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PART I: INTRODUCTION

CHAPTER I. INTRODUCTION

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CHAPTER I. INTRODUCTION

A. PURPOSE, SCOPE, AND ARRANGEMENT OF MANUAL

1. Purpose and Scope

The Uranium Recovery Technical Manual has been prepared to provide a documentation of the fundamental technical bases and general features of uranium recovery facilities (including uranium removal facilities, the TBP Plant, and the UO_3 Plant) at Hanford Works. The manual is intended for use as a means for training and educating personnel unfamiliar with the processes and as a reference handbook for the use of personnel responsible for the operation of the plant.

The material contained in this manual was assembled by Chemical Development, Separations Technology Unit, between December 1950 and October 1951.

2. Arrangement

The manual is divided into five parts as follows:

Part	Title
I	Introduction
II	Process
III	Plant and Equipment
IV	Process Control
V	Safety

Part I contains a summary of general information about the plant and process and is designed to provide the reader with a synoptic view as an aid in understanding the subsequent parts.

Part II contains a step-by-step description of the processes with statements and discussions of the scientific and engineering principles involved, and outlines of procedure, including remedies for any off-standard conditions.

Part III describes the plant layout, equipment arrangement, and individual equipment pieces.

Part IV describes the instruments and analytical methods used for process control.

Part V describes process hazards and the methods used to safeguard against them.

Each part contains one or more chapters. A total of twenty-four chapters is included in the five parts.

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Pages are numbered to designate the chapter number (i.e., Chapter I page numbers begin with 101, Chapter II with 201, etc.). A table of contents is listed on the first page of each chapter. Tables and figures are located at the end of each chapter, the tables preceding the figures. The tables are numbered in one separate series for each chapter, as are the figures (e.g., Table II-1, Table II-2, followed by Figure II-1, Figure II-2, etc.). References to material containing more detailed information on specific points are listed at the end of chapters to which they are pertinent, just before the tables and figures.

A subject index, in alphabetical order, is included in the back of the manual for quick reference to specific points.

B. FUNCTION OF THE PLANT

1. General

The function of the Uranium Recovery Plant is to produce a relatively pure uranium trioxide powder from the uranium irradiated in the Hanford piles and processed, for plutonium recovery, through one of the Bismuth Phosphate Plants or the Redox Plant.

The uranium from the Bismuth Phosphate Plants is stored in underground tanks in the form of a uranium-bearing waste, consisting of sludge and supernatant liquor which contain a large fraction of the radioactive fission products and traces of the plutonium formed in the pile-irradiation of the uranium. Facilities for removal of this uranium waste from underground storage constitute one of the three major components of the plant.

The second major component of the Uranium Recovery Plant is the TBP Plant, in which the uranium in the waste removed from underground storage is decontaminated from the fission products and residual plutonium by a solvent-extraction process.

The third major component of the Uranium Recovery Plant is the UO_3 Plant, in which uranyl nitrate solutions produced by the TBP and Redox Plants, meeting the required purity and radioactivity specifications, are converted to uranium trioxide (UO_3) powder by calcination.

2. Design Production Capacity and Yield

2.1 Uranium removal facilities and TBP Plant

The uranium removal facilities and the TBP Plant are designed to process the approximately 5900 short tons of uranium in underground storage (as of January 1, 1952) at an average rate of 8 short tons/day. The maximum instantaneous production rate used as the design basis is based on an assumed 80% operating time efficiency, i.e., 20% down time for repairs, maintenance, etc. Thus the maximum instantaneous design production capacity is 10 short tons of uranium per day. The removal

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facilities and the TBP Plant are designed to recover at least 95% of the uranium in underground storage. The estimated uranium loss in the TBP Plant alone, at a 10-ton/day instantaneous uranium processing rate, is about 1%.

Uranium removal and processing through the TBP Plant at instantaneous rates as low as 2.5 tons/day is feasible (with only one of two parallel TBP-Plant processing lines operating). Operation at rates exceeding the maximum instantaneous design production capacity is also feasible, with the sacrifice of a few per cent more uranium loss in the waste streams. The estimated TBP-Plant uranium loss at 12 tons/day (instantaneous rate) is about 2 to 3%, as compared with about 1% at 10 tons/day.

2.2 UO_3 Plant

The UO_3 Plant is designed for an average production rate of up to 10.5 short tons of uranium per day -- 8 tons/day from the TBP Plant and 1 to 2.5 tons/day from the Redox Plant -- with an estimated yield of over 99%. The maximum instantaneous production rate used as the design basis is based on an assumed 80% operating time efficiency, the same as for the rest of the Uranium Recovery Plant. Thus the maximum instantaneous design production capacity is 13.125 short tons of uranium per day. The UO_3 Plant may be operated at any production rate below full capacity. The extent to which the production rate may be increased above the maximum instantaneous design capacity is subject to technical considerations discussed in Chapter VIII and cannot be reliably estimated at the time of this writing.

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3. Feed Material

The feed to the Uranium Recovery Plant consists of uranium wastes from the Bismuth Phosphate Plants and the uranium product of the Redox Plant.

3.1 Uranium wastes from Bismuth Phosphate Plants

The Bismuth Phosphate Plants have been used since start-up of Hanford Works in 1944 for recovering plutonium from uranium slugs irradiated in the Hanford piles. The uranium accompanied by the bulk of the radioactive fission products is discharged from the Bismuth Phosphate Plants in a slightly alkaline metastable waste solution (with a pH of about 10.5), composed of the following ingredients in the approximate proportions indicated:

Constituent	Lb./Short Ton U
UNH	4220
HNO_3	170 to 210
H_2SO_4	700 to 810
H_3PO_4	730 to 1110
$NaNO_3$	130 to 210
NaOH	1560 to 1600
Na_2CO_3	3960 to 4060
H_2O	about 27,000 to 28,000

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The waste volume associated with 1 ton of uranium is about 4000 gal.

The metastable waste solution is stored in underground tanks, where solids — mainly complex sodium uranyl phosphocarbonates — separate and settle down, forming a sludge. About 75% of the uranium is contained in the sludge and the remaining 25% in the supernatant liquor. The feed to the Uranium Recovery Plant comprises both the sludge and the supernate.

The fission-product radioactivity associated with the uranium is a function of the irradiation history of the parent slugs and of the time elapsed since irradiation. The ranges of radioactivities involved are approximately as follows:

Age, Years	Irradiation Level, Mw.-Days/Ton	Fission-Product Radioactivity, (Theoretical) Curies/G. U Beta	Gamma	Remarks
7	200	2.8×10^{-3}	6×10^{-4}	Oldest, least radioactive waste available.
2	200	1.1×10^{-2}	3.9×10^{-3}	This is approximately the most highly radioactive feed that can be successfully decontaminated from fission products in the TBP Plant to meet specifications for recovered uranium.
2	400	1.9×10^{-2}	6.5×10^{-3}	

The plutonium content of the uranium wastes is about 2 to 4 grams per ton of uranium.

For more detailed information on the nature and composition of the uranium wastes the reader is referred to Chapter II.

3.2 Uranium product of the Redox Plant

The uranium product of the Redox Plant, as received for processing in the UO_3 Plant, is an aqueous solution of approximately 60 weight per cent UNH (uranyl nitrate hexahydrate). This UNH solution is sufficiently free of both radioactive and non-radioactive contaminants to require no purification before concentration and calcination. A typical analysis is as follows:

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Constituent	Approximate Concentration
Beta-emitting fission products	Less than 10^{-7} (theoretical) curies/g. U (30% of natural uranium beta)
Gamma-emitting fission products	Less than 5×10^{-8} (theoretical) curies/g. U (300% of natural uranium gamma)
Pu	10 parts/billion parts U
HNO_3	10,000 p.p.m.*
Na	1,000 p.p.m.*
Al	1,000 p.p.m.*
Fe	1,000 p.p.m.*

*) Based on U.

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4. Uranium Product (UO_3)

The product from the UO_3 process is dry, powdered uranium trioxide (UO_3). Product quality specifications are not available at this writing. The expected composition and properties of the recovered uranium trioxide are approximately as follows (based on uranium from the Redox and BiP Plant combined in the ratio of 2.5 tons to 8 tons):

Component or Property	Concentration or Value
Beta-emitting fission products	8×10^{-8} (theoretical) curies/g. U (24% of natural uranium beta)
Gamma-emitting fission products	4×10^{-8} (theoretical) curies/g. U (240% of natural uranium gamma)
Pu	Less than 100 p.p.b.
Na	200 p.p.m.
$PO_4^{\equiv}$	150 p.p.m.
Fe	1000 p.p.m.
S, Mo, Cr, W, Si, B, Mn	100 p.p.m. each
H_2O	Less than 0.1%
U_3O_8	0.1 to 0.3%
UO_3 (purity)	At least 97%
Particle size	More than 80% through 80 mesh
Bulk density	3.5 to 4.0 g./cu.cm.

C. PLUTONIUM SEPARATION PROCESSES

Two processes for the separation of plutonium from the uranium and highly radioactive fission products with which it is associated in the irradiated uranium slugs from the 100-Area pile operations are used at [redacted] the bismuth phosphate process, which has been in operation [redacted] and the Redox process, scheduled to begin processing pile-[redacted] uranium early in 19[redacted]

1. Bismuth Phosphate ($BiPO_4$) Process

The bismuth phosphate process separates only plutonium from the pile-irradiated slugs. The uranium, still associated with the bulk of the fission products, is stored in underground tanks to await recovery.

The primary principle upon which this process is based is that plutonium in the IV valence state may be carrier-precipitated on a $BiPO_4$ or LaF_3 cake, while when in the VI valence state it remains in the supernatant liquid when $BiPO_4$ or LaF_3 is precipitated from solution.

A brief description of the process is given below:

(a) The irradiated uranium slugs are dissolved in nitric acid.

(b) Pu(IV) is carrier-precipitated with $BiPO_4$ from the metal solution. The uranium-bearing supernate is neutralized and sent to underground storage tanks as the $BiPO_4$ Process first extraction cycle waste. The Pu-$BiPO_4$ cake is dissolved in HNO_3.

(c) The fission-produce radioactivity still associated with the plutonium is further reduced by processing the plutonium through two "decontamination cycles". Each cycle consists of two $BiPO_4$ precipitations; the first from a Pu(VI) solution so that the plutonium remains in solution, the second from a Pu(IV) solution so that Pu is carried on the $BiPO_4$.

(d) The Pu from the last "decontamination cycle" product cake is dissolved in HNO_3 and oxidized to Pu(VI). $BiPO_4$ and LaF_3, in turn, are then precipitated to achieve additional decontamination of the plutonium from fission products.

(e) The Pu is reduced to the (IV) valence state and carrier-precipitated with LaF_3. The LaF_3-Pu cake, now decontaminated from all but slight traces of the fission products, is metathesized to the hydroxide with KOH and then dissolved in HNO_3 to obtain a product solution suitable for the final isolation process.

A complete description of the bismuth phosphate process is contained in Section C of the H.E.W. Technical Manual(1).

The neutralized supernate from the first $BiPO_4$ precipitation, which contains the uranium and about 90% of the fission-product radioactivity from the irradiated slugs, is one of the feed materials to be processed in the Uranium Recovery Plant.

2. Redox Process

The Redox process recovers both plutonium and uranium from pile-irradiated slugs. Redox is a solvent-extraction process, employing an

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immicible organic solvent, hexone (methyl isobutyl ketone), as an extractant for both plutonium and uranium. The primary principles upon which this process is based are: (a) uranyl nitrate and the nitrates of plutonium in the IV or VI valence state can be made to distribute preferentially from an aqueous phase into hexone by the addition of a salting agent (aluminum nitrate) to the aqueous phase and (b) plutonium in the III valence state and the fission products always favor the aqueous phase, even when the aqueous phase contains high concentrations of salting agents.

A brief description of the Redox process is given below:

(a) The irradiated uranium slugs are dissolved in HNO_3. The metal solution is then partially decontaminated from the fission products Ru, Zr, and Nb by "head-end" treatment procedures (oxidation of Ru to the volatile oxide, RuO_4, which is removed by sparging; and scavenging of the solution with coformed MnO_2, which carries Zr and Nb and is removed by centrifugation).

(b) The metal solution is separated into three aqueous streams in the First Solvent-Extraction Cycle. These streams contain respectively essentially all the plutonium, essentially all the uranium, and the bulk of the fission products. The separation is effected as follows: U and Pu are extracted into hexone in the first extraction contactor (IA Column) while the bulk of the fission products are carried into the aqueous waste stream. The hexone-phase effluent from this column flows to a second contactor (IB Column) where plutonium is reduced to the III valence state and thus leaves in the aqueous effluent while the uranium leaves in the hexone. The uranium is then stripped into an aqueous stream (possible because the aqueous phase contains no salting agent) in a third contactor (IC Column).

(c) Both the uranium and plutonium streams from the First Solvent-Extraction Cycle are then given their final decontamination treatments in the Second and Third Uranium and Second and Third Plutonium Solvent-Extraction Cycles. Each cycle contains an extraction column for the separation of the U or Pu from fission products and a stripping column to place the U or Pu back into an aqueous phase.

After passing through the third Redox solvent-extraction cycles (or, possibly, after the second cycles) the uranium solution is decontaminated sufficiently to be fed directly to the UO_3 Plant and the plutonium solution is suitable as feed to a final isolation process.

A complete description of the Redox process may be found in the Redox Technical Manual(2).

D. PRINCIPLES AND OUTLINE OF THE URANIUM RECOVERY PROCESS

The uranium recovery process is designed to recover the uranium from the uranium-bearing effluents of the Bismuth Phosphate and Redox Plants in

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a form suitable for shipment off-site. The uranium recovery process is composed of three component processes: the removal of bismuth phosphate process uranium wastes from underground storage, the decontamination of the uranium from the plutonium and fission products with which it is associated in this waste (TBP process), and the conversion of the decontaminated uranium from the TBP and Redox processes to uranium trioxide powder (UO_3 process). In the following subsections the basic principles of these processes are briefly explained and the steps which make up these processes are outlined. This section is intended only as an introduction to the uranium recovery process, more complete information being contained in Part II (Chapters II through XII).

1. Basic Principles

1.1 Uranium removal from underground storage

The uranium waste from the $BiPO_4$ process is removed from the underground storage tanks by sluicing the uranium-bearing precipitate with its own supernatant liquid.

The uranium wastes from the $BiPO_4$ process are stored in a number of underground cascade storage tanks. Each cascade contains 3, 4, or 6 tanks, connected at the overflow points, in series. The neutralization of this uranium waste to a slightly alkaline condition (pH about 10.5), to prevent corrosion of the mild-steel-lined tanks, has resulted in the precipitation of a sludge, which contains approximately 75% of the uranium, mostly in the first tank of each cascade series. This sludge is readily dissolved in nitric acid, but, because of the rapid corrosion rates of the steel-lined tanks when in contact with acidic solutions, the sludge must be removed before acid dissolution. It is expected that the sludge will be essentially all removed by sluicing with recirculated supernatant liquid to form a pumpable slurry, an operation similar to placer mining. An alternative method for sludge removal is dissolution in water and/or solubilizing agents, such as sodium bicarbonate.

1.2 TBP process

The TBP process utilizes the preferential extractability of uranyl nitrate by tributyl phosphate (TBP) to separate uranium from the plutonium and fission products with which it is associated in the $BiPO_4$ process wastes.

The salts of uranium consist chiefly of two classes: (a) the uranous, U^{+4}, and the uranyl, UO_2^{+2}. Uranium is capable of existing in other valence states, but only the tetravalent and hexavalent forms are comparatively stable in aqueous solutions. U^{+4} is a strong reducing agent; it therefore follows that it is difficult to reduce UO_2^{+2} to U^{+4}. $UO_2(NO_3)_2$, the product of the dissolution of uranium in nitric acid, is very soluble in aqueous solutions and forms an organic-soluble complex with tributyl phosphate ($UO_2(NO_3)_2 \cdot (TBP)_2$). When aqueous solution are contacted with organic solutions of TBP (i.e., solutions of TBP in inert organic diluents), the uranium can be made

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to distribute preferentially into the organic phase by adding a salting agent (nitric acid or a nitrate salt) to the aqueous phase. Under these conditions, the plutonium, when reduced to the III valence state, and the fission products still favor the aqueous phase. This preferential distribution, and the non-reducibility of UO_2^{+2} under conditions where plutonium is reduced to the III valence state, makes possible the separation of uranium from plutonium and the fission products in the TBP process.

1.3 UO_3 process

The UO_3 process utilizes high temperatures to convert concentrated uranyl nitrate from the Redox and TBP processes to the solid trioxide, UO_3.

Uranyl nitrate, $UO_2(NO_3)_2$, may be converted to uranium trioxide, UO_3, at high temperatures (approximately 400°F.) by the following reaction:

$$UO_2(NO_3)_2 \xrightarrow{\text{heat}} UO_3 + \text{nitrogen oxides} + \text{oxygen}$$

The exact proportions of the several components of the effluent gases are dependent upon the conditions of the reaction, temperature being the most important determining factor. This reaction is utilized in the UO_3 process to convert uranium to a form suitable for shipment off-site.

1.4 Simplified flowsheet

Fig. I-1 is a simplified flowsheet for the entire Uranium Recovery Plant. The path of uranium from the underground storage tanks and from Redox to the final uranium product is shown across the top of the figure, and is labeled "Uranium Recovery". The operations illustrated are conducted in three locations: in the removal facilities at the various $BiPO_4$ process tank farms, in the TBP Plant, and in the UO_3 Plant. Also shown are the flow diagrams for auxiliary processing operations: HNO_3 recovery (UO_3 Plant), solvent treatment (TBP Plant), and waste treatment (TBP Plant).

This flowsheet shows the code letters used to identify the process streams entering and leaving the TBP-Plant solvent-extraction columns. For example, the three feed streams to the decontamination column (the RA Column) are the RAS (scrub) stream, the RAF (feed) stream, and the RAX (extractant) stream. The first letter, "R", identifies the uranium recovery process. The second letter, "A", "C", or "O", identifies the column, i.e., the RA (decontamination), RC (stripping), or RO (solvent recovery) column. The last letter identifies the stream. Influent stream abbreviations end in F, X, or S, which stand for feed, extractant, and scrub, respectively. Effluent streams end in U, W, or O, which stand for uranium, waste, and organic respectively. Thus the RAF is the uranium-containing feed stream to the RA Column and the ROO is the purified organic effluent from the RO Column.

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1.5 Decontamination

The main function of the TBP Plant solvent-extraction battery is to decontaminate the uranium-bearing feed from fission products and plutonium. The factor by which the concentrations of radioactive contaminants is reduced is termed the "decontamination factor" (D.F.), which may be expressed mathematically as follows:

$$D.F. = \frac{\text{Radioactivity (or plutonium) initially present}}{\text{Radioactivity (or plutonium) present at step in question}}.$$

Either the gamma or the beta radiations may be used as an index of the fission product radioactivity present, and the decontamination factor thus determined is termed a "gamma D.F." or "beta D.F." The D.F. based on plutonium is termed the "Pu D.F." A logarithmic method of expressing decontamination factors is also used, and is related to the D.F. by the following expression:

$$dF = \log_{10} (D.F.)$$

Therefore a D.F. of 10^5 is equivalent to a dF of 5, D.F. 20 equals dF 1.3, etc.

2. Uranium Removal From Underground Storage

The purpose of the waste removal facilities is to remove and, as much as possible, homogenize the waste uranium sludge and supernate from the $BiPO_4$ process underground storage tanks. This is accomplished by sluicing the sludge with high-pressure streams of supernate to form a removable slurry.

The removal of uranium from each series of cascade tanks is carried out as follows:

(a) The supernate in each series of cascade tanks is circulated through each tank in the cascade until it attains a uniform composition.

(b) The supernate is pumped from the first tank in the series to a storage tank, thereby uncovering the precipitated sludge.

(c) The sludge is then slurried by a process of sluicing, using supernate pumped at 100 lb./sq.in.ga. pressure through nozzles inside the tanks. The slurry formed in this manner is pumped to an accumulator tank, where the solids partially settle out. The supernate is continually reused for sluicing until the correct concentration of solids (about 1 part solids to 7 parts supernate) is reached in the accumulator tank.

(d) The slurry is then transferred from the accumulator tank to a dissolver tank containing HNO_3.

(e) Steps (c) and (d) are repeated until the waste storage tank is nearly empty. A slight heel, which cannot be reached by

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the slurry pump because of the dished bottom of the storage tank, is removed via a steam jet.

(f) If any considerable portion of the sludge cannot be removed by the above slurrying procedure, it may be dissolved by adding water or a solubilizing agent such as ammonium or sodium bicarbonate. The resulting solution may then be jetted to the accumulator tank.

3. Feed Preparation

The purpose of the feed preparation step is to prepare a feed solution suitable for the TBP Plant solvent-extraction cycle from the slurry removed from underground storage.

The blended sludge and supernate slurry is slowly fed to an agitated dissolver tank containing nitric acid. This tank contains an excess over the amount of acid required to dissolve the sludge. The excess nitric acid acts as a salting agent in the first column of the extraction cycle (RA Column). The "reverse strike" procedure (adding slurry to acid) is used to prevent excessive foaming and an initially high gas evolution rate, which occurs if nitric acid is added to a tank containing waste slurry.

After dissolving, the acidified feed solution is adjusted in acidity, if required, and concentrated by evaporation to about 70 per cent of its original volume if the TBP Plant is operating at TBP-HW No. 4 Flowsheet (Fig. I-2) conditions. The concentrated feed solution is then centrifuged for the removal of any solids. The resulting solution is suitable as feed to the RA Column. A typical analysis (TBP-HW No. 4 Flowsheet) is as follows:

Component	Molarity
UNH	0.27
H^+	2.96
Na^+	4.07
SO_4^{-2}	0.26
PO_4^{-3}	0.26
NO_3^-	5.71
Cl^-	0.023

It is also possible to use unconcentrated feed to the RA Column. This scheme is shown on the TBP-HW No. 5 Flowsheet (Fig. I-3).

4. Solvent-Extraction

4.1 Introduction

The purpose of the TBP solvent-extraction cycle is to separate the uranium feed solution into two aqueous streams, one containing decontaminated uranyl nitrate and the other containing the radioactive fission

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products and other undesirable ions which are associated with the uranium in the underground waste storage tanks.

The solvent-extraction cycle has been designed to operate under the conditions of either the TBP-HW No. 4 (Fig. I-2) or the TBP-HW No. 5 (Fig. I-3) Flowsheets or modifications of either which may include the processing of feeds made up from slurries containing any ratio of sludge to supernate. Operation on dilute solution (such as supernate alone) may, however, necessitate a reduced uranium processing rate. The outline presented under 4.2, below, is based on the TBP-HW No. 4 Flowsheet (Figure I-2). However, it also applies to the TBP-HW No. 5 Flowsheet or other variations which may possibly be used.

4.2 Solvent-extraction flowsheet description

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The concentrated feed solution from the feed preparation step (RAF) is continuously pumped to the RA Column. It enters the column at a feed point intermediate between the top and bottom of the column. A countercurrent flow of approximately 12.5 per cent TBP dissolved in a hydrocarbon diluent (RAX), introduced at the bottom of the column, extracts the uranium while the bulk of the fission products, plutonium, and other undesirable ions remain in the aqueous phase. An aqueous scrub stream (RAS) containing nitric acid is introduced at the top of the column to scrub residual traces of the fission products and plutonium from the rising uranium-containing TBP stream. This scrub stream also contains the ferrous ammonium sulfate and sulfamic acid necessary to reduce plutonium and hold it in the relatively inextractable III valence state. In this manner the bulk of the fission products, plutonium, and other undesirable ions (SO_4^{-2}, PO_4^{-3}, etc.) leave the column in the aqueous effluent (RAW) and the uranium leaves in the TBP stream (RAU).

The RAU stream, containing uranium and a slight amount of nitric acid, flows by gravity from the top of the RA Column into the bottom of the RC Column. In the RC Column the rising organic stream is contacted with a countercurrent downward-flowing stream of water (RCX) which, because it contains no salting agent, strips uranium back into the aqueous phase. The aqueous effluent (RCU), containing approximately 6 weight percent $UO_2(NO_3)_2 \cdot 6H_2O$ (i.e., UNH) is the product stream from the TBP Plant solvent-extraction cycle and is one of the feed streams to the UO_3 Plant.

The TBP extractant stream to the RA Column (RAX) is diluted with an inert hydrocarbon diluent to form a 10 to 15 volume per cent solution of TBP for the following reasons:

(a) The density of TBP is approximately the same as water, thus it must be diluted to a lower density to make countercurrent flow possible in the solvent-extraction columns.

(b) Higher concentrations of TBP in diluent have less satisfactory physical properties (i.e., density and viscosity) than 10 to 15% mixtures.

(c) It is more difficult to strip the uranium from organic solutions containing higher percentages of TBP.

(d) Use of TBP in concentrations below 10 per cent results in more dilute uranium solutions which require larger processing equipment for a given rate of production.

4.3 Pulse columns

The RA and RC Columns employed in the TBP Plant are a relatively new type of solvent-extraction contactor. These columns are filled with perforated plates (1/8-in. holes, 23 percent free area), spaced two inches apart parallel to each other and perpendicular to the axis of the column. The inlet streams to these columns are fed to the column at constant rates. However, a cyclic pulse is superimposed on one of the streams by means of a moving-piston pulse generator. This pulsing forces the organic phase through the holes in the perforated plates for about one-half of the pulse cycle and allows the aqueous stream to flow in the opposite direction during the other half of the cycle. This causes vigorous mixing of the aqueous and organic phases, which is very favorable for solvent-extraction. Because of the pulse flow mechanism involved, these columns are termed "pulse columns".

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The pulse column is much more effective per unit height than the usual packed columns used for solvent-extraction processes, for example in the Redox process. Thus the RA pulse column in the TBP Plant is only 21 ft. in height as compared to a required height of about 50 ft. for a conventional packed column capable of the same performance.

Pulse columns were chosen for the TBP Plant so that installation of the solvent-extraction equipment in the existing 221-U Building Canyon could be made with only relatively minor structural revisions. Installation of packed RA Columns would have necessitated deepening the cells containing the two RA Columns by approximately 30 feet.

5. Concentration of Recovered Uranium

The purpose of the recovered uranium concentration step is to reduce the volume and increase the concentration of the decontaminated UNH solutions from both the TBP and Redox Plants to a UNH concentration suitable for feed to the calcination pots. The concentration is effected by evaporating water and nitric acid from the combined solutions.

The UNH solution from Redox (60% UNH) and from TBP (6% UNH) are blended and held in heated storage tanks, before being fed to the UNH concentrators. This solution is continuously fed to either one of two first-stage concentrators, where it is concentrated to about 55 to 65% UNH. It is then concentrated to approximately 80 to 100% UNH in a single, small, final evaporator. This concentrated UNH solution is the feed to the calcination (UO_3 conversion) step.

The two-stage concentration of UNH was provided as a means of combatting the corrosive nature of hot concentrated UNH solutions. The

first two, large concentrators are expected to withstand the corrosive effects of boiling UNH solution up to 55 to 65% UNH. The single, small, final concentrator is considered expendable, and may easily be replaced when required.

The nitric acid in the overhead vapors from the three UNH concentrators is recovered for reuse in the process. These vapors, which average approximately 2 weight per cent HNO_3, are fed to the two nitric acid fractionating columns. Aqueous 40% HNO_3, recovered from the calcination step (see Subsection D7, below) is also fed to these columns. The bottom effluent streams from these fractionators are approximately 60 weight per cent HNO_3. This recovered HNO_3 is reused for slurry dissolution at the uranium removal facilities.

6. Calcination

The final step in the uranium recovery process is the conversion (calcination) of the concentrated UNH solution to solid UO_3. This is accomplished in electrically heated decomposition pots at temperatures of about 400°F.

The eighteen electrically-heated 55-KW. decomposition pots (used in parallel) are each filled with about 50 gallons of concentrated uranium solution (approximately 80 to 100% UNH) from the uranium concentration step. The pots are heated for about two hours until the charge reaches a temperature of 400°F. The temperature is then held constant until decomposition is complete, a period of about three hours. While heat is supplied to a pot, it is constantly stirred to prevent caking on the walls of the pot. Gases evolved from the pots during the calcination step are fed to a nitric acid absorption column.

The UO_3 powder resulting from this step is unloaded from the pots via a pneumatic conveyor system and loaded into drums for shipment.

7. Nitric Acid Recovery From Calcination

Nitric acid is recovered from the fumes evolved during calcination and from the overhead vapors from the uranium concentrators (see above). This recovered nitric acid is reused in the process for dissolving the uranium slurry in the feed preparation step.

The off-gas from the calcination step is fed, after cooling, to an HNO_3 absorption column, where the NO_2 evolved during the conversion of UNH to UO_3 is absorped in water to form HNO_3. Air from the bleacher unit (see below) is also fed to the bottom of the column to oxidize the NO in the entering gas to NO_2 and thus permit its absorption. The acid stream from the absorption column is then countercurrently contacted with air in the bleacher unit, which oxidizes some dissolved NO to NO_2 and sweeps the rest out of solution, to be returned to the absorption column. The bottom effluent from the bleacher unit,

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containing approximately 40% HNO_3, is fed to the HNO_3 fractionators, where it joins the overhead vapor from the UNH concentrators and is concentrated to 60% HNO_3, suitable for reuse in the process.

8. Solvent Treatment

The 10 to 15 per cent TBP in hydrocarbon diluent solution employed as the solvent in the TBP solvent-extraction cycle must be reused for economic reasons. The purpose of the solvent treatment step is to treat the spent solvent so that it is suitable for reuse in the process.

The spent solvent stream from the RC Column (RCW) contains traces of the fission products and plutonium and also solvent decomposition products formed as a result of contact of the solvent with process solutions. Known impurities in the solvent stream, which are deleterious to process performance, result from the hydrolysis of TBP when in contact with nitric acid solutions as follows:

$$\underset{\text{TBP}}{(C_4H_9)_3PO_4} \longrightarrow \underset{\text{DBP}}{(C_4H_9)_2HPO_4} \longrightarrow \underset{\text{MBP}}{C_4H_9H_2PO_4} \longrightarrow H_3PO_4$$

Also, continued exposure of the hydrocarbon diluent to nitric acid solutions may result in the formation of nitrated hydrocarbons, which may affect process performance adversely.

The spent solvent is continuously treated in the RO Column. The solvent, introduced at the bottom of the column, is countercurrently contacted with an aqueous scrub solution which removes fission products, plutonium, and solvent impurities from the solvent. The most effective composition for the aqueous scrub stream is yet to be determined. Dilute acids, salts, and bases have all proven effective in "cold" pilot-plant studies. Tentatively, it has been proposed that a dilute solution of Na_2SO_4 be used as the scrub solution. The aqueous effluent (ROW) from the RO Column is sent to the waste treatment step. The organic overhead (ROO) is returned to the process for use as RAX.

Facilities are also provided for batch-wise chemical treatment of the solvent with aqueous chemical solutions if additional treatment is necessary, for adjustment of the TBP concentration, and for the addition of make-up solvent to replace lost solvent.

9. Waste Treatment and Disposal

The function of the waste treatment step is to reduce the volume of wastes which, because of their high levels of radioactivity, must be confined in underground storage tanks. Other liquid wastes from the Uranium Recovery Plant, which contain only slight traces of radioactivity, are discharged to underground cribs (concentrator and fractionating column overheads) or discharged to open ditches or ponds (cooling water and steam condensates) and require no routine treatment.

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The only two highly radioactive waste streams from the Uranium Recovery Plant are the aqueous waste streams from the RA and RO Columns (RAW and ROW). These two streams are combined and neutralized with NaOH before concentration. Neutralization is necessary to minimize corrosion in the waste evaporator and in the underground storage tanks. The neutralized waste is concentrated by evaporation and returned to the underground waste storage tanks which originally contained the $BiPO_4$ process uranium waste. The volume of returned waste is approximately the same as the original uranium waste volume.

E. THE URANIUM RECOVERY PLANT

Two of the three major components of the Uranium Recovery Plant — the TBP Plant and the UO_3 Plant are located in the 200 West Area of the Hanford Works, approximately 30 miles from Richland, Washington. Parts of the uranium removal facilities are located in both the 200 West and 200 East Areas. A detailed map of the Hanford Works and plot plans of the 200 East and 200 West Areas are contained in Chapter XIII. Chapters XIII through XVIII of this manual contain a detailed description of the plant and its equipment.

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1. General Plant Layout

The facilities for the removal of underground uranium wastes are located at the tank farms (241-B, -BX, -BY, and -C in the 200 East Area; 241-T, -TX, and -U in the 200 West Area) filled from the "B" and "T" Bismuth Phosphate Plants. Facilities for blending and dissolution of these wastes are located adjacent to the 241-BX and 241-C tank farms in the 200 East Area and adjacent to the 241-U and 241-TX tank farms in the 200 West Area. The TBP and UO_3 Plants are located in U Area, a part of the 200 West Area, in Buildings 221-U and 224-U respectively. These buildings were originally constructed to be used as a Bismuth Phosphate Plant. All process solution transfers between these various processing areas of the Uranium Recovery Plant are made through pipelines enclosed in underground concrete encasements. Connections to and from these pipelines are made through reinforced concrete diversion boxes.

There are two other buildings of interest to the Uranium Recovery Plant in the 200 West Area: these are the 222-S Laboratory Building, which handles the analytical requirements for the Plant; and the Redox Plant, Building 202-S, which supplies one of the feed streams to the UO_3 Plant.

1.1 U Area layout

The layout of the U Area (which is a part of the 200 West Area) is shown on Figure I-4. This layout drawing shows the relative location of the TBP Plant (221-U Building), the UO_3 Plant (224-U Building), the 222-U Laboratory (which has no connection with the Uranium Recovery Plant), and some of the auxiliary facilities.

The layout of the TBP and UO_3 Plants is discussed under 1.3 and 1.4, below.

The functions of the auxiliary facilities shown on Figure I-4 are as follows:

Facility	Function
203-U UNH Storage	Storage of decontaminated UNH solutions from the Redox and TBP Plants for feed to the UO_3 Plant.
203-UX UN Storage	Storage of UN feed to calcination step. Storage of off-standard uranium solution from calcination pots for recycle to TBP Plant or UO_3 Plant.
211-U and -AU Tank Farms	TBP Plant chemical storage and aqueous make-up facilities.
241-WR Underground Storage Vault	Storage of acidified feed from the tank farms, concentrated high-radioactivity wastes and recovered HNO_3 to be routed back to the tank farms, and low-radioactivity wastes to be sent to cribs.
241-UX-154 Diversion Box	Diversion box for routing process streams to and from the TBP Plant and the 241-WR Storage Vault.
270-W Crib Waste Neutralizer	Facilities for neutralization of condensates with $CaCO_3$ before cribbing.
271-U Service Building	Contains offices and aqueous make-up facilities for the TBP Plant.
275-UR Warehouse	TBP Plant dry chemical storage.
276-U Solvent Make-Up and Treatment	Facilities for the make-up and auxiliary treatment of the TBP solvent.
291-U Sand Filter, Fans, and Stack	Disposal of ventilation air from 221-U, 224-U, and "hot" tanks in 241-WR.
2714 Warehouse	Storage of UO_3 product.

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1.2 Layout of underground removal facilities

Figure I-5 is a simplified layout drawing of the 241-U tank farm, 241-UR removal facilities, and 244-UR Process Tank Vault where the uranium slurry from the tanks is blended and dissolved. The removal facilities in this area are similar to those installed at the 241-B, -BX, -BY, -C, -T, and -TX tank farms. Process tank vaults 244-BXR, -CR, and -TXR, similar to 244-UR, are also installed at the 241-BX, -C, and -TX tank farms.

Each uranium-containing tank is equipped with a sluice pit for a high-pressure sluicing nozzle; a pump pit, for a slurry pump and another sluicing nozzle; and a heel pit for a steam jet for removing the "heel" of solution from the bottom of the tank. The nine uranium-containing tanks in this area are connected through three diversion boxes to a master diversion box 241-UR-151, which in turn connects to the 244-UR Process Tank Vault. Returning concentrated waste from the TBP Plant is also routed through this box. All piping in this area is laid in underground concrete trenches. The underground waste tanks are vented through individual vent exhaust systems, comprised of a Fiberglas filter, exhaust fan, and local stack. The tanks in the Process Tank Vault are vented through Fiberglas filters to the 291-UR ventilation fan and stack.

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1.3 TBP Plant (221-U) layout

The TBP Plant, Building 221-U, is a multistoried, predominantly reinforced concrete structure, approximately 810 ft. in length. Figure I-6 is a simplified sketch of the building layout.

The building has two major portions: the process portion which contains the "hot" process equipment and the regulated work zones, and the service portion which houses personnel and equipment necessary for remote operation of the process portion.

The Canyon cells house the processing equipment for feed concentration and centrifugation, solvent-extraction, waste treatment, and solvent treatment. Piping connections between cells are made through the cell walls and the pipe trench. Because of the large volumes of solution which must be handled to process uranium at the instantaneous design rate of ten tons per day, two process lines have been installed in the building (each capable of processing five tons of uranium per day) so that the smaller equipment sizes necessary to fit the Canyon cells could be used. Also, the installation of two process lines was desirable to give the TBP Plant greater flexibility of operation and a greater range of feasible processing rate. The function of each Canyon section (a section contains two cells) is noted on Figure I-6.

The regulated work zones consist of areas where limited contact of personnel with radiation and radioactive contamination is allowed under carefully prescribed and monitored conditions. The Canyon deck level and the Canyon Crane Gallery are both classed as regulated work zones. The SWP (regulated work) Lobby (located at the northwest end of the operating gallery) is the central point used for entrance to the Canyon.

The service portion of the building includes the Operating, Pipe, and Electrical Galleries. Other service areas are located adjacent to the 221-U Building in 271-U.

1.4 UO_3 Plant (224-U) layout

The UO_3 Plant, Building 224-U, is a concrete structure housing the equipment for UNH concentration, calcination of the UNH to UO_3, and loading of the UO_3 product as well as equipment for the recovery of nitric acid from the concentration and calcination steps. A simplified layout of the building is shown as Figure I-7.

2. Special Features of the Plant

2.1 Shielding

The high levels of radioactivity associated with the process streams necessitates that the underground removal and TBP Plant facilities be shielded to prevent personnel from receiving excessive amounts of radiation.

The process equipment at the underground removal facilities is shielded with earth and concrete. Other outside facilities, such as process solution storage vaults, diversion boxes, and pipe lines, are also shielded with earth and concrete. The TBP Plant process equipment is shielded by the concrete cell walls and cover blocks. The shielding reduces radiation intensities to less than 0.1 mr./hr. in non-regulated zones and, normally, to less than 1.0 mr./hr. in regulated work zones.

Process solutions and solids in the UO_3 Plant are essentially free from fission products and therefore require no special shielding. However, process equipment areas in this building are classed as regulated work zones since the radiation levels may, in some cases, be as high as 1 to 2 mr./hr.

2.2 Remote operation

The location of the underground removal and TBP Plant process equipment (underground and behind concrete shielding) requires that this equipment be operated by remote control. The remote operational controls are similar to those employed in the Redox process and in highly-automatic process industries.

Processing operations are, for the most part, controlled from the Control Houses at the removal facilities and from the Operating Gallery in the TBP Plant. Some of the processing operations at the removal facilities, however, are controlled from above the tanks. Some of the methods and devices employed for remote operation are briefly described below.

At the underground removal facilities, steam jets and electrically-operated pumps submerged in the process liquid are used for solution and slurry transfers. A system of interlocking controls keeps any pump from overfilling any of the tanks. The slurry pumps in the waste tanks are raised or lowered by remotely operated cables, to stay in the correct position relative to the tank liquid level. The slurrying nozzles,

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moved by an electrically-operated mechanism, may be pointed to spray any part of the tank bottom. Progress of the slurrying operation may be viewed through a periscope. Differential pressure instruments are used to indicate the total weight and specific gravity of solutions Solutions are sampled via vacuum jets which draw the solutions into shielded sampler boxes.

In the TBP Plant, solution transfers are also made via steam jets and submerged pumps. Flow rates of streams which must be closely regulated are controlled from the Operating Gallery by recording-controlling instruments which receive an impulse indicating the flow rate from rotameters (solvent-extraction column streams) and orifice meters (other streams) and in turn actuate air-operated valves. The position of the organic-aqueous interface in the columns is controlled by recording-controlling instruments which are actuated by air-bubbling dip tubes in the column tops and in turn control the flow rate of the column aqueous exit stream with an air-operated valve. Agitator, pump, and pulsing unit motors are controlled electrically in the usual manner. Weight factor and specific gravity instruments and samplers are operated in a manner similar to those at the removal facilities.

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2.3 Remote maintenance

The process equipment used in the uranium removal facilities and the TBP Plant is designed to require a minimum of servicing and maintenance. However, when maintenance is required, it can be accomplished remotely with the aid of gantry cranes at the underground removal facilities or a 75-ton capacity crane in the TBP Plant Canyon. Piping connections are made with jumpers fitted with special connectors which may be tightened or loosened with a crane-operated impact wrench. Agitators and pumps are held in place with large nuts which may also be removed with an impact wrench. The TBP Plant tanks are positioned by guides built into the cells and may be lifted out after piping jumpers have been removed. Replacement parts are prefabricated to fit in place. The crane operators, protected by shielding or distance, view operations through a periscope or mirrors.

Radioactivity levels in the UO_3 Plant are sufficiently low to permit contact maintenance.

2.4 Fire and explosion protection

The TBP process employs a moderately flammable organic solvent: TBP diluted with a kerosene-type hydrocarbon. While the high flash point (about 150°F. Tag closed cup) and low volatility of this solvent tend to limit the flammability hazard, several protective features for the prevention of fire or explosion have been incorporated in the TBP Plant. Among these are the adequate ventilation of the process tanks and processing areas, to prevent the build-up of any potentially hazardous vapor concentrations, and the use of explosion-proof or totally enclosed electrical equipment (conforming to or exceeding National Electrical Code Class I, Division 2 specifications) in solvent areas.

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Details on the fire and explosion safety features of the TBP Plant may be found in Chapter XXIV.

2.5 Uranium oxide dust control

The finely ground UO_3 powder produced in the UO_3 Plant is toxic. In the case of natural uranium, respiratory protection is required if the concentration in air rises above 3×10^{-5} micrograms/ml.

The exhaust air system in the UO_3 Plant is designed to keep the concentration of UO_3 dust in the air below the highest permissible level so that masks will not be required in normal operation.

REFERENCES

(1) HW-10475-C H.E.W. Technical Manual, Section C. Author not stated. 1944.

(2) HW-18700 Redox Technical Manual. Author not stated. July 10, 1951.

(3) HW-19400 An Introduction to the TBP and UO_3 Plants. D. R. Gustavson. Dec. 20, 1950.

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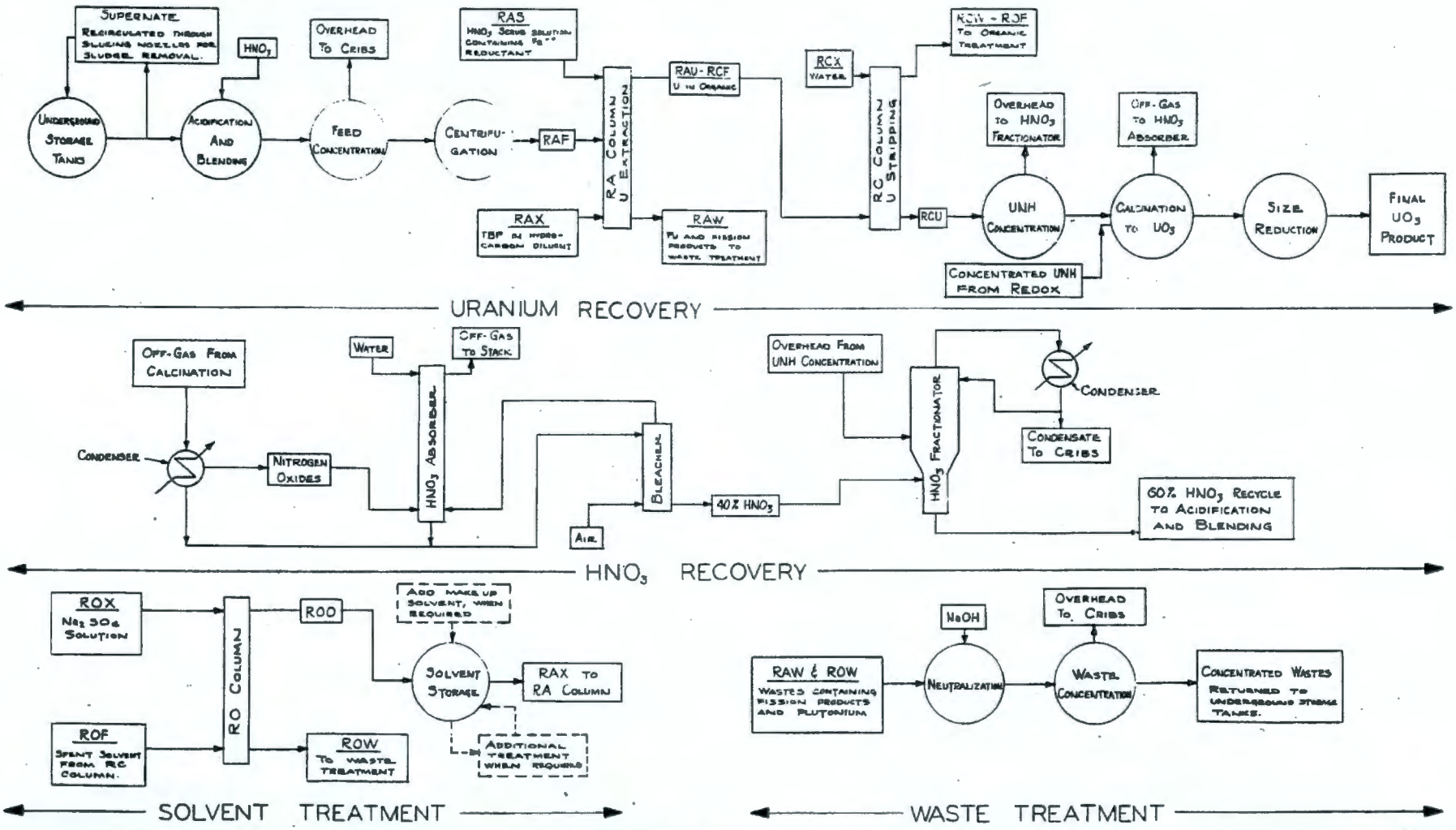
FIGURE I-1

SIMPLIFIED URANIUM RECOVERY PLANT FLOWSHEET



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[redacted] DECLASSIFIED

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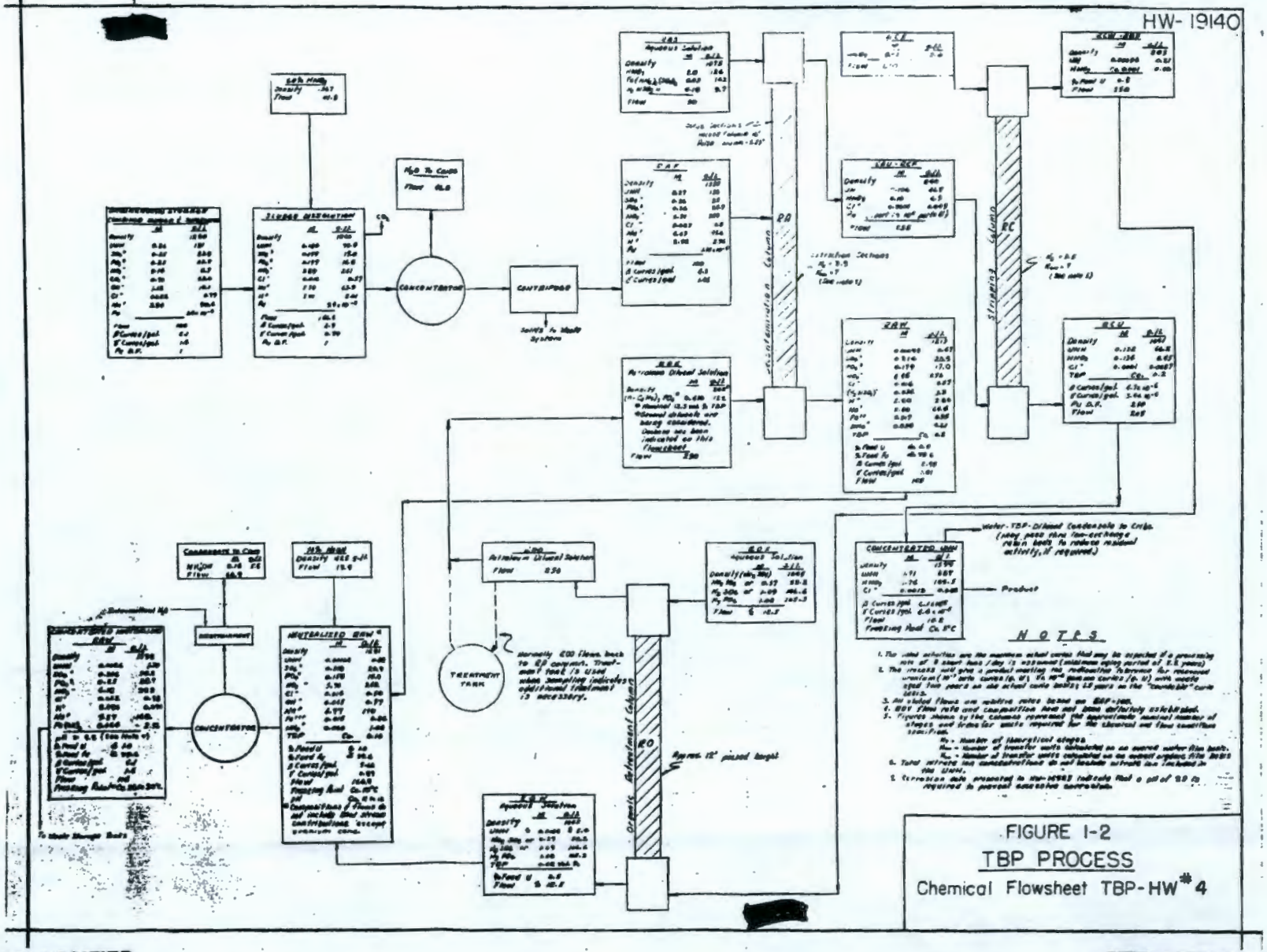

FIGURE 1-2

TBP PROCESS

Chemical Flowsheet TBP-HW#4

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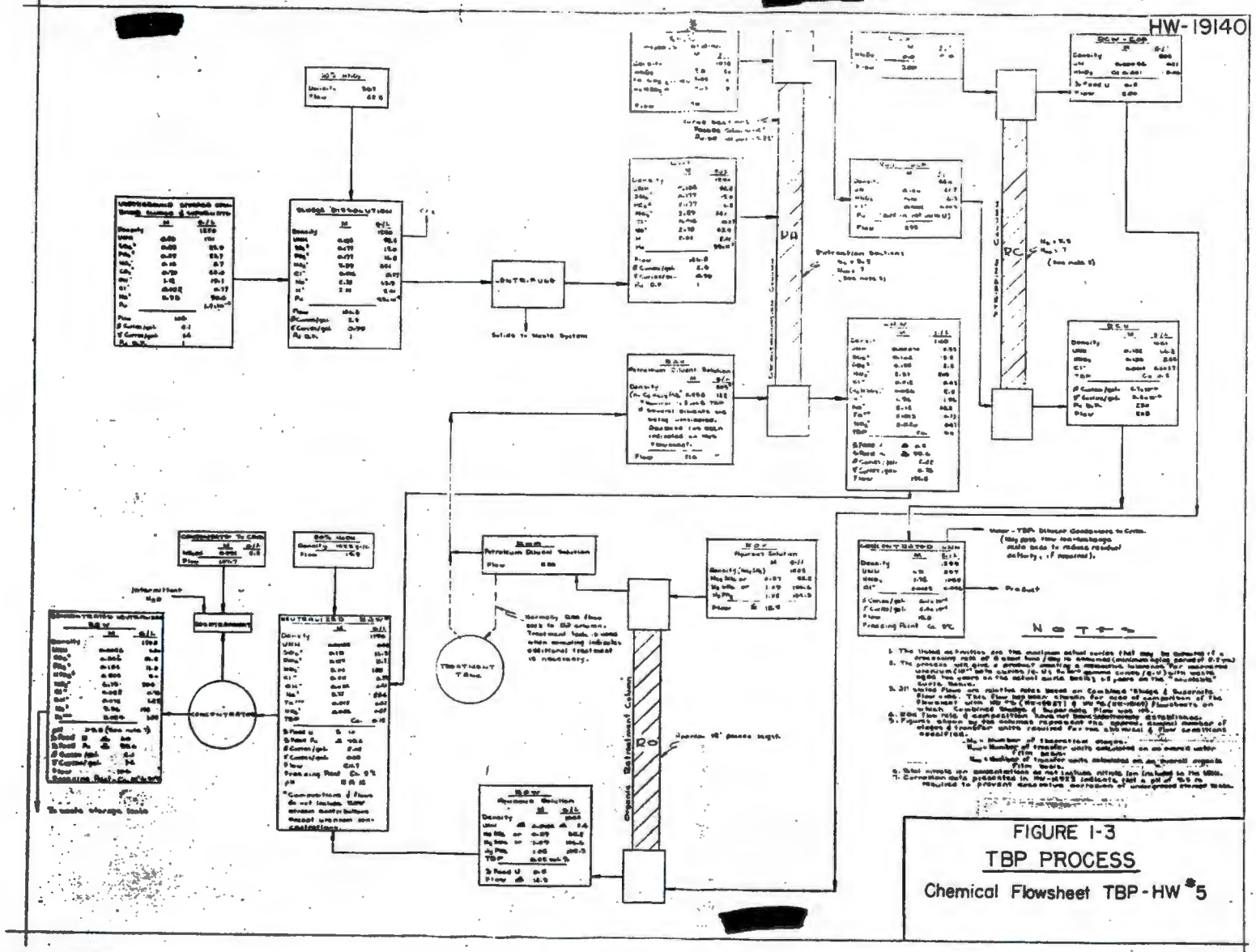

FIGURE 1-3

TBP PROCESS

Chemical Flowsheet TBP-HW #5

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FIGURE I-4

SIMPLIFIED URANIUM [illegible] AREA)

