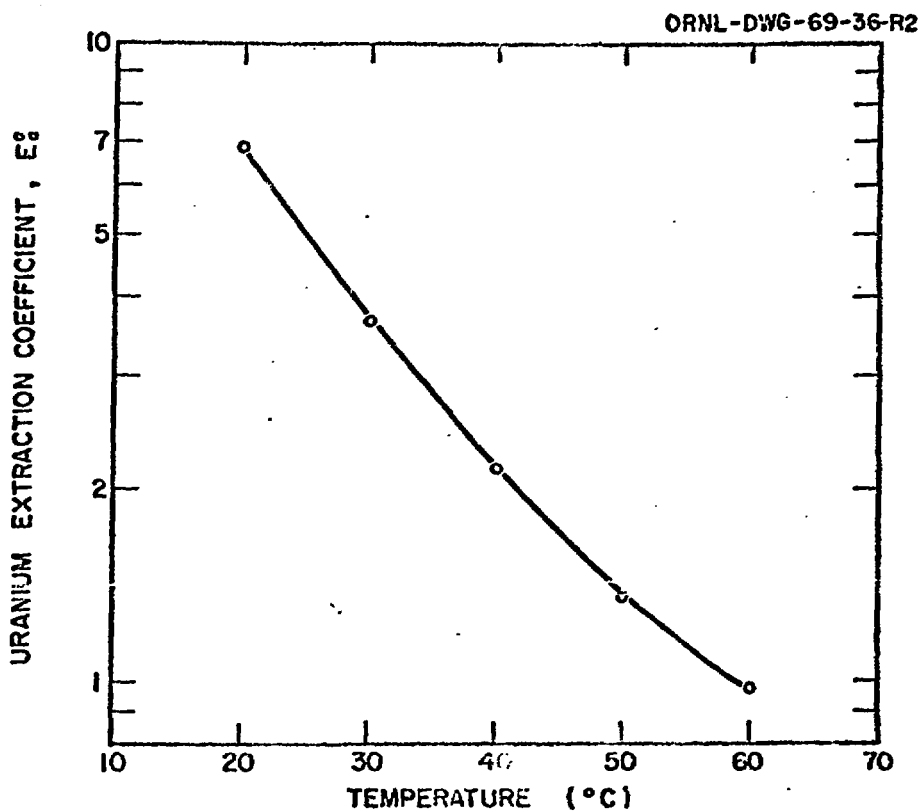


Fig. ⁵ Effect of Temperature on Uranium Extraction from Company A
Acid with 0.2 M D2EHPA--0.05 M TOPO--NDD.

