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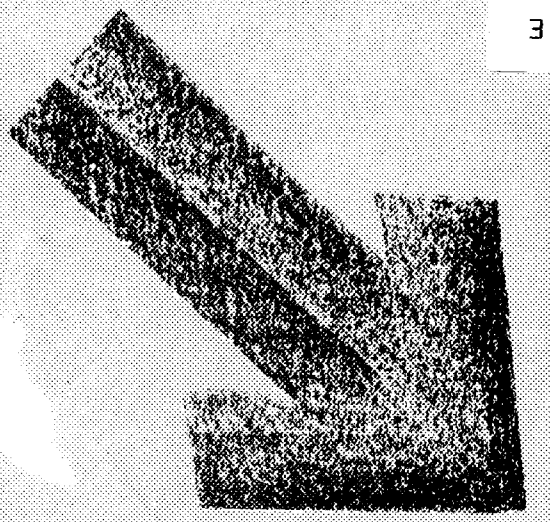

ORNL-1367 (Rev.)
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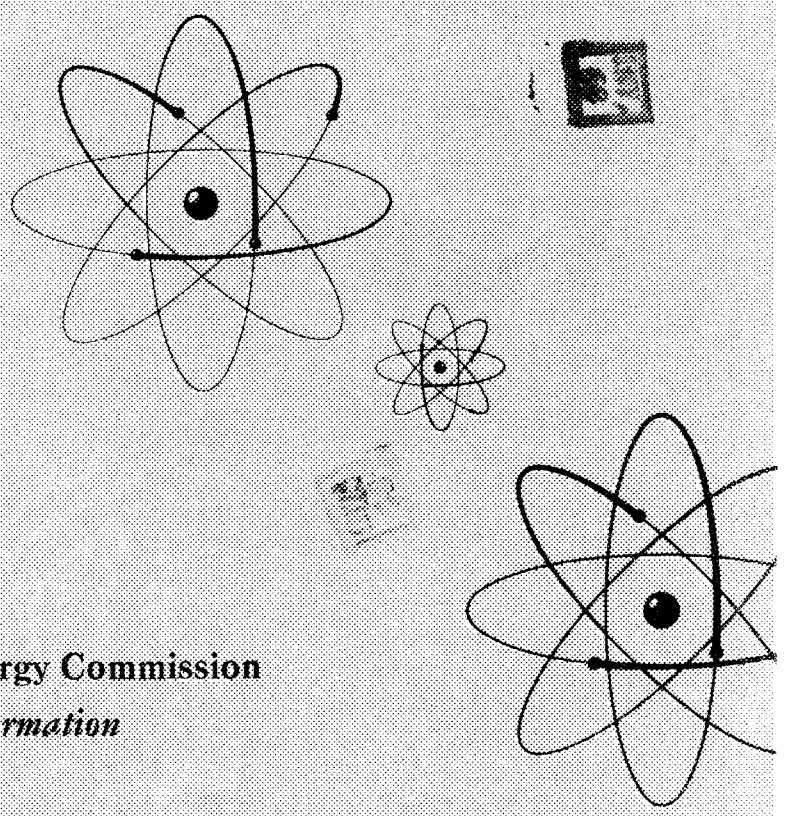

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CHEMISTRY—SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM

ORNL-1367(Rev.)

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

PROGRESS REPORT: LABORATORY DEVELOPMENT OF THE THOREX PROCESS

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0.0 Abstract

This progress report presents data and conclusions obtained during preliminary laboratory development of the Thorex process, which was required to separate and decontaminate thorium, uranium-233, and protactinium from irradiated thorium metal. Tentative chemical flowsheets are described.

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1.0 Introduction

The purpose of the laboratory development work presented in this report was to establish chemical conditions required for a plant process which has been designated as the "Thorex process." These conditions would be designed to separate and decontaminate thorium-232, uranium-233, and protactinium-233 from short-cooled neutron-irradiated thorium, i.e.,

$$Th^{232}(\underline{n},\gamma)Th^{232} \xrightarrow[23.5\ m]{\beta^-} Pa^{233} \xrightarrow[27.4\ d]{\beta^-,\gamma} U^{233}(\underline{n},\underline{f}) \longrightarrow F.P.'s$$

The process was needed for the isolation of the fissionable U^{233} isotope for power development, the highly radioactive Pa^{233} for decay to isotopically pure U^{233}, and (2) the natural Th^{232} for re-use as a source in "breeder" type reactors. The scope of the laboratory work included the development of (a) the type of process and approach to the problem, (b) the primary chemistry involved in various steps, and (c) certain chemical and physical data required for unit operation and/or pilot plant demonstrations of the process.

The type of process chosen was basically a solvent-extraction separation involving tributyl phosphate in an inactive diluent, and combining the essential features and knowledge of both the Redox and Purex processes for uranium and plutonium separation. However, the unique problems associated with the handling of the very active Pa^{233} isotope required the additional study and use of (a) other solvents, (b) surface adsorption, and (c) ion exchange.

The prime responsibility of the laboratory group was the evolution of a final Thorex chemical flowsheet which would represent the optimum experience with respect to: (a) a compatible system of chemistry for thorium, uranium, and protactinium separation, (b) the engineering feasibility of the process based on pilot plant experience, and (c) the economic installation and operation of process plants. Consultation in weekly Thorex Committee meetings with representatives of the Unit Operations, Pilot Plant, and Design Sections (Chemical Technology Division) has been important in guiding the progress of flowsheet development. Chemical flowsheets of the Interim-23 process and two alternate approaches to a Thorex process are presented in the Summary of this report.

The assistance of members of the Analytical Chem. and Chem. Divisions in the various phases of this development is gratefully acknowledged. Special thanks are due to L. T. Corbin, G. R. Wilson, W. Laing, R. W. Stoughton, P. Thomason, C. Burros, S. Reynolds, and C. Feldman.

The cooperation and assistance of other members of the Chemical Technology Division are also acknowledged.

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2.0 Summary

Metal dissolving, the usual first consideration in separation processes, has not been studied to date by the laboratory group owing to the adequate treatment of this subject in earlier ORNL work. However, the Unit Operations group, in parallel Thorex studies, has investigated the feasibility of simultaneous dissolving of aluminum jackets and thorium slugs in nitric acid containing F^- and Hg^{++} ions. This procedure, with batch or continuous operation, has appeared to be an integral engineering concept in Thorex process development.

Three solvent-extraction process flowsheets (Figs. 2.0-1, 2, and 3) have been derived from the laboratory development to date: (1) the Interim-23 process, which has already received Unit Operations, Design, and Pilot Plant testing; (2) Thorex process No. 1, which has received testing only in laboratory countercurrent contactors; and (3) Thorex process No. 2, which has progressed only through laboratory study and initial Unit Operations demonstrations.

The Interim-23 process, designed only for U^{233} recovery and decontamination, was based on a 1.5% TBP extraction of U^{233} from a feed prepared by dissolving both the aluminum jackets and thorium slugs in 13 N HNO_3 containing fluoride and mercury catalysts. Silica gel adsorption is used for final protactinium decontamination, and Dowex-50 resin for the U^{233} product concentration and isolation (developed by D. C. Overholt). Pilot Plant results have indicated (a) overall U^{233} losses of less than 0.5%, (b) thorium separation factors of $>10^5$ ($<0.003\%$ Th in the final product), (c) overall β and γ decontamination factors of $10^{5.5}$ through the solvent extraction step, $\sim 10^{7.5}$ through the silica gel step, and $>10^{7.5}$ through the resin concentration step.

The Thorex process No. 1, a tentative approach to thorium-U^{233}-protactinium separation and decontamination, featured the following steps, in order: (1) Pa^{233} extraction in diisobutyl carbinol, (2) U^{233} extraction in 5.0% TBP, and (3) Th^{232} extraction in a 45% TBP—15% benzene—40% Amsco solvent. Although this process appeared potentially adequate from the standpoint of separation and decontamination, certain objectionable engineering and chemical features were evident.

Engineering problems involved the necessity for: (a) operational control of three different solvents; (b) three sets of solvent vessels for storage, pumping, holdup, and chemical treatment; and (c) six first-cycle columns, four of which would be definitely "hot." Chemical problems involved: (d) the incomplete stripping of protactinium from the carbinol; (e) the need for aromatics, e.g., benzene, in the extractant to prevent two-phase organic layers when the TBP was saturated with thorium; (f) incomplete protactinium decontamination in the thorium step owing to its TBP extractability in acidic systems; and (g) the uncertain attainment of equilibrium, or steady state, in the complicated TBP-Th-HNO_3 system.

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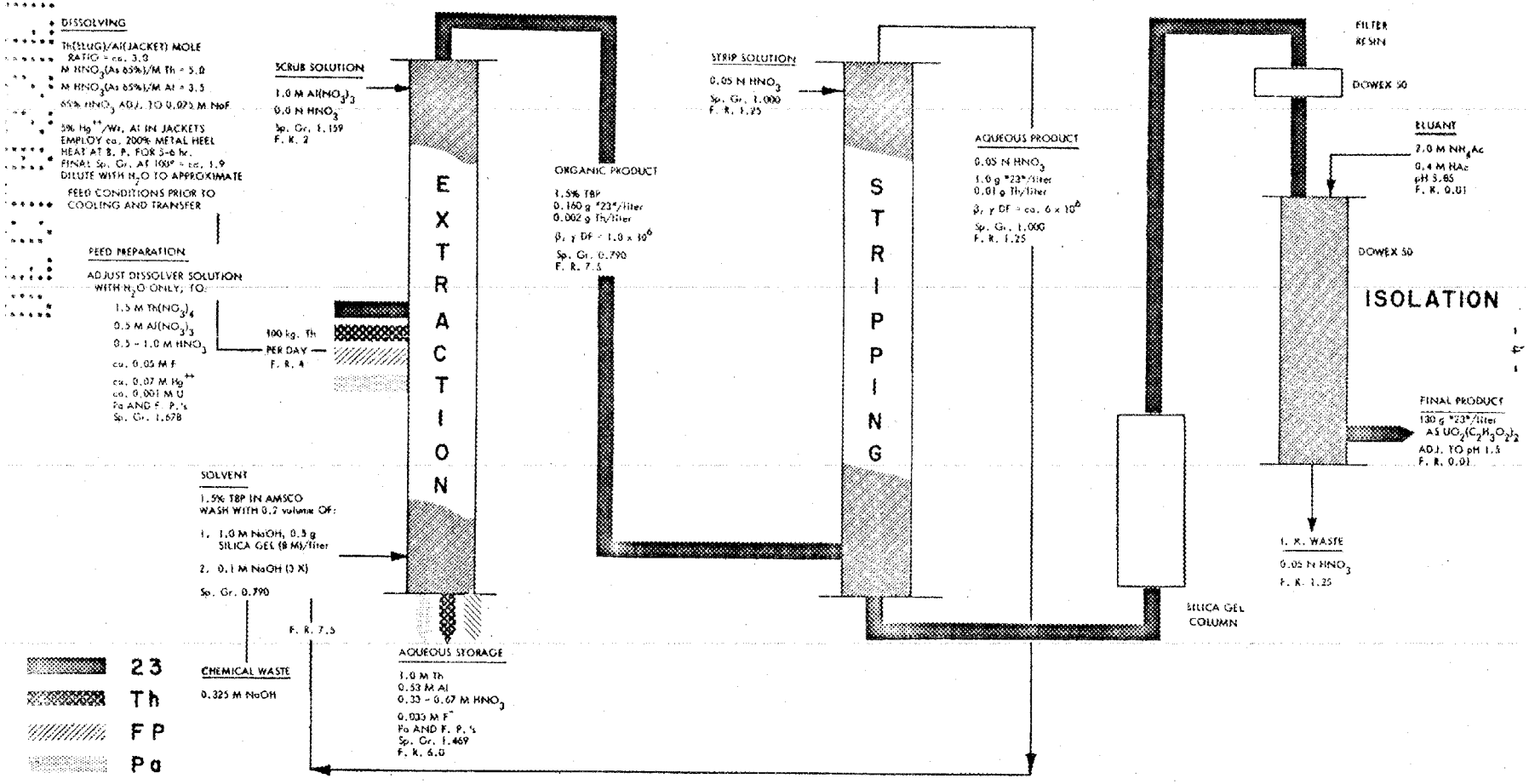
INTERIM 23 FLOWSHEET



TENTATIVE THOREX FLOWSHEET No I

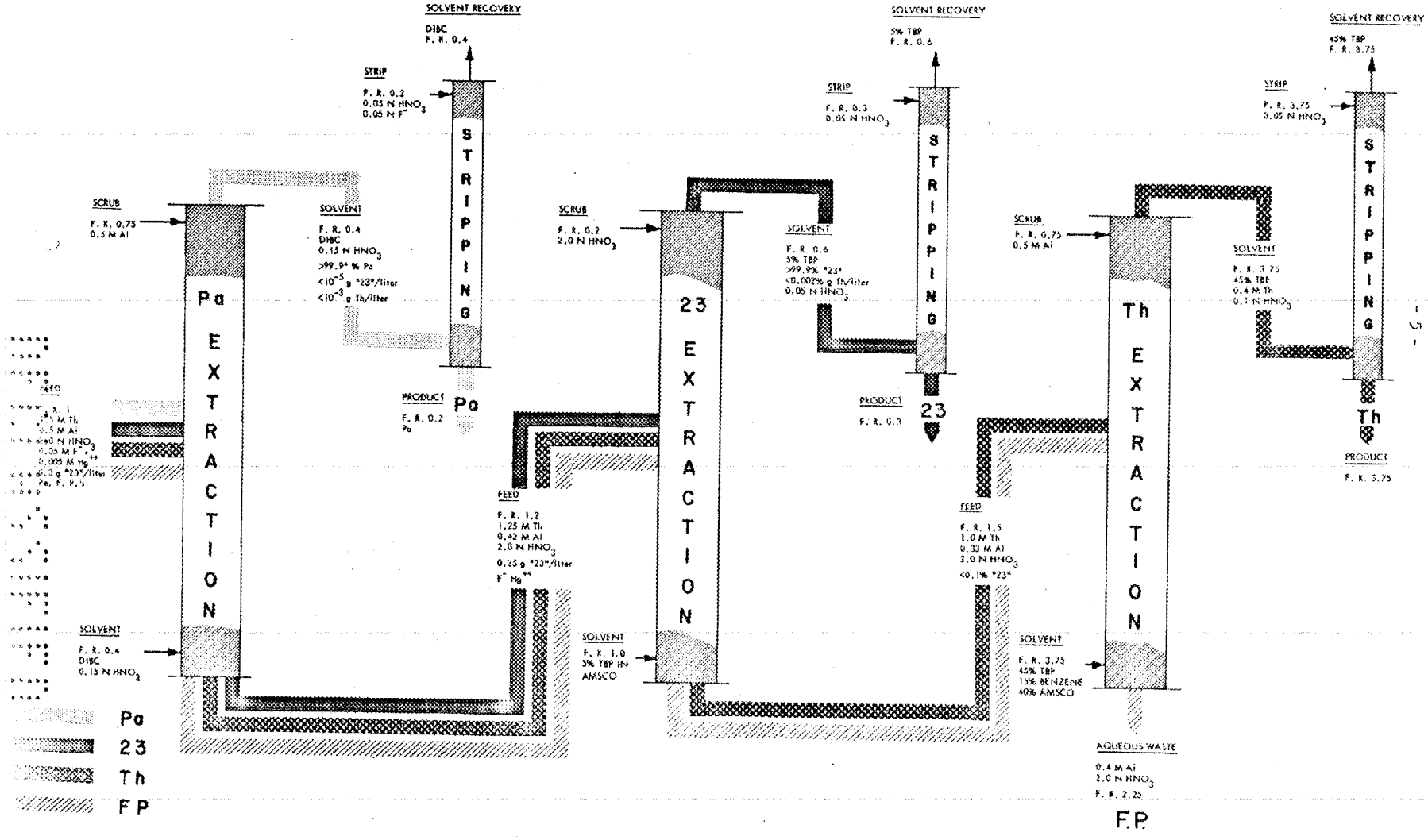
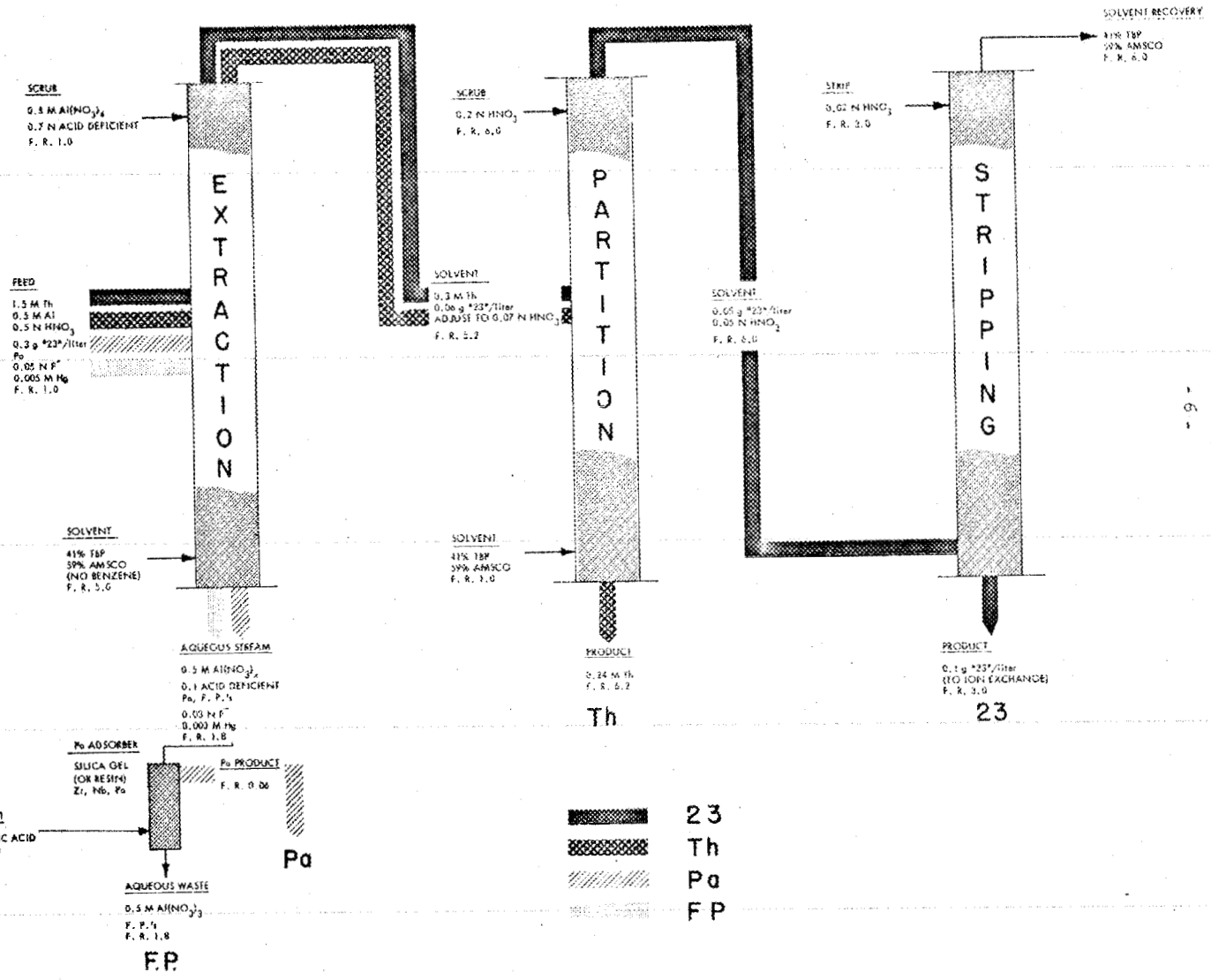


FIGURE 2.0-5

TENTATIVE THOREX FLOWSHEET No 2



Step 1 above provided Pa recovery of $>10^4$, with thorium and U^{233} separation factors of $>10^5$. About 85% of the niobium, 5% of the zirconium, 1% of the ruthenium, and 0.0% of the total rare earth fission products were extracted with the protactinium. Step 2 provided U^{233} losses of <0.1%, thorium-U^{233} separation factor of $>10^4$, and a β-γ DF of $>10^5$. Step 3 was not proved satisfactory with respect either to β-γ decontamination or to steady-state operation. Laboratory work on this flowsheet has been discontinued at the present.

Thorex process No. 2, the favored process on the basis of engineering feasibility, made use of a single solvent and the following successive steps: (1) thorium and U^{233} extraction and separation from protactinium and fission products by use of concentrated TBP (41 to 55%), (1a) protactinium adsorption on silica gel, (2) thorium partition from U^{233} by preferential stripping, using dilute HNO_3, and (3) U^{233} stripping in very dilute nitric acid.

A drastic change in the chemical behavior of protactinium was a requisite in this process. Protactinium, which will normally contribute more than 90% of the gross β activity in Thorex feeds, was observed to be more than 90% extractable in the acidic thorium-TBP systems, as illustrated by the third step in Thorex process No. 1. A method for converting protactinium to an inextractable species was thus required to allow an initial step for separating thorium and U^{233} from protactinium and fission products. Such an approach was naturally desirable, if not mandatory, to permit (a) a needed reduction in the number of hot columns and (b) the use of a single plant solvent. Since laboratory studies of protactinium behavior had indicated an ionic-polymeric equilibrium which was subject to rapid disproportionation with changing pH, an acid-deficient system, similar to that utilized in the ORNL Redox process, was chosen to shift this equilibrium toward the polymer species. The desired effect of decreased extractability was realized.

Extraction conditions for step 1 were thus established to maintain: (a) a highly acid-deficient aluminum nitrate scrub section to hold protactinium extraction factors (O/A) below 1.0; (b) a slightly acid-deficient extraction section to limit protactinium and fission product extractability and prevent thorium hydroxide precipitation or losses; (c) sufficient aluminum nitrate salt strength throughout the system to maintain thorium extractability; and (d) appropriate flow ratios and solvent capacity to prevent, without benzene addition, a two-phase organic separation. Step 1a required no aqueous feed adjustment, and the silica gel bed area and capacity were governed by process flow rates. Step 2 mainly required the proper adjustment of flow ratios and strip solution acidity to remove thorium and yet maintain U^{233} extraction in the organic phase. Step 3 required principally a flow ratio adjustment of the solvent and a very dilute nitric acid strip solution.

Step 1 was demonstrated to provide an easily maintained steady state, thorium and/or U^{233} losses of less than 0.1%, gross β D.F.'s greater than 10^4,

and protactinium D.F.'s of 10^5. Step 1a permitted 99% protactinium recovery by adsorption. Step 2 allowed a thorium-U^{233} separation factor of greater than 10^4, and any protactinium extracted in Step 1 was observed to follow the thorium stream, so that a protactinium D.F. of greater than 50 for the U^{233} stream was obtained. (Th^{234} activity in short-cooled Hanford-irradiated thorium may limit the β D.F. of the thorium stream to about 10^2.) Step 3 allowed U^{233} losses of less than 0.1%. The degree of the thorium-U^{233} separation in step 2 as well as of U^{233} losses in step 3 appeared to be critically dependent on solvent treatment, i.e., on finite removal of TBP hydrolysis products. Operability of the solvent-extraction steps of this process flowsheet has been demonstrated in 2-in. pulse columns.

Detailed discussions of these three flowsheets, and variations, may be found in Sec. 5.0.

3.0 Principles of the Separations Process (J. E. Savolainen, A. T. Gresky)

The Thorex process is being developed to recover, in high purity, Th^{232} and the products which it forms on neutron irradiation, i.e., U^{233} and Pa^{233}. The predominant nuclear reaction which occurs on neutron irradiation of thorium is $Th^{232}(n,\gamma)Th^{233}$. The Th^{233} decays to U^{233} by the following scheme:

$$Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233}$$

The accompanying nuclear reactions are shown in Fig. 3.0-1.

Some of the isotopes which are produced by the accompanying reactions are Th^{234}, U^{234}, and U^{232}. Mixed fission products which are radioactive are also produced by the neutron fission of U^{233}.

The presence of Th^{234} limits the radioactive decontamination of the irradiated thorium that can be attained by chemical processing. Uranium-232, which will be one of the U^{233} impurities, decays with a relatively short half-life to daughters which emit high-energy α particles. These high-energy α particles can bring about (α,n) reactions with impurities having a low atomic number (Fig. 3.0-2). The neutrons formed by these (α,n) reactions may cause an effective lowering of the critical mass of the U^{233}.

The fission of U^{233} has a yield distribution which varies from that of U^{235} and Pu^{239} (Fig. 3.0-3). The chemical separations problems associated with U^{233} fission products therefore are expected to be somewhat different from those associated with Pu^{234} or U^{235}.

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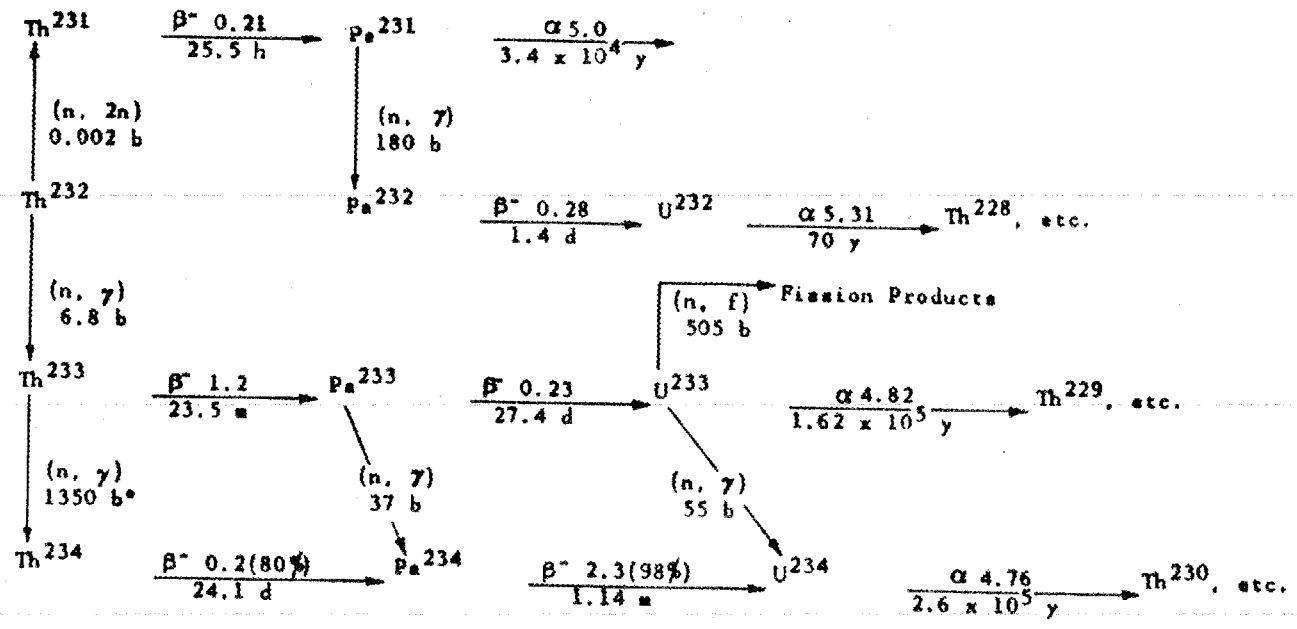
FIGURE 3.0-1

SOME NUCLEAR REACTIONS RESULTING FROM NEUTRON IRRADIATION OF Th^{232}

Energies of radiations are given in MEV's following the type of radiation.
Neutron-capture cross-sections are given in barns with the reactions.



*Reference 3.

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FIGURE 3.0-2

IMPURITY TOLERANCES FOR LIGHT ELEMENTS IN U^{233}: EFFECTS OF U^{232} CONTENT

Data from Ref. 4. Plot indicates relative impurity tolerances of the light elements under various conditions of isotopic purity and storage. Tolerances are based on probabilities of (α, n) reactions with isotopes of these elements.

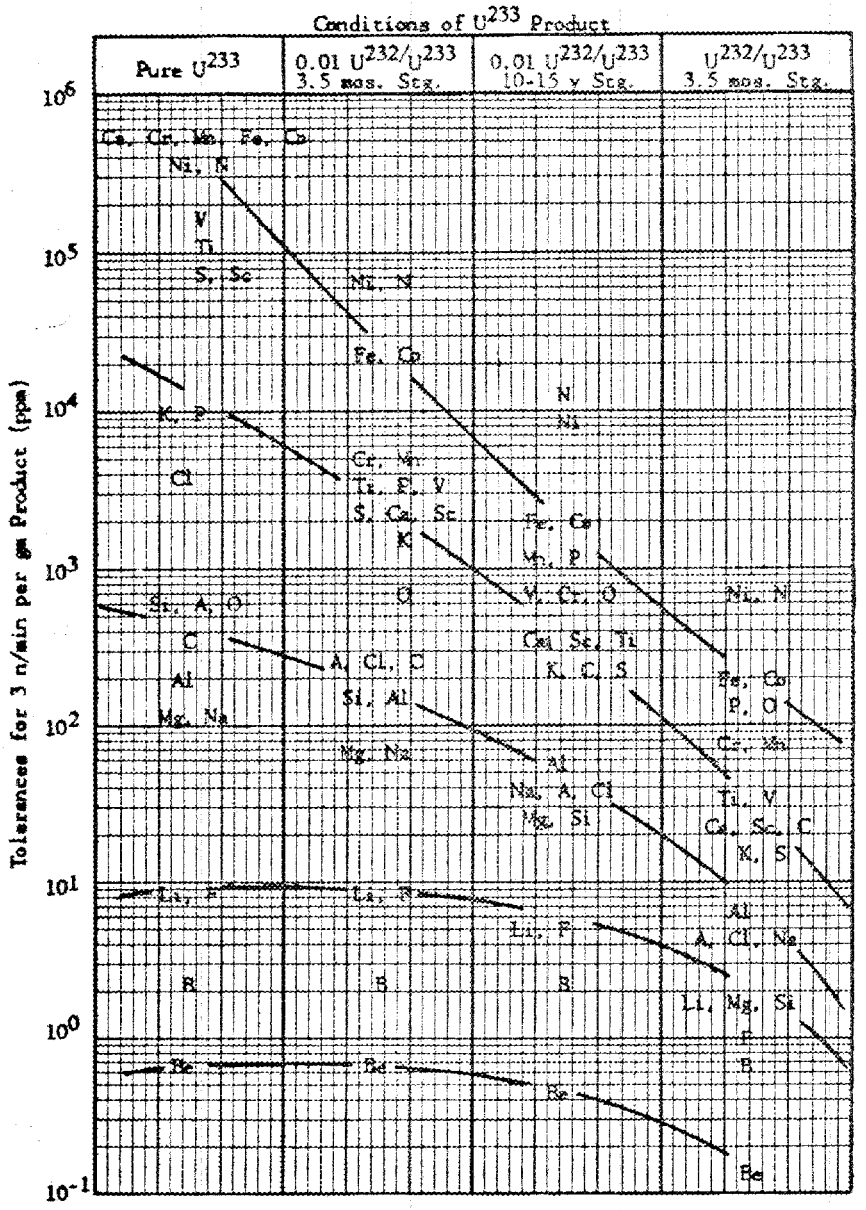

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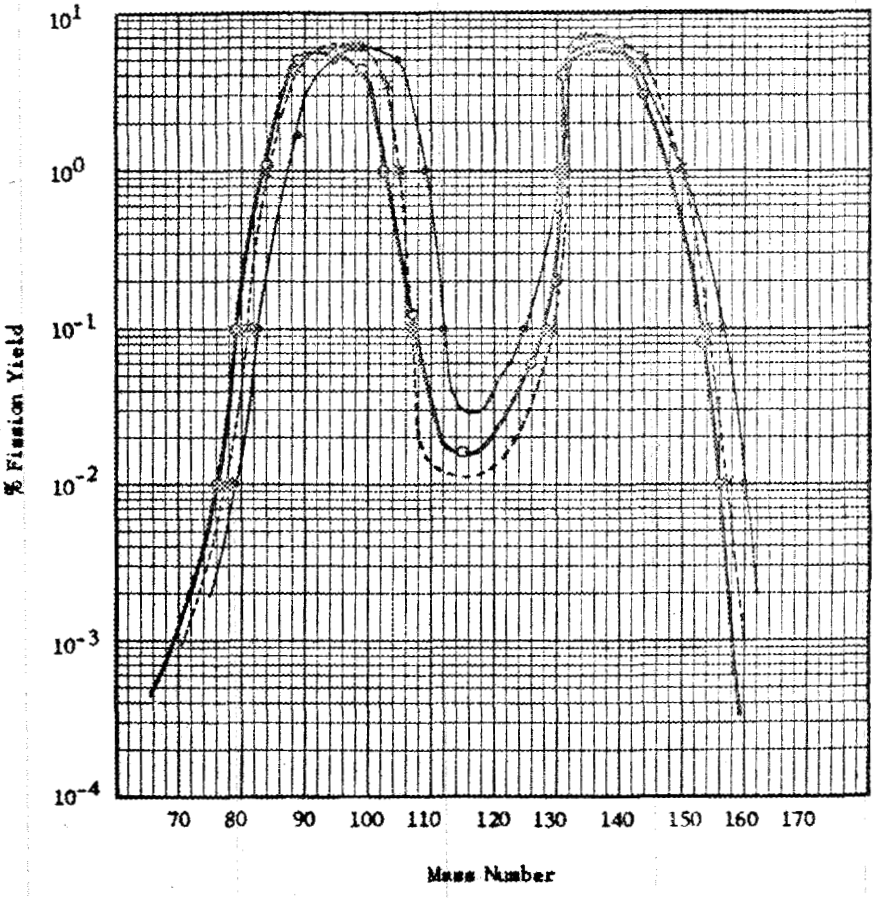
FIGURE 3.0-3

MASS YIELD CURVE FOR U^{233} FISSION
COMPARED WITH OTHER FISSIONABLE MATERIALS

Curves, taken from data in National Nuclear Energy Service, Div. IV, Vol. 9, Books 2 and 3, show fission yield curves of Pu^{239}, U^{235}, and U^{233}. Curves indicate isotopic shift toward lighter mass numbers in the group of light fission fragments. This shift is reflected in variations of the fission product spectrum and limiting contaminants of the Thorex (U^{233}), Purex (Pu^{239}), and 25 (U^{235}) processes.



• Pu^{239}
x U^{235}
o U^{233}

The yield of the total potential of fissionable material, i.e., U^{233} and Pa^{233}, as a function of the irradiation time and the neutron flux density is shown in Fig. 3.0-4. The mass of protactinium present in the neutron-irradiated thorium as a function of the neutron-flux density and the irradiation time is shown in Fig. 3.0-5. Graphic calculation may be made to determine the Pa^{233} level after subsequent cooling by using the slope of the protactinium decay curve. Figure 3.0-6 gives the amount of U^{233} present in irradiated thorium as a function of the flux and time at the end of the irradiation period. The amount of Pa^{233} and U^{233} produced by neutron irradiation of thorium for 100 and 150 days with a flux of 10^{13} n/cm^2/sec is shown in Fig. 3.0-8. The subsequent decay of the Pa^{233} is also indicated. The amount of fission products increases rapidly as a function of the flux and irradiation time (Fig. 3.0-7). A comparison of the curie production and decay of Pa^{233} and La^{140} is shown in Fig. 3.0-9.

The restrictions which are placed on the process are those common to processing high levels of radioactive materials which require biological shielding: (1) The equipment required to be in contact with the radioactivity should have a minimum number of parts which require servicing or replacement after operations start, e.g., valves, agitators, centrifuges, filters, pumps, and transfer jets; (2) after the thorium metal has been dissolved, the radioactive process solutions should not require extensive analyses or treatment before or after entering the process equipment; (3) these radioactive solutions should be confined to a minimum number of the units of the total equipment; (4) the process should be operable continuously over a wide range of conditions with a minimum of externally applied compensations for these variables. It is desirable to have a minimum number of steps in the process. Waste volumes and the size of the equipment should be kept at a minimum by operating at as high concentrations as possible. Separations processes in the order in which they satisfy these requirements are:

1. Solvent extraction
2. Ion exchange or surface adsorption (fixed bed)
3. Electrodeposition
4. Distillation or sublimation
5. Coprecipitation

Solvent extraction is considered to have the greatest advantages for the major separation steps. Ion exchange and adsorption afford means of isolating a constituent with large volume reductions after bulk separation from the other constituents. These separations are more adaptable than precipitations since no filtering medium is required. One drawback, which is not insurmountable, is the batch type operation required at the present time. Electrodeposition, although convenient, does not appear applicable. Distillation can be used with only a few substances and is not applicable. Sublimation of one of the components of a system from the others, such as of protactinium from thorium, requires that the bulk thorium be in the form of a compound such as a halide or

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FIGURE 3.0-4

PRODUCTION OF U^{233} AND Pa^{233} IN IRRADIATED THORIUM AS A FUNCTION OF FLUX AND TIME. Data from ORNL-34[1]

The sum of $Pa^{233} + U^{233}$ represents the total potential fissionable material produced by thermal-neutron irradiation of thorium.

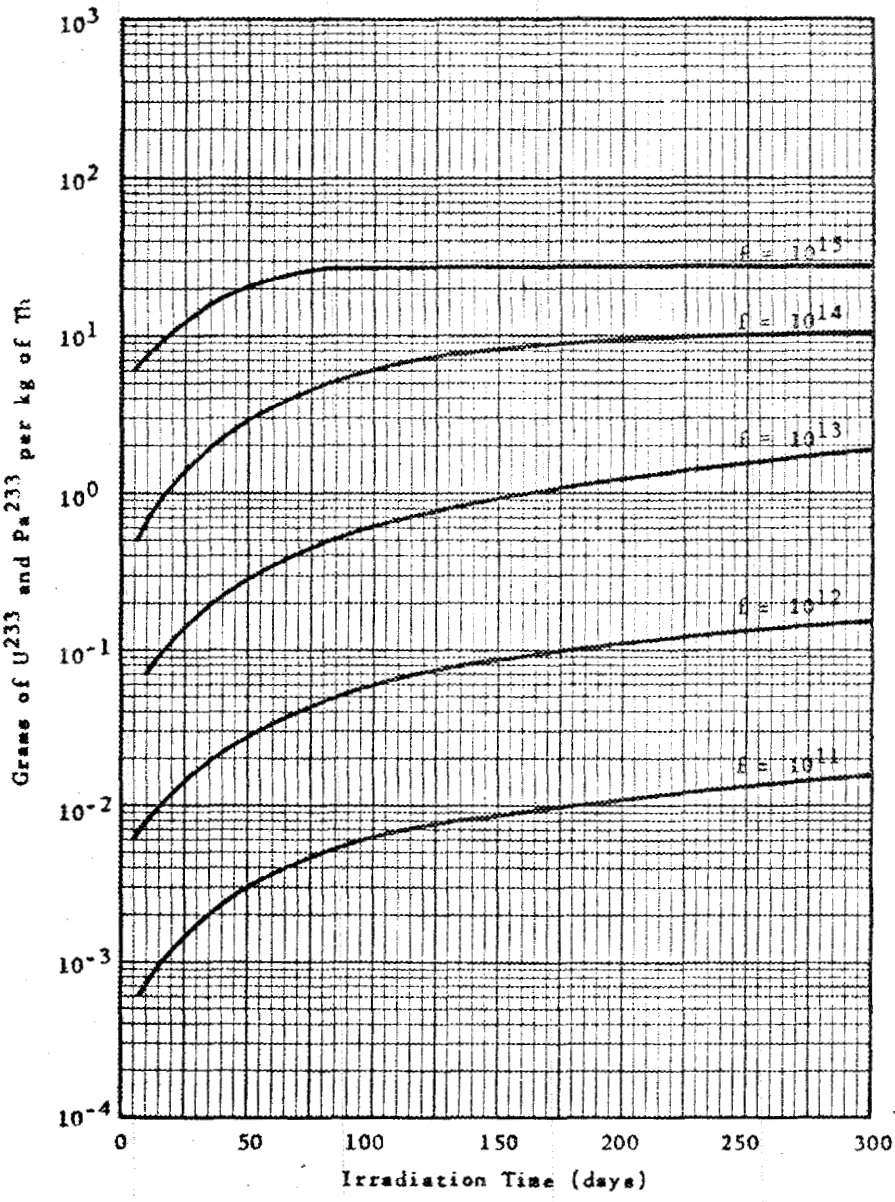

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FIGURE 3.0-5

PRODUCTION OF Pa^{233} IN THORIUM AS A FUNCTION OF FLUX AND TIME. Data from ORNL-34[1]

The slope of the Pa decay line can be used for graphical calculation of Pa^{233} content at various cooling periods after discharge.

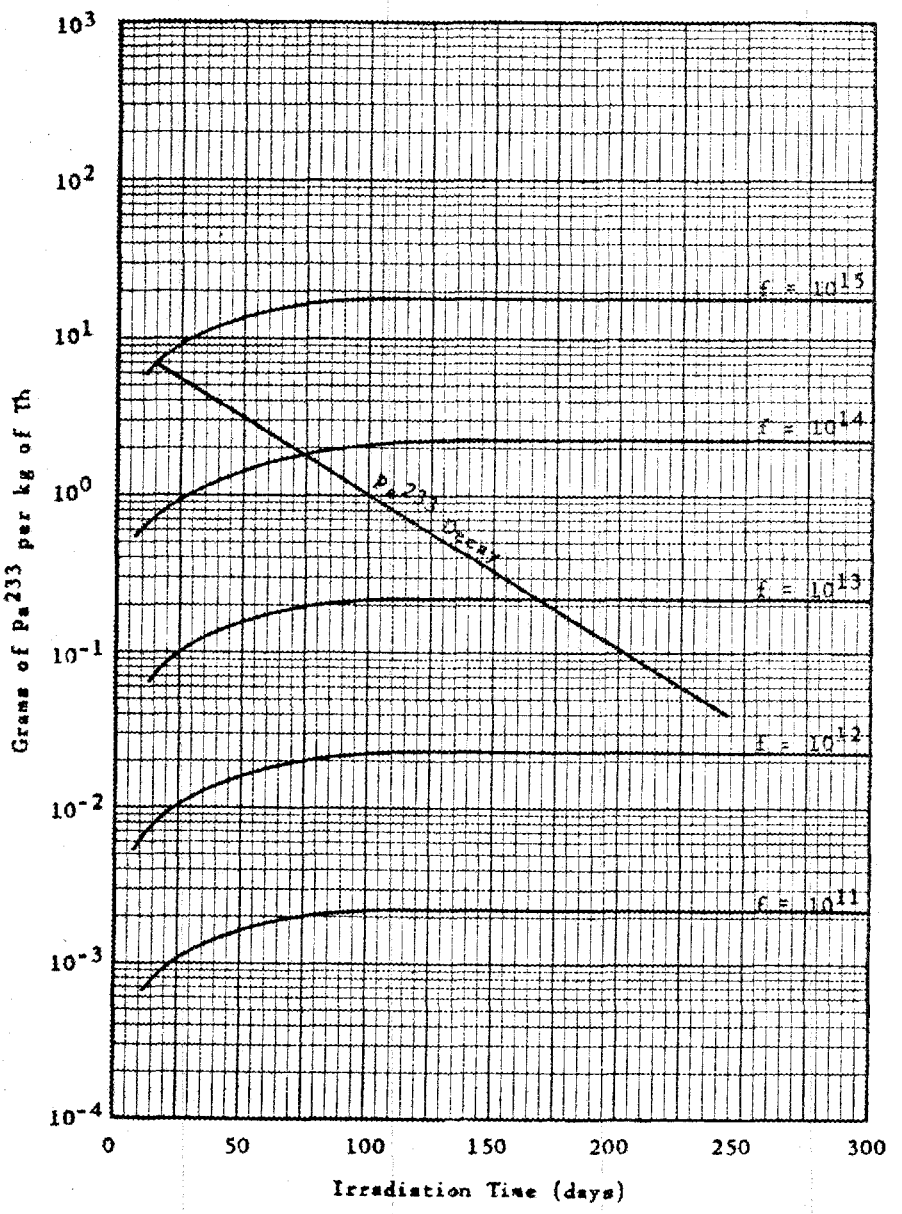

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FIGURE 3.0-6

PRODUCTION OF U^{233} IN THORIUM AS A FUNCTION OF FLUX AND TIME. Data from ORNL-34[1]

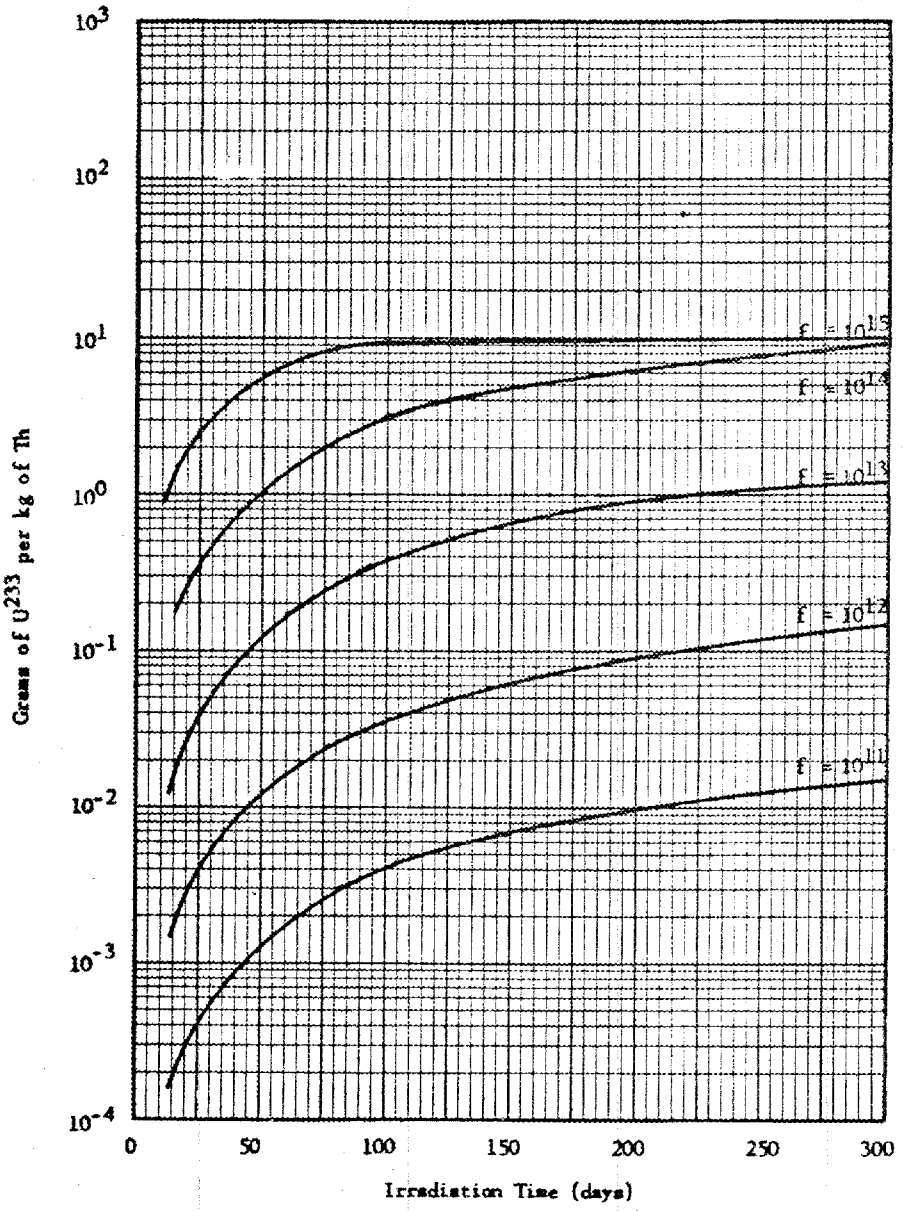

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FIGURE 3.0-7

PRODUCTION OF U^{233} FISSION PRODUCTS IN THORIUM AS A FUNCTION OF FLUX AND TIME. Data from ORNL-34[1]