REF. DWG: H-2-40774

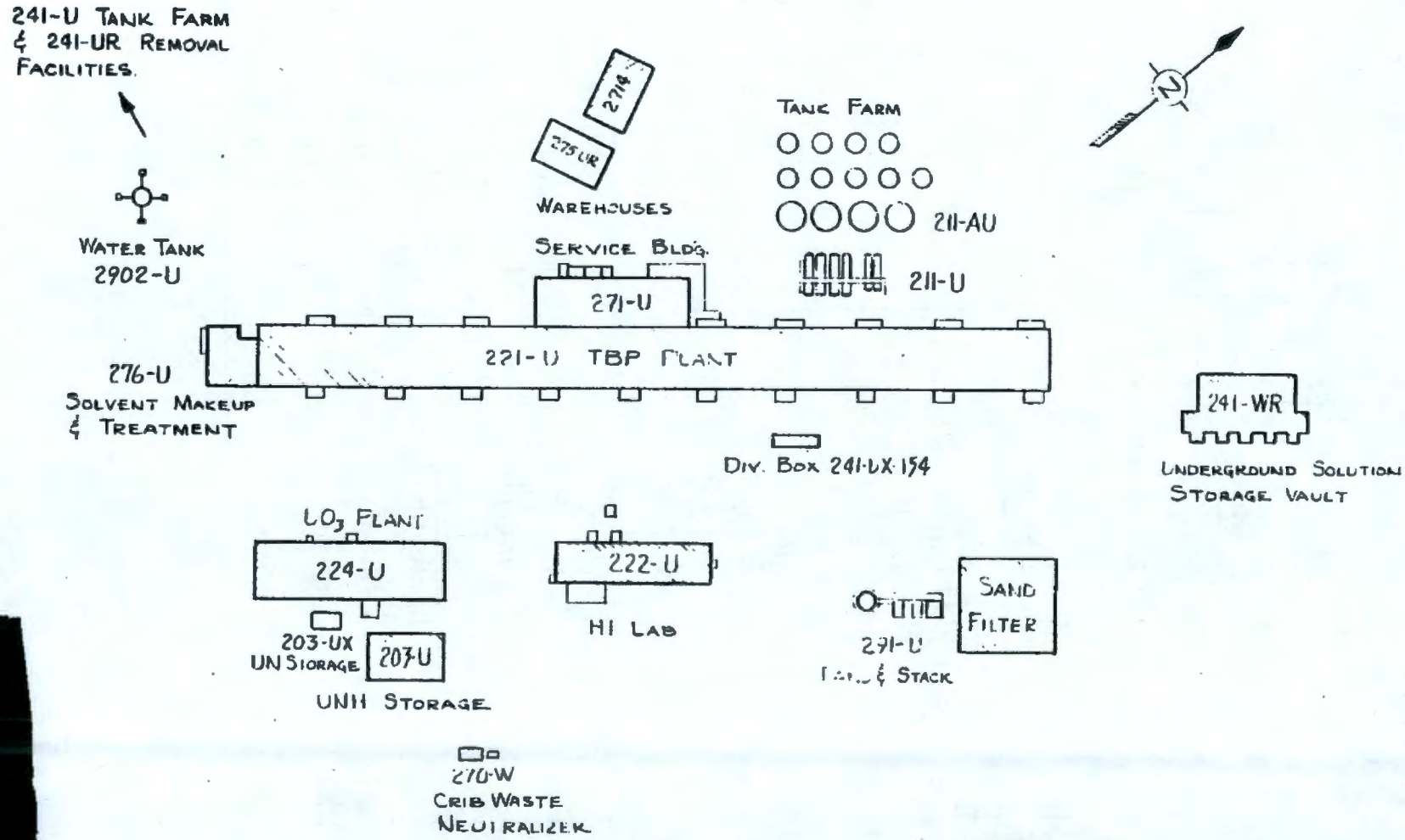

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FIG. I-4

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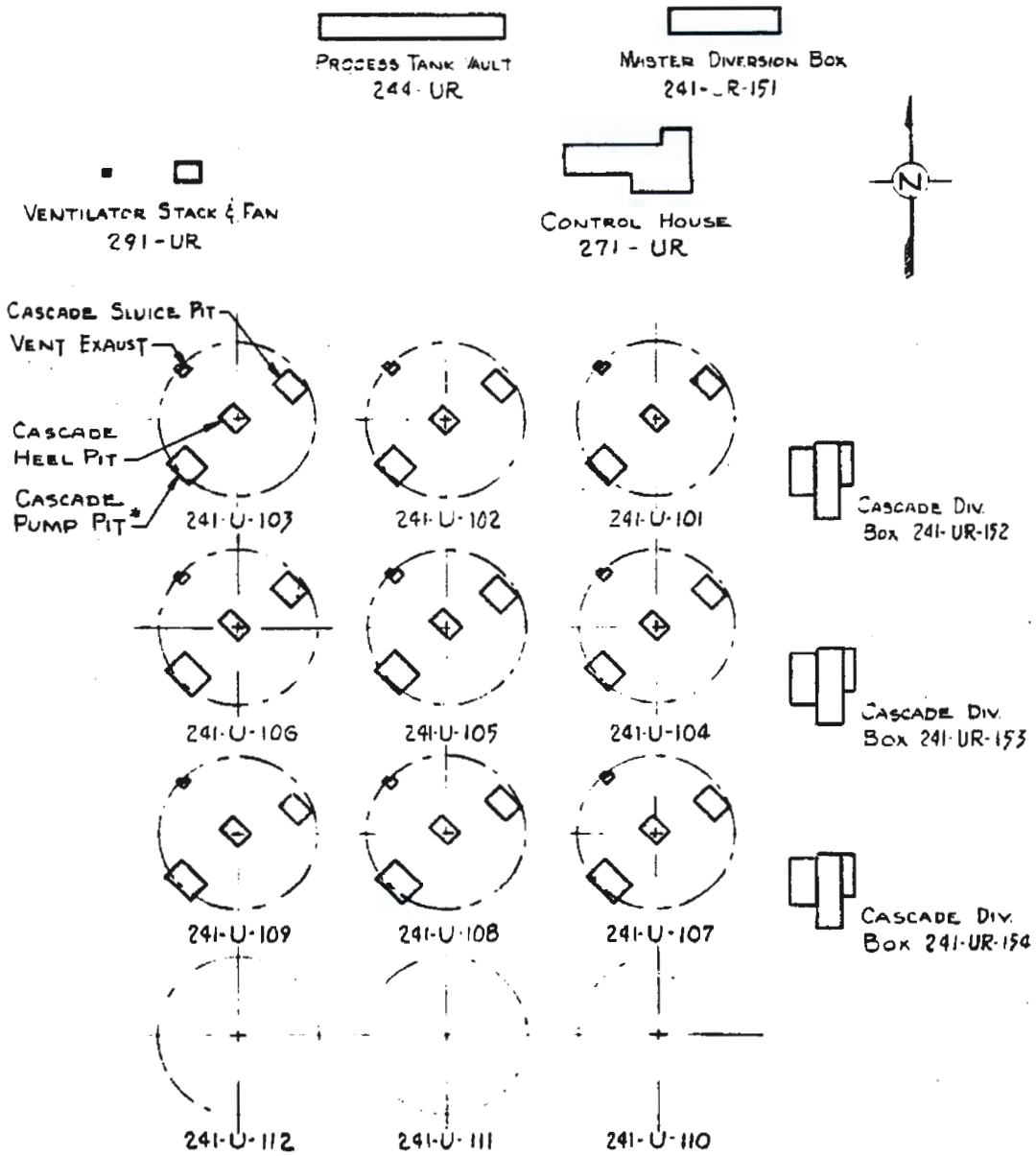
FIGURE I-5

SIMPLIFIED LAYOUT

UNDERGROUND STORAGE TANKS & REMOVAL FACILITIES, 200-U AREA

REF DWG: H-2-40000F



* THE CASCADE PUMP PIT CONTAINS A SLUICING NOZZLE IN ADDITION TO THE PUMP

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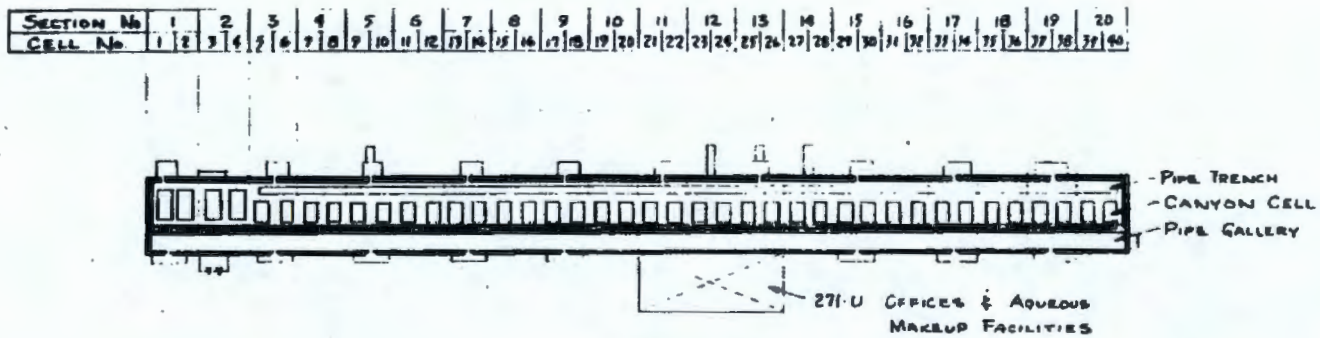
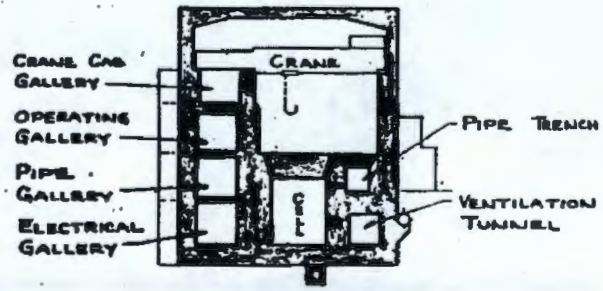
FIGURE I 6

SIMPLIFIED TBP PLANT (221 U BUILDING) LAYOUT

REF. DWG: SK-2-6177



PLAN AT SECOND FLOOR



CANYON CROSS SECTION

SECTION FUNCTIONS

1. EMPTY	11. WASTE NEUTRALIZATION
2 R.R TUNNEL	12 WASTE SAMPLING
3. FEED RECEIVING	13 WASTE RECEIVING
4. FEED & WASTE HOLDUP	14. FEED CENTRIFUGATION
5. SUMP SOLUTION HOLDUP	15. URANIUM SAMPLING
6. FEED EVAPORATION	16. URANIUM RECEIVING
7. FEED EVAPORATION	17. SOLVENT EXTRACTION
8. EVAPORATION (SPARE)	18. SOLVENT TREATMENT
9. WASTE EVAPORATION	19. SOLVENT EXTRACTION
10. WASTE EVAPORATION	20. SOLVENT TREATMENT

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FIGURE I-7

SIMPLIFIED UO_3 PLANT (224 U BUILDING) LAYOUT

BASIS: SK-2-50044

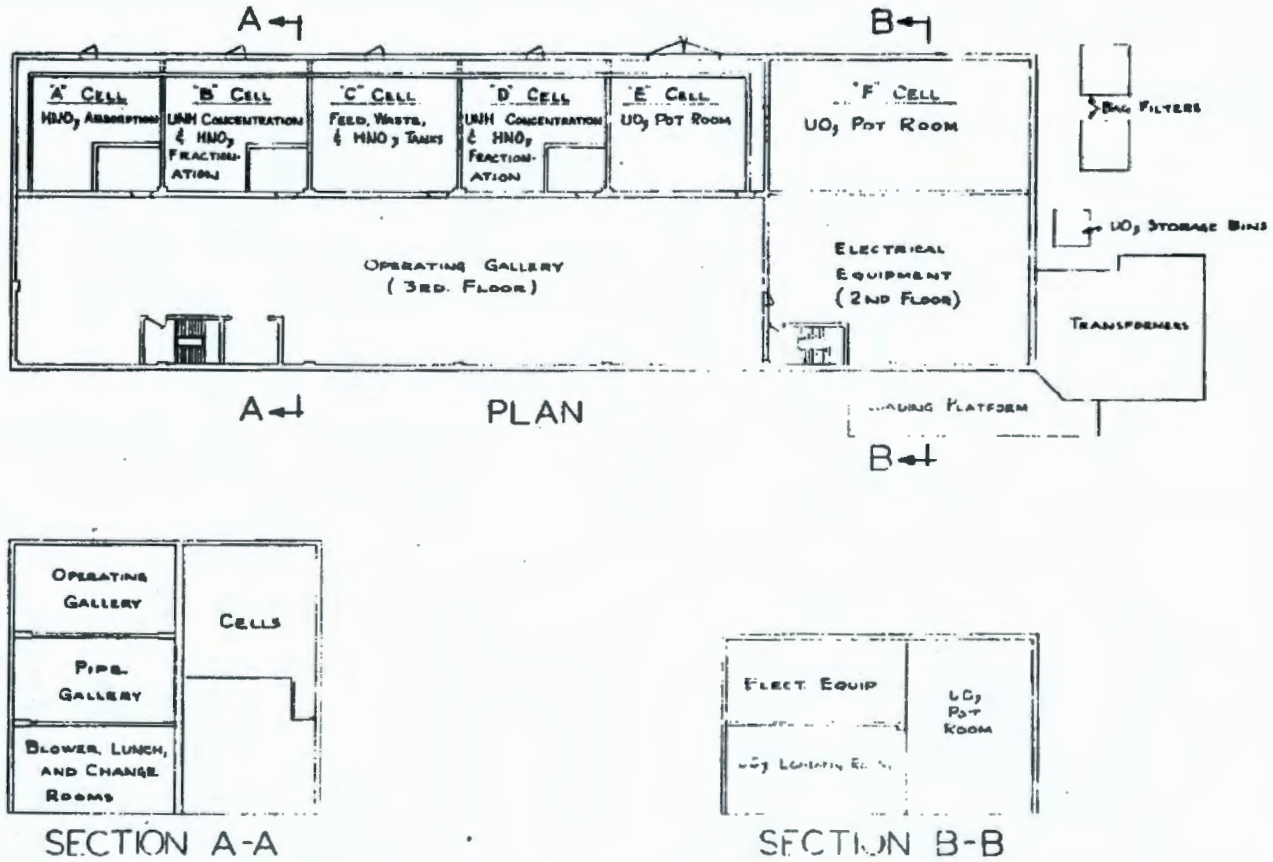

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FIG I-7

PART II: PROCESS

CHAPTER II. URANIUM REMOVAL FROM UNDERGROUND STORAGE

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CHAPTER II. URANIUM REMOVAL FROM UNDERGROUND STORAGE

A. COMPOSITION AND PROPERTIES OF STORED URANIUM WASTES

1. Origin and Nature

1.1 Origin of the uranium wastes

In the Bismuth Phosphate Plants plutonium and uranium are separated in the first extraction step. The plutonium is removed with the centrifuge cake for further purification. The centrifuge effluent containing the bulk of the uranium (ca. 99.9%) and fission products (ca. 90%) along with excess H_3PO_4, HNO_3, H_2SO_4, and $NaNO_2$ is neutralized by 50% NaOH and 30% Na_2CO_3 solutions to form a metastable solution at a pH of 10.5 and temperature of approximately 60°C., which is then jetted (at approx. 35°C.) via an underground pipeline to storage in underground tanks arranged in cascades of 3 to 6 tanks.

Over a period of 6 1/2 years of operation, from December 1944 to June 1, 1951, approximately 5160 short tons of uranium have been transferred in 21.2 million gallons of waste to the underground storage tanks. At the present (June 1951) processing rate of 4 short tons of uranium metal per day, another 740 tons of uranium are expected to be stored underground in the remaining 7 months of 1951, giving a total of about 5900 tons of uranium to be processed by the Uranium Recovery Plant. Uranium wastes were stored at a rate of about 2 short tons/day (700 to 800 short tons/yr.) during the first 5 years of operation. This rate has been approximately doubled during the last year (1951), to about 1400 short tons stored per year. The following is a chronological inventory of uranium metal stored in underground waste storage tanks:

Date	Total Short Tons U	Production Rate, Short Tons/Yr.
Jan. 1, 1946	700	700
Jan. 1, 1947	1400	700
Jan. 1, 1948	2150	750
Jan. 1, 1949	2900	750
Jan. 1, 1950	3700	800
Jan. 1, 1951	4500	800
Jan. 1, 1952	5900*	1400*

*Estimated: 350 days x 4 short tons/day = 1400 short tons.

1.2 Nature of wastes

When jetted from the Bismuth Phosphate Plant waste neutralizer to underground storage, the waste solution has an average composition by weight of 10.7% UNH, 1.96% $SO_4^=$, 1.94% $PO_4^{\equiv}$, 0.71% NO_3^-, and 3.5% $CO_3^=$, and a pH of 10.5. Most of the insolubles, such as SiO_2, and $NaUO_2PO_4$ (believed

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to be the main component of soft sludge), and $Na_4UO_2(CO_3)_3$ (believed to the main component of hard sludge), separate from the metastable solution and settle out in the first tank of a cascade. (Each cascade is made up of 3, 4, or 6 tanks of 55,000, 530,000, or 759,000 gal. capacity.) After the first tank in a cascade is full, some insoluble material in the supernate cascades to the next tank where additional separation and settling of solids takes place. However, there are practically no solids in the third tank of a 3-tank cascade. The approximate sludge levels in the 75-ft. diameter (16 or 22.7 ft. deep) tanks are indicated in Table II-1 and summarized below:

Type of Cascade	Sludge Level, Ft.					
	1st Tank	2nd Tank	3rd Tank	4th Tank	5th Tank	6th Tank
3-tank	4.0	1.9	0	-	-	-
4-tank	7.7	3.7	0	0	-	-
6-tank	9.0	4.0	1.0	0	0	0

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1.3 Effects of aging on uranium waste temperature and composition

Owing to the radioactive heating effect of the fission products, the temperature of the uranium wastes in underground storage rises until conditions of steady-state heat transfer from the storage tanks to the surroundings are essentially established. At the time of the approximate establishment of this steady state, which occurs within two to three months after a cascade is filled, the temperature of the uranium wastes is at a maximum. After this the temperature of the wastes gradually declines as the fission products decay to lower radioactivity levels. While the maximum temperature reached is subject to variations of about 10 to 20°F. as a result of seasonal variations in the temperature of the surrounding ground, it is determined mainly by the radioactivity of the waste. The approximate maximum temperatures reached by uranium wastes resulting from slugs with an integrated exposure of 200 Mw.-days/ton and "cooled" for 90 days are as follows:

Type of Cascade	Maximum Temperature, °F.					
	1st Tank	2nd Tank	3rd Tank	4th Tank	5th Tank	6th Tank
3-tank	170-180	100-125	80-100	--	--	--
4-tank	175-180	100-125	100-120	90-100	--	--
6-tank	190-200	95-105	90-95	85-90	80-85	70-80

The gradual decline of the temperature after attainment of the maximum may be illustrated by the following values for the first tank in a three-tank cascade under the above conditions:

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Time After Filling of Cascade	Temperature, °F.
2 months*	170-180
1 year	130-140
2 years	105-115
3 years	90-100
5 years	85-95

*) Maximum temperature

On the basis of the high temperature of the first tank in a cascade and some direct analytical data it is believed that about 75% of all radioactive fission products are precipitated in the sludge of this first tank of the series. As the tanks cool, more and more $Na_4UO_2(CO_3)_3$ is dissolved by the supernate. Thus the chemical composition of sludge and the ratio of hard to soft sludge are constantly changing, tending toward an equilibrium as the storage tank temperature approaches that of the surrounding ground. As the composition of the sludge changes complementary changes take place in the composition of the supernate.

The gross composition of the stored uranium wastes is discussed in Subsection A3, and the effect of aging on fission-product radioactivity in Subsection A4.

1.4 Effect of aging on physical properties

As the composition of the stored wastes change, their physical properties are also altered. A decline in tank temperature results in: (a) a decrease in the amount of hard sludge and, thus, a decrease in the sludge-to-supernate volume ratio; (b) an increase in the density of the supernate and a decrease in sludge density; (c) a decrease in the ratio of hard to soft sludge. The properties of sludges and supernates are discussed in more detail in Subsections A5 and 6 below.

2. List of Stored Wastes

A list of all underground storage tanks filled with uranium wastes from the start of Hanford operations (1944) through June 1951 is presented in Table II-1, along with data on dates of filling, sludge and liquid depths, and uranium content.

Summation of the data in Table II-1 indicates that a total of 21,200,000 gal. of uranium waste, consisting of about 2,600,000 gal. of sludge and 18,600,000 gal. of supernatant liquid, have accumulated in underground storage to June 16, 1951. Of the 5200 tons of uranium in these wastes about 3800 tons (or 73%) are contained in the sludge. Thus the average uranium content of the sludge is about 2.9 lb./gal., while that of the supernate is about 0.15 lb./gal. About half the uranium in each cascade is in the first tank of the cascade.

[redacted]

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[redacted]

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Because of the difficulty of obtaining accurate measurements and representative samples on such large heterogeneous masses by remote-control methods, the data on sludge levels and distribution of uranium between tanks and between sludges and supernates are subject to some uncertainty. Their accuracy is estimated at about ±10%.

3. Bulk Constituents

The chemical components from which the uranium wastes have been synthesized are reliably known from the Manufacturing Divisions' operating records. However, the chemical composition of the sludges and supernates in the several tanks of the various underground storage tank cascades are known only imperfectly, from analytical investigations handicapped by the difficulty of obtaining by remote-control methods representative samples from large heterogeneous masses in the tanks.

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3.1 Synthesis data

The proportions of chemicals from which the uranium wastes have been synthesized have changed slightly from time to time with modifications of the $BiPO_4$ process first extraction cycle procedure. The most significant of these changes, made in January 1946, involved an approximately one-third reduction in the amount of H_3PO_4 used per ton of uranium. The proportions of chemicals which entered into the uranium wastes according to the procedure largely followed from the start through January 1946[6] and according to that followed in the main from then to the present (June 1951)[26] are indicated in the table below.

Constituent	Lb./Short Ton U: Procedure Through January 1946	Lb./Short Ton U: Procedure Since January 1946
UNH	4220	4220
HNO_3	177	210
H_2SO_4	700	804
H_3PO_4	1107	736
$NaNO_3$	137	210
NaOH	1673	1561
Na_2CO_3	3966	4056
Total	11,980	11,797

Final stored volume = about 4,000 gal./short ton U.

3.2 Analytical data

The scant information on the composition of uranium waste sludges and supernates is illustrated by the typical analytical data tabulated below and summarized more fully in Table II-1 and II-3.

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Composition of T Cascade Supernate(7)
(Filled 1945, Sampled 1948)

Component	Moles/Liter First Tank	Second Tank	Third Tank
U	0.028	0.090	0.11
Na	3.1	2.9	3.3
PO_4	0.33	0.26	0.27
SO_4	0.25	0.18	0.23
CO_3	0.43	0.51	0.91
NO_3	0.56	0.77	0.60

Composition of Tank 101-T Sludge(7)
(Cascade filled 1945. Sampled 1948)

Component	Mols/Kg. of Sludge Inlet, 3 Ft. from Bottom	Inlet, 2 Ft. from Bottom	Inlet, 1 Ft. from Bottom	Outlet, 1 Ft. from Bottom	Outlet, Just off Bottom
U	0.68	0.86	1.53	1.45	1.53
Na	4.5	5.0	6.0	6.6	6.4
PO_4	1.35	1.07	0.51	0.17	0.16
SO_4	0.20	0.13	0.08	0.08	0.06
CO_3	0.26	0.43	1.92	4.3	4.4
NO_3	Not reported				

4. Radioactive Constituents

4.1 General

The underground stored uranium waste contains most (more than 90%) of the fission products formed as a result of exposure of uranium slugs in the 100 Area piles. The radioactive concentration of the underground stored uranium wastes is subject to considerable variation since it is dependent upon a number of variables including the power level maintained in the pile, the period of pile exposure, and the elapsed time ("cooling") after discharge from the pile. Although the piles have been operated at various power levels the greatest part of the underground stored uranium waste resulted from the processing of slugs which had received either 200 megawatt-days/ton integrated exposure over a period of 180 days or 400 megawatt-days/ton integrated exposure over a period of 360 days. The 200 megawatt-days/ton material was processed from plant startup to January 1949 while the 400 megawatt-days/ton material was processed from November 1949 to June 1951. The total radioactive fission-product content of the pile metal 90 days after discharge from the piles is approximately 226,000 and 282,500 (theoretical) curies/ton for the [illegible]0 and 400-megawatt-day/ton material, respectively.

[redacted]

Decay curves for gross beta and gamma activity and for a number of the radioactive isotopes important to the Uranium Recovery process have been calculated and are shown in Figure II-1 (also see Table II-2). The quantity of fission products originally present was based on a uranium exposure of 400 megawatt-days/ton over a period of 360 days. Theoretical or "absolute" curies as well as "countable" curies are shown for the total beta and gamma radiation. The activities of specific isotopes are presented in terms of "countable" curies.

A theoretical (or absolute) curie is defined as the radioactivity of a source of radiation which decays at such a rate that 3.7×10^{10} atoms change per second. It is almost exactly the radioactivity of the amount of radon in equilibrium with 1 gram of radium. Because of the limitations of ordinary radiation counters, absolute curies are difficult to determine. The "countable" curies, in terms of which most of the data in Figure II-1 are expressed, have the practical advantage of being subject to comparatively easy and reproducible determination. Determination of the number of "countable" curies, in the sense in which the term is used here, involves the "counting" of the sample under specified conditions with standard counting instruments, such as the B.G.O. counter in use at Hanford Works. The counting conditions are specified in detail in Document HW-17091 (8). The counting efficiency of the standard counters, and hence the ratio of absolute to "countable" curies, is a function of the particle (or quantum) energy of the radiation measured. Although it is not possible to assign exact values to this ratio, the following are approximate values for beta particles and gamma rays of some typical energies:

Particle or Quantum Energy, M.e.v.	Ratio of Absolute to "Countable" Curies	
	Beta	Gamma
0.1	∞ (not counted)	10
0.15	50	8
0.6	4	3
2.0	2	1.2

The conversion of "countable" to absolute curies is further discussed in Document HW-17091(8).

4.2 Sludge and supernate radiochemical analyses

The radiochemical concentrations in the sludges and supernates of the various tanks in the underground waste storage cascades, like the chemical concentrations, are known only imperfectly since analytical investigations have been handicapped by the difficulty of obtaining representative samples of the large heterogeneous masses in the tanks by remote-control sampling methods.

The information on the radiochemical compositions of uranium waste sludges and supernates is illustrated by the typical analytical data tabulated below and summarized more fully in Table II-2. [redacted]

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Radiochemical Concentrations of T Cascade Supernate(7)

(Filled 1945. Sampled 1948)

Radiochemical Analysis	Counts/(Minute)(Ml.) First Tank	Third Tank
Gross Beta	1.45×10^7	2.82×10^7
Gross Gamma	4.93×10^4	4.03×10^4
Gross Alpha	7.85×10^3	5.2×10^3
Ce Beta	2.35×10^6	1.37×10^7
Cs Beta	8.59×10^6	7.39×10^6
Nb Beta	8.97×10^4	3.67×10^4
Ru Beta	3.53×10^6	5.08×10^6
Sr Beta	1.85×10^5	3.04×10^5
Zr Beta	1.95×10^3	1.49×10^4

Radiochemical Composition of Tank 101-U Sludge(7)

(Cascade filled 1947. Sampled 1949)

Radiochemical Analysis	Counts/(Min.)(Mg. of Sludge) Inlet, 4 Ft. from Bottom	Inlet, 3 Ft. from Bottom	Inlet, 2.7 Ft. from Bottom	Outlet, 3 Ft. from Bottom
Gross Beta	3.13×10^6	5.15×10^5	1.35×10^6	2.93×10^6
Gross Gamma	8.6×10^2	1.49×10^2	4.35×10^2	9.58×10^2
Pu Alpha	94.4	56.2	89.0	112
Ce Beta	2.11×10^6	2.46×10^5	9.35×10^5	2.26×10^6
Cs Beta	7.74×10^4	1.39×10^4	5.38×10^4	9.48×10^4
Nb Beta	1.78×10^3	2.88×10^2	1.26×10^3	4.07×10^3
Ru Beta	8.48×10^4	1.62×10^4	3.61×10^4	8.97×10^4
Sr Beta	8.80×10^4	4.26×10^4	7.74×10^4	1.16×10^5
Zr Beta	3.25×10^3	4.98×10^2	1.46×10^3	4.03×10^3
Other Beta (obtained by difference)	8×10^5	2×10^5	2×10^5	4×10^5

5. Properties of Sludges

A number of the physical properties of sludges believed to be of process importance during the removal and processing of the underground stored uranium wastes have been reported for a sample of 101-U sludge by ORNL.(23) Although the conditions under which the sludge in the various tanks was produced varies appreciably, the physical properties discussed below for 101-U sludge should prove applicable (for order-of-magnitude approximations at least) for other tanks containing sludges.

5.1 Apparent density and consistency

Two types of sludge were found in the sample of 101-U Tank sludges; namely soft and hard sludges. Soft sludge (approximately 60 weight per

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cent of the sludge analyzed) is an easily slurried solid consisting chiefly of sodium uranyl phosphate crystals having a definite needle-like structure. Hard sludge is a dense, hard agglomerate of crystalline carbonate material (believed to be mainly $Na_4UO_2(CO_3)_3$). The crystals are imperfectly formed.

The sludge on the bottom of the tanks is packed down and contains less liquor than the sludge above. Samples taken at the bottom of Tank 101-U contain approximately 80 per cent solids while samples taken at 1 foot, 2 feet, and 3 feet from the bottom contain approximately 70, 50, and 45 per cent solids, respectively.

Consistency measurements were made on samples of the hard sludge using a "Precision" Universal Penetrometer fitted with a standard A.S.T.M. needle. Although considerable variation was noted in the hard sludge its consistency is approximately that of blackboard chalk. (A 400 g. loading of the needle gave penetrations varying from 0.4 to 1.7 mm. for hard sludge compared with 1.3 mm. penetration for blackboard chalk.)

The density of hard sludge was found to be approximately 3.0 g./ml. The density was determined at room temperature by supernate displacement in a graduated cylinder. The soft sludge density was found to be approximately 1.8 g./ml. In determining soft sludge density, large lumps of hard sludge were removed by passing the sludge through an 8 mesh screen, the sample was centrifuged in an International clinical centrifuge (30 min. at approximately 700 G), and the supernate was removed before the soft sludge volume and weight were determined.

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5.2 Solubility of principal sludge components

As currently planned the sludges will be removed from the underground stored tanks as a sludge-supernate (or, perhaps, sludge-water) slurry. If, however, the sluicing methods prove inadequate for the removal of all the sludge (e.g., tank heel removal, local deposits not broken up by sluicing nozzles), techniques may be adopted which will dissolve the sludge in the underground storage tanks. Hence, the solubilities of the sludges have been presented in the following discussion.

Since $Na_4UO_2(CO_3)_3$ and $NaUO_2PO_4$ are believed to be the main components of the "hard" and "soft" underground stored uranium sludge, respectively, the solubilities of these compounds in different solvents have been studied at various temperatures and solvent concentrations. The upper graph shown on Figure II-3 indicates the retrograde solubility (i.e., decrease in solubility with increase in temperature) of $Na_4UO_2(CO_3)_3$ in water and in a solution of 0.5 M Na_2SO_4 and 0.5 M Na_2CO_3. As indicated, the solubility of $Na_4UO_2(CO_3)_3$ is considerably greater (4 to 6 fold) in water than in the carbonate-sulfate solution. The solubility of $Na_4UO_2(CO_3)_3$ in various solvents at 30°C. is tabulated below:

Solvent	Solubility, G. $Na_4UO_2(CO_3)_3$/Liter Saturated Solution
H_2O	143.8
0.51 M Na_2CO_3	73.6
0.41 M $NaHCO_3$	88.3
0.48 M $(NH_4)_2CO_3$	200.1

[redacted]

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On the lower graph of Figure II-3 the solubility of $NaUO_2PO_4$ in sodium carbonate solutions at 28 and 50°C. is shown. At 28°C. the solubility increases with Na_2CO_3 concentration from less than 1 g. U/l. at 0 M Na_2CO_3 to approximately 53 g. U/l. at 1.3 M, then decreases at higher carbonate concentrations.

5.3 Laboratory sludge solubilization batch data(15)(16)(24)

From the data presented in 5.2, above, it may be noted that $Na_4UO_2(CO_3)_3$ is more soluble in water than in carbonate solutions while the opposite is true for $NaUO_2PO_4$. In the small scale laboratory experiments for which data are tabulated below an effort was made to determine the relative effectiveness of various solvents for dissolving simulated soft ($NaUO_2PO_4$) and hard ($Na_4UO_2(CO_3)_3$) sludges. For the experiments the synthetic sludge was composed of 90.6 weight per cent $Na_4UO_2(CO_3)_3$ and 4.04 wt. per cent $NaUO_2PO_4$. The volume of solvent used to dissolve the sludge was the amount theoretically required to dissolve all the $Na_4UO_2(CO_3)_3$ present in the sludge sample. For a given sludge sample size, solvent volumes 1.9, 1.6 and 0.7 times the volume used in the water experiment were used for the Na_2CO_3, $NaHCO_3$, and NH_4HCO_3 experiments, respectively. (See solubility data in 5.2 above).

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Solubilization of Sludge

Solvent	H_2O	0.52 M Na_2CO_3	0.40 M $NaHCO_3$	0.45 M NH_4HCO_3
Shaking time, hr.	64.5	64.5	64.5	18.5
% U dissolved	91.6	90.9	99.0	85.8
% $Na_4UO_2(CO_3)_3$ dissolved	97.2	92.3	99.7	86.46
% $NaUO_2PO_4$ dissolved	0.0	68.5	88.8	74.68
Grams $Na_4UO_2(CO_3)_3$ dissolved per 100 ml.	13.98	6.79	8.85	17.29
Grams $NaUO_2PO_4$ dissolved per 100 ml.	0.0	0.23	0.38	0.66

The data in the above table indicate that $Na_4UO_2(CO_3)_3$ may be dissolved by any of the solvents while Na_2CO_3, $NaHCO_3$, and NH_4HCO_3 are increasingly better for the dissolution of $NaUO_2PO_4$.

5.4 Pilot-plant sludge solubilization studies(15)(18)

Pilot-plant studies were conducted by the Kellex Corporation in a 1/80-scale waste storage tank on incubated simulated wastes to develop a method of sludge solubilization which would be applicable for use within the Hanford "hot" waste tanks. In the studies incubated simulated sludge was placed in the tank, water was added, and liquor was circulated through the tank. When the concentration of the liquor approached saturation (i.e., further dissolution could have been accomplished only with considerably [redacted] circulation) a portion of the liquor was withdrawn and replaced

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with an equal volume of water. When the greater portion of the water-soluble $Na_4UO_2(CO_3)_3$ was removed, the liquor was removed and replaced with $NaHCO_3$ which dissolved the $NaUO_2PO_4$ and any $Na_4UO_2(CO_3)_3$ remaining.

The results from two runs, following the general pattern outlined above, are shown on Figure II-4. Run No. 3 was conducted at approximately 25°C. while Run No. 5 was made at approximately 50°C. Sludges were prepared for the runs by incubating simulated "cold" waste of the following composition for periods of 34 and 50 days at 80°C. before filtering for Runs No. 3 and No. 5, respectively:

Component	Grams/Liter
UNH	146.0
$NaNO_3$	4.7
HNO_3	5.3
$SO_4^{=}$	26.5
$PO_4^{\equiv}$	22.7
NaOH	54.0
Na_2CO_3	177.0

As expected from the retrograde solubility data discussed under 5.2, above, more concentrated uranium solutions were obtained faster at 25° than at 50°C. For example, in Run No. 3 at 25°C. liquor containing approximately 40 g. U/l. was obtained after only 150 hours of recirculation, while in Run No. 5 solution containing approximately 35 g. U/l. was produced after 250 hours of recirculation.

During Run No. 3 essentially all of the sludge was dissolved at the completion of the run. Of the 320 g. of uranium originally present in the simulated sludge sample, 89% was dissolved by water and the remaining 11% was dissolved by $NaHCO_3$.

Run No. 5 was terminated before all the uranium was dissolved (82% of the 430 grams of uranium dissolved after 750 hr.). However, there was little doubt that complete solubilization would have been accomplished with additional operation.

5.5 Sludge insolubles

Silicon dioxide is expected to be the major water and nitric acid insoluble component present in the underground stored uranium sludges. It enters the bismuth phosphate process in the slug bonding layer or as an impurity in the various chemicals used in the process. To determine an "order-of-magnitude approximation of the SiO_2 concentration present in the stored wastes, analyses were made on three Bismuth Phosphate Plant waste samples (8-3-WS) by the Hanford Works Analytical Division during October and November 1949. These samples indicated total SiO_2 concentrations (both soluble silicates and insoluble SiO_2) ranging from 60 to 220 milligrams per liter. Insoluble SiO_2 may collect on the bottom of the various tanks during acidification and blending or it may be separated from solution in the feed centrifuge before it enters the solvent-extraction columns.

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6. Properties of Supernates(23)(11)(1)(7)

The properties of Hanford stored uranium waste supernates are subject to considerable variation since the sludge-supernate equilibrium is dependent upon the temperature existing in the tanks as well as the chemical composition of the stored wastes.

6.1 Supernate density

The densities of the supernate in the 101-T, 102-T, and 103-T Tanks were measured in the waste storage tanks with a densitometer. The density as well as the $Na_4UO_2(CO_3)_3$ concentration (see 6.3 below) of the supernate in the last two tanks of the cascade was considerably greater than that in the first tank. The densities existing in the tanks are listed in the table below together with the temperature at which they were measured:

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Tank	Supernate Density, G./Ml.	Supernate Temperature, °F.
101-T	1.14	144
102-T	1.23	96
103-T	1.21	86

ORNL investigations on "hot" samples of 101-U Tank(23) and Hanford Works investigations on simulated supernate(11) have indicated densities ranging from approximately 1.13 g./ml. at 70°F. to approximately 1.11 g./ml. at 140°F.

6.2 Supernate viscosity(23)

The temperature-viscosity relationship for a 101-U supernate was determined by ORNL. The viscosities were measured with a Fenske-Ostwald viscosimeter. As shown by the plots on Figure II-5, the viscosities ranged from 5.9 centipoise at 74°C. to 1.5 centipoise at 25°C.

Viscosity measurements on a synthetic supernate prepared by the incubation of simulated waste solution for 6 months at 80°C. at Hanford Works gave a viscosity of 1.77 centipoise at 25°C.(9) The viscosity was measured with a Saybolt viscosimeter.

6.3 Solubility of $Na_4UO_2(CO_3)_3$ in supernate

As indicated on Figure II-6, the concentration of $Na_4UO_2(CO_3)_3$ in the hot (sometimes as high as 140 to 220°F.) supernate of the first tank in a filled cascade is less than the concentration present in the second and third tanks of the cascade (0.025 M in the first tank of the T Cascade as compared with 0.09 M and 0.11 M respectively in the second and third). This phenomenon is caused by the retrograde solubility of $Na_4UO_2(CO_3)_3$ and incomplete precipitation in the first tank. Although during cascade filling

most of the precipitation takes place under the high-temperature (precipitation-favoring) conditions present in the first tank, some of the waste solution cascades to the second (and third) tank before precipitation is complete in the first tank.

In the second tank, which is at a lower temperature since the major part of the fission products are left behind in the first tank, the supernate holds more $Na_4UO_2(CO_3)_3$ when equilibrium is attained at the lower temperature.

7. Physical Properties of Slurries

7.1 Apparent density(9)(24)

The apparent densities of slurries prepared from both actual and simulated metal waste supernate and sludge increased from about 1.1 to 2.0 g./ml. as the sludge concentration increased from 0 to 100 per cent.

Increased temperature slightly decreased the apparent density. Thus with an underground slurry with a supernate-to-sludge volume ratio* of 8:1 an increase in temperature from 25 to 65°C. decreased the apparent density of the slurry from 1.19 to 1.17 g./ml. The effect of solids concentration on the apparent density of a typical simulated slurry is presented in Figure II-7.

7.2 Apparent viscosity(9)(11)(14)(24)

Apparent viscosity or consistency of a slurry is its resistance to flow at any given flow or shear rate and is a measure of the combined effects of adhesion and cohesion. The apparent viscosities of waste metal slurries increased with increasing solid content and decreased with increasing shear rate, duration of agitation, and temperature.

At a constant shear rate, an increase in sludge concentration from a supernate-to-sludge volume ratio of 4:1 to 0.3:1 increased the apparent viscosity of a typical underground slurry from 40 to 2900 centipoises as measured with a Brookfield Synchroelectric viscometer with a No. 3 spindle. The apparent viscosity of the slurry of 0.3:1 supernate-to-sludge volume ratio decreased from 2900 to 1570 centipoises with an increase of spindle speed from 6 to 60 rev./min.

The apparent viscosity of an actual underground metal waste slurry increased from 19 to 36 centipoises during 10 hr. agitation, while further agitation produced almost no additional increase. The supernate-to-sludge volume ratio decreased from 7:1 to 2.3:1 during 23 hr. of agitation due to comminution or recrystallization of the solid phase, which apparently

*) It is noted that the supernate-to-sludge ratios given in this subsection cannot readily be interpreted in terms of liquid-solid ratios, since the liquid content of the sludges is not exactly known.

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resulted in an increased liquid content of the sludge. A similar test with a synthetic slurry of the same weight per cent solids content showed a slight decrease in apparent viscosity (from 15 to 13 centipoises) during prolonged agitation and the supernate-to-sludge volume ratio did not change within the limits of experimental error.

Increased temperature reduces the apparent viscosities of slurries. For example, a temperature increase from 20 to 59°C. decreased the apparent viscosity of a slurry of 0.3:1 supernate-to-sludge volume ratio from 1520 to 970 centipoises.

Slurries flowing in pipe line viscometers had apparent viscosities exhibiting the same trends as those observed using a Brookfield viscometer, but the numerical values were much lower. The apparent viscosities of a synthetic slurry flowing in a pipe are plotted as a function of velocity in Figure II-8. As shown in Figure II-8, the apparent viscosities in pipeline flow approached the viscosity of the supernate at velocities above 3.5 and 7 ft./sec. in 1-in. and 1/2-in. i.p.s. pipes, respectively. As the flow rate decreased into the viscous range the apparent viscosity increased sharply.

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7.3 Settling characteristics(12)(14)(24)

Settling rates of waste metal slurries vary widely, depending upon the concentration of solids, the source of the slurry, the degree of agitation, and, to a lesser extent, temperature. Reported settling rates range from 1 to 60 in./hr. of clear solution for slurries ranging from 3.6:1 to 76:1 in supernate-to-sludge volume ratio.

Simulated and actual underground metal waste slurries, each containing the same weight proportion of solids and having an initial supernate-to-sludge volume ratio of 7:1, produced initial settling rates of 10 and 34 in./hr. of clears, respectively. After one hour of agitation, the settling rate of the simulated slurry increased to 25 in./hr. and the rate of the actual metal waste slurry decreased to 6 in./hr. of "clears". After 23 hr. of agitation, the settling rates were 13.5 and 1.2 in./hr. of clears for the simulated and actual underground slurries, respectively, and the supernate-to-sludge volume ratio of the underground slurry changed from 7:1 to 2.3:1 while the ratio of the simulated slurry did not change appreciably.

The effect of temperature on settling rates is negligible within the accuracy of the available data.

7.4 Erosive characteristics(13)

Synthetic metal waste slurries with a supernate-to-sludge volume ratio of 8:1 flowing in 1/2-in. i.p.s. iron pipe at velocities of 12 to 15 ft./sec. have been shown to produce less than 30 mils/yr. erosion in 90° short (1-5/8 in.) radius bends, and almost no erosion in straight sections. Somewhat greater rates would be expected at higher sludge concentrations and increased velocities.

Erosion rates obtained from mechanical abrasion tests with various

slurries gave the relative index listed below. The slurries were of 8:1 supernate-to-sludge volume ratio, except the concentrated RAW, which contained about 1 weight per cent solids.

Relative Erosion Index*

Diatomaceous Earth	16
Kaolin	1.6
Simulated Metal Waste	1.00
Concentrated Neutralized RAW	0.44

*) The "relative erosion index" is the ratio of penetration per unit time of a slurry to that of synthetic metal waste slurry. The penetration was measured as the maximum depth of penetration of neoprene rubbing at a uniform rate on cast bronze submerged in a slurry.

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B. REMOVAL PROCEDURE

1. General

At the time of the projected start-up date for the uranium recovery process, approximately 5,900 tons of uranium in bismuth phosphate process waste form will be stored in underground tanks. During the storage period the neutralized homogeneous bismuth phosphate waste solutions will have separated into a supernatant liquid and a sludge layer which settles to the bottom of the storage tanks. In order to ensure a uniform uranium solution feed to the Uranium Recovery process, the waste removal process involves several principal operations; (1) homogenization of supernate, (2) sluicing the sludge with supernate to obtain a slurry, (3) dissolution of the slurry with nitric acid, (4) blending the acidified solution with homogenized supernate to obtain the desired uranium concentration, and (5) removing the waste metal heels in the underground tanks.

The first equipment for the removal, blending, and acidification of stored uranium wastes was installed at the 241-U-101 series cascade. In addition to the 241-U facilities, storage provisions for the acidified waste removed from the U-101 Cascade are installed in a new underground vault (241-WR) located adjacent to 221-U Building. The equipment thus provided is known as construction Phase I and is intended to pilot operating techniques to be employed in subsequent waste removal installations. Construction Phase II includes the facilities necessary for the removal of the uranium wastes from the remaining waste cascades in 241-U, T, TX, B, BX, BY, and C Tank Farms. Three additional slurry accumulation, blending, and acidification units are provided in Phase II. One is near 241-TX to serve the T and TX Farms, a second in the vicinity of 241-B, BX, and BY to serve these areas, and a third at 241-C.

In order to transfer material between the 200 East and West Areas a pipe line transfer system with intra-area tributaries was constructed as Phase III. Additional lines to cribs and interconnections between 241-WR Storage Vault and the 221-U and 224-U operating facilities were also installed as a part of Phase III construction.

As previously indicated, stored uranium wastes will be removed

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initially from the 241-U-101 cascade. The exact sequence by which other tank cascades will be processed cannot be defined clearly at the present time, since the number of operating sluicing areas required to meet recovered metal production is highly dependent upon the success of initial operations in the U-101 cascade. The sluicing procedure followed for removal of the uranium wastes, however, is essentially the same for all waste removal areas. The technique for removing the waste material employs the principal operations previously outlined, and discussed in more detail below. Reference should be made to Figure II-9, the engineer's flow sketch for 241-C Farm. The equipment shown schematically in Figure II-9 is typical of the waste removal installations located in both 200E and 200W Areas with the exception of the 20-ft. tanks (TK-C-201, 202, 203, and 204 shown in Figure II-9) which are located in 241-C Farm only. The procedure covers the proposed method of waste removal from these smaller tanks in addition to the larger 75-ft. diameter cascade tanks.

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2. Process Description – 75-ft. Tanks (26)

2.1 Mixing of supernates

The bulk of the solids precipitated from the neutralized bismuth phosphate wastes lie in the first tank with small amounts appearing in the second tank in any waste tank cascade. Consequently, the supernatant liquid in equilibrium with these solids varies from tank to tank in the series. In order to insure a uniform feed solution composition for the Uranium Recovery (TBP) process, the supernatant liquid may be homogenized by pumping the solution from tank to tank in series. This is accomplished by using the submerged 600 gal./min. sludge pumps suspended in each storage tank. The inter-tank circuit is set up through jumpers in the cascade diversion box. Since the sludge pumps are of a low head type which cannot force a large solution volume through the sluicing nozzles, the supernate is admitted to each tank through a separate inlet line. At a 600 gal./min. pumping rate it is estimated that 3-1/2 days will be required to turn over the total volume of supernate twice to ensure adequate mixing.

2.2 Transfer of supernate

After the supernatant liquid has been homogenized a portion of the supernate is pumped to an empty waste tank for temporary storage in order to expose the sludge layer prior to the sluicing operation. The transfer of supernate is made by pumping from the last cascade tank to an empty tank (TK-TX-115 in the West Area, TK-BY-109 in the East Area) via the Slurry Accumulator, TK-001. The supernate from the first cascade tank is then (after proper jumper change) transferred to the last cascade tank by gradually lowering the sludge pump to follow the liquid level until the sludge is exposed. At the end of this transfer, 35,000 gallons of supernate are allowed to remain in TK-001 for initial sluicing liquid.

2.3 Sluicing and removal of sludge

Sludge removal is accomplished by recycling 35,000-gallon batches of supernate from the Slurry Accumulator under about 100 lb./sq.in. pressure through either of two 1-3/8-inch firehose-type nozzles inserted into the

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upper portion of the cascade tank through existing 12-inch tank nozzles. Each nozzle has a capacity of about 500 gal./min. at 100 lb./sq.in. inlet pressure and may be remotely adjusted for azimuth and elevation so that its stream may be directed for maximum sluicing efficiency. A motor-operator is provided which may be attached to the azimuth adjustment mechanism on either nozzle to cause it to scan slowly within a predetermined angle.

As the sludge is broken up and slurried by the sluicing supernate, the resulting suspension is removed from the underground storage tank by the sludge pump and discharged to the Slurry Accumulator. The liquid in the Accumulator is then recycled back to the sluicing nozzle until a slurry is produced which contains sufficient solids for charging the Blend Tanks, TK -002 and 003. Liquid level control in the Slurry Accumulator is maintained by opposed-action, air-operated diaphragm valves located in the sludge pump discharge and by-pass line. The valve action is such that a throttling action on the pump discharge valve caused by high level in the Accumulator will open the by-pass valve, and discharge slurry back into the underground waste tank being processed. The sludge pump maintains a minimum solution level above the sludge in the cascade tank for optimum sluicing efficiency. This operation may be observed by means of an illuminated 2.5-power periscope inserted into the top of the tank.

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During the sluicing and removal of sludge from the first tank of a cascade, the supernate from the second and third tanks is consumed in slurrying and blending so that the layer of sludge in the second tank of the cascade is exposed. This sludge is sluiced and removed in a manner similar to the procedure followed for the first tank. During the later stages of sluicing and blending of the contents of the first or second cascade tanks, the supernate originally transferred to an empty cascade tank is returned to the last tank in the cascade being processed via the Slurry Accumulator. It is expected that three tanks in a cascade can be emptied in about 80 days, and four tanks in 120 days; thus maintaining a production rate of 5 tons/day of uranium in acid solution per area.

2.4 Transfer and dissolution of slurry

The 50,000 gallon Slurry Accumulator is equipped with baffles and has a hold up capacity of about one hour. During the sluicing operation some concentration of suspended material will occur through residence time settling. When the solids in the slurry reach a uranium metal concentration of 75 to 100 grams/liter, as indicated by weight factor and specific gravity instrumentation, recirculation is stopped. In addition to the bubbler type weight factor and specific gravity instrumentation, a strain gauge which relates deflection of the tank supports to weight of the tank and its contents is provided to supplement weight factor measurements. The slurry is then agitated and transferred batchwise to the Blend Tanks by means of one or two steam jets, each discharging into a separate 15,000 gallon dissolving and blending tank.

Prior to the transfer of slurry from the Accumulator, the Blend Tanks are charged with nitric acid from Nitric Acid Tank, TK-004, in an amount sufficient to provide the proper acidity for a batch of finished feed

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solution, and the required amount of slurry is jetted into the acid. The addition of slurry is made to the acid in order to control the rate of carbon dioxide evolution resulting from the acidification. Severe foaming would occur in the Blend Tanks if nitric acid was added to a batch of slurry. Agitation and cooling through cooling coils is provided to insure prompt dissolution of the solids and removal of heat of reaction (ca. 24 B.t.u./lb. of slurry). Carbon dioxide and other gases released during dissolution are removed through glass-wool filters and discharged to the atmosphere through a stack.

When dissolution is complete, clear supernate is added to the Blend Tanks from one of the cascade tanks to adjust the dissolved slurry to the required metal concentration. The finished blended solution is removed from the Blend Tanks by submerged pumps which discharge through the master diversion box into existing underground piping in the West area farms, or through lines provided from the East area farms, to four feed storage tanks in the 241-WR diversion station. For each waste processing system in the East area (241-BXR, 241-CXR) a 50,000 gallon Process Pump Tank TK-011 has been provided for surge capacity while pumping the acidified solution at a constant rate to 241-WR storage facilities.

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The acidification step is treated in more detail in Chapter III.

2.5 Removing storage tank heel

After all of the sludge in a cascade has been removed to the minimum pump suction level, a steam jet inserted through a hole in the center of the tank dome removes substantially all of the remaining material reposing in the dished bottom of the tank. The jet discharges directly to the Slurry Accumulator, by-passing all diversion boxes.

3. Process Description -- 20-Ft. Tanks

In the case of the four individual 20-ft. diameter tanks in the 241-C Farm, the waste removal system is designed for a somewhat modified schedule of operation since jets are used instead of pumps to remove the slurry.

3.1 Removal of supernate

The recovery of wastes from these tanks is scheduled between the completion of operations in the TK-C-101 cascade and the start-up of operations in the TK-C-104 cascade. A "heel" left in the Slurry Accumulator from the preceding TK-C-101 cascade operation is used as the prime mover for the liquid sludge jet in TK-C-201. The sluicing nozzle valve is closed and supernate is jetted to the Slurry Accumulator. As the liquid level in the Accumulator reaches a near-maximum level, the additional supernate is jetted from the Accumulator into the Blend Tanks which have been charged with nitric acid. The acidified supernate is transferred to the 50,000-gallon Process Pump Tank and held for blending with subsequent charges.

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3.2 Sluicing and removal of sludge

After the sludge has been uncovered, the valve to the sluicing nozzle is opened and the sluicing operation is carried out. Supernate is used in this instance for both sluicing and as the prime mover of the sludge jet.

3.3 Transfer and dissolution of slurry

Upon completion of the sluicing operation, the sludge-laden material in the Accumulator is jetted to the Blend Tanks for dissolution in nitric acid. A heel is left in the Accumulator to prime the pump for supernate removal from the next tank (TK-C-202). The dissolved material is pumped to the 50,000 gallon Process Pump Tank where it is blended with subsequent batches until the Pump Tank is full. Transfer is made to the 241-WR storage tanks via the East-West underground lines.

The remaining tanks (TK-C-202, 203, 204) are processed in the same manner.

4. Possible Difficulties and Remedies

The design of the waste removal facilities was based mainly on "know-how" and assemblages of equipment believed capable of doing the job. Apart from the studies made on the properties of sludges, supernates, and slurries which are discussed in Section A of this Chapter, no closely applicable development work was pursued upon which design could be based.