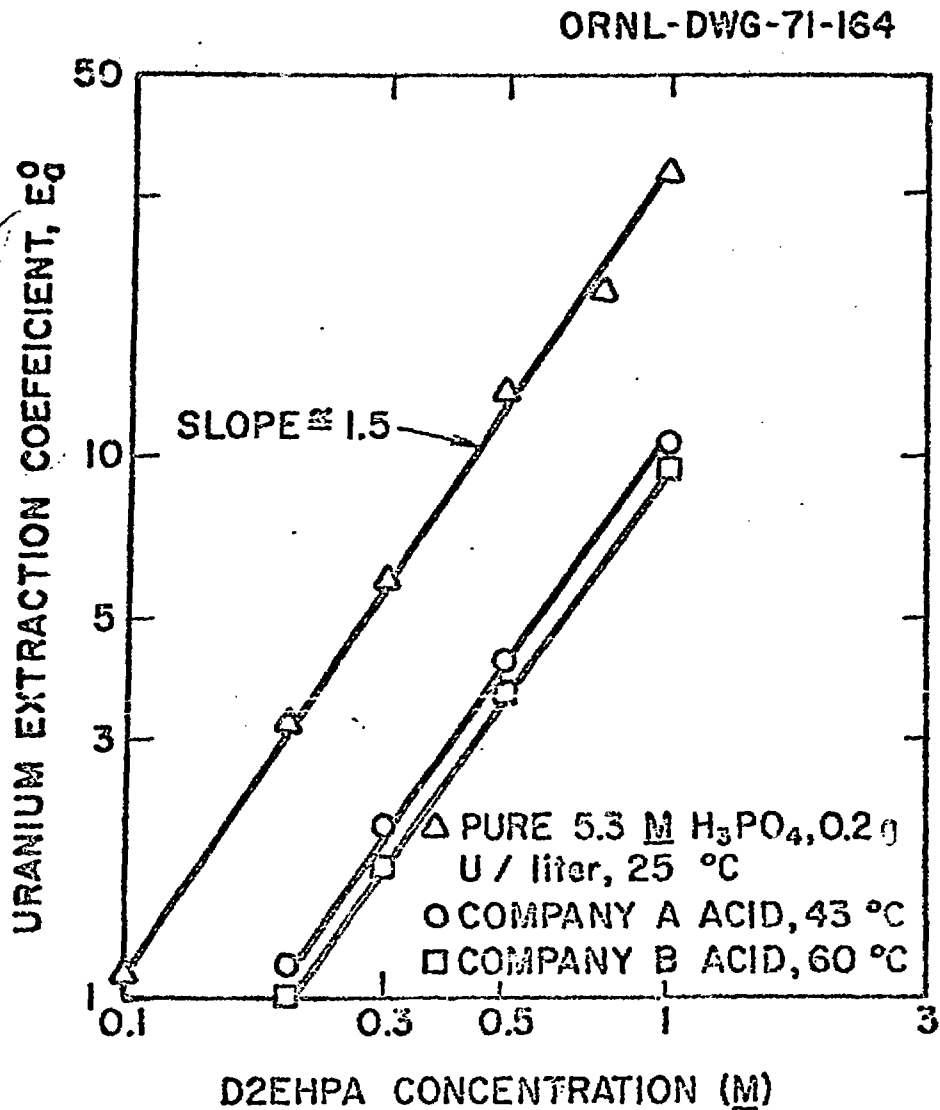
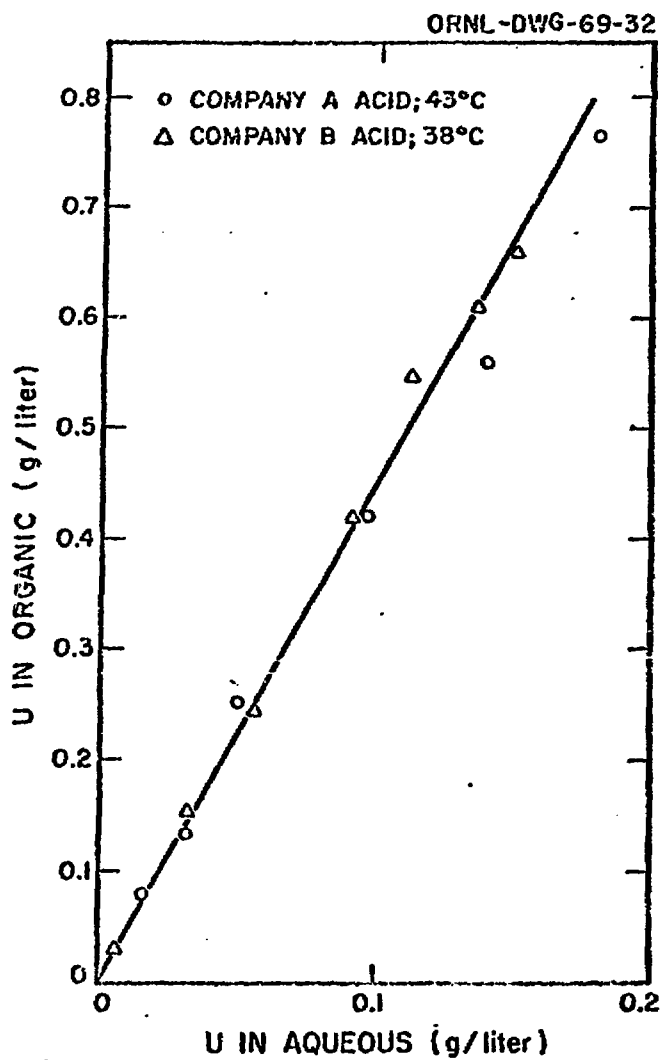


Fig. 6. Effect of D2EHPA Concentration on Uranium Extraction.