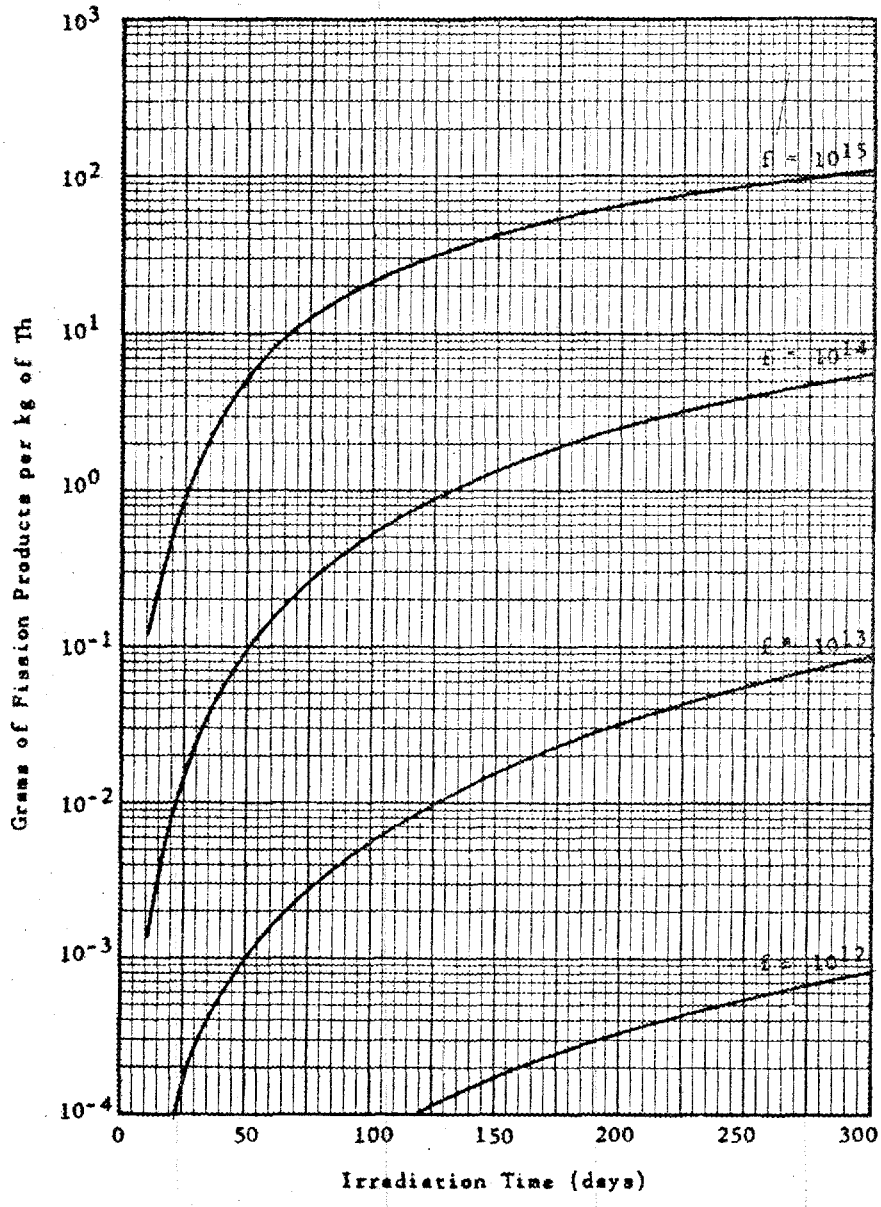

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FIGURE 3.0-8

GROWTH AND DECAY CURVES FOR Pa^{233} AND U^{233} FROM THORIUM IRRADIATION

Curves obtained from ORNL CF-52-1-31[6]

σ Th_c 7 barns
σ 23_f 500 barns
σ 23_t 550 barns
flux 10^{13} neutrons/cm^2/sec

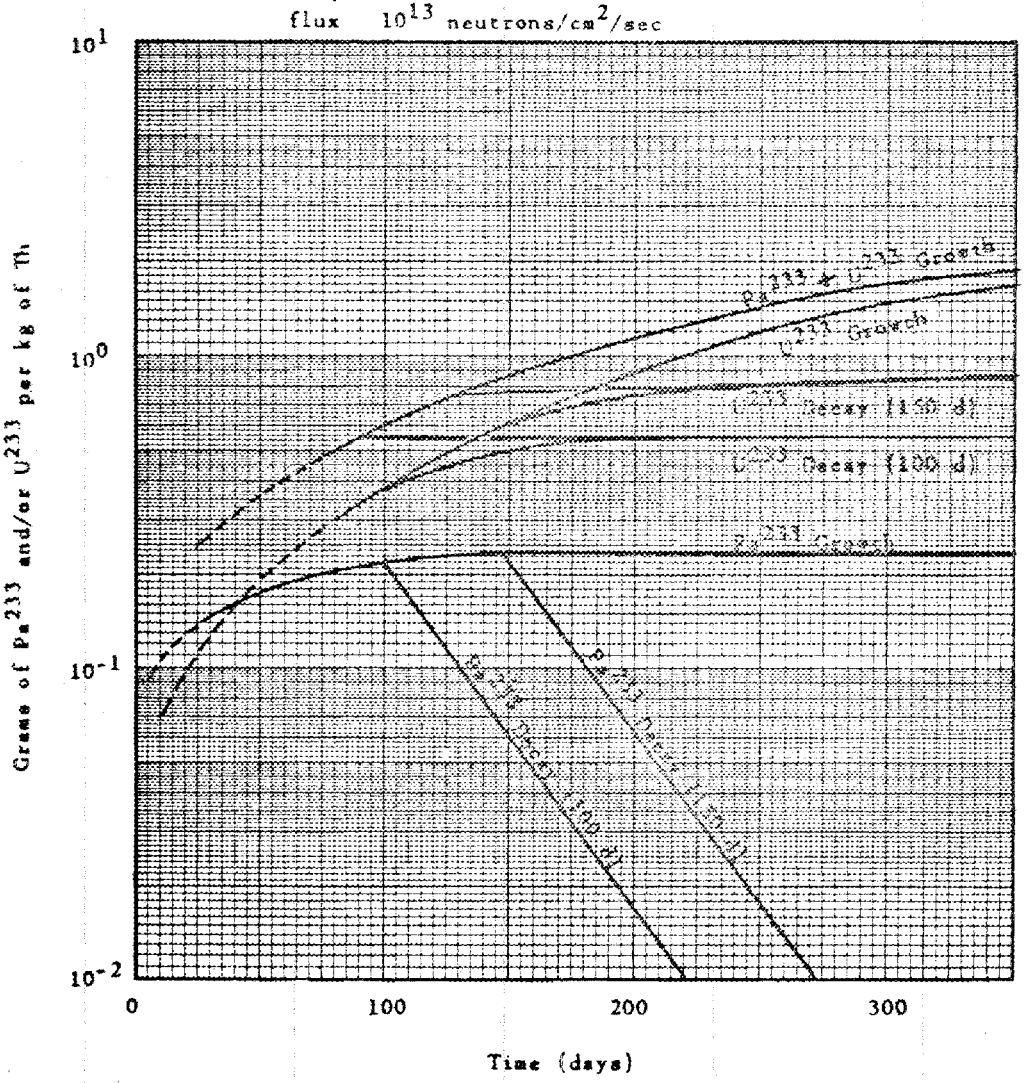

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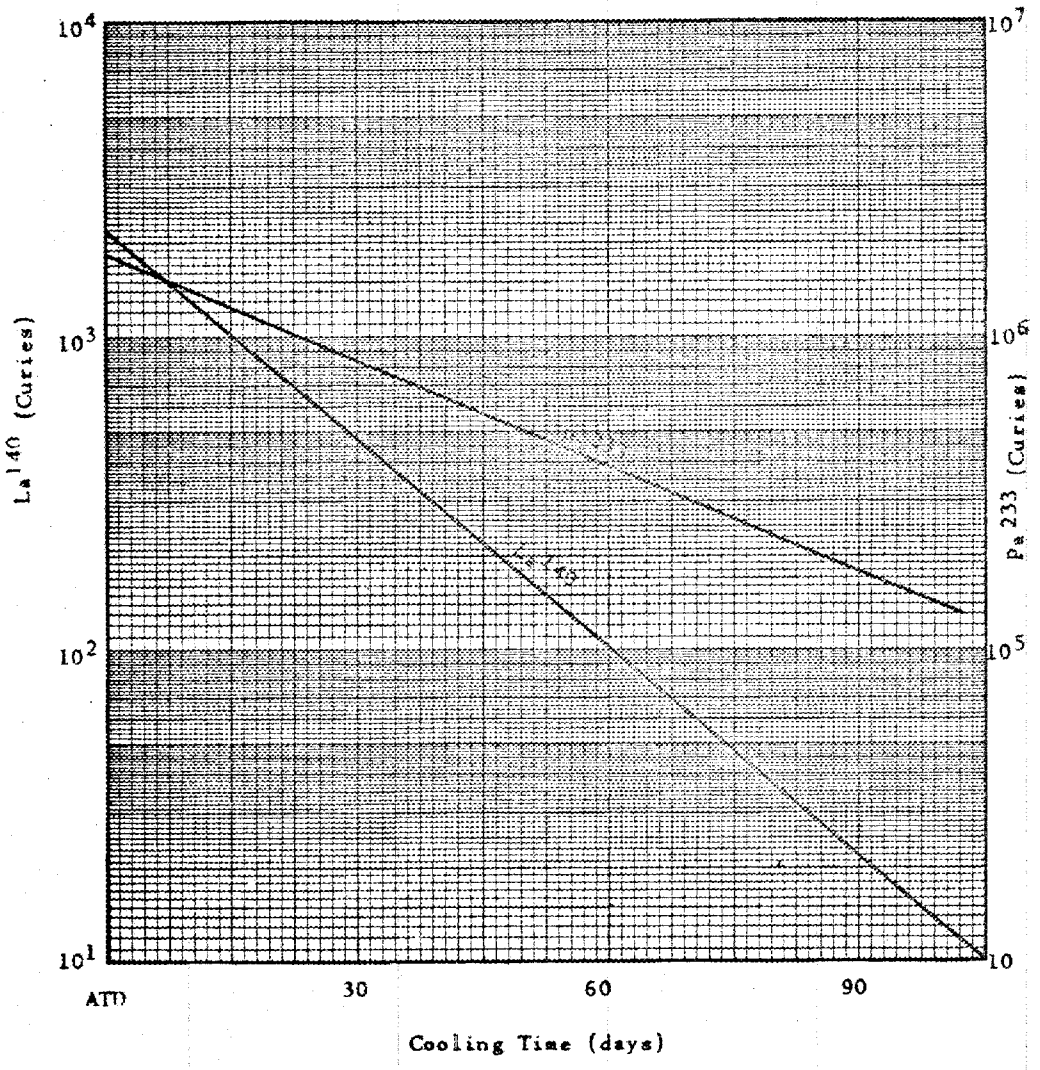
FIGURE 3.0-9

APPROXIMATE CURIE QUANTITIES OF La^{140} AND Pa^{233} VS COOLING TIME

Curves taken from ORNL CF-52-1-31[6]

Curves indicate (1) the relative advantage of Pa over fission product production as a source of high beta and gamma activity, and (2) the limiting nature of the La^{140} gamma activity in shielding considerations for short-cooled material.

Basis: 200 kg of thorium
150 days irradiation
Flux of 10^{13} n/cm^2/sec



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oxide so that the protactinium halide can be formed and sublimed. The separation of precipitates is difficult to carry out in the presence of high levels of radioactivity. Servicing of the filtering medium or the centrifuges used in the separation of a precipitate must be considered as well as methods of redissolving a precipitate and separating the components of a coprecipitate.

Solvent extraction was selected for the Thorex process since (1) operations can be carried out continuously, (2) handling of fluid flows can be controlled readily, and (3) prior engineering experience indicates its practicality.

3.1 Solvent Extraction Principles (J. E. Savolainen)

In solvent extraction of ideal solutions the ratio of the concentrations, C_1 and C_2, of a component in the two liquid phases is a constant at constant temperature:

$$C_1/C_2 = \text{a constant}$$

This constant is called the distribution constant (D.C.) or partition coefficient. If more than one component is involved in ideal solution, the Nernst law of independent distribution applies, in that each component distributes itself independently of the others. However, the behavior of the systems which are used in the separation and the purification of the materials with which this study is interested are not ideal solutions. Some of the components are present in such large amounts that the one phase becomes saturated, which alters the distribution of the other components. Evidence presented in Sec. 3.2.2 shows the complexity of the interaction which occurs in some solvent-extraction systems. The observed nonideal behavior of the systems prompted a classification of solvent-extraction systems to aid the development of processes in which these systems are used.

The types of solvent-extraction systems in which a material is partitioned between an aqueous and an organic phase may be classified according to the type of species in which the extracted material exists in the two phases and the type of interaction with the organic solvent. Four tentative classes of systems can be considered:

1. Carbon tetrachloride and other nonpolar, water-immiscible solvents can extract iodine, bromine, chlorine, or chromyl chloride from aqueous solutions. The colors exhibited by these materials are similar to those exhibited in the gaseous or vapor state. This indicates that these materials may exist as gas-like molecules in the organic phase. The nonpolar carbon tetrachloride molecule is expected to have practically no interaction with these molecular substances.

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2. The extraction of a metal chelate, or inner complex, by a nonpolar solvent, e.g., benzene or carbon tetrachloride, is widely used in analytical procedures.[7] In these cases the extracted metal ion forms a compound with the chelating agent so that electrical neutrality is attained, co-ordinate positions are occupied, and the metal is enclosed in a particle having high solubility in an organic solvent.

3. The extraction of metal salts by solvents whose molecules have a large electric moment may be pictured as follows: The metal ion in solution combines with a sufficient number of anions to produce a neutral complex, which is ordinarily expected to be labile or unstable in an aqueous solution. However, certain molecules, e.g., an ether or tributyl phosphate, with large electric moments and a single point of negative charge can fit into the remaining co-ordinate positions surrounding the metal ion. The salt-like complex is thus expected to be stabilized and may exhibit high solubility in the organic phase. In this type of solvent extraction the polar solvent molecule is used to stabilize a salt-like molecule and give the co-ordinated compound properties that permit solubility in a nonpolar diluent solvent. This is presumably exhibited in the systems in which tributyl phosphate is used as a solvent to extract uranyl nitrate or thorium nitrate into a diluent solvent such as carbon tetrachloride or a liquid hydrocarbon. The effect of the dielectric constant of the diluent on the electric moment of the active solvent molecule is expected to influence the extraction reaction equilibrium.

4. Another type of solvent extraction, which is dependent on the existence of ions in both the aqueous and the organic phase, requires that the solvent molecules have sufficient dipole moment so that the bulk solvent exhibits a moderate dielectric constant. An electrolyte can be extracted in an ionic state into the organic phase if the ionic radii are sufficiently large to compensate for the lower dielectric constant. The interaction of the solvent and the extracted electrolyte is that which is common between an electrolyte and a dielectric medium.

The above classification indicates the extreme classes of solvent-extraction behavior. A specific system may exhibit a hybrid behavior when it consists of two or more of the defined classes, or of some other class not described here.

The mathematical expressions depicting the reactions which govern the distribution of a substance between an organic and an aqueous phase may be relatively complicated. This theoretical information, as well as empirical data,

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is in a usable form when it predicts the amount of material which can be transferred from one liquid phase to another. In this report the ratio of the concentration of a specific material in the organic phase over the concentration in the aqueous phase is the distribution coefficient, D.C.(O/A), of the material. The extraction factor, E.F.(O/A), is the ratio of the total amount of material in the organic phase over the total amount in the aqueous phase. The extraction factor is related to the distribution coefficient:

$$\text{D.C.(O/A)} \times \frac{\text{volume of organic phase}}{\text{volume of aqueous phase}} = \text{E.F.(O/A)}$$

In a continuous countercurrent extraction system, the ratio of the volume flow rates of the two phases can be used in the above expression.

The decontamination factor, DF, is the measure of the increase in the product purity attained in an overall process or in one of its steps. This is generally calculated as the ratio of the amount of contaminant per unit weight of product before and after the process. The separation factor, S.F., is calculated on the same basis as the decontamination factor, but generally refers to the decrease in the contamination of a constituent present in macro concentrations.

3.1.1 General Survey (J. E. Savolainen)

Several systems for the extraction of uranium, thorium, and protactinium from aqueous solutions have been studied for the separation and purification of these materials. The extraction of thorium and uranium from nitrate solutions using diisopropyl ketone has been reported;[8] however, decontamination from protactinium was poor. The purification of thorium nitrate by extraction with hexone from an aqueous solution containing calcium nitrate and nitric acid has also been reported.[9] However, at high thorium and nitric acid concentrations a spontaneous oxidation reaction occurred with the hexone and nitric acid, which constituted a safety hazard. Solvents which may be used for the separation of uranium from thorium have been studied,[10] and those showing preferential extraction of uranium over thorium were 2-ethylhexyl acetate, ethyl benzoate, n-butyl ether, and β, β-dichloroethyl ether. Tributyl phosphate diluted with butyl ether has been used[11, 12] for the extraction of thorium; however, hexane as a diluent was reported[13] to provide greater solvent stability and appeared to be the best extractant[14] for the recovery of thorium and uranium. High nitric acid concentrations were reported[15] to be required to salt the thorium and the uranium into the organic phase.

3.1.2 TBP Extraction (J. E. Savolainen)

Tributyl phosphate was judged the best available solvent for the Thorex process, which required principally the extraction of thorium nitrate.

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Early studies of TBP extraction of heavy metals were discouraging owing to the physical problems of mixing caused by high viscosity. To bring about separation of two liquid phases after they are contacted, it is advantageous for the density difference between them to be as great as practical. For this purpose a diluent having a density either greater or less than that of the aqueous solution was needed, and hydrocarbon solvents containing no unsaturated compounds appeared to offer the greatest advantages.

3.2 Thorium Separation

Thorium forms only one series of salts, i.e., those of the tetravalent state. The thorium ion forms insoluble salts with carbonate, phosphate, and oxalate ions and has a tendency to form complexes with excess carbonate, oxalate, sulfate, or phosphate ions in acidic or neutral solutions. Complexes may be formed with fluoride, thiocyanate, and nitrate ions. Thorium also has a tendency to form double salts and basic salts.

Precipitation methods for the separation of thorium from uranium and protactinium have been reported. Thorium can be separated from uranium by precipitating thorium oxalate from acid solutions; however, protactinium is carried from solution by this precipitate.[16] At 1.5 to 1.8 M HNO_3 concentrations dense precipitates are obtained and can be filtered or centrifuged, while at lower acid concentrations, e.g., 0.4 to 0.6 M, the volumes of the precipitate are twice as large.[17, 18]

Thorium can be precipitated from aqueous solutions by hydrogen peroxide. When made in alkaline or neutral solutions, the precipitates are gelatinous, while in acid solutions they are in a dense form.[19] Peroxide precipitates made in sulfate solutions are stable and do not peptize on being washed with water. The composition of the peroxide precipitate made in moderately concentrated sulfuric acid solutions is presumably $Th(OO)SO_4 \cdot 3H_2O$; however, it is reported[20] that the composition varies with the sulfuric acid concentration. The composition of the precipitate also depends on whether the thorium or hydrogen peroxide is present in excess at the time of precipitation.

Thorium may be separated from both protactinium and uranium by precipitating thorium fluoride from acid solutions with hydrofluoric acid. These conditions, however, would introduce severe corrosion problems to the process development program.

For process considerations, precipitates which require further processing by dissolving and reprecipitation are not desirable, since the radioactivity present in the supernatants or filtrates require that they be stored until the radioactivity decays to a tolerable level. Also, separation of a precipitate from radioactive materials in solution is generally not completely effective, since trace quantities of these materials tend to become embedded in the precipitate or to wet the precipitate after filtration.

Studies of ion-exchange methods for thorium separation have been reported[21] in which an Amberlite IR-1 resin column was used. The thorium absorbed by the column was eluted with a potassium acid sulfate solution. The tetravalent thorium ion is held by a cation exchange resin very tightly and is usually eluted with a complexing agent.

In general, solvent extraction chemistry and techniques appear to offer the best procedures for separations processes.

3.2.1 Solvent Extraction of Thorium (J. E. Savolainen)

The extraction of thorium nitrate into an organic solvent from an aqueous phase has been proposed in process development studies. Extraction of thorium is similar to that of uranium, although uranium tends to be extracted more readily than thorium by organic solvents from solutions containing nitrate ions. A solvent which extracts thorium nitrate will therefore also extract uranyl nitrate. It has been inferred,[22, 23] from the extraction behavior of thorium in the presence of solvent-soluble nitrate salts, that the extraction mechanism may be dependent on the existence of a thorium nitrate complex anion.

The use of methylisobutyl ketone has been reported[17, 24] for the extraction of thorium from aqueous solutions using nitrate salts as salting agents; however a spontaneous oxidation reaction of the ketone at high thorium nitrate and nitric acid concentrations constituted a safety hazard.[9] Also, protactinium is reported[8] to be extracted by methylisobutyl ketone, which limits the thorium decontamination.

3.2.2 Extraction with TBP (J. E. Savolainen)

The use of tributyl phosphate as a solvent for the recovery and purification of thorium as well as uranium has been reported.[12, 13, 25] Pure TBP containing thorium nitrate has a density nearly the same as that of aqueous solutions; therefore the separation of phases was slow when highly concentrated TBP was used as the organic phase. Various organic diluents have been used to increase the density difference between the TBP and the aqueous phase in order to eliminate this phase separation problem. Carbon tetrachloride has been used to make the organic phase more dense than the aqueous phase; and hydrocarbon diluents, as well as butyl ether, have been used to make the organic phase less dense.

3.2.2a Nature of the TBP-Thorium Complex

The nature of the mechanism of the extraction reaction has been studied by using dilute (7.5% by volume) TBP solutions in hexane. The results indicate that the overall extraction reaction is

$$Th^{4+}_{aq} + 4NO^{-}_{3aq} + 4TBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot 4TBP_{org}$$

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The complex $Th(NO_3)_4 \cdot 4TBP$ is thus considered as being the primary complex which is extracted. It has been inferred[22, 23] that some of the thorium nitrate may extract into methylisobutyl ketone as a complex anion analogous to the uranyl ion behavior; however, qualitative measurements show that, in the dilute TBP system, conductivities are less than 10^{-6} ohm/cm^3, and the contribution of the ionic component to the extraction mechanism would be negligible in this case. At higher TBP concentrations ionic material may nonetheless be present, owing to the existence of higher dielectric constants.

The complex which is extracted in dilute TBP is assumed to have a co-ordination number of 8 and a cubic configuration, with the TBP and the nitrate ions occupying alternate corners of the cube. With all the co-ordinate positions of the thorium ion occupied by either nitrate ions or the TBP dipoles, the complex is assumed to be stabilized. The TBP in the complex permits its solubility in an organic solvent. At high thorium and/or TBP concentrations other reactions are assumed to take place, and will be discussed in the following sections.

3.2.2b TBP Extraction (J. E. Savolainen)

The general reactions governing the extraction of both nitric acid and thorium nitrate by dilute TBP were studied in order to furnish a background for the more complicated process systems.

The extraction of nitric acid is expected to follow the sequence of reactions

$$H^+_{aq} + NO^-_{3aq} \rightleftharpoons HNO_{3aq} \qquad (1)$$

$$HNO_{3aq} \rightleftharpoons HNO_{3org} \qquad (2)$$

$$HNO_{3org} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP \qquad (3)$$

giving an overall reaction,

$$H^+_{aq} + NO^-_{3aq} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP \qquad (4)$$

Studies indicate that the composite equation holds in the region of dilute TBP, e.g., 7.5% by volume in hexane, and at moderate nitric acid concentrations in the aqueous phase, e.g., 1 to 2.5 M. At higher equilibrium acid concentrations, e.g., >8.0 M, apparently uncomplexed nitric acid exists in the organic phase.

At higher TBP concentrations, e.g., >10% by volume, the simple reaction of Eq. (4) becomes more complicated. The distribution coefficient as a function of the aqueous nitric acid concentration is not a smooth curve but shows definite inflections. These inflections occur at organic phase concentration ratios of HNO_3/TBP equal to 1/4, 1/2, and 3/4, the integral nature of which suggests pre-complex or aggregate structures. This behavior introduces an uncertainty in the predicted behavior at high TBP concentrations, not only of the nitric acid extraction but also of any organic-soluble nitrate salts present, such as thorium nitrate and uranyl nitrate, which would be extracted simultaneously (Sec. 7).

In a system of three extractables, e.g., HNO_3, $Th(NO_3)_4$, and $UO_2(NO_3)_2$, it may generally be considered that the components compete for TBP, as follows:

$$H^+_{aq} + NO^-_{3aq} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP_{org}, \qquad E^o_A = 0.177 \qquad (1)$$

$$Th^{4+}_{aq} + 4NO^-_{3aq} + 4TBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot 4TBP_{org}, \quad E^o_A = 0.85 \qquad (2)$$

$$UO^{2+}_{2aq} + 2NO^-_{3aq} + 2TBP_{org} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP_{org}, \quad E^o_A = 7.7 \qquad (3)$$

However, in the TBP-thorium system at equilibrium with aqueous concentrations above 2.5 N NO^-_3, it was evident that a change occurred in the mechanism of $Th(NO_3)_4$ extraction. This change has been postulated as a mechanism of polymerization.

3.2.2c Polymerization of TBP-Thorium (J. E. Savolainen)

At high thorium nitrate concentrations in the organic phase, at which the TBP/Th ratio becomes less than 4, and when a normal hydrocarbon diluent is used, two organic phases may appear. The dense organic phase contains practically all the TBP and the thorium nitrate, while the light organic phase contains only small amounts of TBP and thorium nitrate.

To account for a TBP/Th ratio of less than 4, that of the primary complex, a polymerization reaction is assumed to occur. The co-ordination number 8 of the thorium ion is expected to remain constant in this reaction. Two of the primary complexes, having a cubic configuration, are apparently coupled together by nitrate ions at two adjacent corners of each cube, liberating two TBP molecules, as follows:

$$2\left[Th(NO_3)_4 \cdot 4TBP\right] \rightleftharpoons \left[Th(NO_3)_4 \cdot 3TBP\right]_2 + 2TBP$$

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The polymerization reaction may continue, forming polymers of a higher order. As the polymerization number increases, the TBP/Th ratio approaches 2.0 as a limit. The tetramer, $4Th(NO_3)_4 \cdot 10TBP$, has appeared as an observed limit.

Polymer chains which are close to each other in a normal hydrocarbon solvent may exert attractive forces analogous to van der Waals' forces. These forces may overcome the solvation by the normal hydrocarbon diluent and bring about the formation of a dense phase by a process analogous to the condensation of a vapor.

If an aromatic solvent such as benzene is present in the diluent, an induced dipole can be formed in the ring structure of the aromatic molecule. This aromatic molecule with its induced dipole can then be attracted along the thorium nitrate-TBP polymer chain and solubilize the polymer chains, preventing the formation of a dense phase.

3.3 Uranium-233 Separation (J. E. Savolainen)

Uranium exhibits valence states of III, IV, V, and VI; only the IV and VI states are stable in aqueous solutions. The existence[26] of the UO_2^+ ion in aqueous solutions and its optimum stability range,[27] pH 2 to 4, have been reported; however the concentration of this ion is very low, e.g., 10^{-6} M, when at equilibrium with U(IV) and U(VI). The hexavalent uranium ion in aqueous solutions forms uranates with alkalies and uranyl compounds with acids.

The most effective method of separating uranium from aqueous solutions is by solvent extraction of uranyl nitrate. Considerations of other methods of separation show that direct precipitation of uranium from solutions with dilute concentrations are ineffective.[28]

Volatility methods have been used on a small scale for uranium and protactinium separation from thorium.[29, 30] The thorium is converted to an oxide or fluoride from which volatile protactinium and uranium fluorides can be removed by a stream of hydrogen fluoride at an elevated temperature.

Ion exchange methods are useful in the final isolation and volume reduction steps in the recovery of uranium; however, the separation of uranium from large amounts of thorium by use of fixed resin beds does not offer advantages over that by solvent extraction.

3.3.1 Solvent Extraction of U^{233} (J. E. Savolainen)

A common method of separating and purifying uranium involves solvent extraction of uranyl nitrate by diethyl ether from aqueous solutions. Many other

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solvents have been found to extract $UO_2(NO_3)_2$,[31] e.g., ethers, alcohols, ketones, and esters. Alcohols which are immiscible with water tend to have the property of preferential extraction of protactinium in the presence of uranium and thorium, indicating that a different type of extraction occurs with protactinium.

Results of diethyl ether extraction of uranium from aqueous thorium solutions show the influence of various inorganic nitrates used as salting agents. The data indicate that uranium extraction decreases when thorium is present as compared with a system having no thorium. This may be interpreted as indicating thorium and uranium competition for solubility in the organic phase. High nitrate ion concentrations increase the extractability of thorium at the expense of uranium, which indicates a higher order of dependence of the thorium extraction mechanism on nitrate ion concentration.

3.3.2 The TBP-Uranium System (J. E. Savolainen)

The solvent which has the greatest promise in regard to separation from impurities, ease of operation, and chemical stability is tributyl phosphate dissolved in an inactive solvent such as a hydrocarbon or carbon tetrachloride. To exploit the extraction properties of the TBP, use is made of a saturation effect; i.e., the preferential extraction of uranium is used to reduce the amount of impurities which are extracted with the uranium. When the amount of TBP is sufficient to extract only the most extractable material, the contamination by other materials will be reduced. In conjunction with this saturation effect, the nitrate ion dependency of the thorium extraction reaction can be used to reduce the amount of thorium which is extracted with the uranium, thus enhancing separations.

It has been reported[32] that diluents with low dipole moments allow high distribution coefficients for the TBP extraction of uranium. The extraction reaction of uranium can be written as

$$UO_{2aq}^{2+} + 2NO_{3aq}^{-} + 2TBP_{org} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP,$$

and has an equilibrium constant of K = 7.7 at 25°C when the organic phase consists of 20% TBP in carbon tetrachloride. By comparison, the reaction by which nitric acid is extracted,

$$H_{aq}^{+} + NO_{3aq}^{-} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP_{org},$$

has an equilibrium constant of K = 0.177.

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3.4 Protactinium Separation (J. E. Savolainen)

Protactinium-233 is an intermediate in the nuclear reaction by which U^{233} is produced from Th^{232}:

$$Th^{232}(n, \gamma)Th^{233} \xrightarrow[2.35\ m]{\beta^-} Pa^{233} \xrightarrow[27.4\ d]{\beta^-} U^{233}.$$

This protactinium isotope will constitute the bulk of the radioactivity present in short-cooled irradiated thorium. Its presence will constitute a problem in the recovery of U^{233} unless it is allowed to transform to uranium during a long decay period. The recovery of the Pa^{233} would serve as a source of high levels of radioactivity and also as a source of small amounts of isotopically pure U^{233}.

Protactinium exists in two valence states, IV and V. Protactinium(V) appears to be the more stable state and protactinium is expected to be in this state in the process solutions. It is considered to be a homologue of tantalum, resembling the latter in many of its chemical properties, e.g., its great tendency to hydrolyze in neutral and slightly acid aqueous solutions, to precipitate as a hydrous oxide at high concentrations, and to form hydrated colloids at low concentrations.

The conclusive identification of PaO_2, $PaCl_4$, and PaOS establishing the IV valence state for protactinium, has been reported.[33] The reduction of Pa(V) salts to Pa(IV) by $CrCl_2$, $TiCl_3$, and zinc amalgam has also been reported.[34] It is stated that the aqueous solution chemistry of protactinium(IV) resembles zirconium rather than tantalum.[35]

The recovery of protactinium from thorium nitrate solutions by coprecipitation with hydrous manganese dioxide and with thorium iodate has been reported.[30] The effective separation by manganese dioxide diminishes at high concentrations of nitric acid and thorium nitrate.[36,37]

The apparent existence of two different states of protactinium has been reported[38] as a result of experiments in which a zirconium iodate precipitate was found to carry that fraction of the protactinium from solution which was inactive to other chemical reactions. The fraction which was carried with the iodate was not extracted into diisopropyl ketone. This behavior suggests the existence of a polymerized or colloidal form of protactinium in solution. In this extraction the protactinium adhered to the surfaces of the apparatus, probably because of the low acid concentrations.

The absorption of 88 to 94% of the protactinium present, from a solution 0.14 to 0.4 M in uranyl nitrate, by IR-1 resin saturated with uranyl ion has been reported.[39] One gram of IR-1 ion-exchange resin absorbed about 50%

of the protactinium from 50 ml of solution containing 15 g of thorium nitrate and 1 M in nitric acid. The protactinium may be present as a radiocolloid since ionic absorption from solutions of such high ionic strength would be expected to be negligible. Possible methods for the separation of radiocolloids from ionic materials are suggested, e.g., ultrafiltration, dialysis, or adsorption on large-surface-area solids from which the colloid can be removed by the use of complexing agents. The absorption of protactinium by ion-exchange resins at low acid concentrations has also been observed.[40] Under these conditions carrying on manganese dioxide precipitates or extraction with diisopropyl ketone did not take place.

3.4.1 Solvent Extraction of Protactinium (J. E. Savolainen)

Investigations of the solvent extraction of protactinium by various solvents showed[41] that diisopropyl carbinol gave the best distribution coefficients for the extraction from nitric acid solutions, and that the highest distribution coefficient occurred near 3 M HNO_3 concentrations. High fluoride ion concentrations in the presence of thorium did not change the distribution coefficient materially, but high temperatures were found to decrease the distribution coefficient. Water-immiscible alcohols apparently extracted protactinium from aqueous solutions quite readily.

The extraction of protactinium by TBP was used for its isolation.[42] The distribution coefficient was dependent on the acid concentration of the aqueous phase, as in the extraction with other solvents. The variation of the distribution coefficient with acid concentration was indicative that the extraction of protactinium into organic solvents could be controlled by the aqueous acid concentration. The TBP concentration was also an important factor controlling the distribution coefficient.

3.5 Associated Problems in the Thorex Process

The following discussion deals with general limiting features and associated problems which have affected laboratory development of the extraction process.

3.5.1 Dissolution of Aluminum-Jacketed Thorium Slugs (J. E. Savolainen)

The thorium is neutron-irradiated in the metallic state in the form of aluminum-clad rods. The initial step in the separations process is the dissolving of the aluminum and the thorium in nitric acid. To bring about the rapid dissolution of the two metals it is necessary to add catalysts to the nitric acid.

In most previous separations processes, the aluminum jackets, i.e., those

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bonded to uranium slugs by Al-Si alloys, have been removed in an initial, separate step by a caustic dissolution; sodium nitrate is included to prevent hydrogen evolution:

$$Al + 0.85NaOH + 1.05NaNO_3 \longrightarrow NaAlO_2 + 0.9\ NaNO_2 + 0.15NH_3 + 0.2H_2O$$

whereas $Al + NaOH + H_2O \longrightarrow NaAlO_2 + 1.5H_2$. With unbonded aluminum jacketed thorium slugs, simultaneous dissolution of both the aluminum and thorium was possible with two catalysts, Hg^{++} and F^- ions. The reaction with aluminum was

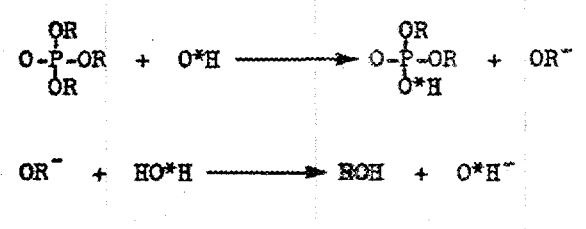
$$Al + 3.75HNO_3 \xrightarrow{Hg^{++}} Al(NO_3)_3 + 0.225NO + 0.15N_2O + 0.1125N_2 + 1.875H_2O$$

The Hg^{++} ion is apparently reduced by the aluminum metal to Hg, which amalgamates the surface and prevents the usual formation of passive aluminum oxide films.

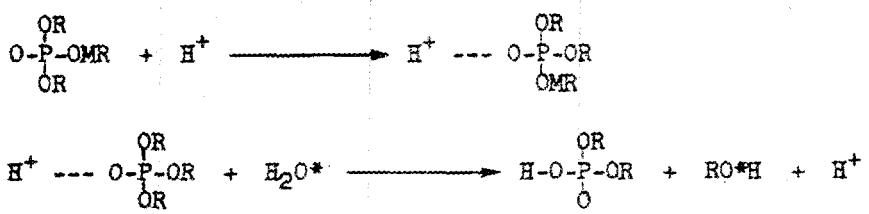
The primary thorium reaction has not yet been analyzed accurately. Nitric acid consumption at about 5 moles per mole of thorium and gas production at about 0.5 mole per mole of thorium has been indicated in Unit Operation studies. The gas composition in one dissolving run was 51% N_2, 32% NO, 3% NO_2, 8% N_2O, and 6% H_2. In this work the thorium dissolving procedure was based on earlier studies at ORNL.[41, 43] In a batch dissolving step sufficient metal was used to allow a 200% metal heel. Nitric acid at a concentration of 13 M, with 0.05 to 0.10 M F^- catalyst, was used. After reacting for 7 hr the dissolver solution was about 2.3 M in Th^{4+} and 1.5 M in free HNO_3. The mole ratio of acid to metal in the reaction was 4.7 to 5.8, with an average ratio of 5.3 from eight dissolvings.

3.5.2 Decomposition Products of TBP (Hydrolysis)

The decomposition products of tributyl phosphate which are expected to be present in the extraction of thorium nitrate are those formed by hydrolysis reactions. The initial hydrolysis reactions of alkyl phosphates have been studied using O^{18} to trace the mechanism of the reaction.[44] In alkaline solutions essentially 100% of the hydrolysis follows the mechanism



In autocatalytic hydrolysis and acid hydrolysis, 70% of the reaction results from splitting of the O-R bond of the ester:



The primary hydrolysis of a trialkyl phosphate apparently is catalyzed by both hydrogen and hydroxyl ions.

Results have been reported which indicate that in basic solutions the rate of formation of the di- and tribasic phosphoric acids from a trialkyl phosphate is much less than the rate of formation of the monobasic acid. However, in acid solutions the hydrolysis reaction continues to form the di- and tribasic acids also.

Studies have shown[45] that 0.004 M TBP in 5 M aqueous nitric acid solutions at 75°C was 50% decomposed in 40 to 50 hr. In a similar solution using hydrochloric acid 50% decomposition required only 10 hr. The difference in the reaction rate may be due to differences in the hydrogen ion activity. These decomposition rates at 75°C are substantially greater than those at room temperatures.

The decomposition products of tributyl phosphate have been found to cause precipitates, e.g., thorium mono-butyl or dibutyl phosphate, in the countercurrent extraction of thorium nitrate.[46] Decomposition products also form stable organic soluble compounds with the uranyl ion which are difficult to strip from the organic phase with aqueous nitric acid solutions.

The behavior on thorium extraction indicates that these decomposition products are accumulated within the countercurrent extraction system so that concentrations are reached which are sufficient to cause precipitation of thorium salts. To ensure the operation of the thorium extraction system and the uranium stripping step it was desirable to eliminate these decomposition products.

Washing with concentrated caustic solutions, e.g., 1.0 M NaOH, causes the formation and partial extraction of sodium butyl phosphates in the organic phase. Further washing with dilute (0.1 M) NaOH or Na_2CO_3 allows a distribution of these salts which favors the aqueous phase. Finite removal of the substances apparently depends on countercurrent washing procedures. Final washing with water is usually required to ensure removal of entrained caustic, which would accentuate hydrolysis during solvent storage. Because of the autocatalysis of the decomposition reaction, it appeared advisable in any case to use the solvent as soon as possible after treatment.

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3.5.3 Saturation in the TBP-Th-U-HNO_3 System
(W. T. McDuffee, J. E. Savolainen)

The extraction of nitric acid has been found to follow the overall reaction

$$H^+_{aq} + NO^-_{3aq} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP_{org},$$

and that of the uranyl nitrate

$$UO^{2+}_{2aq} + 2NO^-_{3aq} + 2TBP_{org} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP,$$

while that of thorium nitrate appears to be

$$Th^{4+}_{aq} + 4NO^-_{3aq} + 4TBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot 4TBP_{org},$$

with subsequent effects which can be explained by "polymerization" reactions similar to

$$X\left[Th(NO_3)_4 \cdot 4TBP\right] \rightleftharpoons X\ Th(NO_3)_4 \cdot (2X + 2)TBP + (2X - 2)TBP$$

The effects that thorium saturation of the organic phase would have on the distribution coefficients can be deduced from the nitrate ion and TBP dependencies. As the organic phase becomes saturated, the thorium distribution coefficient will decrease. If the thorium nitrate concentration is increased in the aqueous phase after the organic phase has been saturated with a large amount of thorium and small amounts of uranyl nitrate, the distribution coefficient of the uranium can be expected to decrease somewhat, because (a) the uranium extraction has a second-order dependency on the aqueous nitrate ion concentration, while (b) the thorium extraction has a fourth-order dependency. The TBP dependency of the thorium extraction is expected to vary, decreasing as the thorium concentration increases. These effects will result in the "salting out" of a portion of the uranium from the organic back into the aqueous phase.

The reactions by which nitric acid is extracted are expected to be

$$H^+_{aq} + NO^-_{3aq} \rightleftharpoons HNO_{3aq}, \qquad (1)$$

$$HNO_{3aq} \rightleftharpoons HNO_{3org}, \text{ and} \qquad (2)$$

$$HNO_{3org} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP_{org}. \qquad (3)$$

At very high acid concentrations it is expected that a portion of the acid may be extracted in an uncomplexed form in the organic phase; however, it would generally consume the TBP by the formation of the $HNO_3 \cdot TBP$ complex. A large portion of the nitric acid is thus extracted into the organic phase at the expense of thorium extraction.

From the point of view of solvent capacity it would be of advantage if the salting effect could be obtained with a nitrate which is not extracted into the organic phase. Subsequent stripping of the organic phase would be simplified by the absence of high acid concentrations.

3.5.4 Salting Effects (W. T. McDuffee, J. E. Savolainen)

A nitrate salt affects the extraction of thorium and uranyl nitrate by increasing the nitrate ion concentration and by changing the activity coefficient of the salts in the aqueous phase which are extracted by the organic phase. The extraction reactions of uranyl and thorium nitrate are dependent, respectively, on the second and fourth power of the nitrate ion concentration. The aqueous ion concentrations of the proposed process solutions are in that range where the activity coefficients increase with increasing ionic strength.

If nitric acid is used as a salting agent all its potential nitrate ions do not contribute to the nitrate ion concentration or the ionic strength of the aqueous solution because a large portion of the acid is in an associated form. Also, a portion of the nitric acid is extracted by the TBP phase.

Analysis of data from experiments showing the effects of salting agents on the distribution of thorium nitrate between 30% TBP in hydrocarbon solvent and an aqueous phase gave an empirical expression for the extraction coefficient as a function of the salting agent (Fig. 3.5.4-1). In these systems the concentration of nitric acid and thorium nitrate were below the saturation limit of the TBP phase. Plots of the logarithm of the distribution coefficient of thorium as a function of the nitrate ion concentration have slopes which vary with the charge of the cation of the salting agent. These slopes are:

Salting Agent	Slope of log E_A^0 vs. Normality of NO_3^-	Ratio of Slopes (Related to Monovalent Ion)
$NaNO_3$	0.417	1
$Ca(NO_3)_2$	0.588	1.41
$Al(NO_3)_3$	0.833	1.99
$Th(NO_3)_4$	1.18 (calcd)	2.83 (calcd)

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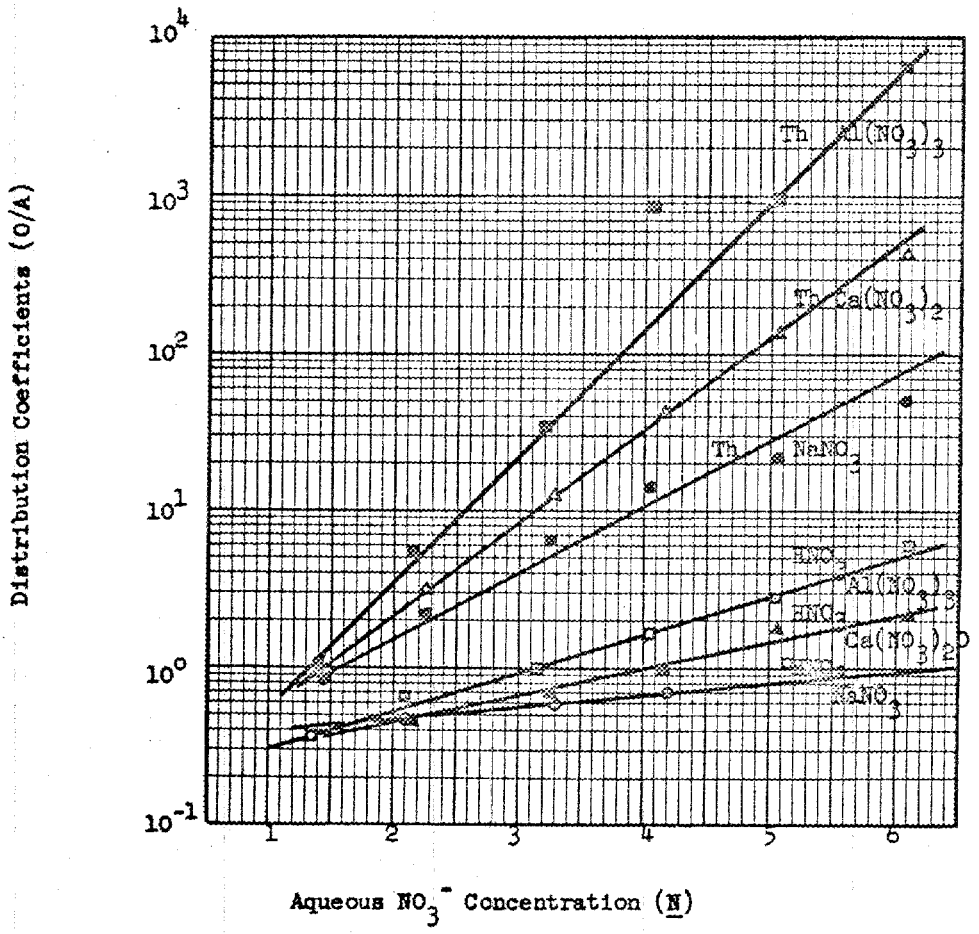
Fig. 3.5.4-1 Distribution Coefficients of Thorium and HNO_3 as a Function of the Salting Agents $NaNO_3$, $Ca(NO_3)_2$, and $Al(NO_3)_3$.

Initial Conditions:

Aqueous phase: 0.1 M $Th(NO_3)_4$, 0.2 M HNO_3, 1.0 to 6.0 M NO_3^- as Na, Ca, and Al nitrate

Organic phase: 1.0 M TBP in Amsco

Organic/aqueous ratio: 1.0



o $NaNO_3$
▲ $Ca(NO_3)_2$
□ $Al(NO_3)_3$

The increase in the ratio of the slope with increasing cation charge of the salting agent is equal to $(\sqrt{2})^{c-1}$, where c is the cation charge. The salting effect which thorium nitrate has on its own extraction is calculated from this relation. The following equation describes the effect of "salting" on the thorium distribution coefficient when using (a) 30% TBP in a hydrocarbon solvent, (b) low thorium concentrations, and (c) greater than 1.15 N equilibrium nitrate ion concentration:

$$\log E_A^0 \text{ Th} = (N - 1.15)(0.417)(\sqrt{2})^{c-1} - 0.097,$$

where N is the nitrate ion normality and c is the charge of the cation of the solute. Similar relations are expected to hold for different TBP concentrations.

3.5.5 Problems in Steady-State Equilibrium

(W. T. McDuffee, J. E. Savolainen)

TBP extraction of uranium, thorium, and nitric acid from an aqueous solution takes place simultaneously in a countercurrent extraction column, and the relative solvent affinity is in the order listed. Those materials which are extracted by the organic phase and which are present in high concentrations, e.g., thorium and nitric acid, will have the greatest influence on the changes of the column behavior as the steady state of the column operation is approached or attained.

Distribution coefficient changes, owing to (a) varying degrees of solvent saturation and (b) varying salting strength throughout the column, permit an unusual type of reflux operation, as follows: (1) As the two phases are contacted initially, a large fraction of the thorium and a smaller fraction of the nitric acid will be extracted from the aqueous phase; (2) as fresh organic solvent contacts this aqueous phase again a larger fraction of the nitric acid can be extracted; (3) when this portion of the organic phase contacts a new portion of the aqueous phase and extracts more thorium, the nitric acid from the organic phase will pass back into the aqueous phase; and (4) as the column continues operation, a higher concentration of nitric acid will build up below the region of high thorium concentration, which in turn will increase the extraction of thorium into the organic phase. This constitutes the general mechanism of "reflux" in the TBP-extraction systems.

By definition the steady state of the column is reached only when the constituent concentrations in the two phases, along the entire column, no longer vary. Before the steady state is reached, the behavior of the extraction column may vary over wide limits with respect to thorium recovery and decontamination. Some of the fission products, such as zirconium and the rare earths, may behave in a manner similar to that of nitric acid, so that regions of high concentrations develop below the region where thorium saturates the

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organic solvent. This constitutes the usual mechanism of "decontamination by saturation" in the TBP system, as exemplified and utilized in the Purex process.

If thorium accumulates in the column it will force the region of high nitric acid concentration toward the bottom of the column, where it will be removed by the aqueous raffinate leaving the column. The rate of thorium accumulation in the column may be slow, i.e., 1 or 2 percent of the feed amount per volume change. Then the prediction of column behavior from the conditions in the entering and exit streams becomes very uncertain, and dependent on high accuracy in analytical determinations and flow-rate measurement. Therefore the complete behavior of an extraction column operating with the Th-HNO_3-TBP system cannot be predicted at present with sufficient accuracy from batch equilibrium data alone. The steady-state condition cannot be readily calculated, in view of the complex interdependency of the extraction of the individual components.

However, the behavior of a column can be pictured by a countercurrent "profile," in which (a) the total equivalents or (b) the concentrations of the extractable materials in each phase are plotted as functions of the distance along the "column." Applications which explain this method of approach to column behavior are found in Sec. 4.1.2. These graphic plots will permit an empirical analysis of stage-by-stage distribution and, it is hoped, an approach to eventual mathematical treatment of steady-state problems in the HNO_3-Th-TBP system.

3.5.6 The Acid-Deficient System (A. T. Gresky, J. E. Savolainen)

An "acid-deficient" aluminum nitrate system was used in the ORNL Redox process to provide a degree of fission product decontamination unattainable in neutral or acidic systems for uranium recovery. In the Thorex development use has been made of a similar chemical device to provide optimum protactinium and fission product decontamination.