Perhaps the single most important potential difficulty confronting the waste removal operation is the plugging of lines, nozzles, or pumps with nodules of hard sludge known to be present in the underground tanks. The fact that these harder materials are soluble in water, or sodium carbonate solutions, will allow the judicious use of these solubilizing agents to attempt a remedy for an equipment stoppage caused by plugging. The erosive and corrosive properties of the materials handled received consideration during design. No difficulties are anticipated from erosion of pipe, since the penetration rate at the fluid velocities encountered are sufficiently low that the pipe will outlast the sluicing operation in any cascade. Important known potential mechanical difficulties have been precluded wherever possible in the design of agitators and pumps by the use of proper seals and bearings. The remedial measures taken for the correction of mechanical failures will have to be based on field observation.

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Table II-2

FISSION-PRODUCT RADIOACTIVITY AS A FUNCTION OF AGE

Source of Data: HW-17091

Basis: (a) Pile metal at 400 megawatt-days/ton integrated exposure over 350 days.

(b) Radioactivities are stated per short ton of uranium.

Isotope	Half Life	Ratio = Abs. Curies / Count. Curies Beta[b]	Gamma[d]	After 90 Days "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta[a]	Gamma[c]	After 1 Year "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta	Gamma	After 2 Years "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta	Gamma
Sr^{89}	54.5 days	1.33	--	14,090	--	10,635	--	383	--	290	--	5	--	4	--
$Sr-Y^{90}$	25 yr.	1.76	--	2,690	--	1,530	--	2,840	--	1,500	--	2,565	--	1,456	--
Y^{91}	57 days	1.30	--	17,725	--	13,635	--	555	--	425	--	7	--	5	--
$Zr-Nb^{95}$	65 days	6.76	5.0	22,180	41,600	3,280	8,360	1,040	1,890	157	400	24	45	4	9
Ru^{103}	38.7 days	32.30	2.5	37,630	38,100	1,150	15,450	2,440	2,770	90	1,110	56	59	2	24
Ce^{143}	45 days	5.00	3.0	7,180	3,590	1,440	1,200	92	45	20	15	--	--	--	--
$Ru-Rh^{106}$	290 days	1.03	1.5	2,230	770	2,160	510	1,130	390	1,095	260	455	166	470	110
Ce^{144}	130 days	1.54	--	80	--	55	--	17	--	10	--	3	--	2	--
Cs^{135}	2.7 yr.	6.90	7.0	60	60	10	--	40	49	5	7	38	38	5	5
$Sn-Te^{129}$	32 days	1.20	7.0	550	1,620	455	270	1	4	1	1	--	--	--	--
$Cs-Ba^{137}$	33 yr.	4.30	2.7	1,220	1,140	270	420	1,200	1,120	266	415	1,173	1,090	260	404
Ba^{140}	12.8 days	2.47	3.0	430	110	170	--	--	--	--	--	--	--	--	--
La^{140}	1.68 days	1.46	1.5	540	560	360	360	--	--	--	--	--	--	--	--
Ce^{141}	28 days	5.06	10.0	5,310	6,240	1,045	640	5	5	1	1	--	--	--	--
Pr^{143}	13.8 days	2.56	--	620	--	245	--	--	--	--	--	--	--	--	--
$Ce-Pr^{144}$	275 days	1.83	10.0	47,270	22,720	25,815	2,270	23,630	11,360	12,900	1,140	9,400	4,515	5,135	453
Nd^{147}	11.8 days	3.05	3.0	100	85	35	--	--	--	--	--	---	--	--	--
Pm^{147}	3.7 yr.	16.70	--	4,090	--	280	--	4,010	--	240	--	3,372	--	202	--
Sm^{151}	20 yr.	0.00	--	160	--	--	--	100	--	--	--	155	--	--	--
Eu^{155}	2 yr.	28.60	12.0	90	90	--	--	70	70	--	--	48	48	--	--
			Total	165,845	116,865	62,570	29,480	37,724	17,793	17,000	3,350	17,333	5,864	7,545	1,005
	Total (Beta + Gamma)			282,510		92,050		55,517		20,350		23,297		8,550	

Isotope	After 4 Years "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta	Gamma	After 8 Years "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta	Gamma	After 12 Years "Cooling" Abs. Curies/Ton Beta	Gamma	Count. Curies/Ton Beta	Gamma
Sr^{89}	--	--	--	--	--	--	--	--	--	--	--	--
$Sr-Y^{90}$	2,427	--	1,379	--	2,173	--	1,230	--	1,943	--	1,144	--
Y^{91}	--	--	--	--	--	--	--	--	--	--	--	--
$Zr-Nb^{95}$	--	--	--	--	--	--	--	--	--	--	--	--
Ru^{103}	--	--	--	--	--	--	--	--	--	--	--	--
Ce^{143}	--	--	--	--	--	--	--	--	--	--	--	--
$Ru-Rh^{106}$	84	28	51	16	3	1	3	1	--	--	--	--
Ce^{144}	--	--	--	--	--	--	--	--	--	--	--	--
Cs^{135}	23	23	3	3	8	8	1	1	--	--	--	--
$Sn-Te^{129}$	--	--	--	--	--	--	--	--	--	--	--	--
$Cs-Ba^{137}$	1,127	1,050	250	388	1,033	964	230	357	953	887	212	329
Ba^{140}	--	--	--	--	--	--	--	--	--	--	--	--
La^{140}	--	--	--	--	--	--	--	--	--	--	--	--
Ce^{141}	--	--	--	--	--	--	--	--	--	--	--	--
Pr^{143}	--	--	--	--	--	--	--	--	--	--	--	--
$Ce-Pr^{144}$	1,496	720	909	72	37	18	20	2	1	1	--	--
Nd^{147}	--	--	--	--	--	--	--	--	--	--	--	--
Pm^{147}	2,327	--	139	--	1,100	--	65	--	518	--	31	--
Sm^{151}	145	--	--	--	126	--	--	--	110	--	--	--
Eu^{155}	25	25	--	--	8	6	--	--	2	2	--	--
Total	7,654	1,847	2,660	480	4,490	1,008	1,530	360	3,523	890	1,387	329
Total (Beta + Gamma)	9,501		3,140		5,490		1,810		4,413		1,716	

NOTES:

(a) The countable beta curie is defined by counting each isotope under the following conditions:

(1) Using a counting instrument which operates through a 2 mg./sq. cm. window. [Under this condition the beta ray absorption loss in the window will range from 49% for 0.15 M.e.v. particles to 10% for 0.6 M.e.v. beta particles]. Such a counting instrument may be of the mica-window, Geiger-Muller type.

(2) Taking the counting measurements on 100 mg./sq. cm. sample. (Under this condition the beta ray self absorption loss in the sample ranges from 98% for 0.15 M.e.v. particles to 72% for 0.6 M.e.v. beta particles.)

(3) Adequately correcting for all other counting variables, such as geometry, etc.

(b) Countable beta curie factor for each isotope (obtained by applying the above conditions). The countable beta curies are obtained by dividing the calculated absolute curies by this factor.

(c) The countable gamma curie is defined by counting each isotope under the following conditions:

(1) Taking the counting measurements on a 100 mg./sq. cm. sample.

(2) Using enough shielding (1.8 gm./sq. cm. of aluminum) to shield the maximum energy beta rays (3.55 M.e.v. for Rh^{106}) from the counting instrument.

(d) Countable gamma curie factor based on (a) and (b) above. It may be noted that the countable gamma curie factor is considered less exact than the beta curie factor because there is less experimental data upon which to base the gamma factor.

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Table II-3

COMPOSITION OF URANIUM WASTES IN UNDERGROUND STORAGE TANKS

Source of Data: HW-14157

Source of Sample	Date Sampled	Non-Radioactive Constituents: Moles/Liter for Supernate; Moles/Kg. for Sludge							Mol Ratio U/PO_4	Radioactive Constituents: Counts/Min./Ml. for Supernates; Counts/Min./Mg. U for Sludges												
		U	Na	PO_4	SO_4	CO_3	NO_3	Bi		Gross Beta	Gross Gamma	Gross Alpha	Pu Alpha	Ce Beta	Cs Beta	Nb Beta	Ru Beta	Sr Beta	Zr Beta	Tm Beta	Other Beta(c)
101-T Supernate	7-47	0.0282	--	0.405	0.298	--	--	$< 10^{-6}$	0.070												
101-T Supernate	8-47	0.0244	--	0.368	--	--	--		0.066												
101-T Supernate	11-48	0.0282	2.06	0.33	0.248	0.45	0.56		0.085	1.45×10^7	4.93×10^4	7.85×10^3	--	2.28×10^6	6.59×10^6	8.97×10^4	3.53×10^6	1.85×10^5	1.95×10^3	--	--
102-T Supernate	7-47	0.101	--	0.33	0.282	--	--	$< 10^{-6}$	0.31												
102-T Supernate	8-47	0.0918	--	0.304	--	--	--		0.30												
102-T Supernate	11-48	0.0903	2.92	0.263	0.177	0.507	0.771		0.343												
103-T Supernate	7-47	0.112	--	0.356	0.260	--	--	$< 10^{-6}$	0.313												
103-T Supernate	8-47	0.103	--	0.341	--	--	--		0.302												
103-T Supernate	2-48	0.111	3.31	0.267	0.225	0.912	0.663		0.416	2.82×10^7	4.03×10^4	8.20×10^3	--	1.27×10^7	7.39×10^6	3.67×10^4	9.08×10^6	3.04×10^5	1.49×10^4	5.20×10^5	1×10^6
103-U Supernate	2-49	0.084	1.48	0.106	0.115	0.33	0.37		0.80	7.40×10^6	1.61×10^4	--	1.58×10^3	1.10×10^6	3.54×10^6	7.12×10^3	1.35×10^6	9.90×10^4	1.47×10^3	--	1×10^6
103-U Supernate	2-49	0.084	1.61	0.105	0.115	0.30	0.38		0.80	6.42×10^5	1.78×10^4	--	1.53×10^3	1.04×10^6	3.78×10^6	8.48×10^3	1.40×10^6	2.70×10^4	1.38×10^3	--	2×10^5
101-T Sludge I-???	8-48	0.471	8.04	1.17	0.25	0.05	0.62		0.406	1.70×10^6	5.80×10^4	1.44×10^2	--	9.10×10^5	8.24×10^4	5.05×10^2	4.25×10^4	2.24×10^5	3.36×10^3	1.49×10^5	3×10^5
101-T Sludge I-???	8-48	0.563	3.7	1.41	0.23	0.02	0.26		0.398	2.15×10^6	3.88×10^2	1.51×10^2	--	7.22×10^5	3.59×10^4	1.44×10^3	3.09×10^4	3.92×10^5	4.75×10^3	--	1×10^6
101-T Sludge I-3'(a)	11-48	0.881	4.52	1.35	0.20	0.263	--		0.504												
101-T Sludge I-2'	11-48	0.857	5.04	1.07	0.125	0.427	--		0.801												
101-T Sludge I-1'	11-48	1.53	5.06	0.505	0.08	1.92	--		3.03												
101-T Sludge O-1'(b)	11-48	1.45	6.57	0.170	0.06	4.25	--		8.5												
101-T Sludge O-Bottom	11-48	1.53	6.35	0.18	0.06	4.38	--		8.8												
101-U Sludge I-4'	2-49	1.38	5.52	0.64	0.0292	3.02	0.03		2.18	3.13×10^6	8.80×10^2	--	94.40	2.11×10^6	7.74×10^4	1.78×10^3	8.48×10^4	8.80×10^4	3.25×10^3	--	8×10^5
101-U Sludge I-3'	2-49	1.11	4.09	0.52	0.0214	2.77	0.05		2.13	8.18×10^6	1.49×10^2	--	56.20	2.46×10^5	1.39×10^4	2.68×10^2	1.82×10^4	4.26×10^4	4.88×10^2	--	2×10^5
101-U Sludge I-2' ??'	2-49	1.15	5.35	0.86	0.0285	2.70	0.56		2.05	1.35×10^6	4.35×10^2	--	69.00	9.35×10^5	5.38×10^4	1.28×10^3	2.61×10^4	7.74×10^4	1.46×10^3	--	2×10^5
101-U Sludge O-3'	2-49	1.12	4.79	0.35	0.0316	0.68	0.03		2.04	2.93×10^6	8.58×10^2	--	112.00	2.28×10^6	9.48×10^4	4.67×10^3	8.97×10^4	1.16×10^5	4.03×10^3	--	4×10^5
102-U Sludge I-1''	2-49	0.445	4.74	1.43	0.0529	1.15	0.05		0.311	1.75×10^6	5.42×10^2	--	108.00	1.16×10^6	5.00×10^4	1.38×10^4	4.68×10^4	1.58×10^5	1.46×10^3	--	3×10^5
102-U Sludge O-1''	2-49	0.639	3.79	1.11	0.0365	1.50	0.03		0.576	4.07×10^5	1.64×10^2	--	50.00	2.74×10^5	2.42×10^4	2.85×10^2	1.83×10^4	4.88×10^4	1.70×10^2	--	4×10^4

Legend:

(a) 1 - Inlet sample; dimension is depth of sample measured from bottom of tank.

(b) O- Outlet sample; dimension is depth of sample measured from bottom of tank.

NOTES:

(a) Counting Conditions:

Alpha: Simpson proportional counter, 52% geometry.

Beta: Mica end-window G-M; 16.2% geometry.

Gamma: Mica end-window G-M; Al-Pb-Al sandwich on first shelf, sample on second shelf; geometry not stated.

(b) To convert the stated counts to microcuries (per unit volume for supernates, per unit weight for sludges), multiply beta counts by 4.45×10^{-6} and alpha counts by 8.7×10^{-7}.

(c) By difference.

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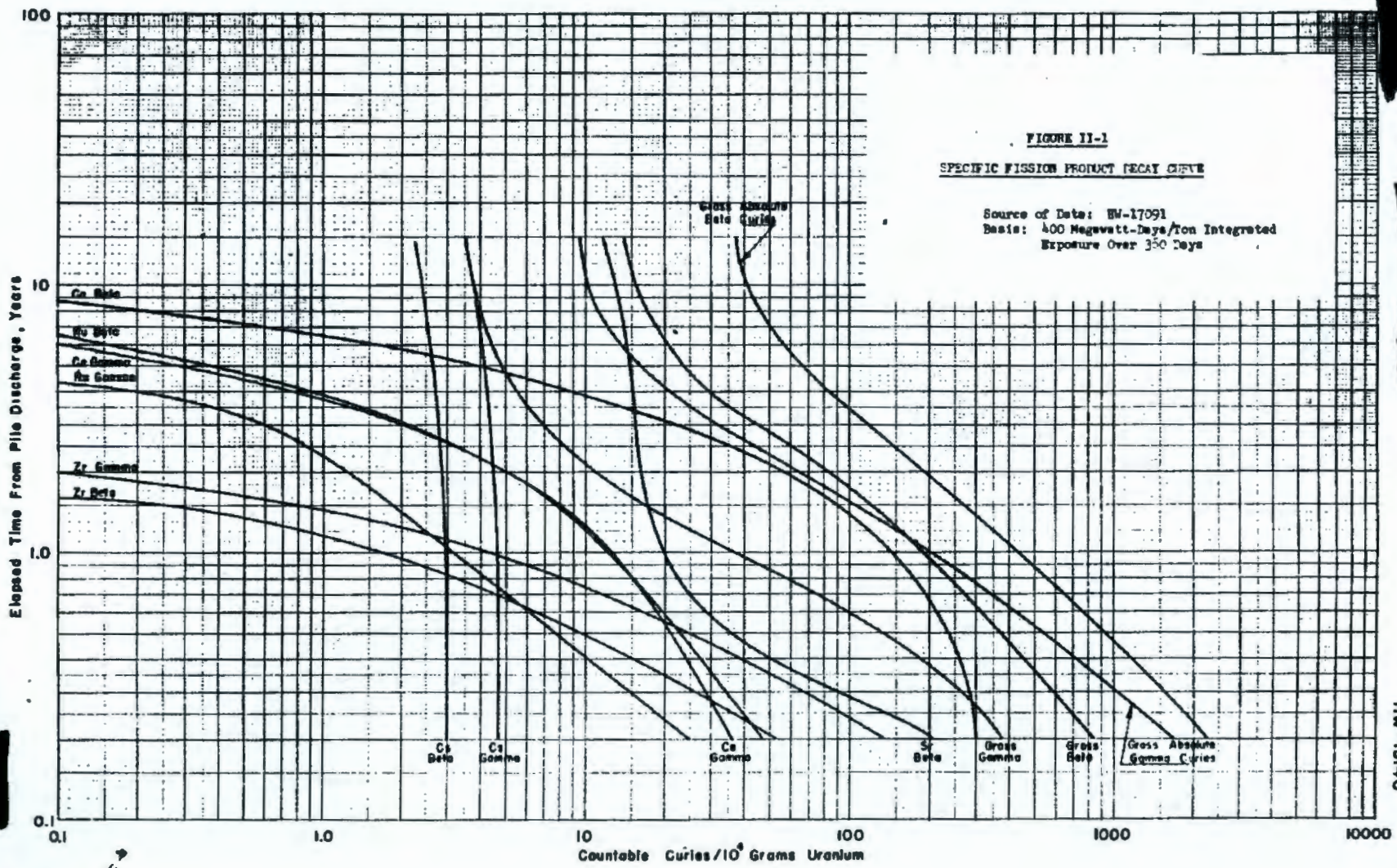

FIGURE II-1

SPECIFIC FISSION PRODUCT DECAY CURVE

Source of Data: HW-17091
Basis: 400 Megawatt-Days/Ton Integrated Exposure Over 350 Days

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FIGURE II - 2

VARIATION IN SLUDGE COMPOSITION WITH DEPTH

SOURCE OF DATA: K-337

SAMPLES FROM TANK 101-T INLET

TAKEN NOV. 18-19, 1948

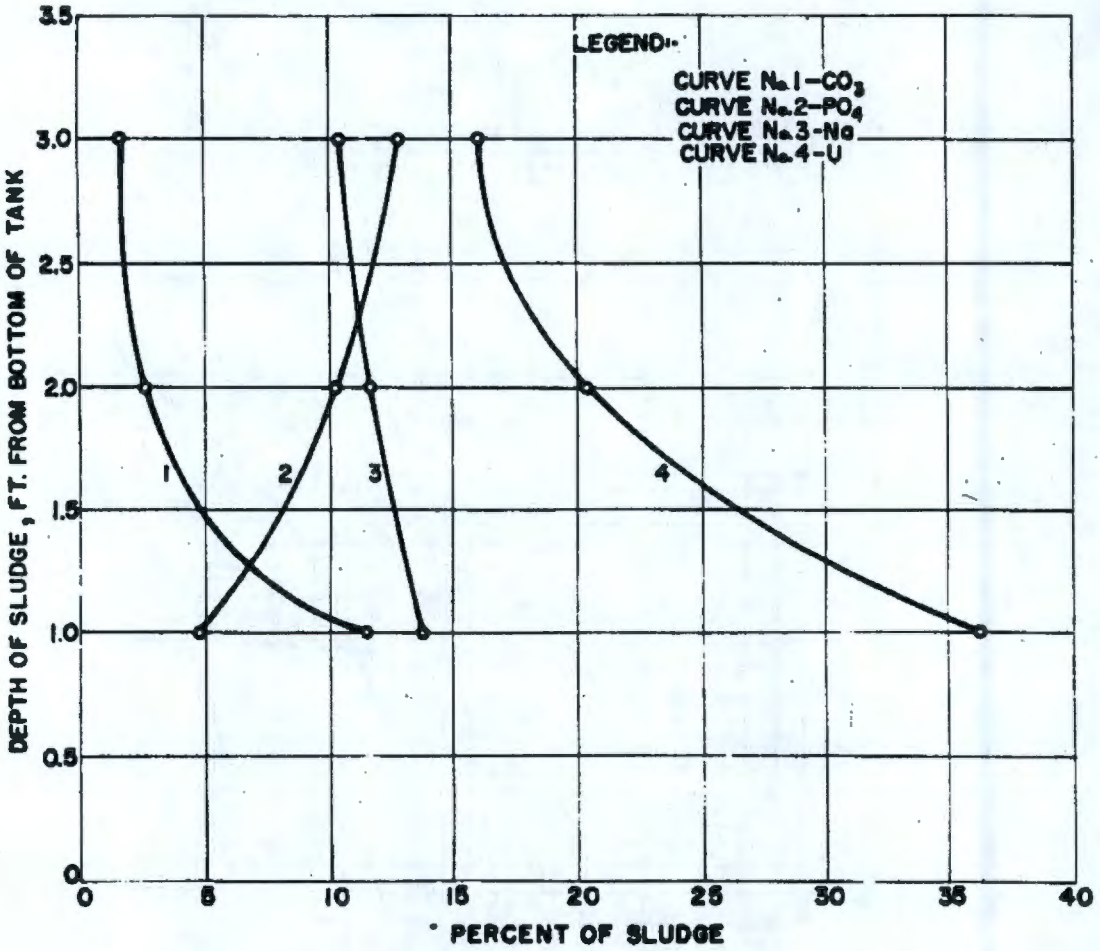

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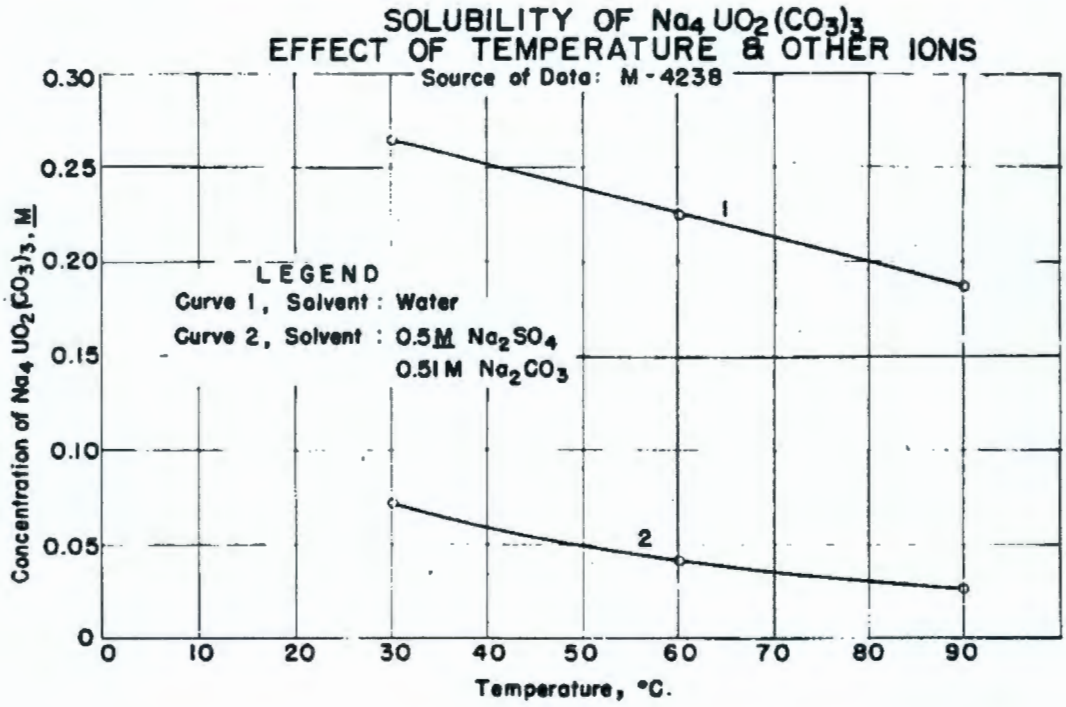
Figure II-3

SOLUBILITY OF SLUDGE COMPONENTS



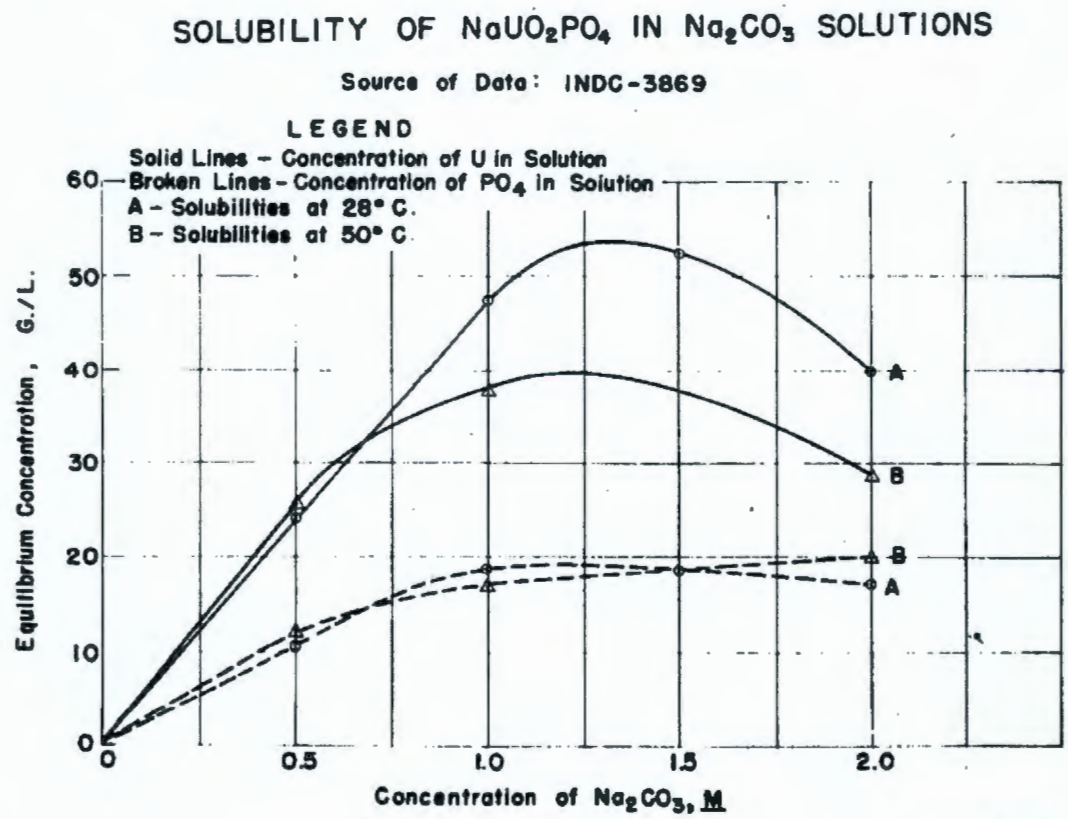


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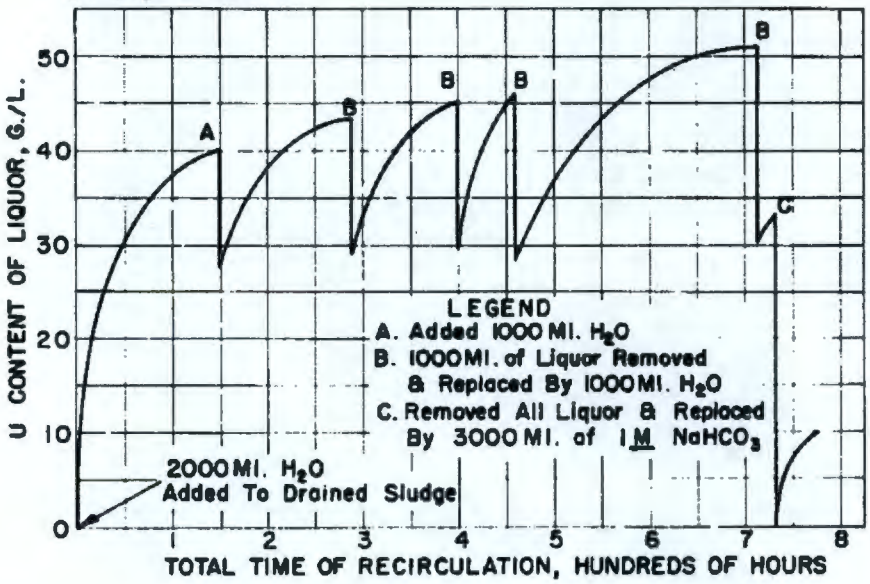
Figure II - 4
DISSOLUTION OF SLUDGE FROM INCUBATED SIMULATED WASTE

RUN Nº 3 AT ROOM TEMPERATURE

Incubation: 34 Days at 80° C.

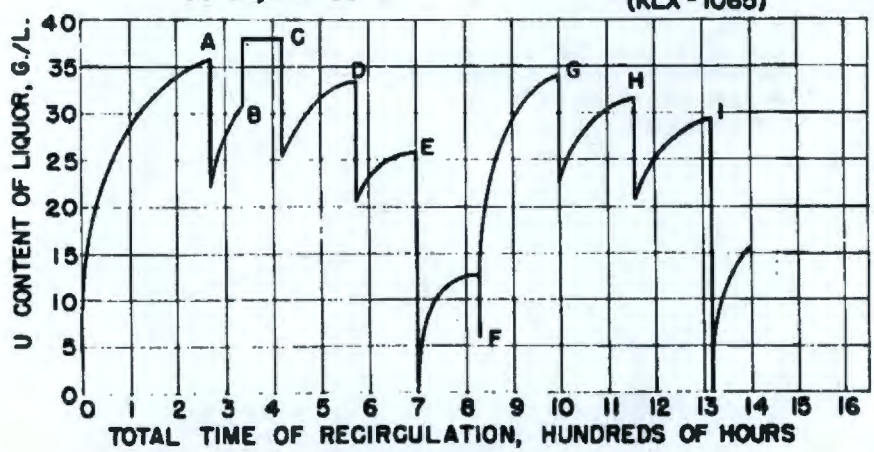
Source of Data: INDC-3681



RUN Nº 5 AT 50° C

Incubation: 50 Days at 80° C.

Source of Data: INDC-4256 (KLX-1065)



L E G E N D

A. Volume Reduced to 2000 Ml. Added 1000 Ml. H_2O.
B. Pump Failed. All Liquid In Tank.
C. Volume Reduced to 2000 Ml. Added 1000 Ml. H_2O.
D. Volume Reduced to 2000 Ml. Added 1000 Ml. H_2O.
E. All Solution Removed. Added 1000 Ml. H_2O.
F. Volume Increased to 2000 Ml. & Made 1.25 M In $NaHCO_3$.
G. Added 1000 Ml. 1.25 M $NaHCO_3$.
H. Volume Reduced to 2000 Ml. Added 1000 Ml. 1.25 M $NaHCO_3$.
I. All Solution Removed. Added 3000 Ml. 1.25 M $NaHCO_3$.

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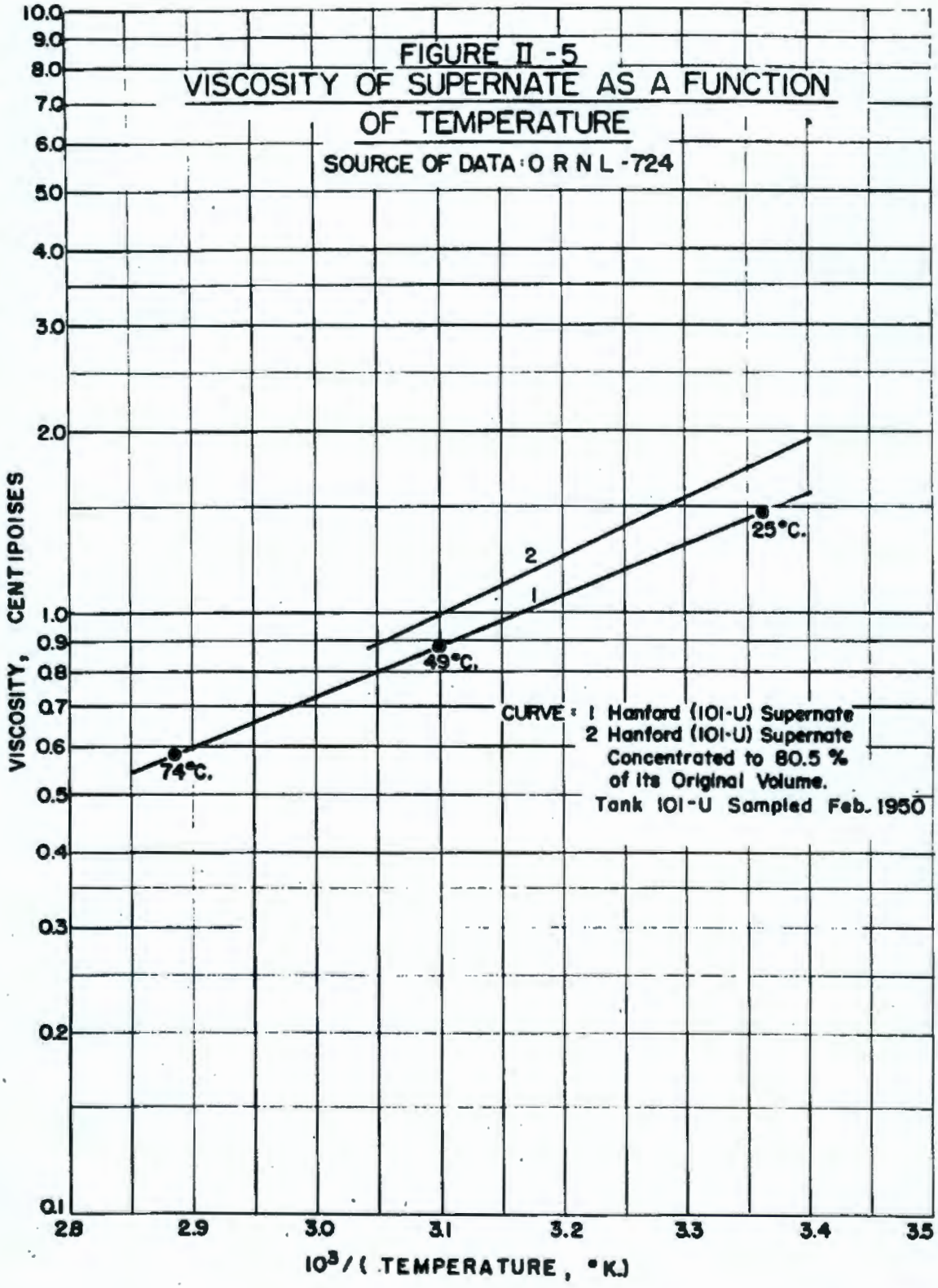

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FIGURE II-6

SOLUBILITY OF $Na_4UO_2(CO_3)_3$ IN SUPERNATE AS A FUNCTION OF TEMPERATURE

SOURCE OF DATA: HW-14157, GEH-12988

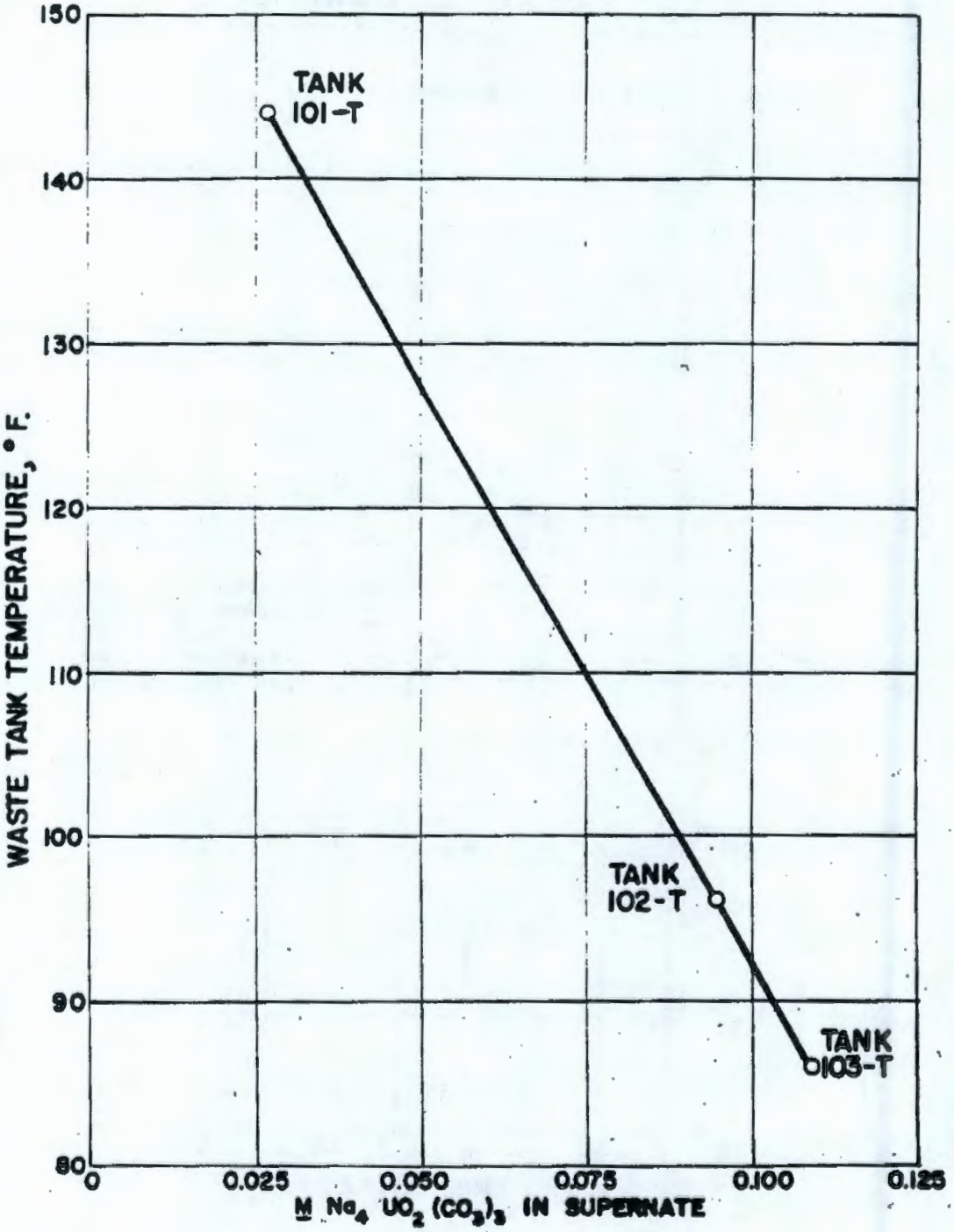

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Figure II - 7

APPARENT DENSITY OF SIMULATED METAL WASTE SLURRIES
EFFECT OF SOLIDS CONCENTRATION

(Data from HW-18367)

Material: Supernate and sludge from simulated metal waste (initial composition; 0.29 M UNH, 0.40 M $NaPO_4$, 0.25 M $NaSO_4$, 0.97 M $NaCO_3$, 0.16 M $NaNO_3$, 0.34 M $NaHCO_3$), incubated 6 months at 80 ± 5° C.

Legend:

⊙ 25° C.
× 40° C.
△ 65° C.

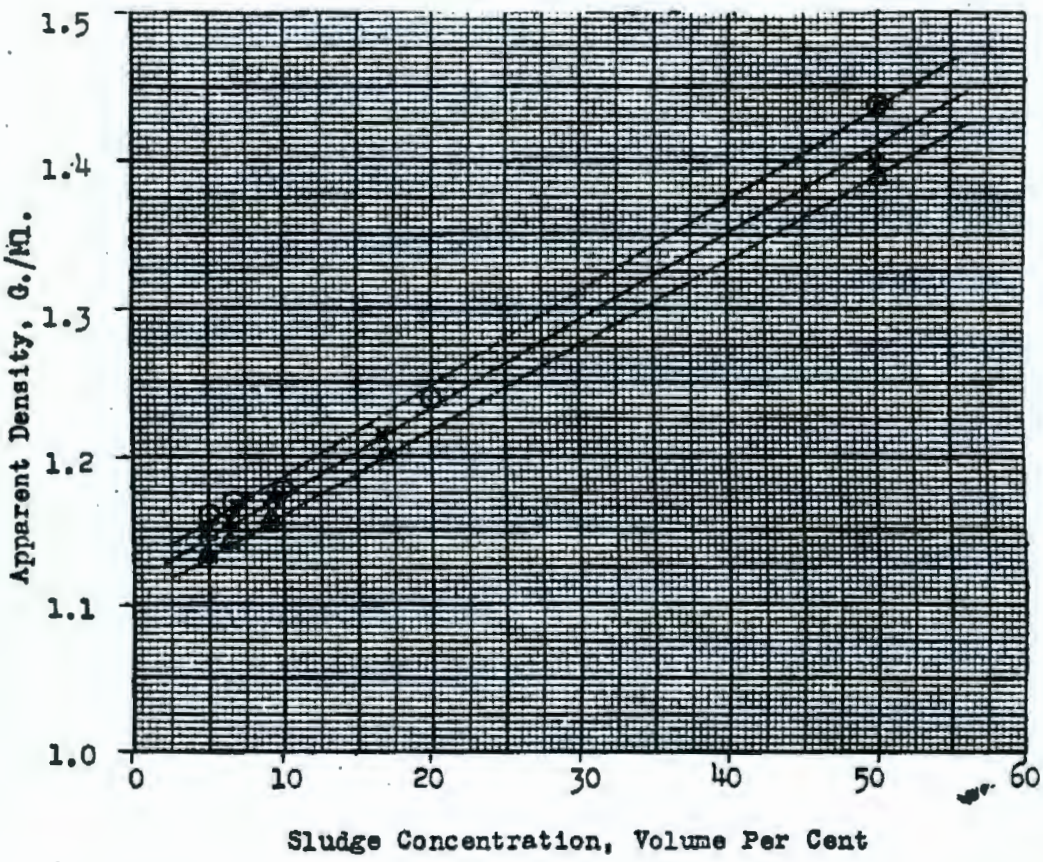

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Figure II-8

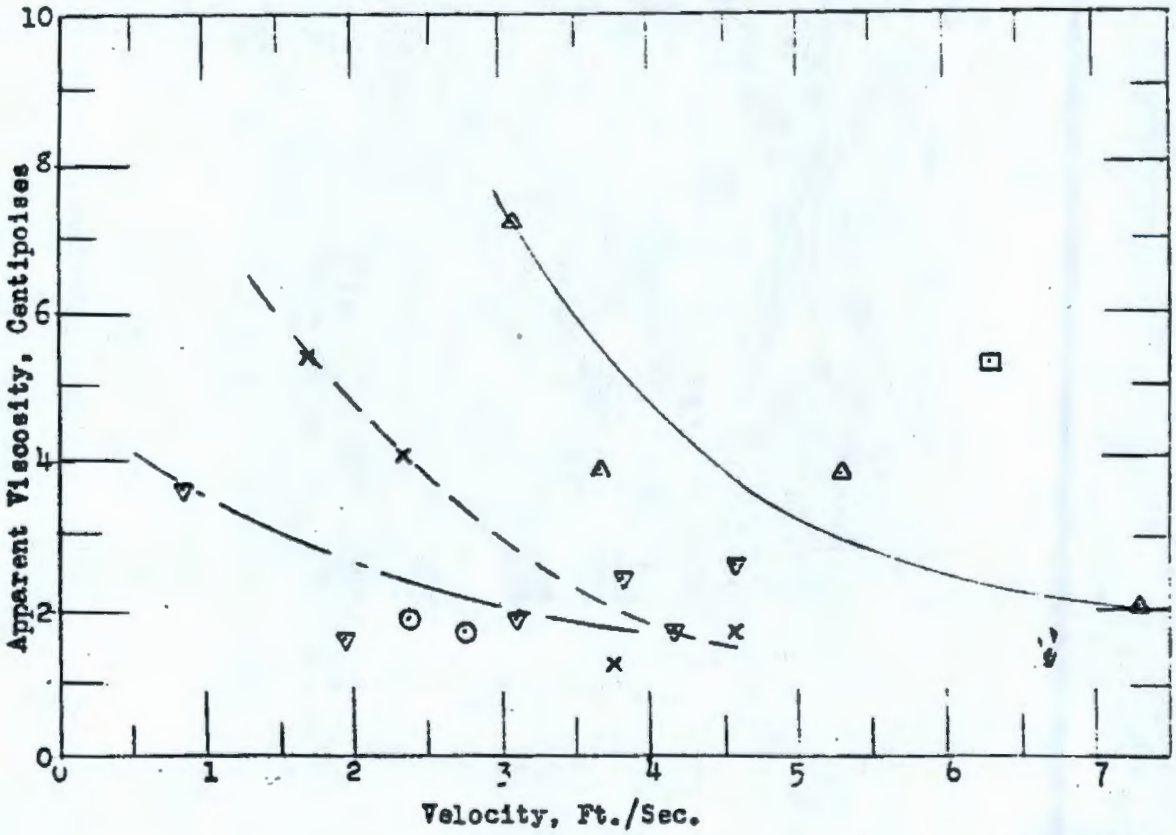
APPARENT VISCOSITY OF SYNTHETIC METAL WASTE SLURRIES
EFFECT OF VELOCITY IN PIPES

(Data from HW-17775)

Test Method: Pipeline viscometer. Apparent viscosities were calculated from pressure drop versus velocity data, using a Reynolds No. curve prepared from supernate calibration data, and assuming the supernate to have a constant viscosity of 1.77 centipoises.

Material: Supernate and sludge from simulated metal waste (initial composition; 0.29 M UNH, 0.40 M $NaPO_4$, 0.25 M $NaSO_4$, 0.97 M $NaCO_3$, 0.16 M $NaNO_3$, 0.34 M $NaHCO_3$), incubated 4 months at 80 ± 5° C.

Legend:
- △ ½ in. pipe; 0.44 supernate-to-sludge volume ratio.
- ⊡ ½ in. pipe; 1.17 supernate-to-sludge volume ratio.
- ⊙ 1 in. pipe; 2.29 supernate-to-sludge volume ratio.
- × 1 in. pipe; 4.15 supernate-to-sludge volume ratio.
- ▽ 1 in. pipe; 5.85 supernate-to-sludge volume ratio.



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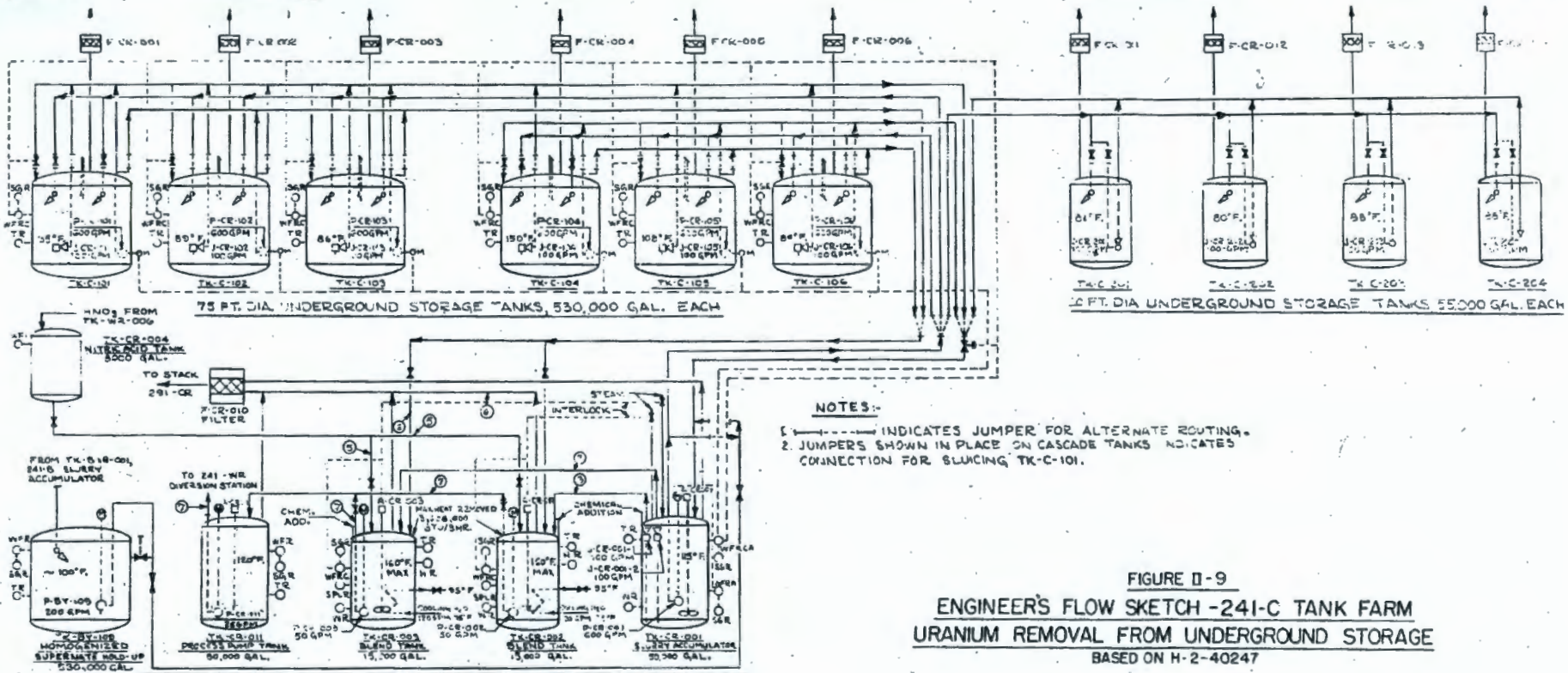

NOTES:-

1. ---------- INDICATES JUMPER FOR ALTERNATE ROUTING.
2. JUMPERS SHOWN IN PLACE ON CASCADE TANKS INDICATES CONNECTION FOR SLUICING TK-C-101.

FIGURE II-9

ENGINEER'S FLOW SKETCH -241-C TANK FARM URANIUM REMOVAL FROM UNDERGROUND STORAGE

BASED ON H-2-40247

TABLE 1

UO2	318,000
NO3	2[illegible],400
SO4	3[illegible],000
PO4	2[illegible],000
CO3	4[illegible],500
OH	5[illegible],500
Na	1[illegible],700
Al	1[illegible],700
TOTAL	[illegible]
SP. GRAV.	1.2[illegible]
SP. GR. TEMP'RT.	85°-130°

TABLE 2

UO2	10,000
NO3	[illegible]
SO4	[illegible]
PO4	[illegible]
CO3	[illegible]
OH	[illegible]
Na	[illegible]
Al	[illegible]
TOTAL	[illegible]
SP. GRAV.	[illegible]
SP. GR. TEMP'RT.	[illegible]

* - DAILY REMOVAL COMBINED ① & ②. ** INCLUDE JET DILUTION

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PART II: PROCESS, continued

CHAPTER III. FEED PREPARATION

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CHAPTER III. FEED PREPARATION

A. ACIDIFICATION

1. General

Approximately 23 million gallons of waste containing 5900 tons of uranium metal will have been accumulated as of January 1, 1952, in the Underground Storage Tanks of the Bismuth Phosphate Plant. Originally highly acidic, these wastes have been neutralized with NaOH and Na_2CO_3, and during the subsequent period of storage they have formed complex precipitates of sodium uranyl carbonates and phosphates, which have been deposited in strata as a function of their relative solubilities. A discussion of the origin, nature, and characteristics of these stored uranium wastes is presented in Chapter II.

In the process of removing the waste from underground storage (procedure discussed also in Chapter II) the sludge and the supernatant liquid are mixed to form a slurry or suspension representing as closely as possible homogenization of the contents of each tank cascade. This slurry is treated with 60 per cent nitric acid to dissolve the solids and produce a homogeneous solution, which may then be used directly as the aqueous uranium feed to the solvent-extraction battery, or may be concentrated and further treated as desired.

The stipulated flowsheet conditions, e.g., Flowsheet TBP-HW No. 4, are idealized compositions representing sludge and supernate slurried in the ratio in which they exist in the Underground Storage Tanks. (The over-all sludge-to-supernate volume ratio is estimated to be about 1 to 7). In actual practice, the compositions available may vary between the limits of all sludge to all supernate, depending upon the success of the sluicing operation in the homogenization of the liquid and solid phases. In the event it becomes necessary to use water as the sluicing agent, feed streams for the acidification procedure will then consist of (a) supernate, and (b) water-slurried sludge.

The following table presents the compositions (before acidification) of (a) sludge, (b) supernate, and (c) slurried sludge and supernate combined in the proportion necessary to meet flowsheet specifications. The sludge presented in this table is a material of high density (ca. 2.6 g./cu. cm.), which when slurried with supernate in the ratio of 1 volume of sludge to 15.7 volumes of supernate, gives the combined composition, as shown. It is recognized that appreciable deviations from these compositions will be encountered in individual tanks (and cascades) as a result of differences in aging periods as well as the alterations in the bismuth phosphate process flowsheets which have been made from time to time, and which have thus effected corresponding changes in the waste composition. (See Chapter II for more complete information.)

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Composition of Slurry, Sludge, and Supernate Before Acidification

Component	Combined Sludge and Supernate (Slurry)			Supernate			Sludge*		
	M	G./L.	Lb./Gal.	M	G./L.	Lb./Gal.	M	G./L.	Lb./Gal.
U	0.26	61.9	0.52	0.08	19.0	0.16	3.1	733	6.11
Na^+	3.93	90.4	0.75	3.33	76.6	0.64	13.4	307	2.56
PO_4^{-3}	0.25	23.7	0.20	0.20	19.0	0.16	1.0	95	0.79
SO_4^{-2}	0.25	24.0	0.20	0.26	25.0	0.21	0.1	13	0.11
CO_3^{-2}	0.70	43.0	0.36	0.49	29.3	0.24	4.0	241	2.01
NO_3^-	0.66	40.9	0.34	0.85	52.7	0.44	6.3	391	3.26
Cl^-	0.02	0.7	0.01	0.02	0.88	0.01	--	--	--

*Estimated density of 2.63 g./cu. cm.

The acidification step may be accomplished either by the addition of acid to the slurry (the direct strike), or the addition of slurry to the acid (the reverse strike). For reasons explained under A4, below, the reverse strike was selected for the acidification procedure.

A tabulation of the composition of acidified feed is presented below as a function of the type of uranium waste being processed. The compositions are based on acidification with 60 per cent HNO_3 to produce a final solution containing 2.01 M H^+. The amount of nitric acid required is based on the absence of hydroxyl ions or basic salts in the original waste.

Average Composition Of Slurry, Sludge, and Supernate After Acidification

Component	Combined Sludge and Supernate (Slurry)			Supernate*			Water Slurried Sludge**		
	M	G./L.	Lb./Gal.	M	G./L.	Lb./Gal.	M	G./L.	Lb./Gal.
U	0.20	47.0	0.40	0.14	33.3	0.28	0.38	90.4	0.75
Na^+	3.00	69.0	0.58	5.72	132	1.10	1.66	38.2	0.32
PO_4^{-3}	0.19	18.0	0.15	0.34	32.3	0.27	0.12	11.4	0.095
SO_4^{-2}	0.19	18.2	0.15	0.44	42.2	0.35	0.01	1.15	0.01
NO_3^-	3.59	226	1.88	5.14	319	2.65	3.78	234	1.95
Cl^-	0.017	0.6	0.005	0.034	1.21	0.01	--	--	--
H^+	2.01	2.01	0.017	2.01	2.01	0.017	2.01	2.01	0.017
Free HNO_3	1.06	66.8	0.56	0.11	6.93	0.06	1.63	103	0.86
Titratable HNO_3	1.82	115	0.96	1.67	105	0.87	1.89	119	0.99

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*) Acidified to 1.0 M H^+ followed by a two-fold concentration (to 0.14 M U) to permit a higher production rate. This represents the maximum degree of concentration possible since further evaporation produces a solid phase. (See Chapter IV.)