Conditions: Organic and aqueous phases mixed 5 min at a phase ratio of 1:1. Ratio of TOPO:D2EHPA in the organic phase was constant at 1:4. Company A and Company B acid samples were 6 molar in H_3PO_4 .



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Fig. 7. Isotherm for Extraction of Uranium from Wet-Process Phosphoric Acid with 0.5 M D2EHPA--0.125 M TOPO--NDD.

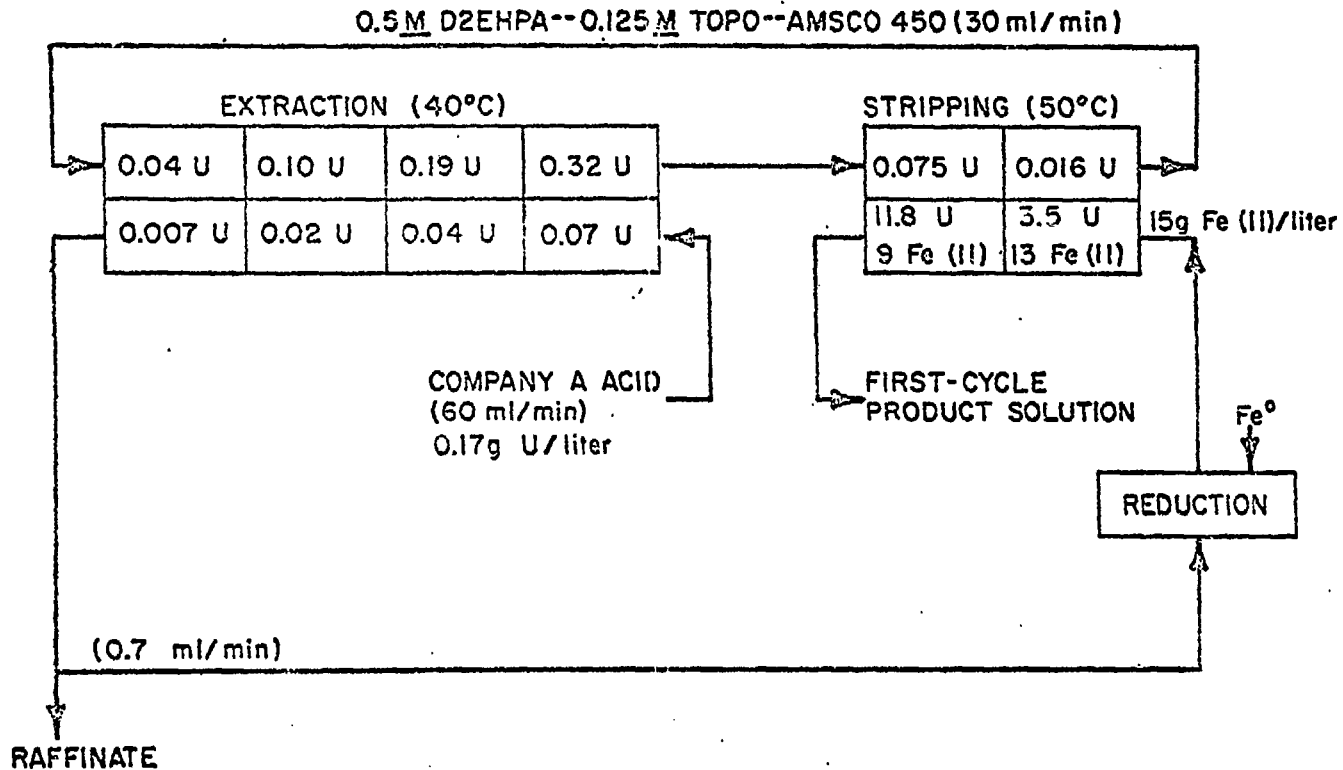


Fig. 8. Demonstration of First-Cycle Flowsheet. Numbers in blocks show concentration in grams per liter at steady state.