A method has been reported[47] for preparing aluminum dihydroxy nitrate solutions, i.e., $Al(OH)_2NO_3$ or $AlONO_3 \cdot H_2O$, by dissolving aluminum metal with mercury catalysis into aluminum nitrate solutions. A typical solution has a composition of 4.62 M Al, 5.56 M NO_3^-, and 8.35 M OH^-, and has a pH of about 2.0. It has been reported[48] that thorium hydroxide precipitates from aqueous solutions at pH 3.5. It is thus expected that thorium nitrate, provided the thorium is in equilibrium with an extractable species, will remain soluble in an aqueous solution of acid-deficient aluminum nitrate, the use of which would afford maintenance of a fairly constant pH in an extraction system.

3.5.6a Hydrolysis of $Th(NO_3)_4$ and $Al(NO_3)_3$ (J. E. Savolainen)

The hydrolysis reactions of the thorium ion have been investigated and interpreted,[49] from pH data of dilute-solution ions in perchloric acid, on

the basis of the reaction

$$Th^{4+} + 3H_2O \rightleftharpoons ThO^{2+} + 2H_3O^+,$$

$$2Th^{4+} + 3H_2O \rightleftharpoons Th_2O^{6+} + 2H_3O^+.$$

Equilibrium constants of these two reactions are 3.1×10^{-8} and 2.7×10^{-5}, respectively. Calculations indicate that, at a pH of 2.0 and a bulk thorium concentration of 1 M, a substantial fraction, about 0.7, of the thorium may be in the Th^{4+} form. Since the Thorex process solutions contain large concentrations of nitrate ions, the formation of intermediate thorium nitrate complexes, which enhance the extractability of the thorium, will reduce the fraction of thorium which may be present as hydroxy complexes.

The relatively high acidity of the aluminum hydroxy nitrate solutions indicates that the aluminum ion undergoes hydrolysis reactions. The types of aluminum hydroxy ions and their behavior in aqueous solution will require further investigation. The extraction behavior of thorium, uranium, and protactinium from these solutions may be influenced by the aluminum hydroxy ions. The ionic strength of these solutions and the degree of hydration of the aluminum hydroxy ion complexes are expected to influence the activities of the extractable salts. The mono- and the dihydroxy aluminum salts may behave as di- and monovalent ions. This would cause the effective ionic strength to be lower than that calculated from the bulk concentrations by assuming the aluminum to be present as the simple trivalent ion. The effects of the salting agents (Sec. 3.5.4) presumably cannot be extended as yet to predict the salting effects of the aluminum hydroxy nitrate salts.

3.5.7 Specific Gravity as a Function of Thorium, Aluminum, and Nitric Acid Concentrations (J. E. Savolainen)

An equation was developed for calculating the specific gravity of the feed solutions from the concentrations of the constituents:

$$\text{Sp gr } (20^\circ C) = 0.373 \times \underline{M}\ Th + 0.126 \times \underline{M}\ Al + 0.0195 \times \underline{M}\ HNO_3 + 1.031$$

The concentration range in which this equation can be used is 1.2 to 2.0 M Th, 0.2 to 0.8 M Al, and 0.75 to 1.5 M HNO_3. The specific gravity calculated from this equation may vary by ±0.008 units, or about 0.5%, from the experimentally determined value. A temperature variation of ±3 from 20°C causes a variation of about 0.002 units. An error of 3% in the thorium analysis introduces a larger error than the error inherent in the equation. The thermal coefficient of expansion is apparently dependent on the composition (also see Sec. 7.3).

The equation can be expressed in grams of thorium and aluminum per liter:

$$\text{Sp gr } (20^\circ C) = 0.00161 \times g\ Th/l + 0.00467 \times g\ Al/l + 0.0195 \times \underline{M}\ HNO_3 + 1.031$$

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3.5.8 Thorium-234 as a Limiting Contaminant (J. E. Savolainen)

The thorium, after neutron irradiation, is expected to contain some of the Th^{234} isotope. This isotope has radiation properties somewhat similar to Pa^{233}, and may limit the radioactive decontamination of the thorium product after chemical processing. Thorium-234 is produced by the following reactions:

$$Th^{232}(n,\gamma)Th^{233}, \quad \sigma_c = 6.8 \text{ barns} \qquad (1)$$

$$Th^{233}(n,\gamma)Th^{234}, \quad \sigma_c = 1350 \text{ barns} \qquad (2)$$

The subsequent decay reactions are

$$Th^{233} \xrightarrow[23.5\ m]{\beta^-\ 1.2\ Mev} Pa^{233} \xrightarrow[27.4\ d]{\beta^-\ 0.2\ Mev} U^{233} \xrightarrow[1.62 \times 10^5\ y]{\alpha} Th^{229}, \text{ etc.}$$

$$Th^{234} \xrightarrow[24.1\ d]{\beta^-\ 0.2\ Mev} Pa^{234} \xrightarrow[98\%\ 1.14\ m]{\beta^-\ 2.32\ Mev} U^{234} \xrightarrow[2.6 \times 10^5\ y]{\alpha} Th^{230}, \text{ etc.}$$

A small fraction, i.e. 0.12%, of the Pa^{234} decays by γ emission to UZ, which has a 6.7-hr half-life, transforming by β emission to U^{234}.

The rate of production of Th^{234} is proportional to the square of the neutron-flux density, while the rate of production of the Pa^{233} is proportional to a corresponding first power. Since the half-lives of these two radioactive species are comparable, the Pa^{233}/Th^{234} ratio at the reactor equilibrium will be maintained during decay. Thus the β and γ decontamination factors, which can be achieved by chemical processing of the short-cooled irradiated thorium, will decrease with increasing neutron-flux densities. Calculations from reported nuclear constants have indicated, for instance, that the Pa^{233}/Th^{234} ratio will be (a) 10^5 for a 10^{13} flux and (b) 10^3 for a 10^{14} flux, and so β and γ D. F.'s for processed Th^{232} necessarily will be limited to values corresponding to these ratios.

3.5.9 Crud Problems (J. E. Savolainen)

In most solvent-extraction systems certain impurities and suspended solids have a tendency to adhere to the liquid-liquid interface. These solids and impurities accumulate in those parts of the phase-contacting equipment where the phases are separated, and in such amounts as to create semirigid masses of suspended solid particles and emulsions. These accumulated masses of undesirable material, of widely variant chemical and physical properties, are generally

called "cruds." Since these cruds may become dispersed in the product stream and contaminate the product with ionic and radioactive materials, elimination of them by chemical or mechanical means is a necessity.

Spectrographic analyses of certain cruds which form in the Thorex extraction show high concentrations of chromium, iron, and silica as well as phosphorus and thorium. It may be expected that organic acid decomposition products, organic acid salts, and silicic acid can accumulate at liquid-liquid interfaces and cause crud formation. Solids which can be wetted by both liquid phases can stabilize emulsions which cause cruds. Surface-active agents which bring about the partial wetting of solid particles may be a factor in this latter problem.

Chemical methods of reducing this crud problem may be found, i.e., complexing of the ionic constituents which are found in the cruds. Surface active or emulsion-inhibiting agents, which will aid in the preferential solvent-wetting of the suspended solids, may also be of value. Mechanical means of accumulating and removing the cruds formed in the equipment, to prevent their carry-over by the product stream, may be a necessity.

3.6 Isolation (J. E. Savolainen)

After the irradiated thorium has been processed through the primary separation steps, the Th^{232}, U^{233}, and Pa^{233} products will be present in relatively large volumes of aqueous solutions, and the uranium and protactinium will be present in very dilute concentrations. These require isolation from the bulk solutions of the primary separations processes and decontamination from certain impurities, e.g., corrosion products, which may have been introduced during processing.

Evaporation of the water can be used as a volume reduction step, but no increase in product purity will result. Corrosion products and degradation products from dissolved organic materials remaining from the separation steps may also be formed and/or concentrated in such a step.

Precipitations of dilute constituents generally require carriers and necessitate further manipulations in the isolation step. However, precipitation of a concentrated constituent, such as thorium, may be advantageous.

Ion exchange affords a ready means of isolating a dilute constituent from an aqueous phase. Elution can be carried out so as to bring about substantial volume reductions as well as increased purity.

3.6.1 Uranium-233 Isolation (J. E. Savolainen)

The feasibility of U^{233} isolation by an ion exchange process has been

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demonstrated during plant operation of the Interim-23 Process.[56] Substantial decontamination and concentration of the product are obtained by preferential elution.

In general the process has involved: (1) absorption of U^{233} by Dowex-50 cation exchange resin from a feed of 0.05 N HNO_3 containing about 1.0 g of uranium per liter; (2) elution at 40 to 50°C with 2.0 M ammonium acetate—0.4 M acetic acid at pH 5.85 to produce a solution containing about 130 g of uranium per liter; (3) precipitation of uranium peroxide by addition of 30% H_2O_2, followed by filtration; and (4) final conversion to the product $UO_2(NO_3)_2$ by addition of nitric acid. The absorption step was complicated by the presence of aluminum, thorium, or iron, which were able to effectively displace the uranium from the resin.

3.6.2 Protactinium Isolation (S. S. Brandt, J. E. Savolainen)

In the proposed Thorex process, protactinium remains in the aqueous solution after the separation of thorium and uranium in the first extraction step. The subsequent separation of the protactinium from this solution containing the fission products can be either a solvent extraction or a surface adsorption process.

The solution containing protactinium may be acidified with nitric acid and the protactinium extracted with a TBP-diluent phase. Subsequent stripping into an aqueous phase, followed by precipitation or evaporation, may afford a means of concentrating this constituent. Extraction in carbinols, e.g., DIBC, also offers a feasible method (see Secs. 3.4.2 and 4.3.1).

Another method of separating the protactinium depends on its surface adsorption properties in solutions with relatively low hydrogen ion concentrations. At a hydrogen ion concentration as low as pH $\sim$2.0, the protactinium is present mostly as a radiocolloid and adheres to the surfaces of solids. Silica gel offers a large surface for adsorption, and resolution of the adsorbed protactinium by complexing agents affords a means of obtaining high concentrations of this constituent. Complications of an adsorption system for protactinium isolation include process crud and/or thorium contamination of the bed.

Primary limitations on the Pa^{233} product have been tentatively associated with the mass of solid impurities; i.e., the total weight of the product should not exceed twice the weight of the protactinium metal present. Elimination of bulk contaminants, such as thorium, uranium, silica, or corrosion products, is thus a necessity and will likely require a final laboratory-scale purification step, e.g., fluoride distillation of PaF_5.

3.6.3 Thorium Isolation (J. E. Savolainen)

The thorium in solution after separation by the solvent extraction process

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may be either dehydrated and/or denitrated by evaporation, or isolated by precipitation as the oxalate from nitric acid solutions. Concentration of the $Th(NO_3)_4$ product solution by evaporation is considered undesirable owing to nitric acid degradation of entrained solvents, but can be made adaptable by proper handling. Reported information[17, 18] indicates that thorium oxalate precipitated in a 3 to 4 M nitric acid solution is freed of most impurities, especially iron and uranium. Also, the precipitates made at 1.6 to 1.8 M nitric acid are readily filtered and have a high density. The thorium oxalate precipitate, after being washed, may be dried at 120 to 130°C.

A possible alternate isolation procedure involving ion exchange is being considered as a concentration and decontamination step for the Thorex development. Such a step would be especially desirable as a second decontamination cycle, thus eliminating complicated feed-preparation problems inherent in the usual two-cycle solvent-extraction systems.

4.0 Process Development Studies (A. T. Gresky)

This section presents a compilation of experimental data and conclusions which have evolved during the Thorex process development. Specific studies of variables affecting the various process phases, limiting features of the systems, and problems of a general nature are discussed. These details of underlying problems are intended to clarify or support choices of process concepts, conditions, and flowsheets as presented in Secs. 2.0 and 5.0. Since thorium was the "bulk" product involved in the process as constituted, and thereby governed the basic principles of operational technique, discussion of its process chemistry are considered first. Studies of the process chemistry of uranium, protactinium, and certain fission products of U^{233} are then considered to further define the scope and limitations of the Thorex problem. Problems of associated nature, and which are integral parts of important incidentals of the broad development, are discussed as a separate group.

4.1 Thorium Extraction in TBP (W. T. McDuffee)

Solvent extraction processes related to uranium or thorium separation have to date been concerned principally with the nitrate system, owing generally to chemical engineering requirements; aluminum-jacketed thorium metal, oxide, or oxycarbonate slugs must therefore be converted to this system by nitric acid dissolution. Whether the aluminum jackets are to be dissolved (a) separately by sodium hydroxide, or (b) together with the thorium by nitric acid (fluoride and mercury catalyzed) is an engineering consideration related to economics and feasibility of hot waste solution storage. That is, aluminum nitrate in hot wastes limits volume reduction, whereas nitric acid alone does not. This consideration has appeared important in the development of the Thorex process as presently conceived. Tentative processes using (1) a Th-HNO_3 system and

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(2) a Th—acid-deficient $Al(NO_3)_3$ system appear as possible alternates and thus emphasize a choice of waste economy versus process operability. The following discussion concerns principally the tributyl phosphate extraction of $Th(NO_3)_4$ from aqueous nitric acid and/or aluminum nitrate solutions.

4.1.1 Effects of TBP Decomposition Products (W. T. McDuffee)

The principal products of hydrolysis of TBP are di- and monobutyl phosphate. The thorium nitrate reaction products of DBP and MBP are both more stable than the analogous product or complex of TBP. The $Th(NO_3)_4$-MBP product is apparently not extracted strongly from the aqueous phase and usually remains as an emulsifying, colloidal precipitate, whereas the $Th(NO_3)_4$-DBP product appears also as a colloidal precipitate but tends to follow the organic phase.[45] These precipitates would represent a process thorium loss since (a) $Th(NO_3)_4$-MBP is not removed from the aqueous waste stream, and (b) the $Th(NO_3)_4$-DBP, although following the organic extractant, is not readily stripped from the organic phase. The presence of certain colloidal materials in either or both phases in a separation process ordinarily promotes (a) the formation of emulsions, (b) the physical carry-over of solids into product streams, and (c) poorer overall decontamination efficiencies. This is objectionable in the decontamination of thorium from protactinium because of the tendency of protactinium fractions to seek and to adhere to almost any solid surface it contacts. This means that the TBP must be freed from its hydrolysis products prior to its use as an extractant.

MDP and DBP may be removed from diluted TBP solvents by washing with a one-fifth volume of 1.0 M NaOH solution followed by three one-fifth volumes of 0.1 M Na_2CO_3 or NaOH solution. The function of the latter washes is to provide a low salt-strength, essentially nonemulsifying, washing medium for removing the sodium salts of the DBP and MBP formed by the sodium hydroxide. Countercurrent wash columns are recommended for plant operation.

Owing to the significant rates of TBP hydrolysis[50] and the deleterious properties of the products, it was recommended that only fresh treated solvent be used in Thorex processing.

4.1.2 Solvent Saturation and the Two-Phase Organic Problem (S. S. Brandt, W. T. McDuffee)

TBP alone is miscible in all proportions with Amsco 123-15 diluent, a kerosene fraction which is referred to as "Amsco" in the remainder of this report. Up to the point at which extracted thorium is associated as $4TBP \cdot Th(NO_3)_4$ in the Amsco-diluted TBP (20 to 54% by volume), the complex is also miscible in all proportions with the diluent. However, as the TBP/Th ratio is lowered toward 3.5 by further saturation, the complex becomes only partially miscible; the miscibility decreases with decreasing TBP/Th ratios, approaching complete immiscibility at about 2.5. This immiscibility was manifested in diluted TBP solvents

as a two-phase organic system, i.e., a light phase of diluent depleted of TBP and a heavy phase made up principally of "polymerized" complexes, e.g.,

$2Th(NO_3)_4 \cdot 6TBP$, $3Th(NO_3)_4 \cdot 8TBP$, $4Th(NO_3)_4 \cdot 10TBP$, or $5Th(NO_3)_4 \cdot 12TBP$ (Sec. 3.2.2c).

This solvent separation would create unusual density or viscosity effects and would be expected to complicate aqueous-organic mixing, e.g., in pulse-column operation. This effect would thus essentially limit the operability of a "saturated" TBP system, which is a normal requirement for effective β and γ decontamination.

All the TBP-thorium complexes were completely miscible in benzene. It was also possible to prepare a benzene-Amsco diluent mixture which would be miscible in all proportions with any TBP-thorium complex by proper choice of the Amsco-benzene ratio (see Figs. 4.1.2-1, 2, and 3). It was determined that if the diluent mixture contained 15% by volume of benzene, the mixture was miscible at room temperature with all the TBP-thorium complexes known to date (see Fig. 4.1.2-4). Thus, systems containing this aromatic would become operable under any conditions of TBP saturation with thorium, and any degree of thorium reflux would be allowable.

Benzene is more volatile than Amsco, has a much lower flash point, and its use introduces fire, toxicity, and explosion hazards. These disadvantages limit, if not nullify, the use of benzene in plant operation. The flash point of 30% TBP, 15% benzene, 55% Amsco was 38°F as opposed to 149°F for 30% TBP, 70% Amsco. Use of other aromatic ring compounds would also be limited, because of the same disadvantages, as well as low stability to nitric acid and probable irradiation-decomposition.

Effects of other organic compounds on the two-phase formation are shown in Figs. 4.1.2-5 and 6.

4.1.3 Solvent Capacity in the TBP-Th-U-HNO_3 System (W. T. McDuffee)

$HNO_3 \cdot TBP$, $UO_2(NO_3)_2 \cdot 2TBP$, and $Th(NO_3)_4 \cdot 4TBP$ have been considered as the "normal" TBP complexes of these three inorganic substances (Sec. 3.2.2). In the four-component system, i.e., TBP-Th-U-HNO_3, these substances would be expected to compete in the above molecular ratios for the TBP "capacity" in the process solvent on the basis of their relative bond strengths and ionic concentrations in the aqueous-organic system. However, the gradual "polymerization" of the thorium complex to the tetramer, $4Th(NO_3)_4 \cdot 10TBP$, is observed as high nitrate equilibria are approached. This points to a more probable ratio of $Th(NO_3)_4 \cdot 2.5TBP$ for its solvent saturation or capacity considerations. Several investigators have favored a 3:1 complex for TBP:Th for such considerations.

Table 4.1.3-1 and Fig. 4.1.3-1 record distribution data obtained in a

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Fig. 4.1.2-1 Effect of Benzene Addition on Two-Phase TBP-Diluent Systems. A: light phase; B: heavy phase; C: single phase. Conditions: 15 ml of a 50-50 TBP-Diluent solution first saturated with $Th(NO_3)_4+HNO_3$; to resulting two-phase organic layer benzene added until single-phase system obtained

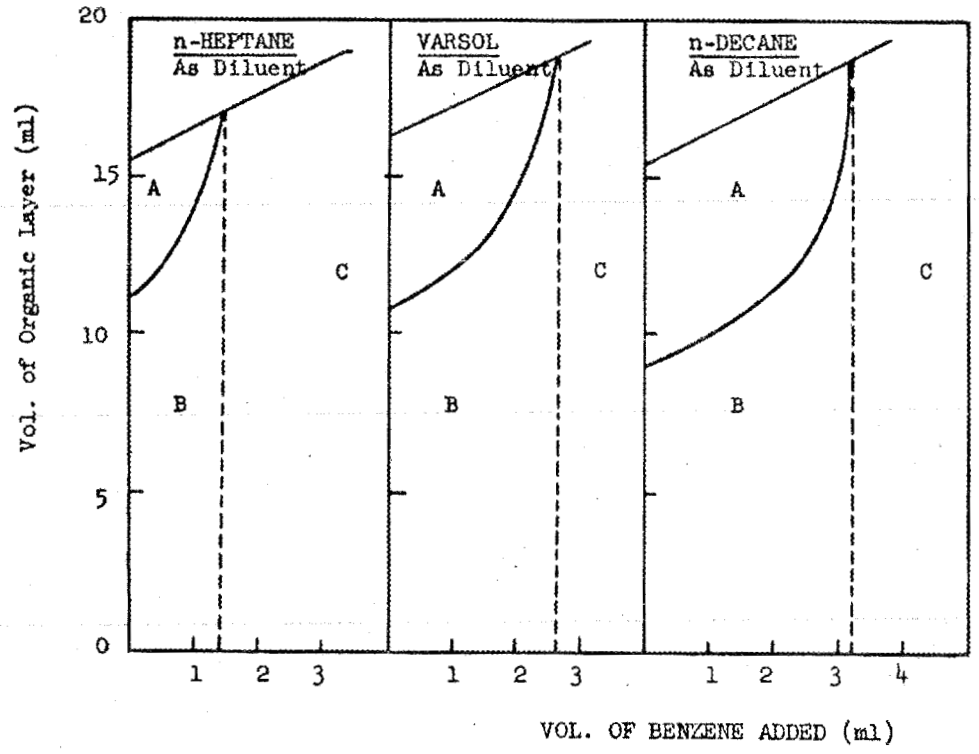

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Figure 4.1.2-2

DWG. 13348

BENZENE/TBP RATIOS REQUIRED FOR SINGLE-PHASE SYSTEMS

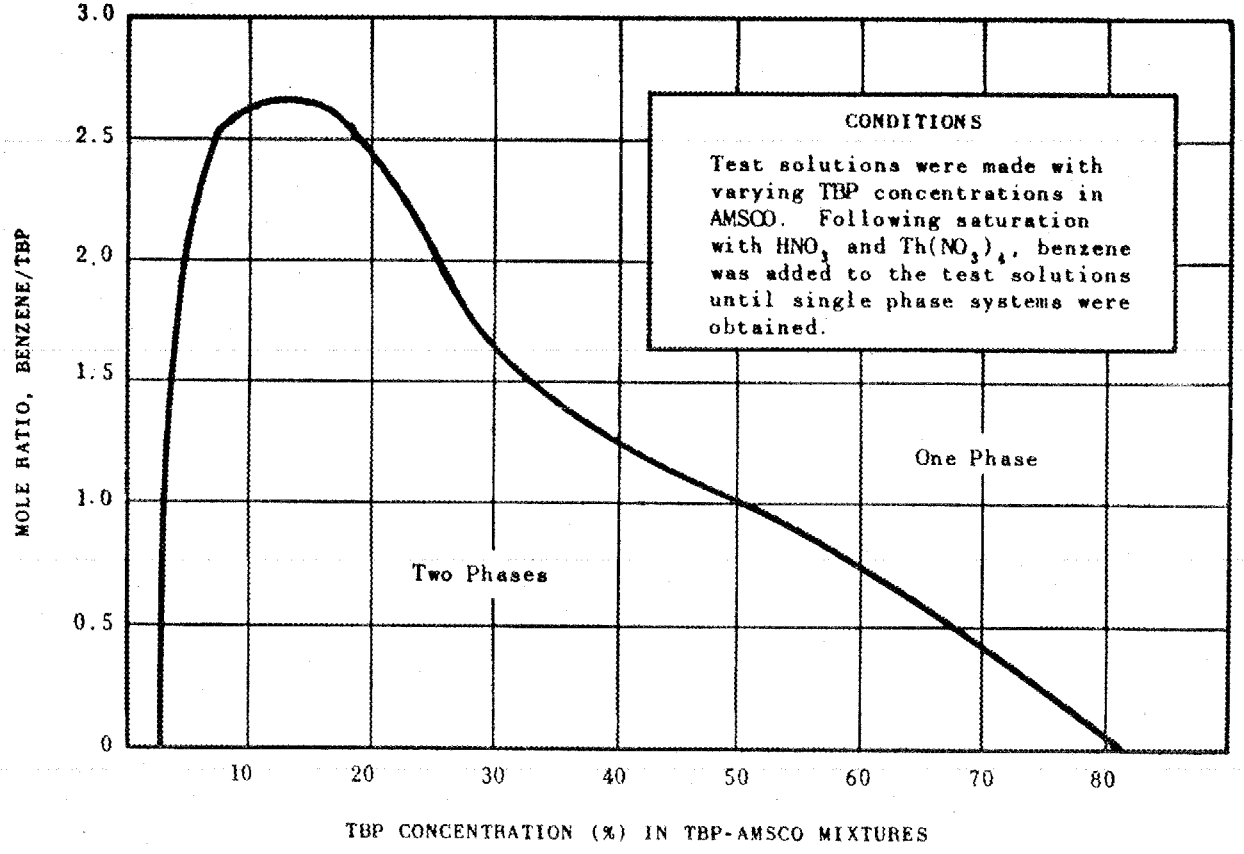

Fig. 4.1.2-3 Effect of Benzene Additions to Various TBP Concentrations in Amsco. A: light phase; B: heavy phase; C: single phase.

Conditions: Each test solution made up by adding to a 7.5-ml sample of TBP a volume of Amsco to give the designated TBP concentration; each solution saturated with HNO_3 and $Th(NO_3)_4$ before beginning benzene additions

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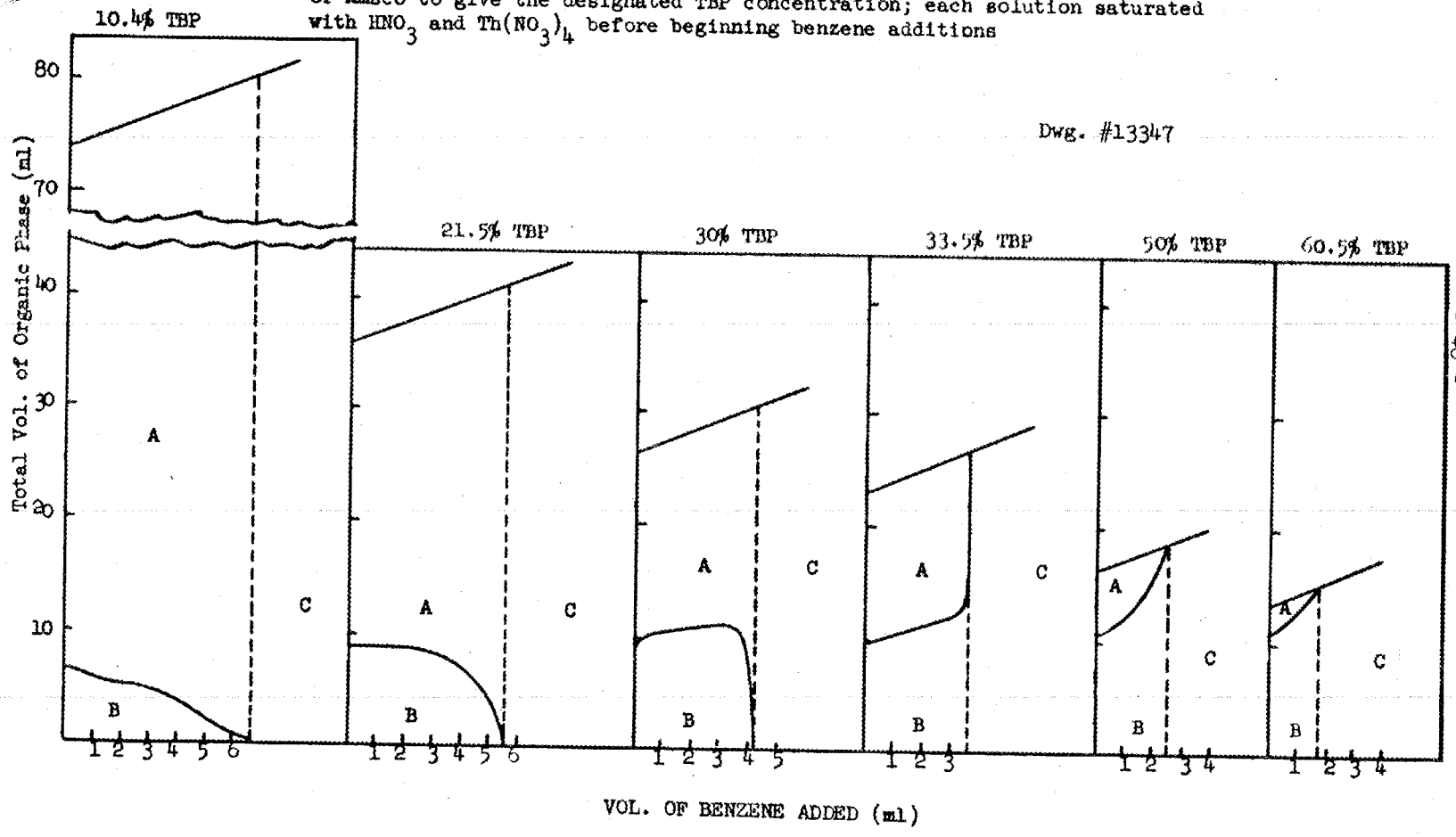

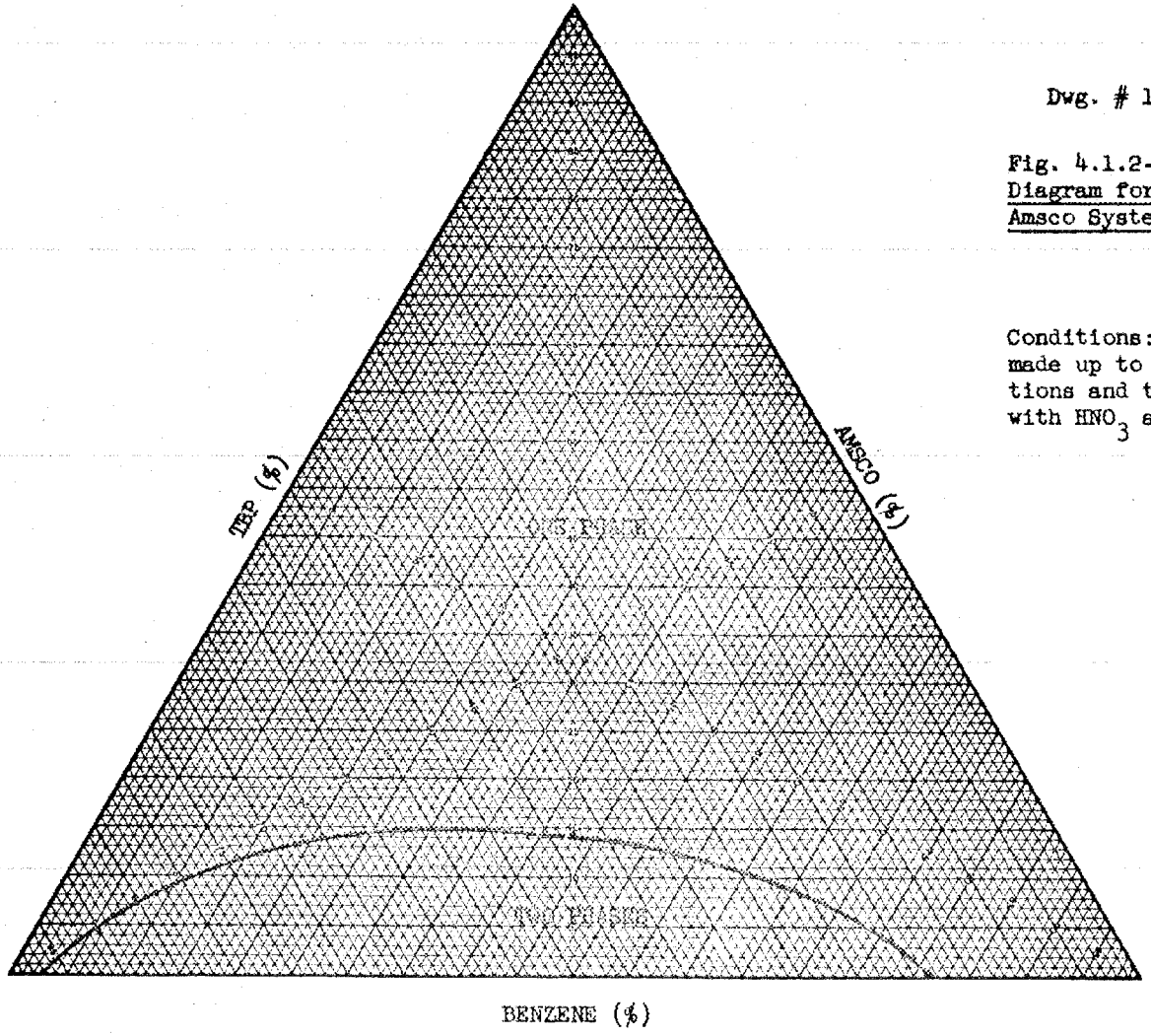

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Fig. 4.1.2-4 Phase Diagram for TBP-Benzene-Amsco System.

Conditions: Test solutions made up to desired proportions and then saturated with HNO_3 and $Th(NO_3)_4$

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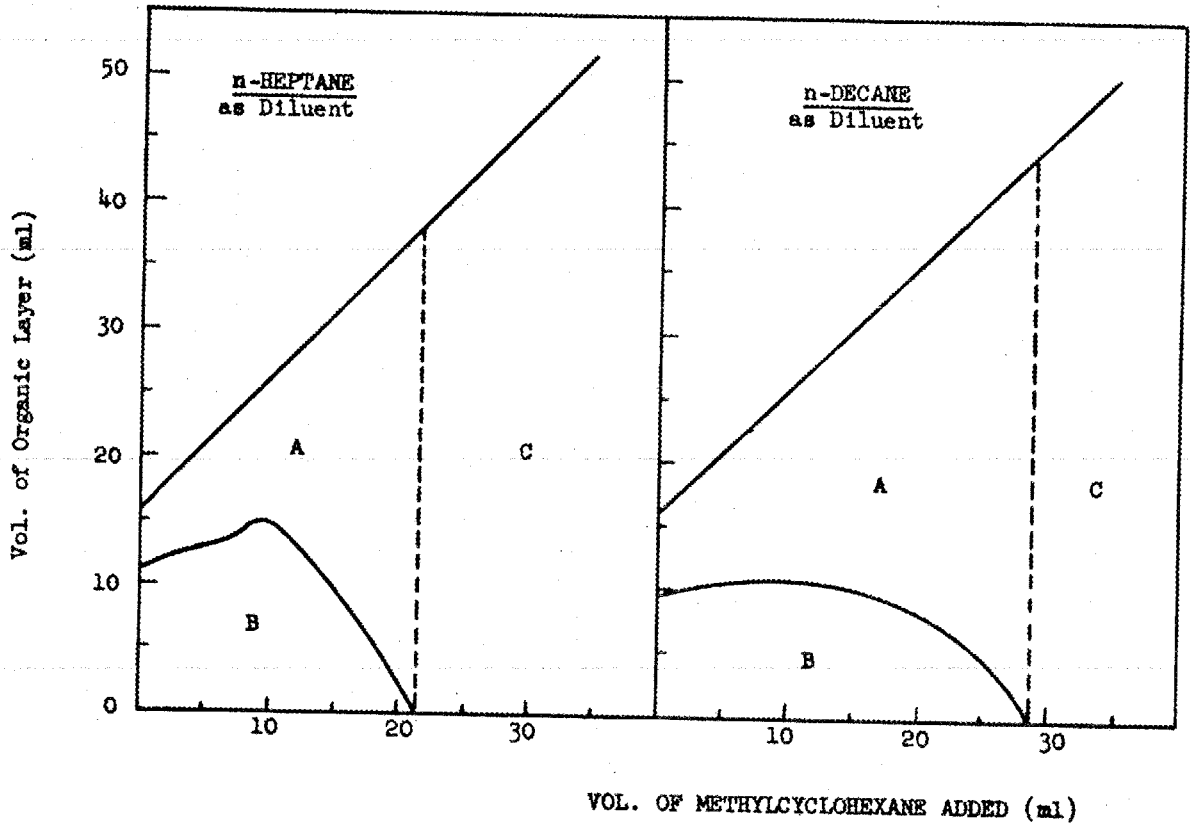
Fig. 4.1.2-5 Effect of Methylcyclohexane Addition on Two-Phase TBP-Diluent Systems.
A: light phase; B: heavy phase; C: single phase.

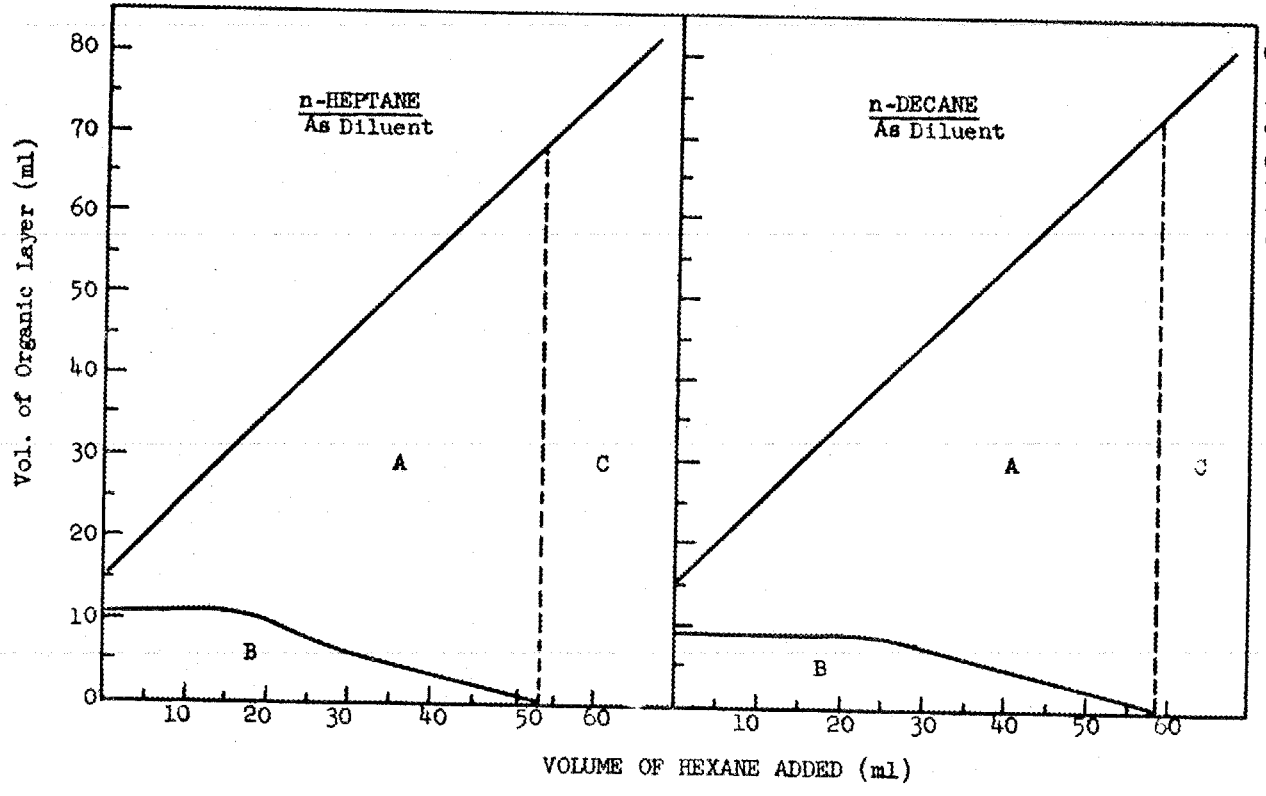
Dwg. #13034



Conditions: 15 ml of 50-50 TBP-diluent solution saturated with $Th(NO_3)_4$ + HNO_3; MCH added to the two-phase organic layer until single-phase system obtained

Dwg. #13035

Fig. 4.1.2-6 Effect of Hexane Addition on Two-Phase TBP-Diluent Systems.
A: light phase; B: heavy phase; C: single phase.



Conditions: 15 ml of 50-50 TBP-diluent solution saturated with Th $Th(NO_3)_4+HNO_3$; hexane added to the resulting two-phase organic layer until single-phase system obtained.

Dwg. 15890

Fig. 4.1.3-1 Distribution Coefficients (O/A) of Thorium and Nitric Acid in 27.3% (or 1.0 M) TBP, 15% Benzene, 57.7% Amsco.

Curves indicate a fairly constant ratio of Th D.C./HNO_3 D.C. of about 2.0, between 2.0 N and 7.0 N equilibrium NO_3^- aq. Compare with curves in Fig. 4.1.3-2.

Conditions: Aqueous phases containing equimolar ratios of $Th(NO_3)_4$ and HNO_3 contacted with equal volumes of the 1.0 M TBP solvent (thorium and H^+ analyses recorded in Table 4.1.3-1)

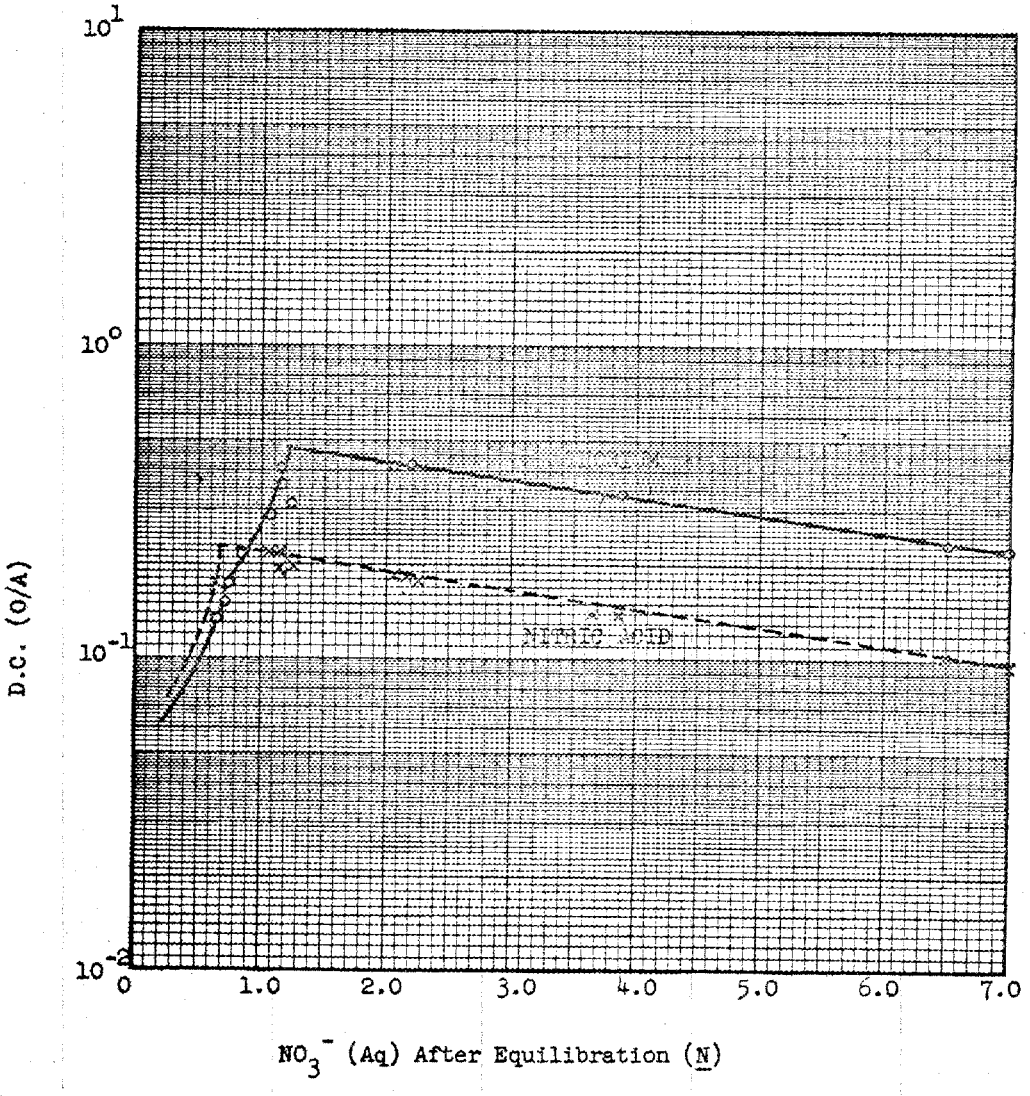


Table 4.1.3-1

Extraction of Thorium and Nitric Acid in 1.0 M (27.3%) TBP—15% Benzene—57.7% Amsco

Conditions: Aqueous phases having a Th/HNO_3 mole ratio of 1.0 at varying total concentrations were contacted with equal volumes of solvent; equilibrium NO_3^- normality in aqueous phase calculated from thorium and HNO_3 analyses

Equilibrium NO_3^- (aq.) (N)	Thorium Distribution			HNO_3 Distribution		
	Org. (M)	Aq. (M)	D.C. (O/A)	Org. (M)	Aq. (M)	D.C. (O/A)
0.648	0.017	0.126	0.135	0.025	0.144	0.174
0.718	0.021	0.139	0.151	0.026	0.162	0.161
0.747	0.025	0.146	0.171	0.029	0.163	0.178
0.783	0.027	0.152	0.179	0.031	0.175	0.177
0.824	0.034	0.159	0.214	0.041	0.188	0.217
1.073	0.059	0.207	0.285	0.051	0.245	0.208
1.116	0.084	0.207	0.406	0.063	0.288	0.218
1.144	0.078	0.214	0.364	0.057	0.288	0.198
1.212	0.069	0.238	0.290	0.051	0.260	0.196
1.216	0.075	0.238	0.315	0.051	0.264	0.216
2.076	0.170	0.399	0.426	0.089	0.480	0.186
2.155	0.174	0.414	0.421	0.085	0.499	0.171
2.155	0.173	0.414	0.419	0.094	0.499	0.188
2.175	0.182	0.414	0.440	0.096	0.519	0.185
2.279	0.186	0.440	0.423	0.094	0.519	0.182
3.666	0.230	0.710	0.324	0.119	0.826	0.144
3.845	0.241	0.745	0.324	0.117	0.865	0.135
3.854	0.241	0.745	0.324	0.117	0.874	0.134
3.873	0.254	0.752	0.336	0.121	0.865	0.140
3.873	0.254	0.752	0.336	0.117	0.865	0.135
6.504	0.300	1.261	0.238	0.153	1.460	0.105
6.992	0.300	1.354	0.222	0.156	1.576	0.099
7.011	0.300	1.354	0.222	0.156	1.595	0.098
7.212	0.305	1.395	0.219	0.159	1.632	0.097
7.232	0.308	1.395	0.221	0.184	1.652	0.111

TBP-aqueous system containing equimolar ratios of $Th(NO_3)_4$ and HNO_3 at varying total concentrations. Distribution coefficients (O/A) for $Th(NO_3)_4$ were about a factor of 2 higher than those for nitric acid. Final saturation conditions attained in the 1.0 M TBP solvent, accounting for a 4% volume increase, was calculated as 0.184 M HNO_3/0.184 M TBP and 0.308 M $Th(NO_3)_4$/0.776 M TBP, which correspond to complexes of TBP·HNO_3 and 2.52TBP·$Th(NO_3)_4$, respectively. The latter ratio compares roughly to the tetramer $4Th(NO_3)_4$·10TBP.

Table 4.1.3-2 and Fig. 4.1.3-2 record similar distribution data obtained in a system containing equimolar ratios of $UO_2(NO_3)_2$, $Th(NO_3)_4$, and HNO_3. The ratio of the distribution coefficients (O/A) for $UO_2(NO_3)_2/Th(NO_3)_4$ in 2.0 M TBP was observed to increase from 19 to 35 as solvent saturation was approached, and the uranium effectively "salted-out" the thorium from the organic phase. This effect is evidently related to the marked increased in fission product decontamination as a function of percent saturation in uranium-TBP systems, e.g., as in the Purex process. The data also reflect a large difference in HNO_3 equilibria, solvent capacities, and efficiencies of decontamination by saturation in the uranium-HNO_3 and thorium-HNO_3 systems of TBP extraction.

Although the U^{233} concentrations in Thorex feeds are negligibly small, the problem of controlling TBP saturation and capacity in a countercurrent thorium-HNO_3-TBP system becomes exceedingly complicated. Control of HNO_3 reflux, with its attendant effects on thorium distribution and recovery, has appeared to be very difficult in multistage high-saturation systems. Use of large solvent excesses, i.e., low-saturation systems, would perhaps allow an operable process but would certainly provide for poor fission product separations.

The above-mentioned problems and their effects on "steady-state" extraction conditions, as well as the problems associated with the two-phase organic formation, were factors leading to a choice of aluminum nitrate salting and acid deficiency as Thorex process concepts.

4.1.4 Distribution Coefficients and Countercurrent Studies

(W. T. McDuffee)

Progress reports from Batelle Memorial Institute[58,59] record extensive batch equilibrium data for the TBP-Th-HNO_3 systems, and this work was not duplicated by the ORNL laboratory group. However, the apparent futility of predicting countercurrent extraction behavior in the TBP-HNO_3-Th system, on the basis of simple batch equilibria alone, led to the choice of an empirical approach to process development, which was based on batch countercurrent "profiles." These profiles, which are essentially plots of $Th(NO_3)_4$ and HNO_3 distribution at various contacting stages, revealed the importance of accurate adjustment of: (a) solvent capacity, (b) thorium and nitric acid concentrations of feeds, (c) aqueous salting strength, and (d) flow ratios. Conversely, the Th-$Al(NO_3)_3$-TBP system was shown by this method to be very easily controlled in countercurrent operation. Figures 4.1.4-1 and 2 show a sketch of the countercurrent equipment and a diagrammatic explanation of the laboratory operation as used in various Thorex studies.

Dwg. #15891

Fig. 4.1.3-2 Distribution Coefficients (O/A) of Uranium, Thorium, and Nitric Acid in 54.5% (2.0 M) TBP, 15% Benzene, and 30.5% Amsco. Curves indicate a marked depressant effect of uranium saturation on thorium extraction and a smaller effect on nitric acid extraction. Thorium-nitric acid curves should be compared with those in Fig. 4.1.3-1.