**) Slurried with water to give a uranium concentration of 0.50 M before acidification. Although not necessarily the optimum feed composition, this represents an attainable and desirable feed. The maximum uranium concentration permissible will be determined by solubility relationships which have not been defined for $U:PO_4$ ratios that are significantly greater or less than unity. (See Chapter IV.)

The three commonly used methods of expressing the acidity of dissolved uranium waste are defined as follows:

(a) H^+ is the total hydrogen ion concentration in solution, with HNO_3, H_2SO_4, and H_3PO_4 considered as being 100 per cent ionized.

(b) Free HNO_3 is the total hydrogen ion concentration, less twice the sulfate and three times the phosphate concentration, and is based on the following compounds in solution:

$$HNO_3,\ H_2SO_4,\ H_3PO_4,\ NaNO_3,\ \text{and}\ UO_2(NO_3)_2.$$

(c) Titratable HNO_3 is the total hydrogen ion concentration, less the phosphate concentration, and is based on the following compounds in solution:

$$HNO_3,\ Na_2SO_4,\ Na_2HPO_4,\ NaNO_3,\ \text{and}\ UO_2(NO_3)_2.$$

2. Stoichiometry

The molecular species existing in the sludge are largely complex sodium uranyl phosphates and carbonates. The following typical reactions occur on acidification:

(a) $Na_4UO_2(CO_3)_3 + 6HNO_3 \longrightarrow 4NaNO_3 + UO_2(NO_3)_2 + 3H_2O + 3CO_2$

(b) $NaUO_2PO_4 + 3HNO_3 \longrightarrow NaNO_3 + UO_2(NO_3)_2 + H_3PO_4$.

The nitric acid required (on the basis of these reactions) and the amounts of CO_2 evolved are presented in the following table as a function of the type of uranium waste being processed. The data are based on the recovery of 10 short tons of uranium per 24-hour day. The slurry dissolution rate corresponds to 52 pounds of uranium per minute, this value being derived from the homogenized slurry addition rate to the Blend Tank of 100 gallons per minute. The final acidity is 2.01 M H^+ for the resultant solution of slurry and water-slurried sludge, and 1.0 M H^+ for the supernate.

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HNO_3 Requirements and CO_2 Evolution

	Type of Uranium Waste Processed		
	Slurry (0.26 M U)	Supernate (0.08 M U)	Water-Slurried Sludge (0.50 M U)
Rate of Feed Addition, Gal./Min. for 5.4 Hr./Day.	100	325	52
Amount of 60% HNO_3 Required per Day, Gallons.	12,500	20,500	6,000
CO_2 Evolution During Feed Addition (Reverse Strike), Cu. Ft./Min.	230	520	110

The evolution of CO_2 is uniform under reverse strike conditions, but at the same slurry dissolution rate under direct strike conditions CO_2 evolution reaches a peak which is estimated to be three times as high[13].

3. Heat Evolution

The heat evolved in the acidification of slurry (7-to-1 supernate-to-sludge volume ratio) is about 13 gram-calories per gram of slurry or 23.4 B.t.u./lb.[13]. This corresponds to a temperature increase of 16°C. under adiabatic conditions.

4. Methods of Addition and Course of Physical Changes

As previously stated, two methods of acid addition were considered which were (a) the direct strike (addition of acid to the slurry), and (b) the reverse strike (addition of slurry to the acid). The serious disadvantages of the direct strike are (a) the formation of a highly viscous intermediate state, (b) the high peak evolution of CO_2, and (c) excessive foaming. These undesirable conditions are avoided in the reverse strike, which was therefore selected as the optimum operating procedure.

4.1 Viscosity

As illustrated in Figure III-1, viscosity as a function of slurry acidification under direct strike conditions reaches a maximum of 850 centipoises at a pH of 1. When the reverse strike is employed, the viscosity is approximated by a linear decrease from 2.0 (viscosity of 50 per cent HNO_3) to 1.5 centipoises for the final solution (Figure III-2).

4.2 pH

A pH profile of the solution under direct strike conditions is also

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shown in Figure III-1. Precipitation of the uranium begins at a pH of 9 and results in a highly viscous suspension at a pH of 1. The sharp break which occurs between the pH limits of 1 to 4 has been proposed as a supplemental method for controlling the final acidity of the solution[6]. Under reverse strike conditions, the solution remains acid throughout the dissolution period, decreasing from the original 13 M (60%) to 1.06 M free HNO_3.

4.3 Foaming

Foaming is slight under reverse strike conditions. At a slurry addition rate of 100 gal./(min.)(sq.ft.) of acid surface area, the foam height is less than one inch[13]. In contrast, on rapid addition of acid to slurry, the resulting mixture increases to 7 to 10 times its original volume as a result of foam formation.

5. Method of Control

5.1 Introduction

The dissolving step is so controlled that the resultant feed solution for the RA system exhibits the maximum stability with the minimum excess acid content. Too low an acidity (i.e., the addition of too much slurry to a given volume of 60 per cent HNO_3) results in a solution from which precipitates will be formed as a function of time depending upon the final acidity, e.g., slurry acidified to 1.8 M H^+ is stable only for a period of about 12 days[15]. Since facilities exist at the 241-WR Diversion Vault and in the TBP Plant (Building 221-U) for the detection and adjustment of the acidity, it is essential only that sufficient HNO_3 be present during the initial acidification to maintain a stable solution for the period of transfer from the Blend Tanks to the 241-WR Diversion Vault. On the other hand, the use of excessive amounts of acid (greater than the final 2 M H^+ concentration required to give an indefinitely stable solution) is economically undesirable and has also been shown to be unnecessary from both the chemical and operational standpoints.

5.2 Turbidity

A turbidimetric method is used to control the final acidity of the solution. The rate of dissolution under reverse strike conditions is very rapid, and thus the change from a single to a two-phase system at the end point permits a method of control[17]. Slurry is added to the acid in the Blend Tank until the formation of a permanent precipitate is indicated by a turbidimeter. The suspension is then back-titrated with enough HNO_3 to dissolve the solids, and supernate and HNO_3 are added, if required, to adjust the solution to the desired uranium concentration (0.18 M, density = 1.26 g./cu. cm.). At the time of this writing, incomplete data are available as to the relative amounts of acid and slurry necessary to produce the required turbidity as a function of slurry composition; however, the data available indicate that a satisfactory degree of control is possible.

5.3 pH

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An alternative method of control is provided with the inclusion of pH electrodes in the Blend Tank, in addition to the turbidimeter. In the procedure employing pH control, slurry is added to the acid in the Blend Tank until the sharp increase in pH, occurring between pH 1 and pH 4, is noted (see Figure III-1). Nitric acid is then added in an amount required to produce a feed containing 2.01 M H^+. (Approximately one gallon of 60% HNO_3 is required for every five gallons of Blend Tank solution to produce the desired acidity starting with a pH of approximately 1.) The density of the solution is determined, and acid and supernate are added, if necessary, to adjust the solution to the desired uranium concentration. The major disadvantage of this method is the questionable reliability and reproducibility of the readings obtained with the glass electrode in highly radioactive solutions, and in the presence of the suspended solids encountered near the end point.[2][9][17]

5.4 Laboratory control

Control of the dissolution by means of laboratory analytical results is feasible but undesirable because the time required for the analyses would considerably extend the time cycle beyond that fixed for this step by process design. Although more time consuming than the turbidity and pH methods described in A5.2 and 5.3 above, the following analytical control method may be used to monitor slurry dissolution. The total amount of 60% HNO_3 required to produce the proper batch size is pumped into the Blend Tank. After approximately half the slurry expected to be needed is added to the HNO_3, the Blend Tank is sampled. From the uranium and HNO_3 analyses on the sample the volume of slurry which must be added to produce the required feed composition may be calculated.

B. CONCENTRATION

1. General

The acidified feed solution is very dilute in uranium. The exact composition may vary between wide limits (probably between 0.03 and 0.7 M)[8], depending upon the supernate-to-sludge ratio and the particular Underground Storage Tank cascade from which the material being processed originates. Ultimately, the "hot" aqueous wastes from which uranium has been removed must be restored underground. To accomplish this operation in the most economical manner, concentration of the aqueous waste stream is a virtual necessity in order to avoid the economically disadvantageous situation of requiring more storage capacity than has been made available by removal of uranium-bearing material from the Underground Storage Tanks.

Two methods of volume reduction are indicated in Chemical Flowsheets TBP-HW No. 4[11] and TBP-HW No. 5[12], presented in Chapter I. Partial concentration of the dilute uranium feed stream with the remainder of the volume reduction accomplished by concentration of the neutralized aqueous waste stream is shown by TBP-HW No. 4. An equivalent over-all volume reduction accomplished entirely by concentrating the neutralized aqueous waste stream is shown by TBP-HW No. 5. The conditions specified in TBP-HW No. 4 involve the advantages of reduced volumes to be handled in the step [redacted]equent to feed concentration, and somewhat more efficient

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solvent-extraction column operation as a result of about 10 per cent higher nitric acid concentration in the RA Column. The feed concentration equipment design is based on the TBP-HW No. 4 Flowsheet, because this represents a more conservative approach. It is also possible to operate the plant on the basis of the TBP-HW No. 5 Flowsheet.

It should be emphasized that the TBP-HW No. 4 and No. 5 Flowsheets represent idealized conditions for a design basis. In actual operation the supernate-to-sludge ratio may vary widely from day to day, resulting in a fluctuating feed stream composition. However, both the process and equipment are sufficiently flexible to handle any ratio from 100 per cent supernate to 100 per cent sludge with appropriate changes to RA Column flow rates and to feed acidity.

The succeeding discussion is based upon the TBP-HW No. 4 Design Flowsheet conditions. Methods of handling variations from this idealized case are presented in Subsection D2.

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2. Solubility Limitations

The solubility relationships of the dissolved salts in the dilute uranium feed solution impose a definite limitation upon the degree of concentration which can be attained without solids precipitation. Reference is made to Chapter IV for a discussion of the properties of uranyl nitrate solutions containing nitric acid and sodium, sulfate, phosphate, and nitrate ions; the effect of degree of feed solution concentration upon RA Column operation is also discussed in Chapter IV.

As discussed in Section A, above, the hydrogen ion concentration (free hydrogen ion or hydrogen associated with salt radicals) in dilute uranium feed solution is such (about 2 M) that all salts are in solution at room temperature. The component of the solution nearest to a saturation concentration at TBP-HW No. 4 conditions is a uranyl hydrogen phosphate (believed to be $UO_2HPO_4 \cdot 4H_2O$).[10] During volume reduction of the solution by evaporation, $UO_2HPO_4 \cdot 4H_2O$ becomes less saturated in the solution because of an increase in concentration of the hydrogen ion (up to about 3 M). If the acidity were increased above that shown on TBP-HW No. 4 by additional concentration, sodium nitrate would eventually reach its solubility limit. However, as discussed in Subsection 3, below, the corrosion problem may make it impossible to concentrate to acidities greater than about 5 to 6 M.

The salt $(UO_2)_3(PO_4)_2$ exhibits retrograde solubility characteristics, i.e., the solubility decreases with increasing temperature. All evidence to date indicates that solid phase formation during concentration will not be caused by the formation of the retrograde soluble salt $(UO_2)_3(PO_4)_2$.[15]

Other components of the feed solution (principally $SO_4^{=}$) will probably offer no important solubility limitations to feed concentration, as compared to uranyl phosphate or sodium nitrate.

3. Corrosion Limitations

In addition to the limitations on degree of feed concentration imposed by solubility relationships, another practical limitation, corrosion of components of the Concentrator, exists. Stainless steel is corroded rather rapidly by the chloride ion. The effect increases with increasing temperature, chloride ion concentration, and nitric acid concentration. The concentration of the chloride ion in the uranium wastes stored underground has been determined to be from 0.5 to 0.8 gram /liter, resulting from impurities in process chemicals (chiefly in sodium hydroxide and sodium carbonate).[14]

Under the concentration conditions specified in the TBP-HW No. 4 Flowsheet, the expected corrosion rates on the 309S Cb tubes and shell of the Concentrator are on the order of 1 to 10 mils/year.[16] These corrosion rates are not excessive, especially in view of the short-term nature of the plant. If acid concentration or chloride content were to increase by a factor of 2 or 3, the corrosion of the Concentrator might be excessive under the operating conditions employed.

C. CLARIFICATION

It is probable that some undissolved solids will be present in the acidified uranium feed solution. The solids will most likely consist of such foreign materials as sand, concrete, bits of glass, and larger pieces, such as pH electrodes, that may have been dropped into the tanks during monitoring of the tank contents.

All feed solution must pass through perforated plates in the solvent-extraction Pulse Columns. (See Chapters V and XV for a description of the equipment.) The holes in the plates are 1/8 inch in diameter, and they are self-purging to a degree (due to liquid velocity and cyclic reversal of direction of flow through the holes); nevertheless, an upper limit on solids particle size is imposed to prevent plugging the holes.

Centrifugation may be relied upon to accomplish what gross particle removal is required. A 40-inch Bird Centrifuge (similar to those used in the Bismuth Phosphate Plants) is provided for each of the two parallel processing lines. The Centrifuge is described in Chapter XVI. It may operate at either 1740 rev./min., producing a peripheral force of 1730 times gravity, or 870 rev./min., producing a peripheral force of 430 times gravity. At the nominal feed flow rate of 13 gal./min. through each Centrifuge, the holdup time of liquid in the bowl is about 5 minutes. This residence time is sufficient to remove any particles large enough to interfere with column operation. High solution clarity is not attained, nor is it deemed necessary for the TBP process.

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D. PROCEDURE

1. Normal Procedure

1.1 General

The normal operating procedure described here is based upon the stream flows and compositions indicated in Chemical Flowsheet TBP-HW No. 4 (presented in Chapter I) and upon the procedures implied by the engineers' flow sketches of the uranium waste removal operation (Chapter II) and of the uranium recovery process (Chapter VI).

It is recognized that uranium feed stream compositions will vary considerably from the arbitrary normal as defined above, with a resultant variance in the volumes involved for a given production rate (normally 10 tons uranium/day, instantaneous rate). However, with few exceptions feed preparation procedures remain the same. Variations from normal procedures caused by non-uniformity of feed solution compositions are discussed in Subsection D2.

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1.2 Acidification

As discussed in Chapter II, a total of four slurry accumulation-acidification tank groups are provided for processing the slurry removed from the four Underground Waste Tank Farms. The following discussion applies to the equipment associated with the 241-U Tank Farm, but the general procedure description applies equally well to other Tank Farms and their associated equipment. The following discussion is based on the engineers' flow sketch on uranium waste removal in Chapter II.

After the contents of the Slurry Accumulator, TK-UR-001, have been recycled through a 241-U Cascade until the uranium concentration has reached 75 to 100 grams/liter as described in Chapter II, about 5000 gal. of slurry are jetted from TK-UR-001 into about 3000 gal. of 60% nitric acid in one of the two Blend Tanks, TK-UR-002 or TK-UR-003, depending upon which is available at the time. The quantities quoted are based upon 5 short tons uranium/day since it is assumed that 5 additional tons/day will enter the processing system from one of the other Underground Storage Areas (241-B, 241-C, or 241-T). An interlock between the Blend Tank agitator motor circuit and the slurry transfer jets in the Slurry Accumulator prevents slurry transfer unless the Blend Tank agitator is in operation. Cooling water is routed through the Blend Tank coil during slurry addition. About 100 per cent freeboard is maintained in the Blend Tanks to provide capacity for containing the foam evolved during the dissolution of the solids from the slurry. About 2000 gal. of clear, homogenized supernate is added from one of the Underground Tanks being processed to the solution in the Blend Tank to adjust the uranium concentration to the average value of about 45 grams/liter. This concentration figure, as well as the quantity of supernate added, may vary considerably. In some instances, Blend Tank sampling may be required to determine the amount of supernate which is to be added.

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The contents of the Blend Tank are pumped to the Feed Receiver Tank, TK-WR-005, located in the 241-WR Diversion Station. This vessel (50,000 gal. capacity) has about 1-1/2 to 2 days capacity (5 ton basis) of acidified solution. (A duplicate Feed Receiver, TK-WR-003, normally receiving from the 200-E Area cascades, has the same capacity.) Acidified solution is normally batched from the Feed Receiver to the Feed Sampler, TK-WR-004, where inventory is accomplished, and thence pumped into one of two Feed Receivers, TK-3-1, TK-3-6, in the 221-U Building.

All of the four process feed vessels (two Feed Receiver Tanks, TK-WR-003 and 005, and two Feed Samplers, TK-WR-002 and 004) in the 241-WR Diversion Station either are or can readily be interconnected; therefore, a great deal of flexibility as to routing of process feed solution is available in the Diversion Station. Each vessel in the Diversion Station is provided with chemical addition lines for adjustment of solution concentrations, if required.

1.3 Feed concentration

Each of the two Feed Receivers, TK-3-1 and TK-3-6, in the 221-U Building contains enough acidified uranium solution to provide 10 hours of operating time at the rate of 5 tons/day. (Since each receiver normally serves duplicate processing lines continuously, a net production rate of 10 tons of uranium per day is attained.) For purposes of this discussion, only one of the duplicate feed concentration systems is described. In the following discussion reference is made to the engineers' flow sketch (Chapter VI) of the uranium recovery process.

Dilute uranium solution is continuously pumped from Feed Receiver "A", TK-3-1, to the Concentrator Feed Tank, TK-6-6, at the rate of about 19 gal./min. The exact flow is controlled by the liquid level in the Concentrator Feed Tank. The solution is continuously pumped from the Concentrator Feed Tank to a long-tube evaporator, Concentrator E-6-1, in the same cell, at a nominal rate of 19 gal./min. The Concentrator bottoms overflow into the Feed Cooler, TK-6-2, at a rate regulated by weight-factor instrumentation on the Concentrator so that a uniform effective liquid level exists in the Concentrator. Overheads from the Concentrator are de-entrained in the vapor space of the Concentrator and then routed into a bubble-cap Stripping Column, T-6-4, where nitric acid is scrubbed from the vapor (and further decontamination of the vapor is attained) by a water reflux added at a manually-controlled rate (3 gal./min., nominally) to the top plate. The acid scrubbed from the Concentrator overheads in the Stripping Column rejoins the concentrated feed solution in the Feed Cooler. The acid-free vapors are condensed in Condenser E-6-5 and routed out of the 221-U Building to one of three Condensate Receiver Tanks, TK-WR-007, 008, and 009, in the 241-WR Diversion Station for eventual disposal to cribs if decontamination tolerances are met. (See Chapter XII for a discussion of the cribbable waste problem.)

Steam flow rate to the Concentrator is controlled by the rate of feed flow to the Concentrator in conformance with the degree of concentration desired (about 30 per cent nominally).

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Partial cooling of the concentrated feed stream is effected in the Feed Cooler, but this vessel serves chiefly as a pump-out tank to the Concentrated Feed Receiver, TK-6-7, located in another cell. Concentrated feed is continuously pumped there at a nominal rate of 13 gal./min., but the exact rate is controlled by the liquid level of the Feed Cooler.

1.4 Feed centrifugation

The Concentrated Feed Receiver, TK-6-7, also serves as a feed tank for the Centrifuge, G-14-1. The Centrifuge is described in detail in Chapter XVI. Uranium solution is pumped to the Centrifuge at a nominal rate of 13 gal./min. Since holdup time in the centrifuge bowl, at this rate, is only on the order of 5 minutes, the Centrifuge rotates at its maximum speed (1740 rev./min.) to produce a force 1730 times that of gravity at the edge of the bowl. Clarified solution continuously overflows the bowl of the Centrifuge and is routed into the Centrifuge Catch Tank, TK-14-2. The liquid level in TK-14-2 controls the rate of feed to the Centrifuge. Chemical addition facilities to the Centrifuge and a jet leading from the Centrifuge to the Waste Utility Holdup Tank, TK-4-6, provide a means for disposing (by dissolving or slurrying out) of solids accumulated in the Centrifuge during normal operation. This material may be either reworked or disposed of to underground waste storage facilities from the Waste Utility Holdup Tank.

Clarified uranium solution is continuously pumped to the RAF Feed Tank, TK-19-6, at a rate governed by the level of TK-19-6 (nominally about 13 gal./min.), for feeding to the solvent-extraction battery.

2. Remedy of Off-Standard Conditions

2.1 Wide fluctuations in uranium content of the feed

It is recognized that considerable variation in uranium content of the feed solution will occur. The combination of liquid-level and weight-factor instrumentation (and possibly sampling) will indicate the approximate uranium concentration in the Slurry Accumulator; samples taken of the acidified feed in the Feed Sampler, TK-WR-004, will indicate the uranium concentration more accurately.

The feed concentration system has the capacity for more concentration than is nominally required. If desired, more-dilute-than-normal feeds may be concentrated further than the normal 30% (within the limitations described in Section B). The flexibility of solvent-extraction procedures, which enables satisfactory extraction of uranium from feed solutions varying widely in composition, may eliminate the need for special remedies in the feed preparation portion of the process.(6) (See Chapter VI for a discussion of the adaptation of the solvent-extraction battery procedure to varying feed uranium concentrations.)

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2.2 Abnormal acid concentration in feed

This condition will be detected in sampling from the Feed Sampler Tank, TK-WR-004. If the acid concentration is too low, more may be added by means of chemical addition facilities to the Feed Sampler Tanks or the Feed Receiver Tanks, TK-3-1 and TK-3-6.

If the acid concentration is too high it may be possible to hold up the solution either in the tanks of the 241-WR Diversion Station or in the Feed Utility Holdup Tank, TK-4-1, until it can be blended with lower-acid-content feed. However, because of the flexibility of solvent-extraction procedures (see Chapter VI) higher-than-normal acid concentration may not necessarily be detrimental (except insofar as feed concentration is limited).

2.3 Failure of feed supply to the Concentrator

In the event of failure of feed supply, as indicated by the weight-factor alarm on the Concentrator Feed Tank, TK-6-6, water may be directed into TK-6-6 and fed to the Concentrator until the situation can be corrected or the Concentrator slowly shut down. This arrangement allows maintenance of the "on the line" status of the Concentrator if the feed supply can be restored within a reasonable time.

2.4 Excessive acidity or radioactivity in condensate

This condition may be detected by pH monitoring and sampling of the condensate stream. It may indicate too high a vapor velocity in the Stripping Column, T-6-4, in which case cutting back on the concentration rate might be required, at least temporarily. Increasing the amount of reflux water may aid in correcting the off-standard condition.

2.5 Total failure of any equipment piece

If any equipment piece fails or is removed from service temporarily for repairs (for example, de-scaling evaporator tubes), the total production load may be thrown upon the duplicate feed preparation line, since the capacity of all equipment associated with each line is sufficient to supply both solvent-extraction batteries.

2.6 Failure of the Feed Cooler pump

This condition is detected by the high-level weight-factor alarm on the Feed Cooler. Because of the limited holdup time in this pump-out tank, an interlock that will shut down the Concentrator Feed Tank pump is provided between the Concentrator Feed Tank pump and Feed Cooler weight-factor instrumentation. Use of the jet spare for the Feed Cooler pump will enable operations to continue until the Feed Cooler pump can be placed back in service.

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Figure III-1

VISCOSITY AND pH AS A FUNCTION OF SLURRY ACIDIFICATION

DIRECT STRIKE- ADDITION OF ACID TO SLURRY

Source of Data: HW-18367

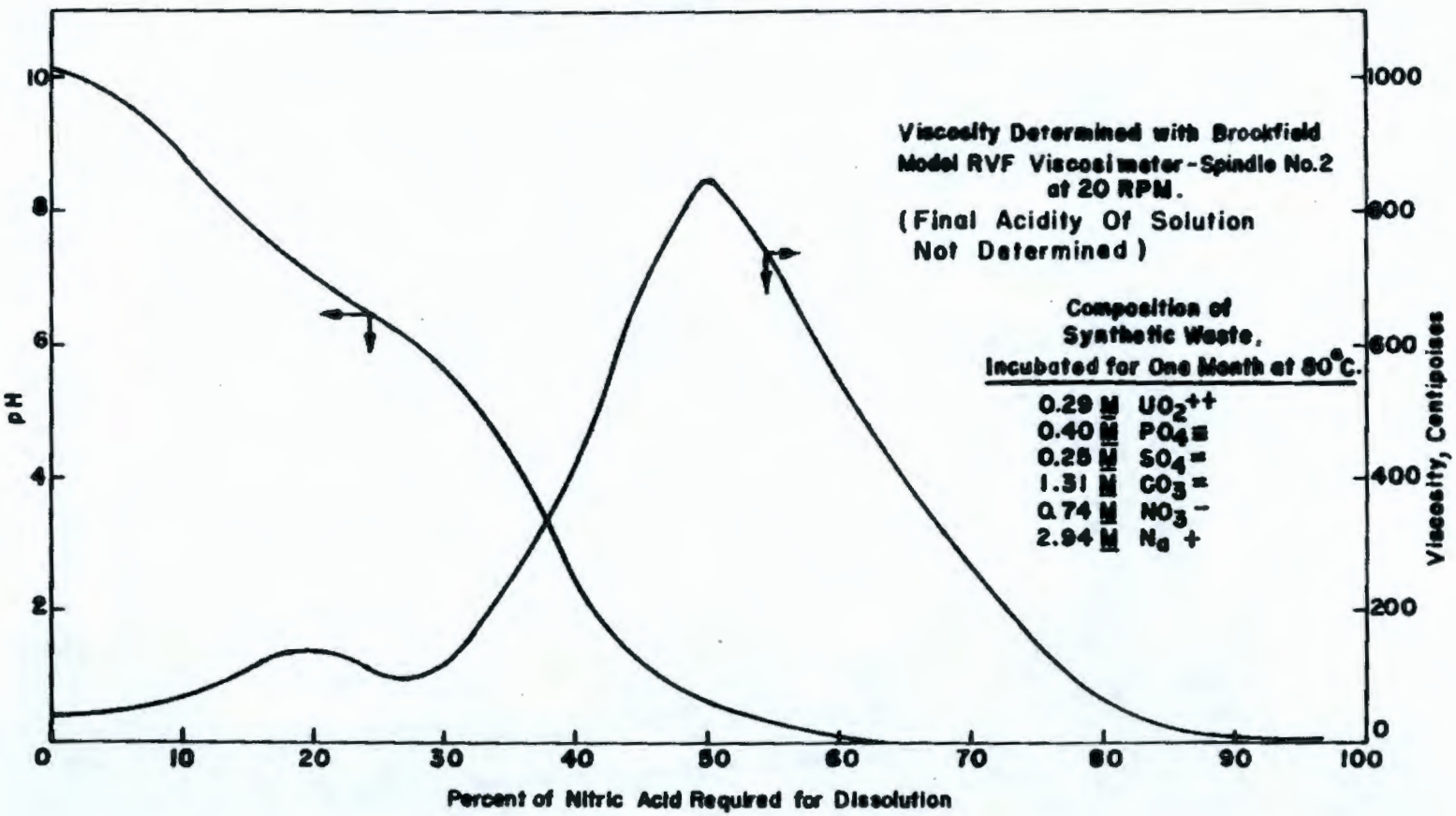

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Figure III-2

DENSITY AND VISCOSITY OF SLURRY
DURING REVERSE STRIKE ACIDIFICATION

Source of Data: R.F. Maness, Informal Communication, July 1951

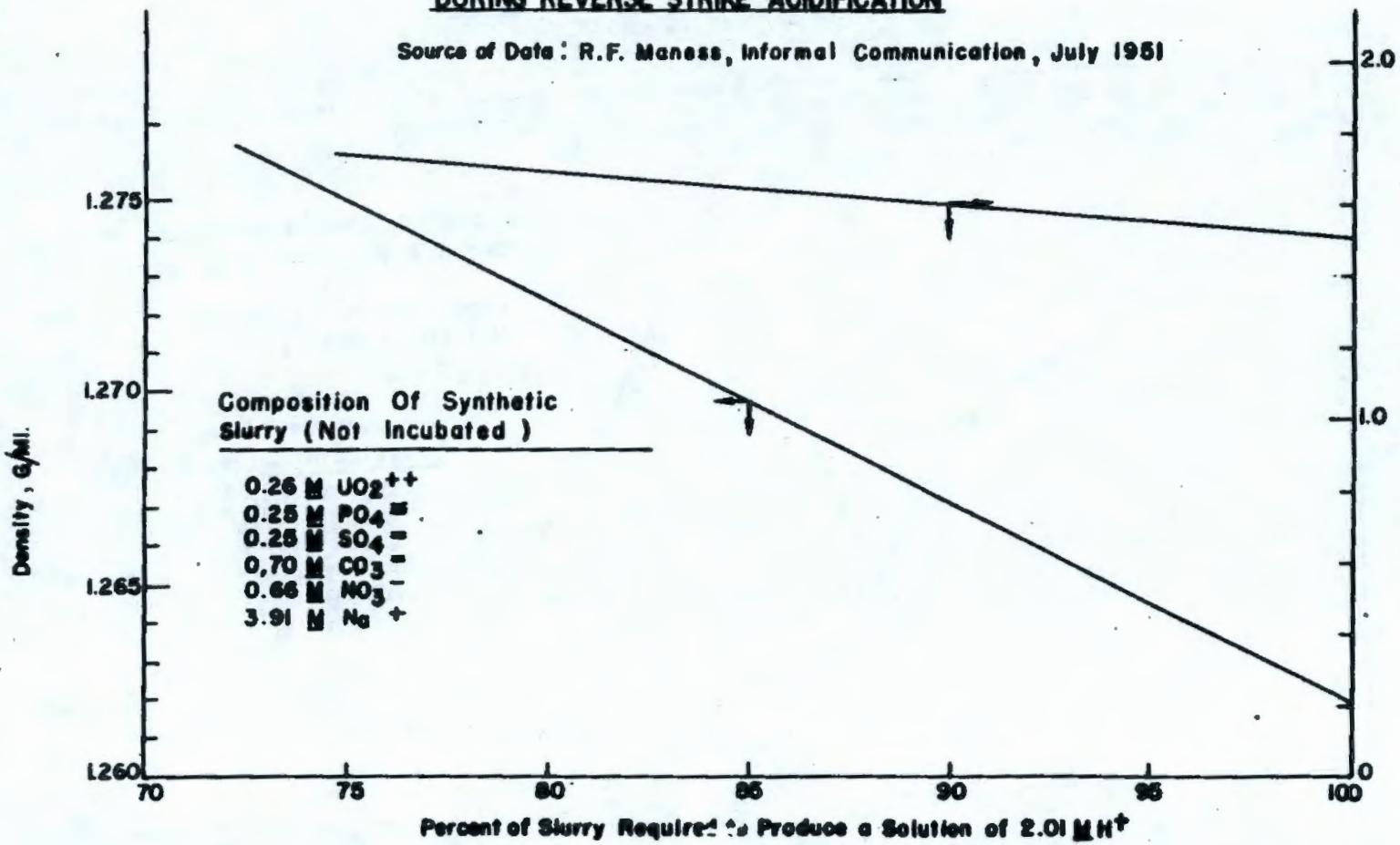

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Figure II-2
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PART II: PROCESS, continued

CHAPTER IV. PROCESS CHEMISTRY (SOLVENT-EXTRACTION)

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CHAPTER IV. PROCESS CHEMISTRY (SOLVENT-EXTRACTION)

A. PROCESS DESCRIPTION

1. Basic Principles

1.1 Introduction

The TBP process utilizes the preferential extractability of uranyl nitrate by tributyl phosphate (TBP) to separate uranium from the fission products and plutonium with which it is associated in the uranium-bearing wastes from the bismuth phosphate process. In the TBP process the uranium is recovered as an aqueous uranyl nitrate solution adequately free from plutonium and the fission-product elements. The present chapter deals with the chemical considerations governing this solvent-extraction process. The important engineering considerations involved in the process are treated in Chapter V, while the actual plant procedure is described in Chapter VI. The present chapter covers only the solvent-extraction steps of the TBP process. The auxiliary steps of feed preparation, aqueous make-up, solvent treatment, and waste treatment and disposal are dealt with in Chapters III, X, XI, and XII, respectively.

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The TBP solvent-extraction process is in certain respects both simpler and more complex than the Redox process. It is simpler in the sense that only two different solvent-extraction columns are involved (the RA and RC Columns), as compared with twelve in the Redox process. Also, the TBP process recovers only one product (uranium) while two separate products (uranium and plutonium) are recovered in Redox. On the other hand, the TBP process is more complex than Redox in the sense that it employs a two-component solvent (TBP in a hydrocarbon diluent) as compared with a single-component solvent (hexone) employed in Redox. Also, the TBP RA-Column system contains a larger number of solutes, which significantly affect uranium extraction, than are present in the Redox columns. Besides HNO_3 and $NaNO_3$, which exert salting effects similar to those of HNO_3 and aluminum nitrate in Redox, the TBP RA-Column system also contains significant concentrations of phosphate and sulfate ions which affect uranium extraction in an adverse (although surmountable) manner.

For a brief outline of the TBP solvent-extraction process, the reader is referred to Chapter I. A more detailed discussion of the process, its chemical variables, and their effects follows in Section A. Section B summarizes the important physical and chemical properties of the process materials. Section C is a presentation of equilibrium data for the mass transfer of process components between the aqueous and solvent phases.

1.2 Solvent-extraction principles

For the recovery of uranium from the solution obtained by acidification of the uranium-bearing waste from the bismuth phosphate process, the use of solvent-extraction involves (a) contacting the aqueous feed solution with an organic extractant to transfer the uranium to the organic phase while leaving fission products and plutonium largely behind, then

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(b) stripping the uranium back into an aqueous phase, leaving the solvent phase available for recovery and re-use. The extractant, consisting of about 12.5 per cent tributyl phosphate by volume in a hydrocarbon diluent, is only sparingly soluble in the aqueous phase. Extraction of uranium into the solvent phase is carried out in the RA Column; stripping of the extracted uranium back into an aqueous phase is effected in the RC Column.

The extraction operation may be carried out in a laboratory beaker by mixing an aqueous uranium feed solution with a solution of tributyl phosphate in a diluent, then allowing the two phases to settle or disengage. The mixing and settling operation represents an extraction "stage", and it is an ideal or theoretical stage if mass transfer equilibrium between the phases ("phase equilibrium") is attained during the mixing and settling operation.

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Multiple-stage countercurrent extraction may be effected by the use of an additional vessel for each additional extraction stage desired. The two-phase system is mixed and settled in each vessel, then the phases are transferred in opposite directions through the series of vessels. Continuous-flow column contactors (such as the RA and RC Columns) perform essentially the same series of operations. However, discrete transfer stages are not apparent in the physical form of the equipment and are not actually involved in the mechanism of the transfer (see Chapter V). The "Height Equivalent to a Theoretical Stage" (H.E.T.S.) is the column height in which the same mass transfer occurs as in the above-described beaker experiment. The H.E.T.S. and the related "Height of a Transfer Unit" (H.T.U.), discussed in detail in Chapter V, are measures of the mass-transfer effectiveness of a solvent-extraction column. The lower the H.E.T.S. for a given system, the shorter will be the total column height required to provide the number of transfer stages necessary to perform a given solvent-extraction separation.

Since the rate of transfer of solute between phases is limited by the area of contact of the two phases, solvent-extraction equipment is designed to provide a large contact area. However, efficient operation requires rapid separation of phases, as well as rapid transfer of solute, and is therefore dependent upon a compromise between fine dispersion to give maximum contact surface between phases, and coarse dispersion to give maximum rate of phase separation. Data on disengaging times may be found in Subsection B7 of this chapter. The pulse column equipment used for phase contacting in the uranium recovery process is discussed in Chapters V and XV.

When the aqueous feed solution is extracted with tributyl phosphate-diluent solution in the TBP RA Column, the aqueous phase salting strength, the cation oxidation state, and the aqueous-organic phase flow ratio (L/V) are controlled to favor extraction of the uranium while retaining the plutonium and fission products in the aqueous phase. However, some transfer of Pu and fission products to the organic phase does occur. Such contamination of the organic product stream is alleviated by contacting the organic extract with an aqueous nitric acid solution containing ferrous ion reducing agent, which returns most of the extracted plutonium and fission products to the aqueous phase. The latter operation is

referred to as scrubbing, and the transfer stages are referred to as scrub stages. Recovery of the uranium and the solvent involves contacting the scrubbed organic uranium extract with water under conditions which return the uranium wholly to the aqueous phase in the RC Column. The solvent is then countercurrently washed in the RO Column for re-use.

1.3 Choice of solvent

1.31 TBP as a solvent

Tributyl phosphate is an excellent solvent for the uranium recovery process because it shows a relatively strong specific uranium solvent action, which is only partly impaired by sulfate or phosphate in the presence of excess nitric acid.(71) Moreover, TBP is stable toward nitric acid and the other components of the uranium recovery process system; it is stable on exposure to radiation, and a TBP-diluent mixture shows a sufficiently low mutual solubility in contact with an aqueous phase.(9) Tributyl phosphate is readily available, sufficiently inexpensive, non-corrosive, non-toxic, and shows a low vapor pressure and high flash point. For a summary of the specific properties of tributyl phosphate see Subsection B1.

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The mechanism of uranium extraction by tributyl phosphate is apparently dependent upon the rapid formation of an organic-soluble coordination complex between one molecule of uranyl nitrate and two molecules of TBP.(24)(68)(71) The maximum, or saturation, solubility is then one mole of uranyl nitrate in two moles of TBP, or about 436 grams of uranium per liter of 100 per cent TBP. The uranium extraction reaction may be expressed by the following equations:

$$UO_2^{++}\ (Aq.) + 2NO_3^{-}(Aq.) \rightleftharpoons UO_2(NO_3)_2(Aq.), \quad \text{- - - - -(1)}$$

$$UO_2(NO_3)_2(Aq.) + 2TBP(Org.) \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP(Org.), \quad \text{- - -(2)}$$

which may be simplified to:

$$UO_2^{++}\ (Aq.) + 2NO_3^{-}(Aq.) + 2TBP(Org.) \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP(Org.), \quad \text{-(3)}$$

neglecting the possible presence of water of hydration and nitric acid in the coordination complex.

1.32 Diluents for TBP

For use as a solvent for uranium recovery, tributyl phosphate must be diluted by an inert liquid.(72) Dilution is either necessary or beneficial for the following reasons: (a) to alter the specific gravity of the solvent phase, which for 100 per cent TBP is so nearly the same as that of water that phase disengagement would be difficult; (b) to decrease the viscosity of the TBP to favor more rapid phase separation and higher diffusion rate; (c) to reduce the tendency of TBP to form an emulsion with an aqueous phase; (d) to reduce the mutual solubility of the aqueous and

organic phases; and (e) to facilitate stripping the extracted uranium back to an aqueous phase. High TBP concentration in the solvent phase extracts more nitric acid in the RA Column which interferes with stripping the uranium in the RC Column.(29)(72) Low solvent TBP concentration gives an unfavorable uranium distribution ratio at the dilute, or bottom, end of the RA Column,(23) which results in higher uranium losses. The optimum TBP concentration range is 10 to 30 per cent by volume with a nominal 12.5 per cent specified by the chemical flowsheets(23)(29) for the aqueous uranium concentrations and salting strengths available, as well as the phase flow ratio desired. (See TBP-HW No. 4 and No. 5 Flowsheets, presented in Chapter I.)

The choice of a diluent is dependent upon a number of factors:

(a) It must be miscible with TBP and show a high solvent action for the uranyl nitrate-TBP complex.

(b) It must be immiscible or only very sparingly miscible with water and aqueous solutions.

(c) It must be unreactive with all the components of the system including nitric acid and be adequately stable toward nuclear radiations.

(d) The diluent should have a low viscosity and a specific gravity materially different from that of water.

(e) It should be non-corrosive, not highly toxic, and not highly flammable.

(f) It should be readily available and inexpensive.

A number of organic liquids have been considered as TBP diluents. These include petroleum fractions, carbon tetrachloride, undecanes, and specific hydrocarbons such as n-hexane. Although specific hydrocarbons are too expensive, various kerosene-type petroleum fractions have been found generally satisfactory. Carbon tetrachloride shows promise as a diluent for tributyl phosphate and may actually be employed in some separations processes developed in the future, although demonstration is still required because of its potentially corrosive action (due to chloride ion). For a comparison of the properties of possible diluents, see Subsection B2.

1.4 Salting

A common method of reducing the solubility of a compound in a given solution is by the "salting" effect of a common ion. Thus the addition of a soluble nitrate to an aqueous solution of uranyl nitrate will reduce the solubility of the uranyl nitrate in the solution. If such an aqueous solution is in contact equilibrium with a solvent phase, the solubility of the uranium in the aqueous phase is decreased relative to the solvent phase, and distribution into the solvent phase is thereby increased. For a more detailed discussion of salting, see the Redox Technical Manual.(47)

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The salting effect required in the TBP process is provided by sodium nitrate supplemented by added nitric acid. The effects of these salting agents in the TBP-process system are discussed below.

1.41 Sodium nitrate

The aqueous feed to the solvent-extraction system contains sodium nitrate (3 to 4 M) formed by caustic neutralization of the uranium waste prior to storage, and by acidification of the excess caustic in the waste on removal from storage for uranium recovery. This sodium nitrate provides approximately one half of the salting strength needed in the RA Column system of the solvent-extraction process for uranium recovery.

1.42 Nitric acid

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Supplementary aqueous salting strength in the TBP process is obtained by increasing the concentration of free nitric acid in the system, since the initial inadequate sodium nitrate salting strength is fixed by the chemical composition of the slurry removed from underground storage and by the amount of dilution or concentration during feed preparation. It is not feasible to supplement the sodium nitrate salting adequately by the addition of metal nitrates from external sources because of feed solubility limitations (although partial substitution of a metal nitrate -- e.g., aluminum nitrate -- for nitric acid would be feasible). Nitric acid is therefore necessary as a salting supplement in order to make possible a desirably low organic-to-aqueous flow ratio (V/L). Furthermore, in spite of higher cost and slightly lower decontamination,(11)(80) nitric acid is preferred to sodium nitrate as the salting agent in the RAS (scrub) stream because of possible sodium contamination of the uranium product when the salt is used.

The salting effect of nitric acid differs somewhat from that of sodium nitrate. The nitrate shows a simple salting effect on uranium, whereas the acid exhibits the added property of influencing the aqueous complexing of uranium by sulfate and phosphate (see under 1.53, below). However, at concentrations which provide sufficient excess acid to counteract the sulfate and phosphate complexing (nominal process conditions), nitric acid and sodium nitrate are approximately equivalent in their salting effect on a mole-for-mole basis.(38) In Subsection C1 the process equilibrium data for uranium are correlated on the basis of total nitrate concentration.

The optimum concentration of free nitric acid in the aqueous phase (1 to 5 M) is a compromise between opposing factors. Acid concentrations above 5 to 7 M are not feasible because of the tendency to precipitate salts, particularly sodium nitrate. Moreover, if the acid is not recovered, high acid salting requires more neutralization of the waste, thereby yielding a larger waste volume. On the other hand, an increase in aqueous acid concentration compensates for the adverse effect of the sulfate and phosphate present in the feed. The excess acid concentration, however, cannot drop below about 1.5 M because of the tendency for uranyl phosphate to precipitate. Low acid salting has the advantages of decreased acid consumption and decreased caustic consumption (in waste neutralization),

as the acid concentration is decreased. The intermediate value of 2 to 3 M nitric acid in the RAF (feed) stream is a suitable compromise. For the specific effects of nitric acid concentration on the distribution of uranium, plutonium, and fission products, see Section C.

1.5 Basis of the TBP process

1.51 Oxidation state

The fundamental basis for the separation of uranium from plutonium and fission products in the TBP process is the fact that the coordination of the uranium, plutonium, and fission products with tributyl phosphate generally increases as the cationic oxidation state is raised. Two exceptions to this general condition are the fact that plutonium (V) is organic insoluble and that under certain conditions the Pu (IV) valence state is more soluble in TBP than Pu (VI).(72) However, by adjustment of the oxidation-reduction potential of the aqueous phase during solvent extraction, the uranium may be maintained in the extractable (VI) valence state while the plutonium and fission products are held in their lower, largely inextractable valence states. Actually, with the exception of ruthenium, the fission-product elements show little tendency to exist in a valence state above (III) under the process conditions. Any oxidized plutonium present is reduced to the (III) state by ferrous ion added to the extraction system via the RAS scrub stream. The plutonium is maintained in the inextractable (III) state and the ferrous ion is stabilized in the system by sulfamate ion, which destroys any nitrous acid present.

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1.52 Tributyl phosphate complexing

An additional basis for the TBP process is the fact that the solvent action of tributyl phosphate for uranium is due to the formation of a definite coordination complex. As noted before, the extraction of uranyl nitrate by TBP from an aqueous solution may be expressed by the following summary reversible equation:

$$UO_2^{++}(Aq.) + 2NO_3^-(Aq.) + 2TBP(Org.) \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP(Org.) \quad \text{- -(3)}$$

Then for the reversible reaction the equilibrium "constant", K, may be expressed by the following relationship in which concentrations are given in molarities:

$$K = \frac{UO_2(NO_3)_2 \cdot 2TBP(Org.)}{\left[UO_2^{++}(Aq.)\right]\left[NO_3^-(Aq.)\right]^2\left[TBP(Org.)\right]^2}, \quad \text{- - - - -(4)}$$

where TBP(Org.) represents the concentration of uncomplexed tributyl phosphate in the organic phase. Since two moles of TBP combine with each mole of uranyl nitrate extracted, the value of the term, TBP(Org.), may be calculated from the following equation:

$$TBP(Org.) = TBP - 2UN(Org.), \quad \text{- - - - - - - - - - - -(5)}$$

where TBP represents the initial total concentration of TBP in the organic

phase and UN(Org.) represents the uranyl nitrate concentration in the organic phase. From the definition of the organic/aqueous distribution ratio for uranyl nitrate, assuming that all the uranyl nitrate in the aqueous phase is completely ionized, the following relationship may be written:

$$E_a^o = \frac{UO_2(NO_3)_2 \cdot 2TBP(Org.)}{UO_2^{++}(Aq.)}, \quad \text{- - - - - - - - - - - - -} \quad (6)$$

where E_a^o = distribution ratio, (g./l. organic phase)/(g./l. aqueous phase). Then substituting in the above equation for the equilibrium "constant", K, the following expression results:[24]

$$K = \frac{E_a^o}{\left[NO_3^-(Aq.)\right]^2 \left[TBP - 2UN(Org.)\right]^2} \quad \text{- - - - - - - - -} \quad (7)$$

By transposition, equation (7) may be expressed as:

$$E_a^o = K\left[NO_3^-(Aq.)\right]^2 \left[TBP - 2UN(Org.)\right]^2 \quad \text{- - - - - - -} \quad (8)$$

or

$$E_a^o = \left[K^{\frac{1}{2}}NO_3^-(Aq.)\right]^2 \left[TBP - 2UN(Org.)\right]^2 \quad \text{- - - - - - -} \quad (9)$$

This relationship is the basis for the correlation of the uranium transfer equilibrium data[38] presented in Figures IV-24 through IV-27 (see under C1.28, below). Since uranyl nitrate does not form a perfect solution in water under process conditions, K is not constant for the equilibrium expressed but varies with the concentrations of the various solution components. The factor $K^{\frac{1}{2}}$ of Equation (9) is plotted as a function of sulfate ion, phosphate ion, tributyl phosphate, sodium nitrate, and nitric acid concentration, in Figure IV-24. The uranium phase equilibrium data are then plotted as a function of $K^{\frac{1}{2}}$ in Figures IV-25, 26, and 27, for use in predicting and evaluating the effectiveness of the RA Column solvent-extraction performance.

Control of the decontamination achieved in the RA Column is accomplished by control of the degree of saturation of the TBP with uranium as well as by control of valence states. While it appears that nitric acid, plutonium, and fission products also extract into TBP by a mechanism similar to that for uranyl nitrate, the latter apparently forms much the stronger coordination bond with the tributyl phosphate. The uranyl nitrate is therefore capable of displacing the other process components from TBP when the solvent is at least about 50 per cent saturated with uranium. Thus the extraction operation must be controlled in such a way that the organic uranium concentration is maintained at a sufficiently high level (above about 50 per cent of saturation) at the feed point of the RA Column.[42][72] This condition requires close correlation between aqueous feed uranium concentration (RAF stream), solvent TBP concentration (RAX stream), and the aqueous-to-organic phase flow ratio (L/V).

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1.53 Sulfate and phosphate in the TBP process

Sulfate and phosphate ions both tend to react with uranyl ion to form complex ions which favor the aqueous phase.(10)(35) The effect of their presence in the stored uranium waste must therefore be at least partly counteracted if the uranium is to be successfully recovered by solvent-extraction. This is accomplished in the present recovery process by the use of tributyl phosphate solvent which, as a strong, organic complexing agent, competes for the uranium with the sulfate and phosphate complexing in the aqueous phase. Also, the use of nitric acid as a salting agent in the TBP process probably has the effect of destroying the sulfate and phosphate complexes in the aqueous phase according to the following equations:

$$UO_2(SO_4)_2^{=} + 4H^+ \rightleftharpoons UO_2^{++} + 2H_2SO_4 \text{ , - - - - - - - - - (10)}$$

$$UO_2(HPO_4)_2^{=} + 4H^+ \rightleftharpoons UO_2^{++} + 2H_3PO_4 \text{ , - - - - - - - - (11)}$$

assuming the uranium complex to be a simple association of two to four sulfate or phosphate anions with the uranyl ion. The uranyl ion is then removed from the reaction as uranyl nitrate by extraction into the organic phase. Under the RA Column conditions, the sulfate and phosphate reduce the uranium organic/aqueous distribution ratio about 5-fold, but satisfactory recovery is still accomplished. For the specific data on the effect of sulfate and phosphate on uranium distribution, see Subsection C1. Phosphate concentrations up to 0.6 M and sulfate concentrations up to 2 M can probably be tolerated in the process by adjustment of operating variables.(23)

2. RA Column

2.1 General

The RA Column is the extraction and decontamination contactor in which uranium is transferred to a TBP-diluent phase, while leaving the plutonium and fission products largely in the aqueous raffinate stream. The contactor is set up as a compound column with the aqueous feed solution (RAF) entering at an intermediate point while the aqueous scrub (RAS) and the organic extractant (RAX) streams enter the column at the top and bottom, respectively. Extraction of the uranium is effected in the lower portion (extraction section) of the column, while the traces of fission products and plutonium extracted along with the uranium are scrubbed back into the aqueous phase in the portion of the column above the feed point (scrub section).

During the conversion of the bismuth phosphate process uranium waste to the TBP solvent-extraction process feed, the solution may or may not be concentrated to yield a higher uranium concentration (see Chapter III). Since the RA Column operation is sensitive to RAF uranium concentration, two flowsheets, TBP-HW No. 4 (concentrated) and TBP-HW No. 5 (dilute), have been prepared. These two flowsheets are compared in the following table of RA Column stream compositions. The essential

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difference in the operation of the two flowsheets is the higher flow rate for the more dilute RAF, which is required to maintain the uranium processing rate and the organic uranium concentration.

RA Column Stream Flows and Compositions

	Flowsheet	
	TBP-HW No. 4[43]	TBP-HW No. 5[45]
RAS Stream:		
Relative flow rate	50	50
Density, g./cu.cm.	1.078	1.078
HNO_3, M	2.0	2.0
$FeSO_4 \cdot (NH_4)_2SO_4$, M	0.05	0.05
H_2NSO_3H, M	0.10	0.10
RAF Stream:		
Relative flow rate	100	146.8
Density, g./cu.cm.	1.383	1.240
UO_2^{++}, M	0.27	0.184
Na^+, M	4.07	2.78
H^+, M	2.96	2.01
$PO_4^{\equiv}$, M	0.26	0.177
$SO_4^{=}$, M	0.26	0.177
NO_3^-, M	6.25	4.26
Cl^-, M	0.023	0.016
Pu, M	6.1×10^{-7}	4.1×10^{-7}
RAX Stream:		
Relative flow rate	250	250
Density, g./cu.cm.[a]	0.803	0.803
TBP, M	0.458	0.458
TBP, Volume %	12.5	12.5

[a] The exact density of the RAX depends on the diluent used. The given value is for Deobase as diluent.

With the above feed stream flow rates and compositions, the RAU product stream from both flowsheets has the same uranium concentration (0.106 M). This uranium concentration represents about 46 per cent saturation of the tributyl phosphate. At the RAF feed point the degree of saturation is about 51 per cent (the excess over the uranium concentration in the RAU being contributed by internal reflux of uranium from the RA Column scrub section).

2.2 Uranium extraction

The TBP process solvent-extraction flowsheet specifies a maximum loss in the RAW of 0.5 per cent of the feed uranium to the RA Column. This loss is affected and controlled by a number of chemical and operating variables which are discussed in the following paragraphs. For a summary of the data concerning the effects of the variables on uranium transfer

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equilibrium, see Subsection C1.

2.21 Effect of uranium concentration

Increasing the aqueous uranium concentration under RA Column extraction section conditions lowers the organic/aqueous uranium distribution ratio, E_a^o.(9)(58)(72) For example, in Figure IV-20A it may be seen that the uranium distribution ratio varies from approximately 1 at the 0.17 M uranium concentration at the top of the extraction section, to about 10 at the 0.0001 M uranium concentration at the dilute end, under TBP-HW No. 4 Flowsheet conditions. If it is considered that the extraction mechanism requires the intermediate formation of molecular uranyl nitrate in the aqueous phase (see 1.31, above), then it may be seen that a large increase in the concentration of highly ionized uranyl nitrate is necessary to produce a small increase in the concentration of molecular uranyl nitrate in the aqueous phase. The result, therefore, is that a proportionately large increase in aqueous uranyl nitrate concentration causes the transfer of only a small amount of uranyl nitrate to the organic phase, and the distribution ratio, E_a^o, is lowered.

The above effect is probably accentuated by the influence of the degree of saturation of the tributyl phosphate with respect of uranyl nitrate. The saturation solubility of uranyl nitrate in 12.5 per cent TBP is about 0.22 M, much less than in water or hexone, and the organic/aqueous distribution ratio, E_a^o, decreases as organic saturation is approached (see Figure IV-20B). (In the Redox process the saturation effect is not apparent owing to the high solubility of uranyl nitrate in hexone.)

Increasing the uranium concentration in the RAF stream tends to increase the stage requirements to achieve a specified uranium waste loss. However, the tendency for increased loss may be counteracted by slightly increasing the RAX extractant flow rate, or by decreasing the RAF feed rate or the RAS scrub rate. Decreasing the aqueous-to-organic flow ratio (L/V) in the extraction section reduces the number of stages required to accomplish the desired separation. A lowered RAS flow rate reduces the amount of uranium carried into the extraction section by reflux from the scrub section, and also increases the effective salting strength in the extraction section.