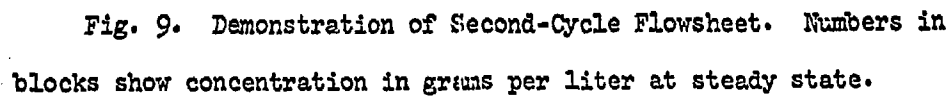


Fig. 9. Demonstration of Second-Cycle Flowsheet. Numbers in blocks show concentration in grams per liter at steady state.

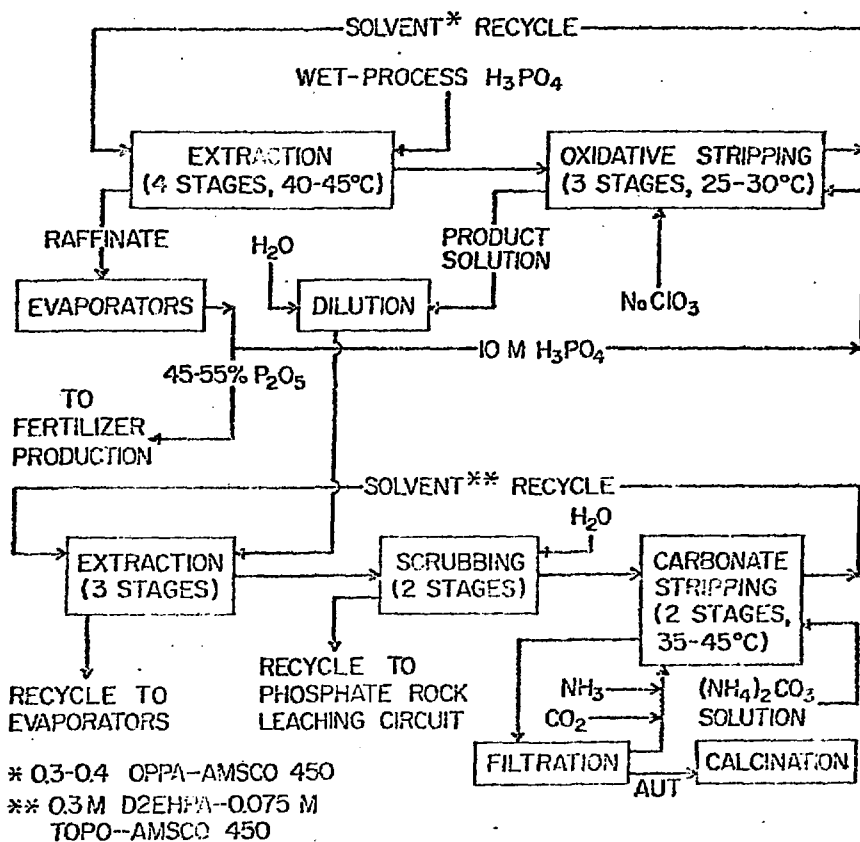
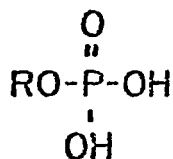


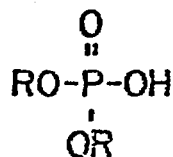
Fig 10 RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID.

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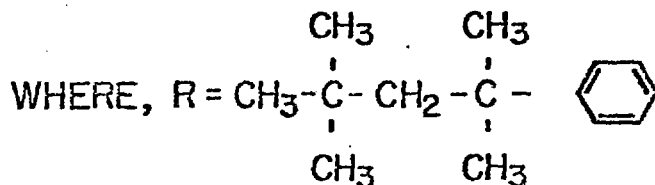
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MONO-ACID PHOSPHATE



DI-ACID PHOSPHATE



OCTYLPHENYL

NOTE: 1. THE OCTYL SIDE CHAIN IS IN PARA POSITION.

