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ISOLATION OF U²³³ FROM THORIUM AND ITS COMPOUNDS

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SEPARATION AND PURIFICATION OF U²³³ FROM

SOLUTIONS CONTAINING THORIUM NITRATE

BY CONTINUOUS COUNTERCURRENT EXTRACTION IN A PACKED COLUMN

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ABSTRACT

The continuous countercurrent extraction of uranium by dibutyl cellosolve from solutions containing thorium nitrate, together with nitrates of aluminum, ammonium, calcium, and hydrogen, was investigated on a laboratory scale. Thorium was removed from the dibutyl cellosolve extract by continuous countercurrent scrubbing with calcium nitrate solution in an upper section of the column.

The efficiency of several types of column packing was investigated. The packings which were studied were 1/16" glass helices, 1/8" glass helices, and split 6 mm glass rings. Using different packings, the HETS was determined for both the extraction step and the scrubbing step at several rates of flow with the aqueous phase continuous and also with the solvent phase continuous. Higher rates of flow invariably resulted in larger HETS values. In the case of the 1/16" glass helices, the HETS was lower with the solvent phase continuous. With the split 6 mm glass rings it was lower with the aqueous phase continuous. With 1/8" glass helices, there was little difference in HETS from the choice of continuous phase.

With the same packing and at similar rates of flow, the HETS for scrubbing was approximately twice the HETS for extraction.

The composition of the aqueous phase influenced not only the distribution coefficient but also the HETS. HETS values must be regarded as specific for given conditions of type of packing, solvent composition, aqueous phase composition, and rate of flow.

The extraction of uranium was 99.4% complete in one test where the height of packed section was 118.5 cm. The pH of the solution was below 0 and the distribution coefficient was 2.03. At similar flow rates in the same apparatus a solution at pH 1.7, which had a distribution coefficient of 1.51, gave only 94.5% extraction.

The thorium content of the extracts was reduced to values as low as 0.2 mg per liter in the upper section of the column. This was a reduction to 1/350 of the thorium content of the extract before scrubbing.

A mathematical relationship between HETS, HTU_{OE} , and HTU_{OW} was developed. Hence it is immaterial whether column design is based on HETS or HTU_{OE} or HTU_{OW} .

On the whole, countercurrent extraction with dibutyl cellosolve, followed by scrubbing the extract with calcium nitrate, was found to be a practical method for separating uranium from thorium and purifying the uranium to any desired degree of purity.

I. INTRODUCTION

Continuous countercurrent extraction is one of the proposed methods for isolation and purification of U^{233} after its formation by neutron bombardment of thorium and subsequent decay of the Th^{233} and the Pa^{233} . Before the present work was started, extensive investigations had been made on the batch extraction of uranium from solutions containing high proportions of thorium using various solvents and various salting agents. On the basis of this past work, this present investigation was made with dibutyl cellosolve as the solvent, and calcium nitrate as a scrub solution. Aluminum and ammonium nitrates were also present in the solutions.

Up to the present time, the principal object of this investigation has been to determine the H.E.T.S. (height of a theoretical extraction stage) and the HTU_{OE} (height of an over-all transfer unit based on extracting phase) for several column packing materials under varied conditions of flow rate and solution composition. This information was needed for the design of a pilot plant column for isolation and purification of U^{233} .

II. SUMMARY

H.E.T.S. and HTU_{OE} values were determined in a laboratory column for 1/16" glass helices, 1/8" glass helices, and split 6 mm glass Raschig rings for flow rates of each phase of 60 to 250 cc per cm^2 per hour. In the case of the glass helices, H.E.T.S. values and HTU_{OE} values were determined for both extraction and scrubbing. In the case of the split 6 mm rings, only the extraction step was investigated. In all cases, values were determined with the solvent as the continuous phase and also with the aqueous solution as the continuous phase.

A 27 mm diameter laboratory column packed with 1/16" glass helices and with a 118.5 cm extraction section and a 92.5 cm scrubbing section was set up and operated in several tests using different aqueous solution compositions, but with the solvent phase continuous in all the tests. The extraction of uranium was 99.4% complete in Test No. 33 where the aqueous phase was below 0 pH and the distribution coefficient was 2.03. Natural uranium at a concentration of 500 milligrams per liter of feed solution was used in this test.

Test No. 36, which was made with U^{233} at a concentration of 0.491 milligrams per liter of feed solution (at a pH of 1.69), gave only 94.5% extraction. This can be attributed largely to the fact that pH adjustment had reduced the distribution coefficient to only 1.506. Since the feed solution was an old one which had been previously extracted with ether, it is possible that decomposition products from the ether had an adverse effect.

The scrub section of the column reduced the thorium content of the extract to 0.2 milligrams per liter in Test No. 35 where the pH of the scrub solution was approximately 1.5. However, in Test No. 36, where the pH of the scrub solution was 3.0, the thorium content of the extract varied between 1.1 and 2.9 to average about 2 milligrams per liter.

III. CONCLUSIONS

Countercurrent extraction with dibutyl cellosolve in a packed column, followed by scrubbing the extract with calcium nitrate solution in an upper section of the column, is a practical method for separating uranium from thorium, and purifying the uranium to any desired degree of purity.

The effect of radioactivity at high radiation levels on dibutyl cellosolve has not been investigated. Neither has the purification of uranium from radioactive fission products been investigated. Although no trouble is anticipated from either of these possibilities, both points will be answered fully in pilot plant work which is scheduled for the near future.

The necessary column height for any extraction process is determined by four factors, viz., the desired percent extraction, the H.E.T.S., the distribution coefficient, and the ratio of solvent phase to feed phase. This investigation has determined the H.E.T.S. for several types of packing for use with several solution compositions on which distribution coefficients have been determined. Thus it is now possible to calculate the required heights of extraction section and scrub section of a column to give any desired percent extraction and any desired degree of purification insofar as the packings and solution compositions which have been investigated are concerned.

For any given packing the H.E.T.S. is variable depending on a number of interrelated factors such as solution composition, viscosity, pH, film diffusion coefficient, rate of flow, and which phase is continuous. Consequently, the H.E.T.S. must be considered as specific for the solution composition and flow rate employed.

As the H.E.T.S. varies with different rates of flow, the HTU_{OE} also varies according to the relation

$$\frac{HTU_{OE}}{H.E.T.S.} = \frac{E - 1}{\ln E}, \text{ where } E \text{ is the Extraction Factor}$$

Thus H.E.T.S., HTU_{OE} , and HTU_{OW} are functions of each other, and it is immaterial whether H.E.T.S., HTU_{OE} , or HTU_{OW} is used as the basis for column design. The results are the same.

H.E.T.S. may be influenced a great deal by the choice of the continuous phase in the operation of the column. With fine glass packing (1/16" helices) much lower H.E.T.S. values are obtained when the solvent phase is

continuous. With 1/8" helices, the H.E.T.S. values are but slightly lower when the solvent phase is continuous. With larger packing (split 6 mm rings) the H.E.T.S. values are much higher when the solvent phase is continuous. The above effects can be explained by assuming that the interfacial area depends on the strength of bridging between the individual particles of packing by the phase which wets the packing preferentially, and on whether the dispersed phase creeps over the surface of the packing in a honeycomb-like structure, or whether it travels as individual droplets.

Higher pH of the calcium nitrate scrub solution results in a higher (aqueous/organic) distribution coefficient for Th, but on the basis of a single column test this effect is counterbalanced by a higher H.E.T.S. for the more basic scrub solution.

IV. REFERENCES TO LITERATURE

Chemical Engineers Handbook, John H. Perry, Editor in Chief. Chapter on Solvent Extraction, pages 1213-1266, Joseph C. Elgin. (Note: On page 1258 of this reference, the statement is made that the rate of flow of oil in the furfural process of refining is 10 to 40 barrels per square foot per 24 hours in a 7 ft diameter column packed with 1-1/2" stoneware rings. This flow rate is 93 to 372 cc per cm² per hour.)

Application of Physico-Chemical Principles to the Design of Liquid-Liquid Contact Equipment, Hunter and Nash, Jour. Soc. Chem. Ind. 51, 285T (1932).

Simplified Calculation of Diffusional Processes, J. A. Colburn, Trans. A.I.Ch.E. 35; 211 (1939).

Liquid-Liquid Extraction in Wetted Wall and Packed Columns, Comings and Briggs, Trans. A.I.Ch.E. 38; 203 (1939).

Limiting Flow in Liquid-Liquid Extraction Columns, Blanding and Elgin, Trans. A.I.Ch.E. 38; 305 (1939).

Liquid-Extraction in Perforated Plate and Packed Columns, Allerton, Strom, and Treybal, Trans. A.I.Ch.E. 39; 361 (1943).

Extraction of Furfural-Water Solutions with Toluene in a Packed Column, O. S. Knight, Trans. A.I.Ch.E. 39; 439 (1943).

Extraction of Acetic Acid by Methyl-isobutyl Ketone in a Wetted Wall Tower, Brinsmade and Bliss, Trans. A.I.Ch.E. 39; 679 (1943).

Liquid-Liquid Extraction in Spray Towers, Johnson and Bliss, Trans. A.I.Ch.E. 42; 331 (1946).

V. REFERENCES TO PREVIOUS WORK WITHIN THE PROJECT

A great deal of work on solvent extraction has been done within the project. The following list of references is by no means a complete bibliography of work done on solvent extraction within the project, but it merely includes those references which have been found directly applicable to the present problem.

- M-12 Investigation on Distribution of $RO_2(NO_3)_2$ between Organic Solvents and Water. C. A. Kraus.
- CD-459 Continuous Extraction of Beta Gunk with Dibutyl Cellosolve. Bredecamp, Capps, Galbreath, and Gates.
- CE-3222 Equipment Development and Semi-Works for Metal Recovery. R. B. Briggs.
- CC-3246 A Pilot Plant for the Purification of Thorium Nitrate by Countercurrent Extraction. A. S. Newton, O. Johnson, W. Tucker, R. W. Fisher, and H. Lipkind.

Drawing of Bellows Pump and Laboratory Column Used at Metallurgical Laboratory.

VI. RAW MATERIALS USED

The solvents used were from the following sources:

Dibutyl Cellosolve	Carbide and Carbon Chemical Corp.
Dibutyl Carbitol	Carbide and Carbon Chemical Corp.
Isopropyl Ether	Carbide and Carbon Chemical Corp.
Ethyl Ether	J. T. Baker Chemical Co.

The other materials used were as follows:

<u>Material</u>	<u>Form</u>	<u>Grade</u>	<u>Source</u>
Aluminum Nitrate	$Al(NO_3)_3 \cdot 9H_2O$	Reagent	J. T. Baker Chemical Co. General Chemical Co. (very little)
Ammonium Nitrate	NH_4NO_3	Reagent	J. T. Baker Chemical Co.
Ammonium Hydroxide	Aqueous Solution	Reagent	J. T. Baker Chemical Co.
Calcium Nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	Reagent	J. T. Baker Chemical Co.
Calcium Hydroxide	$Ca(OH)_2$	Reagent	Mallinckrodt Chemical Works
Thorium Nitrate	$Th(NO_3)_4 \cdot 4H_2O$	Reagent	J. T. Baker Chemical Co. General Chemical Co. (very little)
Nitric Acid	70% Solution	Reagent	J. T. Baker Chemical Co.
Uranyl Nitrate	$UO_2(NO_3)_2 \cdot 6H_2O$	--	Material prepared on project
U^{233} Tracer	Nitric Acid Solution	--	Material prepared on project
Feed Solution for Test No. 36	- See following paragraph.		

The feed solution for Test No. 36 was an old solution which was prepared in the early summer of 1945 by dissolving aluminum jacketed thorium carbonate slugs in nitric acid, adding ammonia to partially neutralize the solution, and then extracting with ether to remove the U²³³. The solution had stood for approximately nine months and most of its Pa content had decayed to U²³³. Just before use, the solution was decontaminated and clarified by MnO₂ precipitation and centrifuging. Then the pH was adjusted with calcium hydroxide. As used, the composition was:

Aluminum	1.29 N
Ammonium	1.29 N
Calcium	1.415 N
Thorium	2.36 N
U ²³³	0.491 mg/liter
Total Nitrate	5.97 N
Sp. Gr. at 23°C	1.45
Viscosity at 23°C	4.32 centipoises
pH	1.69

Viscosity and density data on some of the solution compositions used in the tests were as follows:

8 N Ca(NO₃)₂ Solution

Temperature °C	19°	25°	30°	35°	40°
Viscosity in Centipoises	6.57	5.52	4.82	4.26	3.79
Sp. Gr.	1.45	1.446	1.443	1.441	1.438

Acid Feed Solution

Aluminum Nitrate	1.7 N
Ammonium Nitrate	0.7 N
Thorium Nitrate	3.1 N
Nitric Acid	0.5 N
pH	Below 0

Temperature °C	19°	25°	30°	35°	40°
Viscosity in Centipoises	3.93	3.35	2.95	2.63	2.35
Sp. Gr.	1.421	1.418	1.414	1.411	1.408

After pH adjustment to a pH of 1.8 with lime, the above solution had a density of 1.442 and a viscosity of 3.97 at 23°C.

Dibutyl Cellosolve

Sp. Gr. 0.835 at 20°C

VII. APPARATUS

In brief, the apparatus comprised feed systems for pumping and measuring solvent, feed solution, and scrub solution, and a glass extraction column. These items and their component parts are described separately. Tygon tubing was used for all connections.

Pump

The pump was a bellows type pump constructed by the Clinton Laboratory machine shop. A 0.1 H.P. Bodine Electric Co. motor (Type CR61-2) which was equipped with a variable speed drive was connected through gears and a cam to give a vertical reciprocating motion of $1/8$ " to a horizontal metal plate. To this metal plate there were attached three adjustable screws which contacted the free ends of three brass siphon bellows. These bellows were $11/16$ " O.D. and $27/64$ " I.D. and had 19 corrugations each. The effective cross section was 0.25 square inches. The top ends of the bellows were fixed in place. Thus the height of the adjustment screw determined the compression of the bellows which it contacted.

The opening of each bellows was connected by glass tubing to ground glass check valves. These check valves were made of 10 mm glass tubing, which had been thickened at the valve seats. The connection to the pump was between the two seats. The floats were made of 1-1/2 inch sections of smaller glass tubing and were weighted with mercury which was sealed in.

In the case of the pump for the solvent, the bellows and connection to the check valve were filled with solvent. In the case of the pumps for feed solution and scrub solution, in order to prevent corrosion the bellows were filled with mineral oil. An inverted U tube which was filled with oil was connected to the bellows. The other end of the U tube was filled with the aqueous solution to be pumped and connected to the check valve. The feed inlets of all three check valves were connected to glass tubes extending almost to the floor where they could be dipped into bottles or other open containers of the solution to be pumped.

Feed System for Solvent

A sketch of the feed system for the solvent is shown in Figure I. The outlet from the check valve on the pump line was connected to a tube sealed into the upper portion of a 250 cc flask which served as a pressure equalizer. This flask was fitted with a stopcock (for venting) at the top. A sealed-in glass discharge tube extended to the bottom. This glass tube was connected to a glass laboratory rotameter (Fischer and Porter Co., water capacity 400-7000 cc per hour). The rotameter discharge was connected directly through glass and Tygon tubing to the solvent inlet at the bottom of the column. Regulation of the rate was obtained by adjustment of the screw on the bellows pump.