Conditions: Aqueous phases containing equimolar ratios of $U:Th:HNO_3$ contacted with equal volumes of 2.0 M TBP solvent. Uranium, thorium, and H^+ analyses are recorded in Table 4.1.3-1.

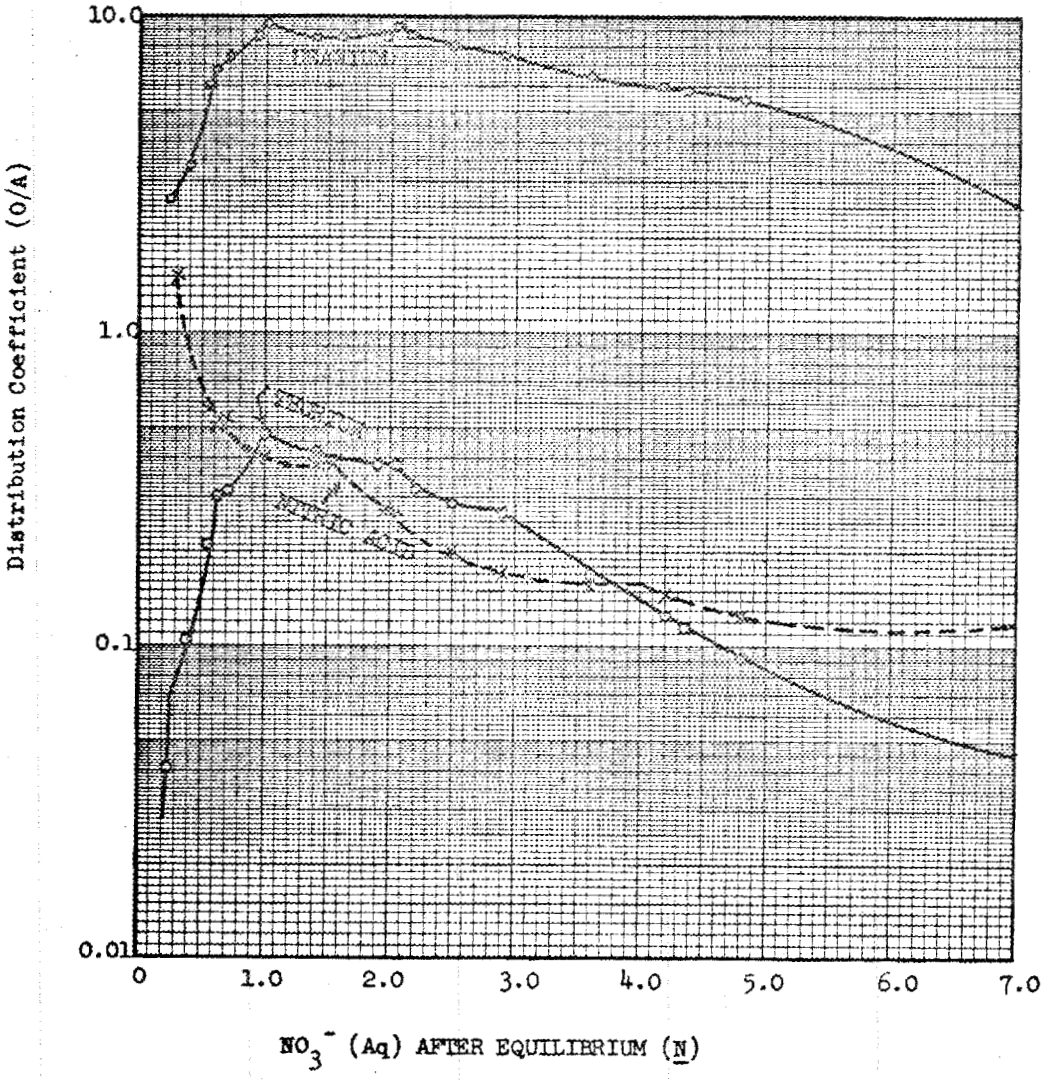


Table 4.1.3-2

Extraction of Uranium, Thorium, and Nitric Acid in 2.0 M (54.5%)

TBP--15% Benzene--30.5% Amsco

Conditions: Aqueous phases containing a U/Th/HNO_3 ratio of about 1/1/1.25 at varying total concentrations were contacted with equal volumes of solvent; equilibrium NO_3^- normality in aqueous phase calculated from uranium, thorium, and HNO_3 analyses

Equilibrium NO_3^- (Aq) (N)	Uranium Distribution			Thorium Distribution			HNO_3 Distribution		
	Org. (M)	Aq. (M)	D.C. (O/A)	Org. (M)	Aq. (M)	D.C. (O/A)	Org. (M)	Aq. (M)	D.C. (O/A)
0.203	0.0240	0.0141	1.695	0.0014	0.034	0.041	0.075	0.04	1.880
0.259	0.0414	0.0152	2.730	0.0039	0.042	0.092	0.075	0.06	1.210
0.378	0.0575	0.0170	3.370	0.0069	0.066	0.104	0.125	0.08	1.560
0.549	0.1090	0.0181	6.050	0.0227	0.096	0.203	0.075	0.13	0.575
0.608	0.1260	0.0188	6.700	0.0315	0.105	0.300	0.075	0.15	0.500
0.687	0.1465	0.0197	7.430	0.0388	0.122	0.318	0.100	0.16	0.625
0.938	0.2110	0.0242	8.720	0.0642	0.160	0.400	0.075	0.25	0.300
0.962	0.2350	0.0242	9.750	0.0790	0.166	0.475	0.100	0.25	0.400
0.967	0.2440	0.0265	9.200	0.0790	0.166	0.475	0.100	0.25	0.400
1.374	0.3060	0.0354	8.620	0.1050	0.246	0.417	0.150	0.32	0.469
1.563	0.3340	0.0384	8.700	0.1100	0.284	0.400	0.140	0.35	0.400
1.919	0.4120	0.0475	8.680	0.1290	0.336	0.385	0.120	0.48	0.250
2.013	0.4380	0.0463	9.450	0.1190	0.360	0.331	0.125	0.48	0.260
2.018	0.3780	0.0431	8.580	0.1210	0.313	0.386	0.100	0.68	0.147
2.099	0.4470	0.0536	8.400	0.1290	0.373	0.348	0.120	0.50	0.240
2.185	0.4570	0.0527	8.680	0.1220	0.390	0.313	0.050	0.52	0.096
2.472	0.505	0.0641	8.000	0.1330	0.431	0.308	0.120	0.62	0.194
2.480	0.480	0.0580	8.270	0.1260	0.446	0.282	0.075	0.58	0.130
2.895	0.564	0.0753	7.50	0.1330	0.511	0.261	0.120	0.70	0.172
3.560	0.648	0.1040	6.24	0.1080	0.638	0.169	0.150	0.80	0.188
4.170	0.695	0.1160	5.98	0.0970	0.772	0.126	0.125	0.85	0.147
4.334	0.694	0.1450	4.78	0.0785	0.811	0.097	0.120	0.80	0.150
4.344	0.695	0.122	5.70	0.0885	0.799	0.111	0.200	0.90	0.222
4.770	0.728	0.135	5.40	0.0788	0.870	0.0902	0.125	1.02	0.122
8.390	0.818	0.485	1.68	0.0518	1.455	0.0356	0.250	1.60	0.157
8.540	0.837	0.550	1.52	0.0532	1.490	0.0357	0.250	1.48	0.169
9.228	0.852	0.678	1.25	0.0579	1.618	0.0358	0.200	1.40	0.143

Dwg. #15893

Fig. 4.1.4-1 Sketch of the Laboratory Countercurrent Contactor and the Lead Shields Used with Radioactive Materials

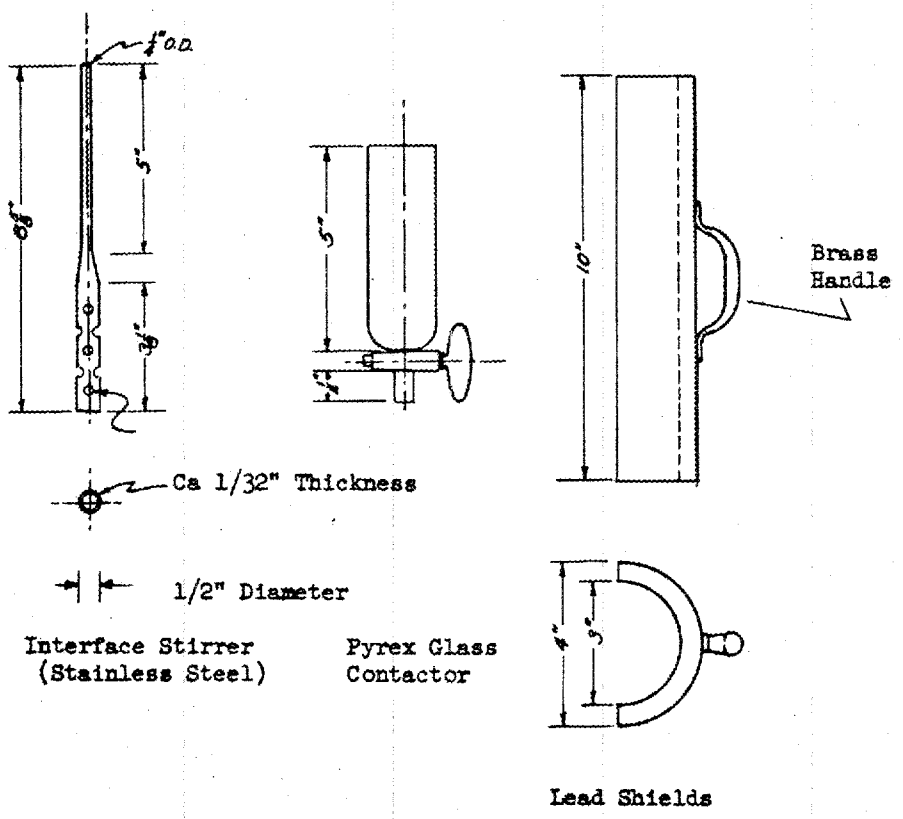


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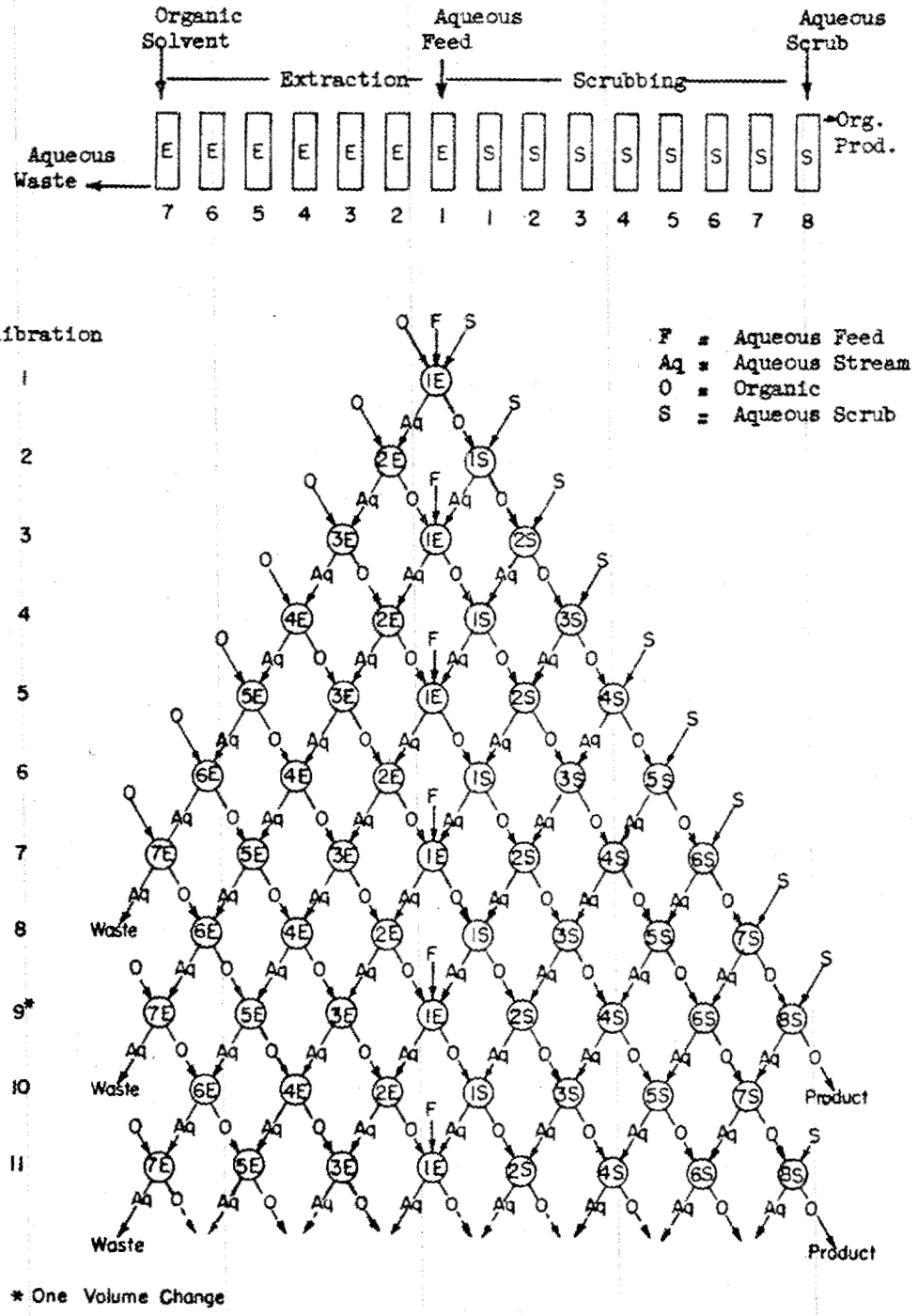
Fig. 4.1.4-2 Diagrammatic Sketch of a Batch Countercurrent Extraction Procedure



4.1.4a The Th-HNO_3-TBP System (Profiles)

(W. T. McDuffee, A. T. Gresky, J. E. Savolainen)

Close correlation of batch countercurrent data with extraction column data has been shown in previous development work. Such data are useful in predicting column behavior with respect to the reflux of extractable components and to steady-state operation. The complex and unusual nature of competing reflux of thorium nitrate and nitric acid in TBP systems required close inspection for an estimation of its behavior. There was a need for a unique organization of analytical data in order to aid in determining when definite equilibrium was attained in various systems.

Representation of the conditions existing in an extraction column at any instant is best shown by a plot of the equilibrium data taken from batch countercurrent runs (see Table 4.1.4-1 and Fig. 4.1.4-3). Such plots have been referred to as "column profiles." In these plots the vertical block diagram in the center represents the various stages and, by convention, those numbered upward represent the scrub stages while those numbered downward represent the extraction stages. The feed is introduced at the first extraction stage, the organic extractant at the bottom extraction stage, and the scrub solution at the top scrub stage. Methods of plotting the analytical data were twofold: (1) as concentrations of the constituents in equivalents per liter, from which by inspection the distribution coefficients (D.C.) could be observed, and (2) as individual concentrations of the constituents times the flow ratios (total equivalents), from which overall material distribution and extraction factors (E.F.) could be observed.

The ordinates were taken at the midpoint of each stage and the abscissas along the horizontal axis in order to represent either the concentration as equivalents per liter or as total equivalents. Since there are two phases to be considered, the data taken from the organic phase were plotted to the right of the block representing the stages and those taken from the aqueous phase were plotted to the left. Since thorium and nitric acid both combine with the TBP, the representation of the content of these substances, by convention, is plotted so that the free nitric acid concentration is shown along the horizontal axis of the column stage in question and the thorium concentration on the same axis, but added to that of the nitric acid, so that two curves are obtained. Then the thorium content is represented by that distance along the horizontal axis between the nitric acid concentration curve and the thorium concentration curve. In those systems which make use of acid-deficient scrubs, the basicity of the phase is represented on the opposite hand of the vertical axis of the phase concerned. The thorium concentration of the phase in these instances is represented by the horizontal distance between the vertical axis of the phase and the thorium curve. This method of representation is justified for the aqueous phase on the basis that the extraction by TBP and the salting strength of the aqueous phase of the system are related to both the concentration of the NO_3^- in the aqueous phase and the molar concentration of the free TBP in the organic phase.

Table 4.1.4-1

Batch Countercurrent Extraction of Thorium, Profile Data

Feed: 2.08 M $Th(NO_3)_4$, 1.0 N HNO_3
Scrub: 1.5 N HNO_3
Organic Phase: 41% TBP, 15% benzene, 44% Amsco
Feed/scrub/organic flow ratio: 2/1/8
Data taken after 7 volume changes

Stage	Organic Phase				D.C.'s(O/A)		E.F.'s(O/A)		Aqueous Phase			
	Thorium		HNO_3	Total[a]					Thorium		HNO_3	Total[a]
	(mg/ml)	(N eq)[b]	(N eq)[b]	(eq)[b]	Th	HNO_3	Th	HNO_3	(mg/ml)	(N eq)[b]	(N eq)[b]	(eq)[b]
8S	82.0	1.414	0.20	12.91	0.73	0.18	5.84	1.44	113.3	1.952	1.09	3.04
6S	88.0	1.519	0.125	13.15	0.44	0.15	3.52	1.20	201.0	3.460	0.835	4.30
4S	104.0	1.792	0.105	15.18	0.49	0.14	3.92	1.12	213.0	3.690	0.775	4.47
2S	114.0	1.967	0.10	16.54	0.35	0.12	2.80	0.96	321.6	5.540	0.826	6.37
1E	133.8	2.300	0.114	19.34	0.30	0.12	0.80	0.32	445.0	7.670	0.96	25.89
3E	125.0	2.155	0.120	18.20	0.28	0.11	0.75	0.29	445.0	7.670	1.08	26.25
5E	114.0	1.967	0.16	17.02	0.35	0.11	0.93	0.29	322.5	5.550	1.44	20.97
7E	39.75	0.685	0.24	7.4	0.80	0.25	2.13	0.67	50.25	0.867	0.97	5.51

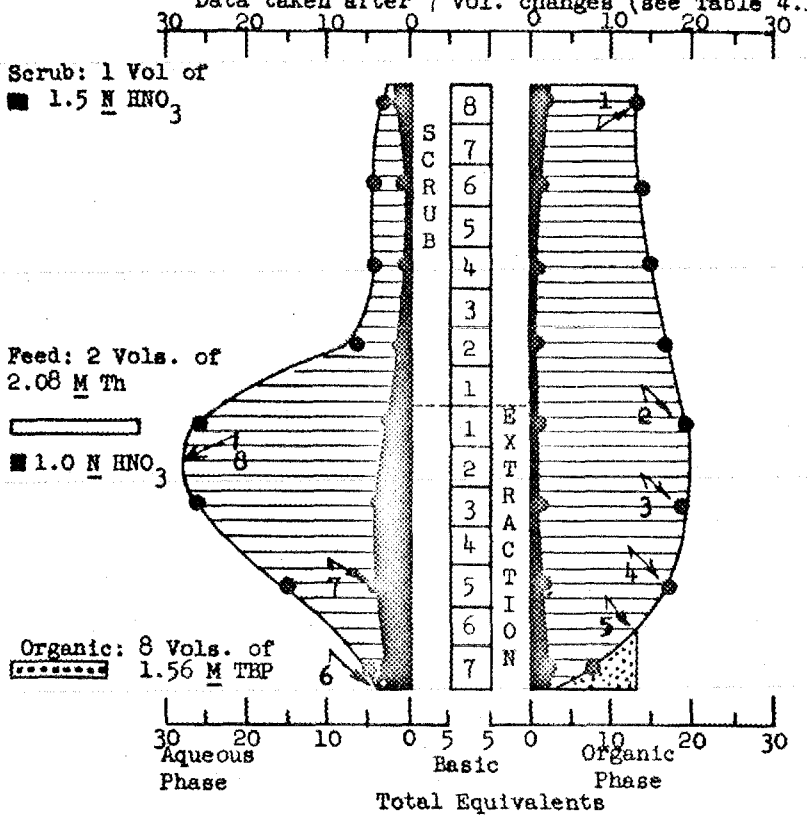
[a]Product of flow rate and sum of thorium and nitric acid equivalents.

[b]Eq = equivalents.

Fig. 4.1.4-3 Extraction Factor Profile of a Batch Countercurrent Extraction of Thorium

Plot shows extraction factors of both thorium and HNO_3 throughout the countercurrent system. The data indicate that 20% of the thorium is remaining in the column, and, therefore, steady state has not been reached.

Feed: 2.08 M $Th(NO_3)_4$; 1.0 N HNO_3
Scrub: 1.5 N HNO_3
Organic phase: 41% TBP, 15% Benzene, 44% Amsco diluent
Feed/scrub/organic = 2/1/8; 7 extraction, 8 scrub stages
Data taken after 7 vol. changes (see Table 4.1.4-1)



1. 0.2 M HNO_3/0.2 M TBP = 1/1
   0.35 M Th/1.36 M TBP = 1/3.75
   Equilibrium Value (calc.) Th/TBP = 1/2.52
2. 0.1 M HNO_3/0.1 M TBP = 1/1
   0.58 M Th/1.45 M TBP = 1/2.5
3. 0.12 M HNO_3/0.12 M TBP = 1/1
   0.54 M Th/1.44 M TBP = 1/2.67
4. 0.12 M HNO_3/0.12 M TBP = 1/1
   0.49 M Th/1.4 M TBP = 1/2.8
5. 0.2 M HNO_3/0.2 M TBP = 1/1
   0.34 M Th/1.34 M TBP = 1/4
6. Thorium Loss
7. HNO_3, 28% excess over input
8. Th, 50% excess over input

Dwg. #15895

The compositions of the feed, scrub, and organic extractant were plotted as blocks on the same scale as that of the contents of the stages, so that the degree of reflux or equilibrium could be obtained by inspection. Uranium which is present in solutions of irradiated thorium is usually present in too low concentrations to be significant in the plots.

With respect to thorium-TBP systems the runs plotted may be broadly classified in the following manner:

1. Acidic feeds

   a. Acidic scrubs, using HNO_3

   b. Neutral scrubs

      i. Using $Al(NO_3)_3$

      ii. Using H_2O

   c. Acid-deficient scrubs, using acid-deficient $Al(NO_3)_3$

2. Acid-deficient feeds

Of these, only the runs using acidic feeds will be discussed here. Acid-deficient feeds were used in the original hexone 23 process[52] and in the ORNL Redox process[53] for the extraction of uranium. Because of the longer dissolving cycle required for the preparation of acid-deficient feeds, these processes were not given serious consideration in the Thorex process.

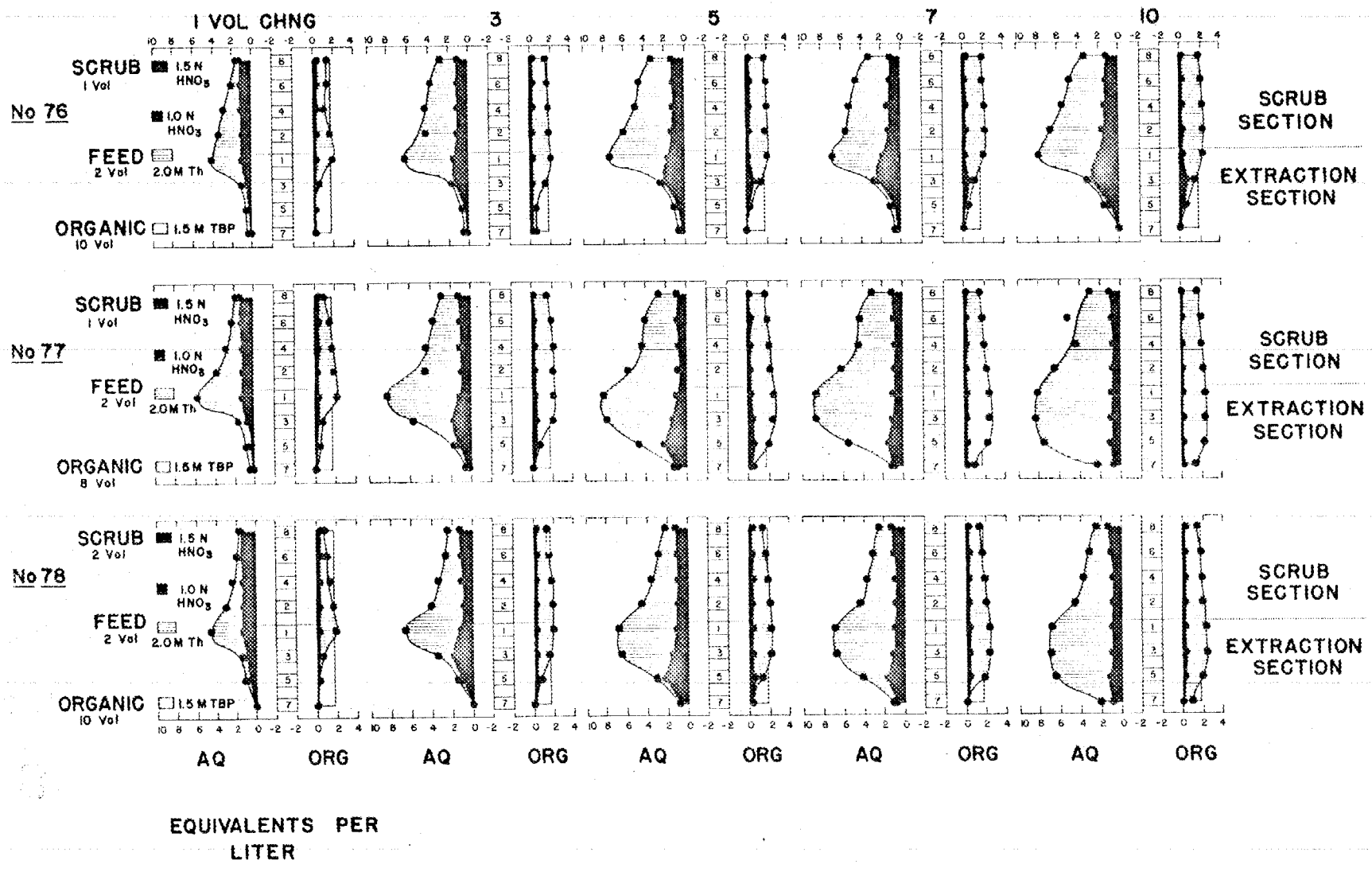
Nitric Acid Scrubbing (W. T. McDuffee)

This system is slow to come to a steady state and is difficult to operate (see Figs. 4.1.4-4 and 5, in which the effects of varying the flow rates are shown). The profiles were taken at the end of the first, third, fifth, seventh, and tenth volume change. In each run, refluxing of the nitric acid was seen, beginning at the feed plate and continuing until the nitric acid concentration increased in the extraction section to a higher concentration than existed in the feed. The thorium concentration remained essentially constant at the feed stage, but, as the run continued, the thorium concentration rose in the extraction section, forcing the point of maximum nitric acid concentration down the extraction section until at the end of the tenth volume change the nitric acid leaving the system exceeded the feed concentration.

In Control Run 76 the system was nearly at a steady state with respect to both nitric acid and thorium after ten volume changes. Flow conditions were calculated to produce an equilibrium organic product stream at a TBP/Th ratio of 3.7/1, neglecting any TBP consumption by HNO_3. The thorium loss to the aqueous waste stream was low (1.2%).

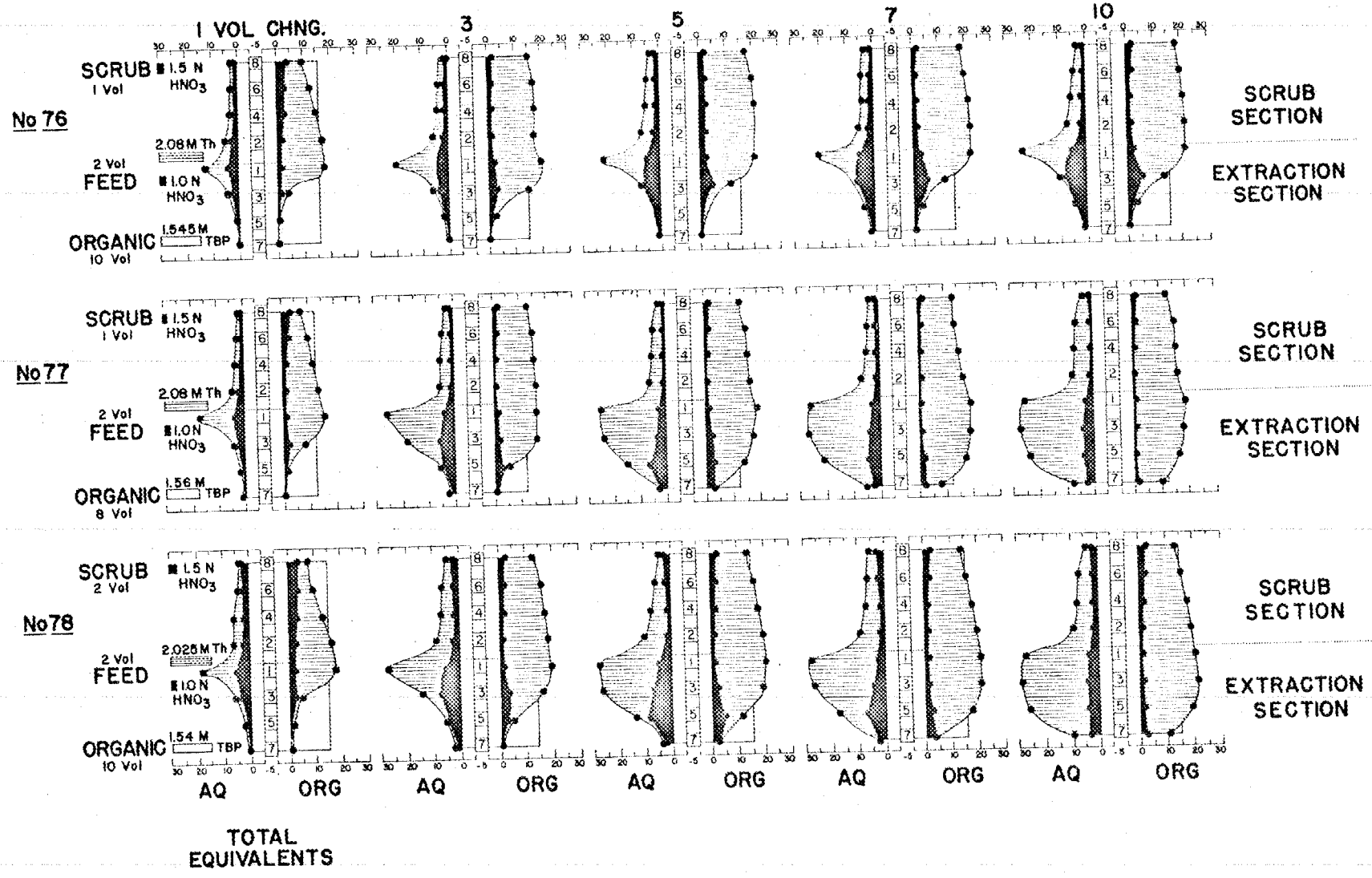
DC PROFILES OF BATCH COUNTERCURRENT EXTRACTION OF THORIUM & HNO_3 IN TBP

Dwg 16411



E F PROFILES OF BATCH COUNTERCURRENT EXTRACTION OF THORIUM & HNO_3 IN TBP

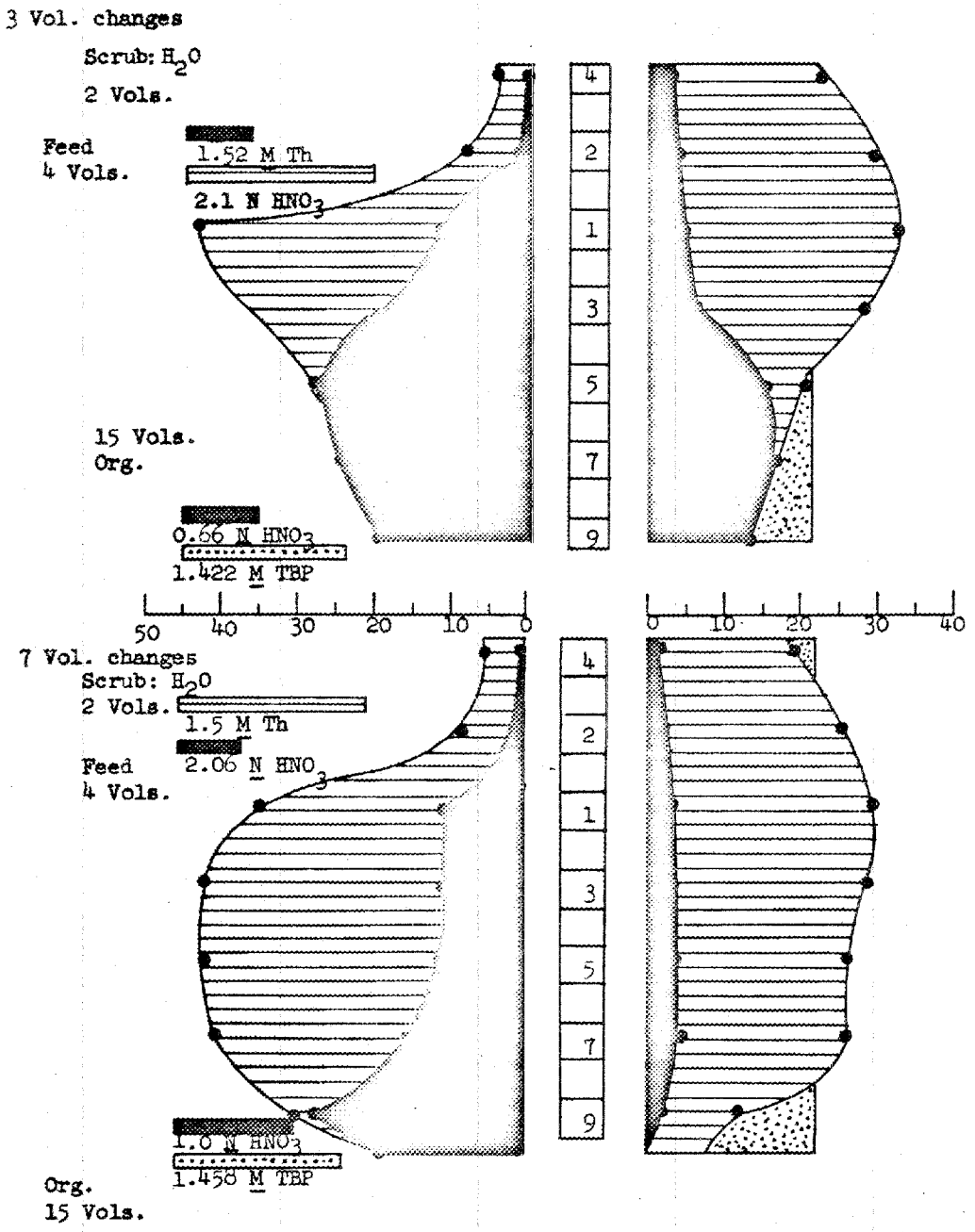
Dwg 15028



Dwg. 15892

Fig. 4.1.4-6 Extraction Factor Profile of Countercurrent Extraction of Thorium Showing the Effect of Using Water as Scrub

Organic: 40% TBP, 40% Amsco, 20% Benzene
Flow rate: Feed/scrub/organic = 2/1/3.75; 4 scrub, 10 extraction stages.



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In Run 77 the organic/feed flow ratio was reduced from 5/1 to 4/1, calculated on an equilibrium basis of a TBP/Th ratio = 3/1, as opposed to that in Run 76. The system progressed in the same manner with respect to thorium and nitric acid but came to a steady state with about 30% of the thorium passing out with the aqueous waste stream.

In Run 78 the effect of decreasing the feed/scrub ratio from 2/1 to 1/1 is shown. In this run the nitric acid maximum appeared at the feed plate, moved down the extraction section, and finally dropped out of the last extraction stage. At the same time that the nitric acid maximum dropped out of the bottom of the column, thorium appeared in the aqueous waste stream, and at the tenth volume change about 29% of the thorium was passing from the column with the aqueous waste stream.

Water Scrubbing (W. T. McDuffee)

This system offered little advantage over nitric acid scrubbing, since the nitric acid in the feed refluxed as before and low extraction factors were obtained because of the low salt strength in the system (see Fig. 4.1.4-6).

4.1.4b The Th-$Al(NO_3)_3$-TBP System (W. T. McDuffee)

In order to (a) supply an inextractable salting agent and (b) allow a combination jacket-removal and slug-dissolving scheme, $Al(NO_3)_3$ was included in both the feed and scrub systems. This afforded (a) high thorium extractability, (b) efficient scrubbing, and (c) easily controlled TBP saturation.

Effects of Acid Deficiency (W. T. McDuffee)

This system offered the greatest advantage in protactinium decontamination, and no deleterious effects on thorium extraction were apparent. The protactinium decontamination to be obtained in the process depended on holding the scrub section highly acid deficient with respect to $Al(NO_3)_3$. Thorium will precipitate from a dilute solution at the acid deficiency of $Al(OH)_2NO_3$; however, in more concentrated nitrate solutions no precipitation occurs. Therefore, in the extraction section of the column where the concentration of thorium is low, essentially neutral or slightly acid-deficient conditions are necessary. It has been found that acid deficiencies of the order of 0.1-0.2 N in an extraction section containing 0.5 M $Al(NO_3)_3$ represent the optimum conditions with respect to protactinium and fission product decontamination and the recovery of thorium. $Al(NO_3)_3$ solutions may be made acid deficient by the dissolution of aluminum metal in Hg-HNO_3 or Hg-$Al(NO_3)_3$ to form $Al(OH)_2NO_3$, which may be used as a neutralizing agent. The highly acid-deficient scrub solutions may maintain the scrub section basic with respect to $Al(NO_3)_3$ and at the same time be used to neutralize free acid in process feeds, thus providing a neutral or only slightly basic extraction section. The latter condition is necessary in order to maintain high thorium D.C.'s (O/A). The salting

strength of $Al(OH)_2NO_3$ is less than that of normal $Al(NO_3)_3$; hence slightly higher concentrations of the former are necessary in process considerations to reproduce salting properties of the latter. Neutralizing the nitric acid entering with the feed raises the aqueous salt strength in the extraction section while at the same time removing the HNO_3 from competition with thorium for the TBP capacity.

The acid-deficient system permits good decontamination of the Th from both fission products and from Pa in a single column. The critical condition lies in the acid deficiency of the scrub section where thorium E.F.'s(O/A) somewhat greater than 1.0 must be maintained. Results obtained in a typical run are shown in Fig. 4.1.4-7. In this run a Pa D.F. of 10^5 was demonstrated. Figure 4.1.4-8 shows the effect of increasing the number of scrub stages and lowering the number of extraction stages.

Salting Effects (W. T. McDuffee)

The effects of acid deficiency of the $Al(NO_3)_3$ scrub, with respect to its salting effects are shown in Figs. 4.1.4-9 and 10. As the acid deficiency of the scrub was increased, the loss in salting strength was indicated by the increase in the thorium content of the aqueous streams, due to lowered thorium D.C.'s. Comparison of the runs represented in Figs. 4.1.4-7 and 8 with those in Figs. 4.1.4-9 and 10 shows the effect of varying TBP concentrations, salt strengths, and acid-deficiencies in countercurrent systems. The acidities of the feeds in Figs. 4.1.4-7 and 8 were at 1.0 N HNO_3, with the result that higher salt strengths were maintained throughout the system and high thorium D.C.'s were obtained.

4.2 Uranium-233 Extraction (A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee)

The distribution of uranium observed in the various solvent systems studied during the Thorex development is reported below. A formalized study of all variables affecting distribution coefficients in these dilute uranium systems has not yet been carried out. Empirical data, as related to required conditions of the Th-U-Pa separations, are nonetheless reported in order to describe the general behavior of U^{233} in various process steps.

4.2.1 Extraction in Carbinols (S. S. Brandt, A. T. Gresky)

Extractability of U^{233}, as well as thorium, in diisopropyl carbinol and diisobutyl carbinol was low enough to allow good separation from protactinium in the systems used for Pa^{233} extraction. Table 4.2.1-1 summarizes the data from the countercurrent runs, which illustrate the essential behavior of U^{233} and thorium in carbinol systems.

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Fig. 4.1.4-7 Extraction Factor Profile of Batch Countercurrent Extraction of Thorium from an Acid-Deficient System

Feed: 1.47 M $Th(NO_3)_4$, 1.02 N HNO_3, 0.52 M $Al(NO_3)_3$
Scrub: 1.0 M $Al(NO_3)_2OH$, 1.4 N Acid Deficient
Organic Phase: 54.4% TBP in Amsco
Feed/scrub/organic flowrate: 1/1/3.75
7 extraction, 8 scrub stages
Data taken after 5 vol. changes

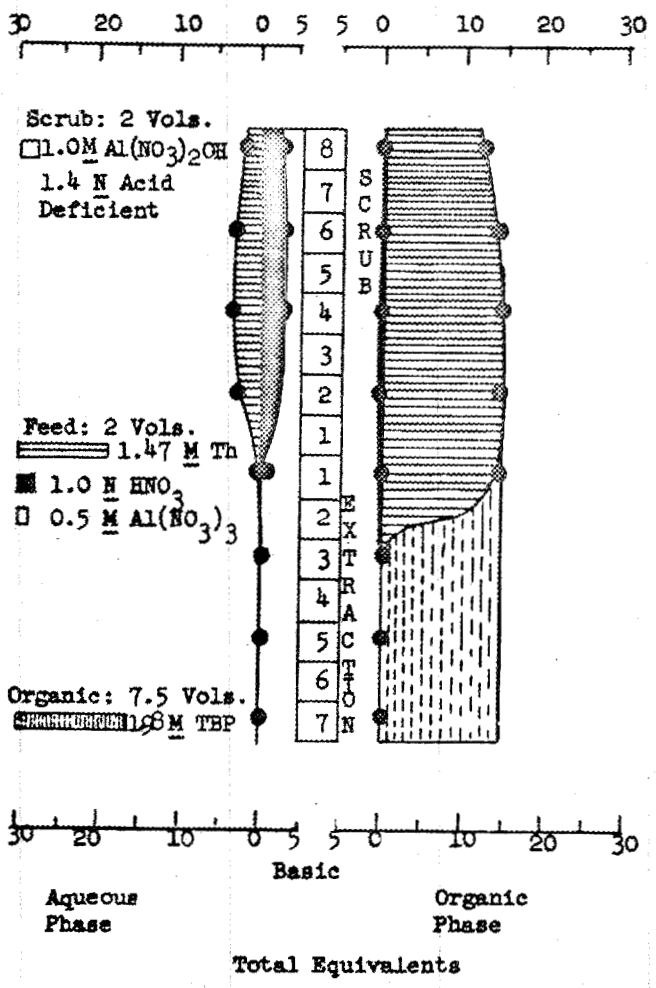

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Fig. 4.1.4-8 Extraction Factor Profile of a Batch Countercurrent Extraction of Thorium from an Acid-Deficient System

Feed: 1.47 M $Th(NO_3)_4$, 1.02 N HNO_3, 0.52 M $Al(NO_3)_3$

Scrub: 1.0 M $Al(NO_3)_2OH$, 1.4 N Acid Deficient

Organic Phase: 56% TBP in Amsco

Feed/scrub/organic flow ratios: 1/1/3.75

3 extraction, 12 scrub stages

Data taken after 5 vol. changes

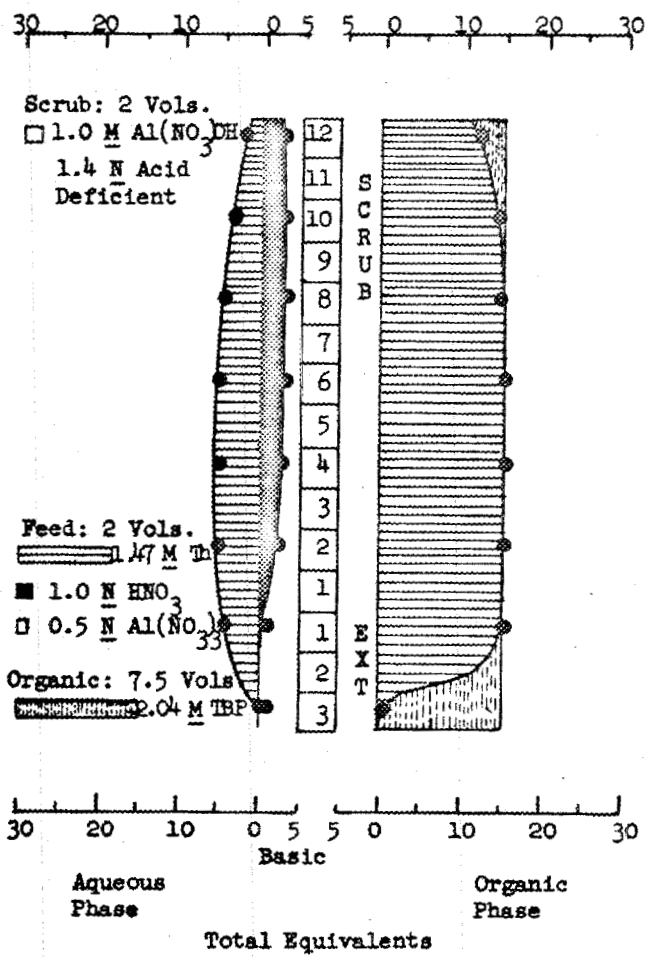

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Fig. 4.1.4-9 Extraction Factor Profile of Batch Countercurrent Extraction of Thorium in an Acid-Deficient System. Data taken after eight volume changes.

Feed: 1.52 M $Th(NO_3)_4$, 0.51 N HNO_3, 0.44 M $Al(NO_3)_3$

Scrub: 0.5 M $Al(NO_3)_2$ OH, 0.72 N Acid deficient; 2 Volumes

Organic: 41.9% TBP in Amsco diluent

Feed/Scrub/Organic Flow Rate: 1/1/5

7 Extraction, 8 Scrub Stages

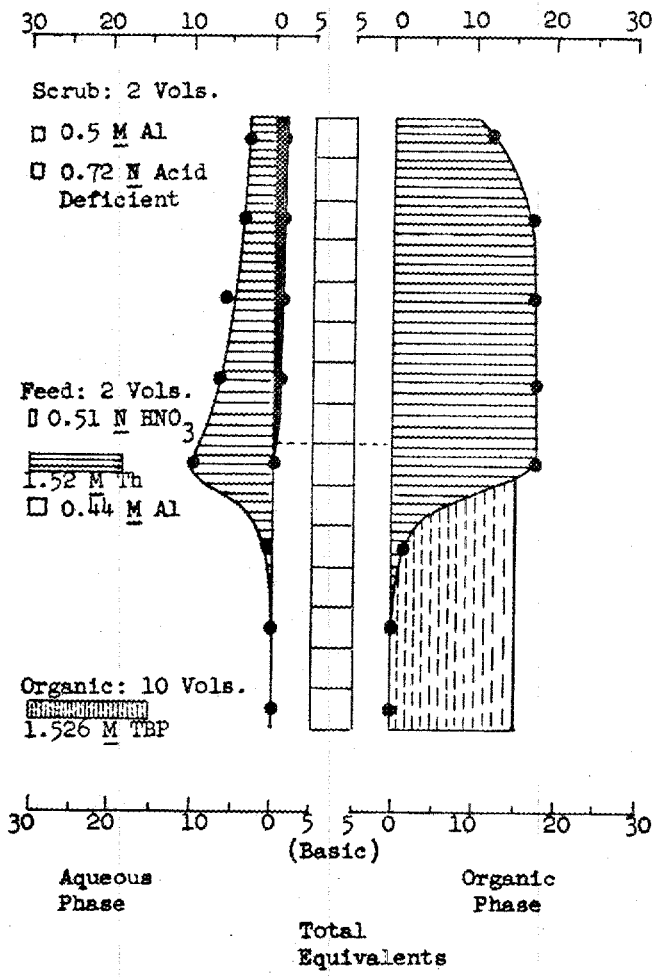

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Fig. 4.1.4-10 Extraction Factor Profile of Batch Countercurrent Extraction of Thorium from an Acid-Deficient System

Feed: 1.52 M $Th(NO_3)_4$ 0.51 N HNO_3, 0.4 M $Al(NO_3)_3$

Scrub: 0.5 M $Al(NO_3)_2OH$, 0.91 N Acid Deficient

Organic Phase: 41.9% TBP in Amsco

Feed/scrub/organic flow ratio: 1/1/5

7 extraction, 8 scrub stages

Data taken after eight volume changes

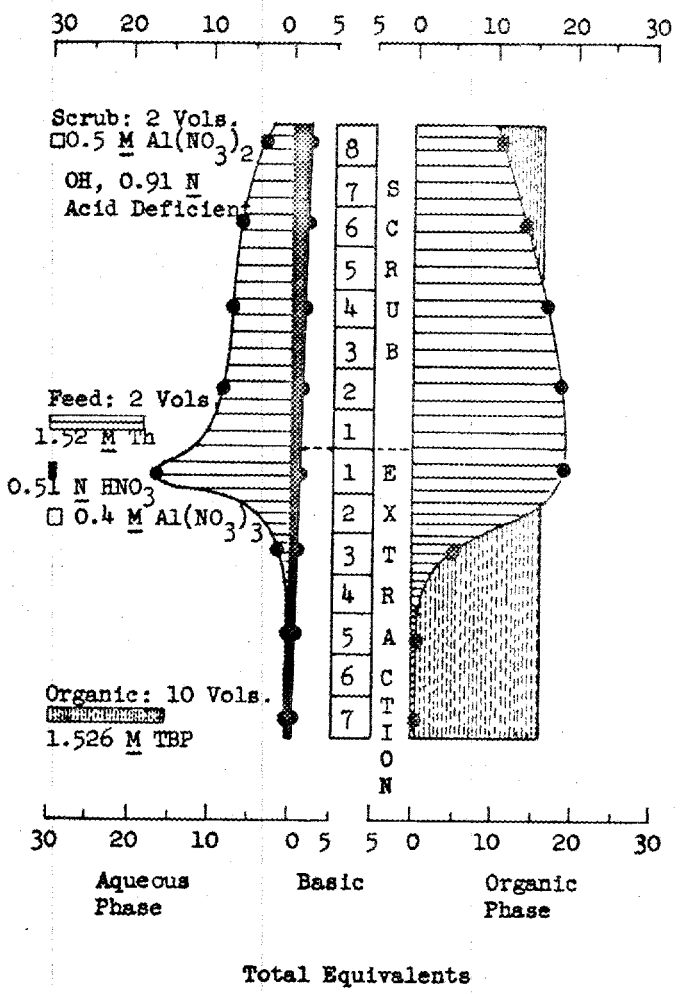

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Table 4.2.1-1

Distribution Coefficients of U^{233}

and Thorium in Carbinols

Conditions: Data are summarized from a number of countercurrent runs which demonstrated protactinium extraction processes; stated equilibrium concentrations were characteristic of extracting and scrubbing stages of the unit

Equil. conc. (aq. phase)	Solvent	U^{233} D.C.(O/A)	Th D.C.(O/A)
1.0 M Th, 3.0 N HNO_3	DIBC	0.45	0.03
1.2 M Th, 2.0 N HNO_3	DIPC	0.81	0.09
4.0 N HNO_3	DIBC	0.01	0.003
4.0 N HNO_3	DIPC	0.1	0.002

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4.2.2 Extraction in Dilute TBP Systems (A. T. Gresky)

The higher extractability of uranium in TBP, with respect to thorium and nitric acid, made possible the use of very dilute systems for separating the small concentrations of U^{233} from bulk thorium, e.g., as in the ORNL Interim-23 process. However, the competition of $Th(NO_3)_4$ and/or HNO_3 for the "free" TBP was observed to be marked, and in some cases outweighed the effects of their salting strength on uranium distribution coefficients. Table 4.2.2-1 reflects this behavior, as observed during the Interim-23 development (also see Figs. 5.1-1, 2, 3, 7, 8, 9, 11).