2. THE OCTYL ISOMER IS SPECIFICALLY 1,1,3,3 TETRAMETHYL BUTYL.

Fig 11 OCTYLPHENYL PHOSPHORIC ACID

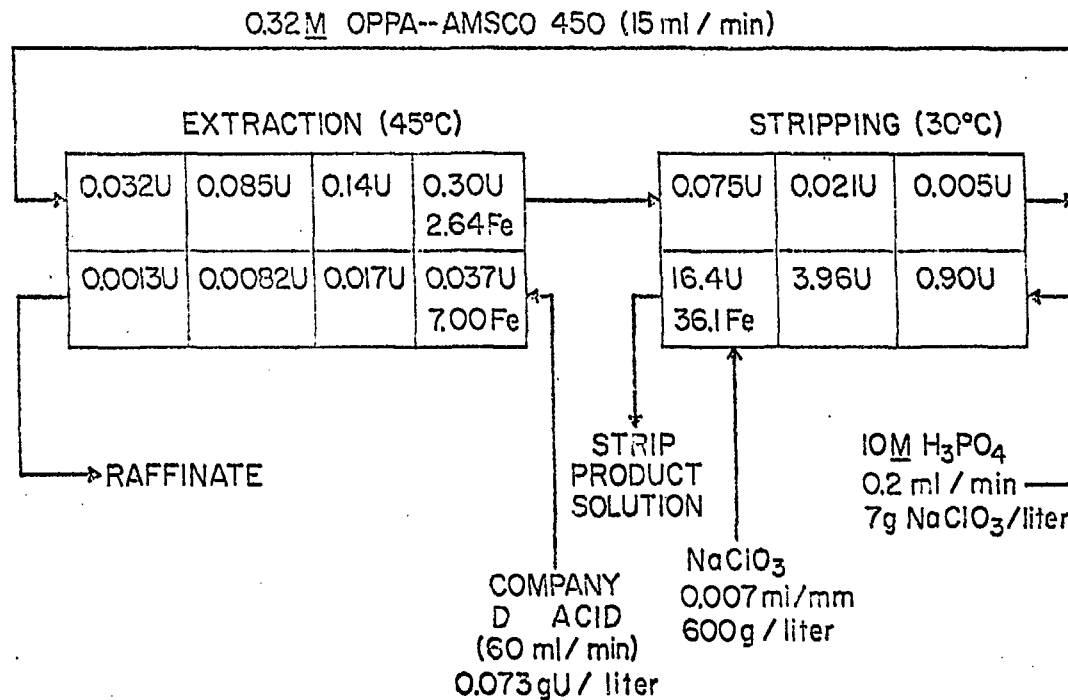


FIG 12 DEMONSTRATION OF FIRST CYCLE FLOWSHEET

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TABLE-1. ANALYSIS OF WET-PROCESS PHOSPHORIC ACID SAMPLES

Acid from Company	Rock Location	Type of Acid	Concentration, g/liter			
			U	Fe(II)	Total Fe	PO ₄
A	Florida	Brown	0.14-0.17	0.3-0.8	7-10	5.0-6.0 <u>M</u>
B	Florida	Brown	0.16-0.19	0.3-2.6	10-12	5.4-6.0 <u>M</u>
C	Florida	Green	0.10-0.13	0.2-0.7	6-7	5.2-5.3 <u>M</u>
D	Florida	Green	0.07-0.09	2.0-3.5	8-9	5.5-5.7 <u>M</u>
E	N. Carolina	Green	0.06	3.4	6.8	5.5 <u>M</u>
F	Western	Green	0.06	2.6	4.5	5.9 <u>M</u>

TABLE 2 ESTIMATED CHEMICAL REAGENT COSTS^d

Assumptions: Overall recovery of 95% of the uranium from acid containing 0.17 g of U (0.20 g of U₃O₈) per liter