Feed System for Feed Solution and Scrub Solution

The feed system was similar for the feed solution and the scrub solution. It is shown in Figure II. The outlet from the check valve on the pump line was connected through glass and Tygon tubing to a glass header which was made of 26 mm glass tubing and was 31 cm in height. There was an overflow discharge opening 10 cm from the top of the tube. This discharged through a U tube into the pump line on the intake side of the check valves. The line connecting the pump discharge and the header was also fitted with a T tube

FIG. 1
DIAGRAMMATIC SKETCH OF FEED SYSTEM FOR SOLVENT

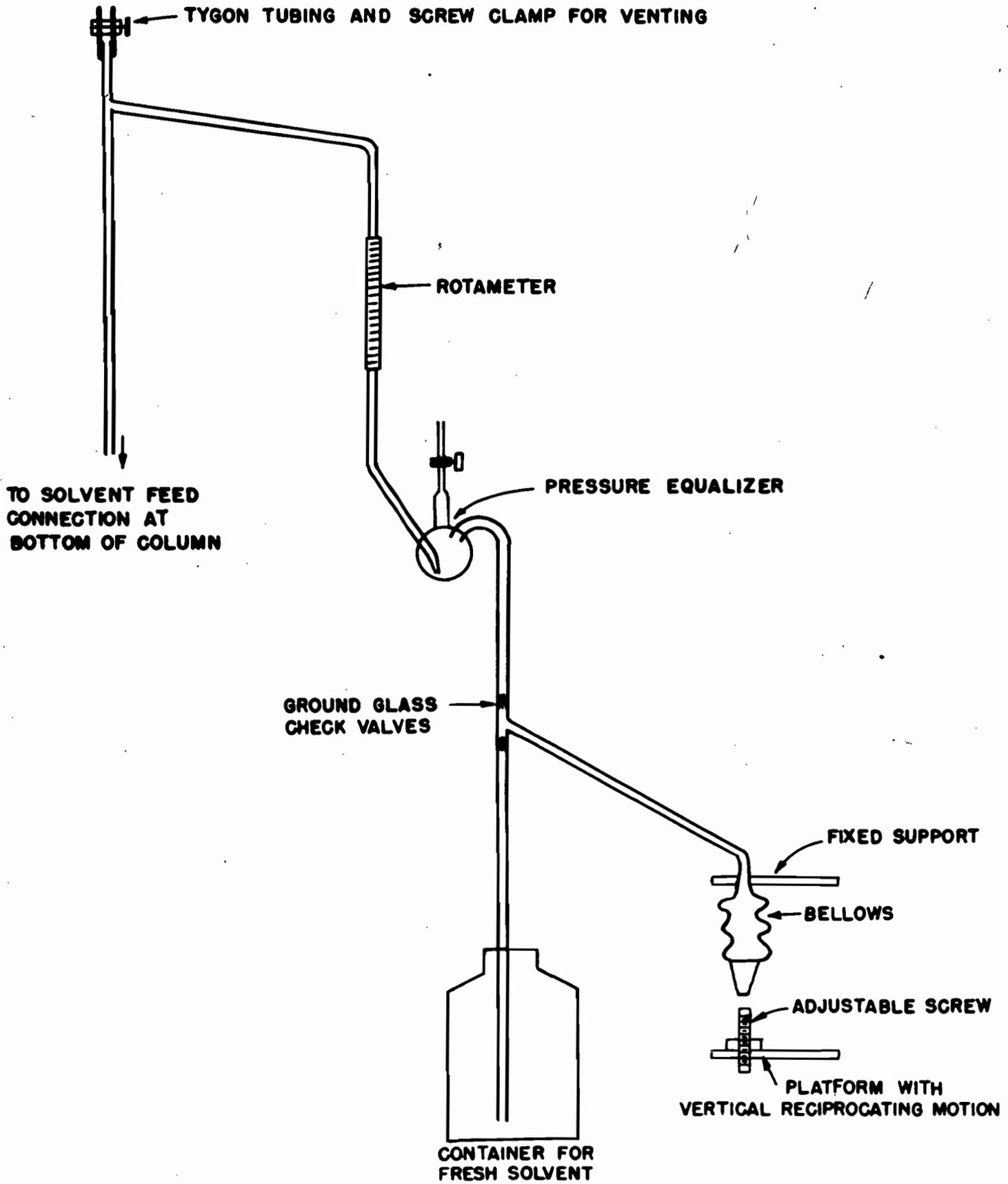
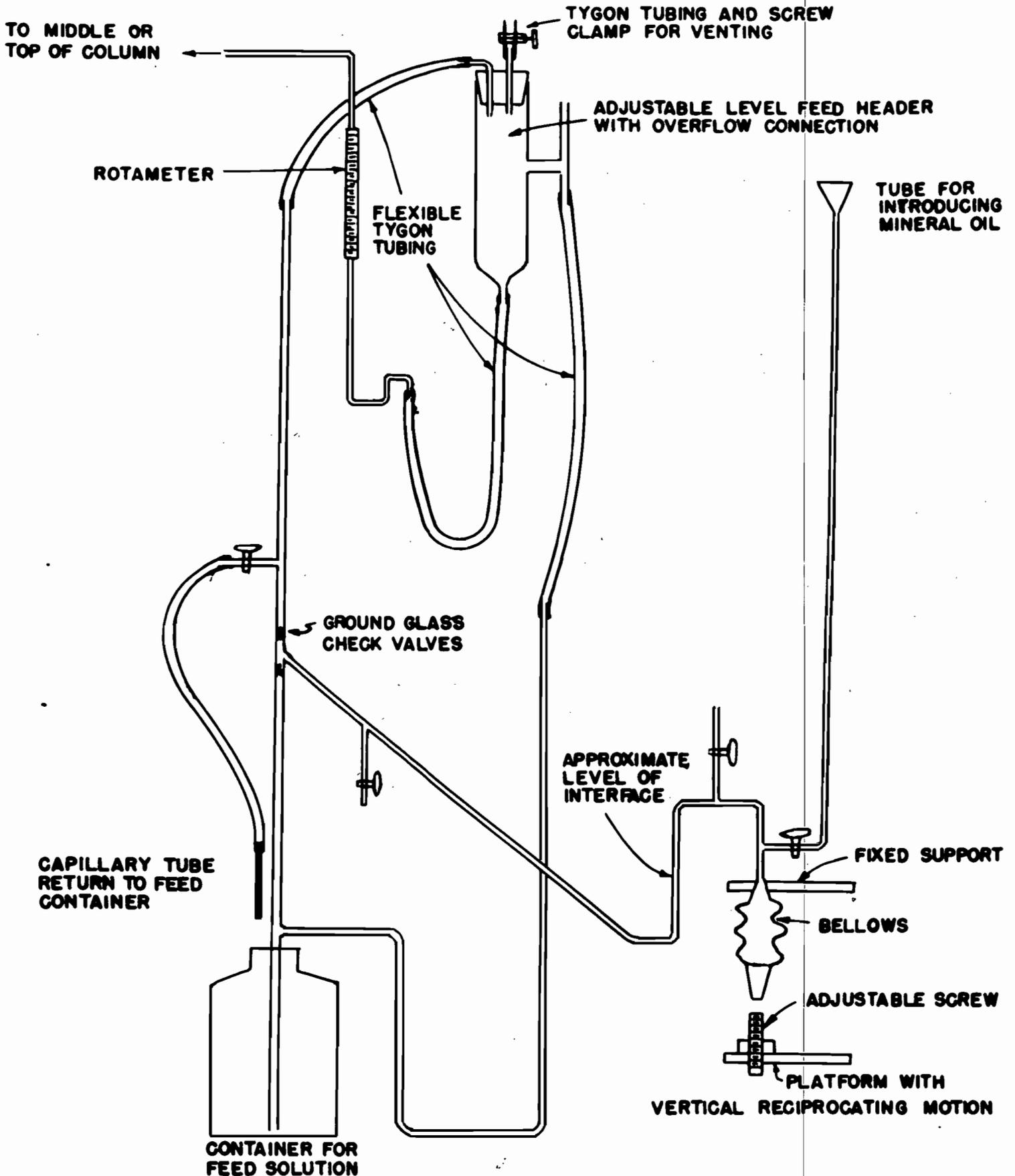


FIG. 2

DIAGRAMMATIC SKETCH OF FEED SYSTEM FOR FEED SOLUTION AND SCRUB SOLUTION



and stopcock which was connected by Tygon tubing to a capillary tube discharging into the vessel containing the feed solution.

The bottom of the glass header was connected to a glass laboratory rotameter (Fisher and Porter Co., water capacity 400 to 7000 cc per hour). The rotameter discharge was connected through glass and Tygon tubing to the extraction column.

In all tests prior to Test No. 31, regulation of the rate was obtained by using the glass header as a vented constant level feed tank and raising or lowering its position as changes in rate were made. Finer adjustments were made by pinching the Tygon tubing with screw clamps.

The column used in Test No. 31 and subsequent tests was taller than the columns used in previous tests, and the head room was insufficient to permit use of the glass header as a constant level feed tank. For these tests, the vent at the top of the header was closed and the overflow discharge was also closed. Regulation of the rate was obtained by splitting the pump discharge between the feed line and the capillary tube returning to the vessel containing the feed solution. Finer adjustments were made by screw clamps on the feed line and on the by-pass line.

Regulation of the flow rate by adjustment of the screw at the bellows pump was found impossible for feed solution and scrub solution. The high viscosity of these solutions causes the check valves to stick at low rates. This makes it necessary to pump at higher rates and then by-pass some of the liquid.

Extraction Column

Several sizes and types of extraction columns were used. These are described in detail in Section VIII of this report.

The position of the interface between the two liquids in all of the columns was controlled by using jacklegs. These jacklegs were merely flexible tubes (Tygon) connected at one end to the raffinate discharge at the bottom of the column and connected at the other end to a T tube which could be raised or lowered to the desired height. The side connection of the T tube was connected to a tube leading to the raffinate receiver. The third opening of the T tube pointed upward and was vented.

The glass helices packing was from the Scientific Glass Apparatus Co. The split 6 mm glass Raschig rings were prepared in the laboratory.

VIII. EXPERIMENTS

A. Methods of Calculation of Extraction Column Data

Several methods of calculation are known for continuous counter-current flow extraction. These methods are all quite complicated for systems

in which the two phases are soluble in each other, but are much simpler for systems employing immiscible liquids. Further simplification occurs when the incoming solvent is free of the material to be extracted.

The most convenient methods of calculation are those based on assumed stepwise operation in terms of the theoretical extraction stage. Continuous countercurrent flow columns may be considered as consisting of a series of perfect batch extraction stages, each of which (except the initial stage) is fed by partially extracted feed solution of the composition discharged by the preceding stage, and by solvent of the composition discharged by the subsequent stage.

The simplest method for the calculation of the number of such theoretical extraction stages is described by Underwood (Industrial Chemist 10; 129 (1934)) and by Hunter and Nash (Jour. Soc. Chem. Ind. 51; 265T (1932)). For the special case where the phases are not miscible and where the incoming solvent is free of the material to be extracted:

$$Z_n = \frac{E - 1}{(E)^{n+1} - 1}$$

where Z_n is the fraction unextracted in the raffinate after the n th stage, n is the number of stages, and E is a value which may be called the extraction factor.

$$E = D \frac{S}{H}$$

where D is the distribution coefficient, S is the quantity of solvent per unit time, and H is the quantity of feed solution per unit time. If Z_n is known, the number of stages may be calculated from

$$n = \frac{\log\left(\frac{E-1}{Z_n} + 1\right) - \log E}{\log E}$$

The height of each stage (H.E.T.S.) is obtained by dividing the height of the packed section of the column by the number of stages.

The above method of calculation was used in this report. As an illustration of the method of calculation, the calculations for portion #3 of Test No. 35 are given in detail.

Basic Data:

Height of extraction section	118.5 cm
Height of scrub section	92.5 cm
Rate of aqueous raffinate discharge	342 cc/hr
Rate of solvent per hour	386 cc/hr
Distribution coefficient for U from batch data	1.455
Distribution coefficient for Th between solvent and scrub solution	230
Distribution coefficient for U between solvent and scrub solution	0.158

Thorium content of feed solution	180 gms/liter
Thorium content of raffinate	109 gms/liter
Thorium content of extract	0.2 mg/liter
Uranium content of feed solution	500 mg/liter
Uranium content of raffinate	8 mg/liter
Estimated thorium content of solvent in equilibrium with mixture of feed solution and scrub solution containing 112.5 gms Th per liter	70 mg/liter

Calculations:

Calculations for Scrub Section of Column

$$\begin{aligned} \text{Rate of flow of feed solution} &= \text{Rate of raffinate} \frac{\text{Thorium content of raffinate}}{\text{Thorium content of feed}} \\ &= 342 \times \frac{109}{180} = 207 \text{ cc per hour.} \end{aligned}$$

$$\begin{aligned} \text{Rate of flow of scrub solution} &= \text{Rate of raffinate} - \text{rate of feed} \\ &= 342 - 207 = 135 \text{ cc per hour.} \end{aligned}$$

$$\begin{aligned} \text{Estimated thorium content of solvent before scrubbing} \\ &= \frac{\text{Thorium content of raffinate}}{112.5} \times 70 = 68 \text{ mg/liter.} \end{aligned}$$

$$\text{Fraction of thorium not scrubbed out} = \frac{0.2}{70} = 0.00294.$$

$$\text{Extraction factor for thorium} = 230 \times \frac{135}{386} = 80.5.$$

$$\text{Number of scrubbing stages} = \frac{\log \left(\frac{80.5 - 1}{0.00294} + 1 \right) - \log 80.5}{\log 80.5} = 1.325.$$

$$\text{H.E.T.S. for scrubbing} = \frac{92.5}{1.325} = 69.8 \text{ cm.}$$

Increase of Effective Uranium Concentration by Reflex from Scrub Section

$$\begin{aligned} \text{Extraction factor for removal of uranium from solvent by scrub solution} \\ &= 0.158 \times \frac{135}{386} = 0.0553. \end{aligned}$$

$$\begin{aligned} \text{Fraction of uranium not removed from extract by scrub solution} \\ &= \frac{0.053 - 1.00}{(0.053)^{2.325} - 1} = 0.948. \end{aligned}$$

$$\text{Fraction of uranium returned to extraction section by scrub solution} = 0.052.*$$

*The above assumption that the number of theoretical stages in the scrub section is the same for uranium and thorium is an approximation, but should be sufficiently accurate in this case, since with a low extraction factor there is little difference between the quantity extracted in one stage and that extracted by an infinite number of stages. Also Sherwood has shown that diffusion coefficients for common inorganic and organic materials in the usual solvents do not vary widely.

Uranium content of aqueous phase at top of extraction section = U content of

$$\begin{aligned} & \text{feed} \frac{\text{volume of feed}}{\text{volume of raffinate}} + \frac{0.052}{0.948} \left(\text{U content of feed} \frac{\text{volume of feed}}{\text{volume of raffinate}} \right. \\ & \left. - \text{U content of raffinate} \right) = 500 \times \frac{207}{342} + \frac{0.052}{0.948} \left(500 \times \frac{207}{342} - 8 \right) \\ & = 303 + 17 \\ & = 320 \text{ mg per liter.} \end{aligned}$$

Calculations for Extraction Section of Column

$$\text{Fraction of uranium left in raffinate} = \frac{8}{322} = 0.025.$$

$$\begin{aligned} \text{Extraction factor for uranium in extraction section of column} &= 1.455 \times \frac{386}{342} \\ &= 1.645. \end{aligned}$$

Number of extraction stages for uranium in extraction section

$$= \frac{\log \left(\frac{1.645-1}{0.025} + 1 \right) - \log 1.645}{\log 1.645} = 5.60.$$

$$\text{H.E.T.S. for extraction} = \frac{118.5}{5.60} = 21.1 \text{ cm.}$$

Another method of calculation was originated by Colburn (Trans. A.I.Ch.E. 35; 211 (1939)). This method is based on the heights of over-all transfer units (H.T.U.) together with over-all diffusion coefficients for transfer of the solute between the phases. Report No. CE-3222 shows the mathematical relationships for this method of calculation and also shows the derivation of the Lyon-Larson equation for H.T.U. calculations.

In brief,

$$\text{H.T.U.} = \frac{L}{K_a} = \frac{h}{\int_{c_1}^{c_2} \frac{dc}{\Delta c}}$$

where h = height of packed section

c = concentration of solute in one phase

Δc = concentration of solute in one phase minus the equilibrium concentration in the same phase corresponding to actual concentration in the other phase

L = volume rate of flow of the phase expressed above

K = over-all diffusion coefficient

a = interfacial area per unit volume of column

K_a = over-all capacity coefficient.

Over-all H.T.U. values, based on concentrations in a single phase are often used. In this case

$$\text{H.T.U.}_{OE} = \frac{Z}{N_{OE}}, \text{ and}$$

$$\text{H.T.U.}_{OW} = \frac{Z}{N_{OW}}, \text{ where}$$

HTU_{OE} and HTU_{OW} are over-all transfer units based on concentrations in the extracting phase and the feed phase, respectively. Z is the height of packed section, and N_{OE} and N_{OW} are the number of transfer units as based on the extracting phase and the feed phase.

The Lyon-Larson equation (Report No. CE-3222) for calculation of H.T.U. and number of transfer units is a simplified form of Colburn's original equation.

$$N_{OE} = \frac{1}{R-1} \ln \frac{R-1+L-LS}{RL-LS} \text{ and}$$

$$N_{OW} = \frac{R}{R-1} \ln \frac{R-1+L-LS}{RL-LS}, \text{ where}$$

- N_{OE} = number of transfer units based on concentrations in the extracting phase
 N_{OW} = number of transfer units based on concentrations in the feed phase
 R = distribution ratio = distribution coefficient multiplied by the ratio of the flow rate of extracting phase to that of feed phase = (E as used in the theoretical stage method of calculation)
 L = loss ratio = ratio of solute concentration in the raffinate to the concentration in the feed
 S = ratio of the amount of solute entering the column in the organic feed to the amount leaving in the raffinate.

H.T.U. may be calculated from the above N_{OE} and N_{OW} values by dividing them into the height of packed section of the column. HTU_{OE} is greater than HTU_{OW} by a factor of R, but the calculated heights of columns are the same by either method.

In those cases where the incoming solvent is free of solute,

$$N_{OE} = \frac{1}{(E-1)} \ln \left[\left(1 - \frac{1}{E}\right) \frac{Y_1}{Y_2} + \frac{1}{E} \right], \text{ and}$$

$$N_{OW} = \frac{1}{1 - \frac{1}{E}} \ln \left[\left(1 - \frac{1}{E}\right) \frac{Y_1}{Y_2} + \frac{1}{E} \right]$$

where Y₁ and Y₂ represent concentrations of the solute in the original feed solution and in the raffinate.

since $\frac{Y_2}{Y_1} = Z_n$, in the expression

$$Z_n = \frac{E-1}{(E)^{n+1} - 1}$$

$$N_{OE} = \frac{1}{(E-1)} \ln \left[\left(1 - \frac{1}{E}\right) \frac{(E^{(n+1)} - 1)}{E-1} + \frac{1}{E} \right]$$

$$N_{OE} = \frac{1}{E-1} \ln \left[\frac{(E-1)(E^{(n+1)} - 1)}{E(E-1)} + \frac{1}{E} \right]$$

$$N_{OE} = \frac{1}{E-1} \ln \frac{E^{n+1} - 1}{E} + \frac{1}{E}$$

$$N_{OE} = \frac{1}{E-1} \ln \frac{E^{n+1}}{E} - \frac{1}{E} + \frac{1}{E}$$

$$N_{OE} = \frac{1}{E-1} \ln E^n$$

$$N_{OE} = \frac{n \ln E}{E-1}$$

$$HTU_{OE} = \frac{H}{N_{OE}}$$

$$H.E.T.S. = \frac{H}{n}$$

$$\frac{HTU_{OE}}{HETS} = \frac{\frac{H}{\frac{n \ln E}{E-1}}}{\frac{H}{n}} = \frac{E-1}{\ln E}$$

Thus for any value of E there is a fixed relationship between HETS, HTU_{OE}, and HTU_{OW}, and if E is known HETS may be converted into HTU_{OE} or HTU_{OW}. For the same percent extraction, the calculated column heights will be the same for both the H.E.T.S. method of calculation and the HTU method of calculation.

Although they were not used in the design of the pilot plant column, HTU_{OE} values as well as HETS values were calculated for most of the experiments covered in this report.