4.2.3 Extraction in Concentrated TBP Systems (M. R. Bennett, W. T. McDuffee)

The distribution coefficients (O/A) of uranium, in the 30 to 50% TBP extraction of the relatively small concentrations of U^{233} found in Thorex solutions, were found to be strongly dependent on: (a) the aqueous salting strength of both extractable and inextractable substances, such as $Th(NO_3)_4$, HNO_3, and $Al(NO_3)_3$, and (b) the relative "saturation" of the TBP by the bulk extractable substances in the system, e.g., $Th(NO_3)_4$ and/or HNO_3. Figure 4.1.3-2 and Table 4.1.3-2 indicate the relative nature of these effects. Generally, owing to its the high extractability and/or complex bond-strength of U^{233}, problems in its extraction by concentrated TBP were associated with stripping conditions which would allow sufficiently low salting strength to permit distribution into aqueous phases. Empirical data, taken from counter-current studies of various process steps, are recorded in Table 4.2.3-1.

4.3 Protactinium Separation (S. S. Brandt)

The successful removal of protactinium from Thorex feed solutions has been accomplished by several methods. These methods, described in the following paragraphs, by no means cover all possibilities. However, they do represent the schemes which are felt to be the most compatible with the proposed solvent extraction processes. These methods fulfill the requirements of (a) good separation of protactinium from the other Thorex feed constituents and

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Table 4.2.2-1

Distribution Coefficients of U^{233} in Dilute TBP

Conditions: Data are summarized from a number of countercurrent runs made during the development of the Interim-23 process; stated equilibrium concentrations represent aqueous extracting, scrubbing, or stripping conditions; data indicate general effects of salting and/or solvent saturation by $Al(NO_3)_3$, $Th(NO_3)_4$, and HNO_3

Equil. conc. (aq. phase)	TBP (%)	U^{233} D.C.(O/A)
1.0 M Al, 0.0 N HNO_3	1.25	2.0
1.0 M Al, 0.0 N HNO_3	1.5	3.0
1.0 M Al, 0.0 N HNO_3	3.0	7.0
1.0 M Al, 1.0 N HNO_3	1.25	1.0
1.67 M Al, 1.0 N HNO_3	2.0	7.8
0.73 M Th, 2.6 N HNO_3	1.5	0.54
0.71 M Th, 3.4 N HNO_3	1.5	0.70
3.0 N HNO_3	1.5	0.25
6.0 N HNO_3	1.5	0.45
2.0 N HNO_3	5.0	1.5
0.05 N HNO_3	1.5	0.02

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Table 4.2.3-1

Distribution Coefficients of U^{233} in Concentrated TBP Systems

Conditions: Data are summarized from a number of countercurrent studies which demonstrated Thorex process steps; equilibrium concentrations of the aqueous phase were characteristic of extracting, scrubbing, or stripping stages of the units

Equil. conc. (aq. phase)	TBP (%)	U^{233} D.C.(O/A)
0.43 M Th, 0.5 M Al, 0.1 M HNO_3	41	19.5
0.03 M Th, 0.6 M Al, 0.17 M HNO_3 def.	52	15.0
0.3 M Th, 0.7 M Al, 1.32 M HNO_3 def.	52	20.0
0.63 M Th, 0.7 M Al, 1.32 M HNO_3 def.	52	16.8
0.125 M Th, 0.26 N HNO_3	52	7.0
0.26 M Th, 0.17 N HNO_3	52	16.8
0.17 M Th, 0.19 N HNO_3	41	9.4
0.23 N HNO_3	52	2.3
0.23 N HNO_3	41	1.9
0.21 N HNO_3	41	1.2
0.1 N HNO_3	41	0.25
0.06 N HNO_3	41	0.08
0.03 N HNO_3	41	0.05
0.025 N HNO_3	54	0.083
0.018 N HNO_3	54	0.037

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(b) maintenance of protactinium in a readily accessible form for isolation. The latter condition allows the protactinium to be easily collected and allowed to decay to U^{233} and subsequently recycled, thus bolstering the overall U^{233} yield from the irradiated thorium.

4.3.1 Extraction in Carbinols (S. S. Brandt, A. T. Gresky)

Previous work had indicated that carbinols provided a high D.C.(O/A) for protactinium while, under the same conditions, allowing comparatively low distribution coefficients for thorium and U^{233}. Much of the laboratory work on protactinium extraction by carbinols was done with DIPC (diisopropylcarbinol). This carbinol was chosen because of its favorable performance in comparison with a variety of other alcohols tested. An investigation of the effect of various parameters on the distribution coefficient of protactinium in DIPC-aqueous systems produced the data plotted in Figs. 4.3.1-1 and 2. Supplementing this, the data given in Table 4.3.1-1 characterized the behavior of the main controlling constituents in Thorex feed solutions in DIPC-aqueous systems. These data indicate that in the case of nitric acid, thorium, and U^{233} the D.C.'s(O/A) were directly proportional to the thorium concentration and inversely proportional to the acidity of the aqueous feed. The reverse situation held for protactinium. This behavior was quite favorable for the separation of protactinium from thorium and uranium in Thorex feed solutions.

An indication that the affinity of DIPC for protactinium was not due to a complexing action is shown in Table 4.3.1-2. It was concluded that DIPC extracts protactinium from aqueous solutions by means of a solvating action, the efficiency of which is more than proportionately reduced by dilution with an inert solvent.

While DIPC was quite specific for protactinium extraction, it was considered to be somewhat unstable in the presence of nitric acid and it was not commercially available in high purity or quantity. A substitute for DIPC was found in DIBC (diisobutylcarbinol). A comparison of the protactinium and nitric acid distribution coefficients (Fig. 4.3.1-3) shows an equivalence of protactinium extraction in DIBC and DIPC. The nitric acid distribution coefficient in DIBC was lower than in DIPC, which would allow for a more conservative or optimum use of nitric acid in an extraction process. Other advantages of DIBC over DIPC are:

1. Higher flash point
2. Greater stability in the presence of nitric acid
3. Greater availability in higher purity
4. Lower cost

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Fig. 4.3.1-1 Distribution of Protactinium in DIPC-Aqueous Systems: Effect of Nitric Acid and Thorium on Protactinium Distribution Coefficient (O/A). The thorium isobars are the lines, the ends of which are designated by numbers that represent the thorium normality of the respective isobars. The heavy line represents the protactinium DC (O/A) as a function of nitric acid concentration alone. Note: This figure shows that (1) the presence of thorium in aqueous solutions of protactinium has a depressant effect on the protactinium DC (O/A); and (2) the protactinium DC (O/A) is more sensitive to changes in nitric acid concentration than in changes of thorium concentration at equivalent total nitrate ion levels.

Conditions: Equal volumes of aqueous solution and DIPC equilibrated in a batch contactor; phases separated and analyzed.

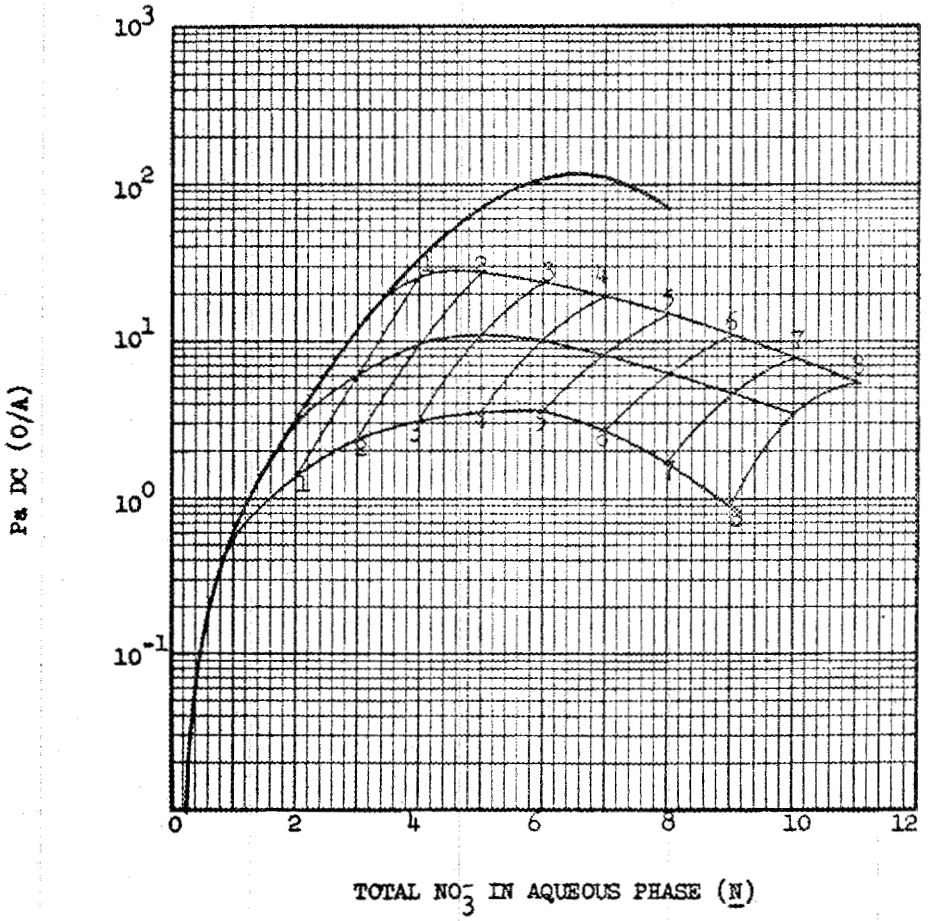

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Fig. 4.3.1-2 Distribution of Protactinium in DIPC - Aqueous Systems: Effect of Nitric Acid and Aluminum on Protactinium DC(O/A). The heavy line represents the protactinium DC(O/A) as a function of nitric acid concentration alone. Note: The light curve shows that, in a HNO_3-Al-Pa solution at a given total NO_3^- concentration, the maximum increase in the protactinium DC(O/A) is obtained with 1.0 N Al; e.g., at 4 N total NO_3^- the protactinium DC(O/A) was equivalent for the following solutions: (1) 1 N Al-3N H^+; (2) 2 N Al-2 N H^+; (3) 3 N Al-1 N H^+.

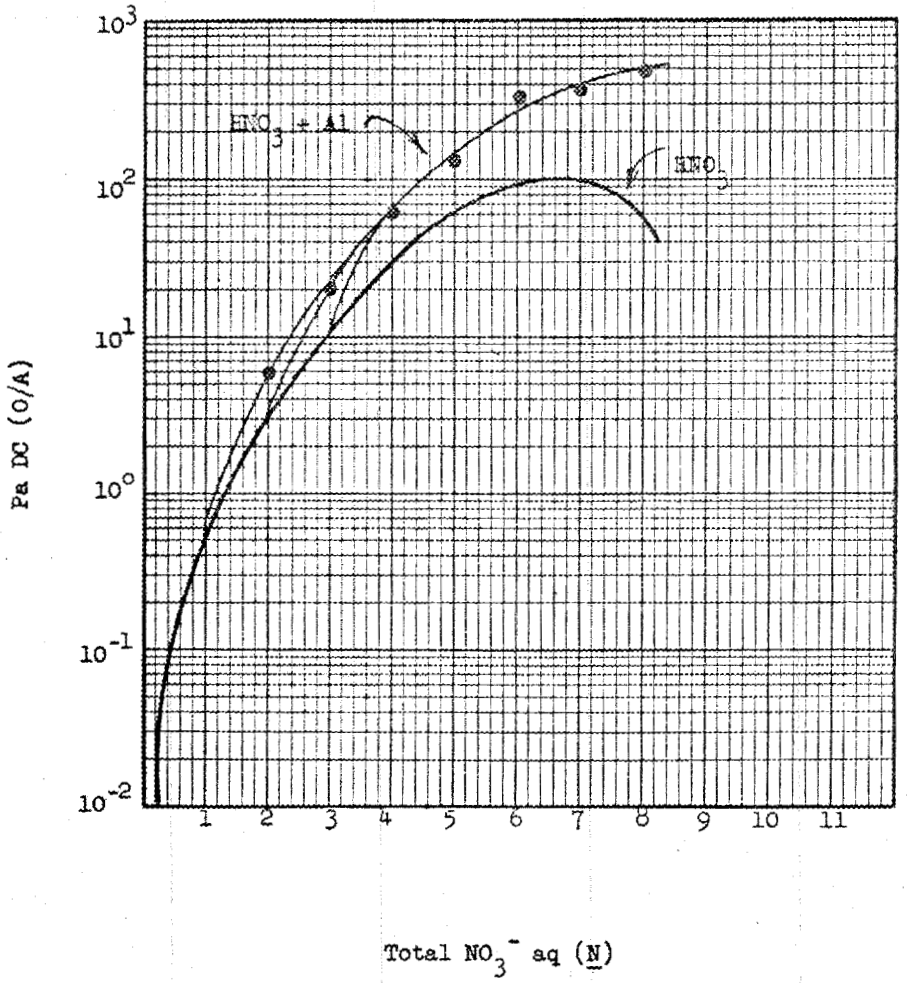

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Fig. 4.3.1-3 Distribution of Protactinium and Nitric Acid in Carbinol-Aqueous Systems. • DIPC; o DIBC

Conditions: Equal volumes of protactinium solutions of varying acidities and of carbinol equilibrated in a batch contactor; phases separated and analyzed

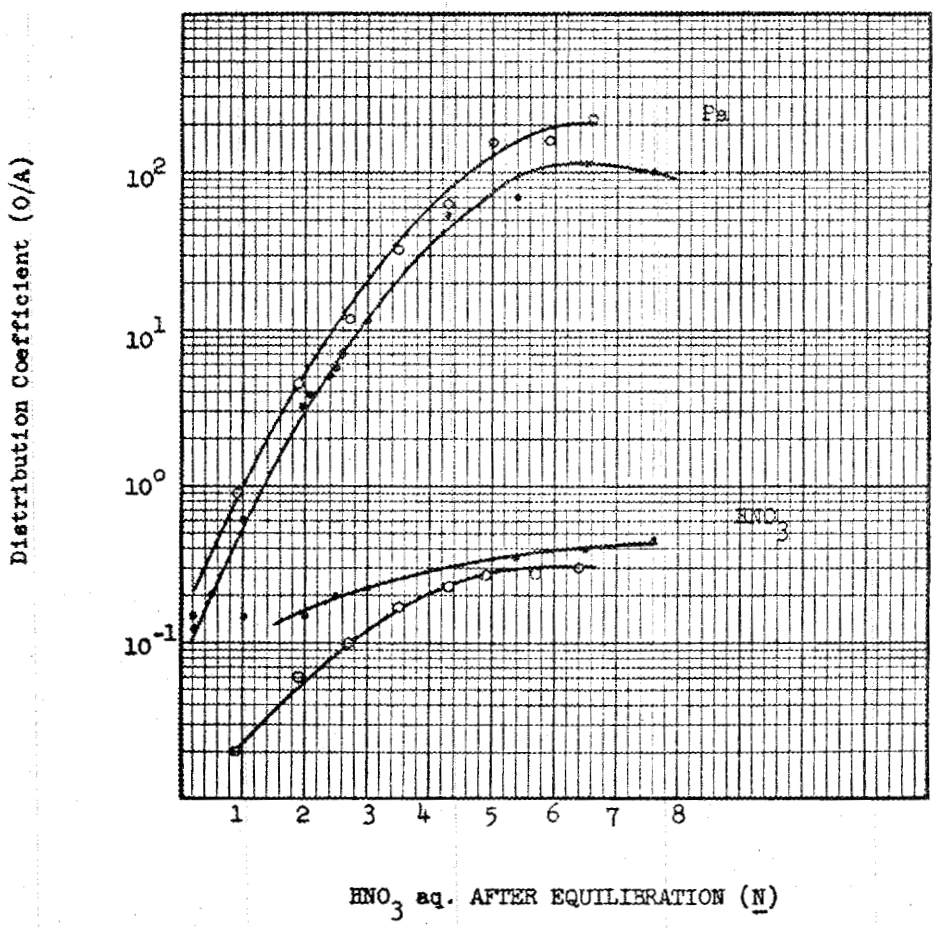

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Table 4.3.1-1

Extraction of Nitric Acid, Thorium, U^{233}, and Protactinium in DIPC:

Effect of HNO_3 and $Th(NO_3)_4$ Concentration on D.C.'s (O/A)

Conditions: equal volumes of aqueous solutions and DIPC contacted for 30 min; the phases separated and analyzed

Subheadings in table refer to concentrations in aqueous solutions prior to contact with DIPC

HNO_3 (N)	HNO_3 D.C. (O/A)			Th D.C. (O/A)			U^{233} D.C. (O/A)			Pa D.C. (O/A)		
	1 M Th	1.5 M Th	2 M Th	1 M Th	1.5 M Th	2 M Th	1 M Th	1.5 M Th	2 M Th	1 M Th	1.5 M Th	2 M Th
1.0	0.83	1.70	2.93	0.012	0.085	0.061	0.23	2.41	7.28	3.5	2.8	1
2.0	0.85	1.48	---	0.012	0.027	---	0.31	2.07	---	10	6.4	3.4
3.0	0.77	1.23	---	0.012	0.058	---	0.38	1.63	---	20	10	5.5

Table 4.3.1-2

Protactinium Distribution as a Function of Percentage of DIPC in Amsco

Conditions: equal volumes of organic (DIPC-Amsco) and aqueous solutions containing 3 N HNO_3, 3 N Th, and protactinium tracer contacted

DIPC in Organic Phase (%)	Pa D.C. (O/A)	
	Observed	Calculated[a]
100	33	(33)
50	1.5	16.5
10	0.01	3.3
2	0.0004	0.66

[a]Calculated on a probable basis of "complex" behavior.

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No work was done to give a specific comparison of the thorium and U^{233} distribution coefficient in DIPC and DIBC-aqueous systems; however a few batch countercurrent runs using DIBC were carried out to evaluate overall Thorex process conditions. Results indicated that somewhat higher thorium and U^{233} separation factors were feasible (see Table 4.2.1-1).

The effect of fluoride ion on protactinium distribution coefficients in carbinol-aqueous systems was investigated to determine whether the fluoride catalyst, added during thorium slug dissolution, exerted any influence in subsequent operations. The data collected in this study indicated that fluoride ion depressed the protactinium extraction markedly except in the presence of thorium. Aluminum inhibited the effect of fluoride to some extent. The data are given in Table 4.3.1-3.

4.3.2 Extraction in TBP (S. S. Brandt, A. T. Gresky)

Most of the work concerned with the extraction behavior of protactinium in TBP-aqueous systems has been of an empirical nature. The behavior of protactinium in dilute TBP-HNO_3 systems is described later in Figs. 5.1-10 and 11. The distribution coefficients of U^{233} were sufficiently different from those of thorium and protactinium to permit good separation of U^{233} from the other two.

The extractability of protactinium in more concentrated (30 to 50%) TBP-HNO_3 systems was considerably higher as shown in Fig. 4.3.2-1. The distribution coefficients of protactinium were of the same order of magnitude as those of thorium under similar conditions. Extraction of both constituents from the aqueous phase was possible, but subsequent separation of the two components by selective stripping was not feasible since changes in the distribution coefficients were essentially equivalent. Use of acid-deficient aluminum nitrate--TBP systems has presented the only feasible approach to thorium-protactinium separations. In this case, definite fractionation of protactinium forms was observed, and the most extractable species exhibited sufficiently low distribution coefficients in highly acid-deficient scrubbing solutions to permit good separation of protactinium from the thorium and uranium.

4.3.3 Adsorption on Silica Gel (S. S. Brandt)

The removal of protactinium from aqueous solutions, e.g., the Pa-F.P. stream from Thorex Flowsheet No. 2, has been studied by adsorption methods. This work has indicated that protactinium is readily adsorbed and eluted when silica gel is used as the adsorbent. Feed conditions studied to data have been (a) 0.5 M Al, 0.1 N HNO_3, and (b) 0.5 M Al, 0.1 N HNO_3 deficient.

Silica gel was chosen as the adsorbent because of its high affinity for rare earths, zirconium, niobium, and related elements.[54] Figure 4.3.3-1

Table 4.3.1-3

Effect of Fluoride on Protactinium D.C. (O/A) in DIPC-Aqueous Systems

Conditions: Equal volumes of organic and aqueous solutions contacted for 15 min; phases separated and analyzed

Subheadings in table refer to concentrations in aqueous solutions prior to contact

HNO_3 (N)	Pa D.C. (O/A)							
	H_2O		2 M Th		1 M Th		1 M Al	
	No F^-	0.05 N F^-	No F^-	0.05 N F^-	No F^-	0.05 N F^-	No F^-	0.05 N F^-
1	1.1	7×10^{-4}	1	1	4	3	4.8	0.7
2	---	---	3.4	3	12	10	---	---
3	20	6×10^{-3}	5.5	5.6	19	17	---	---

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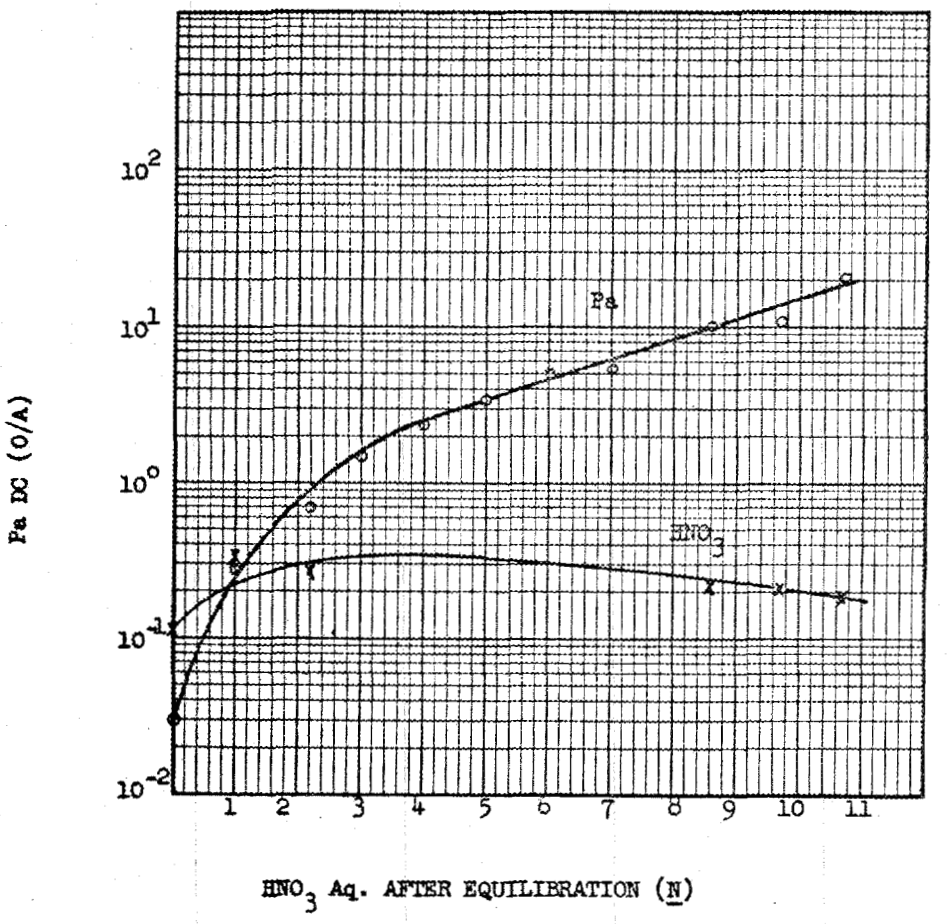
Fig. 4.3.2-1 Distribution of Protactinium in TBP-Aqueous Systems. In other experiments high thorium saturation of the TBP in thorium-HNO_3-TBP systems was not effective in decreasing the protactinium DC (O/A). Cerium, ruthenium, zirconium, and fission product DC's (O/A) are markedly reduced by high thorium-TBP saturation.

Conditions: Equal volumes of protactinium solutions of varying acidities and of organic solvent (50% TBP-50% Amsco) equilibrated in a batch contactor; phases separated and analyzed.



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shows the effect of flow rate on retention of protactinium on a silica gel column. The column dimensions and/or flow rates were not optimum, and only 85% of the protactinium was retained. A column of 1.0 cm diameter and 38 cm length, used in a subsequent test, adsorbed >99% of the protactinium at a flow rate of 1.3 ml/min/cm^2.

Most of the protactinium feed solutions used in evaluating the adsorption conditions have been acid deficient; however, a comparison of adsorption and elution characteristics under both acid-deficient and acidic conditions was made. While no difference was noted in adsorption, as measured by retention, there was a marked difference in the elution of protactinium with 4% oxalic acid solution. Figure 4.3.3-2 describes the comparative elution behavior of protactinium which had been adsorbed from (a) acidic and (b) acid-deficient feed solutions. The elution curve of the protactinium which was adsorbed from an acid-deficient feed indicated that it was adsorbed in a more distinct band than that adsorbed from an acidic feed. This observation was further evidence of the existence of two distinct forms of protactinium, as described in Sec. 4.3.4. The comparison thus favored a process system in which protactinium would be adsorbed from an acid-deficient feed, e.g., the Pa-F.P. stream of Thorex Flowsheet No. 2.

One test run was made to determine the protactinium capacity and breakthrough characteristics of a silica gel column. The test was run long enough to give results which were quite optimistic for process yield considerations. The data are plotted in Fig. 4.3.3-3. The breakthrough point at about 60 ml of feed per milliliter of adsorbent may be explained as the breakthrough of a particular species of protactinium, thought to be "ionic." The 4% oxalic acid elution curve from this capacity test shown in Fig. 4.3.3-4 is similar to curve No. 1, Fig. 4.3.3-2, which depicted the elution of protactinium adsorbed from an acid-deficient feed. More than 99% of the protactinium was eluted in a total volume equal to 1/16 of that of the original feed solution. Excluding the displacement volume and tail, 99% of the protactinium was eluted in a volume equal to 1/40 of that of the feed.

The effects of Thorex feed constituents, e.g., F^-, Al^{3+}, and Th^{4+} ions, on protactinium adsorption behavior were briefly investigated. Exploratory tests indicated no adverse effects of fluoride or aluminum ions. Although thorium did not affect protactinium adsorption, its presence was observed to complicate the elution step. Thorium remaining in the column at the end of adsorption and/or subsequent washing was observed to form occluding precipitates when contacted with the 4% oxalic acid eluting solution. Protactinium recovery and isolation from the Pa-F.P. streams would then perhaps be limited, or dependent on efficient and constant removal of thorium in the extraction cycle. Another practical consideration possibly limiting the use of silica gel columns involves the handling of cruds which will be present in Pa-F.P. streams. Pulse columns have allowed the elimination of undesirable filtration or centrifugation steps for feed clarification, so these streams will normally contain the cruds produced during slug dissolution (see Sec. 4.5.3, paragraph a).

Dwg. #15904

Fig. 4.3.3-1 Effect of Flow Rate on Silica Gel Adsorption of Protactinium.

Column: 0.25 cm i.d. x 30 cm
Adsorbent: 20-mesh silica gel
Feed: 0.5 M Al, 0.1 N acid deficient, 10^6 Pa β c/min/ml;
flow rate 1.6 to 10 ml/min/cm^2

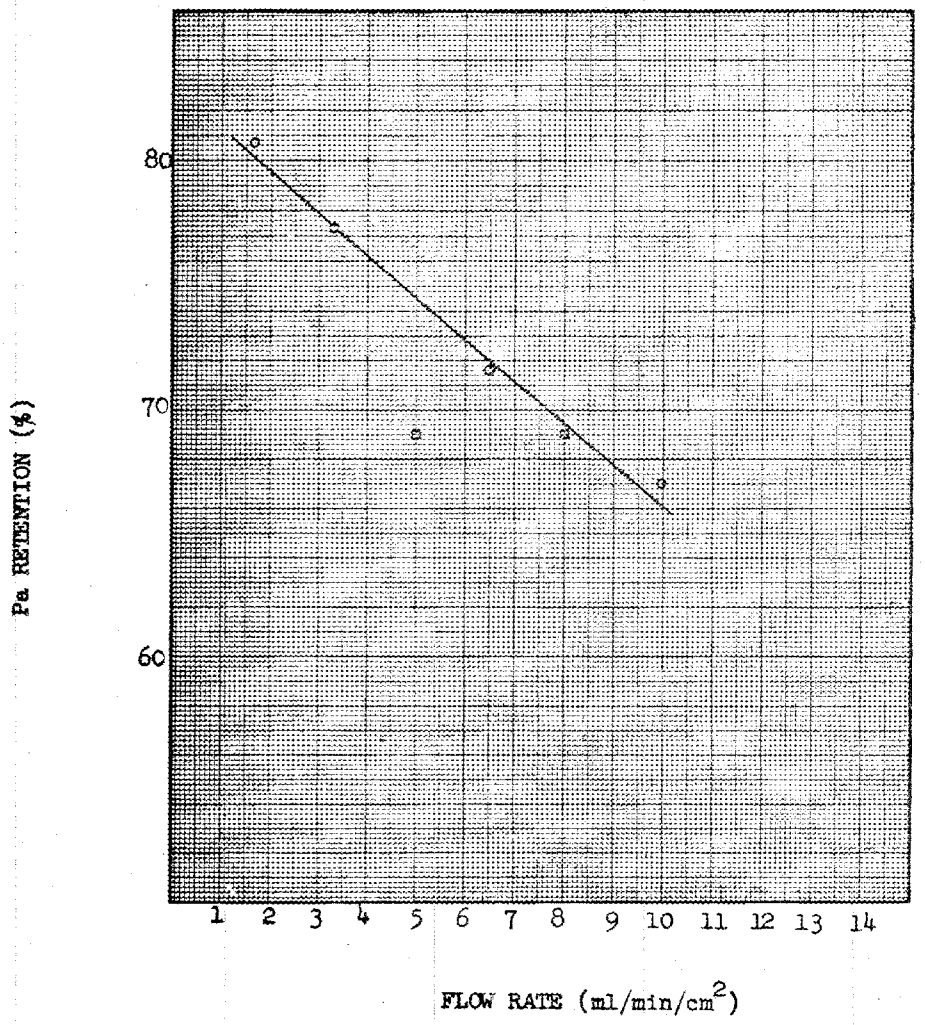

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Fig. 4.3.3-2 Elution of Protactinium from Silica Gel.
Note: Curves are apparently indicative (a) of varying equilibria of ionic-polymeric protactinium species in the adsorption feeds, and thus (b) of a sharper and later breakthrough of the polymeric fraction, suspected at higher levels in the acid-deficient feeds.

Conditions: Protactinium eluted from columns which had adsorbed >99% of the product from equal volumes of (1) an acid-deficient feed and (2) an acidic feed.
Column: 1 cm i.d. x 38 cm filled with 20-mesh silica gel
Adsorption Feed: (1) 0.5 M Al, 0.1 N HNO_3 deficient, 10^5 Pa β c/min/ml;
(2) 0.5 M Al, 0.1 N HNO_3, 10^5 Pa β c/min/ml; flow rate 1 ml/min
Elutriant: 4% oxalic acid; flow rate 1 ml/min
Temperature: 25°C

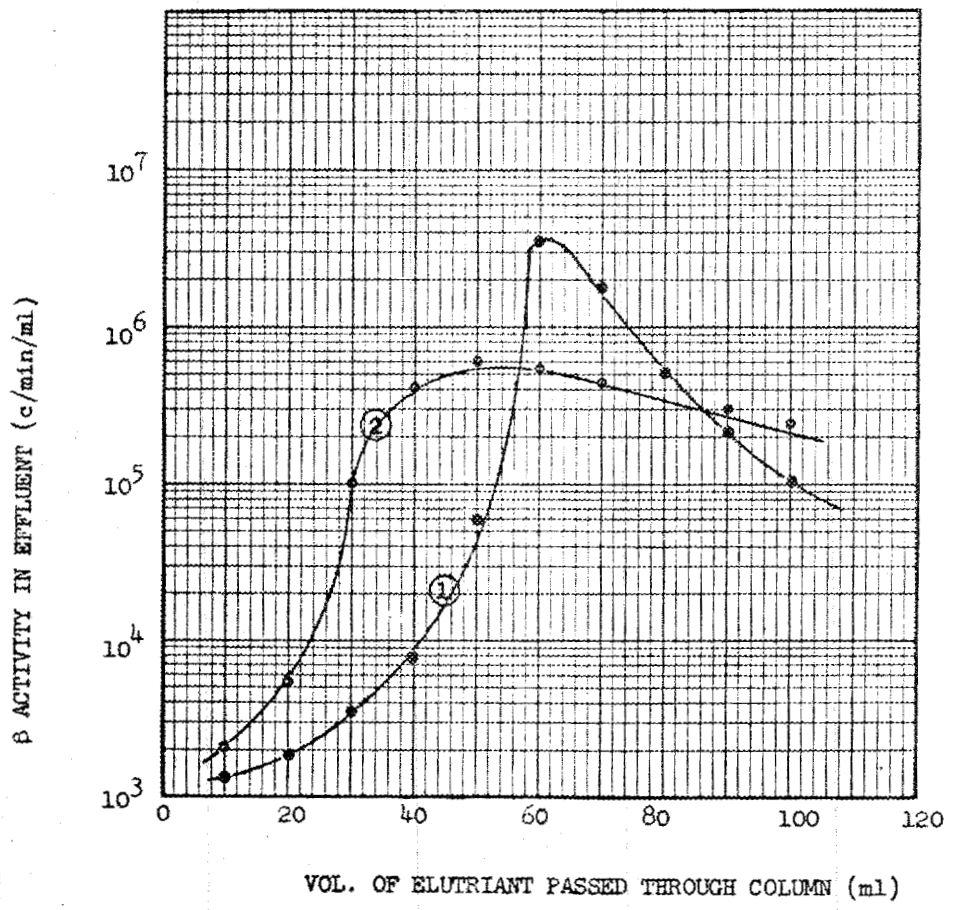

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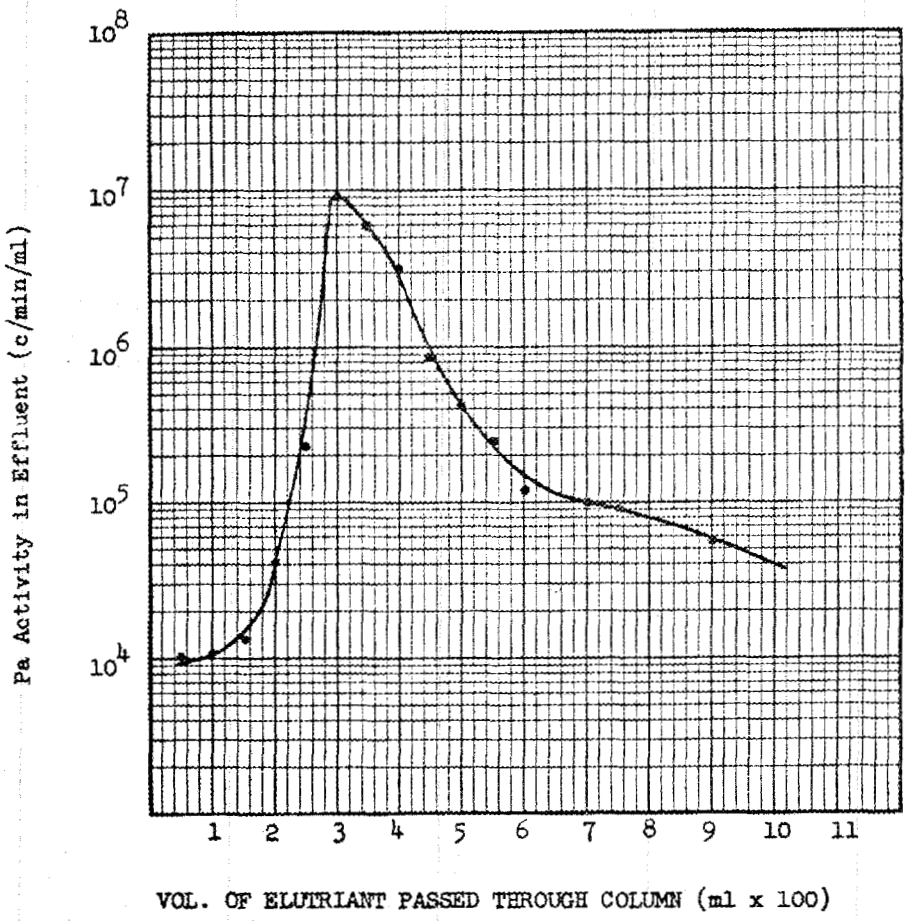
Fig. 4.3.3-3 Adsorption of Protactinium on Silica Gel

Column: 1 cm i.d. x 38 cm
Adsorbent: 20-mesh silica gel
Feed: 0.5 M Al, 0.1 N HNO_3 deficient, 4×10^5 Pa β c/min/ml; flow rate 1 ml/min, total of 9 liters of feed was passed through column
Temperature : 30°C

Conclusion: Breakthrough curve to ~80 throughputs was considered characteristic of an ionic fraction in the feed, whereas the remainder of the curve was characteristic of the polymeric fraction; this correlates with a 10% extraction of Pa observed in the TBP-0.1 N acid-deficient system.

Fig. 4.3.3-4 Elution of Protactinium from Silica Gel

Column: 1 cm i.d x 38 cm
Adsorbent: 20-mesh silica gel on which was adsorbed 90% of the protactinium taken from 9 liters of a feed having an activity of approximately 4×10^5 c/min/ml (see Fig. 4.3.3-3).*
Elutriant: 4% oxalic acid; flow rate 1.3 ml/min/cm^2
Temperature: 30°C



*The sharp breakthrough was considered characteristic of the adsorbed polymeric fraction of protactinium.

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In the Interim-23 plant process, a silica gel column inserted in the BP (U^{233} product) stream was effective in removal of the colloidal protactinium of that stream. The effectiveness of this column is shown in the following tabulation:

Column: 1 by 36 in., 20-mesh silica gel

Flow rate of solution: 9 ml/min/cm^2

Location of Sampling	Gross β	Decontamination Factor
BP stream above silica gel column	1.57×10^5	---
BP stream below silica gel column	6.82×10^3	23

4.3.4 Observed Chemical Behavior (S. S. Brandt, A. T. Gresky)

During the course of protactinium studies, evidence was obtained which indicated the existence of two distinct forms of the element, presumably ionic and polymeric species. These forms apparently exist in an equilibrium which can be shifted in either direction by proper choice of pH conditions. The ionic form, apparently highly extractable in TBP or carbinols, is favored by acidic conditions and exists almost completely at HNO_3 concentrations higher than 3 N. The polymeric form, which is probably a radiocolloid and is generally inextractable, is favored by conditions of low acidity or acid deficiency.

In a brief experiment to characterize polymerization of protactinium, solutions conducive to polymer formation were allowed to stand for several weeks to assure equilibrium and were then extracted with DIPC. Other portions of these solutions were acidified to 3 N HNO_3 and also extracted. The protactinium tracer used in these experiments had been previously stored in a 7 N HNO_3 solution to maintain the ionic species. Results indicated that the polymer, if formed, can easily be shifted to the ionic species by increasing the acidity as follows:

Feed conditions		Pa D.C. (O/A)		
N HNO_3	N $Al(NO_3)_3$	Aged sample	Acidified sample	Control
0	0	0.1	13.9	14
1	0	1	14.5	14
1	1	5	27.7	23

In another experiment, Th-Al-Pa solutions at varying acidities were each extracted with a fourfold volume of 45% TBP, 15% benzene, and 40% Amsco. Following this, each aqueous layer was immediately extracted a second time with an additional fourfold volume of the TBP solution. The results are listed in the following tabulation:

Feed conditions			Pa D.C. (O/A)		Th D.C. (O/A)	
Th (M)	Al (M)	HNO_3 (N)	1st Extraction	2nd Extraction	1st Extraction	2nd Extraction
1.5	0.5	+1.5	0.085	0.085	2.1	5.0
1.5	0.5	+1.0	0.0365	0.0306	2.0	4.1
1.5	0.5	+0.5	0.0114[a]	0.0095	2.3	4.0
1.5	0.5	0.0	0.037	0.0002	1.6	3.2
1.5	0.5	-0.15	0.03	0.00003	1.6	1.6
1.5	0.5	-0.30	0.029	0.00002	1.2	1.1[b]
1.5	0.5	-0.45	0.031	0.00002	1.1	1.0[b]

[a]Doubtful, not rechecked.
[b]Precipitation occurred in aqueous phase.

The data indicate that (a) the first extraction removed the ionic species from the aqueous phase, and (b) left an unbalanced equilibrium in the aqueous phase. In acidic conditions the equilibrium was rapidly regained, as shown by the equivalent distribution coefficients for the second extraction of the acid solutions. In neutral or acid-deficient conditions, after removal of the ionic species, the equilibrium was not regained. The lower protactinium extractability observed at 0.5 N HNO_3 was not rechecked. The data also indicate that, in acidic systems, the protactinium distribution was not markedly affected by thorium saturation of the TBP.

4.4 Fission Product Separation (A. T. Gresky)

The primary problem in β-γ decontamination of the U^{233} and Th^{232} products in the Thorex process has been associated with the usually limiting nature of the protactinium activity, since in short-cooled irradiated thorium the high levels of Pa^{233} essentially minimize the fission product activity levels. The protactinium separation techniques and gross β-γ decontamination have therefore received the greatest part of laboratory study to date. The behavior of individual fission products has been investigated to only a limited extent in various process steps, owing in part to the tedious and difficult analytical

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problems of radiochemical separations of the elements protactinium, niobium, and zirconium as found in certain process streams. A typical radiochemical analysis of activities, after about three months' cooling, was 87.3% Pa, 10.7% total rare earths, 1.2% Ru, 0.5% Nb, 0.3% Zr.

4.4.1 Extraction in Carbinols (A. T. Gresky)

Problems in radiochemical analysis have limited precise determinations of fission product distribution; however, Table 4.4.1-1 indicates the order of extractability of the limiting fission products in diisopropyl and diisobutyl carbinols. In general,[1] the fission products zirconium and ruthenium were most extractable in diisopropyl carbinol, and (2) apparent fractionation, especially of ruthenium and zirconium, was observable by countercurrent separation (see stages E-1 through S-6 in Table 4.4.1-1). Data on niobium were questionable. Total rare earths, ruthenium, and zirconium were less extractable in the diisobutyl carbinol, and niobium appeared as the most extractable species. The data in Table 4.4.1-1, taken from the protactinium extraction step of Thorex Flowsheet No. 1, show the observed F.P. D.C.'s(O/A) in the extraction (E) and scrubbing (S) sections of the countercurrent unit.

4.4.2 Extraction in Dilute TBP Systems (A. T. Gresky)

The distribution of all fission products into 1.5% TBP was very low, as observed in countercurrent studies of the Interim-23 process. However, certain small fractions of Zr and Nb, apparently entrained in the diluent, were observed to contaminate the product stream and the waste solvent. Observed D.C.'s (O/A) in the extraction, scrubbing, and stripping sections of the countercurrent unit are given in Table 4.4.2-1.

4.4.3 Extraction in Concentrated TBP Systems (A. T. Gresky)

Fission product extraction in concentrated TBP is considerably dependent on solvent saturation, aqueous salt strength, and nitric acid concentration. The total rare earth and ruthenium distribution coefficients were most markedly reduced by thorium saturation of the solvent. The distribution coefficients of zirconium appeared to be most strongly affected by nitric acid, in the absence of solvent saturation, and will probably constitute the limiting fission product contaminant in the Thorex process. Niobium appears to be essentially nonextractable. The distribution data from extraction and scrubbing sections in countercurrent flowsheet demonstrations are shown in Table 4.4.3-1. The high extractability of total rare earths, ruthenium, and zirconium in the absence of thorium or TBP saturation (stage E-5, 45% TBP) should be noted. Variations in acidity are seen to have a negligible effect on total rare earth distribution (stage E-5). Table 4.4.3-1 records distribution data from extraction and scrubbing sections in countercurrent flowsheet demonstrations.

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Table 4.4.1-1

Order of Extractability of Limiting Fission Products in DIPC and DIBC

Equil. conc. (aq. phase)	Solvent	F.P. D.C.'s (O/A)			
		TRE	Ru	Zr	Nb
1.36 M Th, 3.0 N HNO_3 (E-1)	DIPC	<0.004	0.2	3.0	0.03(?)
0.1 M Th, 3.6 N HNO_3 (S-2)	DIPC	<0.01	1.8	---	---
3.0 N HNO_3 (S-4)	DIPC	---	3.3	11.0	---
2.3 N HNO_3 (S-6)	DIPC	---	6.5	---	0.5
1.25 M Th, 0.4 M Al, 2.6 N HNO_3 (E-1)	DIBC	0.0002	0.05	0.32	6.0
3.28 N HNO_3 (S-4)	DIBC	<0.01	1.0	0.5	---

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Table 4.4.2-1

Observed Distribution Coefficients of Fission Products in Countercurrent Unit

Solvent: 1.5% TBP

Equil. conc. (aq. phase)	F.P. D.C.'s (O/A)			
	TRE	Ru	Zr	Nb
1.5 M Th, 0.5 M Al, 1.0 N HNO_3 (E-1)	0.00003	<0.02	0.01	0.0002
1.0 M $Al(NO_3)_3$, neut. (Sc-1)	---	---	0.01	0.001
0.05 N HNO_3 (St-1)	---	---	1.4	0.6
0.05 N HNO_3 (St-7)	---	---	2.1	2.9

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Table 4.4.3-1

Distribution Data from Countercurrent Flowsheet Demonstrations

Equil. conc. (aq. phase)	TBP (%)	D.C. (O/A)			
		TRE	Ru	Zr	Nb
0.5 M Th, 0.6 M Al, 2.0 N HNO_3 (E-1)	45	0.006	0.012	0.13	0.02
0.02 M Th, 0.6 M Al, 3.0 N HNO_3 (E-3)	45	0.104	0.06	0.2	0.02
0.6 M Al, 1.5 N HNO_3 (E-5)	45	0.61	0.42	3.45	0.03
0.2 M Th, 1.0 M Al, 0.2 N HNO_3 (S-2)	45	0.006	0.14	1.15	0.7
0.35 M Th, 0.5 M Al, 0.1 N HNO_3 (E-1)	41	0.01	0.03	0.26	0.07
0.05 M Al, 0.03 N HNO_3 (E-5)	41	0.6	0.2	0.04	0.003
0.5 M Th, 0.6 M Al, 0.6 HNO_3-def (S-6)	(activity too low for det'n)				

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4.5 Associated Problems in the Development (M. R. Bennett, A. T. Gresky, W. T. McDuffee)

Certain general features and problems associated with the concept of the Thorex process are presented in the following paragraphs. Some of these problems have received cursory laboratory study, and data are presented. Others are discussed to indicate the degree of prior attention by other groups or the necessity for future laboratory study.