2.22 Effect of nitrate concentration

For a given uranium concentration, raising the total aqueous nitrate concentration increases the distribution of the uranium into the organic phase(9)(64)(65), i.e., produces a larger E_a^o (see Figure IV-21). For example, a 1.0 M increase in nitrate concentration over TBP-HW No. 4 Flowsheet conditions raises the organic/aqueous uranium distribution ratio, E_a^o, by about 10 to 20%. This is true whether the nitrate increase is effected within the range of flowsheet conditions by the addition of sodium nitrate, nitric acid, or both. However, the uranium distribution ratio reaches a maximum at about 5 M nitric acid, and decreases at higher acid concentrations, probably due to the reduction of the activity coefficient of the acid.(72) The influence of nitrate salting on the uranium distribution ratio decreases as the uranium

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concentration increases and approaches saturation in the organic phase. (72) The extraction of uranium is therefore less sensitive to nitrate salting strength ($NaNO_3$ or HNO_3) at the feed plate than it is at the bottom or waste end of the RA Column (see Figure IV-21B).

Due to the nature of the starting material, the uranium concentration in the feed (RAF) to the solvent-extraction system is necessarily low. Then to achieve the per cent TBP saturation required at the feed plate for satisfactory decontamination, the ratio of the aqueous to the organic phase (L/V) must be held to a maximum, or an appreciable amount of uranium must be refluxed in the RA Clumn scrub section. The latter effect is achieved by using insufficient salting strength in the RA Column scrub stream (RAS) to maintain the uranium in the organic phase. However, a reduction in the scrub stream nitric acid concentration necessitates increasing the acid concentration in the RAF (feed) stream in order to maintain the aqueous salting strength in the RA Column extraction section. Furthermore, increasing the uranium reflux in the scrub section may increase the uranium loss in the RAW (waste) stream in spite of maintenance of the extraction section salting strength, if sufficient additional extraction stages are not available in the column. It is apparent that increasing the relative organic flow rate (decreasing the L/V ratio) to compensate for increased losses would reduce the per cent saturation of the TBP. Such a change would thereby nullify the original purpose of reducing the scrub stream salting strength (increasing the scrub reflux) in order to raise the organic uranium concentration at the feed plate.

Uranium losses in the RAW due to low nitrate salting strength in the RA Column extraction section may be counteracted by lowering the aqueous-to-organic ratio (L/V). Lowering the ratio by increasing the RAX relative flow rate has the effect of decreasing the number of transfer stages required to accomplish the desired extraction. Decreasing the RAS scrub stream flow rate reduces the rate of uranium reflux in the scrub section. It also has the effect of increasing the salting strength in the extraction section since the nitrate concentration in the RAS stream is lower than the total nitrate concentration in the RAF stream with which the RAS stream is mixed at the feed point.

2.23 Effect of tributyl phosphate concentration

As may be noted by reference to curves 1 and 2 of Figure IV-21B, the uranium distribution ratio increases slightly with higher TBP concentration.(9)(35) Thus an increase in TBP concentration from 12.5 to 15 volume per cent increases the organic/aqueous uranium distribution ratio, E_a^o, by approximately 30 to 50%.

If the TBP concentration decreases in the RAX stream while the volume flow rate remains constant, the effect on the extraction process is the same as a decrease in the RAX flow rate. In other words, the effect is the same as that of increasing the aqueous-to-organic flow ratio, L/V, and more transfer stages are then required to accomplish the same extraction. A drop in TBP concentration in the RAX stream would then tend to increase the uranium waste loss in the RAW waste stream. Raising the RAX flow rate compensates for a lowering of the TBP concentration.

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2.24 Effect of tributyl phosphate decomposition products

At the concentrations to be expected in the process, the presence of monobutyl and dibutyl phosphates in the solvent has little effect on uranium distribution under RA Column conditions (see under C1.26). High concentrations of DBP, however, may produce a reduction of uranium waste losses. Likewise high concentrations of MBP could result in some precipitation of uranium. Some TBP decomposition products have caused emulsification in the RA system, as discussed in Section F of Chapter V.

2.25 Effect of the diluent

Uranium distribution ratios are not appreciably affected by variations in the composition of the hydrocarbon diluent for TBP.[35][58][72] Waste losses are affected only in so far as stage (or transfer unit) heights may vary somewhat with the physical properties imparted by the diluent to the solvent phase, as discussed in Chapter V.

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2.26 Effect of phosphate and sulfate ions

An increase in the phosphate or sulfate concentration in the aqueous phase reduces the organic/aqueous uranium distribution ratio (E_a^o) and thus results in increased uranium loss from the RA Column. As indicated by the data presented under C1.25, below, and in Figures IV-21A and IV-22A and B, this effect is more pronounced for phosphate than for sulfate. Thus, for example, in the RA Column extraction section a 0.3 M increase in sulfate concentration or 0.1 M increase in phosphate concentration over the TBP-HW No.4 Flowsheet values decreases E_a^o by about 50% and increases RA Column uranium losses about 1.8-fold (on the basis of 7 transfer units in the RA Column extraction section). These anions apparently lower the available aqueous concentration of the uranium by formation of uranyl phosphate or uranyl sulfate complexes which are inextractable by tributyl phosphate. The reactions may be expressed by the following equations:

$$UO_2^{++} + 2HPO_4^{=} \rightleftharpoons UO_2(HPO_4)_2^{=} \quad \text{- - - - - - - -} \quad (10)$$

$$UO_2^{++} + 2SO_4^{=} \rightleftharpoons UO_2(SO_4)_2^{=} \quad \text{- - - - - - - -} \quad (11)$$

although the exact number of anions associated with the uranyl ion is not positively known.

Increases of sulfate and/or phosphate concentration in the RAF stream then would increase RAW uranium losses if not compensated for by sufficient excess nitric acid (2 to 3 M acid for about 0.2 M sulfate and phosphate) or by increasing the RAX flow rate (decreasing the L/V ratio). Lowering the L/V ratio decreases the number of extraction stages required to perform the desired separation.

2.27 Effect of temperature

As shown in Figure IV-23, organic/aqueous uranium distribution ratios, E_a^o, decrease slightly as the temperature of the equilibrated

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extraction system is raised (about two-fold or less as the temperature is raised from 20°C. to 50°C.).(53)(72) However, it should be noted here that the rate of attainment of phase equilibrium is probably controlled by the rate of diffusion in the liquid phases rather than by the rate of the extraction reaction indicated in equation (3) under A1.31.(76) Actually, the advantage in uranium distribution ratio to be gained by extraction at lower temperatures is nullified by the adverse effect of higher viscosity and lower diffusion rates producing higher H.E.T.S. values.(64) A higher operating temperature alters the equilibrium line to require more stages for a given separation but produces lower stage heights thereby making more transfer stages available in a given column extraction system; the over-all effect favors the higher temperature, at least up to the 65°C. studied.

2.28 Effect of aqueous-to-organic flow ratio

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In the tributyl phosphate process, particularly close correlation is required between the relative phase flow rates, the feed uranium concentration, the tributyl phosphate concentration, and the nitric acid salting strength. If a rise in uranium waste losses appears in the RAW stream, the higher waste uranium concentration may be due to a higher aqueous-to-organic phase flow ratio (L/V), a higher aqueous uranium concentration at the feed point, a lower TBP concentration in the RAX, or a lower nitrate concentration in the aqueous phase of the RA Column extraction section. Compensation for these effects can be accomplished by altering the L/V ratio or the salting strength.

Losses from high RAF uranium concentrations may be reduced by lowering the L/V ratio in the extraction section either through lowering the RAF flow rate or raising the RAX flow rate. Such a change decreases the number of stages required to effect the desired extraction. Similarly, if losses appear to be due to a reduction of TBP concentration, then they may be alleviated by increasing the RAX flow rate. Losses due to decreased nitrate salting strength in the extraction section may be counteracted by lowering the L/V ratio either by raising the RAX flow rate or lowering the RAS flow rate.

2.29 Effect of uranium extraction on stream densities

The following table gives the aqueous and organic phase densities, as determined by laboratory countercurrent batch extraction, for seven RA Column extraction and three RA Column scrub stages.(58) The feeds for the two runs simulated composite uranium waste prepared by acidification of combined sludge and supernate. In one of the runs summarized, the feed simulated a solution prepared by concentration after acidification of composite waste. The two runs approximated TBP-HW No. 4 and No. 5 Flowsheet conditions except that the extractant in both cases was 15 volume per cent TBP in Deobase. Plutonium and fission products were absent.

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RA Column Phase Densities, d_4^{25}

Stage	TBP-HW No. 4 Flowsheet Aqueous	TBP-HW No. 4 Flowsheet Organic	TBP-HW No. 5 Flowsheet Aqueous	TBP-HW No. 5 Flowsheet Organic
1	1.019	0.8609	1.1094	0.8605
2	1.1085	0.8646	1.1105	0.8636
3	1.1163	0.8706	1.1130	0.8657
4 (Feed point)	1.2877	0.8733	1.1761	0.8653
5	1.2596	0.8604	1.1600	0.8486
6	1.2496	0.8354	1.1517	0.8266
7	1.2422	0.8222	1.1516	0.8187
8	1.2403	0.8203	1.1516	0.8170
9	1.2365	0.8190	1.1509	0.8170
10	1.2353	0.8180	1.1434	0.8161

It is not feasible to extimate RA Column operating efficiency by means of density variations of the RAW waste stream. The stream density is not sufficiently sensitive to variations in very dilute uranium concentrations; furthermore, due to variable feed make-up from sludge and supernate, the stream density will fluctuate exclusive of variations in the RAW uranium concentration.

2.3 Decontamination from plutonium

The uranium waste slurry contains 1 to 2 per cent of the plutonium originally associated with the irradiated uranium. A Pu decontamination factor of up to 40 is required to yield recovered uranium containing a maximum of one part of plutonium in 10^7 parts of uranium.(22)(25)

Decontamination of the recovered uranium with respect to plutonium requires either the preferential complexing of the plutonium in the aqueous phase, or converting it to the inextractable (III) valence state. The latter method is employed in the TBP process.

Following the converison of the uranium waste slurry to a feed solution for solvent extraction, the plutonium is largely in the organic-soluble Pu(IV) valence state which is the state most extractable by tributyl phosphate (see Figure IV-32). Pu(VI) shows a somewhat lower distribution ratio, E_8, while Pu(III) and Pu(V) are essentially inextractable. Both complexing and reduction to Pu(III) have been checked experimentally in connection with simple Pu decontamination of recovered uranium, as well as to determine the process feasibility of recovering the plutonium by partition of extracted Pu from uranium in an operation comparable to the Redox IB Column separation.(9)(25)(72)(75)

Sulfate and phosphate show some tendency to complex plutonium in the aqueous phase, but, as in the case of uranium, these complexes are destroyed in the presence of excess nitric acid thereby permitting complete Pu extraction. The fluoride and fluosilicate ions have been found to be particularly effective in complexing Pu(IV) in the aqueous phase,

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the distribution ratio being of the same order of magnitude as for Pu(III).(9)(25) However, these complexing agents are objectionable because of equipment corrosion by the fluoride ion.

Reduction of the plutonium to the inextractable Pu(III) state is readily achieved by a reducing agent such as ferrous ion. The rate of reduction is sufficiently rapid (less than 10 seconds) that the reaction may be carried out in the course of the uranium extraction in the RA Column. The reducing agent is therefore added to the solvent-extraction system by way of the RAS scrub stream.

Ferrous ion is unstable in the presence of the RA Column nitric acid concentrations. Oxidation to the ferric state is apparently catalyzed by nitrite ion, and the reduction system may thus be stabilized by the addition of a holding reductant which destroys the nitrite.(6)(7) The sulfamate ion serves very effectively for this purpose. Ferrous ion and sulfamate ion are therefore used together in the RA Column to ensure the existence of all the plutonium in the Pu(III) state in the RA system. Under these conditions the Fe(II) has a half-life of 30 to 50 hours. (9)(37)(75)(82)

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In the Redox process, where the presence of sulfate is detrimental to second cycle plutonium extraction, ferrous sulfamate is used as the reducing agent. In the TBP process, where a small amount of additional sulfate is not harmful, ferrous ammonium sulfate is used as the reducing agent with sulfamic acid added. The latter system is simpler to handle and does not require on-site preparation as does ferrous sulfamate.

In the RA Column some reflux of the plutonium occurs in the scrub section since the Fe(II) is added via the scrub stream and some Pu is extracted at the feed point before reduction is complete. The extent of extraction of Pu(IV) and Pu(VI) is influenced by a number of column variables. The uranium shows preferential complexing with the tributyl phosphate. Therefore, as saturation of the solvent by uranium is approached, the plutonium distribution ratio, E_a^o, is reduced (see Figure IV-33) and less Pu is carried in the extractant.(9)(75) As may be seen in Figure IV-32, nitric acid (or total nitrate ion concentration) tends to salt Pu(III), (IV), and (VI) into the organic phase.(72) The salting effect, however, is markedly reduced as the concentration of the uranium in the solvent approaches saturation.(72) An increase in TBP concentration also increases the plutonium distribution ratio, E_a^o, although again the effect is limited by the uranium saturation of the solvent. Monobutyl and dibutyl phosphate impurities in the organic phase increase the plutonium distrubution ratio, E_a^o, and in so doing reduce the Pu decontamination factor for the RA Column.(44)

2.4 Decontamination from fission products

The ease and extent of fission-product decontamination in the TBP process is dependent upon the age of the uranium waste being processed. For 1 to 1½ year old bismuth phosphate process waste from uranium subjected to 400 megawatt-days/ton integrated exposure over a period of 360 days, zirconium is the decontamination-limiting fission product. For waste

greater than about 1½ years old, ruthenium is the limiting radioactive element.(31)(62)(72) Wastes younger than about 2 years cannot be adequately decontaminated in the TBP Plant because radioactive ruthenium, zirconium, and cerium carry through with the recovered uranium in concentrations which exceed specifications for recovered uranium.

Cerium and niobium are extracted to a certain extent but are largely removed on scrubbing the organic extract. In general, the decontamination achieved in the RA Column is better the lower the fission-product organic/aqueous distribution ratio, and the higher the aqueous/organic phase ratio (L/V) or the higher the uranium saturation of the solvent phase.

Experimental data indicate an anomaly in the effect of nitric acid on decontamination in the RA Column. As in the Redox process, decontamination in the extraction section is better the lower the free acid concentration.(42) On the other hand, fission-product decontamination in the scrub section is better the higher the aqueous acidity.(42) Nitric acid does have a salting effect on gross beta and gross gamma radioactivity (see Figures IV-35 and 36); the salting action is particularly strong for zirconium while showing only slight effect on ruthenium and cerium. However, the salting action of increased HNO_3 in the scrub section is apparently outweighed by some other effects, possibly chemical. For specific distribution ratio data see Subsection C3.

Many characteristics of fission-product (F.P.) decontamination are similar to those for plutonium. Higher uranium saturation of the organic phase improves F.P. decontamination particularly with respect to ruthenium and zirconium.(9)(42)(72) Lowering the RAX tributyl phosphate concentration improves decontamination by decreasing the F.P. distribution ratio, E_8. Low TBP concentrations (below 10 per cent), however, are unfavorable to uranium extraction and seriously limit the column capacity. Complexing agents such as sulfate, phosphate, and fluosilicate tend to hold fission products in the aqueous phase.(9) The latter is true particularly for zirconium while ruthenium is only slightly affected by such agents.

Decontamination performance may be impaired by reaction of the TBP diluent with nitric acid to produce hydrocarbon nitration products. Since the aromatic and olefinic hydrocarbons react most readily with nitric acid, those hydrocarbons are limited to a maximum of 2 per cent by volume as determined by a test involving absorption of these components from the diluent into an H_2SO_4-P_2O_5 mixture (ASTM D-875-46T). No success was obtained in attempts to correlate the Kauri-Butanol Number which has some relation to the aromatic content) with the effect of diluent on decontamination performance. When the olefinic and aromatic hydrocarbons are below the 2 per cent specification limit, the TBP Plant solvent treatment should remove any nitration products formed.

Dibutyl phosphate (as an impurity in the organic stream) lowers the decontamination factor for the RA Column by extracting zirconium particularly.(57) See Subsection C3 for specific data.

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3. RC Column

3.1 General

After extraction and decontamination in the RA Column, the uranium is recovered as an aqueous solution by stripping the RAU stream in the RC Column. The contactor is operated as a simple countercurrent column with the organic and aqueous phases entering and leaving the column at opposite ends. The table below summarizes the column stream compositions, which are identical for the TBP-HW No. 4 and No. 5 Flowsheets.(43)(45)

RC Column Stream Flows and Compositions

RAU or RCF Stream (Organic):	
Relative flow rate[a]	255
Density, g./cu.cm.[b]	0.840
Uranyl nitrate, M	0.106
Nitric acid, M	0.10
Chloride ion, M	0.0001
RCX Stream (Aqueous):	
Relative flow rate[a]	200
Density, g./cu.cm.	1.0
Nitric acid, M	0.01
RCU Stream (Aqueous):	
Relative flow rate[a]	205
Density, g./cu.cm.	1.041
Uranyl nitrate, M	0.132
Nitric acid, M	0.134
Chloride ion, M	0.0001
TBP, g./l.	ca. 0.2
RCW Stream (Organic):	
Relative flow rate[a]	250
Density, g./cu.cm.[b]	0.803
Uranyl nitrate, M	0.00054
Nitric acid, M	ca. 0.001

[a] Based on RAF = 100 for TBP-HW No. 4 Flowsheet;
RAF = 146.8 for TBP-HW No. 5 Flowsheet.

[b] The organic stream densities depend upon the diluent used. The values given are for the use of Deobase as the TBP diluent.

3.2 Uranium stripping

Uranium stripping is accomplished in the RC Column by means of a 0.01 M nitric acid stream. The trace of acid is added to the aqueous stream in order to inhibit emulsification at the dilute end of the column,

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since the nitric acid is essentially completely stripped from the organic stream in the lower portion of the column. Just as the tributyl phosphate shows more affinity for uranyl nitrate than for nitric acid in the RA Column, in the RC Column the uranium is more difficult to strip than the nitric acid. Furthermore, the acid stripped into the aqueous phase makes uranium stripping more difficult. Operation of the RC Column is therefore handicapped if high concentrations of nitric acid are carried over from the RA Column. Thus a 0.1 M increase in the nitric acid content of the RAU stream increases the uranium concentration in the RC Column waste stream (RCW) by approximately 20 per cent (on the basis of 7 transfer units in the RC Column).

The amount of nitric acid carried in the organic RAU-RCF stream is directly proportional to the concentration of the tributyl phosphate as well as being influenced by the extent of uranium saturation of the TBP. The upper limit of the TBP concentration which may be used in the RA-RC system is thus partly controlled by the RC Column operation, which must accomplish complete stripping of the uranium within a reasonable length of column. Uranium stripping in the column is favored by the fact that at low acid concentrations the uranium distribution ratio, E_a^o, becomes much smaller at the dilute end of the column.

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The presence of dibutyl phosphate in the organic stream greatly increases the uranium distribution ratio, E_a^o, under RC Column conditions,(30)(60) and therefore has the effect of increasing uranium waste losses in the RCW stream. Monobutyl phosphate forms a uranium complex which is insoluble in both phases, and promotes the formation of stable organic-aqueous emulsions at the dilute (uranium) end of the RC Column.

Nitration products of hydrocarbon diluents have been found to increase greatly the uranium distribution ratio under RC Column conditions.(60) Diluents high in aromatic or olefin content nitrate on prolonged contact with nitric acid solutions at room temperature. Sodium carbonate and caustic washes have been found effective in reducing the RC distribution ratios for solvent mixtures containing nitration products to more favorable values, but they are still higher than for fresh diluent. Diluents of low aromatic and olefin content are stable to nitration except at elevated temperatures. As the specifications for TBP process diluent limit the aromatic and olefin content to less than 2 per cent by volume, no difficulties resulting from diluent nitration products are anticipated.

The stripping of uranium into water is accompanied by the absorption of heat.(53) Raising the temperature of the transfer system favors the stripping operation both by lowering the distribution ratio, E_a^o, and by decreasing the stage height by lowering viscosities and increasing diffusion rates,(64) although with a temperature change from 77°F. to 110°F. the effect in a 3-in.-diameter pilot-plant column was not significant.(56)

Increasing the aqueous-to-organic flow ratio (L/V) reduces the number of transfer stages required to accomplish the stripping operation, but also produces a more dilute uranium product stream. The phase flow rates are about the same for both phases in the RC Column. Specific data on

the effects of variables on uranium stripping are presented under C1.3.

3.3 Decontamination

The purpose of the RC Column is to strip the uranium back into an aqueous phase, and little additional decontamination is accomplished in the operation. Plutonium and fission products extracted in the RA Column are largely stripped in the RC Column. However, any loss of decontamination due to the presence of dibutyl phosphate in the RA system, tends to be alleviated in the RC system by the fact that the butyl acid phosphate complexes the fission products in the organic phase. In such a case they are at least partially removed in the RCW stream. The same is true for traces of plutonium.

B. PROPERTIES OF PROCESS MATERIALS

1. Tributyl Phosphate

1.1 Introduction

Tri-n-butyl phosphate (TBP) is a viscous, colorless liquid which is produced by the reaction of n-butyl alcohol with either phosphorus oxychloride or phosphorus pentoxide with subsequent caustic treatment and distillation. It is used as the extractant in the uranium recovery solvent-extraction process because of the specificity of the strong complex it forms with uranium. In order to produce an organic phase with the optimum physical and chemical properties, TBP is diluted with a chemically inert petroleum hydrocarbon fraction boiling in the kerosene range. (See Section A of this chapter for more complete information.)

1.2 Specifications

The specifications for TBP are given in the following table:

Tributyl Phosphate Specifications(90)

Butanol content	Reducing normality less than 0.05
Acidity	Less than 0.01 N
Color	Colorless
Water	No turbidity when 1 volume is mixed with 19 volumes of 60° Bé. gasoline at 20°C.
Suspended solids	0
Specific gravity	0.973 to 0.983 (20/20°C.)

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1.3 Physical properties

1.31 General

The physical properties of TBP are presented in Table IV-1. Those properties are listed which are considered to be of fundamental interest in the TBP process.

1.32 Solubility in process solutions

The saturation concentration of TBP in water from a 15 volume per cent TBP-hydrocarbon mixture is 0.23 g./l. at 25°C.(61) The solubility increases as the concentration of TBP in the diluent increases, reaching a value of 0.39 g./l. for 100 per cent TBP. The solubility of TBP in aqueous solutions decreases rapidly with increasing electrolyte concentration in the aqueous phase, as may be seen from the following table:

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Solubility of TBP in Process Solutions at 25°C.

Organic Phase TBP Conc., Volume Per Cent	Solubility of TBP in Aqueous Phase, G./L.				
	H_2O	RCU*	RAW**	3 M HNO_3	2M $UO_2(NO_3)_2$
33.3	0.28	0.19	0.0097	0.21	--
16.6	0.24	0.17	0.0097	0.17	0.01

*0.2 M $UO_2(NO_3)_2$, 0.06 M HNO_3.

**2.6 M HNO_3, 1.9 M $NaNO_3$, 0.2 M Na_2SO_4, 0.2 M Na_3PO_4, 0.03 M NH_4NO_3, 0.02 M $FeCl_3$, 0.03 M NH_2SO_3H.

The solubility of pure TBP in nitric acid solutions decreases to a minimum of about 0.1 g./l. as the acid concentration is increased to 10 M HNO_3. At this concentration the TBP solubility begins to increase rapidly, reaching a value of about 1.3 g./l. in 15 M HNO_3.

1.33 Radiation stability

The exposure of TBP and of TBP-diluent mixtures to a 1.3-M.e.v. electron beam at an intensity level of about 1.3 microamperes per ml. of TBP for 1 second (approximately equivalent to 0.75 curies of irradiation per ml. for 5 minutes) did not seriously affect the TBP, as evidenced by the fact that the distribution ratios of uranium, plutonium, and beta-emitting fission products were essentially the same as into non-exposed solvent.(78) When the total irradiation was increased to 300 microampere-sec. per ml. of solution (approximately equivalent to 170 curies of irradiation per ml. for 5 minutes), the plutonium and beta-emitting fission product holdup in the solvent was increased by a factor of 2 to 20.(79)

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The radiation stability of TBP should be no problem in the TBP Plant as the gross beta and gamma radioactivity of the RA Column feed is only about 6 curies per gallon, or roughly 5×10^{-4} curie per ml. of RAX and the time required for the solvent to pass through the RA Column is less than 5 minutes.

Over-all beta and gamma decontamination factors of 10^4 to 10^5 obtained with Hanford slugs in O.R.N.L. semi-works runs, together with over-all uranium losses of only 0.01 to 0.02 per cent, further confirm the radiation stability of TBP.

1.4 Chemical properties

1.41 General

The chemical properties of TBP are those typical of esters derived from inorganic acids. Hydrolysis, the reaction of principal interest in the TBP process, is discussed in the following section. Tributyl phosphate has no active hydrogen atom and no pronounced surface active properties. The butyl acid phosphates, however, are agents capable of forming strong complexes (notably with uranium) which, in turn, may exhibit unfavorable distribution coefficients and emulsifying characteristics.

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1.42 Hydrolysis

The hydrolysis products of TBP adversely affect fission-product decontamination and uranium losses in the TBP process, as indicated in Section C of this chapter. The hydrolysis proceeds through the dibutyl (DBP) and monobutyl phosphates (MBP) to orthophosphoric acid, the first step being rate determining.(60) Representative hydrolysis rates for a two-phase system are given in the table below for TBP in the presence of 3 M HNO_3 with an aqueous-to-organic volume ratio of 1. The hydrolysis is first-order with respect to HNO_3, and zero or first-order with respect to TBP.

Rate of Hydrolysis of TBP in Contact With 3 M Nitric Acid(61)

Temperature, °C.	Fraction of TBP Decomposed per Day, k	Half-Life (Composite)(a)	Induction Period
25	0.00001(b)	50 to 100 yr.	- - -
76	0.00045	3 yr.(c)	8 days
105	0.0023	7 mo.	2 days

(a) Calculated on the basis of zero-order kinetics.

(b) Calculated value.

(c) The half-lives of dibutyl and monobutyl phosphates under similar conditions are 8 and 18 days, respectively.

The hydrolysis of pure TBP in 3 M HNO_3 (equal volumes) may be estimated at any temperature by the equation:

$$\log_{10} k = -\frac{3210}{T} + 5.86 \text{ - - - - - - - - - - } (1)$$

where k = the fraction of TBP decomposed per day, and T = temperature in degrees Kelvin.

A comprehensive plot of the rates of hydrolysis for the series from tributyl phosphate to orthophosphoric acid is given in Figure IV-1. From an extrapolation of the data, it is apparent that the hydrolysis of TBP at 25°C. over a 30-day interval is immeasurably small.

The rate of hydrolysis in the aqueous phase as compared to the organic phase, is greater by a factor of about 230. However, this is offset by the low solubility of TBP in aqueous solutions (see under B1.32) so that when the two phases are comparable in volume the "effective" hydrolysis takes place in the organic phase. The rate constants for hydrolysis in either phase are summarized in the following table:(60)

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Hydrolysis Constants of TBP

Temperature, °C.	k*(Aq.)	k* (Org.)
25	0.004	0.00002
76	0.06	0.0002
105	0.28	0.0012

*)Fraction decomposed per day per M nitric acid.

The application of the rate of hydrolysis of tributyl phosphate to a system in which a diluent is employed is uncertain, However, it may be assumed that a rate calculated from the data in the preceding tables will give the upper limit.

2. Diluent

2.1 Introduction

The inert diluent for TBP in the TBP process is a highly purified saturated-hydrocarbon mixture, boiling in the kerosene range (190° to 270°C.). Solvents meeting specifications for the diluent are commercially available under trade names such as Deobase, Base Oil C, and Shell Deodorized Spray Base.

2.2 Specifications

The specifications for the diluent are given in the following table:(89)

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Diluent Specifications for the Uranium Recovery Process

Viscosity	2.0 centipoises or less at 25°C.
Flash point	140°F. or higher (Tag or Pensky-Martens closed cup).
Combined olefin and aromatic content	2 per cent by volume or less (ASTM D-875-46T).
Specific gravity	0.8 or less at 25/4°C.

2.3 Physical properties

The physical properties of some commercially available kerosene fractions are given in Table IV-2.(54) Some of these diluents do not meet the specifications in regard to flash point and/or aromatic content.

The following physical properties apply to commerical grade kerosene and are comparable to those of the diluent employed in the TBP process:(3) (6)

Physical Properties of Commercial Grade Kerosene

Heat of vaporization	60 cal./g.
Surface tension	28 dynes/cm. at 20°C.
Interfacial tension (oil-water interface)	48 dynes/cm. at 20°C.
Upper explosive limit in air	6.0 volume per cent
Lower explosive limit in air	1.2 volume per cent
Ignition temperature	490°F.

The boiling range of three commercial diluents are given in Figure IV-2. The vapor temperature is plotted against the percentage of the total volume of each solvent distilled. The curves for Deobase and Shell Deodorized Spray Base are similar, indicating that they are composed of hydrocarbons in approximately the same molecular weight range. The narrow boiling range exhibited by AMSCO 125-90W indicates that it is the result of a more selective refinement than either of the other two diluents.

The vapor pressure of Deobase as a function of temperature is shown in Figure IV-3. Curves are given for three approximately equal distillation fractions of commercial Deobase.

2.4 Chemical properties

Inertness toward chemical reaction with process materials was a major consideration in choosing the diluent. The diluent is composed mainly of paraffin hydrocarbons, the aromatic and olefin hydrocarbons having been almost entirely removed by the manufacturer's treatment. The percentage of naphthenes may vary somewhat depending on the source of the crude oil. The iodine numbers given in Table IV-2 are a measure of the olefin content. At an assumed average molecular weight of 150, the per cent of olefins is approximately 0.7 of the iodine number.

Except for the traces of aromatic and olefin hydrocarbons, the diluent used in the TBP process is chemically unreactive in contact with process solutions at ambient temperatures. The diluent, AMSCO 149-92 Br, which contains about 7 and 1 weight per cent of aromatics and olefins respectively, undergoes nitration when contacted with a 3 M HNO_3-0.01 M KNO_2 solution at 60°C. Following a 5-hour exposure period to these conditions, this diluent is found to contain 0.98 weight per cent nitrogen after one water wash as compared to 0.2 per cent found in TBP when treated in an identical manner.(55) AMSCO 125-90W, which meets the specifications in regard to aromatic and olefin content, will react with 3 M HNO_3 at 105°C.(60) A two-phase system composed of an equal volume of RAX (15 volume per cent TBP in AMSCO 125-90W) and 3 M nitric acid reacts as soon as the boiling point is reached (105°C.), and the reaction proceeds until the nitric acid concentration in the organic phase has changed after 6 days from 2.0 M to 0.07 M, and in the aqueous phase from 1.5 M to 0.5 M. No decomposition is noted under similar conditions at 70°C.

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3. Solvent-Phase Solutions

3.1 Tributyl phosphate-diluent systems

3.11 Introduction

The organic extractant used in the TBP process is a 12.5 volume per cent solution of tributyl phosphate in an inert hydrocarbon diluent. The physical properties of TBP-diluent mixtures, as well as those of solutions of $UO_2(NO_3)_2$ and HNO_3 in the TBP-diluent system, are presented below.

3.12 Physical properties

The density of TBP-diluent mixtures may be calculated from the following equation:(54)

$$d_{Mixture} = 0.972N_{TBP} + N_{Diluent}\ d_{Diluent} \text{ - - - - - - - (1)}$$

where d = density at 25°C., g./cu.cm.
N_{TBP} = volume fraction of TBP, and
$N_{Diluent}$ = volume fraction of diluent.

Values derived from this equation are compared with experimental values in Figure IV-4, in which density is presented as a function of the concentration of TBP in Shell Deodorized Spray Base.

The refractive index of a TBP-Shell Deodorized Spray Base mixture is a linear function of the concentration of TBP as shown in Figure IV-4.(84) As the concentration of TBP increases from 10 to 20 volume per cent, the refractive index decreases from 1.4426 to 1.4403.

The viscosity, η (in millipoises), of TBP-diluent mixtures may be calculated from the equation:(54)

$$\log_{10}\eta_{Mix.} = N_{TBP}\,(1.345 + 0.36\,N_{TBP}) + N_{Diluent}\log_{10}\eta_{Diluent} \text{ - - (2)}$$

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where N_{TBP} = volume fraction of TBP, and
$N_{Diluent}$ = volume fraction of diluent.

The change in viscosity of the extractant with temperature is illustrated in Figure IV-5, where the viscosity is seen to decrease from 2.3 to 0.5 centipoises as the temperature is increased from 15° to 90°C. The temperature coefficient is shown to be approximately equal for extractant and feed.

The flash point of the solvent increases as the concentration of TBP increases (Figure IV-6), and may be estimated from the equation:(54)

$$\Delta T = -T_o^2/2300 \log_{10} N, \quad (3)$$

where T_o = flash point of pure diluent in degrees Kelvin, and
N = mole fraction of diluent.

Figure IV-6 shows the close agreement between experimental and calculated values.

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3.2 TBP - diluent - $UO_2(NO_3)_2$ - HNO_3 systems

3.21 Physical properties

The theoretical saturation concentration of uranyl nitrate in 12.5 volume per cent TBP in diluent is 0.22 M, corresponding to one mole of uranium for each two moles of TBP.

The densities of solutions of uranyl nitrate and/or nitric acid in TBP-diluent mixtures may be calculated from the following equation:(69)

$$d_{25} = d_s + (0.394 - 0.086\, d_s)(M\ UO_2(NO_3)_2) + (0.063 - 0.046\, d_s)(M\ HNO_3), \quad (4)$$

where d_{25} = density of solution at 25°C.,
d_s = density of TBP-diluent solvent at 25°C. (for method of calculation see under B3.12), and
M = concentration in moles per liter.

The following equation may be used to calculate the density of TBP-diluent - $UO_2(NO_3)_2$-HNO_3 solutions at temperatures between 30° and 70°C.:(70)

$$\begin{aligned} d_{t°C.} = d_C &+ (3.20 - 0.005\, t - 0.008\, TBP)\, 10^{-2}\, M\ HNO_3 \\ &- (7.4 + 0.01\, TBP + 0.0045\, UNH)\, 10^{-4}\, t \\ &+ 2.1 \times 10^{-3}\, TBP \\ &+ (6.30 - 0.005\, t + 0.009\, TBP)\, 10^{-4}\, UNH, \quad (5) \end{aligned}$$

where d_C = density of the diluent at t°C.,
t = temperature in °C.,
TBP = concentration of tributyl phosphate in volume per cent,
M = concentration in moles per liter, and
UNH = concentration of uranyl nitrate hexahydrate in grams per liter.

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A density-weight per cent-molarity conversion chart is given in Figure IV-7 for $UO_2(NO_3)_2$ in a 12.5 volume per cent TBP solution in Deobase.(34)(40) Different sets of curves are required for different diluents and for concentrations of TBP other than 12.5 per cent.

The effects of temperature on the densities of feed and extractant are compared in Figure IV-8. The temperature coefficient is approximately equal for the two phases over the temperature range from 25° to 75°C.

The viscosities of solutions of uranyl nitrate in TBP-diluent mixtures are shown in Figure IV-9 as a function of the concentration of $UO_2(NO_3)_2$. Curves are presented for 15, 23, and 46 volume per cent TBP in Deobase, and for 15 volume per cent TBP in AMSCO 125-90W. The rate of change of the viscosity with uranium concentration is seen to increase with increasing TBP concentration.

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4. Aqueous Uranium Nitrate Solutions

4.01 Introduction

Subsequent to the acidification of the uranium waste slurry, the properties of the TBP aqueous feed stream are those of a solution of uranyl nitrate and nitric acid containing the additional ions Na^+, $PO_4^{\equiv}$, and $SO_4^{=}$. Minor components, such as fission products, plutonium, and chloride ion, have no significant effect on the properties discussed in this section. The physical properties of this uranium stream as presented here are of concern primarily in the final feed adjustment step. The effect of these properties on RA Column performance are discussed in Section A of this chapter.

The aqueous system containing only uranyl nitrate and nitric acid is encountered as the aqueous effluent (RCU) from the stripping column, and its physical properties are of importance in the final RCU concentration step (see Chapter VII) as well as in their effect on column performance itself.

Also included below are aqueous systems containing $NaNO_3$ in addition to the components indicated above.

4.02 Solubility

$UO_2(NO_3)_2$ - H_2O system

A saturated solution of uranyl nitrate at 25°C. represents about 72 per cent by weight of $UO_2(NO_3)_2 \cdot 6H_2O$ or 2.6 moles per liter.(4) The solubility of uranyl nitrate is presented as a function of temperature in Table IV-3 and the temperature-solubility phase diagram is included in Figure IV-10.(12)

$UO_2(NO_3)_2$ - HNO_3 - H_2O system

Nitric acid markedly reduces the solubility or uranyl nitrate in water as illustrated in the following table:(4)

Composition of Saturated Aqueous Solutions at 25°C.

In Equilibrium with $UO_2(NO_3)_2 \cdot 6H_2O$ as Solid Phase		In Equilibrium with $UO_2(NO_3)_2 \cdot 3H_2O$ as Solid Phase		In Equilibrium with $UO_2(NO_3)_2 \cdot 2H_2O$ as Solid Phase	
Wt. % $UO_2(NO_3)_2$	Wt. % HNO_3	Wt. % $UO_2(NO_3)_2$	Wt. % HNO_3	Wt. % $UO_2(NO_3)_2$	Wt. % HNO_3
56.08	0	36.28	32.21	27.24	55.24
40.36	12.35	27.18	46.12	23.65	60.38
30.29	25.14	25.79	50.43	22.29	66.71
29.65	28.67	26.77	53.20	22.49	68.83
31.27	29.84	27.49	53.71		
36.72	30.43				
37.99	30.15				

The temperature-solubility phase diagrams for the $UO_2(NO_3)_2$ - HNO_3 - H_2O systems are given in Figure IV-10 for 0.0, 0.3, 1.0, and 3.0 M nitric acid concentrations.(12)(17)

Multi-component systems

The solubility relationships at 25°C. for aqueous solutions containing phosphates and sulfates as well as $UO_2(NO_3)_2$, HNO_3, and $NaNO_3$ are given in Figure IV-14. Uranyl acid phosphate is seen to be the limiting component for low acid solutions, whereas $NaNO_3$ limits the solubility at the higher nitric acid concentrations.

The normal salt $(UO_2)_3(PO_4)_2$ exhibits retrograde solubility, i.e., the solubility decreases with an increase in temperature. However, laboratory experiments designed to simulate plant conditions for the evaporation of acidified uranium waste solutions have shown no conditions under which the solubility is limited by this salt.(51)

4.03 Density

$UO_2(NO_3)_2$ - H_2O system

The densities of aqueous solutions of uranyl nitrate from 0 to 90 weight per cent $UO_2(NO_3)_2$ are presented in Table IV-3. From 0 to 55 per cent $UO_2(NO_3)_2$, the densities are given for 25°C.; from 56 to 90 weight per cent $UO_2(NO_3)_2$, the densities are given at the saturation temperature of the solution.(12)

$UO_2(NO_3)_2$ - HNO_3 - H_2O systems

The density of the $UO_2(NO_3)_2$ - HNO_3 - H_2O system (corresponding to the RCU stream) is presented in Table IV-4 as a function of increasing $UO_2(NO_3)_2$ concentration and decreasing HNO_3 concentration as determined at the saturation temperatures of the solutions.(50) The densities at the boiling points of the solutions are given in Figure IV-11,(12)

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and may be calculated for 25°C. by means of the equation in the following paragraph.

$UO_2(NO_3)_2$ - HNO_3 - $NaNO_3$ - H_2O system

The densities of this system at 25°C. are given in grams/cu. cm. by the following equation:[18]

$$d = 1.0012 + 0.3177\, \underline{M}_{UO_2(NO_3)_2} + 0.03096\, \underline{M}_{HNO_3} + 0.051\, \underline{M}_{NaNO_3} \quad \text{---(1)}$$

This equation gives an accuracy of ± 1 per cent up to a concentration of 5 $\underline{M}$ HNO_3. The effect of temperature on the density of this system is shown in the following equation:[18]

$$d_t = 1.0125\, d_{25°C.} + 0.000145\, t - 0.000500\, t\, d_{25°C.} - 0.0036 \quad \text{---(2)}$$

where t = temperature in °C.

Multi-component systems

The densities at 25°C. for aqueous solutions containing phosphates and sulfates in addition to $UO_2(NO_3)_2$, HNO_3, and $NaNO_3$, are given in Table IV-5. These compositions correspond to the approximate concentrations of the aqueous feed, RAF, to the extraction column (see Chapter III).

4.04 Viscosity

$UO_2(NO_3)_2$ - HNO_3 - H_2O system

The viscosity of the $UO_2(NO_3)_2$ - HNO_3 - H_2O system (corresponding to RCU during the final concentration step) is given in Table IV-4. The viscosity shows a regular increase with increasing $UO_2(NO_3)_2$ concentration and exhibits a 20 to 40 per cent increase with a two-fold increase in shear rate.[50]

$UO_2(NO_3)_2$ - HNO_3 - $NaNO_3$ - H_2O system

The viscosities of this system at 25°C. may be calculated by means of the following equation:[18]

$$\log_{10}\eta = 0.9527 + 0.2426\, \underline{M}_{UO_2(NO_3)_2} + 0.0100\, \underline{M}^2_{UO_2(NO_3)_2}$$

$$+ \left[0.0089 - 0.0023\, \underline{M}_{UO_2(NO_3)_2}\right] \underline{M}_{HNO_3}$$

$$+ \left[0.025 + 0.015\, \underline{M}_{UO_2(NO_3)_2} + 0.005\, \underline{M}_{HNO_3} \pm 0.005\right] \underline{M}_{NaNO_3} \quad \text{---(3)}$$

where η = viscosity in millipoises.

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Multi-component systems

The viscosities of multi-component solutions corresponding to RAF solutions are given as a function of temperature in Figure IV-12.[46][88] The viscosities at 25°C. are given in the following table for (a) RAF corresponding to Flowsheet TBP-HW No. 5, (b) the corresponding aqueous phase at the column aqueous feed inlet, and (c) this same aqueous phase near the bottom of the extraction section.[25]

Viscosities of RAF, RAFS, and RAW at 25°C.

Phase	Composition, M						Density, G./Ml.	Viscosity, Millipoises
	UO_2^{++}	$PO_4^{\equiv}$	$SO_4^{\equiv}$	Na^+	HNO_3	Total NO_3^-		
RAF, TBP-HW No. 5	0.188	0.16	0.18	2.65	3.0	5.19	1.2826	16.4
Aqueous phase at feed inlet, RAFS	0.152	0.10	0.12	1.75	3.2	4.71	1.2407	14.3
Aqueous phase at bottom of extn. section	0.015	0.10	0.12	1.75	3.1	4.34	1.1976	13.2

4.05 Hydrogen ion concentration, pH

$UO_2(NO_3)_2$ - H_2O system

The pH's for this system at 25°C. are given in Table IV-3 for solutions from 0 to 43 weight per cent $UO_2(NO_3)_2$.[12]

$UO_2(NO_3)_2$ - HNO_3 - H_2O system

The pH values of solutions from -0.2 to +0.6 M HNO_3 are given at four levels of uranyl nitrate concentration in Figure IV-13.[20] Sodium nitrate has little effect on the pH of acid solutions of $UO_2(NO_3)_2$. Neutral or acid-deficient solutions of $UO_2(NO_3)_2$, however, show a lowering of pH by about 0.12 pH units per mole of $NaNO_3$.[20]

Multi-component systems

The effect of acid concentration on the stability of multi-component systems (RAF solutions) is illustrated in Figure IV-14.[33][61] In the range of HNO_3 concentrations required to maintain stable RAF solutions, the pH is approximately zero.

4.06 Saturation temperature

$UO_2(NO_3)_2$ - H_2O system

The temperature-solubility phase diagram for this system is given in Figure IV-10.[12]

$UO_2(NO_3)_2$ - HNO_3 - H_2O system

The temperature-solubility phase diagram for this system is given in Figure IV-10 for HNO_3 concentrations ranging from 0 to 3 M.

The $UO_2(NO_3)_2$ - HNO_3 - H_2O system,[21] which constitutes the aqueous uranium effluent (RCU: 0.26 M $UO_2(NO_3)_2$, 0.3 M HNO_3) from the RC Column, is illustrated in Figure IV-15A, where saturation temperature is given as a function of the degree of concentration. Figure IV-15B gives a curve showing the per cent removal of the HNO_3 during the concentration operation. The saturation temperature and composition of RCU are presented in Table IV-4 as a function of degree of concentration from 50 to 89 weight per cent $UO_2(NO_3)_2$.

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$UO_2(NO_3)_2$ - HNO_3 - $NaNO_3$ - H_2O system

Segments of a phase diagram for this system are shown in Figure IV-16. In the concentration range covered, the effect of uranyl nitrate is seen to decrease with increasing nitric acid concentration. The component freezing out along the 0.0 and 1.0 M curves is ice while the component freezing out along the 2.0, 3.0, 4.0, and 5.0 M HNO_3 curves is $NaNO_3$.[85]

Multi-component systems

Multi-component solutions, approximating the composition of aqueous feed to the RA Column, are listed in Table IV-5 where saturation temperatures are given as a function of the concentrations of the various constituents over a range of uranium concentrations from 0.15 to 0.37 M.

The saturation temperature of an RAF solution corresponding to Flowsheet TBP-HW No. 5 (TBP-HW No. 4 before concentration) is shown in Figure IV-15A as a function of the degree of concentration, and in Figure IV-14 the solubility of this multi-component system as a function of acid content is presented for varying Na-to-U ratios when the phosphate, sulfate, and uranium molarities are approximately equal, as stipulated in the flowsheet.

4.07 Boiling points

$UO_2(NO_3)_2$ - H_2O systems

The boiling points of aqueous solutions of $UO_2(NO_3)_2$ are given in Table IV-3 and in Figure IV-11.[12][59]

$UO_2(NO_3)_2$ - HNO_3 - H_2O system

The boiling points of this system from 0 to 80 per cent $UO_2(NO_3)_2$ and from 0 to 60 per cent HNO_3 are given in Figure IV-11.[12]

The boiling points of the $UO_2(NO_3)_2$ - HNO_3 - H_2O system, corresponding to concentrated RCU, are given in Table IV-4 as a function of the degree of concentration from 50 to 89 weight per cent $UO_2(NO_3)_2$. (See Chapter VII for a detailed description of the RCU concentration procedure.)

4.08 Specific heat

$UO_2(NO_3)_2$ - H_2O system

The specific heats of uranyl nitrate solutions from 0 to 4 M (71 weight per cent $UO_2(NO_3)_2$) are given in Figure IV-17.[91] Since the saturation concentration is 2.6 M (56 per cent) at 25°C., specific heat values above that concentration include solid $UO_2(NO_3)_2 \cdot 6H_2O$ which has crystallized out. The specific heat of solid $UO_2(NO_3)_2 \cdot 6H_2O$ at 25°C. is 0.23 calorie/(gram)(°C.). Figure IV-17 includes, also, specific heat curves for HNO_3 and $NaNO_3$.

4.09 Refractive index

$UO_2(NO_3)_2$ - H_2O system

The refractive indices for this system from 0 to 55 weight per cent $UO_2(NO_3)_2$ are included in Table IV-3.[12]

4.10 Molarity - weight per cent conversion

$UO_2(NO_3)_2$ - H_2O system

Conversion curves for $UO_2(NO_3)_2$ and $UO_2(NO_3)_2 \cdot 6H_2O$ are given in Figure IV-18.[12] In view of the very small contribution which nitric acid makes towards the density of solutions of moderate uranyl nitrate concentration (see equation (1) under 4.03, above), the conversion curves of Figure IV-18 may be used for solutions containing up to 2 M HNO_3 with an error of only a few per cent.

If the density of any system is known, the conversion of concentration units for any of the components may be obtained from the general equation:

$$\text{Weight per cent} = \text{Molarity} \times \frac{\text{Formula weight}}{10 \times \text{Density}}$$

where the density (in grams/cu. cm.) and molarity are determined at the same temperature.

5. Aqueous Mixed Sodium Salt Solutions

5.1 Introduction

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The highly acidic aqueous raffinate from the RA Column is neutralized with sodium hydroxide and is then concentrated and stored underground. The degree of concentration possible is directly governed by the physical properties of the resultant concentrate as discussed in the following paragraphs.

5.2 RAW

5.21 Composition

The estimated flowsheet (e.g., TBP-HW No. 4) compositions for RAW are based on the assumption that the aqueous feed to the RA Column is prepared from a slurry of sludge and supernate combined in the ratio existing in the underground storage tanks. However, aqueous feed streams prepared from sludge slurried with water, or prepared directly from concentrated supernate, are conceivable and, as such, represent limiting cases. The composition of RAW may thus vary over wide ranges of concentration as the RAF composition fluctuates between these limits. The variation in RAW composition with flowsheet conditions is shown in Table IV-6 as a function of the RA Column aqueous feed composition.[43][45][56] These compositions do not include any contribution from the RO Column aqueous wastes.

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5.3 Neutralized RAW

5.31 Composition

The compositions of neutralized RA Column aqueous waste for flowsheets TBP-HW No. 4 and No. 5 are given in the following table:[48]

Composition and Saturation Temperature of Neutralized and Concentrated RAW as a Function of Degree of Concentration

Per Cent of RAW Volume					
TBP-HW No. 4 Flowsheet	TBP-HW No. 5 Flowsheet	Saturation Temp., °C.	Na_2SO_4 G./L.	Na_3PO_4 G./L.	$NaNO_3$ G./L.
100	77	14	31.0	25.9	332
80	62	18	38.8	32.4	415
63	49	26	49.2	41.1	527
47	37	36	65.9	55.1	706
45	35	39	68.9	57.6	738
44	34	80	70.5	58.9	755

5.32 Physical properties

5.321 Effect of degree of concentration

The physical properties of neutralized waste are given in Table IV-7 as a function of the degree of concentration[48] which is expressed as the percentage of the volume of RAW and of the original volume of the waste removed from the underground storage tanks.

5.322 Saturation temperatures

The relationship between saturation temperatures and degree of concentration is shown in Table IV-7 and Figure IV-19. The optimum volume of concentrated waste has a saturation temperature of 36°C., representing about 47 per cent of the volume of the RAW (Flowsheet TBP-HW No. 4) and 75 per cent of the volume of the parent stored uranium wastes. Concentration below this point greatly increases the freezing point without materially decreasing the waste volume.

An increase in the sulfate concentration of up to three times the nominal TBP-HW No.4 Flowsheet RAW concentration of 0.21M does not appreciably change saturation temperatures. However, an increase in the phosphate concentration (0.18M under TBP-HN No.4 Flowsheet conditions), either in the presence or absence of a corresponding increase in sulfate concentration, markedly raises the saturation temperature as shown in the following table:(63)

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Saturation Temperature and Boiling Point of Neutralized

RAW Concentrated to 50% of Original Volume (TBP-HW No. 4)

Effect of Added Salts

Salt Added	Saturation Temperature, °C.	Boiling Point, °C.
None	36	111
3-fold $PO_4^{\equiv}$ (a)	46	111
3-fold $SO_4^{=}$ (b)	38	111
3-fold $PO_4^{\equiv}$ (a) plus 3-fold $SO_4^{=}$ (b)	74	111

Notes: (a) Na_3PO_4 added to make the $PO_4^{\equiv}$ concentration 0.54M (i.e., 3 times the TBP-HW No. 4 Flowsheet $PO_4^{\equiv}$ concentration of 0.18M).

(b) Na_2SO_4 added to make the $SO_4^{=}$ concentration 0.63M (i.e., 3 times the TBP-HW No. 4 Flowsheet $SO_4^{=}$ concentration of 0.21M).

5.323 Boiling points

The boiling points of neutralized, concentrated RAW are shown in the table below as a function of the degree of concentration:[63]

Boiling Point of Neutralized RAW (TBP-HW No. 4)

Waste Volume		
Per Cent of Neutralized RAW	Per Cent of Stored Uranium Waste	Boiling Point, °C.
100	159	102
70	111	105
60	95	107
50	79	111
45	71	112
40	63	114

See under 5.322, above, for the effect of added salts on the boiling point of RAW concentrated to 50 per cent of its volume.

5.324 Density

The density of concentrated, neutralized aqueous waste is given in Table IV-7 as a function of degree of concentration.

5.325 pH

Wastes neutralized with 50 per cent NaOH solution, in accordance with flowsheet requirements, exhibit pH's of 11.5 and above.[63] The subsequent concentration step affects the pH of the concentrate only slightly, as shown in Table IV-7.[48] The slight effect on pH is due to the liberation of some NH_3 during the concentration step, as discussed in Chapter XII.

5.326 Viscosity

The viscosity of neutralized, concentrated RAW is given in Table IV-7 as a function of degree of concentration.

5.327 Specific heat

The specific heat of neutralized, concentrated RAW is also given in Table IV-7 as a function of temperature at two degrees of concentration.

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6. Reducing Agents

6.1 Ferrous ammonium sulfate

6.11 Introduction

Ferrous ammonium sulfate hexahydrate is a green, crystalline compound which is introduced as a 0.05M aqueous solution in the RA scrub stream for the purpose of reducing plutonium to the organic-insoluble Pu(III) state. The role of the reducing agent in the RA Column is discussed in Section A of this chapter.

6.12 Physical properties

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Formula	$FeSO_4.(NH_4)_2SO_4.6H_2O$
Molecular weight	392.15 (as the hydrate) 284.0 (as the anhydrous salt)
Melting point	Decomposes at about 100°C.

Solubility in Water[4]

Temperature, C.	G. $FeSO_4.(NH_4)_2SO_4$ Per 100 G. H_2O	$FeSO_4.(NH_4)_2SO_4$, Weight Per Cent
0	12.5	11.1
15	20.0	16.7
25	30.0	23.1
40	33.0	24.8
50	40.0	28.6
70	52.0	34.2

Density of Aqueous Solutions[7]

$FeSO_4.(NH_4)_2SO_4$, Weight Per Cent	$d_4^{16.5}$	d_4^{25}
2	1.015	1.013
4	1.032	1.029
6	1.048	1.045
8	1.065	1.062
10	1.082	1.080
12	1.100	1.098
14	1.118	1.116
16	1.136	---
18	1.154	---

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6.2 Sulfamic acid

6.21 Introduction

Sulfamic acid, or rather the sulfamate ion, $NH_2SO_3^-$, is used in the RA Column as a holding reductant, where its function is to destroy nitrite ion, and hence prevent the oxidation of Fe(II) to Fe(III) by nitrite ion before the plutonium is completely reduced to Pu(III). Section A of this chapter contains a discussion of the chemistry of reducing agents in the RA Column.