HTU_{OE} and HTU_{OW} may also be calculated from the relationships

$$HTU_{OE} = \frac{L_E}{K_{Ea} C_{Eav}(1-X)_{om}}, \text{ or } HTU_{OE} = \frac{L_E}{K_{Ea}} \text{ (approximate)}$$

$$HTU_{OW} = \frac{L_W}{K_{Wa} C_{Wav}(1-Y)_{om}}, \text{ or } HTU_{OW} = \frac{L_W}{K_{Wa}} \text{ (approximate)}$$

where L_E and L_W represent the flow rates of the two phases in cubic feet per hour per square foot cross section of the tower, K_{Ea} and K_{Wa} are dimensionless values of the over-all capacity coefficient, and C_{Eav} and C_{Wav} are average concentrations of the solute in the two phases, and

$$(1-X)_{om} = \frac{X^* - X}{\ln \left(\frac{1-X}{1-X^*} \right)} \text{ and } (1-Y)_{om} = \frac{Y - Y^*}{\ln \left(\frac{1-Y}{1-Y^*} \right)}$$

where X and Y are concentrations of the solute in the extracting phase and the feed phase, and X* and Y* are the concentrations of the solute in the extracting phase and feed phase which would be in equilibrium with the actual concentration in the other phase. Concentrations are expressed as lb mols per cubic foot.

$K_E a$ and $K_W a$ may be calculated from:

$$W = \text{lb mols transferred per hour} = S L_E (X_1 - X_2) \\ = S L_W (Y_1 - Y_2)$$

where S is the cross-section of the column in square feet and X_1 and Y_1 are concentrations of the solute at the top of the column and X_2 and Y_2 are concentrations at the bottom of the tower.

$$W = K_E a \Delta_{CElm} V = K_W a \Delta_{CWlm} V$$

where V is the packed volume of the tower in cubic feet and Δ_{CElm} and Δ_{CWlm} are log mean values of $(X_1^* - X_1)$ and $(X_2^* - X_2)$ and of $(Y_1 - Y_1^*)$ and $(Y_2 - Y_2^*)$

$$\Delta_{CElm} = \frac{(X_1^* - X_1) - (X_2^* - X_2)}{\ln \left(\frac{X_1^* - X_1}{X_2^* - X_2} \right)}$$

$$\Delta_{CWlm} = \frac{(Y_1 - Y_1^*) - (Y_2 - Y_2^*)}{\ln \left(\frac{Y_1 - Y_1^*}{Y_2 - Y_2^*} \right)}$$

B. Experimental Data

1. Test on Column with Packing Supported by Stainless Steel Screen

The first tests on column operation were made with a 16 mm I.D. glass column which was packed with five sections of 1/8" glass helices. Beginning with the lower section, the heights of these sections were 22 cm, 21 cm, 58.5 cm, 21.5 cm, and 22.5 cm. The packing for each section was supported on a 48-mesh stainless steel screen. Glass inlet connections extended to the center of the column below each packed section and above the top section. There were outlet tubes at the bottom of the column and above the top packed section.

The above column was connected to the feed system so that dibutyl cellosolve entered below the bottom packed section, feed solution entered above the lower three sections, and scrub solution entered above the top section. The composition of the feed solution was:

Thorium Nitrate	3.1 N
Aluminum Nitrate	1.7 N
Ammonium Nitrate	0.7 N
Nitric Acid	0.5 N

The scrub solution was 5 N calcium nitrate.

Attempts to operate the column were unsuccessful because there was so much resistance to two-phase flow through the screen supports that the

cellosolve soon discharged through the bottom outlet and the aqueous phase discharged through the solvent outlet at the top of the column. This effect occurred even with very slow rates of flow.

A piece of 48-mesh stainless steel screen was cut round and sealed at the end of a 20 mm glass tube. This screen was then raised and lowered in a beaker containing dibutyl cellosolve and a lower layer of aqueous solution (10 volumes feed solution and 6 volumes scrub solution). The test showed that the screen gave a great deal of resistance to two-phase flow through it. When the tube was filled with cellosolve, the screen could be held considerably below the interface with little or no flow of aqueous phase through the screen. When the tube was filled with aqueous phase and then lowered into cellosolve, there was very little flow of the aqueous phase through the screen.

2. Preliminary Tests on Column with Glass Supports for Packing

A two section column was constructed of 16 mm I.D. glass tubing with glass packing supports. These glass packing supports comprised short pieces of 10 mm tubing which were drawn down in the center, and held in place in the 16 mm tube by indentations in the outer tube. The indentations and 10 mm tube supported about 2.5 cm height of 6 mm glass Raschig rings, which in turn supported 23 cm height of 1/8" glass helices. There was a raffinate discharge connection (to a jackleg) at the bottom of the column and a solvent outlet at the top of the column. The solvent inlet was below the bottom packed section, and the feed solution inlet was above the top section.

This column was connected to the feed system and operated for forty minutes at approximately 600 cc per hour flow of each phase. Phase separation was good, and there seemed to be no resistance to two-phase flow. The interface moved up and down the column as the jackleg was raised or lowered. Changes in rates of flow had but little effect on the position of the interface. This indicated a low resistance to flow.

This same column was used in a test to determine whether perfect clarification of the feed solution would be necessary. Using feed solution from aluminum jacketed thorium slugs which had been centrifuged but which was still somewhat turbid, it was observed that precipitate collected in the packing. Also the rate of flow decreased rapidly at the same head and same jackleg setting. Clear solutions are essential for operation of a column packed with 1/8" (or finer) glass helices.

3. Extraction Tests on 16 mm Diameter Column

A 16 mm I.D. column with five packed sections and with glass supports for the packing was constructed. The packing was 1/8" glass helices. Beginning with the lower section, the height of the packed sections was 22 cm, 24 cm, 58 cm, 23 cm, and 23 cm. There were inlet connections to the center of the column below each packed section and above the top section. There were outlet tubes at the bottom of the column and above the top packed section.

The column was connected to the feed system so that the solvent might be introduced below the bottom section or between the second and third sections from the bottom. A mixture of ten parts by volume of feed solution and six parts of scrub solution entered just above the third section from the bottom. The composition of this mixture of feed solution and scrub solution was:

Thorium Nitrate	1.94 N
Aluminum Nitrate	1.06 N
Ammonium Nitrate	0.44 N
Nitric Acid	0.31 N
Calcium Nitrate	3.0 N
Uranium (added as uranyl nitrate)	312 mg/liter
pH	below 0

Batch extraction tests with the above solution showed that an equal volume of dibutyl cellosolve extracts 67% of the uranium. An equal volume of ether extracts 92% of the uranium.

Six extraction tests were made on this column with dibutyl cellosolve and one test was made with ether.

Since the data from the second test indicated that channelling might be taking place, before any further extraction tests were made the column was operated with colored solutions to see whether channelling could be observed. Iodine was used to color the solvent and methyl orange was used to color the aqueous phase. These observations were made at flow rates of 150 and 300 cc per hour per cm^2 cross-section area. There was noticeable channelling when the aqueous phase was continuous. When the solvent phase was continuous, channelling was observed in those tests in which the packing had not been previously wet with aqueous phase. There appeared to be very little if any channelling in tests where the packing was first wetted with aqueous phase, and then the solvent phase was made continuous through the packing. In one test where the packing had been pre-wetted with aqueous phase, the flow was stopped and the column allowed to stand for forty hours with the solvent phase continuous. No channelling could be observed when operation was resumed.

As a result of the above observation, the packing was pre-wetted in all of the tests where the solvent phase was continuous.

Several tests were made at different flow rates and using different heights of packing. Some of the tests were with the aqueous phase continuous and some with the solvent phase continuous. In all of the tests, the raffinate and extracts were collected in several portions in order to determine whether equilibrium was established during the test.

The results of the tests, together with calculations to show the number of theoretical stages and the height of each theoretical stage, are shown in Table No. I.

TABLE NO. I
EXTRACTION TESTS IN 16 MM DIAMETER COLUMN

Test No.	Portion No.	Time for Collection of Portion (min)	Height of Packing Used (cm)	Contin-uous Phase	Rate of Aqueous Phase (cc per hour)		Ratio Solvent to Aqueous	Extrac-tion Factor	U Con-tent of Raffi-nate (mg per liter)	Percent Extrac-tion	Theo-retical Stages	HETS (cm)	Time of Operation Before Sample Collection Started	Remarks
					Total	Per cm ²								
1*	1	30	104	Aqueous	564	291	1.08	2.19	34.0	67.3	1.99	52.3	0	Column filled with aqueous phase at start.
	2	30	"	"	592	294	1.07	2.17	58.3	81.2	1.55	67.0		
	3	30	"	"	574	286	1.11	2.24	66.7	78.4	1.38	75.4		
	4	30	"	"	572	285	1.11	2.24	71.3	77.0	1.30	80.0		
	5	30	"	"	614	305	1.02	2.07	65.7	78.8	1.40	74.2		
	6	30	"	"	588	293	1.07	2.18	72.3	76.6	1.31	79.4		
	7	30	"	"	570	283	1.12	2.28	57.3	81.5	1.42	73.2		
2*	1	30	58	Aqueous	490	244	1.25	2.53	90	71.2	1.01	57.4	0	Column filled with aqueous phase.
	2	30	"	"	584	291	1.17	2.38	150	52.0	0.60	96.6		
	3	30	"	"	588	293	1.05	2.12	175	44.0	0.51	131		
	4	30	"	"	572	284	1.06	2.16	195	37.5	0.40	144		
	5	30	"	"	574	286	1.07	2.18	190	39.1	0.42	137		
	6	30	"	"	560	279	1.09	2.22	205	34.3	0.36	161		
	7	60	"	"	312	156	0.98	1.99	185	40.7	0.49	119		
	8	60	"	"	280	139	0.97	1.97	165	47.2	0.59	98.4		
3*	1	30	104	Solvent	640	319	0.93	1.89	69	78.0	1.55	67.3	0	Column filled with aqueous phase and this displaced by solvent before starting test.
	2	30	"	"	574	286	1.00	2.04	62	80.0	1.57	66.4		
	3	30	"	"	540	269	1.09	2.21	56	82.0	1.58	65.8		
	4	30	"	"	600	298	0.96	1.95	63	79.1	1.61	64.5		
	5	30	"	"	576	287	0.99	2.01	67	78.6	1.50	69.2		
4*	1	60	104	Solvent	325	162	0.88	1.78	100	68.0	1.15	90.3	0	Rate cut at end of test 3 to start test 4.
	2	60	"	"	320	159	0.96	1.96	37	88.1	2.29	45.3		
	3	60	"	"	325	162	0.94	1.91	38	87.9	2.32	44.6		

* Solvent was dibutyl cellosolve

TABLE NO. VI

DATA ON COLUMN OPERATION FOR TESTS NOS. 33, 34, AND 35

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Portion No.	Time for Collection of Portion (min)	Rate of Aqueous Phase cc per hour		Analysis of Raffinate			Calculated Values for Extraction													Calculated Values for Scrubbing												
							Total Flow (cc per hr)		Ratio Scrub	Ratio Solvent	U Content of Aqueous Phase Before Extracting		Extraction Factor	Per cent Extracted		Per cent Loss in Raffinate		Theoretical Extraction Stages	H.E.T.S. for Extraction (cm)	Solvent Flow Rate cc per hour		Analysis of Extract		Flow Rate of Scrub		Ratio Scrub to Solvent	Estimated Th Content of Solvent Before Scrubbing Based on Previous Tests and Th Content of Raffinate (mg per liter)	Extraction Factor	Per cent of Thorium Removed by Scrubbing		Theoretical Scrubbing Stages	H.E.T.S. for Scrubbing (cm)
							Feed Solu-	Scrub Solu-	Feed	Aqueous	From mix- ture feed and scrub	Corrected for U re- ture fluxed by scrub		Basis Feed	Cor- rected for scrub reflux	Basis Feed	Cor- rected for scrub reflux			Total	per cm ²	U mg per liter	Th mg per liter	Total	per cm ²				Removed by Scrubbing	Not Removed by Scrubbing		
							Total	Per cm ²	U mg per liter	Ca mg per liter	Th mg per liter																					
TEST NO. 33																																
1	60	352	62	40	48	110	215	137	0.64	1.16	306	320	2.34	86.95	87.5	13.05	12.50	1.90	62.3	407	71	290	49	137	24	0.337	295	28.6	83.4	16.6	0.53	175.5
2	30	255	(Interface changed.)			Not calculated)																										
3	60	345	60	<5est4	55	108	207	138	0.64	1.13	300	315	2.30	98.67	98.73	1.33	1.27	4.57	25.9	390	68	325	9	138	24	0.354	292	30.2	96.93	3.07	1.01	91.6
4	55	349	61	<5est2	59	112	217	132	0.61	1.19	311	327	2.41	99.36	99.39	0.64	0.61	5.18	22.9	415	73	315	3	132	23	0.318	300	27.1	99.00	1.00	1.38	67.0
5	15	376	66	<5est2	58	114	238	138	0.58	1.10	316	332	2.24	99.37	99.40	0.63	0.60	5.62	21.1	416	73	290	2	138	24	0.332	305	28.2	99.35	0.65	1.50	61.6
TEST NO. 34																																
1	60	400	70	19	54.4	138	306	94	0.31	1.18	383	406	1.97	95.04	95.32	4.96	4.68	3.55	33.4	470	82	210	32	94	16	0.20	141	56	77.3	22.7	0.37	253
2	60	423	74	11	50.5	114	268	155	0.58	1.04	317	337	1.74	96.53	96.74	3.47	3.26	4.72	25.1	440	77	286	25	155	27	0.352	117	98.6	78.3	21.7	0.33	279
3	60	396	69	12	51.2	116	255	141	0.55	1.01	322	342	1.69	96.27	96.49	3.73	3.51	4.80	24.7	399	70	296	16	141	25	0.353	119	98.8	86.6	13.4	0.44	212
4	60	475	83	17	48.5	120	317	158	0.50	0.85	334	355	1.43	94.91	95.21	5.09	4.79	5.44	21.8	410	72	306	7	158	28	0.385	123	108	94.3	5.7	0.61	151
5	60	440	77	19	56.0	112	274	166	0.61	0.98	312	331	1.64	93.91	94.26	6.09	5.74	4.12	28.8	430	75	310	1.7	166	29	0.386	115	108	98.52	1.48	0.85	109*
TEST NO. 35																																
1	60	345	60	6	67	105	203	142	0.70	1.08	294	310	1.57	97.96	98.06	2.04	1.94	6.56	18.1	372	65	246	<0.2	142	25	0.381	65	87.5	99.692	0.308	1.29	71.7
2	60	354	62	7	64	109	214	140	0.65	1.02	303	320	1.49	97.69	97.81	2.31	2.19	6.90	17.2	362	63	326	0.2	140	25	0.386	68	88.8	99.706	0.294	1.30	71.2
3	60	342	60	8	67	109	207	135	0.65	1.13	303	320	1.64	97.46	97.50	2.64	2.50	5.60	21.1	386	68	307	0.2	135	24	0.350	68	80.5	99.706	0.294	1.33	69.8
4	60	345	60	8	63	110	211	134	0.65	1.10	306	323	1.60	97.39	97.52	2.61	2.48	5.85	20.3	380	67	286	0.3	134	24	0.353	69	81.2	99.710	0.290	1.33	69.7
5	60	350	61	7.5	64	109	212	138	0.65	1.09	303	320	1.59	97.52	97.66	2.48	2.34	6.05	19.6	382	67	286	0.2	138	24	0.362	68	83.2	99.706	0.294	1.32	70.3
6	15	348	61	8.5	66	111	215	133	0.62	1.03	309	326	1.51	97.25	97.40	2.75	2.60	6.40	18.5	360	63	266	0.2	133	23	0.369	69	84.8	99.710	0.290	1.32	70.3

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* Column filled with feed solution at the start of this test and equilibrium for thorium removal may not have been reached in the scrub section of the column even in portion 5.

TABLE NO. I (Cont.)

EXTRACTION TESTS IN 16 MM DIAMETER COLUMN

Test No.	Portion No.	Time for Collection of Portion (min)	Height of Packing Used (cm)	Continuous Phase	Rate of Aqueous Phase (cc per hour)		Ratio Solvent to Aqueous	Extraction Factor	U Content of Raffinate (mg per liter)	Percent Extraction	Theoretical Stages	H.E.T.S. (cm)	Time of Operation Before Sample Collection Started	Remarks
					Total	Per cm								
6*	1	60	58	Solvent	356	177	0.96	1.96	33	89.4	2.44	42.7	1 hr	Column filled with aqueous phase and this displaced by solvent at start of test.
	2	60	"	"	295	147	1.07	2.17	29	90.7	2.35	44.3		
7*	1	150	104	Solvent	119	59	0.99	2.01	15	95.2	3.42	30.4	0	Rate cut after test 6 to start test 7.
	2	60	"	"	114	57	1.01	2.05	6	98.1	4.60	22.6		
	3	30	"	"	112	56	1.02	2.07	6	98.1	4.55	22.6		
10**	1	30	104	Aqueous	660	329	1.14	13.1	17	94.5	1.10	94.5	30 min	Column filled with aqueous phase at start. Better extraction by ether was due to higher extraction factor and not a shorter H.E.T.S.
	2	30	"	"	650	323	1.17	13.4	11	96.5	1.26	82.5		
	3	30	"	"	610	304	1.48	17.0	8	97.5	1.28	81.3		

* Solvent was dibutyl cellosolve

** Solvent was ether

4. Tests on 26 mm Diameter Column with Single Section

In order to determine the H.E.T.S. and HTU_{OE} for several types of packing and at various rates of flow, a number of tests were made on a glass column 26 mm in diameter and 142 cm total height. In some of these tests the extraction step of the process was studied and in other tests the scrubbing step was studied.