4.5.1 Nitric Acid Dissolution of Fuel (M. R. Bennett)

The dissolution of thorium fuel units is the initial step of the Thorex process for separation and recovery of U^{233}, Pa^{233}, and thorium. The thorium metal, normally in the form of aluminum-jacketed cylindrical slugs, is irradiated according to the nuclear reaction

$$Th^{232}(n, \gamma)Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233}.$$

After a cooling period, varying from 30 to 90 days, the metal is charged to a dissolver, and the dissolution is carried out on a batch basis. (A more unusual process for continuous dissolution of thorium metal, and/or jacketed slugs, is now under study by the Unit Operations group and appears to offer worthwhile engineering advantages.) The present methods for slug dissolution include: (a) a two-step process for (1) removal of the aluminum jackets in a 10% NaOH—20% $NaNO_3$ solution and (2) dissolution of the thorium metal in 13.0 M HNO_3 containing 0.075 M F^- ion; or (b) a one-step process in which the jacketed slugs are dissolved simultaneously in the HNO_3 solution containing 0.075 M F^- and 0.005 M Hg^{2+} ions. The latter method, which allows utilization of the dissolved aluminum as a "salting agent" in the Thorex process and permits simpler dissolving techniques, is the procedure currently in use. The slugs are charged into the dissolver and reacted at the boiling point for about 8 hr before dissolution is complete, the product solution being approximately 1.0 M in HNO_3, 2.0 M in $Th(NO_3)_4$, and 0.7 M in $Al(NO_3)_3$. It is then transferred to another tank for final adjustment to Thorex feed specifications. The gases evolved during the thorium dissolution consist mainly of N_2 and NO, with smaller amounts of NO_2, N_2O, and H_2. The total off-gas volume is about 50 liters per kilogram of thorium. Most of the NO_2 evolved is reconverted to HNO_3 and HNO_2 by reaction with H_2O in a downdraft condenser and is refluxed to the dissolver.[55]

4.5.2 Distribution of Beryllium (M. R. Bennett)

The distribution of beryllium in the Thorex separation process was of considerable interest, since beryllium becomes a neutron source by the reactions

$$Be^9(\alpha,\underline{n})C^{12}, \text{ or } Be^9(\gamma,\underline{n})Be^8(2\alpha).$$

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Greater than 10^7 overall beryllium decontamination from U^{233} was considered to be of prime importance, and a separation factor of at least 10^5 over the entire solvent extraction flowsheet was considered mandatory. Tolerance limits for light element impurities in U^{233} products were pointed out in Sec. 3.0 and Fig. 3.0-2.

Feed solutions were spiked with 0.70 g of beryllium per liter (i.e., about 2 g per kilogram of thorium), and its distribution was followed over each of the steps in Thorex process No. 2. Spectrographic analyses of organic and aqueous phases at the feed plate of the thorium extraction cycle indicated a beryllium D.C. (O/A) of about 1.0×10^{-4}. No beryllium was detectable in the organic product from this step. Beryllium in both the aqueous and organic streams of the "preferential strip" step was reported at the minimum detectable limit of 3.0×10^{-5} g/liter. This same limit was found in the final U^{233} product solution from the stripping step before and after a fifty-fold volume reduction. This allowed quotation of an overall separation factor for beryllium of 5×10^5 or greater. (An additional separation factor of 20 was reported from the peroxide precipitation in the U^{233}-isolation step, which indicated that an overall D.F. of 10^7 or higher is possible in the proposed process.)

4.5.3 Crud Problems (A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, J. E. Savolainen)

Several types of crud problems have been encountered during development of the Thorex process, e.g., those associated with the (a) dissolution of metal slugs, (b) decomposition of Amsco, (c) decomposition of TBP, and (d) use of commercial $Th(NO_3)_4 \cdot 4H_2O$ salt in process studies. The behavior of these cruds and the manner in which they affect the process are given in the following paragraphs.

(a) Filtered cruds from metal dissolver solutions contain silicon, thorium, and corrosion products. The material is made up of gray crystalline and siliceous matter, which tends to plug filters easily. The sources of these insolubles are probably both metallurgical contaminants and corrosion products. Filtration of such "hot" solids is an undesirable process feature and is not proposed for plant operations using pulse columns, so the bulk of these cruds will go with the hot aqueous waste stream following thorium extraction. Certain colloidal, surface-active fractions will probably contribute to the usual column interfacial cruds observed in solvent extraction processing. The cruds in the aqueous waste will contribute to problems in a proposed silica gel adsorption step for protactinium recovery, and the interfacial fractions will likely require operational column control and use of de-entrainers or phase separators.

(b) Organic addition compounds and decomposition products of the aliphatic-aromatic diluent, i.e., Amsco, may be formed in the process by oxidation, nitration, and/or nitrite addition in the presence of nitric and nitrous

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acids. Substituted branched-chain aromatic compounds may be suspected as the most unstable diluent fractions which would contribute to a source of these crud formers. Some of these materials can presumably form metal-organic compounds, dye-like compounds, and soaps, which can be removed from the organic phase by washing with caustic solutions or by adsorption on silica gel. Considerable amounts of interfacial, emulsifying cruds have been observed to collect during caustic washing of used TBP-Amsco solvent. Nitro compounds of Amsco were found to contribute to the extraction and retention of activities, as well as to crud formation, so a preconditioning of the diluent to increase its stability toward process conditions has been proposed (see Sec. 4.5.5).

(c) The cruds associated with TBP decomposition products were discussed at length in Secs. 3.5.9 and 4.1.1. Studies of these cruds have emphasized the necessity for judicious consideration of solvent handling with respect to (1) efficient solvent clean-up procedures, and (2) hydrolysis rate effects during TBP hold-up, either in interim storage, in process, or in emergency shutdown of columns. Cruds of this type are formed from strong compounds or complexes with the heavy metals, e.g., thorium, and can contribute to process emulsion formation and product losses.

(d) Cruds associated with the commercial thorium nitrate tetrahydrate salt (mantle grade "TNT") were observed to create drastic problems during early Unit Operations studies of pulse column operation. The difficulties were traced to the use of certain batches of the salt which contained excessive impurities, especially with respect to silicates and phosphates. In these studies, which were concerned with testing the "acid-deficient" Thorex flowsheet, it appeared that soluble or colloidal silicates caused emulsions and the phosphates caused an amorphous precipitation of thorium salts. The difficulties were manifest in the extraction section, where low aqueous thorium concentration and a pH of about 2.5 were characteristic, and contributed to early column flooding or inoperability. Investigation of this problem revealed that the process would "tolerate" the use of TNT's with silicate at about 200 ppm and phosphate at about 100 ppm. Analyses of a suitable and an unsuitable sample are shown below:

Sample	Analysis (ppm of TNT)		Mole Ratio, SiO_2/PO_4
	Silicate	Phosphate	
MG-G	180	75	4/1
MG-B	400	530	5/4

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Restoration of the poor-grade MG-B material, for feasible use in process studies, was accomplished by two different methods: (1) heating the dissolved salt at 110 to 120°C, in the presence of high $Th(NO_3)_4$ and/or HNO_3 concentrations, to dehydrate the soluble silicic acid or silicates and thus eliminate their emulsifying properties; it is pointed out that proposed dissolution procedures would duplicate this condition and thus reduce the deleterious effects of any such materials from metal dissolvings; and (2) extraction of experimental feed solutions (1.5 M Th, 0.5 M Al, 0.5 N HNO_3) with about one-third volume of diisobutyl carbinol—1.0 N HNO_3 was generally sufficient to remove the emulsifying siliceous material. Addition to the feed of ferric ion, in a five- to tenfold excess of the phosphate concentration, was found to complex the phosphates and prevent thorium precipitation in the process streams.

4.5.4 Waste Problems (A. T. Gresky, W. T. McDuffee)

The philosophy of waste disposal, with considerations of health, safety and economy, necessarily affects all approaches to chemical separations processes associated with radioactive materials. During the Thorex process development the problem of disposing of "hot" liquid waste containing solids arose. A compromise has seemed necessary between storage of (a) large volumes of "cold," coating-removal, $NaAlO_2$ wastes with small volumes of radioactive waste concentrates, and (b) no coating-removal wastes with large volumes of radioactive, solids-containing wastes. This compromise is illustrated by (a) an alternate proposal of Thorex Flowsheet No. 1a, as shown in Sec. 5.2, paragraph d, which used nitric acid alone for "salting," as opposed to (b) Thorex Flowsheet No. 2, which required aluminum nitrate salting. A satisfactory balance of waste handling features, with chemical and engineering feasibility, was thus a first-order problem in choosing a final process approach.

The chemical concepts which affected "hot" liquid waste disposal in Thorex process 1a were involved primarily with the dissolving method, which would require separate dissolution of the aluminum jackets, e.g., in a sodium hydroxide—sodium nitrate solution, prior to nitric acid dissolving of thorium metal for the process feed preparation. A rather voluminous amount of cold aluminum-sodium aqueous wastes would thus be produced; however, with excess nitric acid supplying the needed salting strength for subsequent hot extraction steps, final volume reduction and nitric acid recovery would make possible the production of relatively small storage volumes of fission product wastes, as in the Purex process.

The Thorex No. 2 process, on the other hand, would make use of a simultaneous dissolution of aluminum jackets and thorium slugs in nitric acid, thus eliminating the voluminous cold aluminum-sodium wastes but requiring storage or processing of hot aluminum nitrate wastes.

Owing to the more favorable chemical and operational features of the No. 2 process, as discussed in Sec. 2.0, the possibilities for decontamination and

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recovery of aluminum nitrate are being considered as process adjuncts in order to alleviate the hot waste problems. Methods may involve (1) an alternate protactinium recovery step in which additional fission product activities would be extracted from the IAW stream, e.g., with TBP, (2) an ion-exchange step for aluminum separation and decontamination, (3) an aluminum crystallization and concentration step, e.g., from concentrated HNO_3, or (4) a combination of two or three these methods.

In addition to the problems of liquid waste disposal, the removal of gaseous fission product and nitrogen oxides from dissolver off-gases may require some study. A unit to perform this type of function in the Purex process will be tested and may be adaptable to Thorex requirements.

4.5.5 Preconditioning Diluent Amsco (W. T. McDuffee)

Preconditioning of the diluent Amsco, using nitric acid and silica gel treatment, has been found advantageous in obtaining a diluent which is more stable toward nitric acid in process streams. Such treatment also offers advantages in reducing the tendency of β activity to enter the diluent and in rendering the organic solutions more easily stripped free of β activity.

During the plant operation of the Interim-23 process, which used a 1.5% TBP-Amsco solution as the extractant, the organic phase was observed to discolor during runs. Also, after stripping out the U^{233} the extractant was found to retain β and γ activities to an objectionable extent. In another instance, when pure Amsco diluent was used as a displacing medium for a hot feed of high β and γ activities, the diluent quickly became strongly contaminated, although very little mixing of the organic and aqueous phases had occurred.

Amsco diluent is a complex mixture consisting principally of aliphatic hydrocarbons, with small percentages of aromatic and olefinic compounds. The latter compounds are quite reactive toward nitric acid solutions, e.g., Thorex feeds, which may act as oxidizing, nitriting, or nitrating agents. The products of the reaction of nitric acid and Amsco have been found to be nitrogen compounds ($R\text{-}NO_2$) and organic acids[45] when accelerated tests were conducted with 6 N HNO_3 at 70°C.

There was evidence that the presence of nitro compounds in the Amsco diluent increased the extraction of β activity. The difficulty of stripping the activity from the diluent was also enhanced, as shown in Table 4.5.5-1. This table shows that pretreatment of Amsco diluent with 8 M HNO_3 caused increases in the amount of β activity picked up and held through the scrubbing and stripping operations.

Certain data[56] have indicated that washing used 1.5% TBP extractant with 0.1 M Na_2CO_3 improved the β D.F.'s obtained in the subsequent run. This

Table 4.5.5-1

Preconditioning of Amsco Diluent: Effect of Nitric Acid and/or Silica Gel Treatment on Extraction and Retention of β Activity

Conditions: Amsco was pretreated by: (A) one-fifth volumes of 0.0 N, 8 N, 12 N, or 16 N HNO_3, followed by washing with one-fifth volumes of H_2O, 1.0 M NaOH, and 0.1 M Na_2CO_3; and (B) portions of the above were then passed through 45-cm columns of 20-mesh silica gel at a rate of about 2.0 ml/min/cm^2; aqueous feeds, 1.5 M Th—0.5 M Al—1.0 N HNO_3 containing about 10^9 β c/min/ml, were then (1) equilibrated with the Amsco, which was then scrubbed with three passes of (2a) 1.0 M $Al(NO_3)_3$ or (2b) 1 M $Al(NO_3)_3$, 1.4 N acid-deficient, and then (3) stripped with one pass of 0.05 N HNO_3; gross β activity in the organic phase was determined after (1), (2), and (3)

HNO_3 (N)	A					B				
	1	a		b		1	a		b	
		2	3	2	3		2	3	2	3
0.0	6.9×10^3	650	350	100	50	220	380	10	10	0
8.0	6.3×10^5	525	245	445	255	1300	450	20	65	20
12.0	1.6×10^4	260	45	45	55	780	430	45	45	15
16.0	4.6×10^4	2100	765	65	175	55	270	215	50	15

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would indicate presumably that some compound was removed which interfered with the β decontamination. Preliminary data indicate that the presence of HNO_2 accelerates the attack of HNO_3 solutions on Amsco. Treatment of Amsco with 8 M HNO_3 in the presence of small amounts of HNO_2 and 0.5% sulfamic acid indicated that sulfamic acid was not an effective inhibitor of the HNO_3 attack.

Silica gel exhibits a marked tendency to selectively adsorb the olefins and aromatics. Amsco which had been passed through a bed of silica gel showed much improved characteristics. On contact with β-active feeds, the diluent absorbed less activity, and scrubbing and stripping were more efficient (see Table 4.5.5-1). The data show that, regardless of what acid pretreatment the diluent received, the silica gel treatment improved it still further. However, the best results were obtained with diluent which had received only the silica gel treatment.

Thus, it appears that the best method of preconditioning Amsco may consist of treatment with silica gel. The most economical silica gel/Amsco ratios have not yet been determined, but it is felt that effective results can be obtained with low ratios. The data in Table 4.5.5-1 indicate that the deterioration products of the Amsco resulting from HNO_3 attack are also removed by silica gel. It appears that a more stable and effective extractant can be obtained by preconditioning the diluent with silica gel prior to solvent make-up and thereafter treating the used TBP-Amsco solutions with 1.0 M NaOH containing a small quantity of silica gel (about 0.5 g of 8-μ silica gel per liter of sodium hydroxide).

4.5.6 Corrosion Problems (A. T. Gresky)

Owing to the necessity for fluoride catalysis in the nitric acid dissolution of currently used thorium fuels, definite problems of corrosion associated with the very active fluoride ion in processing equipment and storage facilities are anticipated. The extent of the problem with respect to fluoride distribution and concentrations in the process systems will be investigated by the Laboratory group, while materials and equipment corrosion tests will be carried out by the Unit Operations group. Corrosion-depressant effects of thorium ion, aluminum ions, and/or acid-deficient conditions in the process solutions are variables expected to be studied.

5.0 Discussion of Chemical Flowsheets (A. T. Gresky, W. T. McDuffee, S. S. Brandt, M. R. Bennett)

The primary features, present status, and diagrams of the three flowsheets, i.e., Interim-23, Thorex No. 1, and Thorex No. 2, were presented and discussed briefly in Sec. 2.0 of this report. Further critical details and comments concerning each of the process steps are presented below, in outline.

5.1 Interim-23 Process (see Fig. 2.0-1) (A. T. Gresky)

(a) Purpose:

An interim development to provide recovery and decontamination of an emergency requirement of approximately 1500 g of U^{233} from short-cooled, Hanford-irradiated thorium slugs; thorium and protactinium (as aqueous wastes) were to be stored for future recovery, pending development of a Thorex process.

(b) Basic Features:

(1) A simple, rapid slug dissolution and feed preparation; (2) preferential extraction and decontamination of U^{233} from thorium, protactinium, and fission products by use of an acidic thorium-aluminum feed with wide specification limits, a dilute TBP extractant, a neutral aluminum nitrate scrub solution, and a system operable in pulse column contactors; (3) efficient product stripping and concentration by a dilute nitric acid strip system; (4) additional protactinium and fission product decontamination by silica gel adsorption; and (5) additional thorium decontamination and product isolation by ion exchange on Dowex-50 resin. Other primary features of the process involved (6) a preconditioning of the Amsco diluent with nitric acid; and (7) used-solvent recovery and decontamination by treatment with sodium hydroxide and silica gel.

(c) Process Details:

(1) Solvent: 1.5% TBP in an Amsco 123-15 diluent, which was found optimum for good U^{233} recovery and separation from thorium. The Amsco was preconditioned for higher stability to process acidities by initial contact with 10 N HNO_3 in order to reduce crud formation in extraction columns and/or solvent recovery steps. The TBP-Amsco solvent was pretreated and recovered by washing with one one-fifth volume of 1.0 M NaOH (to form sodium salts of the decomposition products MBP and DBP) containing 0.5 g of 8-μ silica gel per liter (to adsorb nitrated organic compounds and/or colloidal activities) and three one-fifth volumes of 0.1 M NaOH or Na_2CO_3 (to strip MBP-DBP salts, silica gel, and fission products from the organic phase). Determination of the percentage of TBP involved a H^+ titration of the organic phase previously saturated to TBP·HNO_3 by equilibration with 8 N HNO_3 (see Figs. 5.1-1 through 6).

(2) Feed solution: 60- to 90-day cooled neutron-irradiated unbonded aluminum-jacketed thorium slugs (about 3 moles of thorium per mole of aluminum) were charged in 200% thorium excess and dissolved at 120 to 115°C in 13 N HNO_3 (5 moles per mole of thorium and 3 moles per mole of aluminum), 0.075 M F^- (thorium reaction catalyst), and 0.005 M Hg^{2+} (aluminum reaction catalyst).

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Dwg. #15908

Fig. 5.1-1 Distribution Coefficients (O/A) of Uranium and Thorium, in Dilute TBP-Thorium System, As Functions of Percentage of TBP. Sharply decreasing uranium and thorium extraction D.C.'s (O/A) below 1.5% TBP may be a result of slower ionic diffusion rates. Contact times were standardized at about 3 min.

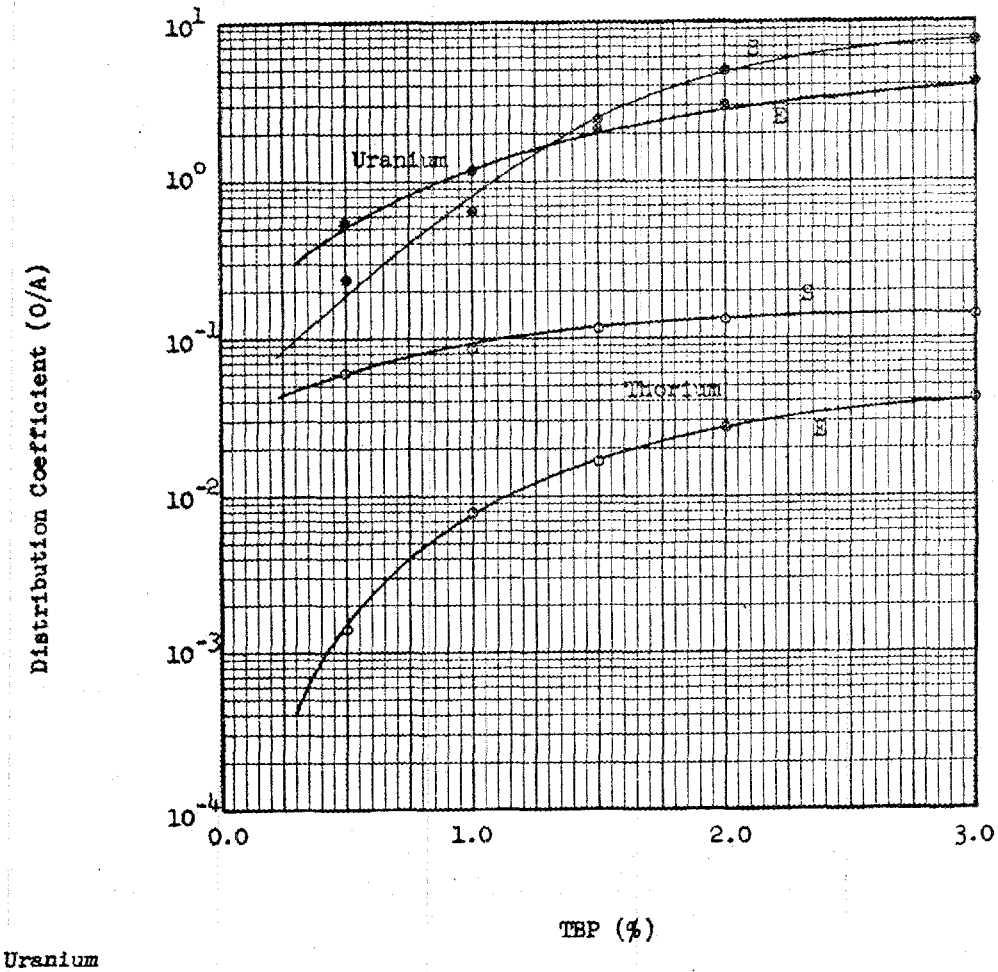
Feed: 0.75 M Th, 0.75 M Al, 0.38 N HNO_3, 1.05 g of U per liter

Scrub: 1.0 M $Al(NO_3)$, 0.0 N HNO_3

Organic Phase: 0.5 to 3.0% TBP in Amsco, neutral

Feed/scrub/organic countercurrent extraction flow ratio = 4/1/5

8 extraction, 6 scrub stages, 2.5 Vol. changes



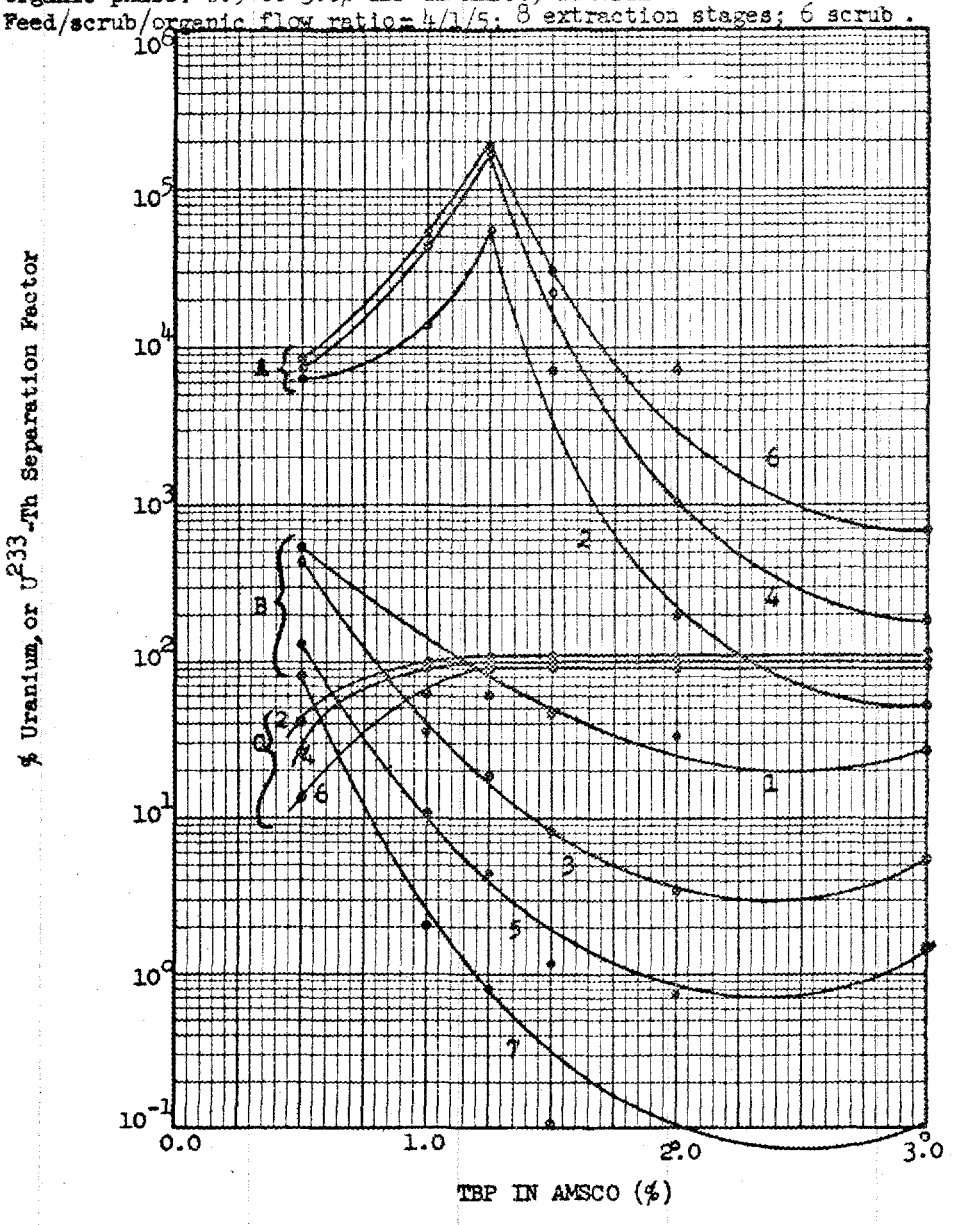
● Uranium
o Thorium
E Extraction Section
S Scrubbing Section

Dwg. #15909

Fig. 5.1-2 U^{233}-Th Separation Factors and U^{233} Recovery and/or Loss, as Functions of Percent TBP and Contact Stages.

(A) U^{233}-Th S.F. at scrub stages 2,4, and 6 (6 = product stream);
(B) % of feed U (aq) at extraction stages 1, 3, 5, and 7 (1 = feed plate);
(C) % of feed U (org) at scrub stages 2,4, and 6; these show >99% recovery with solvents 1.5 thru 3.0% TBP, high losses in 0.5 and 1.0% TBP.

Countercurrent extractions, 6 separate runs; 2.5 vol. changes.
Feed: 0.75 M Th, 0.75 M Al, 0.38 M HNO_3, 1.05 g of U per liter
Scrub: 1.0 M Al $(NO_3)_3$, neutral
Organic phase: 0.5 to 3.0% TBP in Amsco, neutral
Feed/scrub/organic flow ratio = 4/1/5; 8 extraction stages; 6 scrub.



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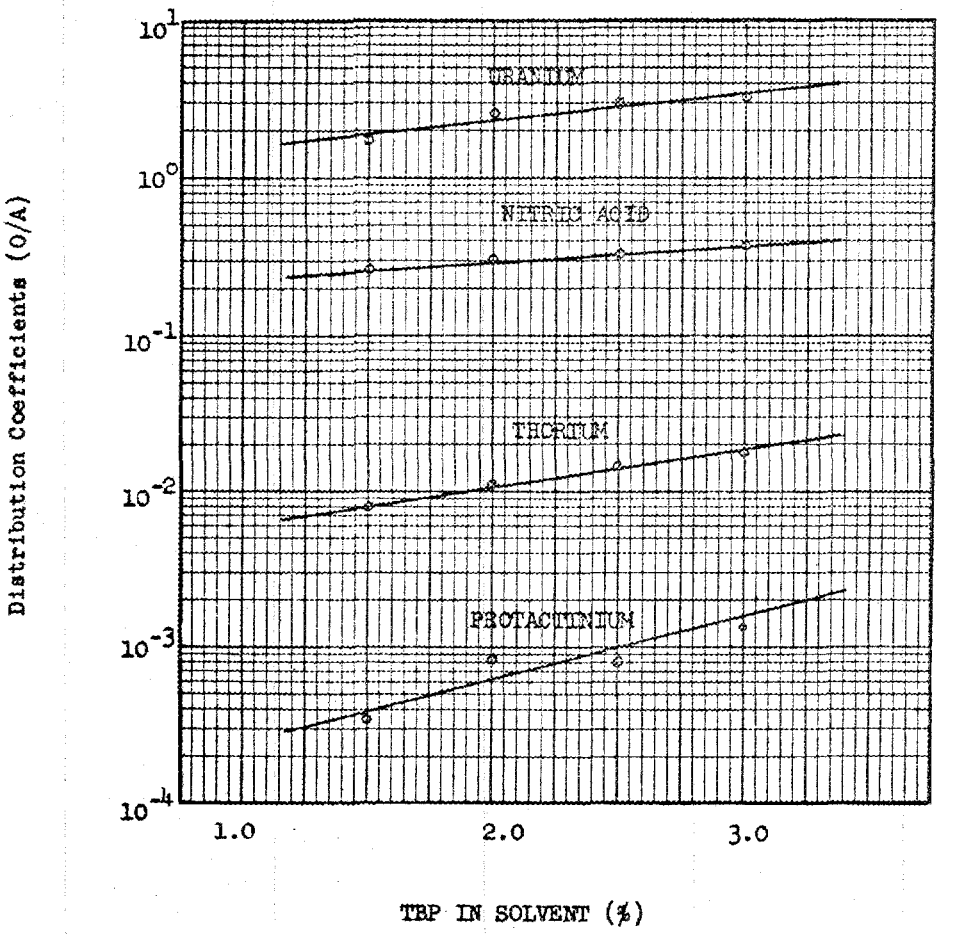
Dwg. #15910

Fig. 5.1-3 Distribution Coefficient (O/A) of U^{233}, Pa^{233}, Thorium, and Nitric Acid in Dilute TBP.

Aqueous phase: 1.2 M Th, 0.45 M Al, 0.8 M HNO_3, 0.8 g of U per liter, and 10^6 Pa β c/min/ml

Organic phase: 1.5 to 3.0 % TBP in Amsco, neutral

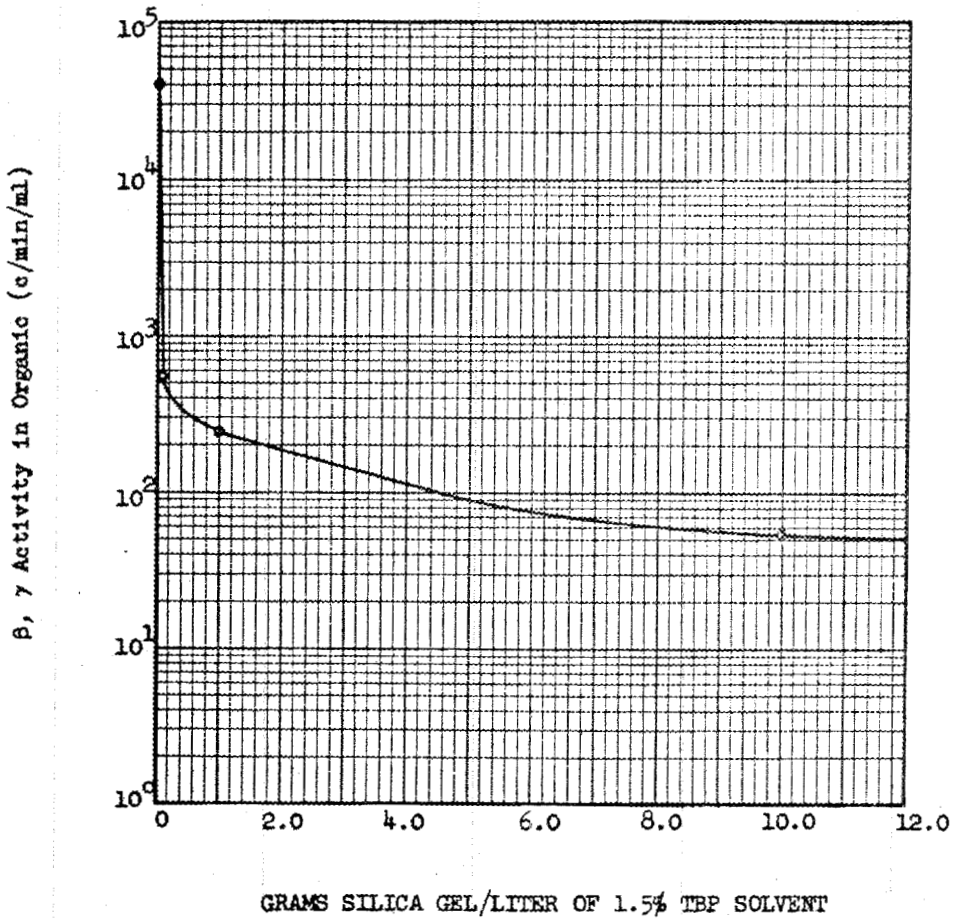
Aqueous/organic extraction ratio: 1/1



Dwg. #15911

Fig. 5.1-4 Beta Decontamination of Used 1.5% TBP by Washing with Na_2CO_3-Silica Gel. Procedure adopted to provide solvent decontamination for the Interim-23 process was as follows: One 1/5-vol. wash with 1.0 M NaOH containing 0.5 g of silica gel per liter; three subsequent washes with 0.1 M Na_2CO_3 alone. Complete removal of silica gel and activities was generally attained.

Conditions: β, γ-contaminated 1.5% TBP washed with equal volumes of 0.1 M Na_2CO_3 containing varying amounts of 8-μ silica gel; β, γ activity in original and washed samples counted in Geiger-Mueller tube.



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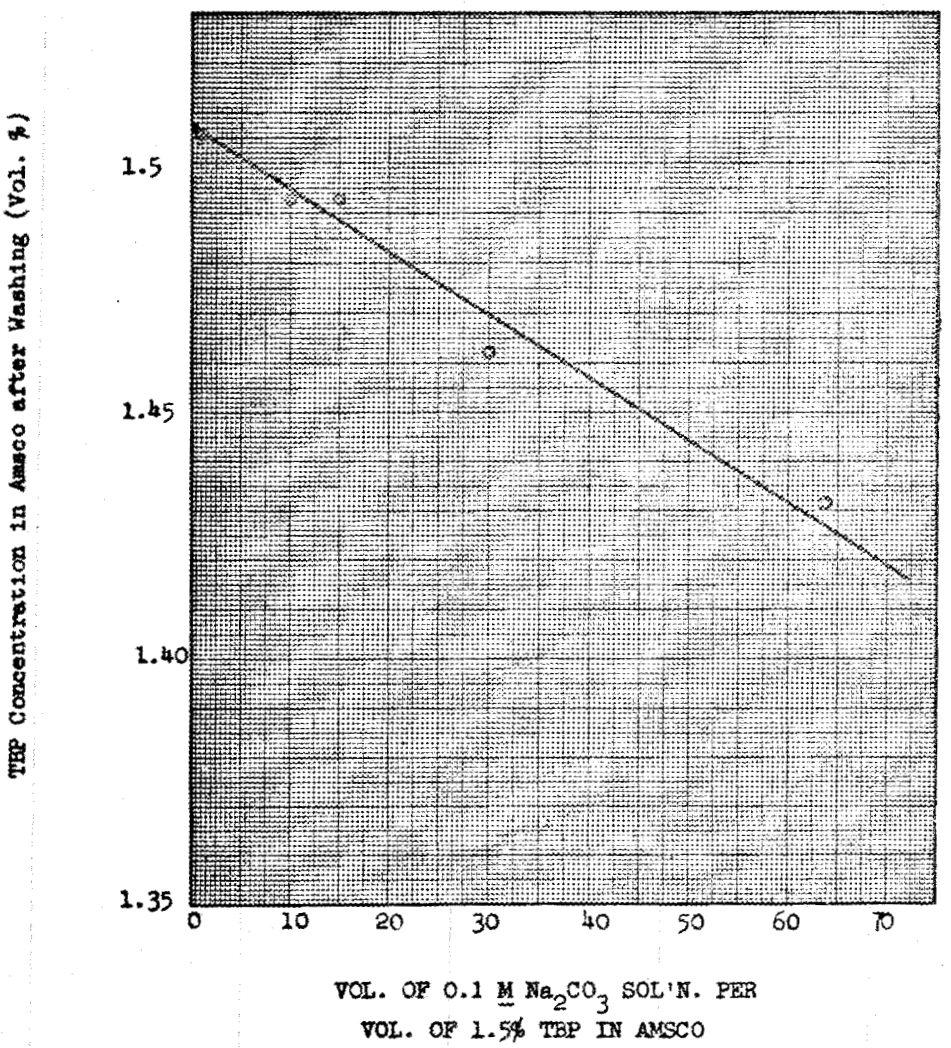
Dwg. #15912

Fig. 5.1-5 Solubility Loss of TBP on Washing 1.5% TBP-Amsco Solvent with 0.1 M Na_2CO_3.

Conditions: Solvent washed with varying volumes of 0.1 M Na_2CO_3 solution.



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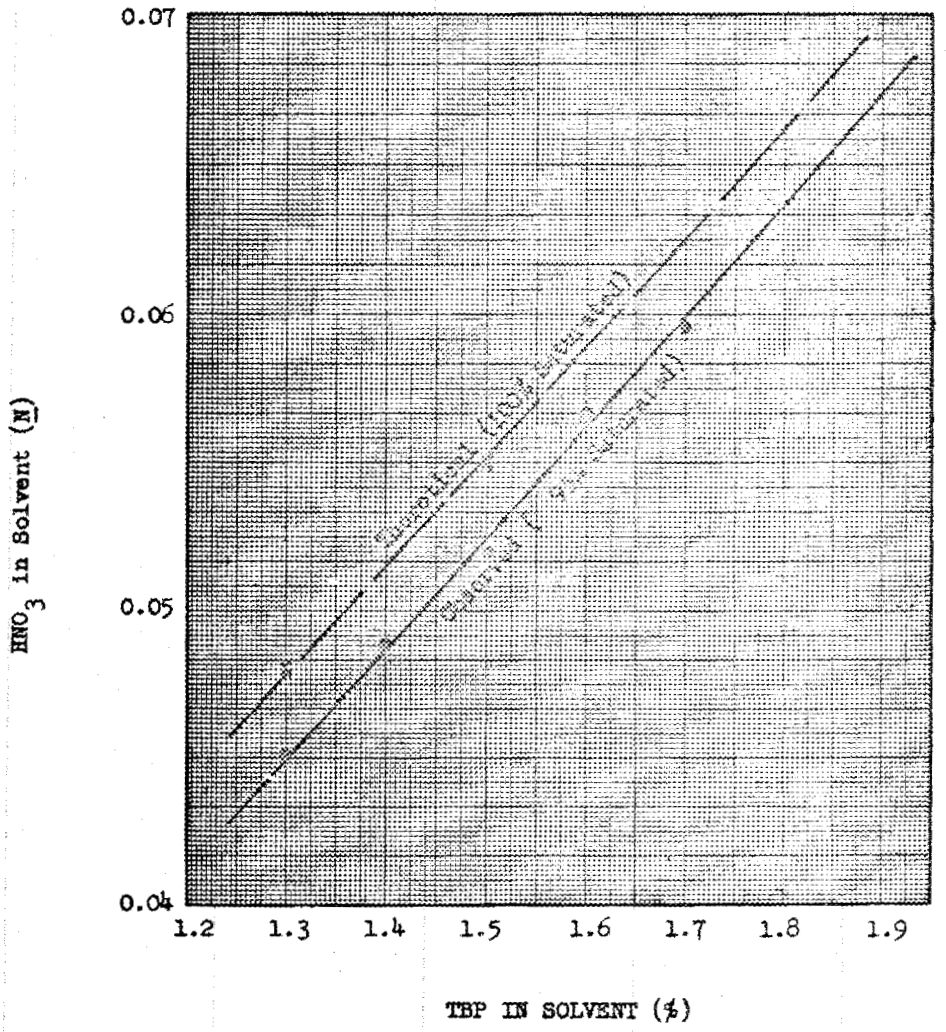
Dwg. #15913

Fig. 5.1-6 Analysis of TBP in Dilute Systems by Nitric Acid Saturation: Plot of % TBP vs. Normality of HNO_3 at >95% Saturation.

Conditions: Solvent set at equilibrium with 8 N HNO_3 solution, then titrated for normality of H^+; this normality is essentially that of the TBP, since HNO_3/TBP at saturation = 1.0; then, % TBP = N HNO_3 x 100/0.95 x N of 100% TBP, i.e., 3.67, or % TBP = 28.65 x N H^+; diluent in the tests was Amsco



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The reaction gases were scrubbed with sodium hydroxide and filtered; dissolution was essentially complete in about 7 hr, leaving a solution of thorium nitrate, aluminum nitrate, and nitric acid at a specific gravity of about 1.9. The dissolver solution was cooled to 90 to 100°C and transferred to a feed preparation tank and adjusted with water to a specific gravity of about 1.68. The final feed conditions were of the order of 1.5 M Th, 0.5 M Al, 0.5 to 1.0 M HNO_3, $\sim 2 \times 10^{10}$ β c/min/ml (11% geometry), and $\sim 2 \times 10^{6}$ U^{233} α c/min/ml (52% geometry); feed acidity and thorium content were somewhat critical with respect to U^{233} distribution in the extraction systems, owing to TBP-saturation effects of $Th(NO_3)_4$ and HNO_3 (see Figs. 5.1-7, 8, and 9).

(3) Scrub solution: 1.0 M aluminum nitrate, neutral. Acid deficiency was observed to decrease protactinium and fission product extraction in the solvent; however, pulse column studies indicated difficult mixing of such a solution with the 1.5% TBP-Amsco. Conditions were such as to maintain U^{233} extraction and permit good separation from thorium, protactinium, and fission products in the scrubbing operation (see Figs. 5.1-2, 10, and 11).

(4) Strip solution: 0.05 N HNO_3. The U^{233} D.C. (O/A) of about 0.02 permitted good product stripping and concentration in a relatively short column. Organic-stable colloidal fractions of protactinium and/or fission products were observed in the stripping operation; however, β and γ D.F.'s of only 2 to 10 were obtained for the product stream.

(5) Silica gel column: 20-mesh silica gel packed in a 1.0-in.-high stainless steel column for use in the 75 to 100 kg of thorium per day plant. This column was placed in the U^{233} product stream from the strip column to adsorb the principally colloidal activities and permit additional β and γ decontamination. No U^{233} was permanently adsorbed or lost in this column.

(6) Protactinium-thorium sorption bed: 0.2 liter of Dowex-50 (60 to 90 mesh, 8% cross-linked) in a 3-in.-diameter, 2-in.-high column. This was placed in the product stream, preceding the product column, to adsorb preferentially any traces of thorium, protactinium, or aluminum not removed or deentrained in previous steps. As the runs progressed, these elements were expected to displace the temporarily adsorbed U^{233}. This permitted considerable ionic and active decontamination of the product and simplified subsequent elution from the product column. The bed was calculated at 100 to 200% excess of that required to hold all the thorium expected in 1500 g of U^{233} product and remained in place for the duration of the initial Interim-23 program; the adsorbed U^{233} was finally to be preferentially eluted, permitting complete product recovery.

(7) U^{233} Product cation-exchange column: 2.4 liters of Dowex-50 (60 to 90 mesh, 8% cross-linked), calculated at 100% excess of desired U^{233} capacity (about 320 g), in a water-jacketed, 3-in.-diameter, 24-in.-high glass column. This was placed finally in the product stream to adsorb and concentrate the U^{233} from ten to thirteen extraction column runs. The light-yellow,

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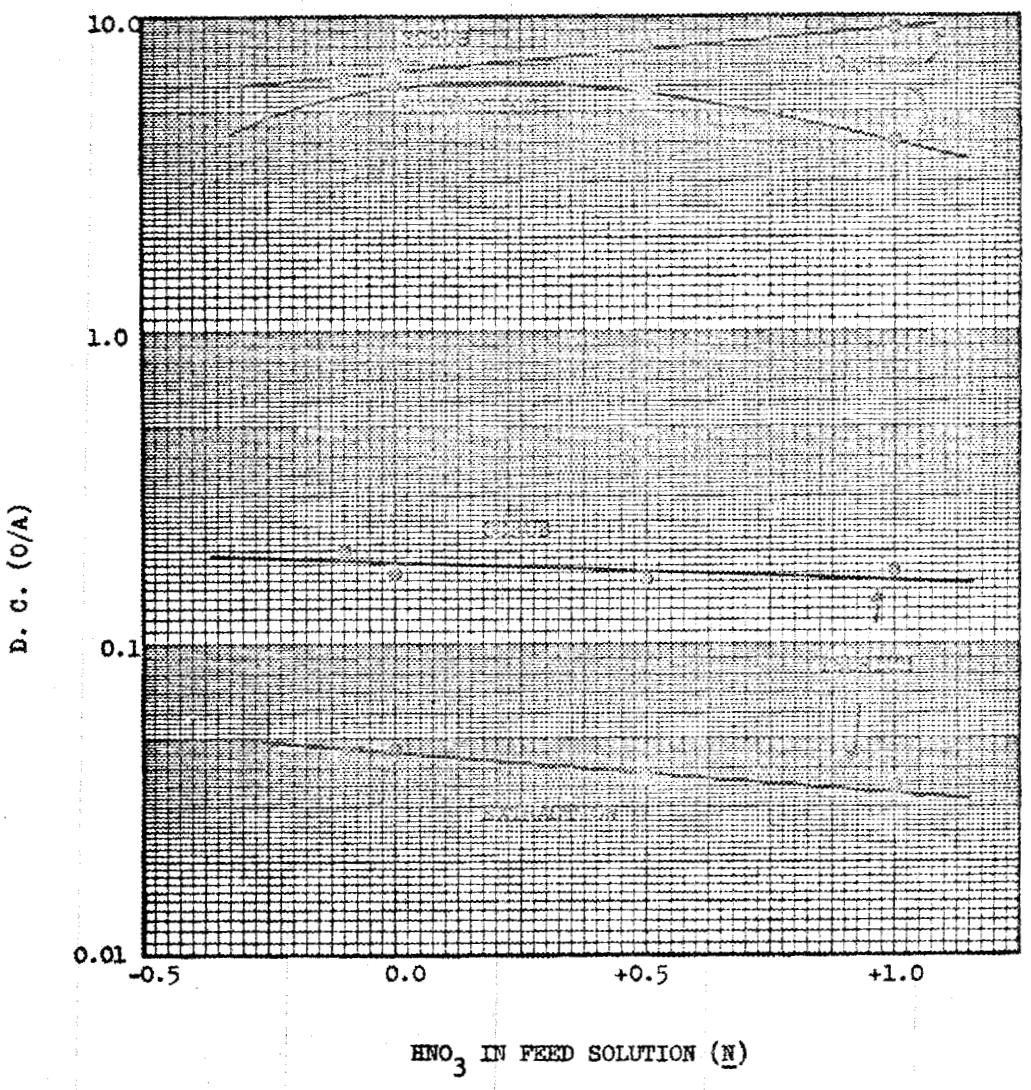
Dwg. #15914

Fig. 5.1-7 Distribution Coefficients (O/A) of U^{233} and Thorium in the Dilute TBP-Th System, as Functions of Normality of HNO_3 in Feed Solutions. Decreasing uranium and thorium extraction D.C.'s (O/A) with increasing acidity was due to competition of HNO_3 for TBP saturation. Increasing uranium scrubbing D.C.(O/A) was due to lower saturation of TBP by thorium.

Countercurrent extraction
Feed: 0.75 M Th, 0.75 M Al, 1.08 g of U per liter, -0.17 to +1.0 N HNO_3
Scrub: 1.0 M $Al(NO_3)_3$, 0.0 N HNO_3
Organic phase: 3% TBP in Amsco, neutral
Feed/Scrub/organic flow ratio: 4/1/5
8 extraction, 6 scrub stages; 2.5 Vol. changes



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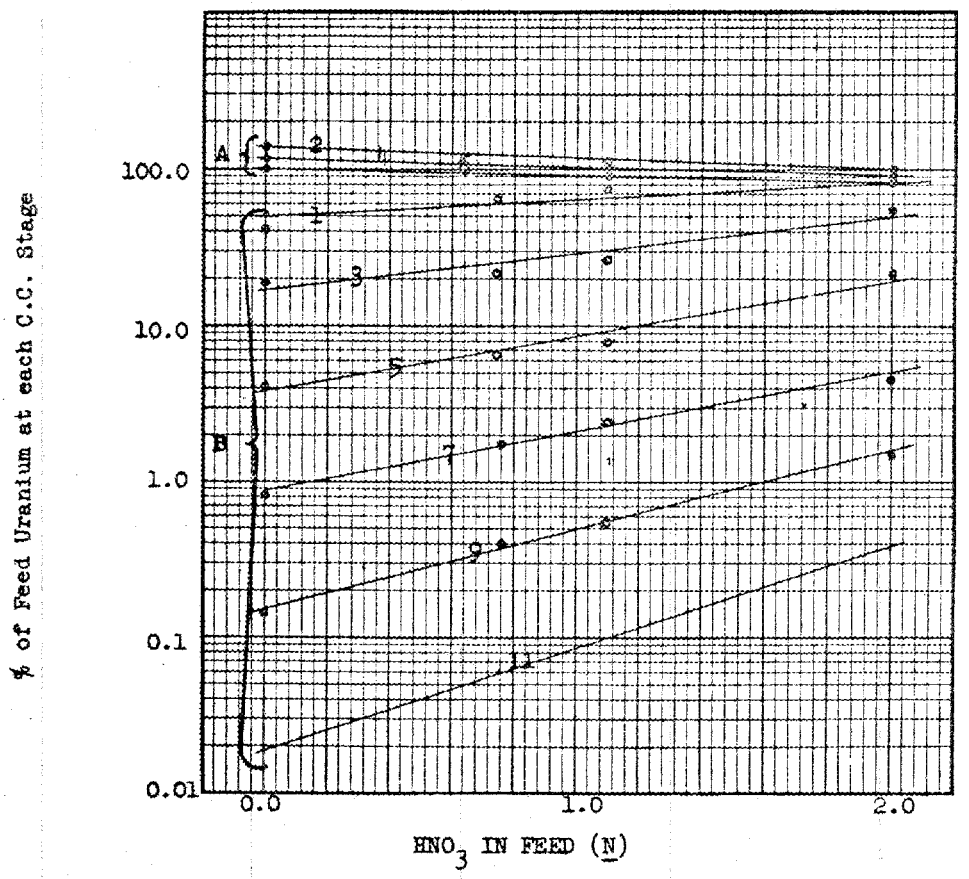
Dwg. #15915

Fig. 5.1-8 Uranium-233 Recovery and/or Loss in the 1.5% TBP-Th System, as a Function of HNO_3 Concentration in Feeds. Runs at 0.0 and 0.75 N HNO_3 gave complete uranium recovery and were at equilibrium. Runs at 1.1 and 2.0 N HNO_3 gave incomplete uranium recovery or had not attained complete equilibrium in 2.5 volume changes. Uranium D.C.'s were apparently reduced sufficiently by TBP-HNO_3 saturation to decrease stage efficiency and to increase uranium losses.