Sulfamic acid is introduced into the RA Column as a 0.10M solution in the aqueous scrub stream.

6.22 Physical properties

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Formula	HSO_3NH_2
Molecular weight	97.09
Appearance	White crystalline solid, non-volatile, non-hygroscopic, odorless[2]
Melting point	205°C., with decomposition[2]
Heat liberated upon dissolution in water	5800 calories per mole

Solubility of Sulfamic Acid in Water[1]

Temperature, °C.	G. Sulfamic Acid Per 100 G. H_2O	Sulfamic Acid, Weight Per Cent
0	14.68	12.8
10	18.56	15.7
20	21.32	17.6
30	26.09	20.7
40	29.49	22.8
50	32.82	24.7
60	37.10	27.1
70	41.91	29.5
80	47.08	32.0

All ordinary salts of sulfamic acid are extremely soluble in water, being in most instances more soluble than the corresponding nitrate or sulfate.

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6.23 Chemical properties

6.231 Acid strength

Sulfamic acid is considered a strong acid, being stronger than phosphoric acid, though weaker than nitric acid.[2] Its pH as a function of concentration is given in the following table.

pH of Aqueous Solutions of Sulfamic Acid

Concentration of Sulfamic Acid, M	pH
1.0	0.41
0.75	0.50
0.50	0.63
0.25	0.87
0.10	1.18
0.05	1.41
0.01	2.02

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6.232 Hydrolysis

Sulfamic acid hydrolizes according to the equation:[1][67]

$$NH_2SO_3^- + H_2O \rightleftharpoons NH_4^+ + SO_4^=$$

The hydrolysis rate at room temperature is slow (about 0.1 per cent per day for either a 1M sulfamic acid or a 1M sulfamic acid—1M HNO_3 solution). A similar rate is found for a 1 M sulfamic acid—1M Al $(NO_3)_3$—0.3M HNO_3 solution. The hydrolysis is a first-order reaction with rate constants at 80°C. of 0.0456 and 0.0825 per hour (i.e., 4.56 and 8.25 per cent decomposed per hour) for 1 and 10 per cent solutions, respectively.[1][14]

6.233 Other reactions

Sulfamate ion reacts rapidly, smoothly, and completely with nitrous acid to give N_2:[67]

$$HNO_2 + NH_2SO_3^- \longrightarrow N_2 + SO_4^= + H_2O + H^+.$$

Warm, concentrated nitric acid reacts with sulfamic acid to produce N_2O gas.[14]

Dichromate, permanganate, and ferric chloride do not attack sulfamic acid.[1][13][67]

A 0.1M sulfamic acid solution ozonated for six hours at room temperature decomposes to the extent of only a few per cent.[28]

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6.3 Ferrous sulfamate

6.31 Introduction

Ferrous ion is used in the TBP process for the selective reduction of plutonium to the organic-insoluble Pu(III) state (see Section A), and is supplied by commercially available ferrous ammonium sulfate.

An alternative to ferrous ammonium sulfate is the combined reducing agent and holding reductant, ferrous sulfamate. This substance is not commercially available, and if required, must be prepared on the plant site.

6.32 Preparation

Ferrous sulfamate is prepared from iron powder and an aqueous solution of sulfamic acid by the following reaction:[19][8]

$$Fe + 2\ HSO_3NH_2 \rightarrow Fe(SO_3NH_2)_2 + H_2 + 24{,}600 \text{ calories}$$

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6.33 Physical properties of ferrous sulfamate

Formula	$Fe(SO_3NH_2)_2$
Molecular weight	248.03
Appearance	The 2.5 M solution is greenish-blue in color.[19]
Solubility	The saturation concentration in water is in the range of 3.6 to 3.8 M at 25°C.[19]

6.34 Reactions and stability

High pH contributes to the stability of sulfamate ion towards hydrolysis, while low pH is necessary for the stability of ferrous ion towards air oxidation and consequent precipitation. The stability of ferrous sulfamate toward ferric precipitation is satisfactory upon maintaining the pH at 2 or slightly less with a 2 to 3 per cent excess of sulfamic acid.[19] The over-all stability of a ferrous sulfamate solution maintained at a pH of 2 in a vessel containing an inert-gas blanket is limited by the rate of hydrolysis of sulfamate ion. This rate, as reported in 6.232, above, is approximately 0.1 per cent per day at room temperature, and increases to over 4 per cent per hour at 80°C. The total amount of sulfate ion in the solution due to hydrolysis will be the sum of that produced during the preparation of the ferrous sulfamate (approximately 1 per cent of the initial sulfamic acid) plus that produced on aging.

The reaction between sulfamate ion and nitrous acid, described under sulfamic acid (under 6.233, above), is the reaction which prevents the oxidation of Fe(II) to Fe(III) through an autocatalytic mechanism involving

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nitrite ion.[67] In 5.0 M HNO_3, where oxidation of Fe(II) to Fe(III) is normally rapid, sulfamate ion maintains the half-life of Fe(II) in the range of 30 to 50 hours.[37]

7. Interfacial Tension and Phase Disengaging Time

7.1 Introduction

The process of liquid-liquid countercurrent extraction involves intimate contact between two essentially immiscible liquids, during which time the solute is transferred from one phase to the other across the phase boundary between the two systems. This desired contact is obtained in the Redox process by dispersing in the continuous phase fine droplets of the organic phase, which, owing to the specific gravity differential between the phases, rise vertically through the more dense descending aqueous phase. Interfacial tension in such a system, analogous to surface tension in distillation and absorption processes, influences the size of the droplets of the discontinuous phase. Smaller droplets are more easily formed with systems of lower interfacial tension, the droplet diameter being proportional to the interfacial tension. Small droplet diameters in turn mean increased interfacial area, resulting in increased solute mass transfer rates across the interface. The final result is manifested in lowered H. E. T. S. and H. T. U. values.

Too fine a dispersion, however, which may result in the formation of an emulsion, is not desirable, owing to unduly increased difficulties of phase separation which outweigh any advantages resulting from the increased interfacial area.[5]

The determination of the emulsion-forming properties of a system is made by measuring the time required for the phases to disengage. The disengaging time correlates approximately with extraction column flooding capacity and entrainment losses. There seems to be no indirect method of determining disengaging times, since no reliable experimental correlation has been found between interfacial tension, density, viscosity, etc., of process streams and their disengaging times.

7.2 Interfacial tension

Interfacial tensions between solvent (15 volume per cent TBP in Deobase) and aqueous process solutions have been determined at 25°C. Data on typical systems corresponding to TBP-HW No. 4 Flowsheet conditions are given in the following table.[16]

Organic-Aqueous Interfacial Tensions

Column	Interfacial Tension, Dynes/Cm. Scrub Inlet	Feed Inlet	Extractant Inlet
RA	16.4	15.1	14.7
RC	---	---	14.7

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The variation in interfacial tension with a change in temperature from 15° to 75°C. was found to be negligible, falling within the limits of experimental error.

7.3 Disengaging time

Disengaging time has been arbitrarily defined as the time required for the separation of an organic from an aqueous phase, when the two have been combined in the appropriate ratio (usually the flowsheet ratio) to a total volume of 50 ml., and inverted in a stoppered, 50-ml. graduated cylinder at the rate of once per second for 20 seconds.[86]

No direct correlation has been established among phase densities, interfacial tensions, and disengaging times, but it has been observed that no appreciable aqueous entrainment in the organic effluent occurs during RC Column runs when the organic holdup time is greater than 7.5 times the disengaging time (TBP-HW No. 4 Flowsheet).[56] Since the organic residence time in the RC Column phase disengaging section is about 11 minutes, aqueous entrainment in the organic phase is not expected to occur unless the disengaging time markedly exceeds 90 seconds.

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Disengaging times measured on effluent stream samples from typical RA and RC Column pilot-plant runs average 40 to 60 seconds.[56] No significant effects on disengaging times of an RA extraction system have been observed when excess $SO_4^{=}$, $PO_4^{\equiv}$, or NO_3^- were added to the aqueous phase.[39]

7.4 Emulsifying impurities

The presence of emulsifying agents in minute quantities has been noted to cause wide variation in the disengaging times of systems of essentially identical macro-composition. The uranium-monobutyl phosphate complex causes stable emulsions in the RC Column when present in the organic phase in amounts of 0.01 volume per cent or greater.[87] Monobutyl phosphate is, however, quantitatively removed from the organic solvent by continuous countercurrent washing in the RO Column with a dilute carbonate or other wash solution, as discussed in Chapter XI. Dibutyl phosphate does not produce an emulsifying effect in the RC system.[87]

There is some indirect evidence (based on Redox process experience) that small amounts of siliceous matter in the RAF (derived from the Al-Si slug bonding layer or from sand blown into the underground uranium waste storage tanks) may cause emulsification in the RA Column. However, dissolving coating removal waste in the RAF so that the RAF contained approximately 100 p.p.m. silica has (in one experiment) exhibited no significant effect on disengaging times in the RA Column system.[86]

8. Heats of Extraction

In the RA Column system at 25°C., about 1 kilocalorie of heat is liberated per mole of $UO_2(NO_3)_2$ transferred from the aqueous phase to the organic phase under conditions approximating those found at the feed point under TBP-HW No. 4 Flowsheet conditions.[53] The transfer of uranium from

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an aqueous phase into a TBP-diluent mixture involves the breaking of uranium-phosphate and uranium-sulfate complexes, the dehydration of uranyl nitrate, and the formation of TBP-uranyl nitrate coordination bonds. The heat effects of bond breaking and formation are compensating so that the over-all heat of transfer of uranium into TBP is small.

In the RC Column system, about 5 to 6 kilocalories of heat are absorbed per mole of uranium transferred from the organic phase to the aqueous phase, over the range of compositions given in Figure IV-23[53]

C. SOLVENT-AQUEOUS PHASE EQUILIBRIA

The solvent-aqueous phase equilibrium data, which are the subject matter of this section, are presented largely in terms of the distribution ratio concept. The symbol E_a^o, used throughout this section, stands for the organic/aqueous distribution ratio, defined as g./l. solute in the organic phase divided by g./l. solute in the aqueous phase.

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1. Uranium

1.1 Introduction

The successful separation of uranium from plutonium and fission products is dependent upon the distribution ratios of these materials between the organic and aqueous phases as a function of the composition of the phases involved in the transfer system. The following tables and figures illustrate the dependency of uranium distribution upon the process variables and are to be compared with plutonium and fission-product data as given under C2 and C3 of this chapter. For a discussion of the basic principles involved in the TBP process and the choice of optimum operating conditions, reference is made to Section A.

1.2 RA Column system

1.21 Effect of uranium concentration

The effect of uranium concentration on the uranium distribution ratio is a function of the degree of saturation of the organic phase with respect to uranium. Saturation of the organic phase corresponds to complete utilization of the tributyl phosphate by complexing two moles of TBP with one mole of uranium.[24] The theoretical maximum solubility of $UO_2(NO_3)_2$ in 12.5 volume per cent TBP in diluent is 0.22 M.

The quantitative effect of uranium concentration on uranium distribution may be seen from the inter-stage data given in Figure IV-20A where the illustrated compositions approximate TBP-HW No. 4 Flowsheet conditions. The uranium distribution ratio, E_a^o, is seen to increase by a factor of 10 on passing from the concentration at the feed point (0.2 M $UO_2(NO_3)_2$) to that at the bottom of the column.

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Uranium distribution in the scrub section varies markedly with the concentration of uranium present in the organic phase (Figure IV-20B). Scrubbing an organic extract, 48 per cent saturated with uranium, with 3 M HNO_3 gives a uranium distribution ratio (org./aq.) of 5.2; whereas for a solvent 100 per cent saturated with uranium, the distribution ratio at 3 M HNO_3 is 1.0. As the solvent approaches uranium saturation, uranium distribution becomes less highly dependent on the nitric acid concentration.(72)

1.22 Effect of nitric acid concentration

In the absence of the $NaNO_3$ produced by feed neutralization, uranium distribution into the organic phase increases as the aqueous phase nitric acid concentration increases, reaching a maximum value at about 5.5 M HNO_3 (Figure IV-21A). At higher nitric acid concentrations a decrease in the uranium distribution ratio (org./aq.) is noted, presumably because of a decrease in the activity coefficient of HNO_3. The effects of sulfate and phosphate on uranium distribution, also illustrated in Figure IV-21A, are discussed under 1.25, below. As shown in Figure IV-21B, nitric acid in the range of 1 to 4 M has only a slight effect on uranium distribution under Flowsheet TBP-HW No. 4 conditions.

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1.23 Effect of tributyl phosphate concentration

The effect of tributyl phosphate (TBP) concentration on uranium distribution under RA Column conditions is illustrated in the following table. As the TBP concentration is increased from 10 to 15 volume per cent, the uranium distribution ratio (org./aq.) is seen to increase by a factor of about 1.7.(72)

Uranium Distribution in the RA Column System

Effect of TBP Concentration

TBP Concentration, Volume Per Cent	Uranium Distribution Ratio, G.U/L. Organic / G.U/L. Aqueous
10	3
12.5	3.6
15	5

1.24 Effect of diluent

With the hydrocarbons employed as diluents in the TBP process, variations in uranium distribution attributable to the diluent employed are negligible.(58)(35)(40)

1.25 Effect of phosphate and sulfate

The effect of the presence of phosphate and sulfate is to decrease uranium distribution into the organic phase, phosphate being more effective

than sulfate in this respect (Figures IV-21A, IV-22A, and IV-22B). This is especially apparent in the dilute uranium region of the RA Column, where an increase in the phosphate concentration from 0.1 to 0.4 M decreases the uranium distribution ratio, E_a°, by a factor of about 3.[35]

1.26 Effect of butyl acid phosphates

Butyl acid phosphates, undesirable hydrolysis products of TBP, form very strong complexes with uranium.[30][60] The effects of these complexes on uranium distribution under RA Column conditions are not apparent due to the high ionic strength of the aqueous phase and the direction of uranium transfer. In the RC Column system, however, the stability of the complexes prevents the transfer of uranium back into the aqueous phase.[75] (See under 1.34, below.)

1.27 Effect of temperature

The effect of temperature on uranium distribution is shown in Figure IV-23. Over the temperature range of 0° to 60°C., uranium distribution into the organic phase is favored by a decrease in temperature, the effect being greater at low uranium concentrations.[53]

1.28 RA Column equilibrium diagrams

Changes in feed composition resulting from variable sludge and supernate compositions and volume ratios (see Chapter III, Section A) require changes in operating conditions in order to realize maximum processing capacity consistent with acceptable uranium losses. The chemical process variables, H_3PO_4, H_2SO_4, HNO_3, $NaNO_3$, $UO_2(NO_3)_2$, and TBP concentrations, are correlated in Figures IV-24 through IV-27. The correlations are presented on the basis of the equilibrium "constant", K, in the equation representing the mechanism for the extraction of uranium by TBP solutions. The extraction is represented by the reaction:[24]

$$UO_2^{++}(Aq.) + 2NO_3^-(Aq.) + 2TBP(Org.) \rightleftharpoons UO_2(NO_3)_2.2TBP \quad (Org.), \text{--}(1)$$

from which an equilibrium "constant" may be calculated and expressed in the following form (see Section A):

$$E_a^\circ = \left[K^{\frac{1}{2}}NO_3^-(Aq.)\right]^2\left[TBP - 2UN(Org.)\right]^2, \text{ - - - - - - - - -}(2)$$

where E_a° = uranium distribution ratio, $\frac{G.U/L.\ Org.}{G.U/L.\ Aq.}$,

K = equilibrium "constant",

NO_3^- = total nitrate concentration in the aqueous phase, M,

TBP = total tributyl phosphate concentration in the organic phase, M, and

UN = uranyl nitrate concentration in the organic phase, M.

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The curves of Figure IV-24 permit the estimation of the equilibrium "constant", K, for varying concentrations of $SO_4^{=}$, $PO_4^{=}$, $NaNO_3$, and HNO_3. The equilibrium curves of Figures IV-25, IV-26, and IV-27, with parameters expressed in terms of K, may then be used in determining uranium equilibria for an organic phase containing 10, 12.5, or 15 volume per cent TBP in diluent.

The curves of Figure IV-24 agree closely with direct experimental data for $K^{\pm} = 1$, but for $K^{\pm}$ values of 0.5 or 2 an error in Y of about 5 per cent is found at an X value of 100 g./l. of $UO_2(NO_3)_2.6H_2O$. This error drops to zero per cent below an X value of 10 g./l., and may be neglected in most run calculations since the major part of the calculation involves the range below 50 g./l. in the aqueous phase.

As an example, the use of the figures is illustrated for a run made under TBP-HW No. 4 Flowsheet conditions. From the known composition of feed and scrub, the concentrations of $PO_4^{=}$, $SO_4^{=}$, Na^+, and H^+, in the aqueous phase may be calculated to be 0.17, 0.17, 2.71, and 2.64 molar, respectively. The use of these $SO_4^{=}$ and $PO_4^{=}$ concentrations in conjunction with Figure IV-24A gives a K_1 value of 1.25. The value of K_2 is determined from Figure IV-24B using the aqueous phase concentrations of "free" HNO_3 and $NaNO_3$. Converting the H^+ M to "free" HNO_3 (H^+ M - $2SO_4^{=}$ M - $3PO_4^{=}$ M) gives a value of 1.79, which in conjunction with the previously determined $NaNO_3$ concentration permits the value of K_2 (1.15) to be read from the chart. The product of K_1 and K_2 gives a $K^{\pm}$ value of 1.44. The product of the $K^{\pm}$ value and the total NO_3^- concentration in the aqueous waste stream (4.45 M) gives a ($K^{\pm}NO_3^-$) value of 6.41. Interpolation between curves 6 and 7 of Figure IV-26 (parameters expressed in terms of $K^{\pm}NO_3^-$) gives the desired equilibrium line.

1.3 RC Column system

1.31 Effect of uranium concentration

The ionic strength of the RC Column system is much lower than that of the RA system; consequently, the effect of uranium concentration on uranium distribution is more pronounced. This is illustrated in Figure IV-28. In the absence of HNO_3 the uranium distribution ratio (org./aq.) increases a thousand-fold as the uranium concentration is increased from 1 to 50 g./l. In the presence of 10 g. HNO_3/l. the effect is reduced due to the salting action of nitric acid[32] [38] (see 1.32, below).

1.32 Effect of nitric acid concentration

By referring to Figure IV-28 it may be seen that HNO_3 increases uranium distribution into the organic phase markedly in the dilute region of the RC Column. At a 0.01 M $UO_2(NO_3)_2$ concentration in the aqueous phase the uranium distribution ratio (org./aq.) increases a thousand-fold as the aqueous phase nitric acid concentration is increased from 0 to 10 g./l.

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1.33 Effect of tributyl phosphate concentration

Increasing the concentration of TBP in the solvent increases uranium distribution into the organic phase. At 100 g./l. $UO_2(NO_3)_2.6H_2O$ in the equilibrated aqueous phase with no HNO_3 present, uranium distribution into the organic phase is increased by a factor of 2 as the TBP concentration is increased from 10 to 15 volume per cent.[36] The effect increases slightly with decreasing uranium concentration.

1.34 Effect of butyl acid phosphates

The deleterious effect of dibutyl phosphate on uranium distribution in the RC Column may be seen from the following data in which an organic phase (RAX), consisting of 15 volume per cent TBP in Deobase containing varying amounts of dibutyl phosphate, was equilibrated with an equal volume of aqueous solution containing 1 or 10 g./l. $UO_2(NO_3)_2.6H_2O$.[52]

Uranium Distribution in the RC System

Effect of Dibutyl Phosphate (DBP)

Organic Phase DBP, G./L.	Aqueous Phase UNH, G./L.	Uranium Distribution Ratio, E_a^o
0.0	1	0.002
0.2	1	0.41
1.0	1	21.0
0.0	10	0.02
0.2	10	0.07
1.0	10	0.22

The presence of small quantities of DBP thus prevents the stripping of uranium back into the aqueous phase, the effect increasing with decreasing uranium concentration.

The complex formed between uranium and monobutyl phosphate is a precipitate insoluble in either phase and, under dilute RC Column conditions, results in the formation of stable emulsions or interfacial scum.[65]

1.35 Effect of temperature

The effect of an increase in temperature is to decrease uranium distribution into the organic phase (Figure IV-23). The effect is relatively slight, an increase from 20° to 40°C. decreasing the uranium distribution only by a factor of about 1.5 at uranium concentrations of about 0.1 M.[53]

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1.36 RC Column equilibrium diagrams

Equilibrium lines for RC Column operation, with 10, 12.5, and 15 volume per cent TBP in the feed, are shown in Figures IV-29 through IV-31. The nitric acid concentrations which are given permit the estimation of uranium equilibria under a wide range of conditions.

The slopes of the equilibrium lines decrease from about 3 to 1 as the nitric acid concentration is increased from 0 to 30 g./l. in the aqueous phase. Similarly, a decrease in the slope of each equilibrium line is found above approximately 30 g./l. $UO_2(NO_3)_2.6H_2O$ in the aqueous phase.

2. Plutonium

2.1 Introduction

Although the bismuth phosphate process uranium waste contains only 1 to 2 per cent of the plutonium initially associated with the uranium, a decontamination factor of about 40 is required in the TBP process to meet the specifications of a uranium-to-plutonium weight ratio of 10^7 in the uranium product. This degree of decontamination is attained by the reduction of Pu(IV) in the RA Column to the essentially non-extractable Pu(III). The reducing agent, Fe(II), is added to the scrub stream along with sulfamate ion which acts as a holding reductant to prevent the premature oxidation of Fe(II) to Fe(III) in the column. The small amount of sulfate ion introduced into the scrub stream by the addition of Fe(II) as ferrous ammonium sulfate has no appreciable deleterious effect on uranium extraction. Consequently, chemical addition to the scrub solution is made in the form of ferrous ammonium sulfate and sulfamic acid instead of the more difficultly prepared ferrous sulfamate.

The following paragraphs show the dependency of plutonium distribution on the several process variables. In many cases the data for Pu(III) are unavailable because of its low distribution into the organic phase.

2.2 Effect of oxidation state

A comparison of the distribution ratios of Pu(III), (IV), and (VI), as illustrated in Figure IV-32, shows the distribution ratio (org./aq.) of Pu(IV) from an aqueous phase containing 1.5 M HNO_3 to be higher than those of Pu(VI) and (III) by factors of 2 and 32, respectively. The distribution ratio of Pu(III) is of particular interest in the TBP process since it is the oxidation state encountered in the RA Column. Its distribution ratio, E_a^o (org./aq.), is low -- on the order of 0.01 at an aqueous phase concentration of 0.0 M $UO_2(NO_3)_2$ and 1 M HNO_3.[75] However, since the presence of trace amounts of the more easily extractable Pu(IV) will give an apparent high Pu(III) distribution ratio, this experimentally measured value for Pu(III) distribution may be considerably in error.

2.3 Effect of complexing agents

The following data show the effect of butyl acid phosphates on Pu(IV) distribution.[27][36]

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Effect of Butyl Acid Phosphates on Pu(IV) Distribution

Aqueous phase: 3 M HNO_3. Equal-volume contacts at 25°C.

Organic Phase	Pu(IV) E
15 vol. % TBP in Deobase	4.63
1 vol. % BAP*, 15 vol. % TBP in Deobase	237
0.1 vol. % BAP*, 15 vol. % TBP in Deobase	63
1 vol. % BAP* in benzene	274
0.1 vol. % dibutyl phosphate in benzene	24.3
0.1 vol. % monobutyl phosphate in benzene	2.1**

* Equimolar mixture of monobutyl and dibutyl phosphates.

** Precipitate containing the bulk of the plutonium formed at the interface.

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In the presence of 0.4 M $UO_2(NO_3)_2$, Pu(IV) distribution into the organic phase is increased only by a factor of 6 by the presence of 1 per cent butyl acid phosphates.[27]

The distribution of Pu(IV) is greatly increased in favor of the aqueous phase in the presence of fluosilicate, the distribution ratio being comparable to that found for Pu(III).[25] The effect of fluoride ion on Pu(IV) distribution is very similar to that of fluosilicate.[9][36][81] In view of the corrosive properties of fluoride ion, however, neither fluosilicates nor fluorides are contemplated for plant use.

2.4 Effect of uranium concentration

Plutonium distribution into the organic phase is depressed in the presence of uranium due to the higher specificity of the TBP-uranium complex.[77] With an aqueous phase 3 M in HNO_3, the Pu(IV) distribution ratio (org./aq.) decreases by a factor of 6 as the degree of uranium saturation of the organic phase is increased from 35 to 80 per cent (Figure IV-33).

2.5 Effect of nitric acid concentration

The effect of nitric acid is to salt plutonium into the organic phase and, as illustrated in Figure IV-33, the effect is pronounced at low uranium concentrations. With an organic phase 40 per cent saturated with uranium, the Pu(IV) distribution ratio (org./aq.) increases from 0.7 to 4.6 as the HNO_3 concentration in the aqueous phase is increased from 1.5 to 5.0 M. This effect, however, is greatly suppressed as the uranium concentration in the solvent nears saturation. The relative salting effect of nitric acid on Pu(III), Pu(IV), and Pu(VI) is compared in Figure IV-32 for Pu distribution in the absence of uranium.

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2.6 Effect of tributyl phosphate concentration

Plutonium distribution into the organic phase increases with increasing TBP concentration. The following data show the effect of TBP concentration on Pu(IV) and Pu(VI) distribution.(75)

Effect of TBP Concentration on Plutonium Extraction

Aqueous Phase: 1.85 M HNO_3, Pu tracer.
Organic Phase: TBP- Gulf BT Mixtures.
Temperature: 20°C.

TBP Concentration, Volume Per Cent	Pu Distribution Coefficient (E_a^o) Pu(IV)	Pu(VI)
2.1	0.04	0.04
5.1	0.31	0.21
10.3	1.45	0.58
15.4	1.90	0.95

3. Fission Products

3.1 Introduction

Successful operation of the TBP process is dependent upon the separation of uranium from fission products and plutonium. The following data show the effects of operating variables on fission-product distribution. (See C1 and C2, above, for uranium and plutonium distribution data.) Fission-product distribution ratios were determined as the ratios of the co./min./ml. of the equilibrated phases. However, to make them comparable to uranium and plutonium distribution data, they are expressed as $\frac{\text{g./l. organic phase}}{\text{g./l. aqueous phase}}$ and will henceforth be designated by the symbol E_a^o. It is to be understood that actual fission-product concentrations have not been determined as g./l.

3.2 Typical fission-product distribution ratios

Representative distribution ratios for gross beta radioactivity and the individual fission products ruthenium, cerium, zirconium, and niobium at the feed point and second scrub stage under conditions approximating those in the RA Column ($PO_4^{\equiv}$ and $SO_4^{=}$ absent) are shown in the table below:(77)

Radioactivity	Distribution Ratio, E_a^o At Feed Point	At Second Scrub Stage
Gross Beta	0.0017	0.11
Ru	0.0045	0.22
Ce	0.00035	0.0058
Zr	0.0064	0.022
Nb	0.00035	- - -

Feed -	0.5 M $UO_2(NO_3)_2$, 3 M HNO_3
Extractant -	15 volume per cent TBP in Varsol, 0.15 M HNO_3
Scrub -	3 M HNO_3
Vol. ratio -	Feed: Extractant: Scrub = 3:10:2

3.3 Effect of uranium concentration

The fission-product distribution ratios are given in Figure IV-34 as a function of the final uranium concentration in the organic phase. The extraction of gross fission products into the organic phase (30 volume per cent TBP in Gulf BT) decreases by a factor of 10 as the degree of uranium saturation of the solvent is increased from 35 to 80 per cent.[81] The same effect may be seen in Figure IV-35, where gross beta and gamma distribution ratios are shown for an extractant consisting of 10.7 volume per cent TBP in methylcyclohexane.[9] As discussed under 3.4, below, the distribution ratios are lower by a factor of 5 to 10 in the latter case due to the lower concentration of TBP.

Ruthenium distribution and, to a lesser extent, zirconium distribution are highly dependent upon the degree of uranium saturation of the solvent as shown in Figure IV-34. Thus, from the standpoint of effective decontamination in the extraction section of the RA Column, it is desirable to maintain the degree of saturation of the solvent with respect to uranium at 50 per cent or greater at the feed point. TBP-HW No. 4 and 5 Flowsheets operate with 51 per cent uranium saturation of the solvent at the feed point and about 8 per cent uranium reflux in the scrub section.

3.4 Effect of nitric acid concentration

The distribution ratios of gross beta and gamma radioactivities into the organic phase from an aqueous phase containing only uranyl nitrate and nitric acid, as shown in Figures IV-35 and IV-36, increase by factors of 5 and 21, respectively, with an increase in the HNO_3 concentration of the aqueous phase from 1.0 to 5.0 M. Ruthenium[75] and cerium[72] distribution ratios show only a small increase with increasing nitric acid concentration, whereas the zirconium[75] distribution ratio, E_a^o, increases from 0.08 to 0.72 over the range of 0.0 to 5.0 M HNO_3 when extracted from aqueous solutions by means of 15 volume per cent TBP. Concentrations of nitric acid in the feed as low as 1.0 M, to take advantage of the high D. F. obtainable, are not permissible due to the possibility of uranyl phosphate precipitation in feed solutions containing relatively high concentrations of uranyl ion (see Section B). Moreover, in the presence of process concentrations of sulfate and phosphate ion (approximately 0.26 M in TBP-HW No.4 Flowsheet) aqueous-soluble uranium complexes are formed which make high concentrations (up to 5 M) of nitric acid desirable in the aqueous phase in order to maintain the uranium distribution ratio, E_a^o, at a value consistent with allowable uranium waste losses. The upper limit to the aqueous nitric acid concentration in the feed occurs in the range of 4 to 7 M depending upon the sodium ion concentration, since acid

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concentrations appreciably greater than this result in the precipitation of sodium nitrate and the reduction of the uranium distribution ratio (see Section B). The TBP-HW No. 4 Flowsheet[43] specifies 2.0 M HNO_3 in the scrub. This, when mixed with feed in the flowsheet ratio, results in an aqueous phase at the feed point approximately 2.5 M in free HNO_3. This concentration is a compromise which takes into account (a) fission-product decontamination, (b) uranium waste losses, (c) column operability, (d) nitric acid consumption, and (e) final aqueous waste volumes.

3.5 Effect of TBP concentration

The distribution of fission products into the organic phase decreases as the concentration of TBP in the diluent decreases at constant uranium saturation of the solvent.[9] This effect is illustrated in Figure IV-36. Despite the lower fission-product distribution ratio, E_a^o, with a solvent containing 5.4 per cent TBP as shown in Figure IV-36, TBP-HW No. 4 Flowsheet[43] specifies 12.5 volume per cent TBP as the extractant, chiefly in order to make possible a satisfactorily low RAX flow rate, which leads to better column operation and higher processing capacity.

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3.6 Effect of diluent

The available data indicate that the choice of diluent, with the exception noted below, will have no significant effect on fission-product decontamination. This conclusion follows from the lack of correlation between the physical and chemical properties of the diluent and the observed decontamination.[77][53][55] For instance, no detrimental effect on decontamination is noted in the use of TBP-CCl_4 mixtures containing aliphatic unsaturates, cyclic unsaturates, and aromatics.[55] However, nitration products of diluents high in aromatic and olefin content are reported to have a deleterious effect on fission-product distribution, decreasing the decontamination factor of gamma radioactivity by a factor of 15 and beta radioactivity by a factor of about 2 on the basis of one extraction and 3 scrub stages.[57] Nitration products that may be formed in the organic stream upon continued use of solvent are removed by scrubbing with caustic and/or carbonate solution followed by washing with water, (see Chapter XI).

3.7 Effect of dibutyl phosphate

Small concentrations of DBP cause an "irreversible" extraction of some fission products, principally zirconium. Extractions from Hanford dissolver solution with 12.5 volume per cent TBP in CCl_4, to which 0.0, 0.01, 0.1, and 1.0 volume per cent DBP were added, gave over-all gamma-emitting fission-product distribution ratios, E_a^o, of 1.7×10^{-3}, 0.011, 0.070, and 0.41, respectively. Beta-emitting fission-product distribution ratios, E_a^o, were 8.4×10^{-4}, 2.5×10^{-3}, 0.014, and 0.033, for the same runs.[55] Cerium and ruthenium are unaffected by these concentrations of DBP; over-all decontamination factors of about 10^5 based on one extraction and 3 scrub stages, have been obtained for each at both zero and one per cent DBP. Ammonium fluosilicate tends to nullify the deleterious effect of DBP on fission-product decontamination,[57] but, due

to the corrosion problems attending the use of fluosilicate, the removal of DBP in the RO Column is relied upon to circumvent the problem.

3.8 Effect of complexing agents

A comparison of the effects of various aqueous-soluble complexing agents on fission-product decontamination is illustrated in Table IV-8. The distribution of zirconium into the organic phase upon extraction is decreased about one hundred-fold by 0.1 M $PO_4^{\equiv}$ ten-fold by 0.01 M $SiF_6^{=}$ and six-fold by 0.1 M $SO_4^{=}$.[53] Little effect on ruthenium distribution is noted. However, after 3 scrub stages the over-all decontamination factors appear to be only slightly improved by the complexing agents. Oxalate ion is as effective as fluosilicate for zirconium decontamination.[9]

4. Nitric Acid

4.1 Introduction

Nitric acid transfer occurs in a manner analogous to that of uranium. However, the TBP-HNO_3 complex is less stable than the TBP-$UO_2(NO_3)_2$ complex, and as a consequence, uranium has a back-salting effect on nitric acid which may be interpreted as a competition between uranyl nitrate and nitric acid molecules for the TBP. The following data illustrate the dependency of HNO_3 distribution on the process variables.

4.2 Effect of uranium concentration

Nitric acid transfer into the organic phase decreases with an increase in uranium concentration (Figures IV-37 and IV-38). A 3-fold decrease in the nitric acid distribution ratio (org./aq.) is noted as the uranium concentration is increased from 0.02 to 0.2 M. The effect is similar under both RA and RC Column conditions.[24][35]

4.3 Effect of nitric acid concentration

Inspection of Figure IV-37 shows that the HNO_3 distribution ratio, E_a^o, decreases with increasing nitric acid concentration (at least up to 4 M) under RA Column conditions. This effect is similar to the saturation effect noted for uranium (Figure IV-20B). The HNO_3 distribution ratio is independent of nitric acid concentration under RC Column conditions (Figure IV-38).

4.4 Effect of tributyl phosphate concentration

A linear relationship is found between HNO_3 distribution ratios and TBP concentrations between 10 and 15 volume per cent.[35] The following data, which were obtained under RA Column conditions, show a 1.5-fold increase in the HNO_3 distribution ratio (org./aq.) over the 10 to 15 volume per cent TBP concentration range.

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Effect of TBP Concentration on HNO_3 Distribution

RA Column System, Aqueous Phase Composition:

UNH 0.01 M; $PO_4^{\equiv}$ 0.22 M; $SO_4^{=}$ 0.22 M; NO_3^- 5.7 M; Na^+ 3.4 M.

Volume Per Cent TBP	HNO_3 E_a^o
10	0.10
12.5	0.13
15	0.15

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5. Others

5.1 Phosphate and sulfate

The distribution of phosphate, as measured by the transfer from acidified uranium waste (5 M in HNO_3) into a 20 volume per cent TBP solution in CCl_4, favors the aqueous phase by a factor of about 1500 (i.e., E_a^o = 1/1500).[24] Analyses of uranium product solutions recovered by the TBP process have shown no phosphate or sulfate present.[73]

5.2 Chloride

Based on laboratory studies of a solution containing 1 g./l. of chloride ion, the distribution ratios (org./aq.) for chloride, determined at points corresponding to the dilute extraction region and feed point of the RA Column under TBP-HW No. 3 Flowsheet conditions, are 0.04 and 0.1, respectively.[49] Approximately 4 per cent of the chloride in the feed enters the scrub section via the solvent. The distribution ratio in the scrub section is on the order of 0.03, giving a calculated concentration of about 0.002 g./l. of chloride in the uranium product stream, on the basis of one scrub stage. Comparable data have been derived from simple and compound column studies conducted at the Hanford Works.[83]

5.3 Metallic ions

The distribution ratio (org./aq.) of iron, as determined by contacts of plutonium-bearing slag and crucible solutions with 15 volume per cent TBP in hexane, is on the order of 0.005. By the same procedure, the distribution ratios of Al, Ca, and Mg were found to be on the order of 0.0003.[15] The distribution ratios (org./aq.) of Ni(II) and Cr(III), determined by equilibrations of pure TBP with an aqueous phase containing 1.6 M HNO_3 and 50g./l. of the metal nitrate, are about 10^{-4}. Under the same conditions, the distribution ratios of Fe(III) and Cu(II) are about 10^{-3}.[66]

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Table IV-1

PHYSICAL PROPERTIES OF TRIBUTYL PHOSPHATE

Source of Data: HW-15079, HW-15172, HW-17822

Nomenclature	Tributyl phosphate, n-butyl phosphate, TBP
Formula	$(n\text{-}C_4H_9)_3\ PO_4$
Molecular Weight	266.32
Density, 25°C.	0.9730 g./cu. cm.
Refractive Index, n_D^{25}	1.4226
n_D^{20}	1.4245
Melting Point	-80°C.
Boiling Point	289°C. at 760 mm. pressure 177°C. at 27 mm. pressure 121°C. at 1 mm. pressure
Flash Point	295°F. (Tag closed cup)
Viscosity, 25°C.	3.32 centipoises
Latent Heat of Vaporization	14,680 calories per mole
Solubility in Water	0.39 grams per liter at 25°C.
Solubility of Water in TBP	64 grams per liter at 25°C.
Surface Tension, 25°C.	25 dynes per centimeter
Vapor Pressure, 100°C.*	0.25 mm. Hg

*) See Figure IV-3 for the variation of vapor pressure with temperature.

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Table IV-2

PHYSICAL PROPERTIES OF DILUENTS

Source of Data: HW-19065

Diluent	Density at 25°C., G./Cu.Cm.	Refractive Index n_D^{25}	Viscosity at 25°C., Millipoises	Boiling Range and Mid-point, °C.	Flash Point Tag Closed Cup, °F.	Aromatic Content, %	Iodine Number
Union Insecticide Base	0.8037	1.4444	16.1	175-269,(229)	133	0.9	1.13
Standard Oil Special Grade "B"	0.7918	1.4382	14.5	179-263,(217)	145	0.2	0.11
Standard Base Oil "C"	0.7933	1.4386	14.9	181-263,(220)	143	1.4	0.07
Deobase (Sonneborn Co., N.Y.C.)	0.7804	1.4344	17.3	198-269,(225)	162	1.0	0.02
Deodorized Spray Base (Shell Chemical Co.)	0.8038	1.4435	19.0	193-260,(232)	150	1.0	0.42
AMSCO 149-92 Br	0.7741	1.4339	11.7	172-242,(200)	119	7.0	1.22
AMSCO 125-90 W	0.7570	1.4226	14.1	186-199,(190)	133	1.0	0.49
Super Sol (Penn. Ref. Co.)	0.7543	1.4217	9.6	162-198,(185)	127	1.9	0.04
Gulf B.T.	0.7606	1.4271	8.9	165-198,(177)	111	9.1	1.07
Stoddard Solvent (Shell Chem. Co.)	0.7765	1.4295	9.2	160-193,(168)	102	1.8	0.48
CCl_4	1.5844	1.4603 20°C.	9.14	77	—	—	—
$n\text{-}C_{10}H_{22}$	0.726	—	11.0	196	115	—	—
$n\text{-}C_{12}H_{26}$	0.746	—	14.0	216	165	—	—

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Table IV-3

PHYSICAL PROPERTIES

$UO_2(NO_3)_2$ - H_2O SYSTEM

Source of Data: CL-697 and HW-19932

Concentration of $UO_2(NO_3)_2$ M*	Weight Per Cent	Saturation Temperature, °C.	Boiling Point, °C.	Density, 25°C.*, G./Cu. Cm.	n^{25}_D	pH, 25°C.
0.0	0	0	100.0	0.997	1.3330	7.0
0.132	5	- 0.5	100.2	1.040	1.3372	2.5
0.276	10	- 1.0	100.4	1.086	1.3420	2.3
0.433	15	- 2.0	100.6	1.137	1.3474	2.0
0.604	20	- 3.0	100.9	1.191	1.3532	1.9
0.794	25	- 5.0	101.3	1.252	1.3597	1.7
1.004	30	- 7.5	101.7	1.319	1.3666	1.5
1.237	35	- 10.5	102.3	1.393	1.3744	1.2
1.499	40	- 14.5	103.1	1.477	1.3830	0.9
1.680	43 (eutectic)	- 18.1	103.8	1.540	1.3886	0.7
1.794	45	- 13.5	104.2	1.571	1.3924	—
2.120	50	+ 1.5	105.4	1.671	1.4025	—
2.491	55	20.0	106.8	1.785	1.4138	—
2.91 *	60	35.0	110.3	1.91 *	—	—
3.38	65	46.5	113.8	2.05	—	—
3.89	70	54.0	118.2	2.19	—	—
4.45	75	58.5	120.0	2.34	—	—
4.90	78.5	60.0	—	2.46	—	—
5.10	80	70.0	—	2.51	—	—
5.39	82	87.0	—	2.59	—	—
5.69	84	100.0	140.0	2.67	—	—
6.02	86	110.0	—	2.76	—	—
6.39	88	118.0	160.0	2.86	—	—
6.76	90	160.0	—	2.96	—	—
—	92	167.0	178.0	—	—	—
—	94	172.0	188.0 (with decomposition)		—	—

*) Above 56% (saturation), density and molarity are given at the saturation temperature.

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Table IV-4

PHYSICAL PROPERTIES

$UO_2(NO_3)_2$ - HNO_3 - H_2O SYSTEM*

Source of Data: HW-18406

Solution Composition, Weight Per Cent		Density, G./Cu. Cm. at Saturation Temperature	Viscosity,** Centipoises		Boiling Point, °C.	Saturation Temperature, °C.
$UO_2(NO_3)_2$	Free HNO_3		100 RPM	50 RPM		
50.7	14.97	—	—	—	118	42.5
61.9	—	—	—	—	120	48.1
64.1	8.18	—	—	—	—	50.5
69.4	5.19	2.26	25	18	120	53.8
73.3	5.69	2.19	—	—	120	59.9
79.9	2.31	2.50	—	—	—	93.5
80.9	—	2.55	42	30	130	96.0
86.0	0.48	2.92	—	—	140	106.0
86.5	-0.10	3.11	45	33	145	106.0
86.5	0.36	2.84	—	—	150	106.0
86.7	0.23	2.92	—	—	150	110.2
88.4	0.36	2.95	60	50	160	- - -
88.9	-0.58	3.17	—	—	160	130

*) These data were obtained from a study of RCU concentration.

**) Determined with a Brookfield Model RVF Viscometer, No. 1 spindle.

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Table IV-5

SATURATION TEMPERATURE AND DENSITY

RAF SYSTEM

Source of Data: HW-17226

Composition, M						Saturation Temperature, °C.	Density, 25°C.
UO_2^{++}	$PO_4^{\equiv}$	$SO_4^{=}$	Na^+	Titratable Acid*	NO_3^-		
0.33	0.35	0.26	3.7	1.8	5.3	0.5	1.3332
0.32	0.33	0.26	3.5	2.3	5.7	2.0	1.3457
0.26	0.26	0.26	3.7	1.3	4.8	-2.5	1.3077
0.32	0.34	0.26	5.5	1.3	6.4	17	1.3913
0.32	0.30	0.26	5.2	1.8	6.9	13	1.4065
0.32	0.32	0.28	4.8	2.2	7.4	21	1.4115
0.33	0.31	0.28	5.1	1.9	7.7	12	1.4149
0.32	0.29	0.33	4.9	2.7	7.0	23.5	1.4325
0.32	1.07	0.35	4.0	3.5	5.7	2.0	1.4006
0.19	0.18	0.19	2.6	6.3	8.5	38	1.4133
0.15	0.15	0.15	2.2	8.5	8.5	50	1.4347
0.19	0.18	0.18	2.6	5.9	8.0	35	1.3961
0.19	0.05	0.22	2.4	6.8	8.5	30	1.3973
0.15	0.04	0.18	2.1	8.4	8.5	39	1.3776
0.19	0.05	0.20	2.4	6.3	8.0	26	1.3776
0.37	0.29	0.64	4.7	2.5	—	8	1.4238
0.33	0.27	0.27	3.6	3.2	6.6	-3.0	1.3729
0.33	0.32	0.26	3.5	4.4	7.8	20	1.4082
0.35	0.32	0.26	5.2	2.2	—	17	1.4251
0.32	0.32	0.25	5.2	3.5	6.9	34	1.4731
0.26	0.29	0.31	4.01	3.51	6.5	16.7	1.3996
0.20	0.23	0.23	2.7	4.13	6.0	-7.8	1.3269

*) See Section A of Chapter III for discussion of methods of expressing acid concentration.

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Table IV-6

COMPOSITION OF RA COLUMN AQUEOUS WASTE

Source of Data: HW-18169, HW-18232, and Run Books 3.00-29-RAU, 3.00-30-RAU, 3.00-122-RAU, and 3.00-123-RAU

Constituent	TBP-HW No.4	TBP-HW No.5	Run No. 30[c]	Run No. 123[c]	Run No. 29[d]	Run No. 122[d]
UNH	0.47[a]	0.35	0.11	0.03	3.25	1.75
$PO_4^{\equiv}$	17.0	12.8	20.64	31.8	29.6	30.7
$SO_4^{=}$	20.5	15.5	5.27	16.7	26.19	29.5
NO_3^-[b]	276.0	209.0	386.3	305.0	365.8	358.4
Na^+	64.4	48.8	34.5	64.4	75.4	70.0
H^+	2.60	1.96	—	—	—	—

(a) All concentrations given in grams per liter.

(b) NO_3^- represents total nitrate less that contained in the indicated UNH concentration.

(c) These data are from runs in which the feed was simulated sludge slurried in water.

(d) These data are from runs in which the feed was simulated, evaporated supernate. For summaries of these runs see HW-19170.[56]

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Table IV-7

PROPERTIES OF CONCENTRATED NEUTRALIZED RAW*

FLOWSHEET TBP-HW No. 4 AND 5

Source of Data: HW-18404, HW-21273,
See Figure IV-19

Volume Per Cent							Specific Heat Cal./(G.)(°C.)	
Neutr. HW-4 RAW	Neutr. HW-5 RAW	Stored Uranium Waste	Saturation Temperature, °C.	Density, G./Ml.	pH, 25°C.	Viscosity,** Centipoises	25°C.	39°C.
—	100	204	4	1.211(25°C.)	11.8	—	—	—
100	78	159	14	1.250(25°C.)	11.8	—	—	—
80	62	127	18	1.355(25°C.)	11.7	—	—	—
63	49	100	26	1.344(30°C.)	11.2	20	0.76	0.74
57	44	90	29	1.365(40°C.)	12.5	—	—	—
50	39	79	34	—	12.6	30	—	—
47	37	74.5	36	1.403(42°C.)	12.2	—	—	—
45	35	71	39	1.405(40°C.)	12.2	35	0.87	0.74
44.6	34.7	70.7	60	1.470(65°C.)	11.6	—	—	—
44	34	70	80	1.500(81°C.)	11.5	—	—	—

*) The solutions were prepared to represent the approximate compositions corresponding to concentration of flowsheet RAW wastes except for the omission of iron and uranium, which are insoluble. The compositions did not include any contribution from the ROW stream. Mole per cents on a water-free basis were: Na_2SO_4, 4.70; Na_3PO_4, 3.67; $NaNO_3$, 91.63.