Beginning at the bottom of the column, the connections and packing arrangement were as follows:

Centimeters from Bottom of Column	Tests on Extraction	Tests on Scrubbing
0.0	Outlet for raffinate (Through a jackleg)	Outlet for aqueous phase (Through a jackleg)
4.0	Inlet tube for solvent	Inlet tube for solvent
8.0	Bottom of glass support for packing	Bottom of glass support for packing
13.0	Bottom of packing	Bottom of packing
88.0	--	Top of packing
89.0	--	Inlet tube (through top of column) for scrub solution
97.0	--	Outlet tube for solvent
129.5	Top of packing	
130.5	Inlet tube (through top of column) for feed	
135.0	Outlet tube for solvent	
142.0	Top of column	Top of column

The packing support comprised indentations in the column which supported a short piece of glass tubing that had been drawn down. This in turn supported fragments of broken glass which supported the packing.

The results of the extraction and scrubbing tests on this column are outlined below.

Extraction tests with dibutyl cellosolve

These tests were all made with dibutyl cellosolve as the solvent and with an aqueous phase of the following composition:

Thorium Nitrate	1.94 N
Aluminum Nitrate	1.06 N
Ammonium Nitrate	0.44 N
Nitric Acid	0.31 N
Calcium Nitrate	3.0 N
Uranium (present as uranyl nitrate)	312 milligrams per liter
pH	below 0

Except that the uranium content is at a higher level, the above composition corresponds to a mixture of six volumes of 8 N calcium nitrate solution (scrub solution) and ten volumes of feed solution of the composition originally contemplated, i.e.,

Thorium Nitrate	3.1 N
Aluminum Nitrate	1.7 N
Ammonium Nitrate	0.7 N
Nitric Acid	0.5 N

Several batch extraction tests with an equal volume of dibutyl cellosolve on mixed feed solution of the composition shown above gave consistent checks and an average value of 67.0% extraction of the uranium.

Tests were made at various flow rates and with various kinds of column packing. During each test, the raffinates and extracts were collected in several portions which were analyzed separately in order to determine whether equilibrium had been established.

For each type of packing to be tested, after the column was cleaned and dried with acetone it was filled from the bottom with sufficient aqueous phase to cover the packing. Then flow of both phases was started and the first series of tests made with the aqueous phase continuous. After these tests were finished, the jackleg was gradually lowered while solvent was being pumped in until the aqueous-solvent interface was below the packed section of the column. Then flow of both phases was adjusted to the desired rates, and tests were made with the solvent phase continuous. Usually, operation was continued for approximately 30 minutes before observation of data was started.

The results of the tests, together with calculations to show the number of theoretical extraction stages and the height of each theoretical stage, are shown in Table No. II.

TABLE NO. II
EXTRACTION TESTS WITH n-BUTYL CELLOSOLVE IN 26 MM DIAMETER COLUMN
WITH SINGLE PACKED SECTION

Test No.	Portion No.	Time for Collection of Portion (min)	Kind of Packing	Height of Packing (cm)	Continuous Phase	Aqueous Rate per Hour (cc)		Ratio Solvent to Aqueous Rate	Extraction Factor	U Content of Raffinate (mg per liter)	Percent Extraction (Based on Raffinate)	Theoretical Stages	H.E.T.S. (cm)	NOE	HTU _{OE} (cm)
						Total	Per cm ²								
23	1	15	Split 6 mm Glass	116.5	Aqueous	1390	261	1.10	2.24	80	74.4	1.19	97.8	0.78	150
	2	15	Raschig Rings	"	"	1370	258	1.15	2.34	54	82.7	1.55	75.0	0.98	119
	3	15	" "	"	"	1430	269	1.06	2.15	70	77.6	1.38	84.7	0.91	128
	4	5	" "	"	"	1403	264	1.11	2.26	78	75.0	1.21	96.3	0.78	149
24	1	30	Split 6 mm Glass	116.5	Aqueous	658	124	1.15	2.33	63	79.8	1.40	83.2	0.88	132
	2	30	Raschig Rings	"	"	756	142	1.00	2.03	52	83.3	1.78	65.0	1.22	95.5
	3	30	" "	"	"	774	146	0.99	2.00	60	80.8	1.64	71.0	1.13	103
	4	10	" "	"	"	800	150	0.98	1.98	65	79.2	1.55	75.0	1.08	108
8	1	45	Split 6 mm Glass	122	Aqueous	540	102	1.19	2.41	57	81.7	1.46	83.4	0.91	128
	2	45	Raschig Rings	"	"	550	103	1.14	2.32	43	86.2	1.80	68.0	1.15	102
	3	45	" "	"	"	507	95.4	1.30	2.64	36	88.4	1.80	68.0	1.06	110
	4	30	" "	"	"	500	94.0	1.31	2.66	29	90.7	2.00	61.0	1.18	99.0
25	1	60	Split 6 mm Glass	116.5	Aqueous	357	67.0	0.99	2.00	55	82.4	1.74	67.0	1.21	96.5
	2	60	Raschig Rings	"	"	337	63.0	1.00	2.03	57	81.8	1.68	69.3	1.16	101
	3	60	" "	"	"	348	65.0	1.14	2.32	46	85.3	1.73	67.3	1.10	106
	4	15	" "	"	"	368	69.0	0.99	2.01	46	85.3	1.95	59.7	1.35	86.5
26	1	15	Split 6 mm Glass	116.5	Solvent	1535	289	1.02	2.07	159	49.0	0.55	212	0.38	310
	2	15	Raschig Rings	"	"	1524	286	1.04	2.12	166	46.8	0.50	233	0.34	342
	3	15	" "	"	"	1507	302	1.08	2.19	164	47.5	0.51	228	0.33	351
	4	5	" "	"	"	1560	312	0.96	1.95	166	46.8	0.54	218	0.38	307
27	1	30	Split 6 mm Glass	116.5	Solvent	830	156	0.94	1.91	144	53.8	0.68	171	0.48	241
	2	30	Raschig Rings	"	"	760	143	1.02	2.07	140	55.1	0.67	173	0.46	255
	3	30	" "	"	"	782	147	1.00	2.03	122	60.9	0.83	141	0.56	207
	4	10	" "	"	"	750	141	1.06	2.16	126	59.6	0.76	153	0.49	236
28	1	60	Split 6 mm Glass	116.5	Solvent	325	61	1.10	2.23	90	71.2	1.08	108	0.70	167
	2	60	Raschig Rings	"	"	315	59	1.05	2.14	80	74.4	1.24	94.3	0.82	142
	3	60	" "	"	"	286	54	0.98	1.99	69	77.9	1.47	79.0	1.02	114
	4	15	" "	"	"	340	64	1.18	2.39	70	77.6	1.26	92.0	0.79	147

TABLE NO. II (Cont.)
 EXTRACTION TESTS WITH DIBUTYL CELLOSOLVE IN 26 MM DIAMETER COLUMN
 WITH SINGLE PACKED SECTION

Test No.	Portion No.	Time for Collection of Portion (min)	Kind of Packing	Height of Packing (cm)	Continuous Phase	Aqueous Rate per Hour (cc)		Ratio Solvent to Aqueous Rate	Extraction Factor	U Content of Raffinate (mg per liter)	Percent Extraction (Based on Raffinate)	Theoretical Stages	H.E.T.S. (cm)	N _{OE}	HTU _{OE} (cm)
						Total	Per cm ²								
17	1	15	1/8" Glass Helices	116.5	Aqueous	1320	248	1.18	2.40	73	76.6	1.22	95.5	0.76	153
	2	15	"	"	"	1280	241	1.18	2.40	40	87.2	1.83	63.6	1.15	102
	3	15	"	"	"	1272	239	1.19	2.41	40	87.2	1.82	64.0	1.14	102
	4	5	"	"	"	1224	230	1.23	2.51	40	87.2	1.77	65.8	1.07	109
18	1	30	1/8" Glass Helices	116.5	Aqueous	600	113	1.25	2.54	33	89.5	1.95	59.7	1.18	98
	2	30	"	"	"	760	143	0.94	1.90	26	91.7	2.85	41.0	2.03	57.3
	3	30	"	"	"	760	143	0.93	1.89	42	86.6	2.20	53.0	1.57	74.0
	4	10	"	"	"	750	141	0.93	1.89	43	86.3	2.17	53.6	1.55	75.0
19	1	60	1/8" Glass Helices	116.5	Aqueous	357	67	0.88	1.80	42	86.6	2.34	49.8	1.70	68.4
	2	60	"	"	"	328	62	1.06	2.16	30	90.4	2.35	49.6	1.56	74.8
	3	60	"	"	"	298	56	1.19	2.41	23	92.6	2.42	48.2	1.50	77.5
	4	15	"	"	"	356	67	0.99	2.01	17	94.6	3.27	35.6	2.25	51.7
20	1	15	1/8" Glass Helices	116.5	Solvent	1508	283	0.97	1.98	33	89.5	2.42	48.0	1.69	69.3
	2	15	"	"	"	1440	271	1.08	2.20	46	85.3	1.81	64.3	1.19	97.8
	3	15	"	"	"	1440	271	1.08	2.20	47	85.0	1.79	65.0	1.18	96.8
	4	5	"	"	"	1440	271	1.08	2.20	47	85.0	1.79	65.0	1.18	96.8
21	1	30	1/8" Glass Helices	116.5	Solvent	730	137	1.08	2.20	24	92.3	2.57	45.3	1.69	69.3
	2	30	"	"	"	652	123	1.17	2.38	20	93.6	2.50	46.5	1.63	71.4
	3	30	"	"	"	754	142	1.07	2.19	25	92.0	2.53	46.0	1.67	70.0
	4	10	"	"	"	810	152	0.93	1.89	20	93.6	3.14	37.2	2.33	50.0
22	1	60	1/8" Glass Helices	116.5	Solvent	310	58	0.87	1.77	10	96.8	4.65	25.1	3.45	33.8
	2	60	"	"	"	403	76	0.91	1.85	11	96.5	4.23	27.5	3.07	37.9
	3	60	"	"	"	358	67	1.02	2.07	5	96.4	4.76	24.3	3.25	36.8
	4	15	"	"	"	372	70	1.00	2.03	4	96.7	5.23	22.4	3.55	32.8
11	1	15	1/16" Glass Helices	116.5	Aqueous	1420	267	1.04	2.12	33	89.4	2.26	51.6	1.52	76.8
	2	15	"	"	"	1428	269	1.03	2.09	92	70.6	1.10	106.0	0.74	157
	3	15	"	"	"	1320	248	1.17	2.37	113	63.8	0.83	141	0.51	228
	4	15	"	"	"	1410	265	1.06	2.17	117	62.6	0.83	141	0.55	212
	5	5	"	"	"	1462	275	1.02	2.08	130	58.4	0.75	155	0.51	230

TABLE NO. II (Cont.)
 EXTRACTION TESTS WITH DIBUTYL CELLOSOLVE IN 26 MM DIAMETER COLUMN
 WITH SINGLE PACKED SECTION

Test No.	Portion No.	Time for Collection of Portion (min)	Kind of Packing	Height of Packing (cm)	Continuous Phase	Aqueous Rate per Hour (cc)		Ratio Solvent to Aqueous Rate	Extraction Factor	U Content of Raffinate (mg per liter)	Percent Extraction (Based on Raffinate)	Theoretical Stages	H.E.T.S. (cm)	NOE	HTU _{OE} (cm)
						Total	Per cm ²								
12	1	30	1/16" Glass Helices	116.5	Aqueous	634	119	1.13	2.29	112	64.2	0.84	139	0.54	215
	2	30	"	"	"	770	145	0.95	1.93	101	67.6	1.06	110	0.75	156
	3	30	"	"	"	820	154	0.87	1.77	116	62.8	0.97	120	0.72	163
	4	10	"	"	"	822	155	0.91	1.86	127	59.4	0.84	138	0.60	194
13	1	60	1/16" Glass Helices	116.5	Aqueous	342	64	0.98	1.98	107	65.8	0.98	119	0.70	168
	2	60	"	"	"	342	64	0.93	1.88	87	72.1	1.25	93.3	0.90	130
	3	60	"	"	"	340	64	1.04	2.11	80	74.4	1.26	92.5	0.82	142
	4	20	"	"	"	351	66	0.98	2.00	82	73.8	1.27	91.8	0.88	133
14	1	15	1/16" Glass Helices	116.5	Solvent	1340	252	1.03	2.09	14	95.5	3.37	34.6	2.29	51.0
	2	15	"	"	"	1290	242	1.11	2.26	27	91.4	2.37	49.2	1.54	75.7
	3	15	"	"	"	1370	258	1.02	2.08	34	89.1	2.27	51.3	1.54	75.8
	4	5	"	"	"	1285	242	1.15	2.34	33	89.4	2.08	56.0	1.33	87.5
15	1	30	1/16" Glass Helices	116.5	Solvent	884	166	0.97	1.96	21	93.3	3.05	38.2	2.14	54.5
	2	30	"	"	"	764	144	1.01	2.06	20	93.6	2.96	39.4	2.03	57.5
	3	30	"	"	"	810	152	0.94	1.91	20	93.6	3.22	36.2	2.28	51.0
	4	10	"	"	"	804	151	1.06	2.15	20	93.6	2.85	40.8	1.89	62.0
16	1	60	1/16" Glass Helices	116.5	Solvent	325	61	1.03	2.10	13	95.8	3.47	33.5	2.34	49.8
	2	60	"	"	"	321	60	0.99	2.01	5	98.4	4.96	23.5	3.43	34.0
	3	60	"	"	"	378	71	0.95	1.92	3	99.0	5.99	19.5	4.24	27.5
	4	15	"	"	"	360	68	0.89	1.80	5	98.4	5.70	20.5	4.16	28.0

In addition to the types of packing used in the above tests, an unsuccessful attempt was made in Test No. 29 to use a packing prepared by mixing equal volumes of -10+20 mesh coke with 1/8" glass helices. The weight proportions of this packing were 177 grams of glass helices and 164 grams of coke. It was reasoned that such a mixture of packing would give intimate contact in the column, since tests had shown that the glass was preferentially wetted by the aqueous phase while the coke was preferentially wetted by the solvent. Test 29 showed that this mixed packing could not be used because there was so much resistance to two-phase flow through the column that the solvent was pushed out through the raffinate discharge at the bottom of the column and the aqueous phase overflowed through the extract discharge line. This occurred at flow rates as low as 300 cc per hour (56 cc per square centimeter of cross-section).

Extraction tests with solvent mixture containing 45% dibutyl carbitol and 55% isopropyl ether.

Three extraction tests were made in the 26 mm column, using the same composition feed solution that was used in the above tests on types of packing, but using a solvent composed of 45% dibutyl carbitol and 55% isopropyl ether.

A batch extraction test with an equal volume of this solvent mixture showed that it extracts 83.3% of the uranium and 0.67% of the thorium.

All three tests in this series were made with the solvent as the continuous phase. Although all of these tests were made satisfactorily, it was observed that this solvent mixture gives appreciable resistance to two-phase flow in the column. This resulted in an unstable interface, which fluctuated an inch or more at irregular intervals but did not go low enough to cause the solvent to escape through the raffinate outlet.

Also, more gas bubbles than usual were observed in the column during this test, but there is not sufficient evidence to attribute this to reaction.

The results of these tests, together with calculations to show the height of each theoretical stage, are shown in Table No. III.

TABLE NO: III
 EXTRACTION TESTS WITH MIXTURE OF DIBUTYL CARBITOL AND ISOPROPYL ETHER
 IN 26 MM COLUMN WITH SINGLE PACKED SECTION

Test No.	Portion No.	Time for Collection of Portion (min)	Kind of Packing	Height of Packing (cm)	Continuous Phase	Aqueous Rate per Hour cc		Ratio Solvent Rate to Aqueous Rate	Extraction Factor	U Content of Raffinate (mg per liter)	Percent Extraction (Based on Raffinate)	Theoretical Stages	H. E. T. S. (cm)
						Total	Per cm ²						
30	1	60	1/8" Glass Helices	116.5	Solvent	348	65	0.98	4.68	6	96.1	2.35	49.5
	2	60	"	"	"	362	68	0.96	4.78	8	97.4	2.19	53.2
	3	60	"	"	"	380	71	0.84	4.22	5	96.4	2.68	43.5
31	1	30	1/8" Glass Helices	116.5	Solvent	790	149	0.99	4.94	17	94.6	1.69	68.8
	2	30	"	"	"	680	128	1.19	5.96	16	94.9	1.57	74.4
	3	30	"	"	"	830	156	0.92	4.59	14	95.5	1.88	62.0
32	1	15	1/8" Glass Helices	116.5	Solvent	1488	280	1.07	5.33	30	90.4	1.28	90.4
	2	15	"	"	"	1540	289	1.07	5.32	24	92.3	1.42	82.0
	3	15	"	"	"	1540	289	1.05	5.26	24	92.3	1.43	81.5

Although this solvent mixture has a better coefficient for the extraction of uranium than dibutyl cellosolve has, the actual percent extraction which it gave was only slightly higher at high flow rates and actually lower at the lowest flow rate than values observed under similar conditions for dibutyl cellosolve extraction (Tests 20, 21, and 22).

After Test No. 32 was complete, operation was continued for several hours in order to obtain a total of two gallons of extract for use in a scrub test.

Scrubbing tests on the removal of thorium from solvent extract by contacting with 8 N calcium nitrate.

Six scrubbing tests were made. Of these, five were with dibutyl cellosolve extract and one with a mixture of 45% dibutyl carbitol and 55% isopropyl ether.

The tests were made in the same 26 mm diameter column used for the study of the effect of kind of packing on the extraction. However, a lower outlet for the solvent was used in the scrubbing tests, since the height of packing employed was only 75 cm.