Countercurrent extractions (4 runs)
Feed: 1.5 M Th, 0.0 to 2.0 N HNO_3, 1.0 g of U per liter
Scrub: 1.0 M Al $(NO_3)_3$, neutral
Organic phase: 1.5% TBP in Amsco, neutral
Feed/scrub/organic flow ratio: 4/1/5
9 extraction, 6 scrub stages; 2.5 Vol. changes

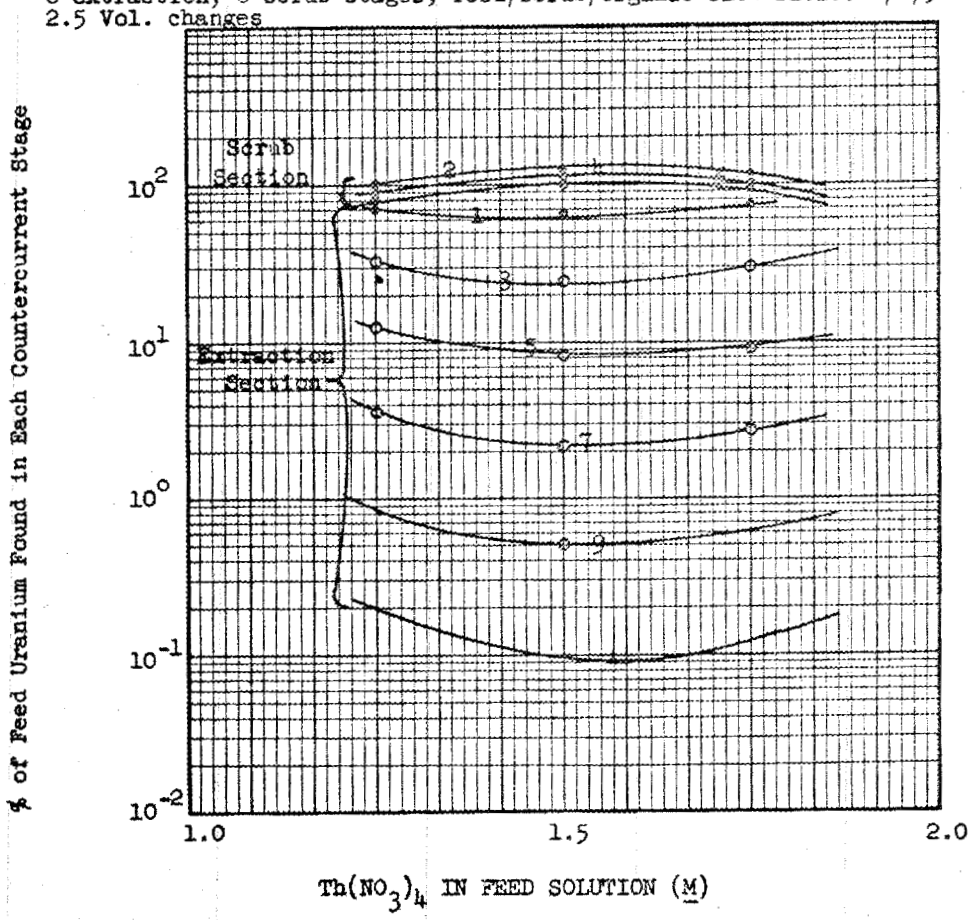


(A) Organic streams at countercurrent scrub stages 2,4, and 6 (6 = U^{233} product);
(B) Aqueous streams at countercurrent extraction stages 1, 3, 5, 7, 9 (1 = feed plate).

Dwg. #15916

Fig. 5.1-9 Percentage of U^{233} Recovered and/or Lost in 15% TBP-Th System, as Function of Molarity of $Th(NO_3)_4$ in Interim-23 Feed Solutions. Note: curves indicate (a) about 99.5% uranium recovery in nine stages with 1.5 M thorium feed; (b) about 80.0% uranium recovery in seven stages with 1.25 M thorium feed; (c) about 90.0% uranium recovery in seven stages with 1.75 M thorium feed. The loss in (b) can be ascribed to decreased extraction D.C.'s (O/A) for uranium, owing to decreased aqueous salt strength, whereas loss in (c) was due to thorium saturation of TBP.

Countercurrent Extractions
Feed: 1.25 to 1.75 M Th, 1.0 M HNO_3, 1.0 g of uranium per liter
Scrub: 1.0 M $Al(NO_3)_3$, neutral
Organic: 1.5% TBP in Amsco
8 extraction, 6 scrub stages; feed/scrub/organic flow ratio: 4/1/5
2.5 Vol. changes



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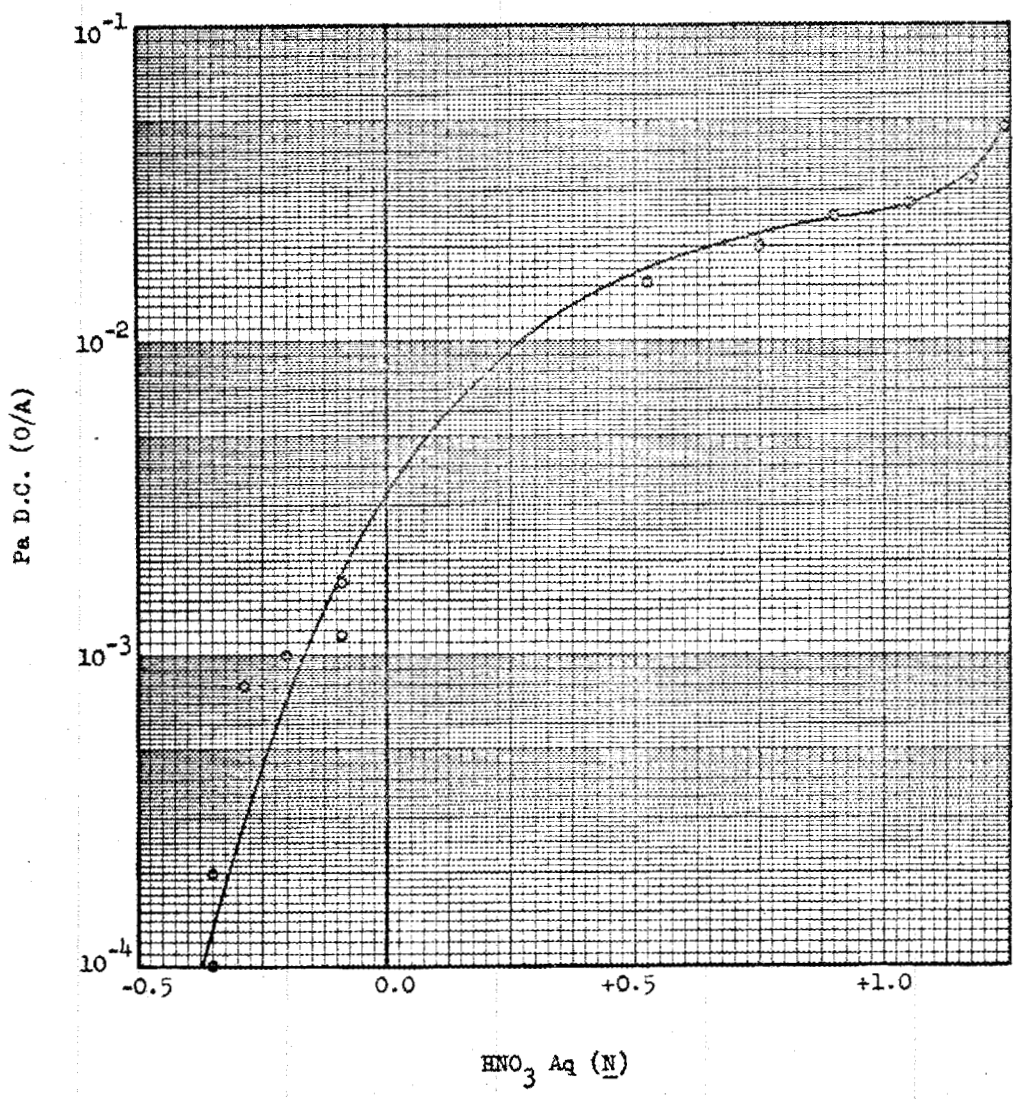
Dwg. #15917

Fig. 5.1-10 Protactinium D.C. (O/A) in 1.5% TBP—1.0 M $Al(NO_3)_3$—System as a Function of H^+ Concentration.

Aqueous phase: 1.0 M $Al(NO_3)_3$, -0.4 to +1.25 N HNO_3
Organic phase: 1.5% TBP in Amsco, 0.0 N HNO_3
Organic/aqueous ratio: 1/1



Dwg. 15918

Fig. 5.1-11 Distribution Coefficients (O/A) of U^{233}, Pa^{233}, and Th, in the Dilute TBP--1.0 M Al $(NO_3)_3$ System, as Functions of Normality of HNO_3 and Percentage of TBP.

Organic phase: 1.5 to 3.0% TBP in Amsco, which had been used in a prior extraction of a feed, 1.2 M Th, 0.8 N HNO_3, 0.45 M Al, 0.89 of uranium per liter, 10^6 Pa β c/min/ml

Scrub solution: 1.0 M $Al(NO_3)_3$, 0.0 to -0.6 N HNO_3

Organic/aqueous ratio: 5/1

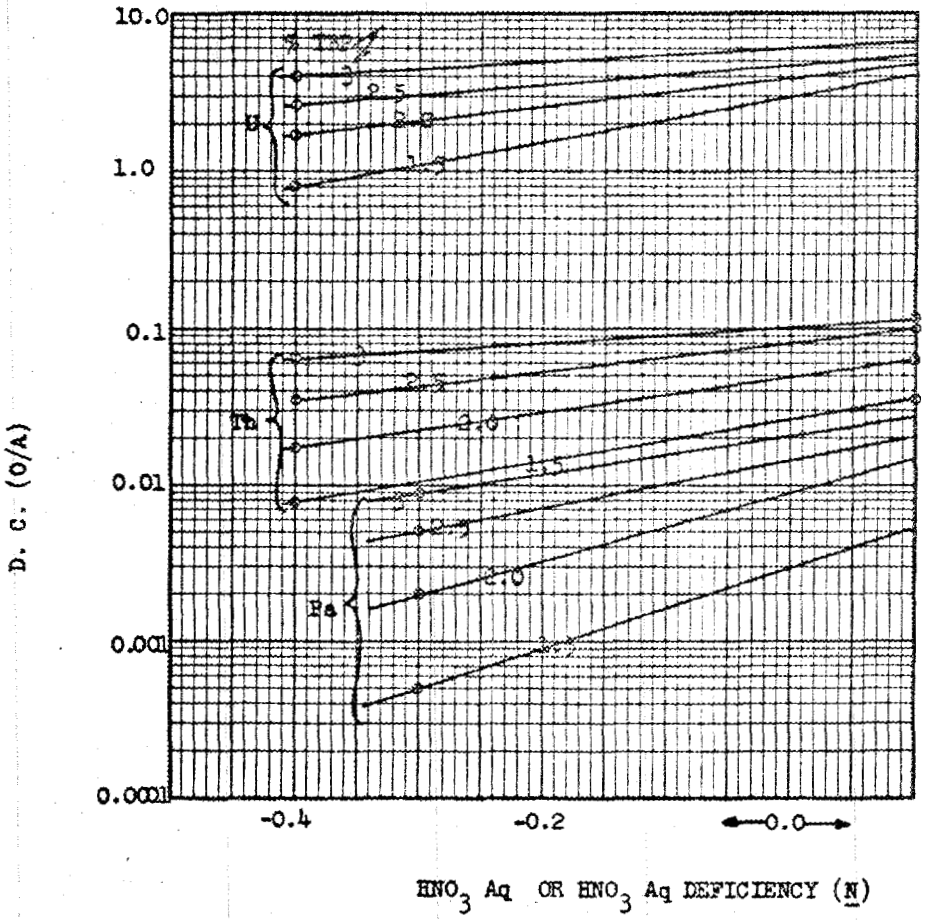


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Table 5.1-1

Typical Analytical Data from Countercurrent

Studies of the Interim-23 Process

Conditions of Countercurrent Run:

Feed: 356 mg Th/ml, 0.29 mg U/ml, 0.4 M $Al(NO_3)_3$, 0.88 N HNO_3, 6.7×10^8 β, γ c/min/ml (in E-1, out E-7)
Scrub: 1.0 M $Al(NO_3)_3$, neut. (in S-6, out E-7)
Organic: 1.53% TBP in Amsco (in E-7, out St-5)
Strip: 0.05 N HNO_3 (in St-5, out St-1)
Flow ratios: F/S/O/St = 4/2/7.5/1.25 Vol. changes = 2.5
Determinations: Th (mg/ml), U (mg/ml), β^- (c/min/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-5	Th	<0.001	<0.001	-	-
	U	<0.0001	0.0003	<0.3	-
	β	1.0×10^3	2.6×10^2	3.9	23.5*
St-3	Th	<0.001	<0.001	-	-
	U	0.0002	0.017	0.012	0.07
	β	1.3×10^3	1.1×10^3	1.2	7.2
St-1	Th	<0.001	0.003	<0.3	-
	U	0.012	0.58	0.021	0.126
	β	1.5×10^3	2.8×10^3	0.54	3.25
Sc-6	Th	0.001	0.01	<0.1	-
	U	0.16	0.078	2.05	7.7
	β	1.6×10^3*	3.0×10^2	5.3	19.8*
Sc-4	Th	0.004	0.03	0.133	0.5
	U	0.18	0.093	1.94	7.3
	β	3.2×10^3	1.6×10^3	2.0	7.5
Sc-2	Th	0.215	2.93	0.073	0.27
	U	0.19	0.084	2.26	8.5
	β	5.0×10^3	2.0×10^4	0.25	0.94
E-1	Th	2.3	240.0	0.01	0.012
	U	0.2	0.103	1.94	2.27
	β	4.5×10^5	4.5×10^8	0.001	0.001
E-3	Th	2.2	245.0	0.01	0.012
	U	0.03	0.012	2.5	2.94
	β	4.5×10^5	4.5×10^8	0.001	0.001
E-5	Th	2.4	239.0	0.01	0.012
	U	0.003	0.0014	2.15	2.53
	β	4.3×10^5	4.5×10^8	0.001	0.001
E-7	Th	2.0	240.0	0.01	0.012
	U	0.0004	0.0002	2.0	2.34
	β	4.2×10^5	4.4×10^8	0.001	0.001

*β-γ was mostly colloidal protactinium activity.

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sharply defined adsorption band of U^{233} was distinguishable and traceable during the progress of the plant operation and was sometimes marked by a thin blue band which was attributed to nickel; accurate estimates of adsorbed product weight were possible by a measure of the band length. The column was loaded downflow at a rate of about 1.2 ml/min/cm^2 to within 2 to 4 in. of the bed bottom, and it was possible to hold losses of U^{233} to less than 0.01%. Alternate columns were removed from the plant product-cubicle to the Isolation Laboratory for final product elution with 2.0 M ammonium acetate—0.4 M acetic acid solution at 40 to 50°C, and final isolation by peroxide precipitation, filtration, and nitric acid digestion.

(8) Miscellaneous: Since aluminum was found to desorb U^{233} strongly from Dowex-50 resin, special precautions involving the use of a phase separator in the product stream from the extraction column were instituted to forestall inadvertent contamination by scrub solutions. And, owing to possible mechanical and chemical difficulties inherent in adsorption techniques, ample solvent de-entrainment and a phase separator were provided in the aqueous strip stream.

Further details of the plant operation of this process are to be reported by the Pilot Plant Section of the Chemical Technology Division.

5.2 Thorex Process No. 1 (see Fig. 2.0-2) (A. T. Gresky, S. S. Brandt, W. T. McDuffee, J. E. Savolainen)

(a) Purpose:

A long-range development to provide (1) an alternate process for the separation, decontamination, and recovery of Pa^{233}, U^{233}, and Th^{232} from short-cooled neutron-irradiated thorium, and (2) a primary study of unique principles and methods of solvent extraction as related to chemical separations of the three elements and fission products. The general approach for this process, as outlined below, was originally considered mandatory in the TBP systems owing to an inability to partition protactinium from thorium.

(b) Basic Features:

(1) A simple, rapid slug dissolution and feed preparation. (2) An initial, high-degree, preferential extraction of the very active Pa^{233} (>90% of gross β and γ activities) from U^{233} and Th^{232} by use of the carbinols, DIPC or DIBC, to permit a separation unattainable by subsequent extraction steps. (3) Preferential extraction and decontamination of U^{233} from the thorium solution by use of a dilute TBP extractant (somewhat similar to the Interim-23 procedure). (4) Thorium extraction and decontamination by use of a more concentrated TBP mixture of the hydrocarbon Amsco and an aromatic, e.g., benzene (to forestall two-organic phase formation at thorium "saturation"). (5) Individual stripping of each of the three products by appropriate aqueous solutions. Other primary features involved (6) preconditioning of the Amsco diluent and (7) a highly important solvent treatment to eliminate decomposition products of TBP.

(c) Process Details:

(1) Solvents: DIBC, in relation to DIPC, was considered the optimum solvent for high protactinium specificity, nitric acid stability, flash-point, availability, and purity. Five percent TBP for U^{233} extraction permitted sufficiently high D.C.'s (O/A) to allow use of nitric acid scrub solutions for partitioning from thorium (Interim-23 conditions of 1.5% TBP and neutral aluminum nitrate scrub solutions were possible alternates). Forty to fifty percent TBP solutions, containing a minimum of 15% benzene, were considered optimum for the bulk thorium extraction and decontamination, to allow sufficient salt capacity, reasonable flow ratios, and operable viscosity ranges. Solvent treatments visualized were occasional water washing and distillation of the used DIBC; preconditioning of the Amsco diluent with 10 N HNO_3, caustic washing, and silica gel adsorption; and careful treatment of TBP solutions for MBP, DBP, and F.P. removal by contacting with 1.0 M NaOH containing 8-μ silica gel and countercurrent washing with 0.1 M NaOH or Na_2CO_3.

(2) Feed solution: Prepared, in general, as outlined in the previous discussion of the Interim-23 process; adjusted in the initial step to permit protactinium extraction and to afford cascading conditions operable in subsequent steps.

(3) Scrub solutions: 2.0 N HNO_3 was sufficiently high in the protactinium step to permit its extraction and partition from U^{233} and thorium, and low enough to reduce nitric acid extraction to a minimum; 2.0 N HNO_3 in the 5% TBP-U^{233} step was near an optimum for U^{233} extraction and thorium partitioning; 0.5 M $Al(NO_3)_3$, or 1.5 N NO_3^-, was essentially required in the 45% TBP-thorium step to provide fission product scrubbing, to prevent high thorium reflux, and to permit at least 1.5 N NO_3^- in the extraction section, thereby ensuring low thorium losses; proper adjustment of flow ratios, to within operable limits for pulse-column operation and to provide optimum salting strengths for a cascading system, was considered desirable, if not mandatory.

(4) Strip Solutions: Very dilute (0.02 to 0.05 N) nitric acid was used in all product streams to permit low salt strengths and distribution favoring aqueous phases, yet to provide sufficient ionic strength to allow good phase mixing. Flow ratios were adjusted to provide low and near-optimum "extraction factors," allowing a maximum volume reduction for each product stream.

(5) Isolation steps: Though not considered in detail to date, owing to an early abandonment of this process approach for operations use, simple evaporation and/or ion-exchange procedures were contemplated.

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Table 5.2-1

Typical Analytical Data from Countercurrent Studies of the Pa^{233} Extraction Step of Thorex Process No. 1

Feed: Thorium, 354 mg/ml; uranium, 0.295 mg/ml; 0.5 M $Al(NO_3)_3$; 2.7 N HNO_3; 4.3×10^6 β/m/ml; 4.2×10^6 Pa β/m/ml (in E-1, out E-7)
Scrub: 2.0 N HNO_3 (in Sc-6, out E-7)
Organic: Diisobutyl carbinol (DIBC), neut. (in E-7, out St-5)
Strip: 0.02 N HNO_3 (in St-5, out St-1)
Feed/scrub/organic/strip flow ratio: 5/1/2/2
2.5 vol. changes
Determinations: Th (mg/ml), U (mg/ml), HNO_3 (N), Pa (c/min/ml), β (c/min/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-5	HNO_3	-	0.05	-	-
	β	1.2×10^3	4.0×10^3	0.3	0.3
St-3	HNO_3	-	0.06	-	-
	β	1.4×10^4	1.5×10^5	0.1	0.1
St-1	HNO_3	<0.01	0.18	<0.05	<0.05
	β	2.0×10^6*	1.1×10^7*	0.2	0.2
Sc-6	Th	<5 γ	<5 γ	-	-
	U	<0.012 γ	0.0001	-	-
	HNO_3	0.16	2.28	0.07	0.14
	Pa	1.1×10^7	1.9×10^6	5.9	11.8
	β	1.1×10^7	2.0×10^6	5.6	11.2
Sc-4	Th	<5 γ	<40 γ	-	-
	U	0.00001	0.00006	0.016	0.032
	HNO_3	0.52	3.28	0.16	0.32
	Pa	1.1×10^7	7.8×10^5	14.7	29.4
	β	1.1×10^7	5.7×10^5	19.1	38.2
Sc-2	Th	<5 γ	1.6	<0.003	<0.006
	U	0.00002	0.045	0.004	0.009
	HNO_3	1.09	4.5	0.24	0.48
	Pa	1.2×10^7	9.0×10^4	129.0	258.0
	β	1.1×10^7	8.9×10^4	125.0	250.0
E-1	Th	7.2	290.0	0.035	0.012
	U	0.12	0.29	0.41	0.14
	HNO_3	1.95	2.65	0.74	0.25
	Pa	8.9×10^6	6.0×10^5	16.6	5.5
	β	8.8×10^6	1.2×10^6	7.6	2.5
E-3	Th	9.3	260.0	0.036	0.012
	U	0.135	0.29	0.47	0.155
	HNO_3	1.97	2.7	0.73	0.24
	Pa	3.0×10^3	2.4×10^4	0.11	0.036
	β	3.0×10^5	7.4×10^5	0.4	0.13
E-7	Th	7.5	264.0	0.03	0.01
	U	0.135	0.295	0.46	0.15
	HNO_3	1.92	2.6	0.74	0.24
	Pa	6.0×10^2	4.4×10^3	0.14	0.05
	β	2.2×10^3	7.0×10^5	0.003	0.001

*β was >95% protactinium activity.

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Table 5.2-2

Typical Analytical Data from Countercurrent

Studies of the U^{233} Extraction Step of Thorex Process No. 1

Feed: Thorium, 255 mg/ml; uranium, 0.29 mg/ml; 0.32 M $Al(NO_3)_3$; 2.6 N HNO_3; 7.0×10^5 β/m/ml, 4.0×10^3 Pa β/m/ml (in E-1, out E-7)
Scrub: 2.0 N HNO_3 (in S-6, out E-7)
Organic: 5% TBP-Amsco (in E-7, out St-5)
Strip: 0.05 N HNO_3 (in St-5, out St-1)
Feed/scrub/organic/strip flow ratio: 12/3/10/2
2.5 vol. changes
Determinations: Th (mg/ml), U (mg/ml), HNO_3 (N), β (c/min/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-5	U	0.00002	0.0008	0.025	0.125
	HNO_3	-	0.05	-	-
	β	-	-	-	-
St-3	U	0.0008	0.085	0.01	0.05
	HNO_3	-	0.06	-	-
	β	-	1.0×10^2	-	-
St-1	U	0.136	1.7	0.08	0.4
	HNO_3	0.07	0.45	0.04	0.2
	β	2.0×10	1.5×10^2	0.13	0.65
Sc-6	Th	0.001	0.008	0.12	0.44
	U	0.34	0.19	1.8	6.0
	HNO_3	0.07	2.0	0.03	0.1
	β	5.0×10	1.9×10^2	0.3	1.0
Sc-4	Th	0.009	0.092	0.1	0.33
	U	0.35	0.195	2.5	8.3
	HNO_3	0.07	1.98	0.03	0.1
	β	7.0×10	1.4×10^2	0.48	1.6
Sc-2	Th	0.114	2.2	0.05	0.17
	U	0.36	0.19	1.9	6.3
	HNO_3	0.07	2.02	0.03	0.1
	β	1.6×10^2	1.3×10^3	0.13	0.43
E-1	Th	8.8	238.0	0.04	0.03
	U	0.38	0.125	3.0	2.0
	HNO_3	0.08	1.95	0.04	0.03
	β	1.1×10^3	6.1×10^5	0.002	0.001
E-3	Th	9.24	220.0	0.04	0.03
	U	0.043	0.014	3.1	2.06
	HNO_3	0.06	1.98	0.03	0.02
	β	5.2×10^2	6.2×10^5	0.001	0.001
E-7	Th	9.2	215.0	0.04	0.03
	U	0.0006	0.0003	2.0	1.33
	HNO_3	0.06	1.9	0.03	0.02
	β	4.7×10^2	6.0×10^5	0.001	0.001

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Table 5.2-3

Typical Analytical Data from Countercurrent

Studies of the Thorium Extraction Step of Thorex Process No. 1

Feed: Thorium, 236 mg/ml, uranium, <0.0003 mg/ml; 0.26 M $Al(NO_3)_3$; 1.35 N HNO_3; 3×10^3 Pa β/m/ml; 6.0×10^5 β/m/ml (in E-1, out E-7)
Scrub: 0.5 M $Al(NO_3)_3$, 0.2 N HNO_3 deficient (in S-6, out E-7)
Organic: 45% TBP, 15% benzene, 40% Amsco, neut. (in E-7, out St-5)
Strip: 0.05 N HNO_3 (in St-5, out St-1)
Feed/scrub/organic/strip flow ratio: 2/1/5/5
2.5 vol. changes
Determinations: Th (mg/ml), HNO_3 (N), β (c/min/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-5	Th	0.025	2.02	0.0124	0.0124
	HNO_3	-	-	-	-
	β	5.5×10	2.8×10^2	0.193	0.193
St-3	Th	11.3	36.3	0.312	0.312
	HNO_3	-	-	-	-
	β	1.6×10^2	4.4×10^2	0.36	0.36
St-1	Th	62.4	92.5	0.7	0.7
	HNO_3	-	0.06	-	-
	β	3.5×10^2	2.0×10^3	0.17	0.17
S-6	Th	93.6	38.8	2.4	12.0
	HNO_3	0.015	0.04	0.375	1.9
	β	1.26×10^3	2.8×10^3	0.445	2.2
S-4	Th	92.5	64.0	1.45	7.2
	HNO_3	0.12	0.36	0.33	1.65
	β	2.0×10^3	6.7×10^3	0.296	1.48
S-2	Th	105.6	83.0	1.27	6.3
	HNO_3	0.19	0.77	0.25	1.25
	β	2.6×10^3	1.4×10^4	0.18	0.9
E-1	Th	111.0	153.0	0.725	1.2
	HNO_3	0.32	1.69	0.19	0.32
	β	4.3×10^3	4.7×10^5	0.01	0.02
E-3**	Th	25.6	5.1	5.0	8.3
	HNO_3	0.855	2.06	0.42	0.7
	β	2.6×10^4	5.9×10^5	0.05	0.08
E-5**	Th	0.425	0.114	3.73	6.2
	HNO_3	0.53	0.72*	0.736	1.22
	β	7.9×10^4	6.7×10^5	0.12	0.2
E-7**	Th	0.029	0.032	0.91	1.5
	HNO_3	0.11	0.07*	1.57	2.6
	β	9.9×10^4	6.4×10^5	0.15	0.25

*Run was not at equilibrium with respect to nitric acid.
**Increasing activities in these stages due to total rare earth, zirconium, and ruthenium extraction.

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(d) Alternate Process - Thorex No. 1a Owing to a late and somewhat better understanding of the "steady-state" problems in TBP-Th-HNO_3 systems, as discussed in Secs. 3.5.5 and 4.1.4a, an alternate procedural flow diagram (Fig. 5.2-1) was drawn to indicate another possible approach to a Thorex process. The principal advantage visualized in this scheme involved elimination of the aluminum nitrate salt from the "hot" waste streams, thereby permitting storage of low volumes of HNO_3-evaporated fission product solutions. Disadvantages would include (1) a more complicated feed preparation step involving caustic jacket-dissolution, and (2) associated storage of large volumes of semi-hot sodium aluminate wastes, as well as those enumerated in Sec. 2.0.

5.3 Thorex Process No. 2 (see Fig. 2.0-3) (A. T. Gresky, W. T. McDuffee, M. R. Bennett, J. E. Savolainen)

(a) Purpose: A long-range development to provide a process, feasible for plant operations, to separate, decontaminate, and isolate Pa^{233}, U^{233}, and Th^{232} from short-cooled neutron-irradiated thorium. Use of a single plant solvent, a small number of unit processes, and simplicity of operation were desired goals.

(b) Basic Features: (1) A simple, rapid slug dissolution and feed preparation; (2) an initial extraction of thorium and U^{233} from fission products and Pa^{233} by use of a 41 to 55% TBP—0.0% benzene solvent and acid-deficient aqueous conditions, principally designed to exploit unique effects of pH on protactinium distribution; (3) separation of protactinium from process solids and partial separation from fission products by silica gel adsorption or TBP extraction from acid media; (4) partitioning of thorium from U^{233} by preferential stripping from the TBP solvent by use of a selective nitric acid strip solution; and (5) stripping of U^{233} from the TBP solvent by use of a very dilute nitric acid solution. The extraction process is very dependent on good analytical control of Th^{4+}, Al^{3+}, and H^+ concentrations, a positive process for solvent purification, and good operational control of flow ratios or rates for process streams. The need for additional solvent-extraction cycles has not been positively established. Isolation steps for the three products are contemplated to involve evaporation for protactinium, evaporation, or precipitation for thorium, and ion exchange for U^{233}.

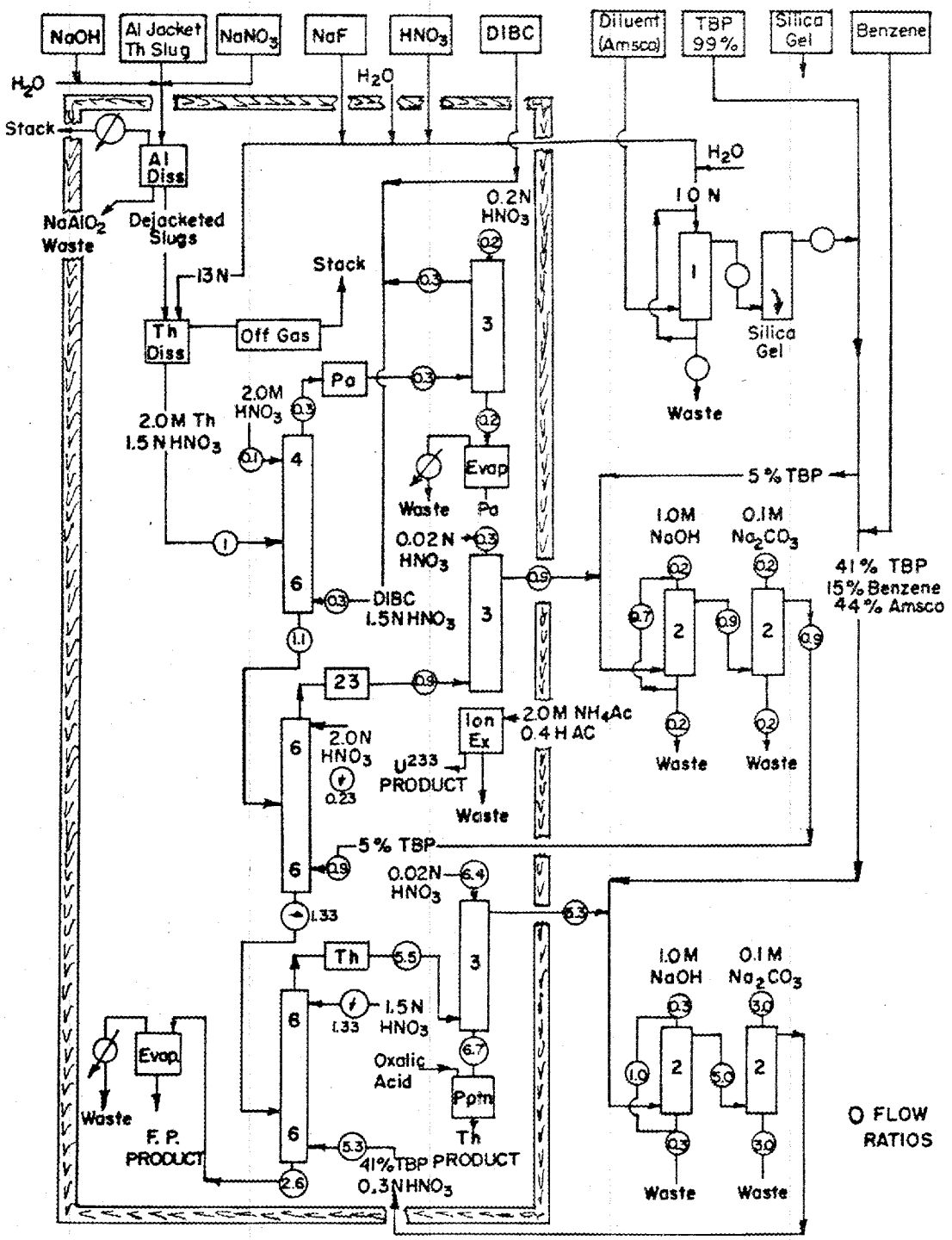
(c) Process Details:

(1) Solvent: 41% (1.5 M) TBP in Amsco 123-15 diluent was chosen originally, in a somewhat arbitrary manner, as a reasonable range for pulse column operation, based on past experience of phase-mixing properties as functions of specific gravities and viscosities; benzene, owing to its undesirable properties, was deleted from the solvent since the acid-deficient chemical system removed the stringent necessity for decontamination-by-saturation and permitted process operation at equilibrium TBP/$Th(NO_3)_4$ ratios of >4.0 (see Secs. 3.2.2b and 4.1.2); operating flow ratios in the extraction

Figure 5.2-1

THOREX FLOWSHEET No IA (Tentative)

Dwg No15149



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column were rather critically established to maintain an equilibrium relation of 5.0 moles of TBP in the solvent phase to 1.0 mole of thorium in the aqueous feed; e.g., the flow ratio of a 1.5 M $Th(NO_3)_4$ feed to 1.5 M TBP solvent was set at 1/5; with no free nitric acid present in the system, it was possible to consider solvent "capacity" essentially on the basis of thorium alone (see Secs. 3.5.3 and 4.1.3); although flow ratios limited the effluent organic stream to a 5TBP/Th complex, normal thorium reflux in the scrubbing operation permitted ratios approaching 4TBP/Th to exist near the feed plate; similar systems using 54.5% (2.0 M) TBP at O/F flow ratios of 3.75, or TBP/Th = 5.0, have been demonstrated as mechanically and chemically operable in a 0.5-in. laboratory pulse column; solvent conditioning and recovery steps were the same as those outlined in Sec. 5.2.

(2) Feed solution: Essentially the same feed preparation step as outlined in Sec. 5.1, except that control of final acidity in dissolver solutions is more critical; aluminum nitrate concentrations in the feed can vary from about 0.4 to 0.7 M without drastically affecting the extraction system; nitric acid concentrations in feeds should not vary too far from 0.5 ±0.05 N; acid deficiency in the scrub solution should be high and of an order, e.g., 0.8 ±0.05 N, to produce an equilibrium acid deficiency, on mixing with an equal volume of feed, of 0.15 to 0.2 N at the feed plate and in the extraction section; feed acidities higher than 0.5 N can be tolerated in the proposed system, but an upward adjustment of the scrub solution with respect to aluminum concentrations and acid deficiency would be necessary.

(3) Scrub solution: 0.6 M $Al(NO_3)_3$, 0.8 ±0.05 N HNO_3 deficient, or 0.6 M $Al(NO_3)_{1.67}(OH)_{1.33}$, produced by a Hg^{2+}-catalyzed dissolution of aluminum metal in nitric acid and/or aluminum nitrate solutions; high acid deficiency was required to allow preferential removal of protactinium and fission products from the organic phase containing thorium and U^{233}.

(4) Strip solutions: 0.2 N HNO_3 solution was used as a preferential stripping agent to partition thorium from U^{233} in the organic phase from the initial extraction step and to permit a relatively low extraction of HNO_3; O/A flow ratios were adjusted to allow essentially complete removal of thorium; a TBP-Amsco solution, at the same TBP concentration as the general process solvent, was used in the preferential stripping step to permit complete recovery of the U^{233} from the aqueous thorium stream; 0.02 to 0.05 N HNO_3 solution was finally used to strip U^{233} from the organic stream; very low salting strength is mandatory in this latter step and necessitates an efficient separation of thorium salts in the previous partitioning step.

(5) Protactinium separation: Alternate proposals include (i) adsorption and concentration in a column containing 20-mesh silica gel (see Sec. 4.3.3), or (ii) extraction by TBP solvent cascaded from the U^{233} stripping step (see Fig. 5.3-1). The colloidal fraction of the fission products zirconium and niobium are expected to be associated with protactinium in alternate (i), and large fractions of the fission products rare earths, ruthenium, and zirconium are

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FIGURE 5,3-1

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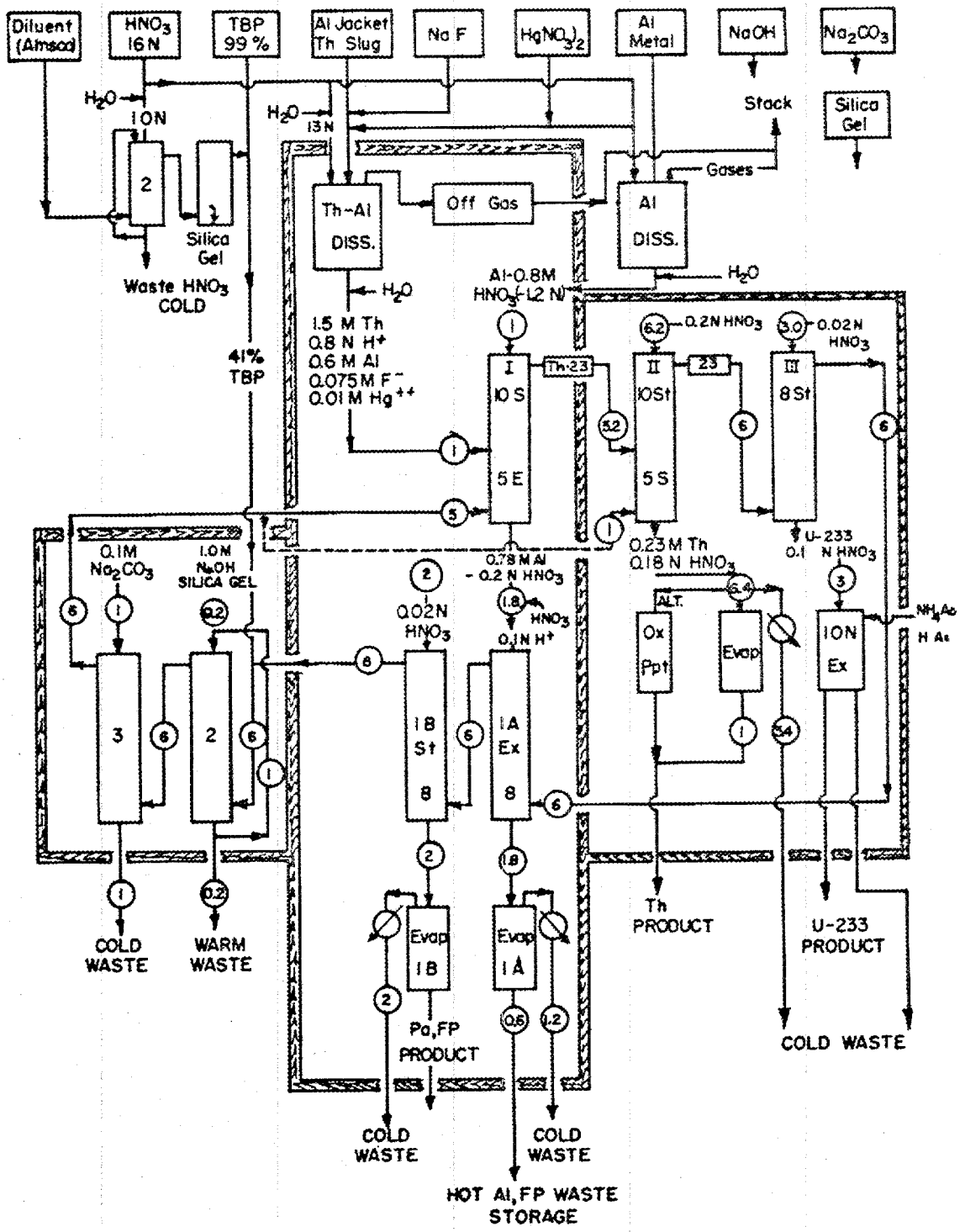
THOREX FLOWSHEET No 2 A

(Alternate Pa Recovery Step)



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extracted with the protactinium in alternate (ii); the protactinium can be eluted from silica gel with 4% oxalic acid or stripped from the TBP solvent with 0.02 to 0.05 N HNO_3, thereby facilitating further concentration and/or isolation steps by evaporation.

Figure 5.3-1 is a procedural flow diagram showing tentative concepts as outlined above. Tables 5.3-1 through 4 give typical analytical data from Thorex process runs.

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Table 5.3-1

Typical Analytical Data from Countercurrent

Studies of the Thorium-U^{233} Extraction Step of Thorex Process No. 2

Feed: Thorium, 358 mg/ml; uranium, 1.0 mg/ml, 0.5 M $Al(NO_3)_3$, 0.52 N HNO_3, 2.9×10^7 β*/m/ml (in E-1, out E-7)
Scrub: 0.5 M $Al(NO_3)_3$, 0.65 N HNO_3 deficient (in S-1, out E-7)
Organic: 41% TBP in Amsco, neut. (in E-7, out S-8)
Feed/scrub/organic flow ratio: 1/1/5
5.0 vol. changes
Determinations: Th (mg/ml), HNO_3 (N), β (c/m/ml), U (mg/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
S-8	U	0.2	-	-	-
	Th	77.6	72.6	1.1	5.5
	HNO_3	-	0.59(b)	-	-
	β	5.0×10^2	1.9×10^3	0.26	1.3
S-6	Th	94.0	112.0	0.84	4.2
	HNO_3	-	0.58(b)	-	-
	β	2.9×10^3***	3.5×10^4	0.08	0.4
S-4	Th	95.2	142.0	0.67	3.3
	HNO_3	-	0.61(b)	-	-
	β	5.8×10^4	1.4×10^6	0.04	0.2
S-2	Th	97.0	140.0	0.69	3.5
	HNO_3	-	0.55(b)	-	-
	β	7.0×10^5	6.8×10^6	0.10	0.5
E-1	Th	89.8	81.2	1.1	2.75
	HNO_3	-	0.1	-	-
	β	1.6×10^6**	1.8×10^7	0.09	0.22
E-3	Th	1.88	0.023	84.0	210.0
	HNO_3	-	0.025	-	-
	β	3.8×10^5	1.7×10^7	0.02	0.05
E-5	Th	<0.001	0.005	-	-
	HNO_3	-	0.03	-	-
	β	2.9×10^5	1.4×10^7	0.02	0.05
E-7	Th	<0.001	0.005	-	-
	HNO_3	-	0.005	-	-
	β	2.0×10^5	1.6×10^7	0.01	0.03
	U	-	0.00003	-	-

*β = 97% protactinium, 2.5% total rare earth, 0.1% zirconium, 0.03% niobium, 0.01% ruthenium.
**β = 99% protactinium, 0.25% total rare earth, 0.25% zirconium, 0.02% niobium, 0.002% ruthenium.
***β = 97% protactinium
(b) = basic, or acid-deficient

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Table 5.3-2

Typical Analytical Data from Countercurrent

Studies of the Thorium-U^{233} Partition Step of Thorex Process No. 2

Organic Feed: 41% TBP in Amsco; thorium, 68 mg/ml; uranium, 1.29 mg/ml; 0.2 N HNO_3* (in E-1, out St-8)
Strip: 0.25 N HNO_3 (in St-8, out E-6)
Organic scrub: 41% TBP in Amsco, neut.
Organic feed/strip/organic scrub flow ratio: 5/5/1
4.0 vol. changes
Determinations: Th (mg/ml), HNO_3 (N), U (mg/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-8	Th	<0.001	0.025	<0.04	<0.05
	U	1.16	0.48	2.4	2.9
	HNO_3	0.05	0.26	0.2	0.24
St-6	Th	0.03	0.2	0.15	0.17
	U	1.64	0.74	2.2	2.65
	HNO_3	0.05	0.26	0.2	0.24
St-4	Th	1.6	9.5	0.17	0.2
	U	1.7	0.42	4.05	4.86
	HNO_3	0.08	0.3	0.26	0.31
St-2	Th	19.2	40.7	0.47	0.57
	U	1.35	0.17	8.0	9.6
	HNO_3	0.09	0.3	0.3	0.36
E-1	Th	49.6	82.4	0.6	0.72
	U	1.6	0.11	14.8	17.8
	HNO_3	0.11	0.5	0.22	0.27
E-3	Th	50.0	82.4	0.6	0.12
	U	0.3	0.02	15.0	3.0
	HNO_3	0.11	0.5	0.22	0.04
E-5	Th	49.0	76.0	0.64	0.13
	U	0.05	0.004	12.5	2.5
	HNO_3	0.11	0.4	0.27	0.05
E-6	Th	-	72.0	-	-
	U	-	0.0016	-	-
	HNO_3	-	0.42	-	-

*HNO_3 is not used in final flowsheet.

Table 5.3-3

Typical Analytical Data from Countercurrent

Studies of the U^{233} Stripping Step of Thorex Process No. 2

Feed: 41% TBP in Amsco; uranium, 0.138 g/liter; 0.03 N HNO_3 (in St-1, out St-8)
Strip: 0.025 N HNO_3 (in St-8, out St-1)
Feed/strip flow ratio: 2/1
Determinations: HNO_3 (N), U (mg/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-8	HNO_3	0.002	0.028	0.07	0.14
	U	<0.0004	0.0005*	-	-
St-6	HNO_3	0.002	0.028	0.07	0.14
	U	<0.0004	0.005*	-	-
St-4	HNO_3	0.002	0.030	0.06	0.12
	U	<0.0004	0.055*	-	-
St-2	HNO_3	0.005	0.048	0.1	0.2
	U	0.0038	0.15	0.03	0.06
St-1	HNO_3	0.01	0.095	0.1	0.2
	U	0.077	0.28	0.27	0.54

*Uncertain

Table 5.3-4

Typical Analytical Data from Countercurrent

Studies of the Protactinium Extraction Step of Thorex Process No. 2a

Feed: 0.75 M $Al(NO_3)_3$, 0.1 N HNO_3, 4.1×10^7 β c/min/ml (3.98×10^7 Pa β/m/ml) (in E-1, out E-8)
Organic: 41% TBP in Amsco, 0.1 N HNO_3 (in E-8, out St-8)
Strip: 0.05 N HNO_3 (in St-8, out St-1)
Feed/organic/strip flow ratio: 1/3/1
3.0 vol. changes
Determinations: gross β (c/min/ml), Pa β (c/min/ml)

Stage	Determinations	Organic	Aqueous	D.C.(O/A)	E.F.(O/A)
St-8	β	3.6×10^4	2.9×10^3	12.0	36.0
	Pa	3.3×10^4	2.0×10^3	16.5	49.5
St-6	β	2.0×10^4	2.6×10^4	0.7	2.1
	Pa	-	-	-	-
St-4	β	4.3×10^3	5.8×10^5	0.007	0.021
	Pa	-	-	-	-
St-2	β	6.2×10^4	1.6×10^7	0.004	0.012
	Pa	5.6×10^4	1.6×10^7	0.0035	0.01
St-1	β	-	4.6×10^7	-	-
	Pa	-	4.1×10^7	-	-
E-1	β	1.4×10^7	5.9×10^6	2.4	7.2
	Pa	1.3×10^7	5.5×10^6	2.4	7.2
E-3	β	1.0×10^6	1.5×10^6	0.67	2.2
	Pa	-	-	-	-
E-5	β	1.6×10^5	4.4×10^5	0.36	1.1
	Pa	-	-	-	-
E-7	β	6.0×10^3	4.0×10^5	0.015	0.045
	Pa	1.1×10^3	3.0×10^4	0.037	0.11
E-8	β	-	3.8×10^5	-	-
	Pa	-	-	-	-

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7.0 Appendix

Certain data and findings obtained during laboratory development studies, but not discussed in detail within the body of this report, are presented in this appendix.