**) Viscosity measured with a Brookfield Model RVF Viscometer using Spindle No. 1 at 100 RPM.

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Table IV-8

EFFECT OF COMPLEXING AGENTS ON DECONTAMINATION

Feed: 0.2 M UNH, 3 M HNO_3, indicated complexing agent
Extractant: 12.5 volume per cent TBP in CCl_4
Scrub: 3 M HNO_3, indicated complexing agent
Feed/scrub/extractant volume ratio = 3/2/10

Source of Data: HW-18880

Complexing Agent	Radio-activity	Distribution Ratio, E_a^o Extraction	1st Scrub	2nd Scrub	3rd Scrub	Over-all Decontamination Factor
None	Gross Beta	8.4×10^{-4}	7.0×10^{-3}	4.3×10^{-2}	9.2×10^{-2}	3.2×10^{5}
"	Zr	2.9×10^{-3}	1.1×10^{-2}	1.4×10^{-2}	5.6×10^{-2}	2.3×10^{5}
"	Ru	2.8×10^{-4}	1.9×10^{-2}	8.6×10^{-2}	0.43	2.0×10^{5}
0.1 M H_3PO_4	Gross Beta	3.3×10^{-4}	2.8×10^{-3}	0.16	0.92	3.0×10^{5}
"	Zr	3.0×10^{-5}	7.8×10^{-2}	0.31	0.09	3.7×10^{5}
"	Ru	3.8×10^{-4}	1.6×10^{-2}	4.1×10^{-2}	0.37	1.6×10^{5}
0.1 M H_2SO_4	Gross Beta	7.1×10^{-4}	4.2×10^{-3}	7.2×10^{-2}	0.29	2.2×10^{-5}
"	Zr	5.3×10^{-4}	1.6×10^{-2}	2.7×10^{-2}	0.12	2.9×10^{-5}
"	Ru	4.0×10^{-4}	4.0×10^{-3}	0.12	0.07	5.0×10^{-5}
0.01 M $(NH_4)_2SiF_6$	Gross Beta	2.5×10^{-4}	5.0×10^{-3}	0.11	0.07	9.1×10^{5}
"	Zr	2.6×10^{-4}	5.2×10^{-3}	9.2×10^{-2}	0.52	3.3×10^{5}
"	Ru	3.2×10^{-4}	1.3×10^{-2}	5.2×10^{-2}	0.14	2.9×10^{5}

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Figure IV-1

RATE OF HYDROLYSIS OF BUTYL PHOSPHATES
IN 3M NITRIC ACID
EFFECT OF TEMPERATURE

SOURCE OF DATA: HW-19959

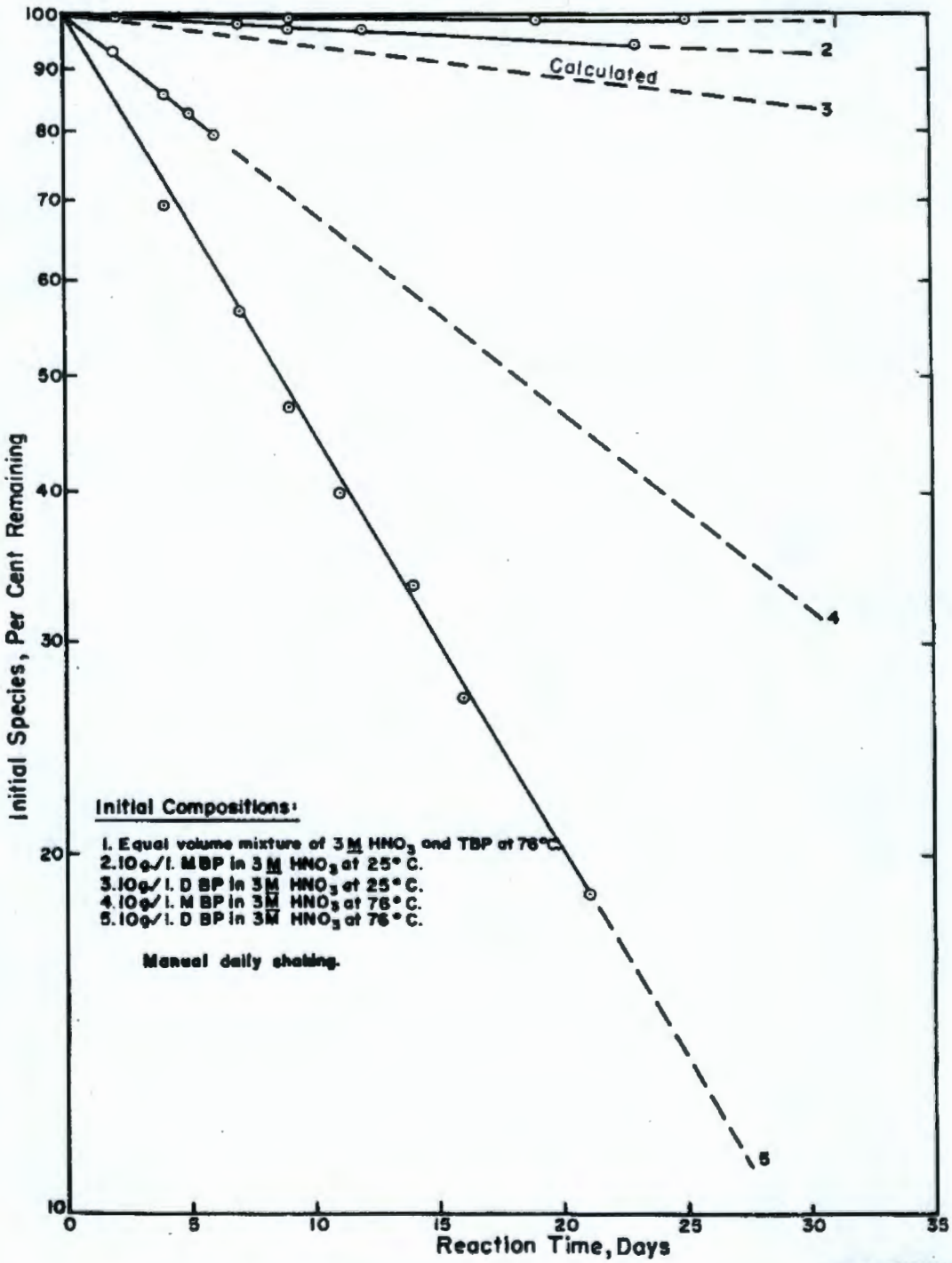

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Figure IV - 2

BOILING RANGES OF DILUENTS

ASTM DISTILLATION

SOURCE OF DATA: HW-19065

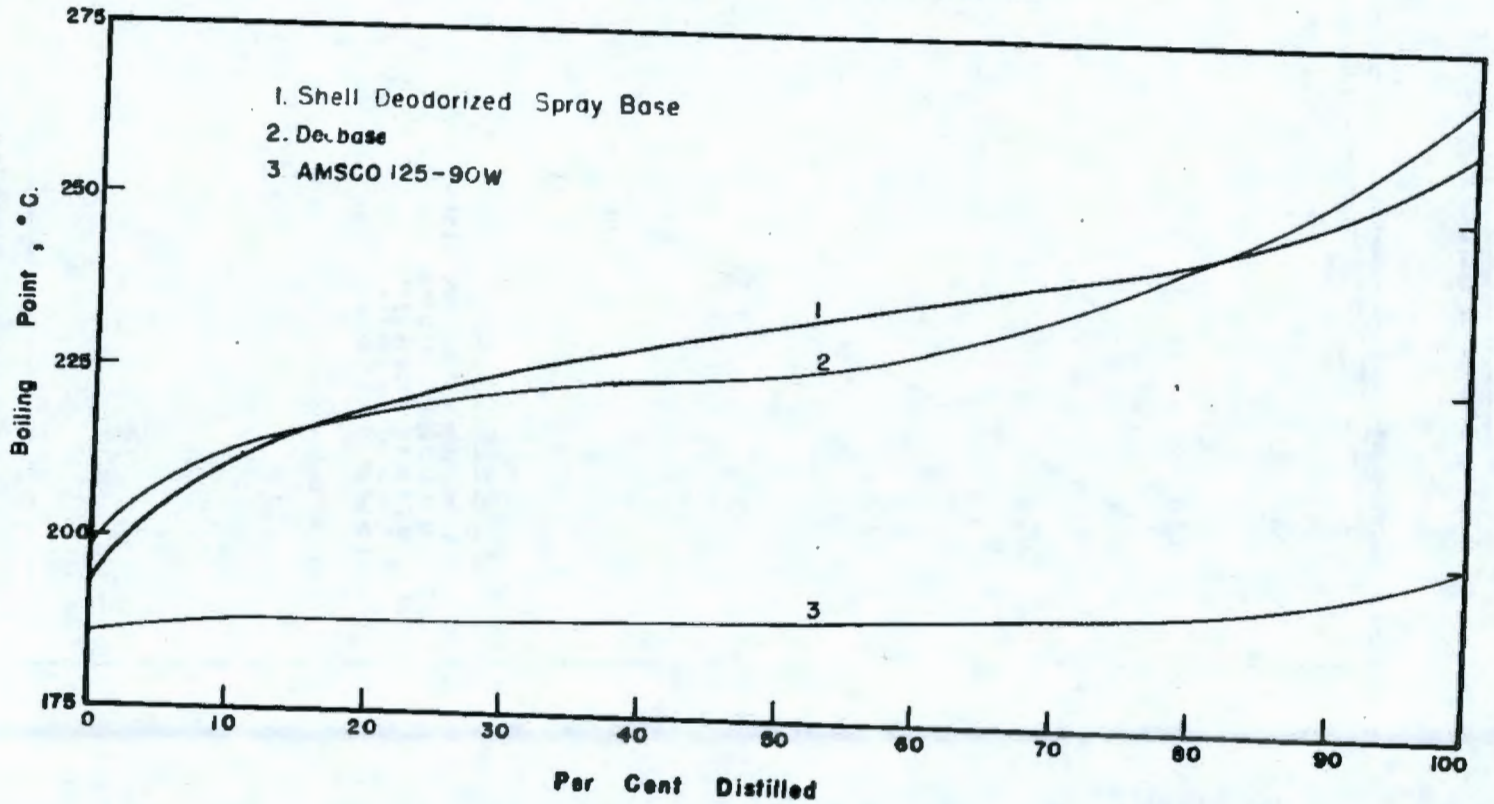

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Figure IV-3

VAPOR PRESSURE OF TBP AND DEOBASE

EFFECT OF TEMPERATURE

SOURCE OF DATA: HW-15172

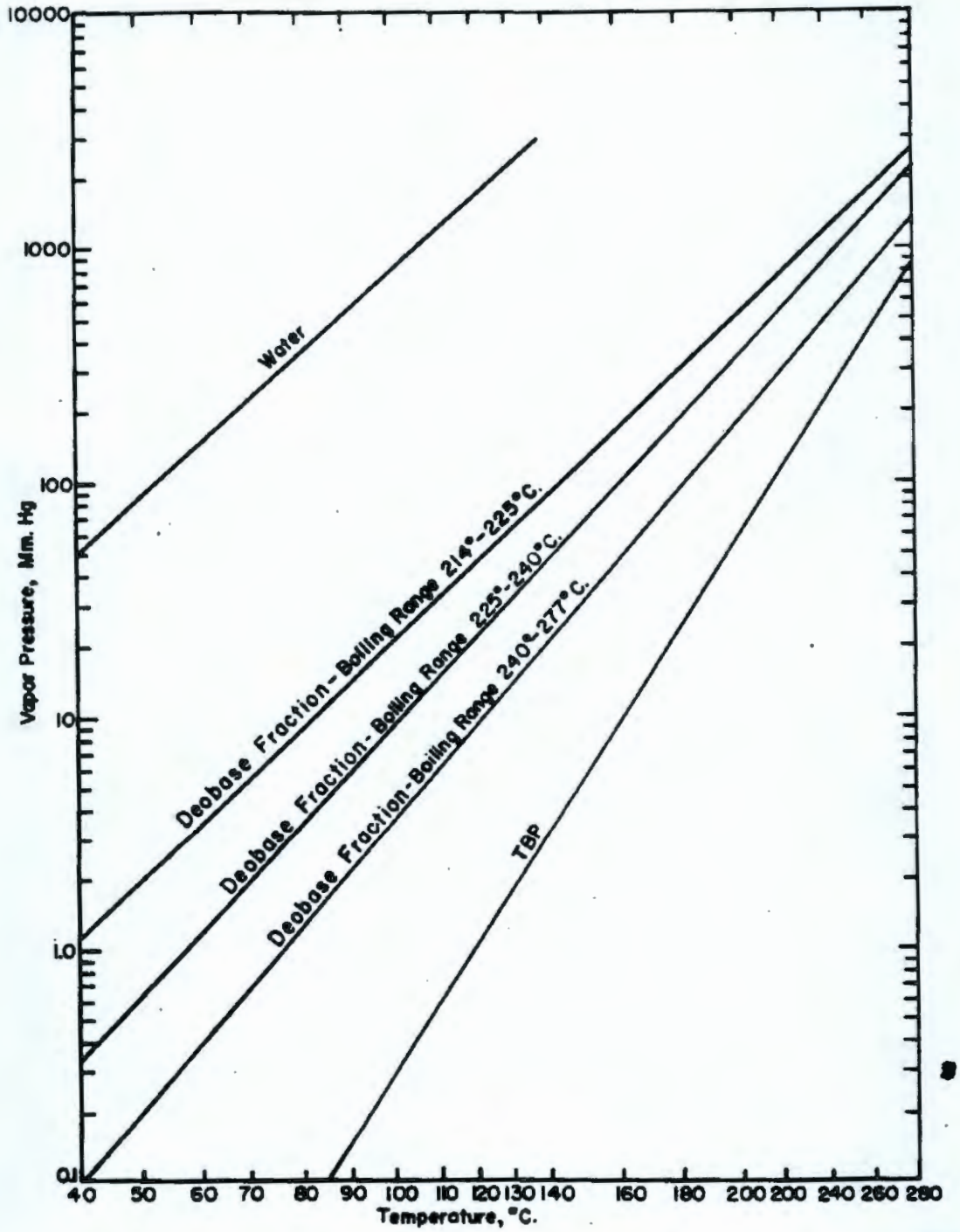

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Figure IV- 4

DENSITY AND REFRACTIVE INDEX OF THE SYSTEM TBP-DILUENT

EFFECT OF TBP CONCENTRATION

SOURCE OF DATA: HW-19065; F. Clagett, Unpublished Data, March 1950

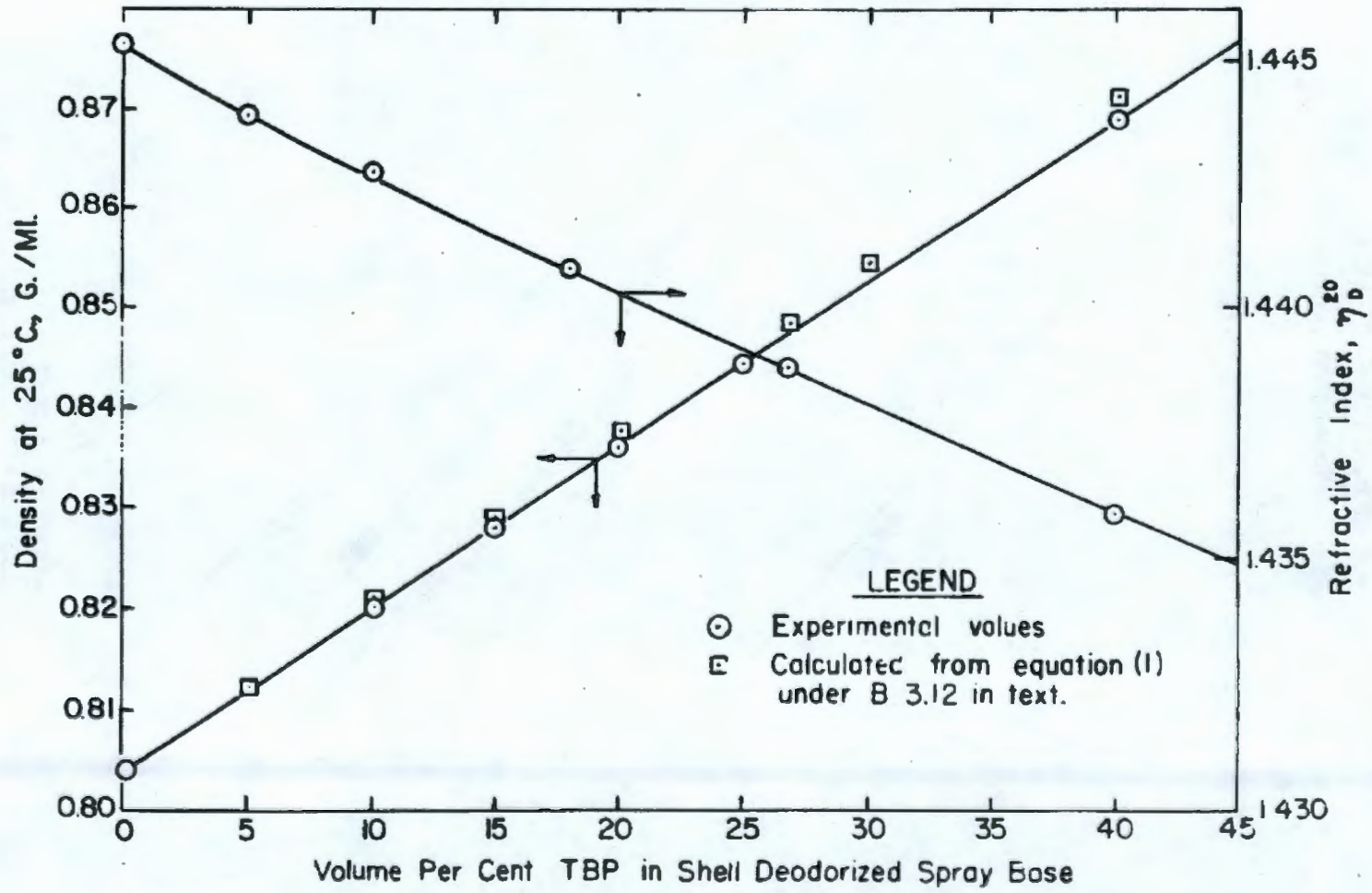

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Figure IV-5

VISCOSITY OF RA COLUMN EXTRACTANT AND FEED

EFFECT OF TEMPERATURE

SOURCE OF DATA: R.F. Maness, Unpublished Data, July 1950

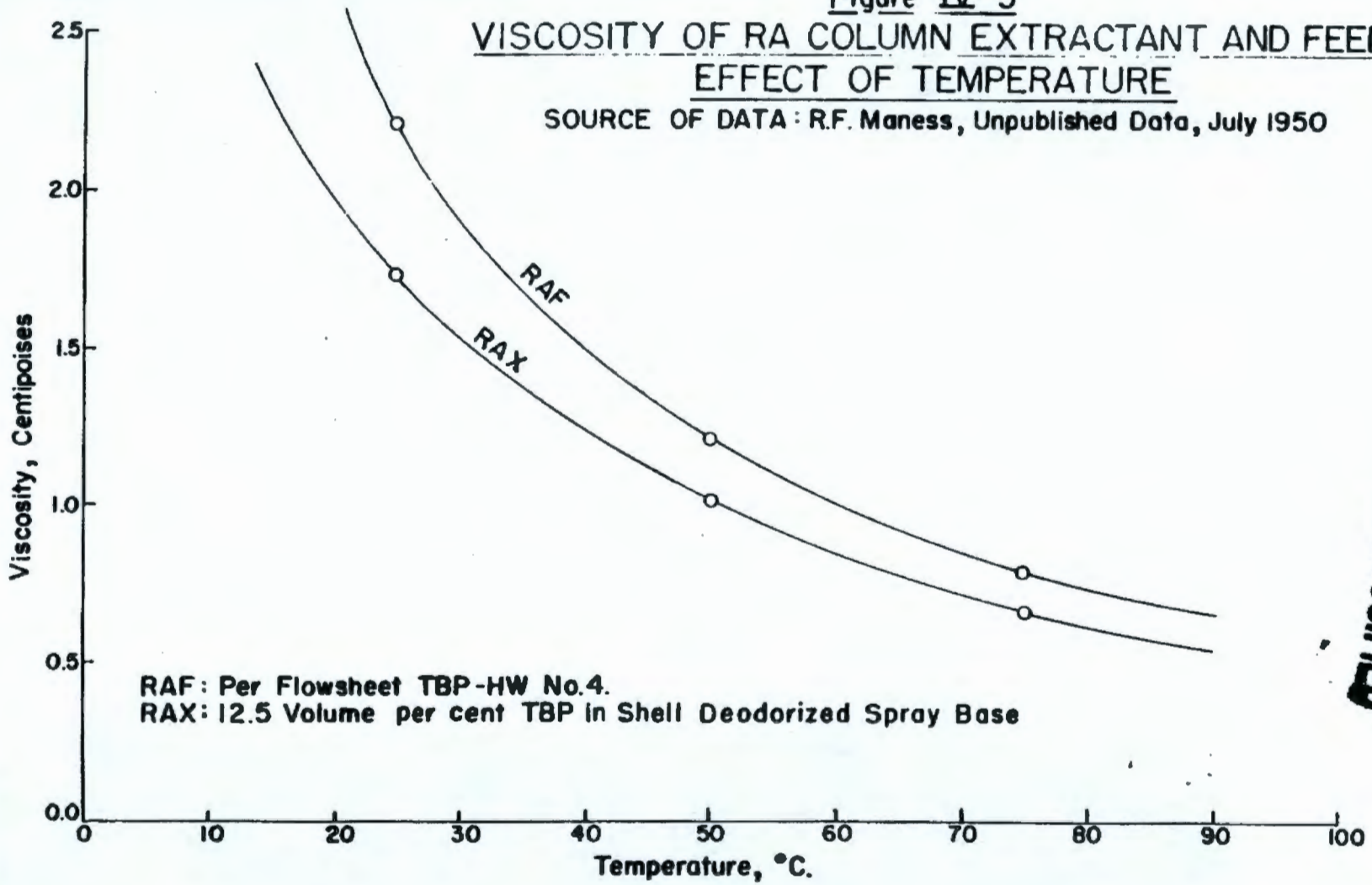

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Figure IV-6

FLASH POINT OF TBP-DILUENT SOLUTIONS

EFFECT OF CONCENTRATION

SOURCE OF DATA: HW 19065; F. Clagett, Unpublished Data, March 1950

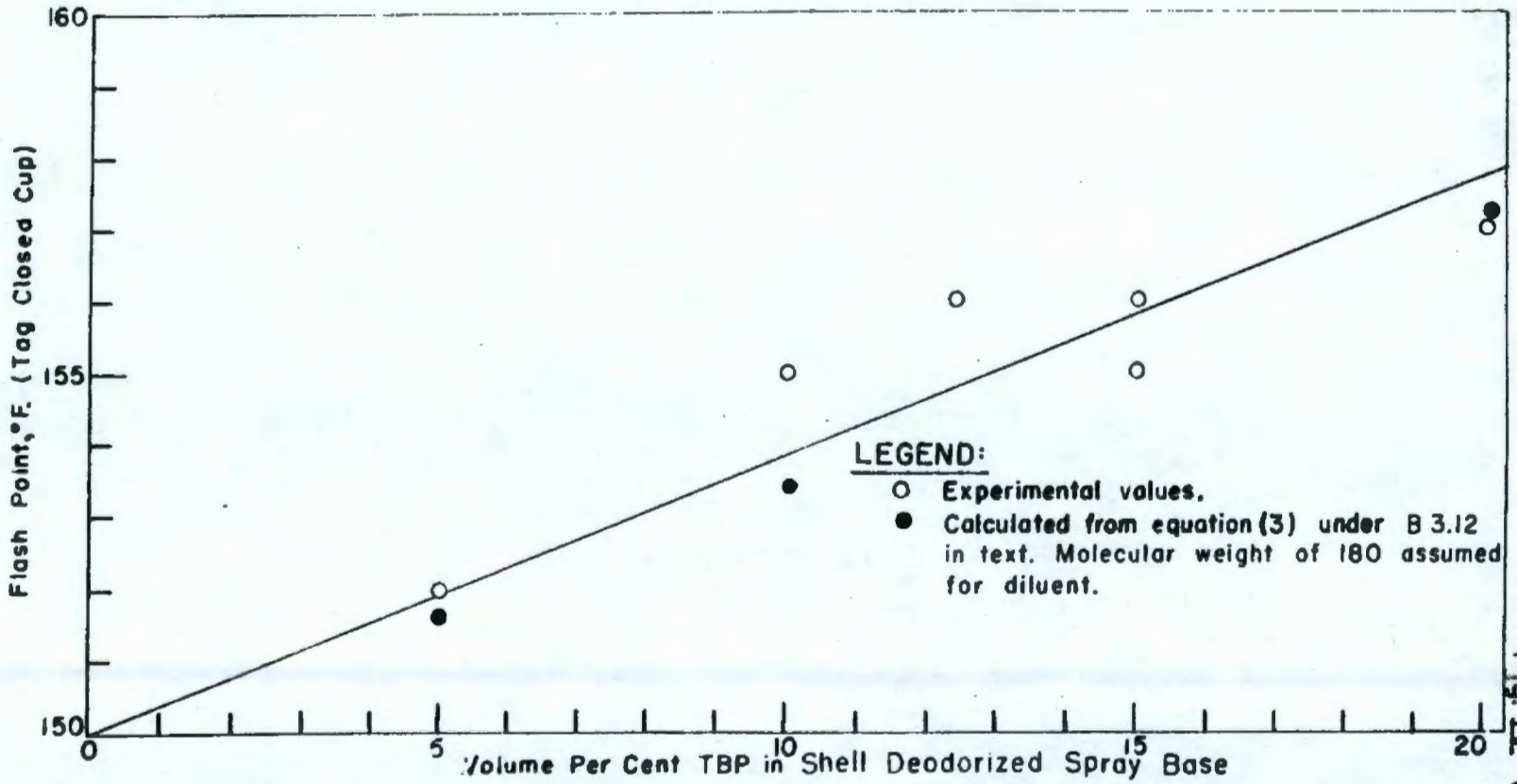

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Figure IV-7

DENSITY-WEIGHT PERCENT-MOLARITY CONVERSION

TBP-DEOBASE-URANYL NITRATE SYSTEM

SOURCE OF DATA: HW-17295; HW-17838

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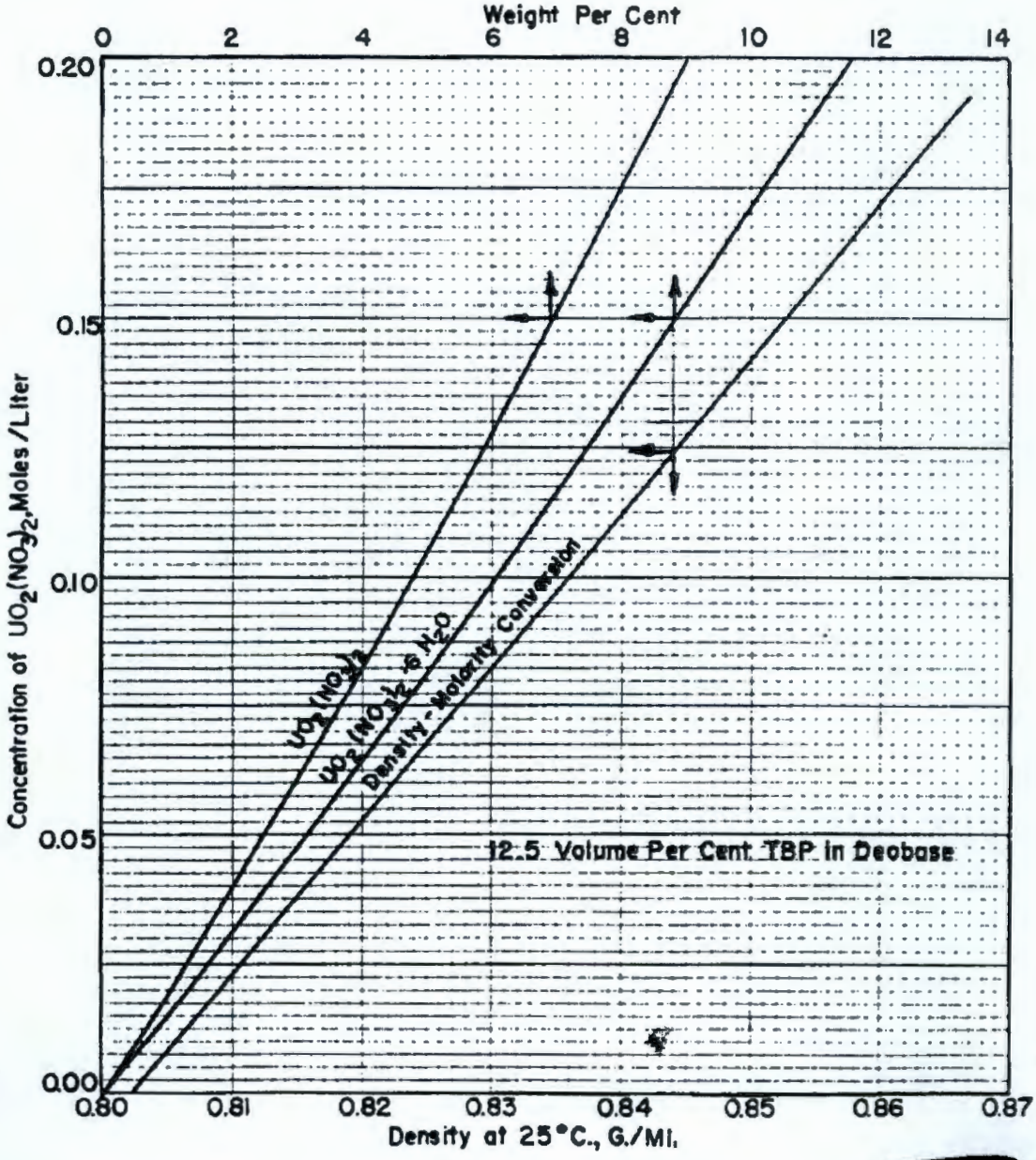

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Figure IV - 8

DENSITY OF RA COLUMN FEED AND EXTRACTANT

TBP-HW No. 4 FLOWSHEET

EFFECT OF TEMPERATURE

SOURCE OF DATA: R.F. Maness, Unpublished Data, July 1950

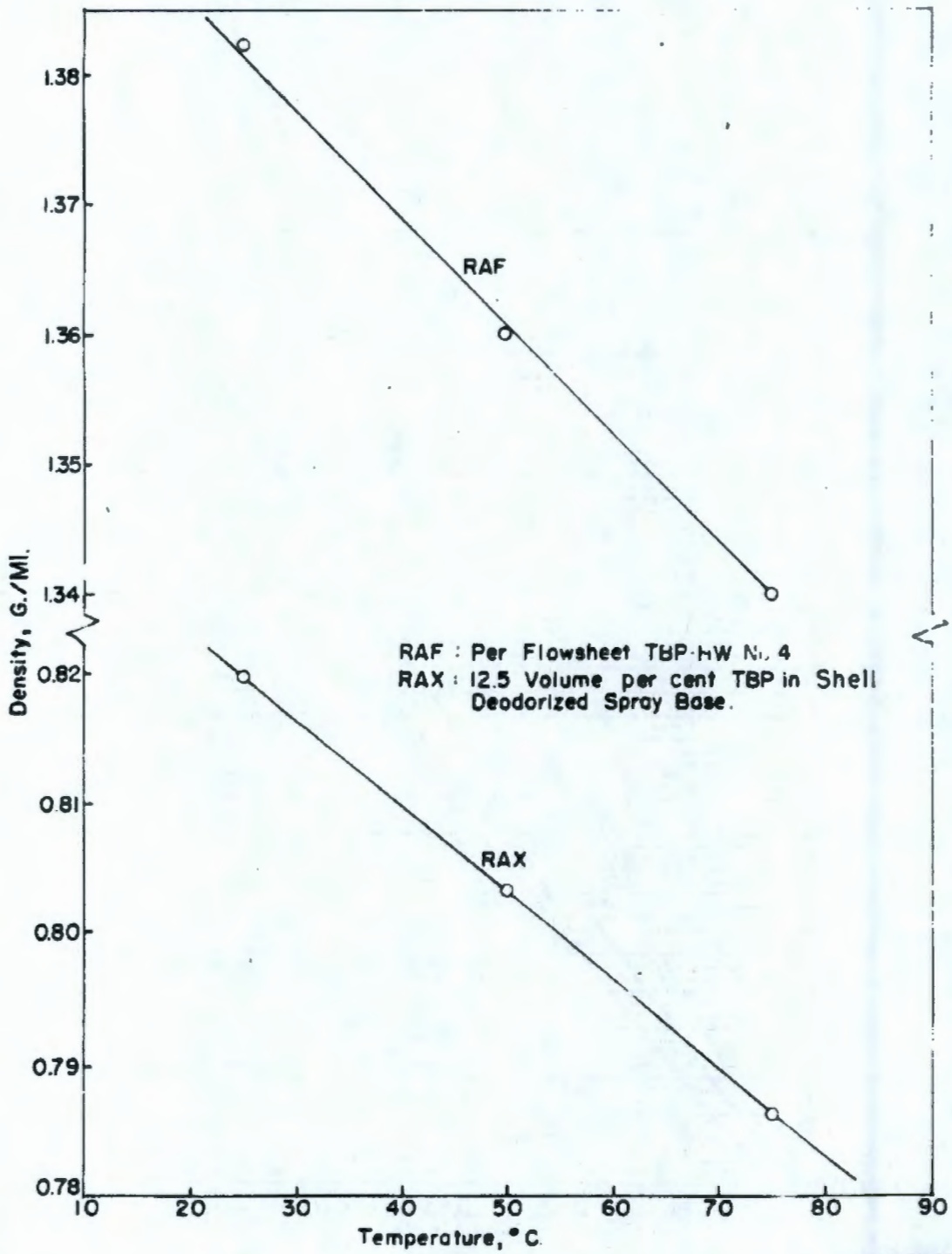

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Figure IV-9

VISCOSITY OF THE SYSTEM TBP-DILUENT-URANYL NITRATE

EFFECT OF URANIUM CONCENTRATION

SOURCE OF DATA: HW-19065

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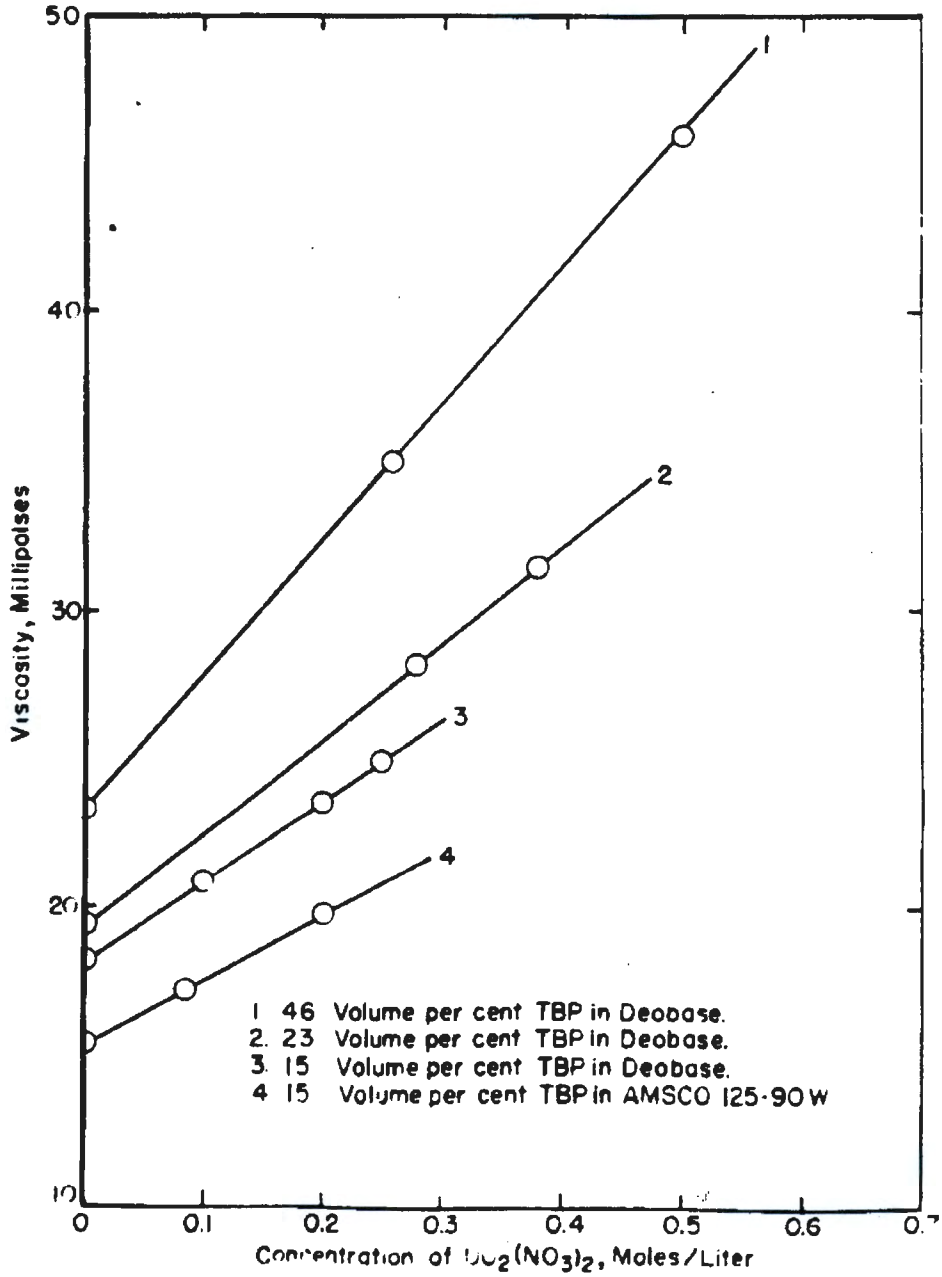

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Figure IV-10

SATURATION TEMPERATURES $UO_2(NO_3)_2 - HNO_3 - H_2O$ SYSTEM

SOURCE OF DATA: HW-8309

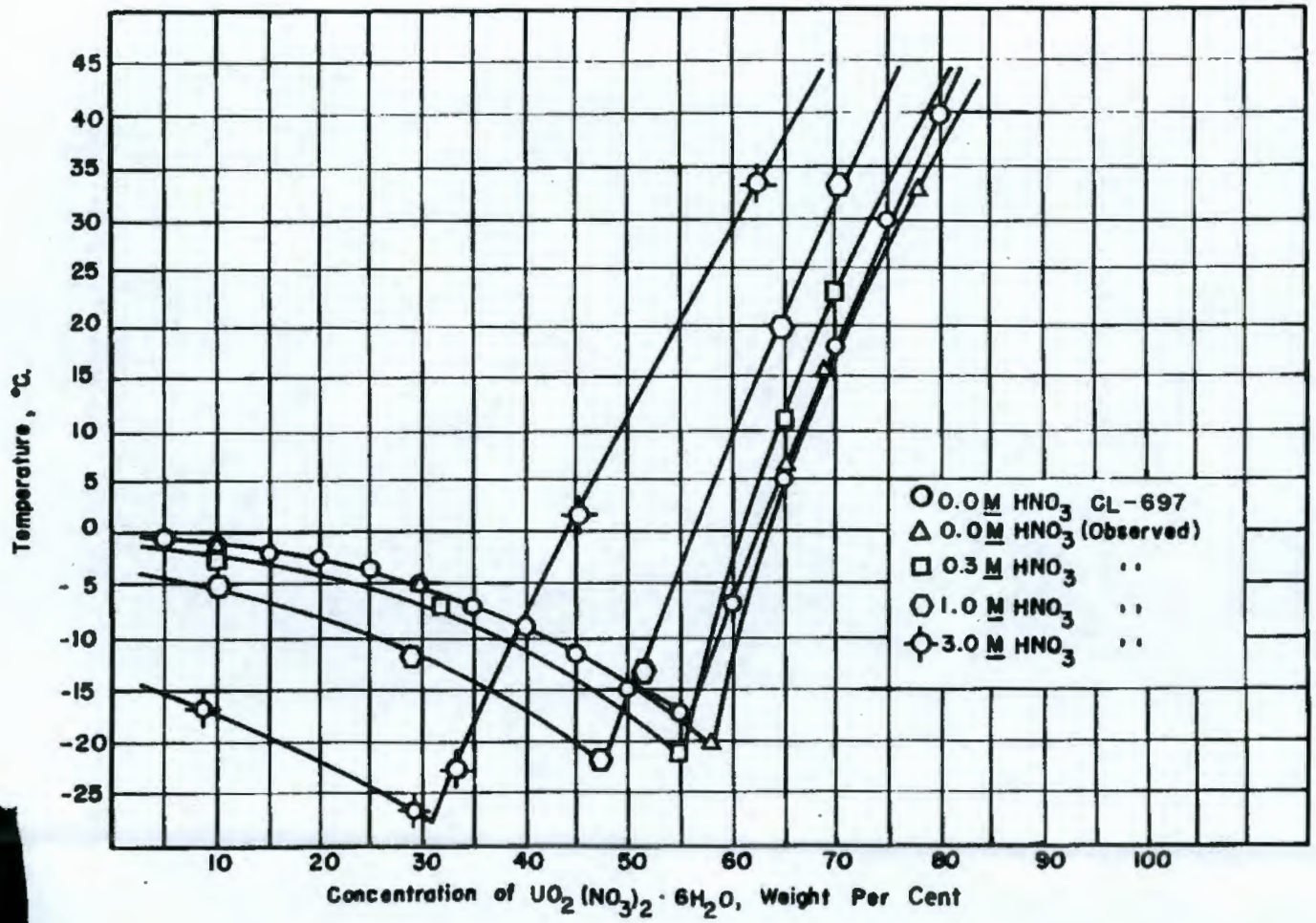

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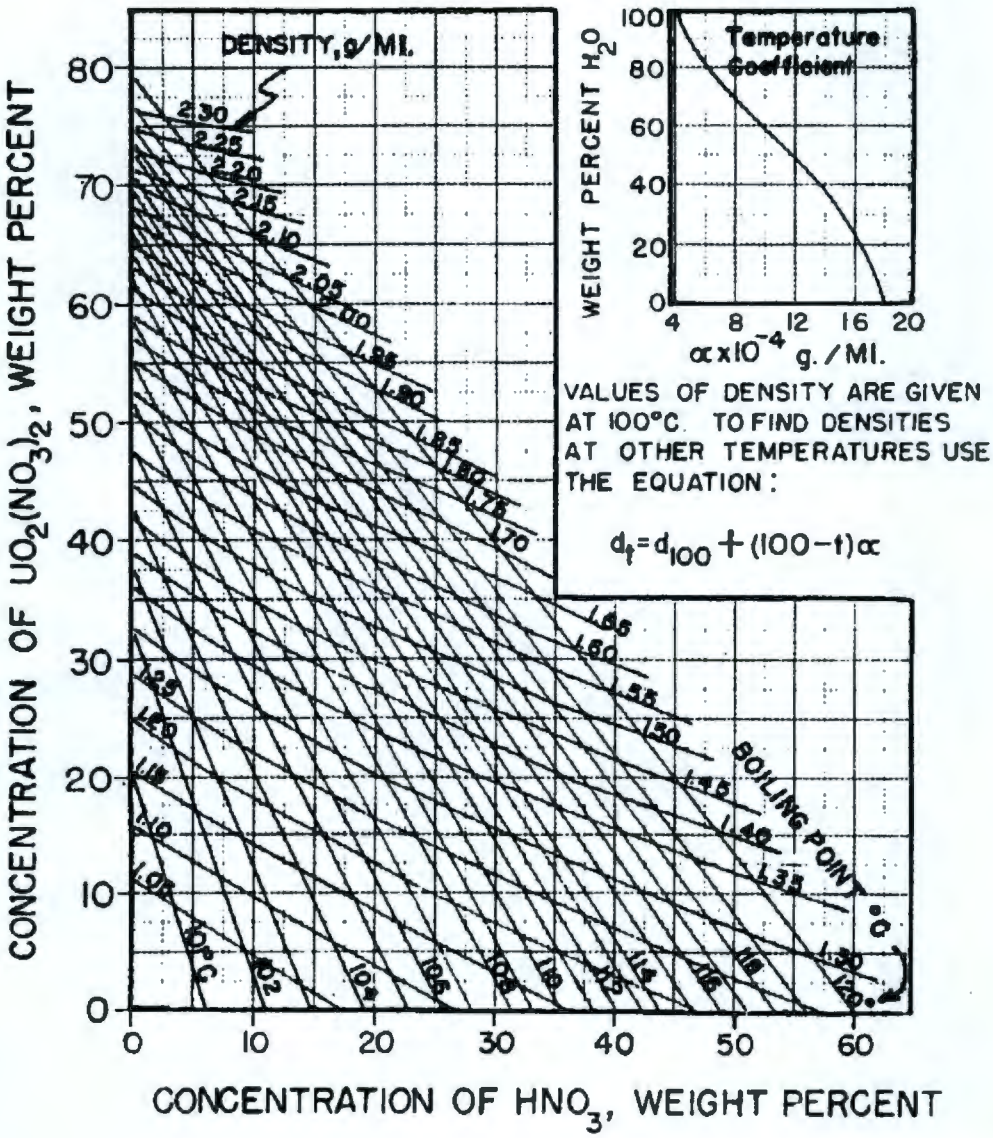
Figure IV-11

BOILING POINT AND DENSITY

$UO_2(NO_3)_2 - HNO_3 - H_2O$ SYSTEM

SOURCE OF DATA: CL-697, Chapter II



VALUES OF DENSITY ARE GIVEN AT 100°C. TO FIND DENSITIES AT OTHER TEMPERATURES USE THE EQUATION:

$$d_t = d_{100} + (100 - t)\alpha$$

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Figure IV-12

VISCOSITY OF RA COLUMN FEED
EFFECT OF TEMPERATURE AND FLOWSHEET

SOURCE OF DATA: HW-18367; R.F. Maness, Unpublished Data, July 1950

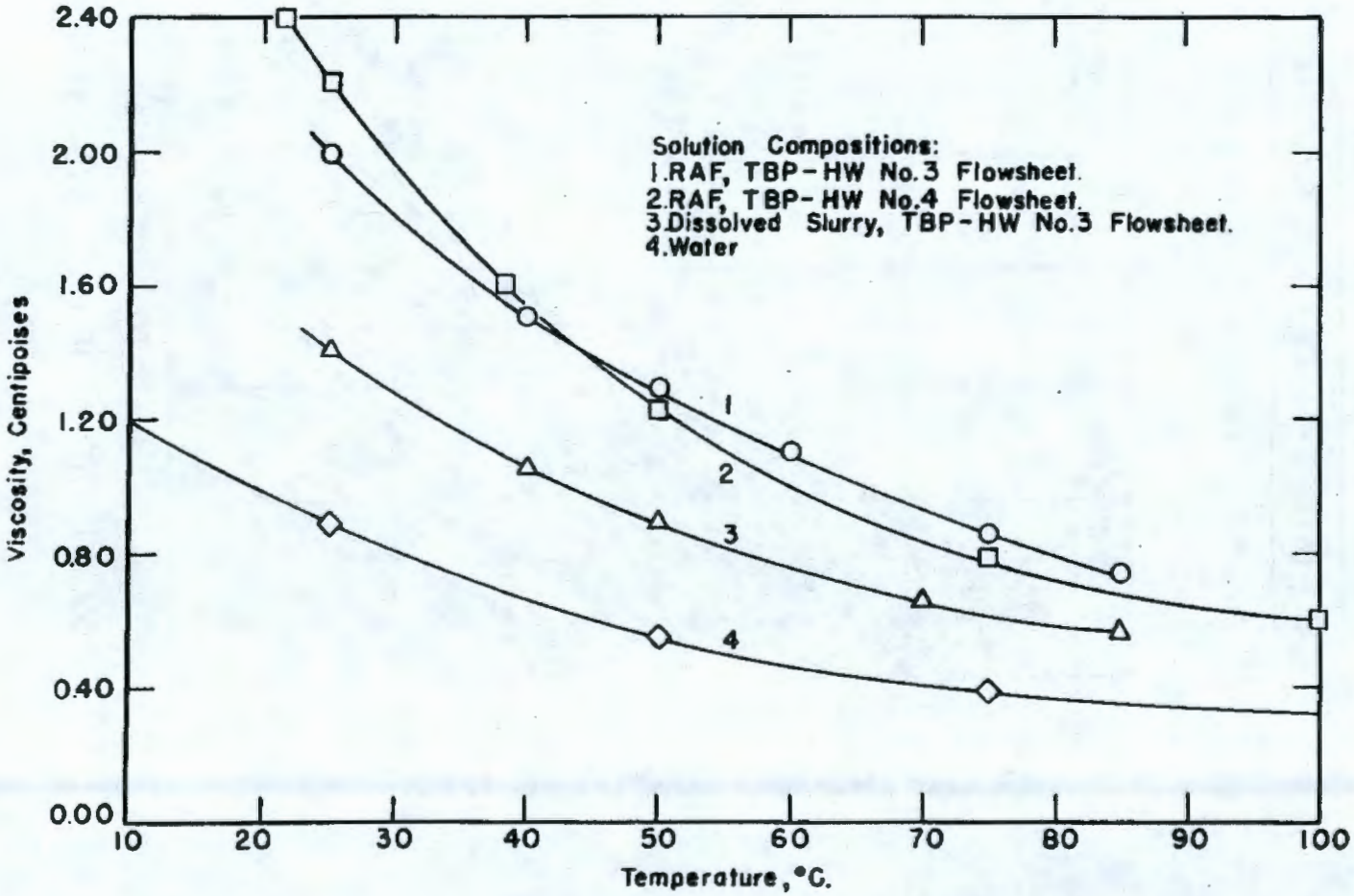

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Figure IV-13

HYDROGEN ION CONCENTRATION

$UO_2(NO_3)_2$ - HNO_3 - H_2O SYSTEM

SOURCE OF DATA: HW-14559

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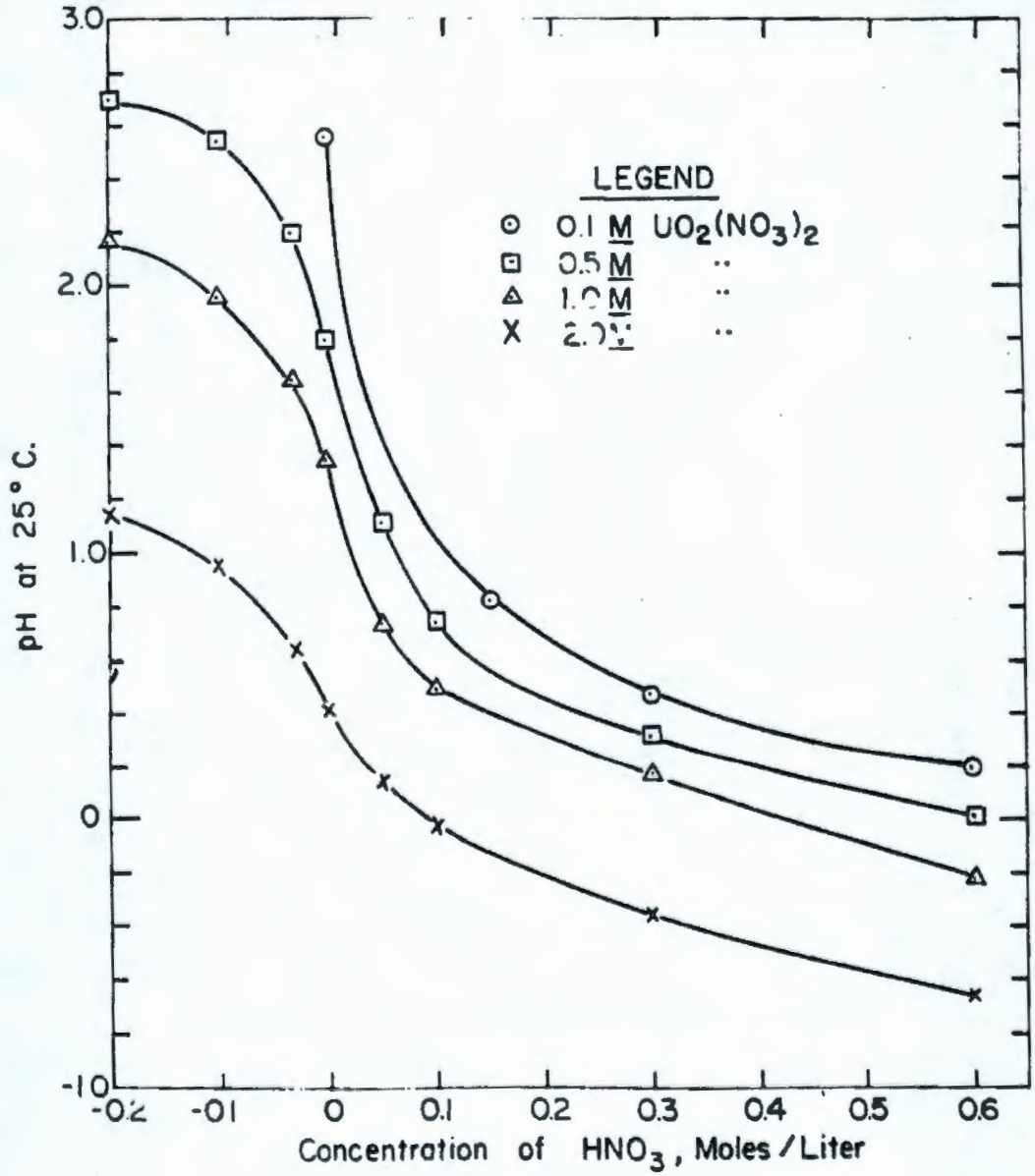

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Figure IV-14

SATURATION COMPOSITION OF RA COLUMN FEED EFFECT OF ACID, SODIUM, AND URANIUM CONCENTRATIONS

SOURCE OF DATA: HW-17226 and HW-18407

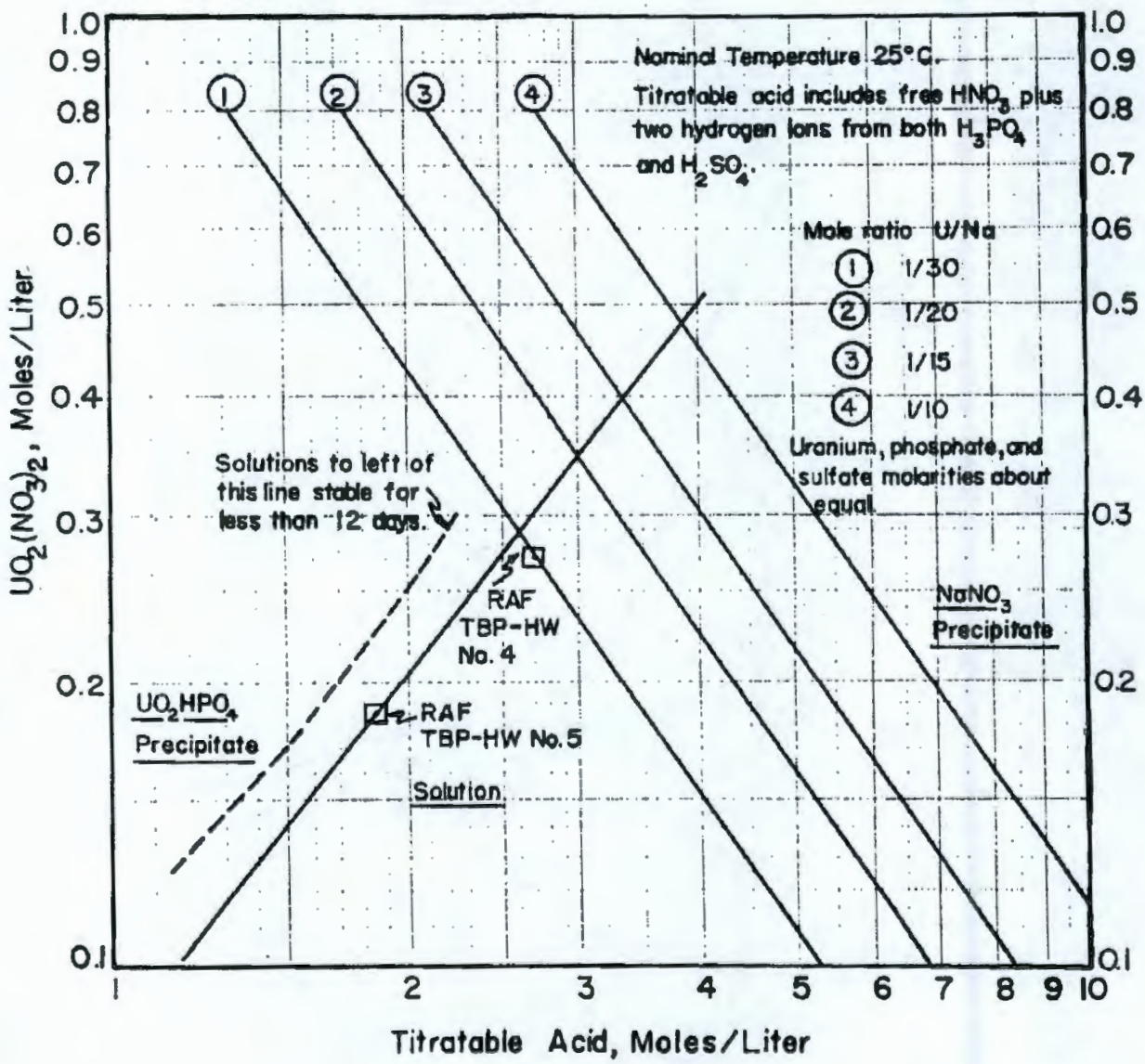

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Figure IV-15A

SATURATION TEMPERATURES

EFFECT OF CONCENTRATION OF RCU AND ACIDIFIED SLURRY

SOURCE OF DATA: HW-15172

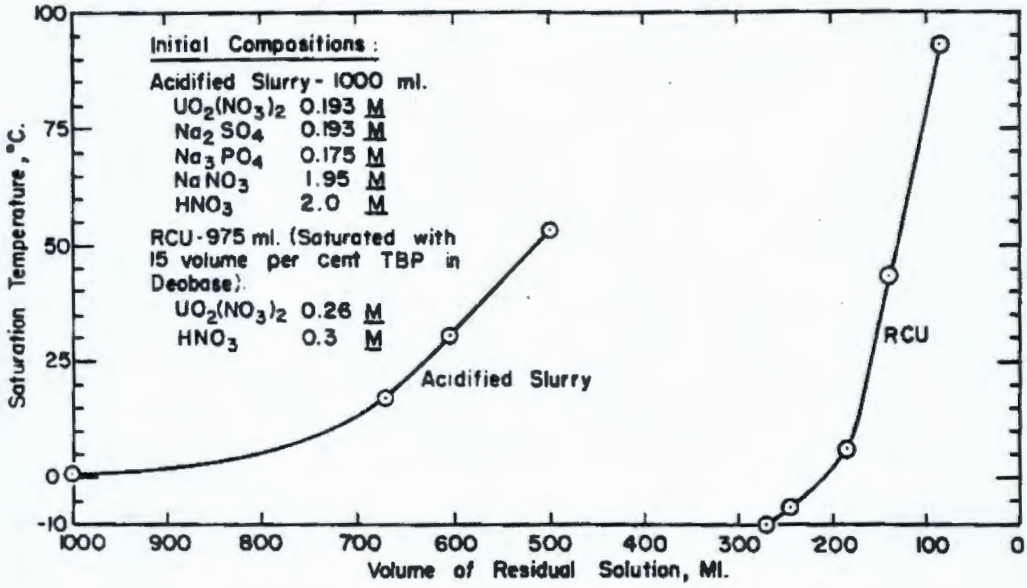

Figure IV-15B

NITRIC ACID REMOVAL BY SOLUTION CONCENTRATION

$UO_2(NO_3)_2$ - HNO_3 - H_2O SYSTEM

SOURCE OF DATA: HW-15172

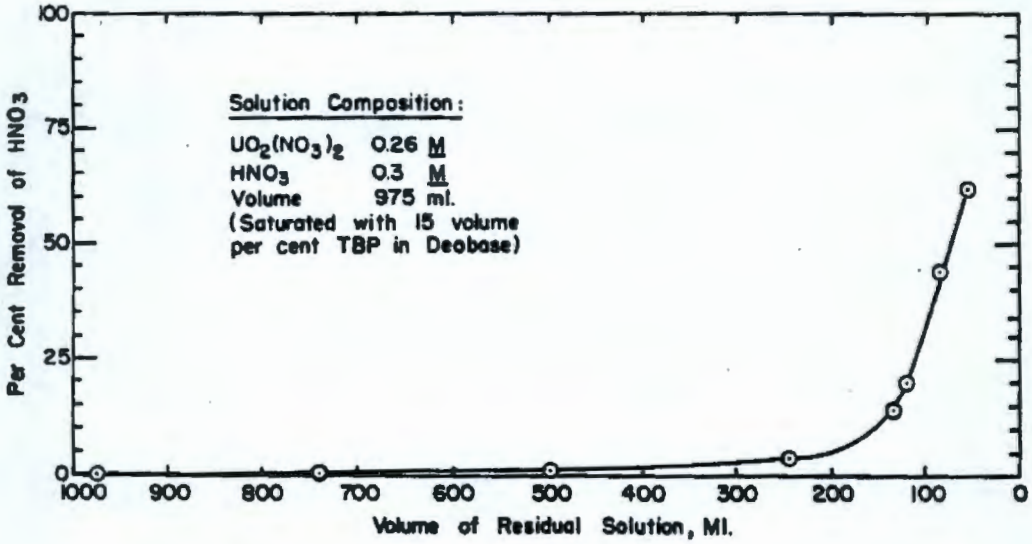

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Figure IV-16

SATURATION TEMPERATURES

$UO_2(NO_3)_2$-HNO_3-$NaNO_3$-H_2O SYSTEM

SOURCE OF DATA: M.H.Curtis, Unpublished Data, July 1950

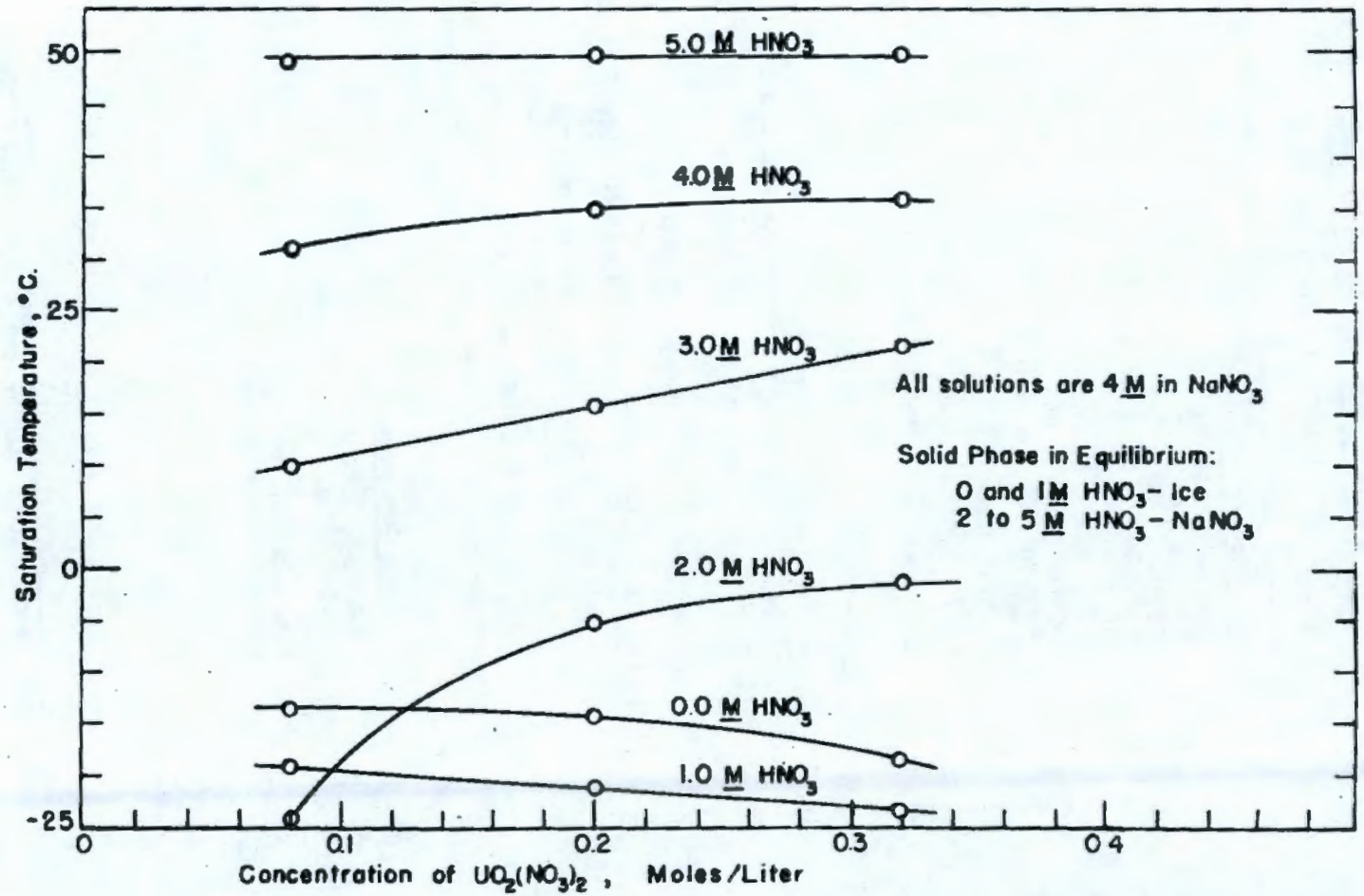

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Figure IV-17

SPECIFIC HEATS OF AQUEOUS PROCESS SOLUTIONS

SOURCE OF DATA: Unpublished Data, C.M. Slansky, October 1948; I.C.T.