Synthetic extracts were used for the tests with dibutyl cellosolve. The extract from Tests 30, 31, and 32 was used for the scrubbing test on the solvent mixture of dibutyl carbitol and isopropyl ether. Eight normal calcium nitrate (pH 1.4-1.6) was used as the scrub solution in all the tests. The composition of the extracts before scrubbing, and data from tests on batch scrubbing, were as follows:

	<u>Dibutyl Cellosolve Extract</u>	<u>Mixed Solvent Extract</u>
Dibutyl Cellosolve	ca. 100%	None
Dibutyl Carbitol	None	45%
Isopropyl Ether	None	55%
Nitric Acid	0.101 N	0.168 N
Thorium	312 mg per liter	560 mg per liter
Uranium	312 mg per liter	285 mg per liter
Percent of U removed by 0.375 volume of 8 N calcium nitrate in batch scrub test	4.93 (average)	3.85
Equilibrium value $\frac{U \text{ aqueous}}{U \text{ solvent}}$	0.14 (average)	0.107
Percent of Th removed by 0.375 volume of 8 N calcium nitrate in batch scrub test	97.3%	94.5%
Equilibrium value $\frac{Th \text{ aqueous}}{Th \text{ solvent}}$	85.	46.5

Column tests were made with 1/16" helices and with 1/8" helices. For each type of packing, tests were made with the aqueous phase continuous and also with the solvent phase continuous. The results of the tests, together with calculations to show the number of theoretical stages and the height of each theoretical stage, are given in Table No. IV.

This tabulation shows that with 1/8" glass helices there is little choice between operation with the aqueous phase continuous or with the solvent phase continuous. With 1/16" glass helices, operation with the solvent phase continuous gave a much shorter HETS. In all cases the HETS for scrubbing was longer than the HETS for extraction at similar flow rates. It is presumed that this was because of the high viscosity of the 8 M calcium nitrate.

TABLE NO. IV

SCRUBBING TESTS ON THE REMOVAL OF THORIUM
WITH CALCIUM NITRATE SOLUTION

Scrub Test No.	Portion No.	Time for Collection of Portion (min)	Kind of Packing	Height of Packing (cm)	Solvent Used	Continuous Phase	Solvent Rate per hour		Ratio Scrub Solution Rate to Solvent Rate	Thorium Extraction Factor	Thorium Content of Solvent after Scrubbing Ng./liter	Per cent of Original Thorium		Theoretical Stages	H.E.T.S (cm)	Uranium Extraction Factor	Calculated Per cent of Uranium Scrubbed Out		N _{oe}	HTU _{oe} (cm)
							Total	per cm ²				Scrubbed out	Not Scrubbed out				By One Theoretical Stage	By Infinite Theoretical Stages		
5	1	60	1/8" glass helices	75 cm	Dibutyl	Aqueous	385	73	0.395	33.6	8.0	97.44	2.56	1.03	72.5	0.055	5.20	5.50	0.111	674
	2	60	1/8" glass helices	"	Cellosolve	"	415	78	0.366	31.1	8.6	97.25	2.75	1.04	72.4	0.051	4.85	5.10	0.118	634
	3	65	"	"	"	"	413	78	0.371	31.5	8.2	97.37	2.63	1.04	71.7	0.052	4.95	5.20	0.118	635
	4	50	"	"	"	"	414	78	0.376	32.0	8.0	97.44	2.56	1.05	71.5	0.053	5.03	5.30	0.117	639
	5	14	"	"	"	"	420	79	0.368	31.3	8.0	97.44	2.56	1.06	71.1	0.052	4.95	5.20	0.120	626
2	1	30	1/8" glass helices	75 cm	Dibutyl	Solvent	750	141	0.355	30.4	4.4	98.59	1.41	1.24	60.4	0.050	4.76	5.00	0.144	521
	2	30	"	"	Cellosolve	"	768	144	0.355	30.4	23.0	92.65	7.35	0.76	98.3	0.050	4.76	5.00	0.088	853
	3	30	"	"	"	"	750	141	0.453	38.5	24.0	92.30	7.70	0.70	108	0.063	5.93	6.30	0.068	1110
	4	30	"	"	"	"	740	139	0.392	33.5	25.0	92.00	8.00	0.71	106	0.055	5.22	5.50	0.077	977
1	1	60	1/8" glass helices	75 cm	Dibutyl	Solvent	357	67	0.381	32.4	4.5	98.79	1.21	1.21	62.0	0.053	5.03	5.30	0.139	538
	2	60	"	"	Cellosolve	"	378	71	0.372	31.6	6.0	98.86	1.14	1.14	66.0	0.052	4.95	5.20	0.145	517
	3	60	"	"	"	"	383	72	0.372	31.6	7.5	98.93	1.07	1.07	70.0	0.052	4.95	5.20	0.147	510
	4	60	"	"	"	"	408	77	0.361	30.7	7.5	98.92	1.08	1.08	69.4	0.051	4.85	5.10	0.151	496
4	1	60	1/8" glass helices	75 cm	Mixed Solvent	Solvent	305	58	0.443	20.6	1.0	99.82	0.18	2.07	36.3	0.047	4.49	4.70	0.320	234
	2	60	"	"	45% Dibutyl	"	365	69	0.392	18.2	10.0	98.22	1.78	1.37	54.8	0.042	4.03	4.20	0.231	324
	3	60	"	"	55% Isopropyl	"	375	71	0.382	17.8	1.0	99.82	0.18	2.18	34.4	0.041	3.91	4.10	0.372	202
	4	60	"	"	ether	"	365	69	0.378	17.6	1.0	99.82	0.18	2.20	34.2	0.041	3.91	4.10	0.376	199
6	1	60	1/16" glass helices	75 cm	Dibutyl	Aqueous	374	70	0.382	32.5	45	85.4	14.4	0.55	137	0.053	5.03	5.30	0.061	1238
	2	60	"	"	Cellosolve	"	377	71	0.387	32.9	39	87.5	12.5	0.59	128	0.054	5.13	5.40	0.064	1168
	3	60	"	"	"	"	355	67	0.403	34.3	36	88.5	11.5	0.60	124	0.057	5.39	5.70	0.064	1170
	4	60	"	"	"	"	363	68	0.386	32.8	37	88.2	11.8	0.60	124	0.054	5.13	5.40	0.066	1133
	5	60	"	"	"	"	358	67	0.377	32.1	35	88.8	11.2	0.62	120	0.053	5.03	5.30	0.072	1045
	6	30	"	"	"	"	350	66	0.360	30.6	35	88.8	11.2	0.63	119	0.050	4.76	5.00	0.073	1030
3	1	60	1/16" glass helices	75 cm	Dibutyl	Solvent	400	75	0.360	30.6	2.2	99.295	0.705	1.44	52.2	0.050	4.76	5.00	0.166	452
	2	60	"	"	Cellosolve	"	392	74	0.388	33.0	1.7	99.456	0.544	1.48	50.7	0.054	5.13	5.40	0.162	463
	3	60	"	"	"	"	400	75	0.390	33.2	1.5	99.520	0.480	1.52	49.5	0.055	5.22	5.50	0.166	453
	4	60	"	"	"	"	382	72	0.388	33.0	1.5	99.520	0.480	1.52	49.4	0.054	5.13	5.40	0.166	451
	5	65	"	"	"	"	397	75	0.368	31.3	1.0	99.680	0.320	1.65	45.5	0.052	4.95	5.20	0.189	398

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5. Tests on 27 mm Diameter Column Operated with Both Extraction Section and Scrubbing Section

The column used in these tests had an over-all height of 256 cm. Beginning at the bottom of the column, the connections and packing arrangement was as follows:

<u>Centimeters from</u> <u>Bottom of Column</u>	
0.0	Outlet for raffinate (through a jackleg).
5.1	Inlet tube for solvent.
8.9	Bottom of glass support for packing.
15.2	Bottom of packing for extraction section. Packing was 1/16" glass helices.
133.7	Top of packing for extraction section.
135.9	Inlet tube for feed solution.
139.7	Bottom of glass support for packing.
146.0	Bottom of packing for scrubbing section. Packing was 1/16" glass helices.
238.5	Top of packing for scrubbing section.
238.8	Inlet tube (through top of column) for scrub solution.
241.0	Outlet tube for solvent.
256	Top of column. Stoppered with two-hole rubber stopper fitted with vent tube and inlet tube for scrub solution.

The general object of the tests on this column was to observe the simultaneous operation of the extraction and scrubbing sections and to check the values of H.E.T.S. which had been determined on the single section 26 mm diameter column.

Tests on the extraction of natural uranium. Tests Nos. 33, 34, and 35.

These three tests were similar except for differences in composition of the feed solution and for minor differences in operation of the column. Test 33 was made with a feed solution which was below 0 pH. The pH of the feed solution was adjusted with ammonia for Test No. 34 and with lime for Test No. 35.

There were differences in the method of starting the operation in the three tests. In Test No. 33, the column was filled from the bottom with raffinate from previous tests. This was displaced by solvent until the interface was in the open section of tube below the packing. Then the flow of feed and scrub was started. After ninety minutes operation at poor rate control, the measurement and collection of raffinate and extract samples was started. Rate control was poor during the collection of portions 1 and 2 but was fairly good for portions 3, 4, and 5.

The column was washed and dried after Test No. 33. The procedure in starting Test No. 34 was similar to that used in Test No. 33 except that the column was filled at the start with a mixture of 10 parts feed solution and 6 parts scrub solution instead of raffinate. Operation was continued for 45 minutes before the measurement and collection of samples were started.

In Test No. 35, the column was started while it was still full of the liquids left from Test No. 34. The scrub was started first and then the solvent. After about fifteen minutes the feed solution was started. Operation was continued for about 45 minutes before the measurement and collection of samples was started.

The data for these three tests are tabulated in Table V and Table VI which follow. Table V lists the composition of the feed solutions, data from batch extractions, data on column size and packing, etc. Table VI lists the flow rates which were observed during the tests, together with analyses of extracts and raffinates, and also shows the results of calculations to determine the efficiency of the column and the h.e.t.s.

TABLE NO. V

Data on Column Construction and Solution Characteristics for Tests Nos. 33, 34, & 35

	Test No. 33	Test No. 34	Test No. 35
Feed Solution Composition:			
Thorium Nitrate	3.1 N	3.1 N	3.1 N
Aluminum Nitrate	1.7 N	1.7 N	1.7 N
Ammonium Nitrate	0.7 N	1.2 N	0.7 N
Calcium Nitrate	--	--	0.9 N
Nitric Acid	0.5 N	--	--
pH	Below 0	1.7	1.8
U (added as uranyl nitrate)	500 mg per liter	500 mg per liter	500 mg per liter
Scrub Solution Composition:			
Ca(NO ₃) ₂	8 N	8 N	8 N
pH	ca. 1.5	ca. 1.5	ca. 1.5
Solvent	Dibutyl Cellosolve	Dibutyl Cellosolve	Dibutyl Cellosolve
Diameter of Column	27 mm	27 mm	27 mm
Area of Column Cross Section	5.72 cm ²	5.72 cm ²	5.72 cm ²
Kind of Packing	1/16" Glass Helices	1/16" Glass Helices	1/16" Glass Helices
Height of Packing for Extrac- tion Section	118.5 cm	118.5 cm	118.5 cm

Table V (Cont.)

	Test No. 33	Test No. 34	Test No. 35
Height of Packing for Scrub Section	92.5 cm	92.5 cm	92.5 cm
U Extraction Factor from Batch Tests	$2.03 \times \frac{\text{Solvent Vol.}}{\text{Aqueous Vol.}}$	$1.67 \times \frac{\text{Solvent Vol.}}{\text{Aqueous Vol.}}$	$1.455 \times \frac{\text{Solvent Vol.}}{\text{Aqueous Vol.}}$
U Extraction Factor for Scrub Solution from Solvent	$0.14 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$	$0.189 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$	$0.158 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$
Thorium Extraction Factor for Scrub Solution from Solvent	$85 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$	$280 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$	$230 \times \frac{\text{Scrub Vol.}}{\text{Solvent Vol.}}$
Estimated Thorium Content of Solvent in Contact with Aqueous Mixture of Scrub Solution and Feed Solution Containing 112.5 gms per liter of Thorium	300 mg per liter	115 mg per liter	70 mg per liter

A comparison of the data for the above three tests reveals the following outstanding points:

- A. Strongly acid solutions (below 0 pH) have a much more favorable distribution coefficient than solutions to which sufficient ammonia or lime has been added to raise the pH to 1.7-1.8.
- B. Adjustment of the pH with ammonia results in a more favorable distribution coefficient than adjustment with lime.
- C. Solutions which have undergone pH adjustment with lime give lower HETP values than unadjusted solutions or solutions which have been adjusted with ammonia. This effect is of sufficient magnitude to result in better overall extraction for solutions adjusted with lime than for solutions adjusted with ammonia, but the overall extraction for solutions adjusted with lime is below the overall extraction for unadjusted solutions.
- D. Adjustment of the pH with either lime or ammonia results in a lower thorium content of the solvent entering the scrub section, and also a more favorable distribution coefficient for the removal of thorium by scrubbing.

Test on the Extraction of Uranium²³³ Test No. 36

This test was similar to Test No. 35 except that the time of operation was much longer (eighty-four hours and forty minutes as compared with five hours and fifteen minutes), and the uranium content of the feed was 0.491 milligrams of U²³³ per liter instead of 500 milligrams of natural U per liter. The history of this feed solution was as follows. During mid-summer of 1945, some aluminum jacketed thorium carbonate slugs which had been bombarded in the pile were dissolved in nitric acid and partially neutralized with ammonia. The resulting solution was extracted with ether, and then the raffinate was allowed to age and produce additional U²³³ by decay of the Pa. This raffinate was diluted and decontaminated and clarified by MnO₂ precipitation and centrifuging. The pH was then adjusted to 1.69 by the addition of lime.

In starting Test No. 36, the column, which had been cleaned and dried, was filled with calcium nitrate solution, and this was displaced by dibutyl cellosolve. The flow of scrub solution was started, and after about thirty minutes the flow of feed solution was started. During the test there were numerous irregularities in flow, and during the greater part of the test the ratio of the scrub solution to feed solution was considerably higher than the desired 0.60. No doubt the changes in the ratio of scrub solution to feed solution influenced the distribution coefficient for uranium extraction, but this effect was not considered in the calculations since batch extraction data were determined for only one mixture, viz., six volumes of scrub solution to ten volumes of feed solution.

The feed solution as used was slightly turbid, and fine brown colored solids collected in the extraction section of the column during the test. Distribution of these solids in the packing indicated channeling in the top 30 centimeters but not below that. In addition to the accumulation of brown solids in the packing, there seemed to be some accumulation of fine white material at the very bottom of the column. The nature of this material was not determined. The quantity was not sufficient to cause any noticeable resistance to flow.

A material balance for the test indicated very good recovery of uranium. This material balance was:

	<u>Milligrams</u>	<u>Percent of Total</u>
Uranium fed to column 16.242 x 0.491	7.96	100.00
Uranium recovered		
Total in extract portions	7.24	90.95
Total in raffinates	0.44	5.53
Total in solutions drained from column and lines at end of test	0.045	0.56
Uranium not accounted for	0.236	2.96

The extracts from the column were passed through an alumina adsorption column for collection and concentration of the U^{233} . This column was 22 mm in diameter and contained 40 grams of -100,200 mesh Fisher's chromatographic adsorption alumina. Adsorption of the U^{233} was virtually complete, and the breakthrough point was not reached during the test. The effluent samples never contained more than 1.0 alpha count per minute per ml. Subsequent leaching of the adsorption column with an alcoholic solution of nitric acid gave a yield of 6.1 mg of U^{233} . This discrepancy of 1.1 milligrams (or 15.2%) between the U^{233} content of the extract and the U^{233} content of the leachings was not explained since the undissolved residue from the adsorption column was discarded before the discrepancy was noticed. However, a later test which is not covered in this report showed substantially complete adsorption from the extract and substantially complete recovery by leaching.

The data for the operation of the column in Test No. 36 are tabulated in Table VII and Table VIII which follow. Table VII lists the composition of the solutions, data from batch extractions, and data on the column size and packing. Table VIII lists the flow rates, the analyses of the extracts and raffinates, and also shows the results of calculations to determine the efficiency of the column and the H.E.T.S.