Chemical	Consumption	Consumption (lbs/lb U ₃ O ₈)	Unit Cost (\$/lb)	Cost (\$ per lb of U ₃ O ₈ recovered)
NaClO ₃	Liquor oxidation (first cycle)	1.0	10	0.10
Iron metal	Stripping	0.5	5	0.03
NaClO ₃ ^a	Liquor oxidation (second cycle)	0.8	10	0.08
NH ₃	Stripping	0.9	4	0.04
CO ₂	Stripping	0.8	3	0.02
D2EHPA	Soluble loss to aqueous	<0.01	100	<0.01
TOPO	Soluble loss to aqueous	<0.01	325	<0.01
Organic phase	Physical losses ^b	0.2 gal	280/gal ^c	0.56
Total		0.3	570	0.85

^a Since the oxygen utilization efficiency in oxidizing with O₂ has not been established, use of NaClO₃ is assumed.

^b Losses by entrainment, spillage, settler clean-outs, etc., assumed to be 0.03% of wet-process acid volume.

^c Assumes an extractant concentration of 0.5 M D2EHPA--0.12 M TOPO; Amsco 450 at \$0.28 per gal.

^d Revised, 1975.

Table 1. Extraction of Uranium from Commercial Phosphoric Acid Solutions with OPPA and DEHPA-TOPO

Organic: 0.32 M OPPA in Amsco 450 or 0.5 M DEHPA--0.125 M TOPO in Amsco 450

Aqueous: Wet-process phosphoric acid samples described in Table I

Conditions: Equal volumes of organic and aqueous phases mixed 5 min at 23°C

Company	Uranium extraction coefficient, E_a^0	
	OPPA ^a	DEHPA-TOPO ^b
A	30	7
B	16	5
C	29	8
D	27	8
E	>30	12
F	>30	10

^aUranium present as U(IV).

^bUranium present as U(VI).

TABLE 4-EFFECT OF MOLE RATIO OF MONO- AND DI- OPPA ON URANIUM EXTRACTION

Organic: Varying ratios of mono- and di- OPPA in Amsco 450

Aqueous: Company A acid

Procedure: Equal volumes of organic and aqueous mixed 5 min at 25°C

OPPA Concentration (M)		Phase Separation Time (sec)	Uranium Extraction Coefficient (%) a	Concentration of Fe in Extract (g/liter)
Mono-	Di-			
0.200	--	900	2.1	0.95
0.175	0.025	900	5.3	1.08
0.150	0.050	400	10	0.94
0.125	0.075	180	16	1.03
0.100	0.100	55	30	1.16
0.075	0.125	50	30	1.43
0.050	0.150	40	37	1.42
0.025	0.175	30	30	1.13
--	0.200	30	2.3	0.29

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TABLE 5 ESTIMATED CHEMICAL REAGENT COSTS

Assumptions: Overall recovery of 93% of uranium from green acid containing 0.10 g of uranium (0.12 g of U_3O_8) per liter or about 1 lb U_3O_8 per 1000 gal of acid.

Chemical	Consumption	Consumption (lb/lb U_3O_8)	Unit Cost (\$/lb)	Cost (\$/lb U_3O_8 recovered)
<u>First Cycle</u>				
$NaClO_3$	Stripping	1.0	10	0.10
OPPA	Soluble loss to aqueous ^a	0.21	75	0.18
Organic Phase	Physical losses ^b	0.30	120/gal ^c	0.36
<u>Second Cycle</u>				
(Costs estimated from previous study)				<0.10
Total				0.64

^a Assumes an equimolar mixture of mono- and di-OPPA with a purity of 85% and a steady state loss of 25 ppm to the aqueous phase.

^b Losses by entrainment, spillage, and settler clean-outs assumed to be 0.03% of the acid volume.

^c Assumes an extractant concentration of 0.34 M OPPA; Amsco 450 at \$0.28/gal.