7.1 The Primary Extraction Mechanisms of Nitric Acid and Thorium Nitrate by TBP (J. E. Savolainen)

These experiments were carried out to elucidate the reactions by which thorium is extracted by TBP from aqueous solutions. Since it was anticipated that nitric acid extraction may influence the thorium extraction, the nitric acid extraction reaction was also investigated.

7.1.1 Nitric Acid Extraction by TBP

The complex of nitric acid that is extracted by TBP is reported to be $HNO_3 \cdot TBP$.[57] In the following work, the extraction system TBP in hexane-aqueous nitric acid was investigated, so that the behavior of the nitric acid may be accounted for in a system which also contains thorium nitrate.

The TBP used in these experiments was purified by washing with dilute caustic, dilute sulfuric acid, dilute ammonium carbonate solution, and water. The TBP was then distilled under vacuum, and the middle cut consisting of 50% of the total original volume was collected for use. The hexane used as the diluent was purified by washing with small portions of cold 95% sulfuric acid until no further coloration of the acid phase was observed. The hexane was washed with water, dried over solid potassium hydroxide, and distilled; the fraction distilling between 66 and 68°C was collected.

The data were obtained for the distribution coefficients of nitric acid in the following manner. Varying amounts of nitric acid were measured into 50-ml glass-stoppered graduated cylinders and diluted with water to the 25-ml mark. Twenty-five-milliliter portions of a TBP-hexane solution were pipetted into each cylinder. The cylinders were placed in a water bath, which was allowed to reach an equilibrium temperature with that of the room over a period of 24 hrs. The cylinders were agitated intermittently, and the phases were allowed to settle at least 30 min before sampling. No aqueous particles could be seen in the organic phase at the time of sampling. The pipetted samples were titrated with standardized sodium hydroxide solution to the phenolphthalein end point. The sampling was carried out in such a way that any temperature changes were minimized. The water bath was equilibrated at room temperature, also, in order to minimize temperature changes. A check maintained on the temperature of the water bath showed no variation in temperature greater than

0.1°C during the period in which the samples were drawn from a series of equilibrated mixtures.

The distribution coefficients obtained, listed in Tables 7.1-1, 7.1-2, and 7.1-3, are plotted in Fig. 7.1-1 as functions of the equilibrium aqueous acid concentration. The points using 10% TBP in hexane were determined and plotted first. The positions of the points for the 10% TBP system preclude the possibility of drawing a smooth curve through these points. The experiments were repeated using 7.5 and 12.5% TBP in hexane as the organic phase. The data indicate that with 7.5% TBP in hexane, the extraction behaves as a simple equilibrium reaction, whereas with 10 and 12.5% TBP another phenomenon is superimposed on the simpler reaction.

Figure 7.1-2 shows the plot of the distribution coefficients as a function of the HNO_3/TBP molar concentration ratio in the organic phase. There are flection points at HNO_3/TBP ratios of 1/4, 1/2, and 3/4, with probable flections at other points. This regular flection of the distribution coefficient curve as a function of the bulk HNO_3/TBP concentration ratio may be the result of the dipole-dipole interaction forces in the organic phase. The distribution curve with 7.5% does not show this behavior because the greater distances between the dipoles in this more dilute solvent reduce the dipole interaction.

With 7.5% TBP in hexane, the extraction is apparently the result of the formation of the $HNO_3 \cdot TBP$ complex. The extraction reaction can be expressed in three steps as:

$$H^+_{aq} + NO^-_3\,aq \rightleftharpoons HNO_3aq$$

$$HNO_3aq \rightleftharpoons HNO_3org$$

$$HNO_3org + TBPorg \rightleftharpoons HNO_3 \cdot TBP$$

Combining the three reactions gives the overall reactions

$$H^+_{aq} + NO^-_{3aq} + TBP_{org} \rightleftharpoons HNO_3 \cdot TBP_{org}, \qquad (1)$$

for which the equilibrium constant may be written as

$$\underline{K}_1 = \frac{[HNO_3 \cdot TBP_{org}]}{[H^+_{aq}][NO^-_{3aq}][TBP_{org}]} \qquad (2)$$

where the brackets refer to activities.

Table 7.1-1

Extraction of Nitric Acid from Aqueous Solution

by 10% TBP (0.367 M) in Hexane at 20°C

Equilibrium Concentrations		Distribution Coefficients,	M HNO_3 org / M TBP org
HNO_{3aq} (M)	HNO_{3org} (M)	E (O/A) HNO_3	
0.49	0.013	0.0266	0.0355
0.94	0.041	0.0436	0.112
1.40	0.088	0.0630	0.240
1.86	0.128	0.0690	0.350
2.36	0.178	0.0755	0.485
2.76	0.204	0.0740	0.557
3.32	0.236	0.0711	0.643
3.88	0.271	0.0700	0.740
4.32	0.284	0.0658	0.772
4.82	0.306	0.0637	0.832
5.22	0.333	0.0638	0.907
5.74	0.348	0.0606	0.948
6.82	0.356	0.0572	0.970
6.76	0.363	0.0537	0.989

Table 7.1-2

Extraction of Nitric Acid from Aqueous Solutions

by 7.5% TBP (0.275 M) in Hexane at 20°C

Equilibrium Concentrations		Distribution Coefficients	$\frac{M\ HNO_{3org}}{M\ TBP_{org}}$	K_1
HNO_{3aq} (M)	HNO_{3org} (M)	E (O/A) HNO_3		
0.33	0.0078	0.0236	0.0284	0.2685
0.62	0.0198	0.0319	0.0720	0.2016
0.90	0.0350	0.0389	0.127	0.1796
1.21	0.0558	0.0461	0.203	0.1733
1.50	0.0765	0.0510	0.278	0.1710
1.82	0.0993	0.0545	0.361	0.1706
2.03	0.115	0.0566	0.418	0.1745
2.40	0.139	0.0579	0.505	0.1766
2.70	0.159	0.0589	0.579	0.1885
3.01	0.177	0.0588	0.644	0.1995
3.34	0.194	0.0581	0.706	0.2155
3.63	0.205	0.0565	0.746	0.2230
3.94	0.219	0.0556	0.796	0.2515
4.20	0.228	0.0543	0.828	0.2725
4.53	0.238	0.0525	0.865	0.311
4.93	0.247	0.0502	0.896	0.356
5.20	0.255	0.0490	0.926	0.462
5.50	0.257	0.0467	0.934	0.465

Table 7.1-3

Extraction of Nitric Acid from Aqueous Solutions by 12.5% TBP (0.457 M) in Hexane at 20°C

Equilibrium Concentrations		Distribution Coefficients	$\frac{M\ HNO_{3org}}{M\ TBP_{org}}$
HNO_{3aq} (M)	HNO_{3org} (M)	E (O/A) HNO_3	
0.233	0.00875	0.0375	0.0191
0.458	0.0208	0.0455	0.0454
0.685	0.0418	0.0610	0.0911
0.904	0.0643	0.0711	0.140
1.126	0.0914	0.0812	0.200
1.344	0.1238	0.0920	0.248
1.544	0.144	0.0932	0.314
1.783	0.168	0.0941	0.366
1.976	0.188	0.0952	0.410
2.216	0.214	0.0966	0.466
2.440	0.242	0.0994	0.529
2.650	0.259	0.0976	0.564
3.09	0.297	0.0960	0.615
3.38	0.320	0.0944	0.696
3.57	0.343	0.0961	0.748
3.78	0.351	0.0929	0.765
4.02	0.363	0.0903	0.792
4.20	0.375	0.0893	0.817
4.53	0.391	0.0864	0.852
4.74	0.400	0.0844	0.872
4.94	0.407	0.0825	0.887
5.18	0.417	0.0805	0.909
5.44	0.424	0.0779	0.925

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Fig. 7.1-1

Nitric Acid Distribution Coefficients as a Function of HNO_{3aq} Concentration

Solvent: TBP in Hexane Temperature: 20°C

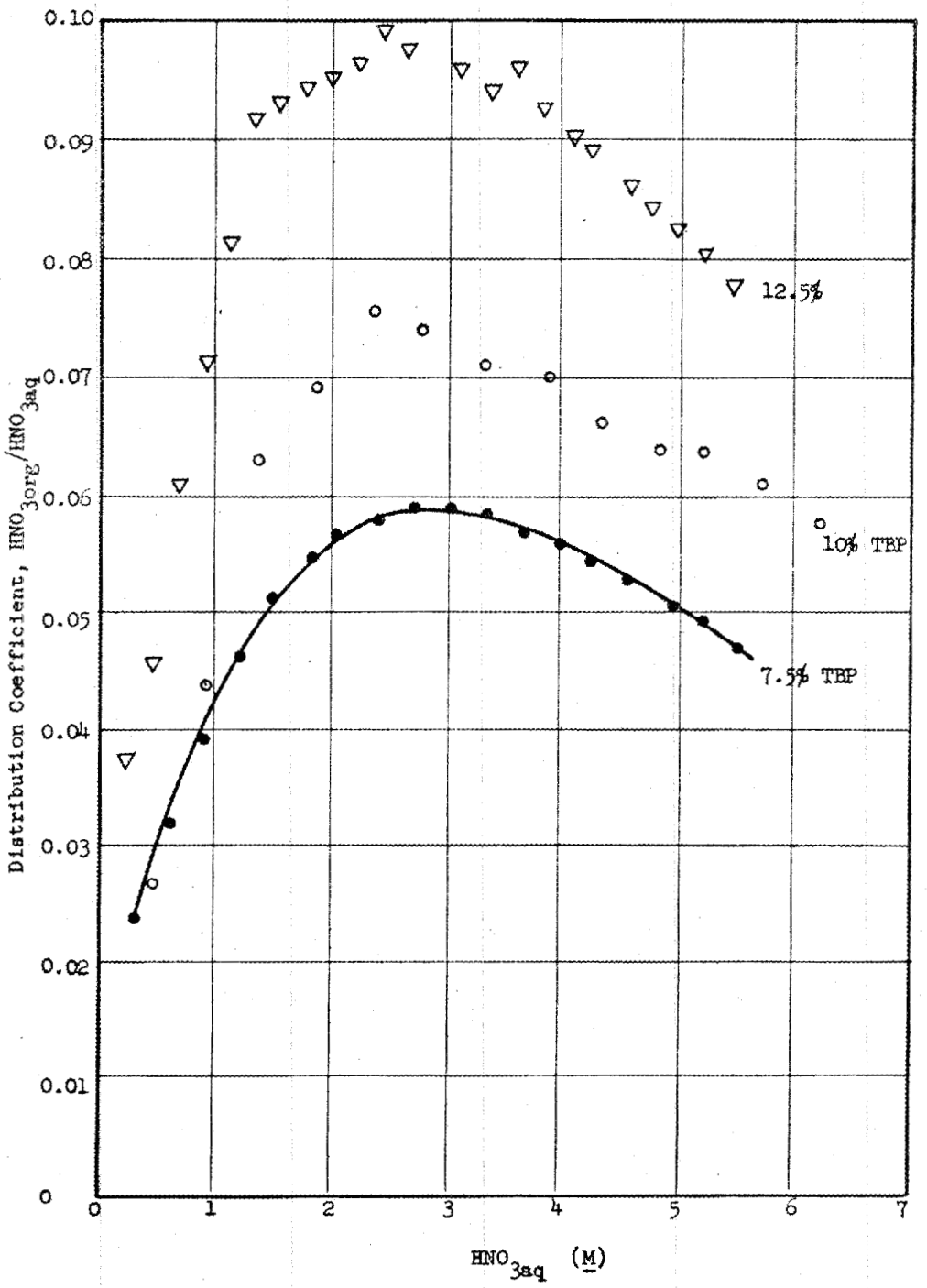

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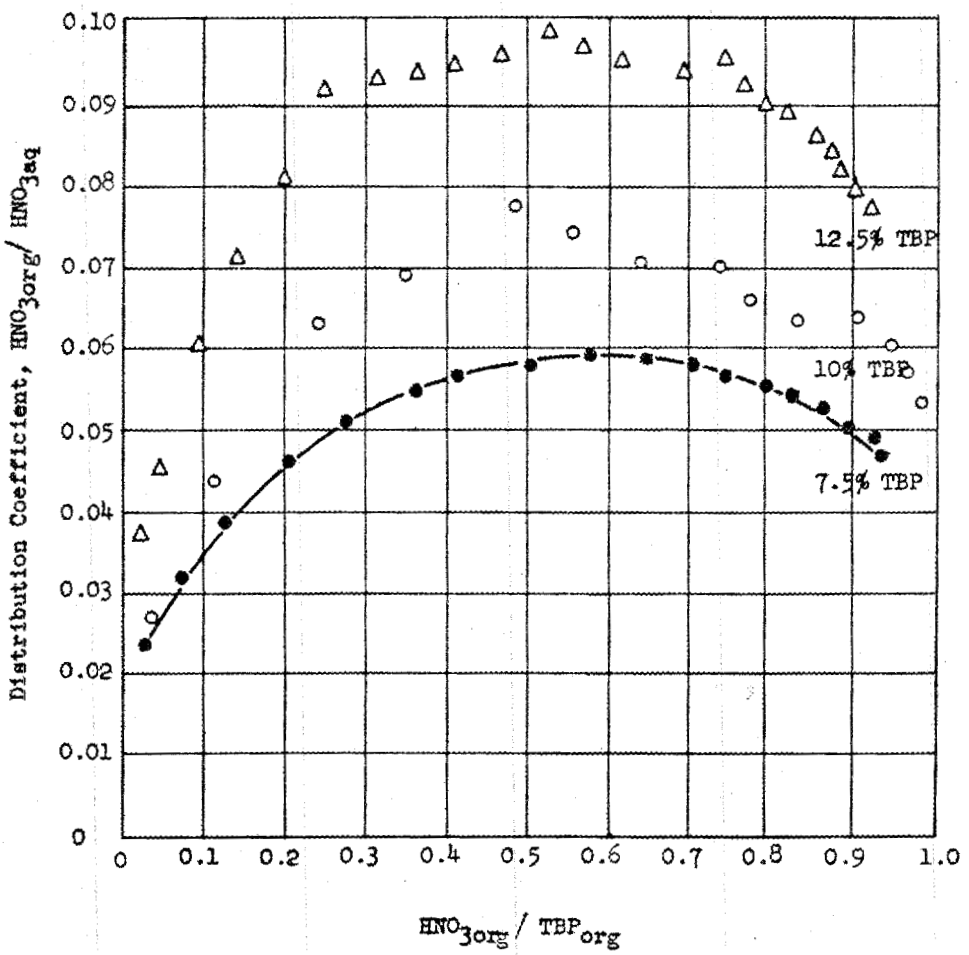
Figure 7.1-2

Nitric Acid Distribution Coefficient as a Function of HNO_{3org}/ TBP_{org} Concentration Ratio



The total TBP will be distributed as follows:

$$(TBP)_t = (HNO_3 \cdot TBP_{org}) + (TBP_{org}) \qquad (3)$$

where the parentheses refer to concentrations. $(TBP)_t$ is the total TBP in the organic phase, $(HNO_3 \cdot TBP_{org})$ is the TBP complexed with the nitric acid in the organic phase, and (TBP_{org}) is the free TBP in the organic phase. To simplify the evaluation of the equilibrium constant, the $\underline{K}$ of Eq. (2) is calculated on the basis of molar concentrations by combining Eqs. (2) and (3) to give

$$\underline{K} = \frac{1}{\left[\frac{(TBP)_t}{(HNO_3 \cdot TBP_{org})} - 1\right] (HNO_{3aq})^2} \qquad (4)$$

It is assumed that the activities are proportional to the concentrations within the range of the experiment. The nitric acid is assumed to be essentially 100% ionized so that the product, $(H^+_{aq})(NO^-_{3aq})$, is almost equal to $(HNO_{3aq})^2$, where (HNO_{3aq}) is the bulk nitric acid concentration in the aqueous phase. The equilibrium constant, $\underline{K}_1$, based on molar concentrations for the nitric acid extraction reaction is plotted in Fig. 3 as a function of the aqueous nitric acid concentration from the data in Table 7.1-2. The plot shows that between 1 and 2.5 $\underline{M}$ nitric acid in the aqueous phase the value of $\underline{K}_1$ does not vary appreciably with changes of the aqueous nitric acid concentration in this range. It was therefore decided to study the thorium nitrate extraction mechanism in this range of nitric acid concentrations.

7.1.2 Thorium Nitrate Extraction by TBP

The extraction of thorium nitrate may be expected to follow a series of reactions:

$$Th^{4+}_{aq} + 4NO^-_{3aq} \rightleftharpoons Th(NO_3)_{4aq}, \qquad (5)$$

$$Th(NO_3)_{4aq} + nTBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot nTBP_{org}. \qquad (6)$$

These can be combined to give the overall reaction,

$$Th^{4+}_{aq} + 4NO^-_{3aq} + nTBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot nTBP_{org}, \qquad (7)$$

Dwg. #13976

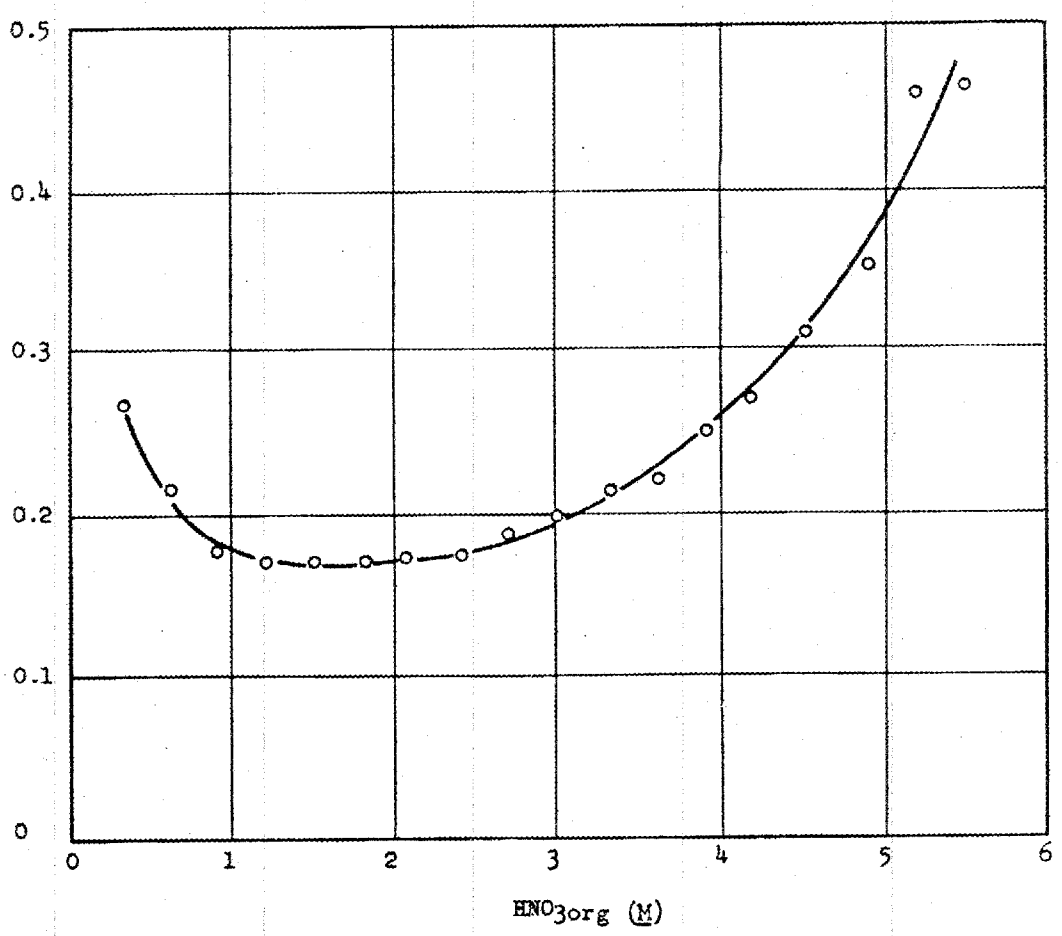
Figure 7.1-3

Equilibrium Constant of Extraction Reaction as a Function of HNO_{3org} Concentration

Based on concentrations, $K = \frac{(HNO_3 \cdot TBP_{org})}{(H^+_{aq})\ (NO^-_{3aq})\ (TBP_{org})}$

Solvent: 7.5% TBP in Hexane

Temperature: 20°C



for which the equilibrium constant would be

$$K_2 = \frac{[Th(NO_3)_4 \cdot \underline{n}TBP_{org}]}{[Th^{4+}_{aq}]\,[NO^-_{3aq}]^4\,[TBP_{org}]^n} \qquad (8)$$

The number n of TBP molecules associated with the thorium nitrate molecule can be determined graphically.

Equation (2) is rewritten as

$$[TBP_{org}] = [HNO_3 \cdot TBP_{org}] \;/\; [H^+_{aq}][NO_{3aq}]\,\underline{K}_1,$$

and is combined with Eq. (8) to give

$$\underline{K}_2 = \frac{[Th(NO_3)_4 \cdot \underline{n}TBP_{org}]}{[Th^{4+}][NO^-_{3aq}]^4 \left[\dfrac{[HNO_3 \cdot TBP_{org}]}{[H^+_{aq}]\,[NO^-_{3aq}]\;\underline{K}_1}\right]^{\underline{n}}} \qquad (9)$$

The thorium distribution coefficient, $\underline{E}$ (O/A)Th, is equal to

$$(Th(NO_3)_4 \cdot nTBP_{org})/(Th^{4+}_{aq})$$

and the nitric acid distribution coefficient, $\underline{E}$ (O/A) HNO_3, is equal to $(HNO_3 \cdot TBP_{org})/(H^+_{aq})$. Assuming that the thorium nitrate is present almost entirely as the Th^{4+} and NO^-_3 ions in the aqueous phase at low thorium concentrations, and that the activities are proportional to the concentrations within the limits of the experiment, then the logarithmic equation can be written on the basis of molar concentrations as an approximation, giving

$$\log \underline{K}_2 + \underline{n} \log \frac{\underline{E}(O/A)HNO_3}{\underline{K}_1(NO^-_{3aq})} = \log \frac{\underline{E}(O/A)Th}{(NO^-_{3aq})^4} \qquad (10)$$

A plot of the log $\underline{E}$ (O/A) $Th/(NO^-_{3aq})^4$ as a function of log $\underline{E}$ (O/A) $HNO_3/\underline{K}_1(NO^-_{3aq})$

should have a slope equal to n of the equations. Figure 7.1-4 plotted from the data in Table 7.1-4 shows the plot of the points obtained from calculations made from data obtained by extracting an aqueous phase 0.05 M in thorium nitrate and varying from 1 to 2.5 M in HNO_3 with an organic phase 7.5% TBP in hexane. The slope of the plot determined graphically is 3.9, which indicates that 4 is the most probable TBP/Th ratio in the complex. The overall reaction in the extraction of thorium nitrate can be said to be

$$Th^{4+}_{aq} + 4NO^{-}_{3aq} + 4TBP_{org} \rightleftharpoons Th(NO_3)_4 \cdot 4TBP \qquad (11)$$

The equilibrium constants based on molar concentrations for the nitric acid and thorium nitrate extraction reactions with TBP are listed for the determined points in Table 7.1-4. In an experiment made to determine the amount of thorium nitrate that can be extracted into 100% TBP, a sample of TBP was equilibrated for 48 hr with an excess of solid thorium nitrate and sodium nitrate. Analysis showed the liquid phase to have a bulk TBP/Th ratio of 2.48.

7.1.3 Discussion:

The equilibrium constant, based on molar concentrations, for the nitric acid extraction by 7.5% TBP shows a variation between that calculated from a system containing no thorium (Table 7.1-2, Fig. 7.1-3) and that of a system containing thorium (Table 7.1-4). The equilibrium constant of the thorium nitrate extraction reaction shows an increase as the nitric acid of the system is increased. These changes in the equilibrium constant may be the result of activity coefficient changes in the aqueous phase.

The manner in which the activity coefficients of either the TBP or the extracted nitric acid complex vary in systems with TBP concentrations 10% and higher is indicated in Figs. 7.1-1 and 7.1-2 by the distribution coefficient curves. This apparent variation of the activity coefficients may be related to dipole interactions. The influence of this behavior on the thorium nitrate extraction is indicated in Sec. 4.1.3. This behavior may be anticipated in solvent extraction systems in which the energy associated with dipole interaction or coupling is comparable to the energy of the complex formation.

Dwg. #13977

Fig. 7.1-4 Graph Showing TBP Dependency of Thorium Extraction (Log Scale) Extraction of Nitric Acid and Thorium Nitrate from Aqueous Solutions by 7.5% TBP in Hexane

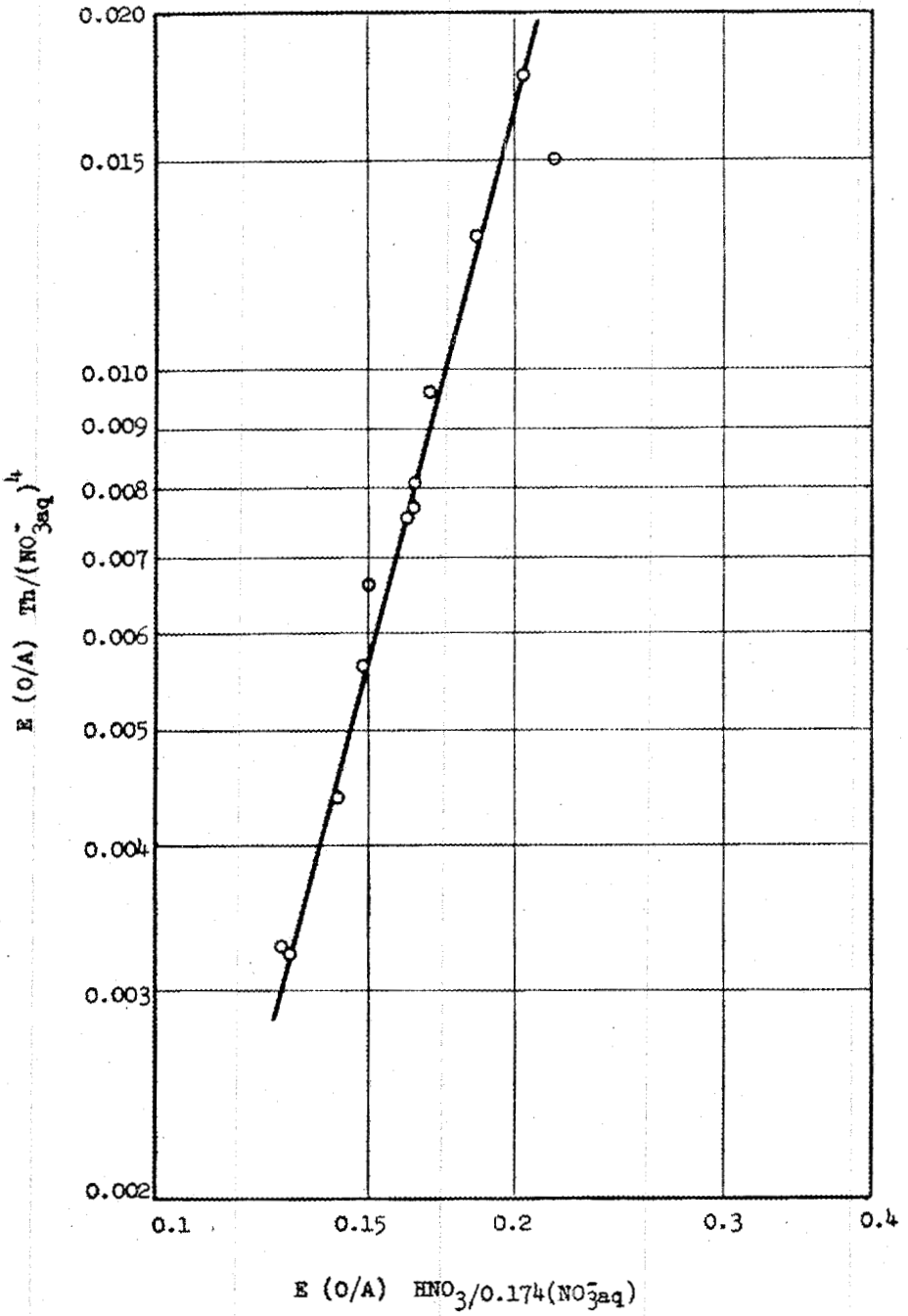


Table 7.1-4

Extraction of Nitric Acid and Thorium Nitrate from Aqueous Solutions by 7.5% TBP (0.275 M) in Hexane

Equilibrium Concentrations				$\frac{E\ (O/A)\ Th}{(NO^-_{3aq})^4}$	$\frac{E\ (O/A)\ HNO_3}{0.174(NO^-_{3aq})}$	Equilibrium Constants	
HNO_{3aq} (M)	$Th(NO_3)_{4aq}$ (M)	HNO_{3org} (M)	$Th(NO_3)_{4org}$ (M)			K_1	K_2
0.96	0.0480	0.0385	0.00151	0.0178	0.200	0.151	0.629
1.17	0.0479	0.0512	0.00215	0.0131	0.1845	0.152	0.607
1.236	0.0461	0.0650	0.00284	0.0152	0.2128	0.186	0.958
1.47	0.0455	0.0710	0.00327	0.00966	0.168	0.153	0.699
1.54	0.0452	0.0757	0.00306	0.00770	0.164	0.153	0.626
1.62	0.0410	0.0825	0.00336	0.00810	0.164	0.160	0.782
1.66	0.0500	0.0875	0.00452	0.00758	0.163	0.168	0.920
1.80	0.0504	0.0940	0.00493	0.00660	0.150	0.189	0.895
1.88	0.0495	0.1005	0.00521	0.00565	0.148	0.169	1.018
2.06	0.0491	0.1115	0.00556	0.00434	0.1412	0.170	1.105
2.28	0.0501	0.1250	0.00621	0.00327	0.1270	0.177	1.425
2.34	0.0501	0.1285	0.00613	0.00322	0.1272	0.181	1.445

7.2 Empirical Expressions for the Mechanism of the $TBP \cdot HNO_3$ Complex Formation (A. T. Gresky)

The equations were derived from data plotted in Fig. 7.2-1 and express HNO_3 D.C.'s (O/A) as functions of the TBP concentration and the $TBP \cdot HNO_{3aq}$ product. Several expressions were required to duplicate observed "peak behavior" in curves.

Range of HNO_{3aq}	TBP/HNO_3 Ratio*	HNO_3 D.C. (O/A) =
(1) 0.0 - 0.25 N	16/1	$0.0[TBP] + 0.375[TBP \cdot HNO_{3aq}] = 0.375[TBP \cdot HNO_{3aq}]$
(2) 0.25 - 0.75 N	8/1	$0.031[TBP] + 0.250[TBP \cdot HNO_{3aq}] = 0.031\ TBP[1 + 8\ HNO_{3aq}]$
(3) 0.75 - 1.25 N	4/1	$0.063[TBP] + 0.125[TBP \cdot HNO_{3aq}] = 0.063\ TBP[1 + 2\ HNO_{3aq}]$
(4) 1.25 - 2.25 N	2/1	$0.188[TBP] + 0.016[TBP \cdot HNO_{3aq}] = 0.188\ TBP[1 + 0.084\ HNO_{3aq}]$
(5) 2.25 - 8.0 N	1/1	$0.25[TBP] - 0.016[TBP \cdot HNO_{3aq}] = 0.25\ TBP[1 - 0.063\ HNO_{3aq}]$

*The tabulated $TBP \cdot HNO_3$ ratio was observed at the peaks found in the experiment using 12.5% TBP.

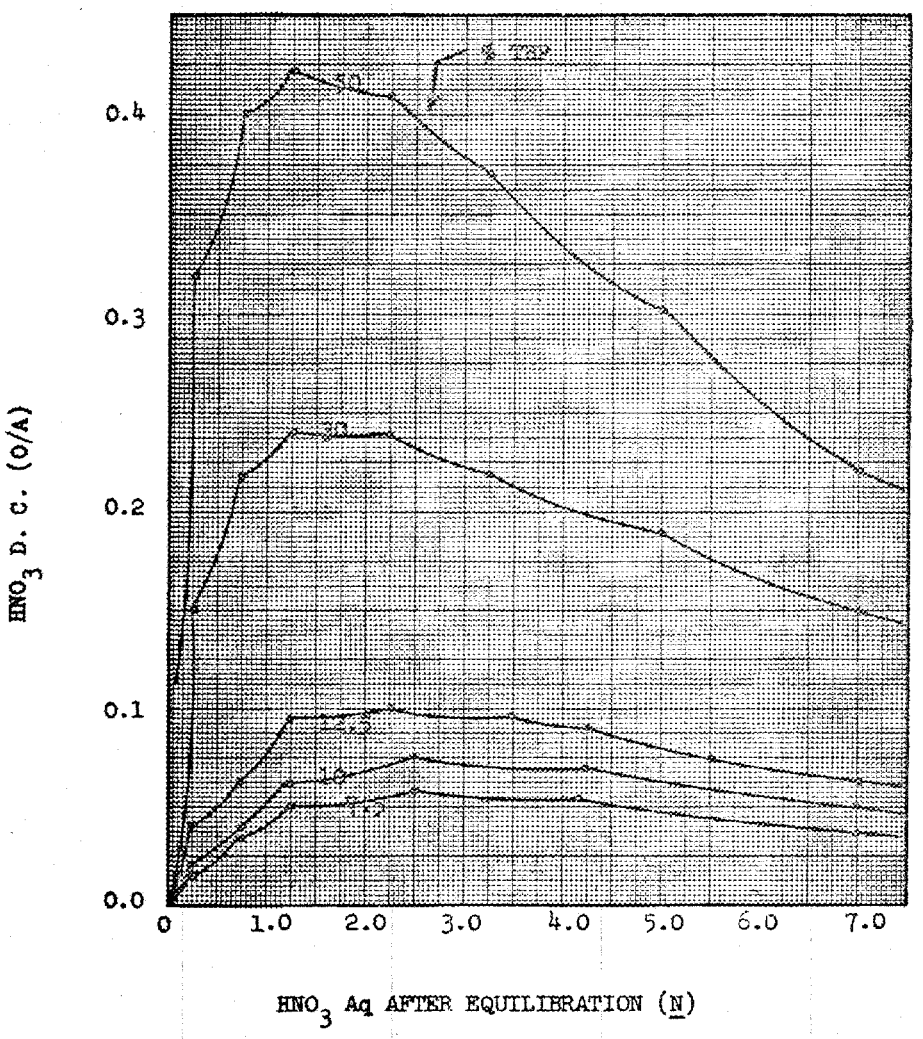
The following correlations were obtained using Eq. (5):

12.5% TBP (0.459 M)			30% TBP (1.1 M)			50% TBP (1.84 M)		
HNO_{3aq}	Obs. D.C.	Calc. D.C.	HNO_{3aq}	Obs. D.C.	Calc. D.C.	HNO_{3aq}	Obs. D.C.	Calc. D.C.
2.216	0.0966	0.0975	2.36	0.233	0.232	2.37	0.385	0.387
3.09	0.096	0.0908	3.5	0.216	0.211	3.43	0.350	0.354
3.78	0.0929	0.0856	4.6	0.196	0.190	4.63	0.313	0.318
4.53	0.0864	0.0799	6.07	0.167	0.163	5.13	0.300	0.302
5.44	0.0779	0.0728				6.78	0.250	0.250

Dwg. #15919

Fig. 7.2-1 Distribution Coefficient (O/A) of Nitric Acid in TBP-Hexane Mixtures as a Function of HNO_3 Aq Normality at Equilibrium. Note: The HNO_3 D.C. (O/A) between 2.0 and 8.0 M HNO_3 aq may be expressed by 0.25 TBP(1-0.063 HNO_3 aq).

Conditions: HNO_3 solutions contacted with 7.5 to 50% TBP-hexane solvent and resulting phases analyzed for H^+ (N)



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7.3 Specific Gravities of Synthetic Dissolver Solutions*

Composition			Specific Gravity		
$Th(NO_3)_4$ (M)	$Al(NO_3)_3$ (M)	HNO_3 (M)	At 15°C	At 20°C	At 30°C
1.20	0.20	0.76	1.5144 (16°C)	1.5104 (21°C)	1.5048 (29°C)
1.20	0.20	1.00	1.5224 (16°C)	1.5184	1.5107
1.20	0.20	1.50	1.5360	1.5313	1.5240 (29°C)
1.20	0.50	.76	1.5579	1.5543	1.5478 (29°C)
1.20	0.50	1.00	1.5623 (15.5°C)	1.5591	1.5517
1.20	0.50	1.50	1.5762 (16°C)	1.5723	1.5642
1.20	0.80	0.76	1.5930	1.5904 (19°C)	1.5835 (29°C)
1.20	0.80	1.00	1.5981 (20.5°C)	1.5958 (20.5°C)	1.5894 (29.5°C)
1.20	0.80	1.50	1.6140 (16°C)	1.6109 (19.5°C)	1.6020
1.60	0.20	0.76	1.6754	1.6707	1.6622 (29°C)
1.60	0.20	1.00	1.6798 (16°C)	1.6744 (21°C)	1.6668
1.60	0.20	1.50	1.6896	1.6860	1.6764
1.60	0.50	0.76	1.7121	1.7096	1.7039 (29.5°C)
1.60	0.50	1.00	1.7158 (16.5°C)	1.7146	1.7077 (29.5°C)
1.60	0.50	1.50	1.7277 (16°C)	1.7248	1.7167 (31°C)
1.60	0.80	0.76	1.7510 (16°C)	1.7460 (19°C)	1.7366
1.60	0.80	1.00	1.7527	1.7487	1.7408
1.60	0.80	1.50	1.7623	1.7571	1.7499
2.00	0.20	0.76	1.8172 (16°C)	1.8126 (20.5°C)	1.8025
2.00	0.20	1.00	1.8209 (14°C)	1.8169 (19°C)	1.8063 (29.5°C)
2.00	0.20	1.50	1.8287 (16°C)	1.8267 (19°C)	1.8185
2.00	0.50	.76	1.8531 (15.5°C)	1.8482	1.8388
2.00	0.50	1.00	1.8561	1.8518	1.8407 (31°C)

*Also see Figs. 7.3-1, 2, 3.

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Fig. 7.3-1 Specific Gravities of Synthetic Dissolver Solutions at 20°C as a Function of Thorium Concentration. Note: Slope = about 0.373 sp. gr. units/M $Th(NO_3)_4$ (see Sec. 3.5.7).

Concentrations of Accompanying Materials:

	0.2 M $Al(NO_3)_3$	0.5 M $Al(NO_3)_3$	0.8 M $Al(NO_3)_3$
0.76 M HNO_3	Curve 1	Curve 4	Curve 7
1.00 M HNO_3	Curve 2	Curve 5	Curve 8
1.50 M HNO_3	Curve 3	Curve 6	Curve 9

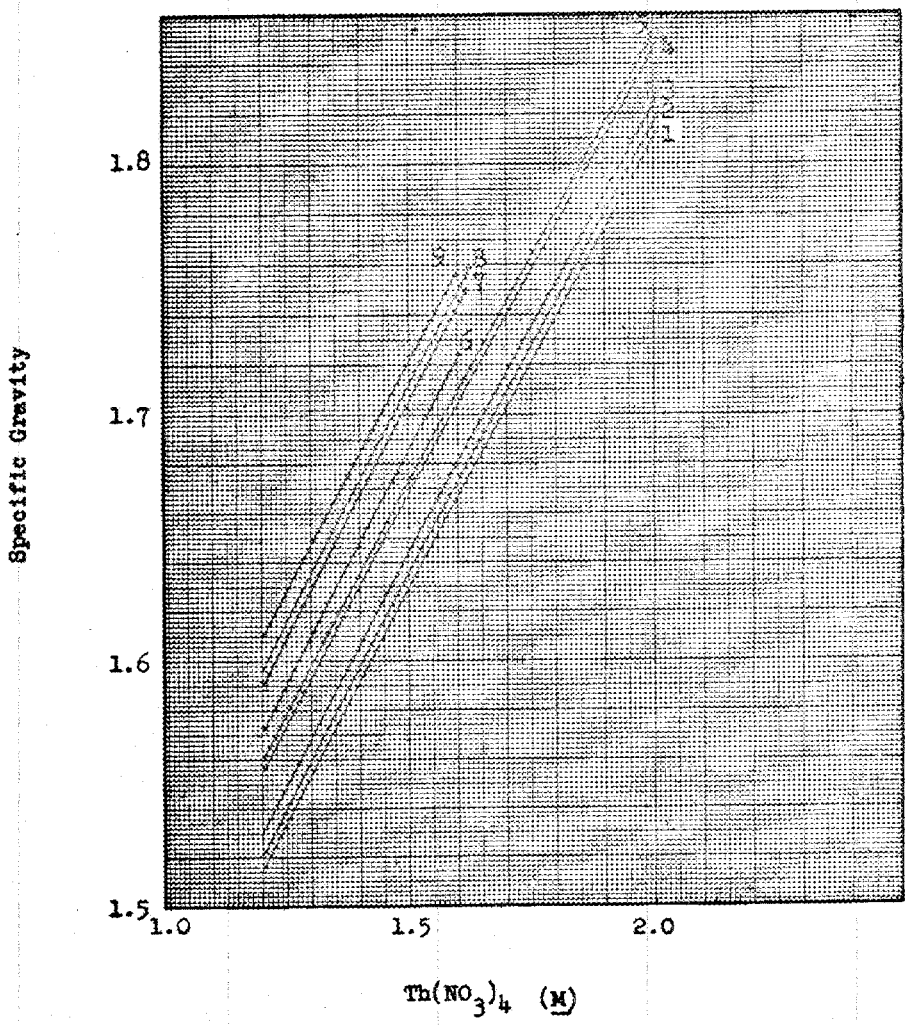

Fig. 7.3-2 Specific Gravities of Synthetic Dissolver Solutions at 20°C as a Function of Aluminum Nitrate Concentration. Slope = about 0.126 sp. gr. units/M $Th(NO_3)_4$ (see Sec. 3.5.7).

Concentrations of Accompanying Materials

	1.2 M $Th(NO_3)_4$	1.6 M $Th(NO_3)_4$	2.0 M $Th(NO_3)_4$
0.76 M HNO_3	Curve 1	Curve 4	Curve 7
1.00 M HNO_3	Curve 2	Curve 5	Curve 8
1.50 M HNO_3	Curve 3	Curve 6	--

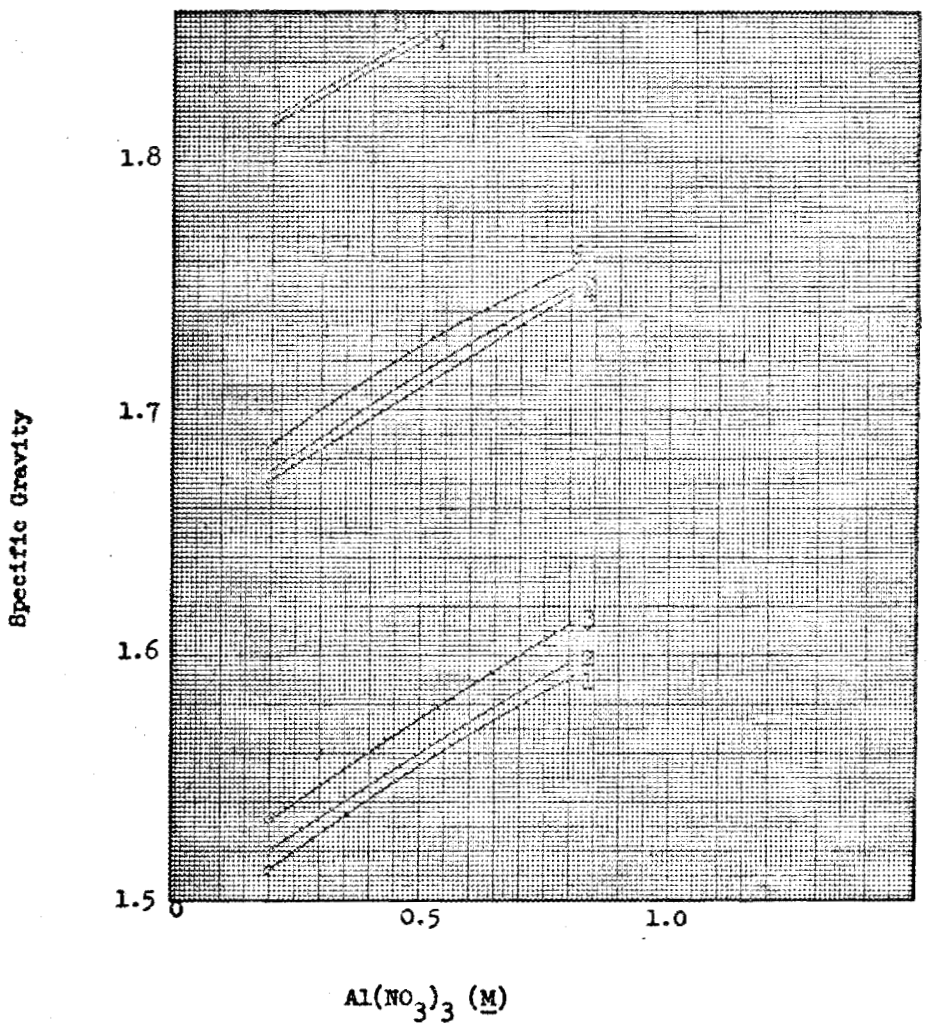

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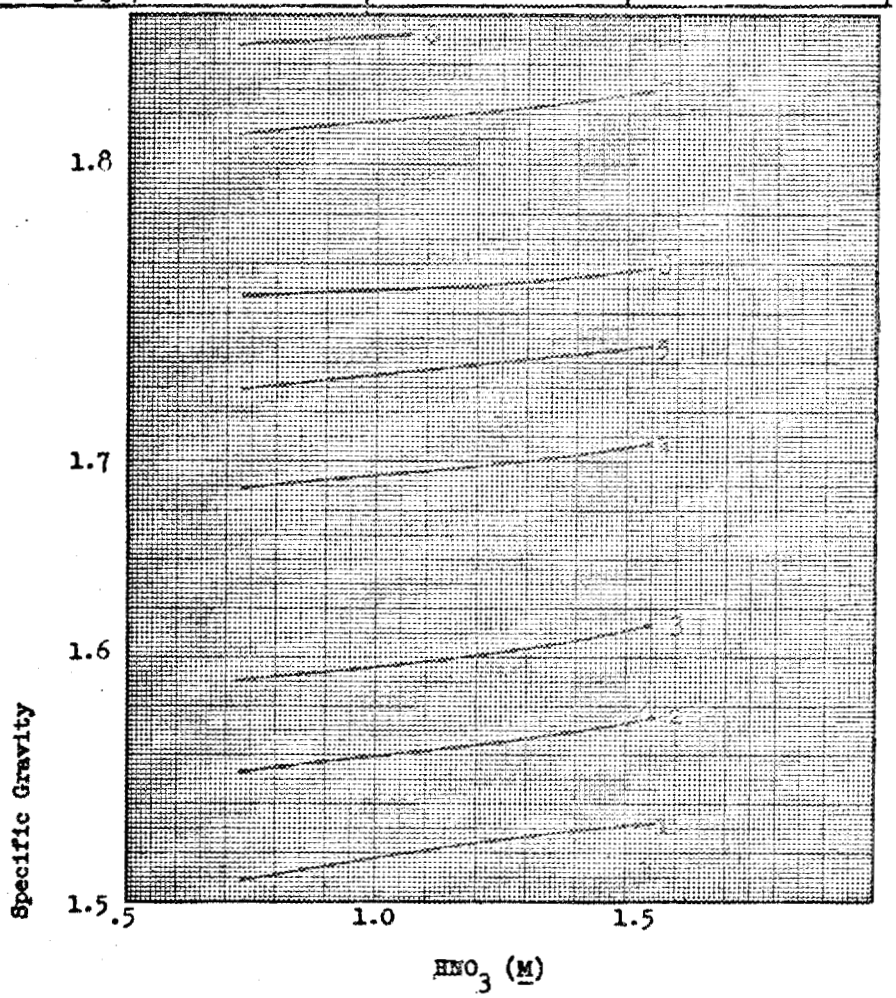
Fig. 7.3-3 Specific Gravities of Synthetic Dissolver Solutions at 20°C. as a Function of Nitric Acid Concentration.

Slope = about 0.0195 sp. gr. units/M HNO_3 (see Sec. 3.5.7)

Concentrations of Accompanying Materials

	1.2 M $Th(NO_3)_3$	1.6 M $Th(NO_3)_4$	2.0 M $Th(NO_3)_4$
0.2 M $Al(NO_3)_3$	Current 1	Current 4	Current 7
0.5 M $Al(NO_3)_3$	Current 2	Current 5	Current 8
0.8 M $Al(NO_3)_3$	Current 3	Current 6	-



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