TABLE VII

Data on Column Construction and Solution Characteristics for Test No. 36

Feed Solution Composition

Total Nitrate Concentration	5.97 N
Thorium Nitrate	2.36 N
Aluminum Nitrate	1.29 N
Ammonium Nitrate	1.29 N
Calcium Nitrate	1.42 N
pH	1.69
U ²³³	0.491 milligrams/liter

Scrub Solution Composition

Calcium Nitrate	8 N
pH	3.0

Solvent

Dibutyl Cellosolve

Diameter of Column

27 mm

Area of Column Cross Section

5.72 cm²

Kind of Packing

1/16" Glass helices

Height of Packing for Extraction Section

118.5 cm

Height of Packing for Scrub Section

92.5 cm

U Extraction Factor from Batch Test

1.506 x $\frac{\text{solvent volume}}{\text{aqueous volume}}$

U Extraction Factor for Scrub Solution from Solvent

0.225 x $\frac{\text{scrub volume}}{\text{solvent volume}}$

Thorium Extraction Factor for Scrub Solution from Solvent

480.0 x $\frac{\text{scrub volume}}{\text{solvent volume}}$

Thorium Content of Solvent in Contact with Mixture of 6 Volumes Scrub Solution and 10 Volumes Feed Solution

86 mg/liter

TABLE NO. VIII
DATA ON COLUMN OPERATION FOR TEST NO. 36

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Portion No.	Time for Collection of Portion (min)	Rate of Aqueous Phase		Analysis of Raffinate		Calculated Values for Extraction										Solvent Flow Rate		Analysis of Extract		Calculated Values for Scrubbing						Portion No.									
		cc per hour	Per cm ²	U Accounts per ml per min	Th gas per liter	Total Flow (cc per hr)	Ratio Scrub	Ratio Solvent	U Content of Aqueous Phase Before		Extraction Factor	Per cent Extracted		Per cent Loss in Raffinate		Theoretical Extraction Stages	H.E.F.S. for Extraction (cm)	Total	per cm ²	U Accounts per ml per min	Th Accounts per ml per min	Flow Rate of Scrub (cc per hr)	Ratio Scrub to Solvent	Estimated Thorium Content of Solvent Before Scrubbing (mg/liter)	Extraction Factor		Per cent of Thorium Removed by Scrubbing	Per cent of Thorium Not Removed by Scrubbing	Theoretical Scrubbing Stages	H.E.F.S. for Scrubbing (cm)					
									Feed	Scrub		Basis Feed	Corrected for reflux	Basis Feed	Corrected for scrub reflux																From mixture feed and scrub	Corrected for U Refluxed	U	Th	Total
1	58	331	58.0	138	41	(Not calculated since conditions could not be constant yet)										413	72.0	360	0.2																1
2	54	341	59.7	134	66	165	176	1.07	1.09	2600	2870	1.64	94.84	95.34	5.16	4.66	4.44	26.7	372	65.0	850	0.1	176	30.8	0.474	66	227	99.85	0.15	1.20	.77	2			
3	60	350	61.2	111	71	181	169	0.93	1.13	2800	3060	1.70	96.03	96.37	3.97	3.63	4.68	25.3	395	69.0	1660	0.3	169	29.5	0.427	71	205	99.58	0.42	1.03	.90	3			
4	60	350	61.2	71	66	169	181	1.07	1.05	2600	2880	1.58	97.27	97.54	2.73	2.46	6.00	19.8	370	64.6	2350	0.3	181	31.7	0.490	66	235	99.55	0.45	0.99	.94	4			
5	60	367	64.2	242	72	193	174	0.90	1.07	2840	3080	1.61	91.47	92.16	8.53	7.84	3.58	33.1	392	68.4	2275	0.7	174	30.4	0.444	72	213	99.03	0.97	0.86	107	5			
6	60	365	63.8	144	71	189	176	0.93	1.02	2800	3070	1.54	94.86	95.31	5.14	4.69	4.86	24.4	374	65.3	2455	0.6	176	30.7	0.470	71	226	99.16	0.84	0.88	105	6			
7	60	353	61.8	134	71	183	170	0.93	1.07	2800	3040	1.61	95.21	95.58	4.79	4.42	4.68	25.3	379	66.1	2430	1.5	170	29.7	0.449	71	215	97.89	2.11	0.72	129	7			
8	177	339	59.4	104	65	161	178	1.11	1.13	2560	2780	1.70	95.94	96.27	4.06	3.73	4.62	25.6	385	67.2	2345	2.3	178	31.1	0.463	65	222	96.46	3.54	0.62	150	8			
9	163	359	62.8	132	68	178	181	1.01	1.02	2680	2910	1.54	95.07	95.47	4.93	4.53	4.94	24.0	368	64.2	2240	2.3	181	31.6	0.491	68	236	96.62	3.38	0.62	150	9			
10	150	352	61.6	130	72	185	167	0.90	1.03	2840	3080	1.55	95.42	95.77	4.58	4.23	5.03	23.5	364	63.5	2400	2.3	167	29.2	0.459	72	220	96.81	3.19	0.64	146	10			
11	180	326	57.1	137	77	184	142	0.78	1.03	3040	3280	1.55	95.48	95.82	4.52	4.18	5.06	23.4	335	58.4	2700	1.9	142	24.7	0.425	77	204	97.53	2.47	0.69	133	11			
12	173	288	50.6	151	76	160	128	0.80	1.18	3000	3250	1.78	94.96	95.35	5.04	4.65	4.00	29.6	341	59.5	2830	2.0	128	22.4	0.375	76	180	97.37	2.63	0.70	132	12			
13	178	307	53.7	123	66	148	159	1.07	1.20	2600	2800	1.81	95.27	95.60	4.73	4.40	4.01	29.6	369	64.4	1950	2.7	159	27.8	0.431	66	207	95.91	4.09	0.60	154	13			
14	178	293	51.3	71	72	154	139	0.90	1.18	2840	3060	1.78	97.50	97.68	2.50	2.32	5.15	23.0	345	60.2	2140	2.2	139	24.3	0.402	72	193	96.95	3.05	0.66	139	14			
15	168	357	62.5	229	74	193	164	0.85	0.92	2920	3200	1.38	92.15	92.83	7.85	7.17	4.71	25.1	330	57.6	2250	1.7	164	28.7	0.498	74	239	97.70	2.30	0.69	134	15			
16	165	375	65.6	193	72	197	178	0.90	0.93	2840	3120	1.40	93.20	93.80	6.80	6.20	4.97	23.9	347	60.6	2830	1.1	178	31.1	0.512	72	246	98.48	1.52	0.76	122	16			
17	158	366	64.1	196	72	192	174	0.90	1.00	2840	3090	1.51	94.51	94.94	5.49	5.06	4.87	24.3	365	63.7	2720	1.9	174	30.3	0.475	72	228	97.36	2.64	0.67	138	17			
18	135	444	77.7	159	70	227	217	0.96	0.86	2760	3050	1.30	94.23	94.78	5.77	5.22	6.26	18.9	382	66.7	2680	1.5	217	37.9	0.568	70	273	97.86	2.14	0.68	135	18			
19	175	365	63.9	157	73	194	171	0.88	1.04	2880	3120	1.57	94.55	94.98	5.45	5.02	4.60	25.7	380	66.4	2830	2.0	171	29.8	0.452	73	217	97.26	2.74	0.67	138	19			
20	155	321	56.2	151	75	176	145	0.82	1.22	2960	3170	1.84	94.89	95.23	5.11	4.77	3.81	31.0	392	68.4	2670	2.9	145	25.3	0.370	75	178	96.14	3.86	0.63	147	20			
21	181	313	54.8	195	72	165	148	0.90	1.13	2840	3050	1.70	93.13	93.60	6.87	6.40	3.65	32.5	354	61.8	1815	2.8	148	25.9	0.419	72	201	96.11	3.89	0.61	151	21			
22	154	375	65.7	102	83	227	148	0.65	0.93	3270	3530	1.40	96.88	97.11	3.12	2.89	7.02	16.9	348	60.8	2642	2.5	148	25.8	0.424	83	204	96.99	3.01	0.66	141	22			
23	145	414	72.4	204	82	248	166	0.67	0.84	3230	3500	1.27	93.69	94.18	6.31	5.82	6.22	19.0	348	60.8	3237	2.7	166	29.0	0.477	82	229	96.71	3.29	0.63	148	23			
24	136	441	77.2	287	81	261	180	0.69	0.75	3190	3490	1.13	91.01	91.77	8.99	8.23	6.70	17.7	332	58.0	3313	2.4	180	31.4	0.542	81	260	97.04	2.96	0.63	146	24			
25	133	451	79.0	257	83	273	178	0.65	1.04	3270	3490	1.57	92.14	92.64	7.86	7.36	3.83	30.9	467	81.5	3565	2.5	178	31.0	0.380	83	182	96.99	3.01	0.67	138	25			
26	138	430	75.3	202	78	245	185	0.76	1.05	3080	3310	1.58	93.43	93.88	6.57	6.12	4.15	28.5	450	78.6	2990	2.4	185	32.4	0.412	78	198	96.93	3.07	0.66	140	26			
27	148	385	67.4	213	85	239	146	0.61	1.08	3350	3570	1.63	93.64	94.03	6.36	5.97	3.81	31.1	416	72.6	2870	2.6	146	25.6	0.352	85	169	96.94	3.06	0.64	146	27			
28	170	350	61.2	180	84	215	135	0.63	0.99	3310	3550	1.49	94.56	94.93	5.44	5.07	4.94	24.0	348	60.8	2820	2.5	135	23.7	0.390	84	187	97.03	2.97	0.67	138	28			
29	160	311	54.4	150	80	182	129	0.71	1.23	3150	3360	1.85	95.24	95.53	4.76	4.47	3.87	30.6	383	66.9	2900	2.3	129	22.6	0.338	80	162	97.13	2.87	0.70	133	29			
30	170	308	53.7	133	83	187	121	0.64	1.20	3270	3470	1.81	95.93	96.17	4.07	3.83	4.23	28.0	368	64.2	2463	2.7	121	21.2	0.330	83	158	96.75	3.25	0.68	137	30			
31	179	292	51.1	162	85	181	111	0.61	1.21	3350	3560	1.82	95.17	95.45	4.83	4.55	3.90	30.3	352	61.5	2353	2.6	111	19.4	0.315	85	151	96.95	3.05	0.69	133	31			
32	176	332	58.0	120	72	175	157	0.90	1.07	2840	3080	1.61	95.78	96.10	4.22	3.90	4.90	24.1	356	62.2	2270	1.9	157	27.5	0.442	72	212	97.36	2.64	0.68	136	32			
33	171	267	46.7	126	85	166	101	0.61	1.36	3350	3540	2.05	96.24	96.44	3.76	3.56	3.77	31.4	363	58.4	2167	2.6	101	17.7	0.280	85	135	96.94	3.06	0.71	130	33			
34	179	327	51.2	133	85	203	124	0.61	1.05	3350	3590	1.58	96.03	96.29	3.97	3.71	5.16	22.9	345	60.2	2507	2.3	124	21.7	0.360	85	173	97.29	2.71	0.70	132	34			
35	183	323	56.5	237	73	172	151	0.86	1.00	2880	3120	1.51	91.77	92.40	8.23	7.60	3.98	29.8	324	56.6	2890	2.0	151	26.4	0.465	73	223	97.26	2.74	0.67	139	35			
36	90	667	116.7	168	47	(Not calculated since this was a cleanup fraction at end of test.)										726	127	2197	4.6															36	

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6. Tests on Orifice Design for Distributor

References to commercial column extraction installations indicate that it is usually not worthwhile to install elaborate devices to distribute the dispersed phase liquid over the area of the column, since general experience has shown that good distribution is established anyway after movement of a distance of four to eight column diameters. In the particular case, however, of operation of a column inside a cell where the height is limited, it is essential that all of the column height operate as closely as possible to maximum efficiency. Therefore, in this particular case distribution of the solution is desirable.

Contemplating use of a distributor designed to maintain a definite head and give flow through small orifices, tests were made to determine the rate of flow of both feed solution and calcium nitrate solution through small stainless steel orifices of different diameters and thicknesses. Tests were made for both vertical and horizontal flow. In all cases the orifice was completely surrounded with dibutyl cellosolve during the tests.

Tests with 8 N Calcium Nitrate Solution

Orifice Diameter	Orifice Thickness	Direction of Liquid Flow	Average Head of Liquid Above Opening (cm)	Rate of Flow cc per opening per minute
0.03125"	0.072"	Vertically Downward	2.8	4.75
"	"	" "	1.4	2.28
"	"	" "	0.7	0. Rate falls to 0 at 1.0-1.2 cm.
0.0468"	0.072"	Vertically Downward	2.8	16.7
"	"	" "	1.6	11.5
"	"	" "	0.7	7.7
0.0468"	0.25"	Vertically Downward	2.9	9.70
"	"	" "	1.5	5.58
"	"	" "	0.7	2.18
"	"	" "	0.6	0.8. Irregular. Flow stops and starts.
0.0468"	0.25"	Horizontal	2.9	7.90
"	"	" "	1.5	2.52
"	"	" "	0.9	0.0. No flow whatever.
0.0468"	0.50"	Vertically Downward	2.9	6.50
"	"	" "	1.5	2.76
"	"	" "	0.9	1.76
"	"	" "	0.5	2.00. (Drains to zero head)

Tests with 8 N Calcium Nitrate Solution (Cont.)

Orifice Diameter	Orifice Thickness	Direction of Liquid Flow	Average Head of Liquid Above Opening (cm)	Rate of Flow cc per opening per minute
0.0468"	0.50"	Horizontal	2.9	5.40
"	"	"	1.5	2.05
"	"	"	0.7	0.77 (Flow irregular)
"	"	"	0.6	0.0 (No flow whatever)
0.0468"	1.00"	Vertically Downward	2.9	4.34
"	"	" "	1.5	2.27
"	"	" "	0.9	1.46
"	"	" "	0.6	1.61
"	"	" "	0.5	1.07 (Rate falls to 0 at 0.3 cm head)
0.0468"	1.00"	Horizontal	2.9	2.22
"	"	"	1.5	0.99
0.0625"	0.072"	Vertically Downward	1.4	21.3
"	"	" "	0.7	13.3
0.0938"	0.072"	Vertically Downward	1.5	52.0
"	"	" "	0.9	36.0

Tests with Mixed Feed Solution

Thorium Nitrate	1.94 N
Aluminum Nitrate	1.06 N
Ammonium Nitrate	0.44 N
Calcium Nitrate	3.312 N
pH	1.8

Orifice Diameter	Orifice Thickness	Direction of Liquid Flow	Average Head of Liquid Above Opening (cm)	Rate of Flow cc per opening per minute
0.03125"	0.072"	Vertically Downward	2.8	6.05
"	"	" "	1.4	3.24
"	"	" "	0.9	0.00 (Flow stops at this head)
0.0468"	0.25"	Horizontal	2.9	10.0
"	"	"	1.5	3.42
"	"	"	1.2	1.27
"	"	"	0.5-0.6	0.0 (Flow stopped)

The phenomena of flow becoming irregular and ceasing at heads slightly above zero is considered due to the effect of surface forces and is a similar action to the previous observation of the resistance offered by a stainless steel screen to two-phase flow.

From the above results a 0.0468" diameter orifice with a metal thickness of 0.25" and with horizontal flow was selected as the best orifice to give a flow of about 2 cc per hole per minute for scrub solution and 3 cc per hole per minute for a mixture of feed solution and scrub solution. Similar flow rates could be obtained by the use of a vertical flow orifice of 0.03125" diameter and a thickness of 0.072", or a vertical flow orifice of 0.0468" diameter and 1.0" thickness. However, stoppage of a horizontal orifice by fragments of broken packing is considered less likely than stoppage of a vertical orifice.

C. Summary of Experimental Data

The above experimental data are summarized in the following tables and graphs.

Table IX and Figure III show the relation between H.E.T.S. and rate of flow for the extraction of uranium by dibutyl cellosolve from acid solutions of the composition originally contemplated. Data for several types of packing are shown.

Table X and Figure IV show the relation between H.E.T.S. and rate of flow for scrubbing thorium from dibutyl cellosolve which has been equilibrated with an aqueous solution of the composition originally contemplated.

Table XI gives H.E.T.S. data for the simultaneous operation of the extraction and scrubbing sections. Data are given for several solution compositions.

Figure V is a series of graphs showing the relation between the percent of material left unextracted and the number of theoretical extraction stages for various values of the extraction factor. Figure VI shows the relationship between the number of HTU_{OG} and the Initial Solute Concentration Solute Concentration of the Raffinate.

Table XII shows the results of calculations to determine the required number of theoretical scrubbing stages to give products of several degrees of purity in regard to thorium content. Values were calculated for three initial thorium/uranium ratios and for two distribution coefficient values. Table XIII is similar to Table XII except that it gives number of HTU_{OG} instead of number of theoretical stages.

FIG. 3.

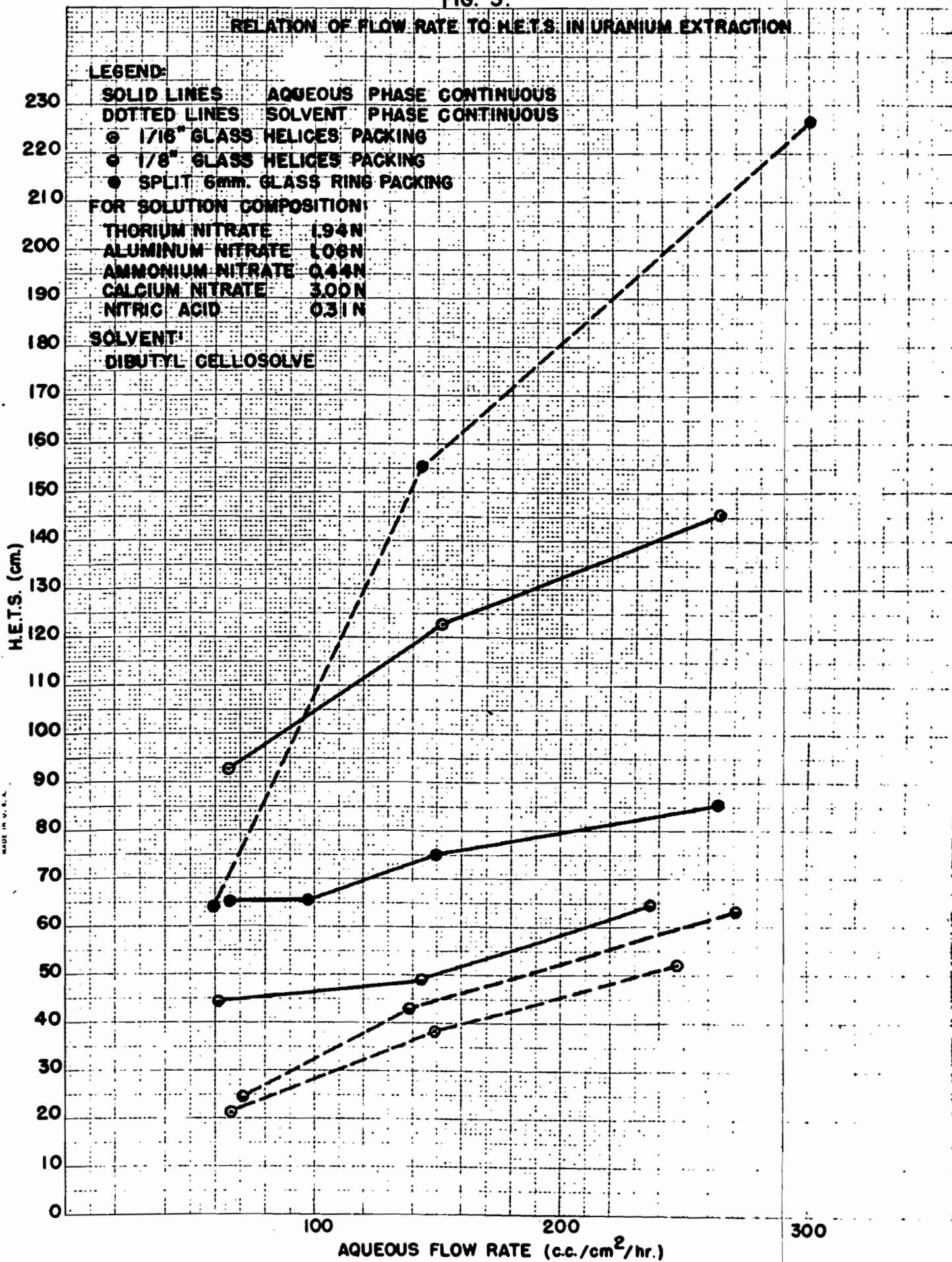


Table IX

Summary of H.E.T.S. Data for Extraction of Uranium by
Dibutyl Cellosolve from Solution Containing:

Thorium Nitrate	1.94 N
Aluminum Nitrate	1.06 N
Ammonium Nitrate	0.44 N
Calcium Nitrate	3.00 N
Nitric Acid	0.31 N
Distribution Coefficient	2.03

Kind of Packing	Aqueous Phase Continuous		Solvent Phase Continuous	
	Flow Rate of Aqueous Phase cc/cm ² /hr	H.E.T.S. (cm)	Flow Rate of Aqueous Phase cc/cm ² /hr	H.E.T.S. (cm)
1/16" Glass Helices	263	146	247	52
	151	123	149	39
	65	93	66	22
1/8" Glass Helices	237	65	271	63
	143	49	139	43
	62	45	71	25
Split 6 mm Glass Rings	264	85	300	226
	150	75	144	156
	98	66		
	66	65	59	65

Table X

Summary of H.E.T.S. Data for Scrubbing Thorium from
Dibutyl Cellosolve after Extraction of Uranium

Solvent Composition:

Dibutyl Cellosolve	almost 100%
Nitric Acid	0.101 N
Initial Thorium Content after Extraction	312 ng/liter
Distribution Coefficient for Thorium (aqueous/organic)	85.0
Distribution Coefficient for Uranium (aqueous/organic)	0.14
Ratio Scrub Solution Volume to Solvent Volume	ca. 0.375

Kind of Packing	Aqueous Phase Continuous		Solvent Phase Continuous	
	Flow Rate of Solvent Phase cc/cm ² /hr	H.E.T.S. (cm)	Flow Rate of Solvent Phase cc/cm ² /hr	H.E.T.S. (cm)
1/16" Glass Helices	67	121	74	48
1/8" Glass Helices	78	71	140	107
			74	70

FIG 4

RELATION OF FLOW RATE TO H.E.T.S. FOR SCRUBBING THORIUM FROM SOLVENT

LEGEND:

- SOLID LINES AQUEOUS PHASE CONTINUOUS
- DOTTED LINES SOLVENT PHASE CONTINUOUS
- 1/16" GLASS HELICES PACKING
- 1/8" GLASS HELICES PACKING

SOLVENT COMPOSITION BEFORE SCRUBBING

- DIBUTYL CELLOSOLVE ALMOST 100%
- NITRIC ACID 0.101 N
- THORIUM 312 mg/liter
- URANIUM 312 mg/liter

SCRUB SOLUTION:

- CALCIUM NITRATE 6N
- pH ca. 1.5

RATIO SCRUB SOLUTION TO SOLVENT
BY VOLUME ca. 0.375

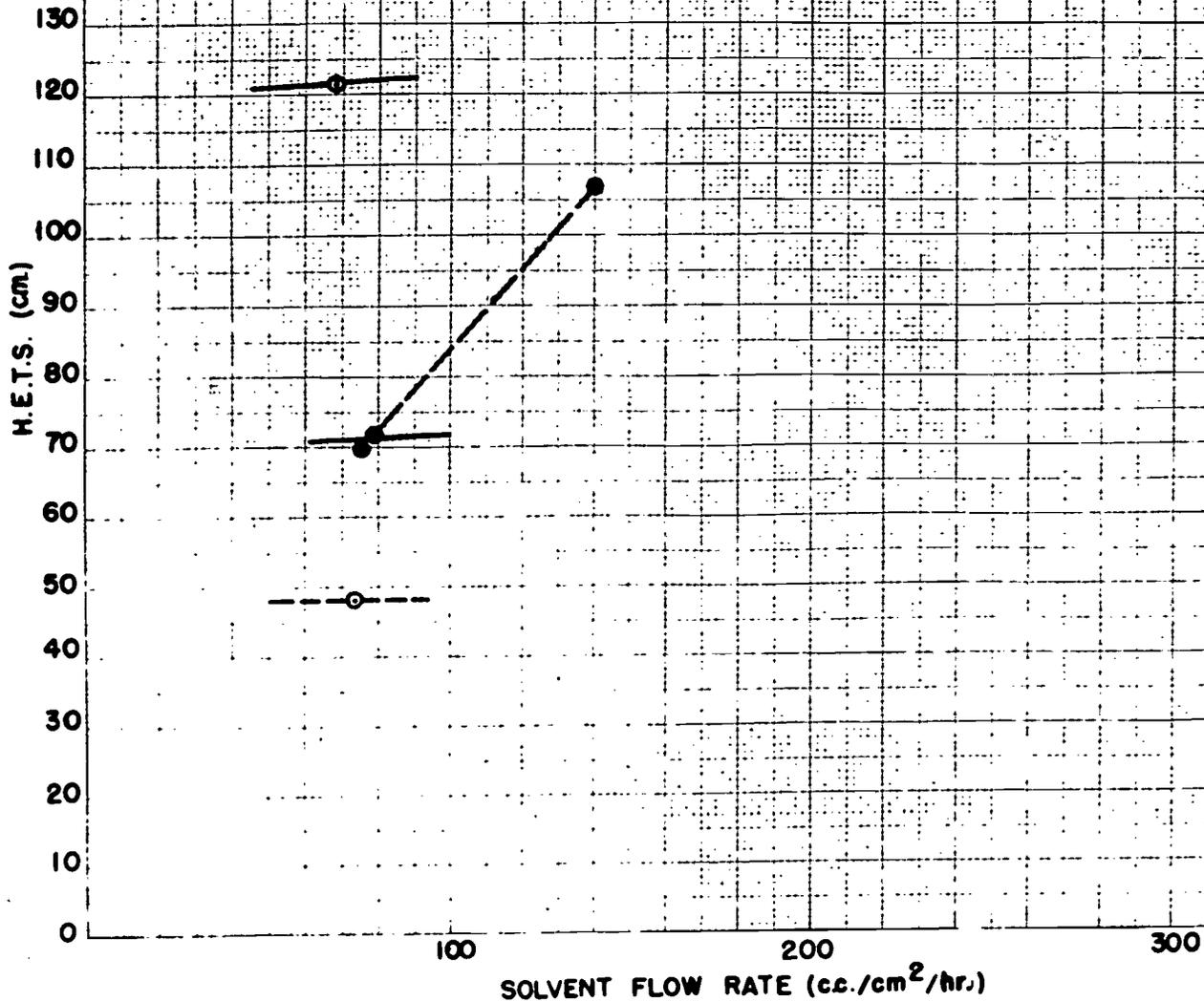
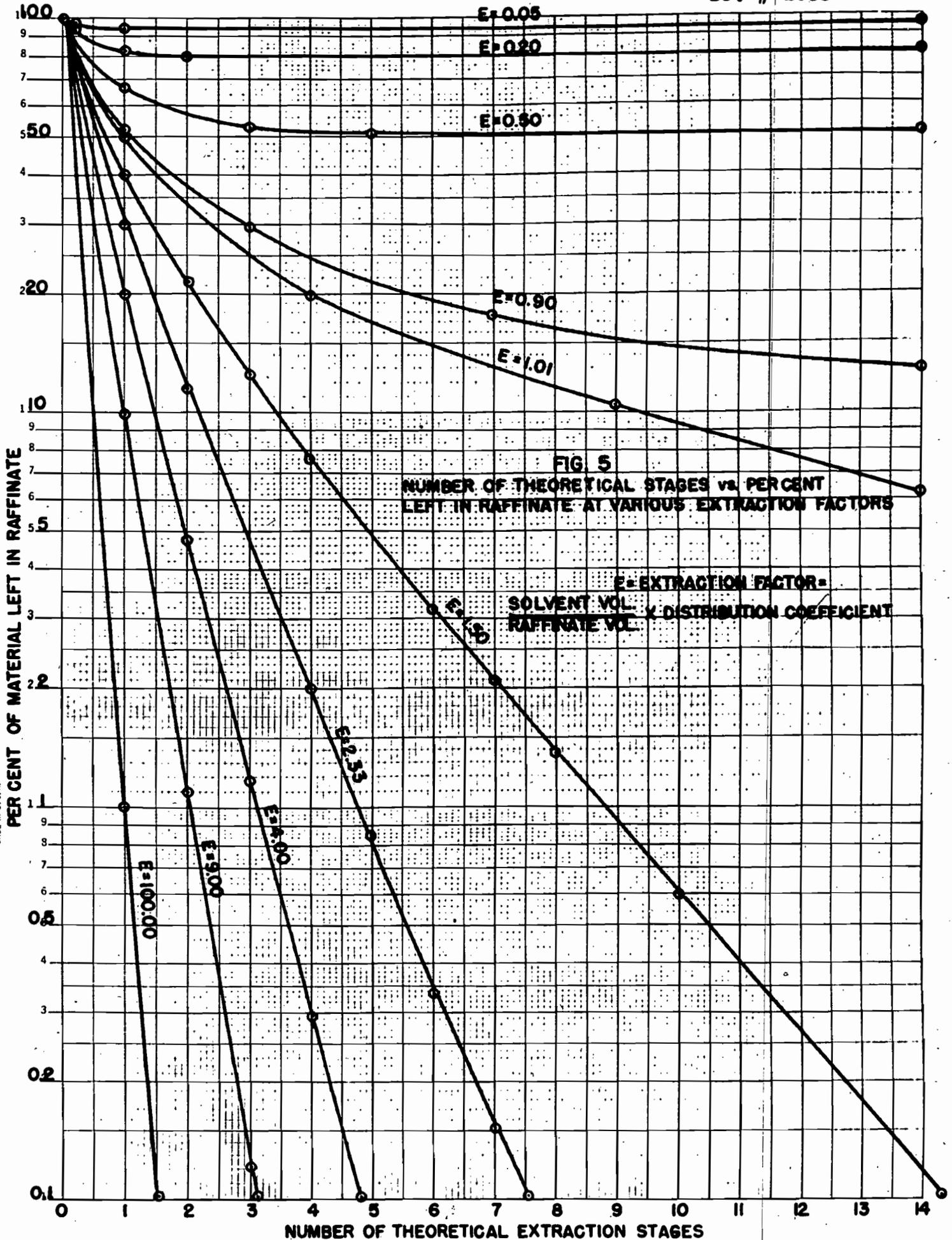


Table XI

Summary of Data for Simultaneous Operation
of Extraction and Scrubbing Sections

Test No.	33	34	35	36
Feed Solution Composition				
Thorium Nitrate	3.1 N	3.1 N	3.1 N	2.36 N
Aluminum Nitrate	1.7 N	1.7 N	1.7 N	1.29 N
Ammonium Nitrate	0.7 N	1.2 N	0.7 N	1.29 N
Calcium Nitrate	None	None	0.9 N	1.415 N
Nitric acid	0.5 N	--	--	--
pH	Below 0	1.7	1.8	1.69
Scrub Solution Composition				
Ca(NO ₃) ₂	8 N	8 N	8 N	8 N
pH	ca. 1.5	ca. 1.5	ca. 1.5	3.0
Average Flow Rate Aqueous Phase (cc/cm²/hr)				
	66	76	61	61
Ratio Scrub to Feed				
	0.58	0.55	0.64	0.81
Thorium Content of Extract Before Scrubbing (mg/liter)				
	ca. 300	ca. 115	ca. 70	ca. 86
Distribution Coefficient for Uranium Extraction				
	2.03	1.67	1.46	1.51
Distribution Coefficient for Uranium for Scrubbing <u>Aqueous</u> Organic				
	0.14	0.19	0.16	0.23
Distribution Coefficient for Thorium for Scrubbing <u>Aqueous</u> Organic				
	85	280	230	480
Kind of Packing				
	1/16" Helices	1/16" Helices	1/16" Helices	1/16" Helices
H.E.T.S. (cm) for Extraction				
	21	25	19	26
H.E.T.S. (cm) for Scrubbing				
	62*	109*	71	129

*May be lower, since it is uncertain whether equilibrium was reached.



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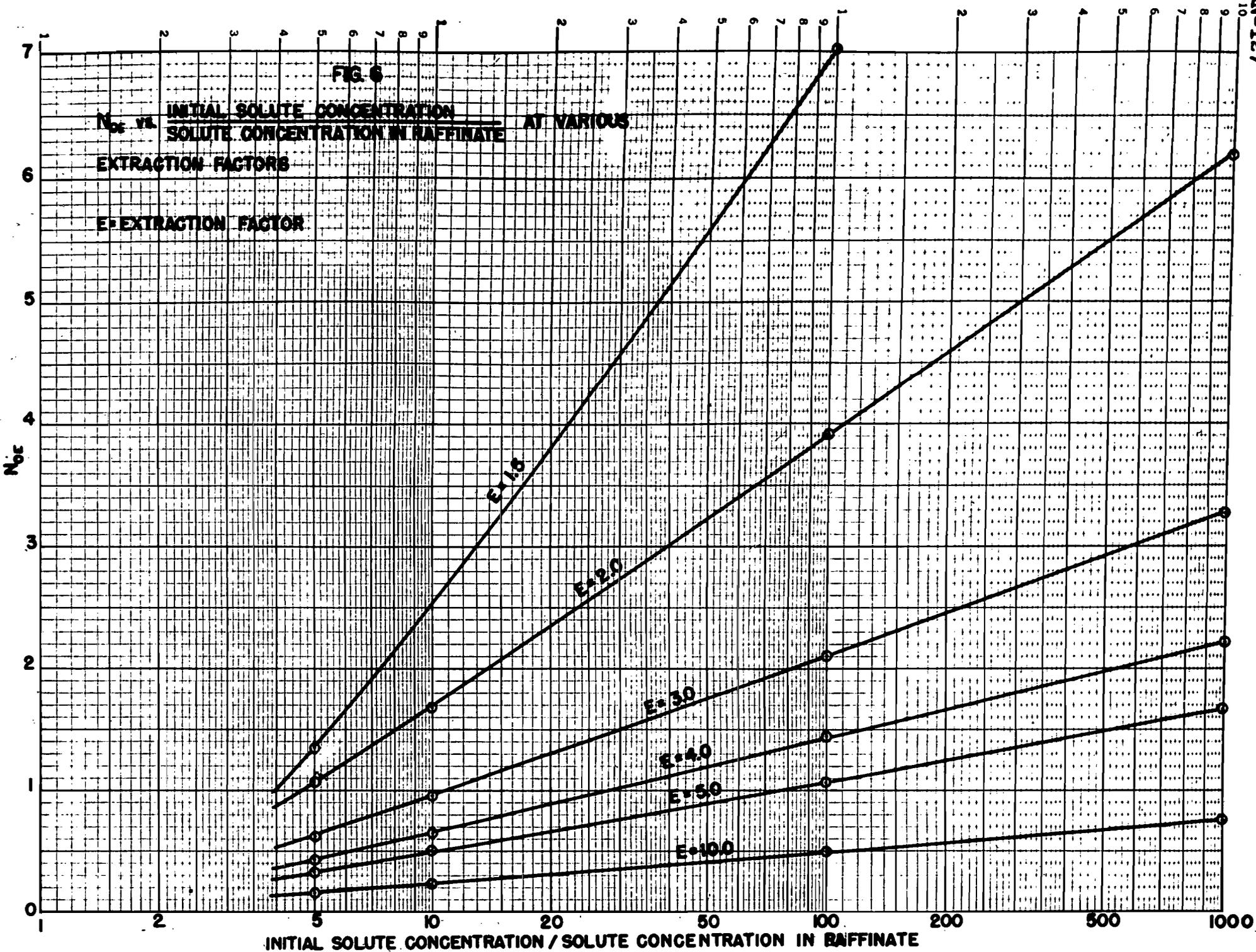


Table XII

Calculated Values for Number of Theoretical Scrubbing Stages
to Separate Uranium and Thorium
to Various Degrees of Purity of the Uranium

Assumed Uranium Distribution Coefficient $\frac{\text{Aqueous}}{\text{Organic}} = 0.2$ in all cases

Assumed Thorium Distribution Coefficient $\frac{\text{Aqueous}}{\text{Organic}}$	85			300		
	4	10	100	4	10	100
<u>Thorium</u> <u>Uranium</u> Ratio in Extract Before Scrubbing						
Number of scrub stages to give 99.% U	1.74	2.01	2.67	1.28	1.47	1.96
Number of scrub stages to give 99.99% U	3.07	3.34	4.00	2.26	2.45	2.94
Number of scrub stages to give 99.9999% U	4.40	4.66	5.34	3.24	3.43	3.92

Table XIII

Calculated Values for the Number of HTU_{OE} Units
to Separate Uranium and Thorium
to Various Degrees of Purity of the Uranium

Assumed Uranium Distribution Coefficient $\frac{\text{Aqueous}}{\text{Organic}} = 0.2$ in all cases

Assumed Thorium Distribution Coefficient $\frac{\text{Aqueous}}{\text{Organic}}$	85			300		
	4	10	100	4	10	100
<u>Thorium</u> <u>Uranium</u> Ratio in Extract Before Scrubbing						
N _{OE} to give 99.0% U	0.198	0.228	0.303	0.0542	0.062	0.063
N _{OE} to give 99.99% U	0.349	0.379	0.454	0.0957	0.104	0.125
N _{OE} to give 99.9999% U	0.500	0.530	0.606	0.138	0.145	0.166

IX. DESCRIPTION OF PROCESS RECOMMENDED

The entire process for the isolation of U^{233} from thorium "carbonate" slugs which have been irradiated with neutrons comprises five principal steps, viz.,

1. Solution of the slugs in nitric acid to form a solution which is 3.23 N in thorium nitrate, 1.77 N in aluminum nitrate, and 1.00 N in nitric acid.
2. Adsorption of the Pa^{233} and the major portion of fission products on MnO_2 , precipitated in situ, removal of the precipitate, and subsequent adjustment of the pH to 1.7 - 1.8 with ammonia or lime or a combination of the two.
3. Continuous countercurrent extraction of the solution, followed by scrubbing the thorium from the extract with calcium nitrate in an upper section of the column.
4. Separation of the U^{233} from the dibutyl cellosolve extract by any one of several methods such as evaporation, stripping with water or ammonium sulfate solution, or adsorption on alumina or other adsorbent. The latter method is preferred for the pilot plant scale of operation.
5. Final purification by a method depending on the means employed for the fourth step.

This report deals only with the extraction and scrubbing step. The other steps have been or will be described in separate reports.

In principle, the extraction step is very simple. The equipment comprises a packed column with a lower section for extraction and an upper section for scrubbing, together with auxiliary equipment for feeding the feed and scrub solutions and the dibutyl cellosolve at controlled rates. There must also be a jackleg or a controlled pressure tank for discharge of the raffinate from the bottom of the column and an outlet at the top of the column for discharge of the extract.

During operation of the column, the dibutyl cellosolve is pumped in at the bottom and rises to the top where it is discharged. The feed solution is introduced in the middle of the column where it mixes with the spent scrub solution and then descends to the bottom and is discharged as raffinate. The scrub solution is added at the top of the column. As the dibutyl cellosolve rises through the lower section, it extracts the uranium from the mixture of feed solution and scrub solution. Also it extracts some thorium. After passing through the lower section, the dibutyl cellosolve continues its ascent and contacts the scrub solution in the upper section of the column. The scrub solution removes substantially all of the thorium from the extract and returns

it to the lower section. At the same time, the scrub solution removes a minor portion of the uranium, returning it to the lower section also. Thus the effective uranium content of the aqueous phase entering the extraction section is always somewhat greater than that corresponding to a mixture of feed solution and scrub solution in the proportions that are fed to the column. The yield must be based on the uranium content of the feed, but calculations to determine the number of stages and the height of each stage must be based on the effective uranium concentration which includes that refluxed by the scrub solution.

As for the design of the column, there are many possibilities depending on the desired percent extraction and the degree of purity of the final product and also on the permissible head room, the method of separating the uranium from the solvent, and the composition of the solutions employed.

On the assumptions that 99% of the uranium is to be extracted and that the product shall be 99% purity (basis uranium and thorium), the following column designs, as shown in Table XIV, would give the desired results for the solution compositions shown.

Table XIV
Column Designs to Give 99% Extraction and 99% Purity of Product

Feed Solution Composition:			
Thorium Nitrate	3.1 N	3.1 N	2.36 N
Aluminum Nitrate	1.7 N	1.7 N	1.29 N
Ammonium Nitrate	0.7 N	0.7 N	1.29 N
Calcium Nitrate	--	--	1.42 N
HNO ₃	0.5 N	0.5 N	--
pH	Below 0	Below 0	1.69
Scrub Solution Composition:			
Calcium Nitrate	8 N	8 N	8 N
pH	ca. 1.5	ca. 1.5	3.0
Kind of Packing	1/16" Glass Helices	1/8" Glass Helices	1/16" Glass helices
Continuous Phase	Solvent	Aqueous	Solvent
Required Stages:			
Extraction	5.64	5.64	8.88
Scrubbing	2.22	2.22	1.235
Height of Sections:			
Extraction	46.9 inches	99.0 inches	90.5 inches
Scrubbing	53.8 inches	62.4 inches	62.5 inches
Total Packed height	8.4 ft.	13.5 ft.	12.8 ft.
Flow Rates (cc/cm²/hr):			
Feed Solution	41.4	38.6	38.4
Scrub Solution	24.9	23.1	23.0
Dibutyl Cellosolve	66.3	61.7	61.4

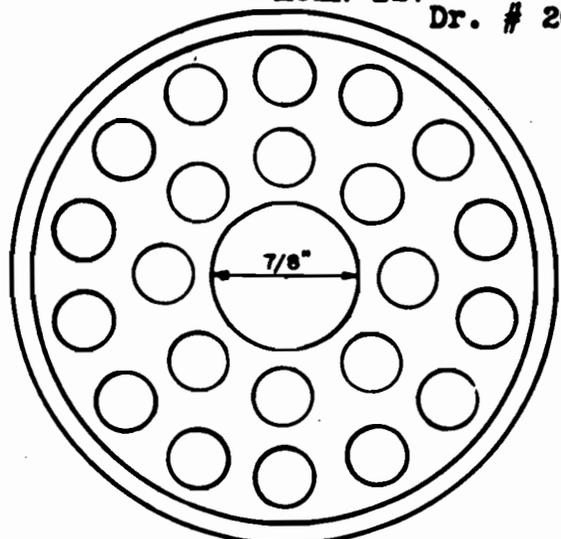
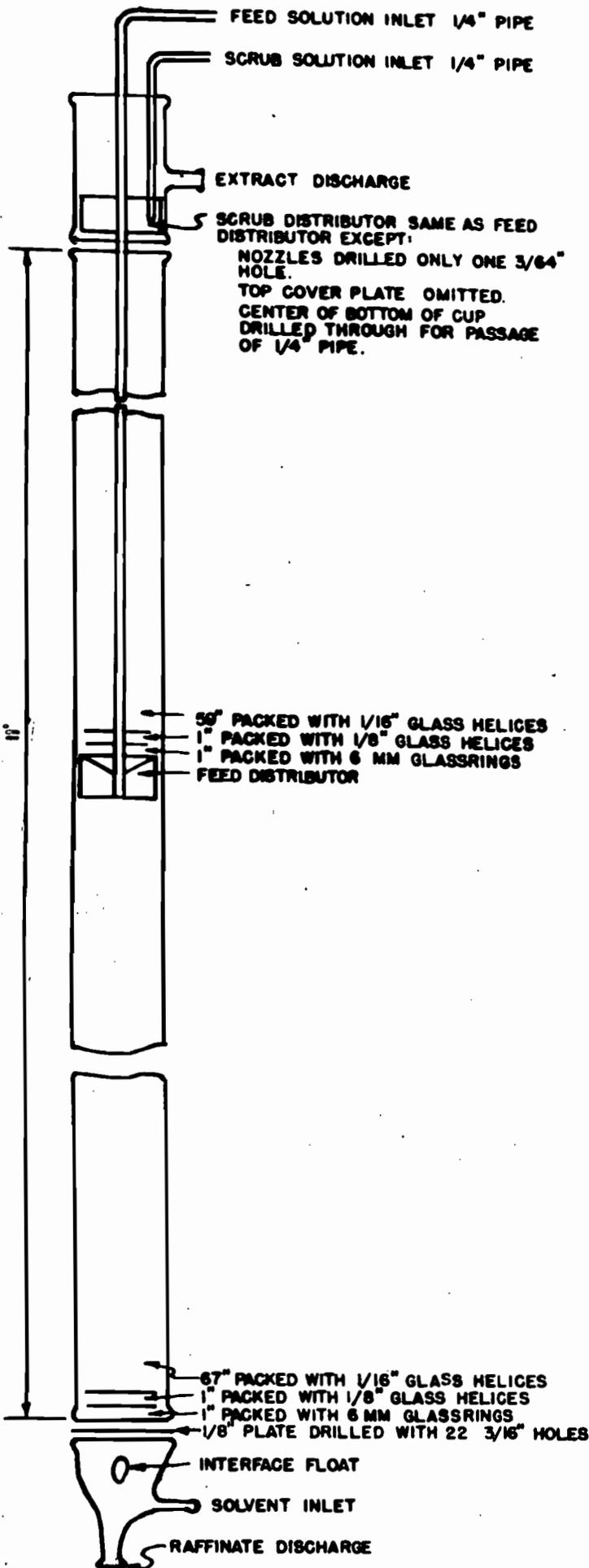
Proposed Column for Pilot Plant Installation

Since lack of head room in the cell where the operation is to be carried out imposes a limitation on the height of the pilot plant column, it is necessary to design this column to fit the cell rather than to fit the operation. The head room is adequate to give well over 99% extraction and well over 99% purity of product for feed solutions at below zero pH as originally contemplated. Unfortunately, such acid solutions give acid extracts which interfere with adsorption of the uranium on alumina in the subsequent step, and if the alumina adsorption process for separation of the uranium from the solvent is to be used, pH adjustment of the feed is necessary. Adjusted solutions, of the compositions tested to date, will require a greater column height to give the same percent extraction. The available head room does not permit 99% extraction and 99% product purity with adjusted solution.

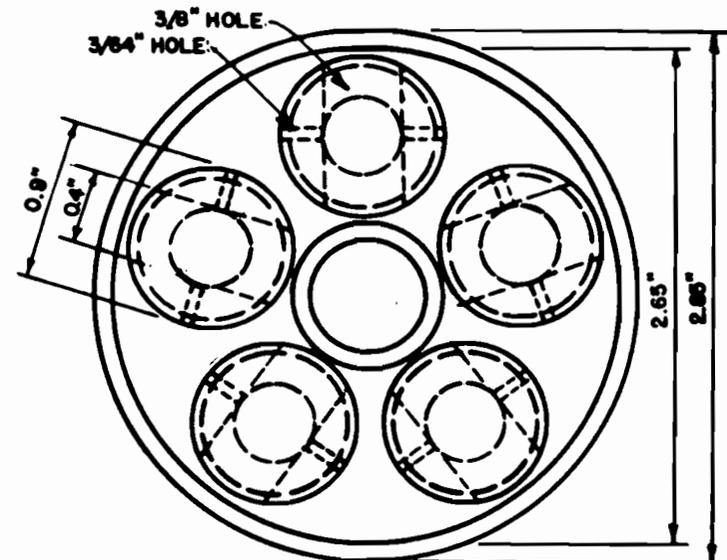
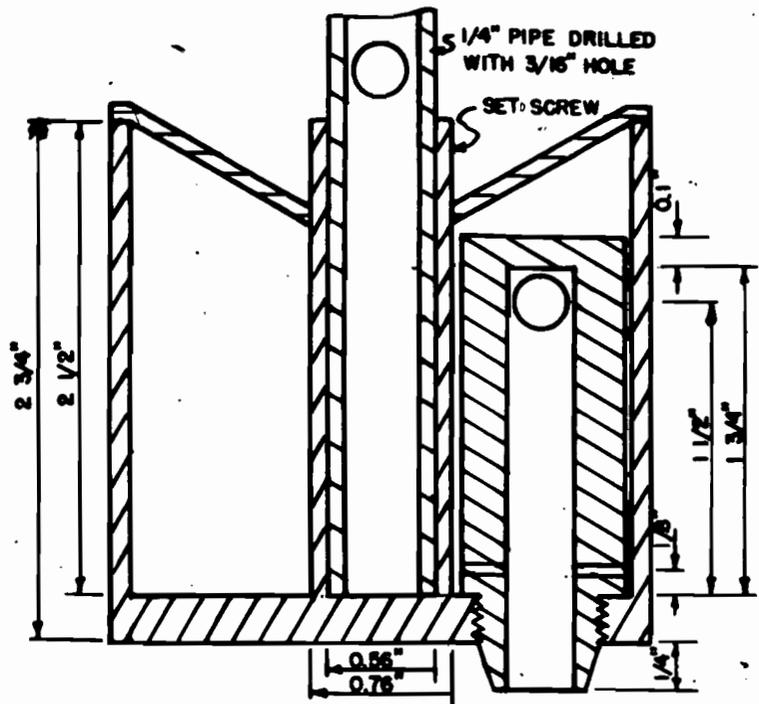
The proposed column for the pilot plant will be made of 3 inch Pyrex glass pipe. The main section will be eleven feet in height and will consist of an eight foot piece and a three foot piece clamped together. At the bottom there will be a 3" x 1" x 1" T for the solvent inlet and the raffinate discharge. At the top there will be a 3" x 3" x 1" T for discharge of the solvent. Connections to these T's will be by gasketed stainless steel flanges. The raffinate will discharge through an adjustable height jackleg constructed of stainless steel and Tygon tubing. The feed solutions and scrub solutions will be introduced through 1/4" stainless steel pipe which enter the open top of the column and extend downward to the desired position where they discharge into stainless steel distributors. The column will be packed with 1/16" glass helices in two sections. The height of the extraction section is to be 68" and the height of the scrub section is to be 60". A sketch of the column is shown in Figure VII. Its expected performance for two types of feed solution is shown in Table XV.

Table XV
Expected Performance of Pilot Plant Column

Composition of Feed Solution:		
Thorium Nitrate	3.1 N	2.36 N
Aluminum Nitrate	1.7 N	1.29 N
Ammonium Nitrate	0.7 N	1.29 N
Calcium Nitrate	--	1.41 N
HNO ₃	0.5 N	--
pH	Below 0	1.69
Composition of Scrub Solution:		
Calcium Nitrate	8.0 N	8 N
pH	ca. 1.5	3.0
Continuous Phase	Solvent	Solvent
Flow Rates (Total for Column, cc/hr)		
Feed Solution	1690	1755
Scrub Solution	1137	1050
Dibutyl Cellosolve	3027	2855



COVER AND PACKING SUPPORT



COLUMN ASSEMBLY
1" = 5"

FIGURE VII

FEED DISTRIBUTOR
1" = 1"

Extraction Stages	8.20	6.66
Scrub Stages	2.48	1.19
Percent Extraction	99.83	97.47
Purity of Product (Basis U and Th)	99.69	96.71

X. DISCUSSION OF THE WORK

This investigation has demonstrated that continuous countercurrent extraction in a packed column is a practical method for separation and purification of U^{233} . Sufficient information is now available to construct a pilot plant. However, the pilot plant which can be designed on the basis of the present information and available facilities has two disadvantages. The most serious of these is that the lack of sufficient head room makes it necessary to operate with the solvent phase continuous. Such a method will require extremely careful control of the interface height, since if the interface dropped too low, a large part of the column contents would immediately "drop out" through the raffinate discharge.

The second disadvantage of the pilot plant column is that fine packing will require almost perfect clarity of solutions if continued operation is to be maintained.

The pilot plant column which is planned will demonstrate extraction as a process and will give information for a full scale column based on the same kind of packing and the same method of operation. It will also give information on the effect of radiation on the solvent and on the decontamination from radioactive fission products. It will not give information for the design of a column with larger packing and designed for operation with the aqueous phase continuous. Such a column would require more height, but its advantages would more than compensate for the increased height. For ultimate large scale operation, there seem to be no valid reasons for any unnatural restrictions on column heights for this operation. This process is subject to the same principles that would apply to the design of columns for other extraction process, with one added provision, i.e., shielding against radiation. One attractive method for this shielding is to sink the column in the ground. Such an installation might consist of an outer stainless steel cylindrical vessel with a suspended pump at the bottom to serve as a safeguard against possible leakage of the column, and an inner stainless steel cylindrical vessel to serve as the column proper. Tubes introduced through the top of the column might serve as inlet and outlet connections, thus decreasing the possibility of leakage from connections on the sides of the column.

XI. RECOMMENDATIONS FOR FUTURE WORK

Plans have already been formulated for future work on several aspects of the problem. These include:

- A. Pilot plant work on the three inch column described in this report. This will give a demonstration on a larger scale and will give data on decontamination from fission products and on the effect of radiation on the solvent.
- B. Laboratory extraction tests on solutions made from thorium metal slugs from which the aluminum jacket has been dissolved with sodium hydroxide solution.
- C. Laboratory batch extraction tests on varied solution compositions in an effort to obtain higher distribution coefficients with adjusted pH solutions. The more promising of these compositions will be tested in the laboratory column.

This work will include a study of other scrubbing solutions and salting agents. Work already in progress on this phase of the problem has indicated that it will be possible to obtain a distribution coefficient of 5.0 or more by using a feed solution containing 3.33 N thorium nitrate, 3.00 N aluminum nitrate, and 0.67 N nitric acid in combination with a scrub solution of 6 N aluminum nitrate which has been adjusted with lime to a pH of 1.3. It is quite possible that use of this solution will permit operation with the aqueous phase continuous and substitution of 1/8" stainless steel helices for the 1/16" glass helices in the pilot plant column.

- D. Laboratory tests on the measurement of the h.E.T.S. of small stainless steel packing.

In addition to the above, before final design of a large scale unit, tests should be made to measure the H.E.T.S. and HTU of larger packing with the aqueous phase continuous for the more promising solution compositions.

Time might also be profitably spent in an effort to find an adsorbent which could be regenerated in place and which would not contaminate the uranium with any other metallic impurity when it was leached with an acid solution of the solvent. Activated carbon and silica gel may have possibilities along this line.

For ultimate large scale operation, water stripping should be given serious consideration. It should be possible to obtain a high volume reduction, together with complete stripping, by using a series of countercurrent water stripping stages with recirculation of the major portion of the water in each stage, permitting only a small fraction of the water discharged from each stage to pass on to the next stage.

XII. ACKNOWLEDGMENT

The workers on this problem are greatly indebted to Messrs. Ward M. Byerly, E. J. Frederick, J. R. Noble, P. F. Thomason, and D. Weinberger

for their assistance on the analytical phases of the work. This assistance included not only a great number of analytical determinations but also revision of the uranium method and development of a completely new thorium method which is suitable for the determination of thorium in quantities as low as 0.1 milligram per liter of extract and possibly even lower.