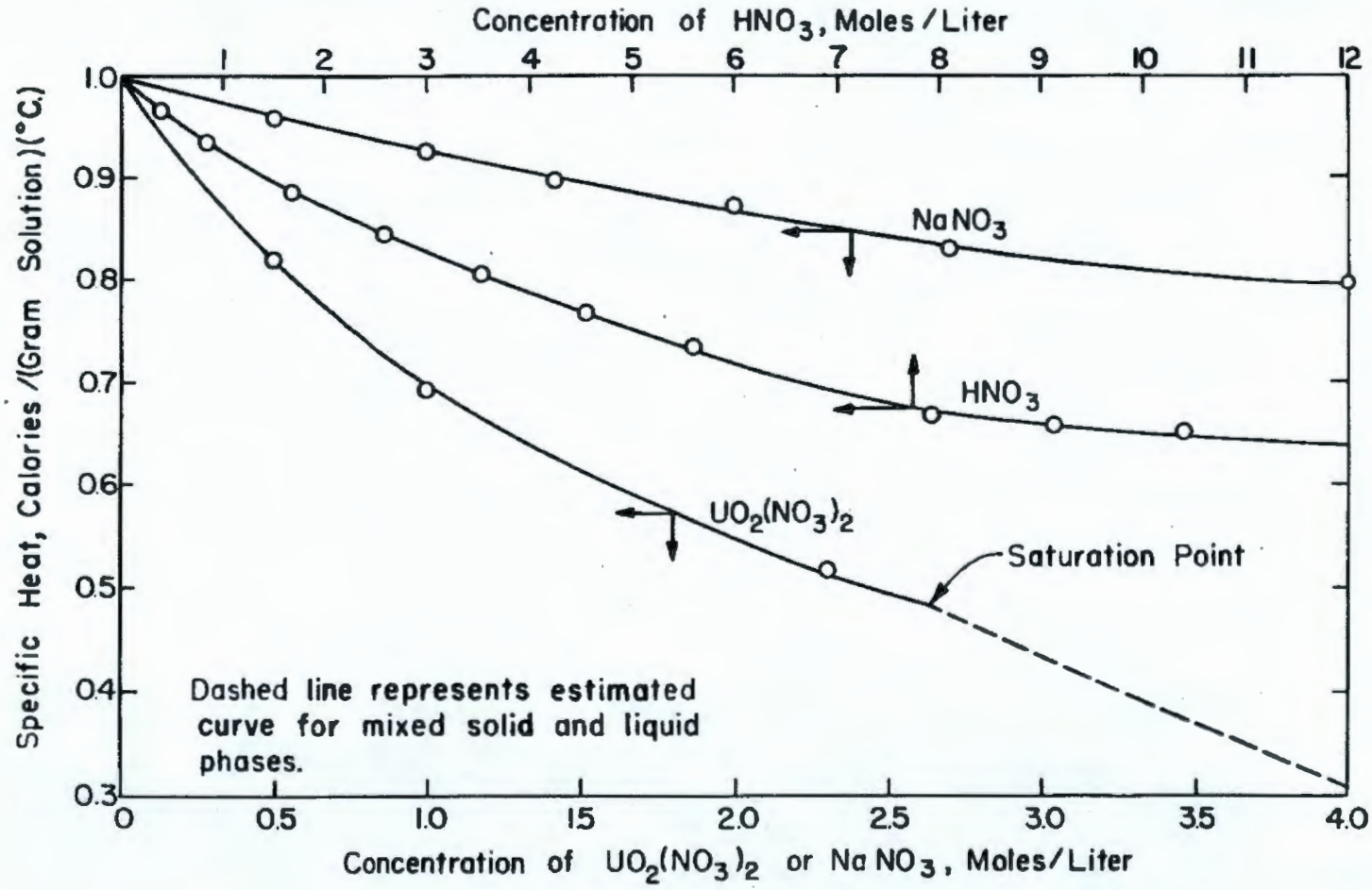

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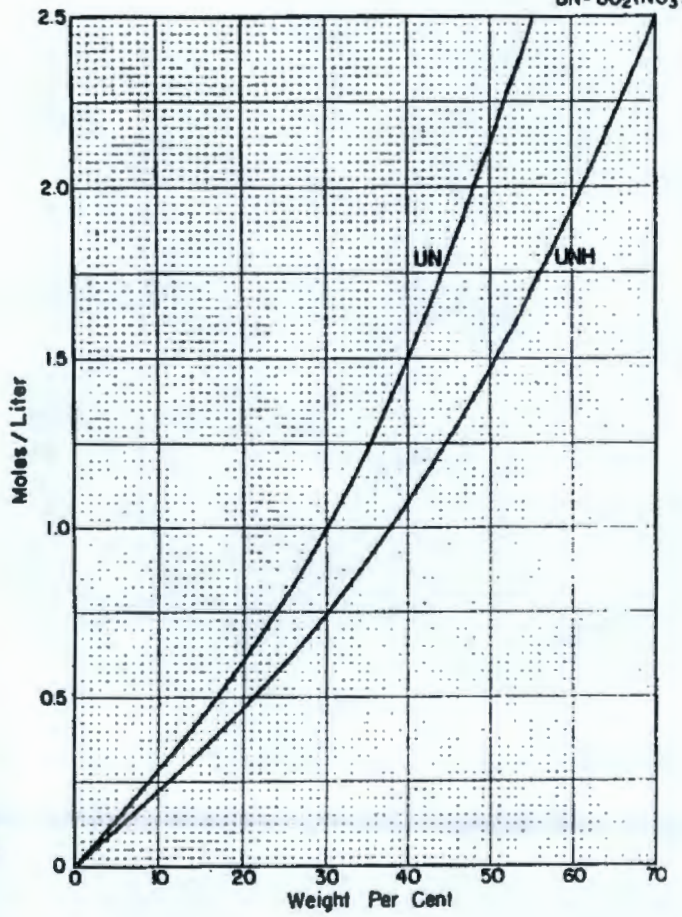
Figure IV-18

AQUEOUS URANIUM MOLARITY-WEIGHT PER CENT CONVERSION

SOURCE OF DATA: HW-11276; CL-697, Chapter II

$UN = UO_2(NO_3)_2$; $UNH = UO_2(NO_3)_2 \cdot 6H_2O$



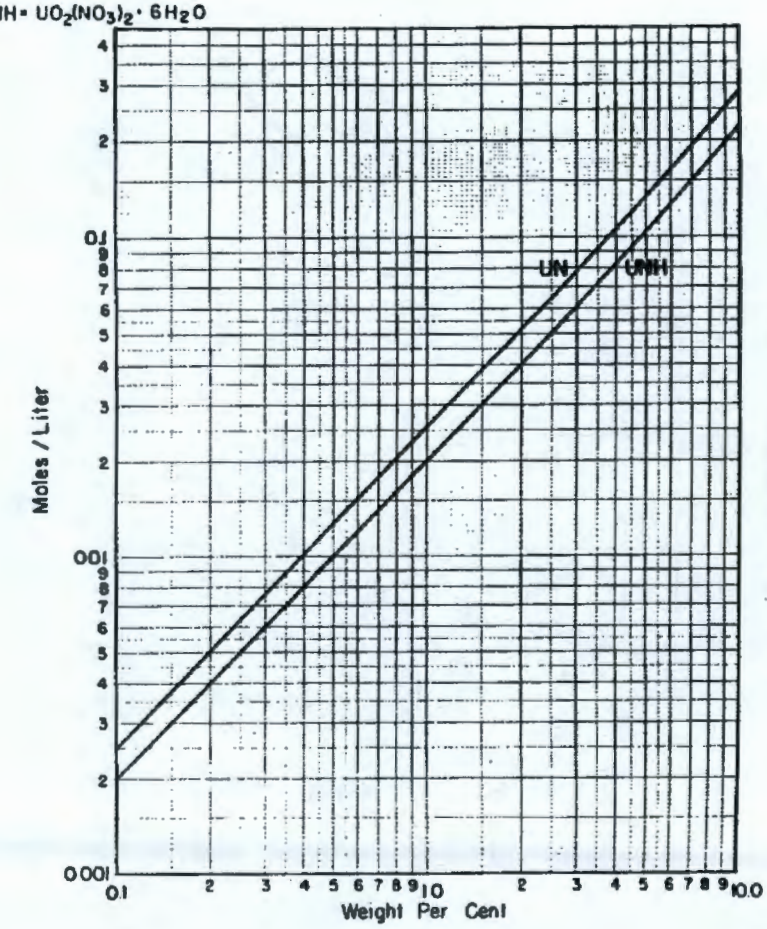


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Figure IV-19

SATURATION TEMPERATURES AND COMPOSITIONS
TBP-HW No.4 AND 5 NEUTRALIZED RAW
EFFECT OF DEGREE OF CONCENTRATION

SOURCE OF DATA: HW-18404

Compositions For TBP-HW No.4 Flowsheet

Volume Per Cent Neutralized RAW	Saturation Temperature, °C.	Na_2SO_4, G./L	Na_3PO_4, G./L	$NaNO_3$, G./L
100	14	30.97	25.94	332.4
80	18	38.71	32.43	415.5
63	26	49.15	41.17	527.6
47	36	65.89	55.19	707.2
45	39	68.82	57.64	738.6
44	60	70.50	58.95	755.4

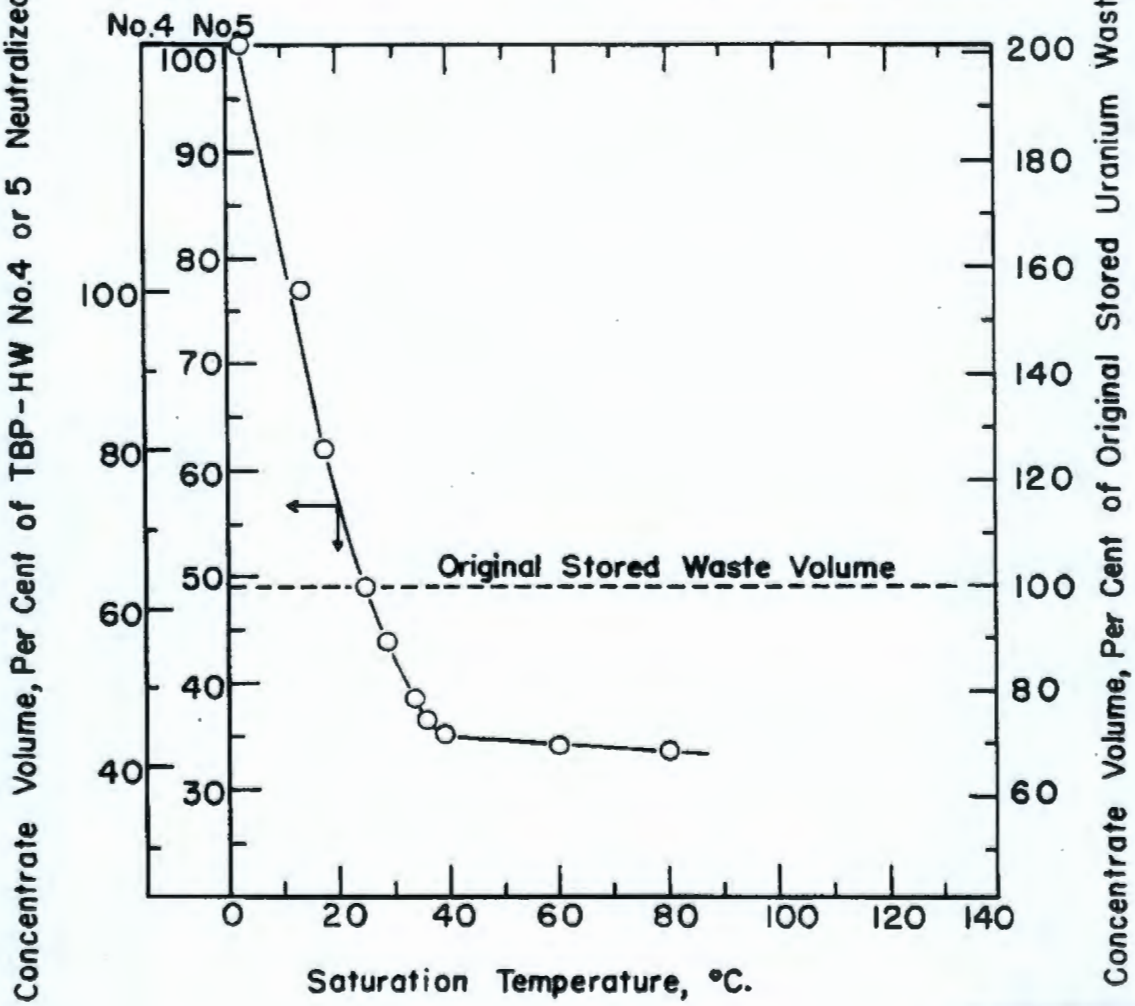

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Figure IV-20A

URANIUM DISTRIBUTION

RA COLUMN SYSTEM

EFFECT OF URANIUM CONCENTRATION

SOURCE OF DATA: HW-19696

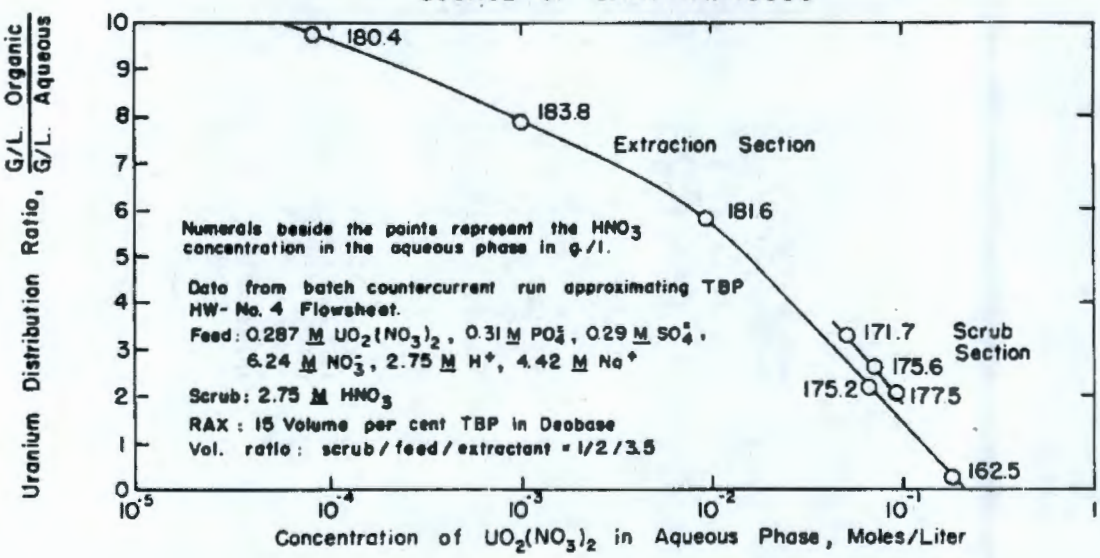

Figure IV-20B

URANIUM DISTRIBUTION

RA SCRUB SYSTEM

EFFECT OF DEGREE OF SOLVENT SATURATION

SOURCE OF DATA: ORNL-260

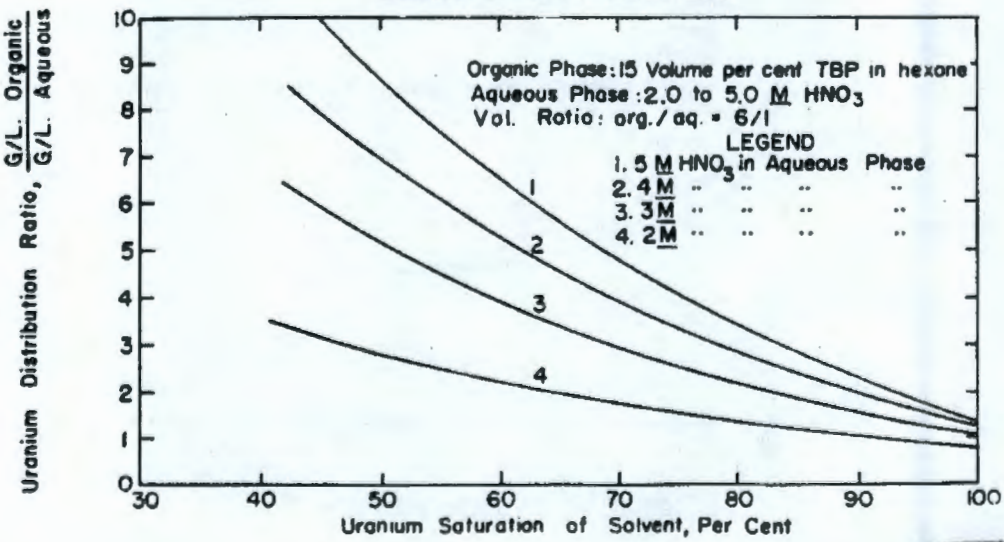

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Figure IV-21A
URANIUM DISTRIBUTION
RA COLUMN SYSTEM
EFFECT OF HNO_3 CONCENTRATION
SULFATE AND PHOSPHATE PARAMETERS
SOURCE OF DATA: ORNL-260

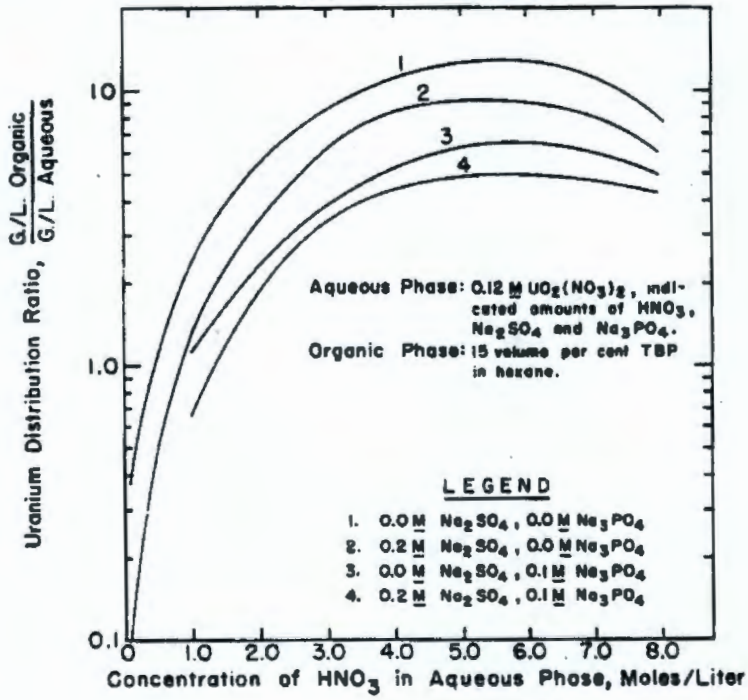

Figure IV-21B
URANIUM DISTRIBUTION
RA COLUMN SYSTEM
EFFECT OF HNO_3 CONCENTRATION
URANIUM AND TBP PARAMETERS
SOURCE OF DATA: HW-17339

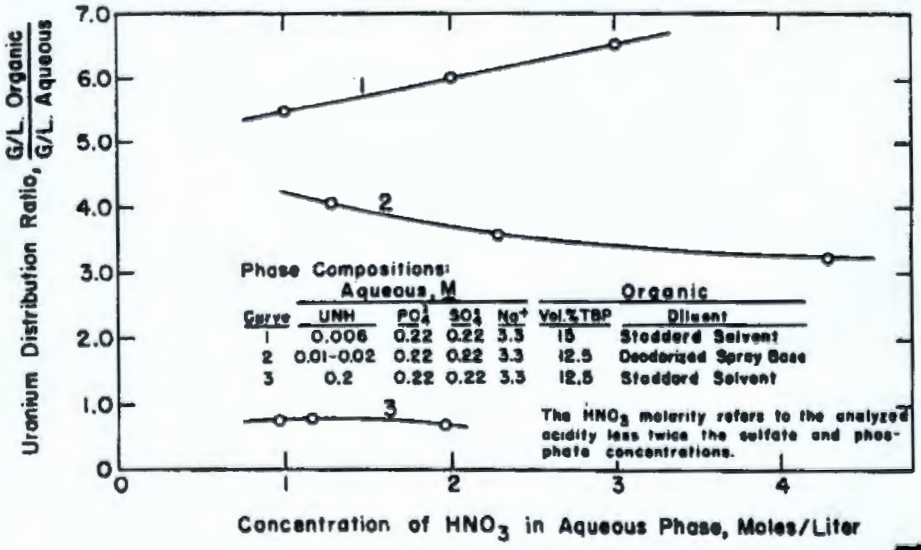

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Figure IV-22 A
URANIUM DISTRIBUTION
RA COLUMN SYSTEM
EFFECT OF PHOSPHATE CONCENTRATION
SOURCE OF DATA: HW-17339

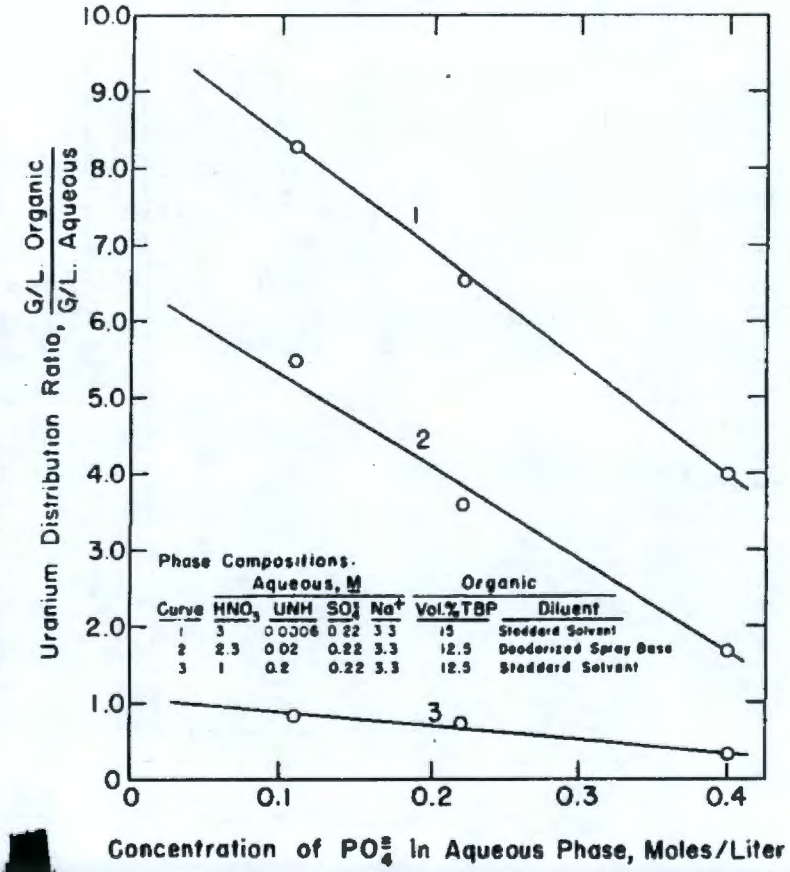

Figure IV-22 B
URANIUM DISTRIBUTION
RA COLUMN SYSTEM
EFFECT OF SULFATE CONCENTRATION
SOURCE OF DATA: HW-17339

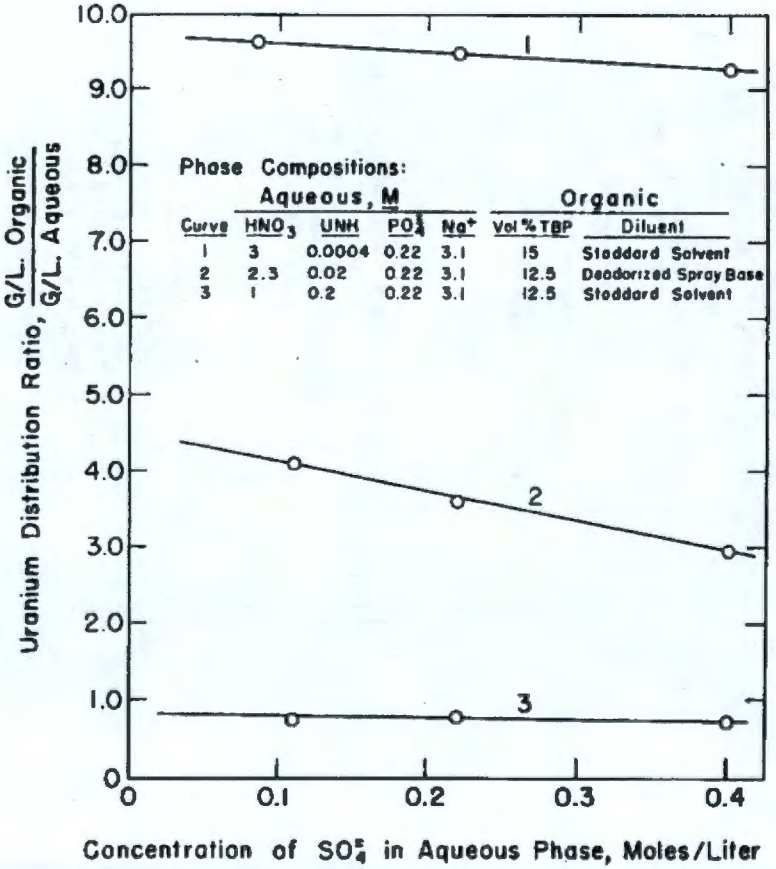

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Figure IV-23
URANIUM DISTRIBUTION
EFFECT OF TEMPERATURE
SOURCE OF DATA: HW-18880

Curve No.	Aqueous Molarity $UO_2(NO_3)_2$	Aqueous Molarity HNO_3	Organic Volume % TBP
1	0.09	0.42	15
2	0.12	RAF (a)	15
3	0.12	—	28
4	0.13	0.1	15
5	0.15	—	15
6	0.75	—	15

(a) RAF composition before equilibration: 142 g. UNH/L, 126 g. HNO_3/L, 27.5 g. $SO_4^{=}$/l., 28.7 g. $PO_4^{\equiv}$/l., 93.7 g. Na^+/l., 342.7 g. total NO_3^-/l.

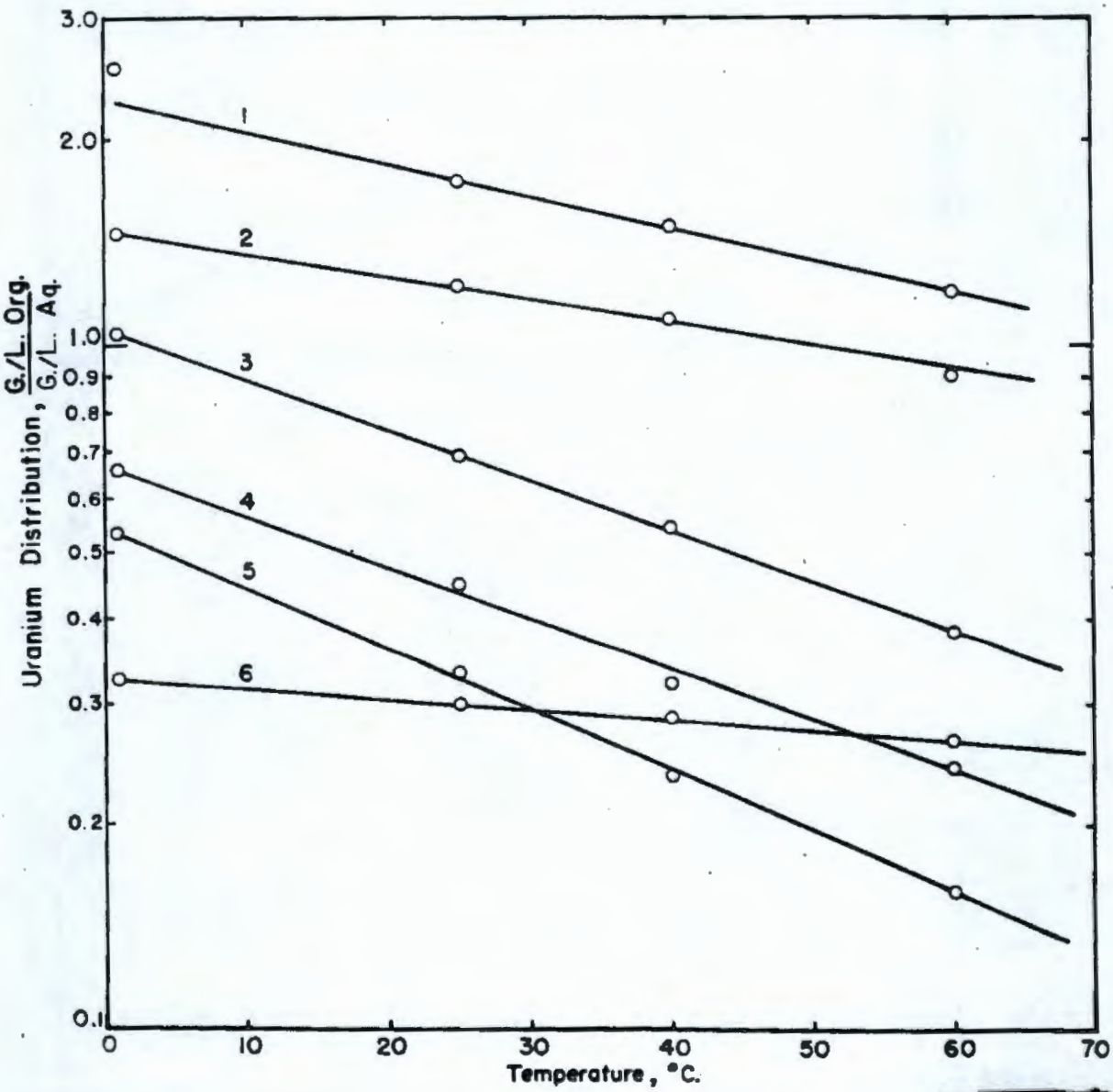

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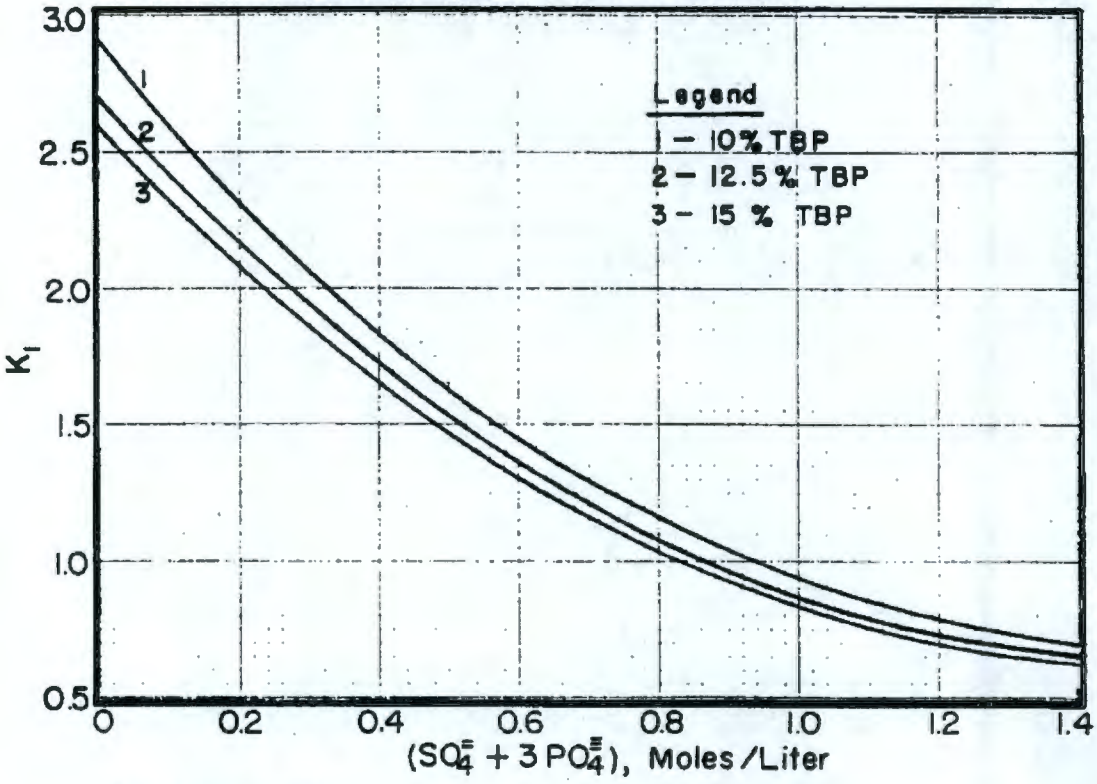
Figure IV-24 A

RA COLUMN PHASE EQUILIBRIUM CHART FOR DETERMINATION OF K_1

SOURCE OF DATA: HW-17747



Directions for use:

1. Determine K_1 from Figure IV-24A interpolating for correct TBP concentration.
2. Determine K_2 from Figure IV-24B interpolating for correct $NaNO_3$ concentration. Assume the following compounds in solution: $NaNO_3$, $UO_2(NO_3)_2 \cdot 6H_2O$, H_3PO_4, H_2SO_4, and "free" HNO_3. (If the acidity is reported as "titratable acid", the free HNO_3 may be calculated by subtracting twice the sulfate and twice the phosphate molarities from the total titratable acid molarity, the third H_3PO_4 hydrogen being assumed to be undissociated in the titration.)
3. Calculate $K^{1/2}$ from $K_1K_2 = K^{1/2}$
4. Use this value of $K^{1/2}$ to interpolate the proper uranium phase equilibrium curve on Figure IV-25, 26, or 27.

Figure IV-24 B

RA COLUMN PHASE EQUILIBRUIM CHART FOR DETERMINATION OF K_2

SOURCE OF DATA: HW-17747

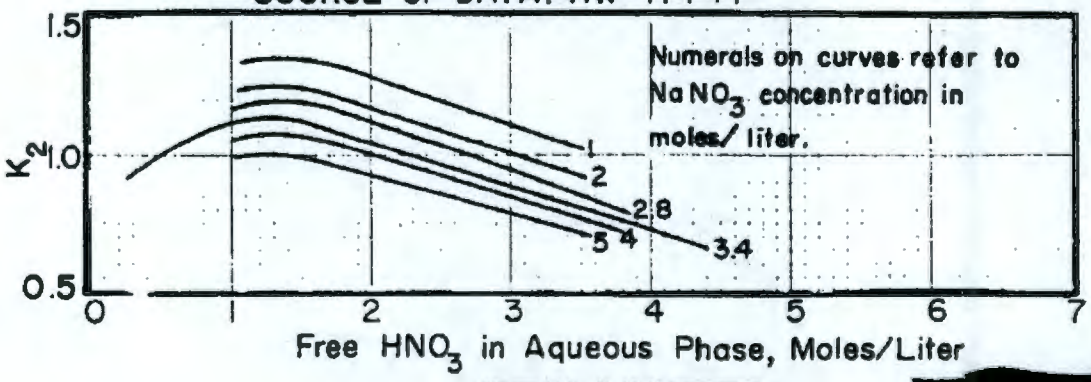


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Figure IV-25

RA COLUMN PHASE EQUILIBRIUM DIAGRAM

10 VOLUME PER CENT TBP IN DILUENT

SOURCE OF DATA: HW-17747

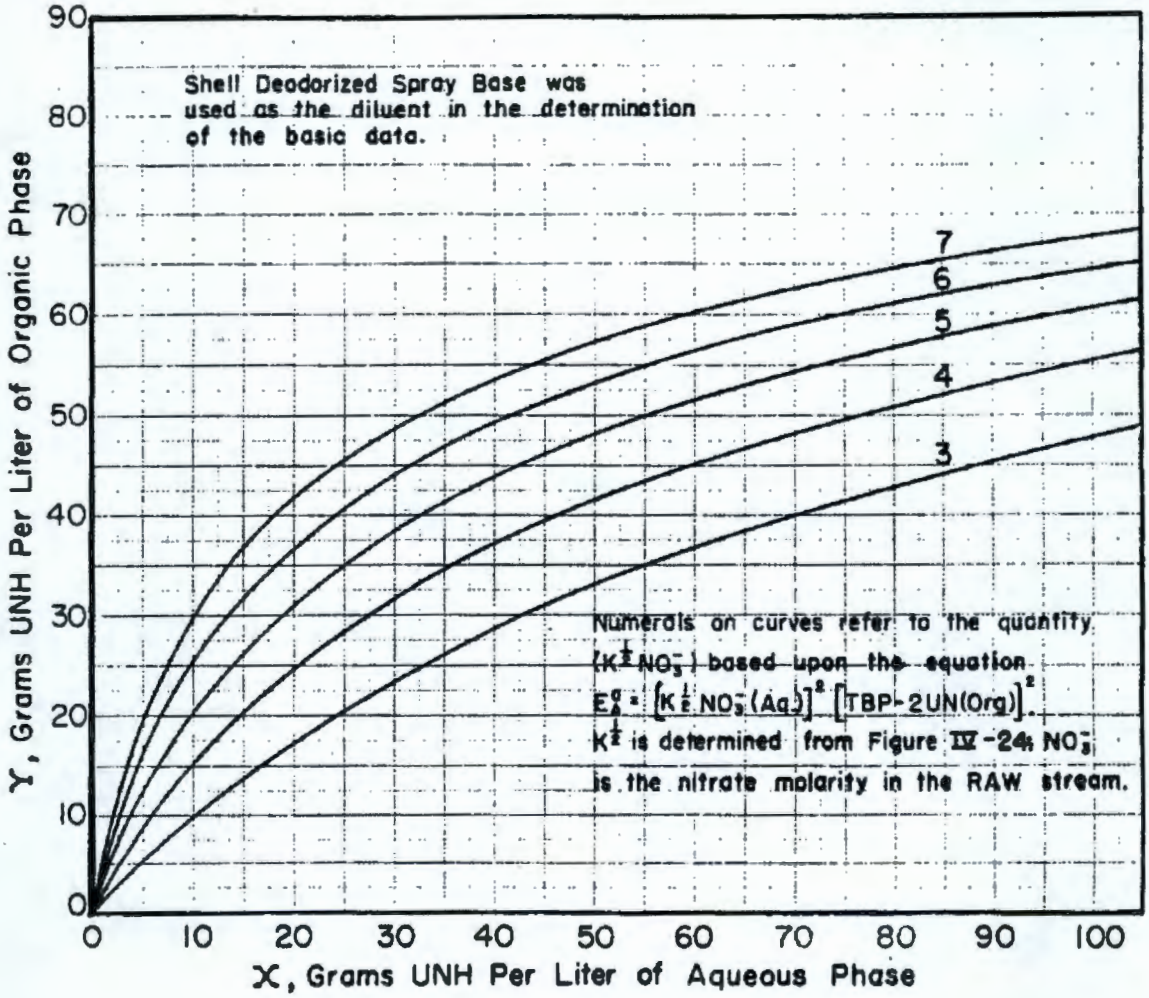

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Figure IV-26

RA COLUMN PHASE EQUILIBRIUM DIAGRAM

12.5 VOLUME PER CENT TBP IN DILUENT

SOURCE OF DATA: HW-17747

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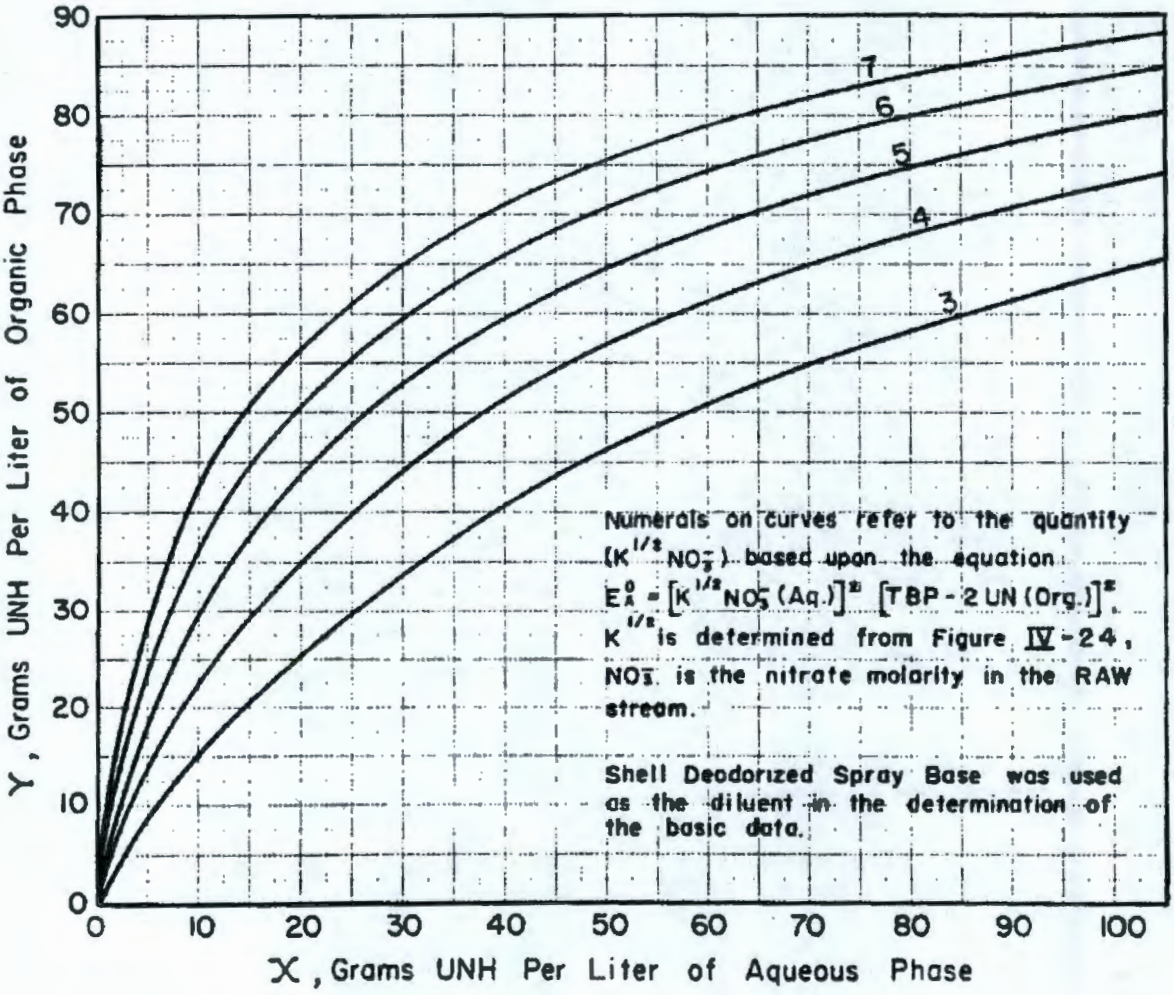

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Figure IV-27

RA COLUMN PHASE EQUILIBRIUM DIAGRAM
15 VOLUME PER CENT TBP IN DILUENT

SOURCE OF DATA: HW-17747

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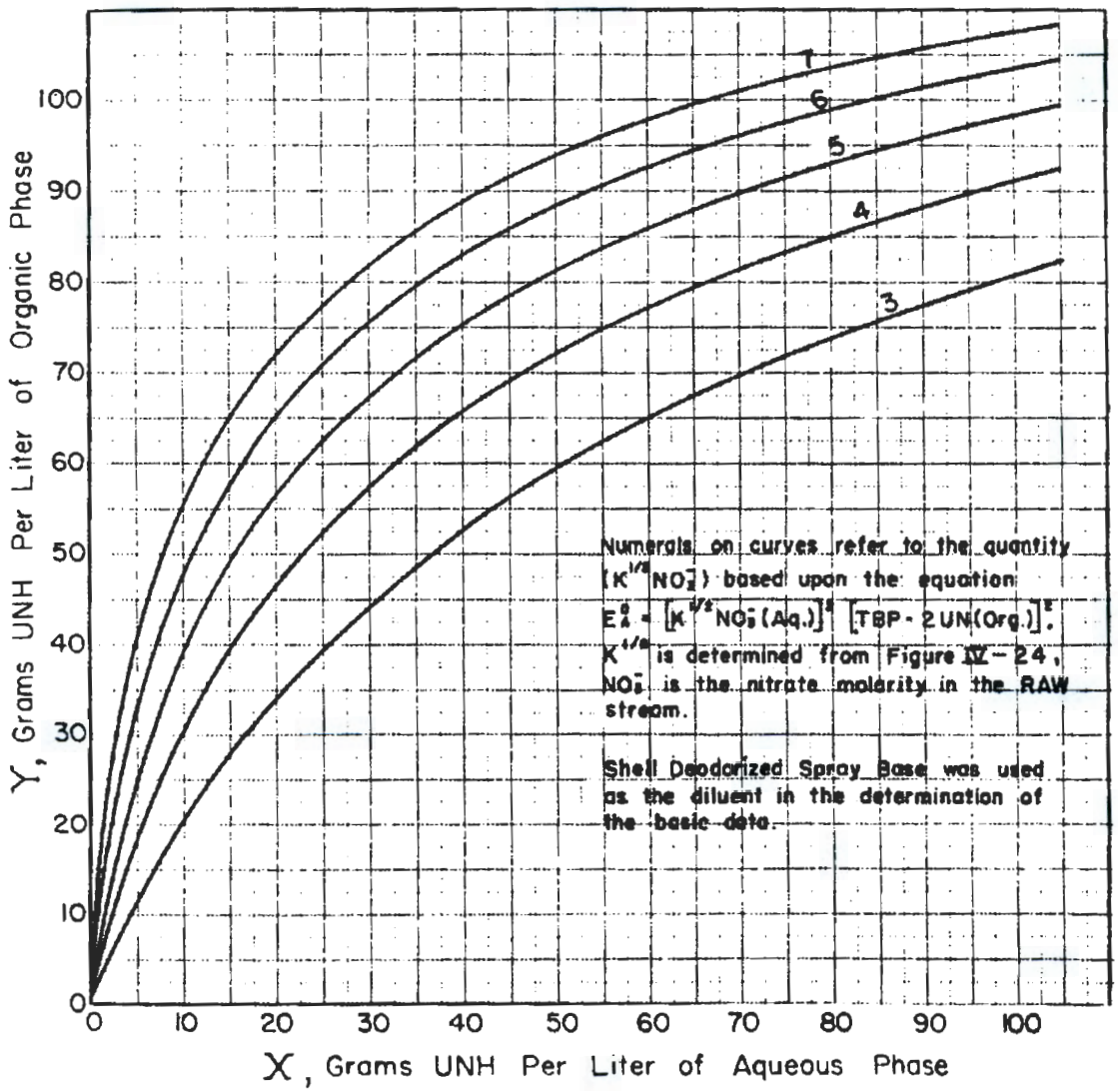

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Figure IV-28
URANIUM DISTRIBUTION
RC COLUMN SYSTEM
EFFECT OF URANIUM CONCENTRATION
SOURCE OF DATA: HW-17179

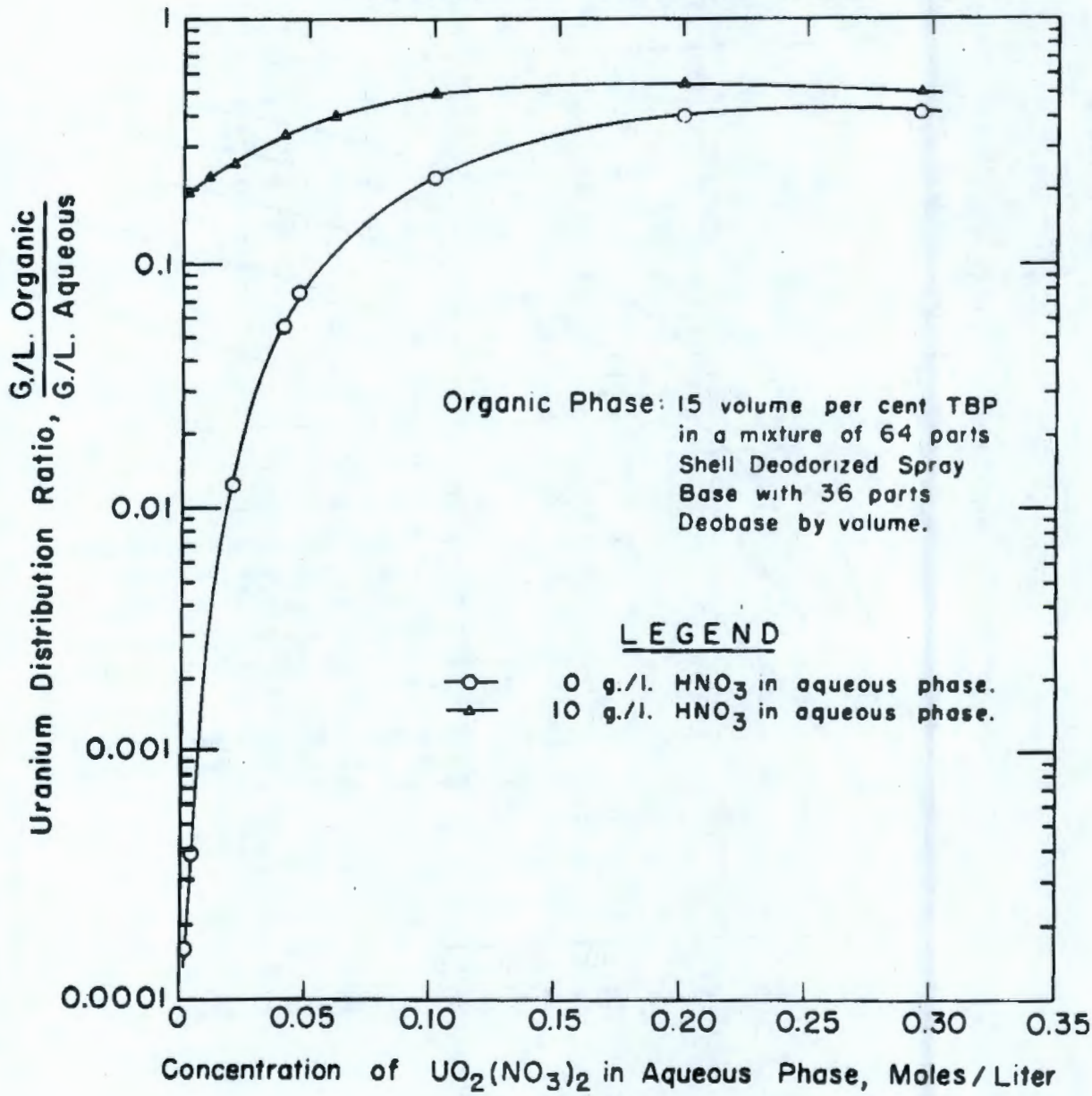

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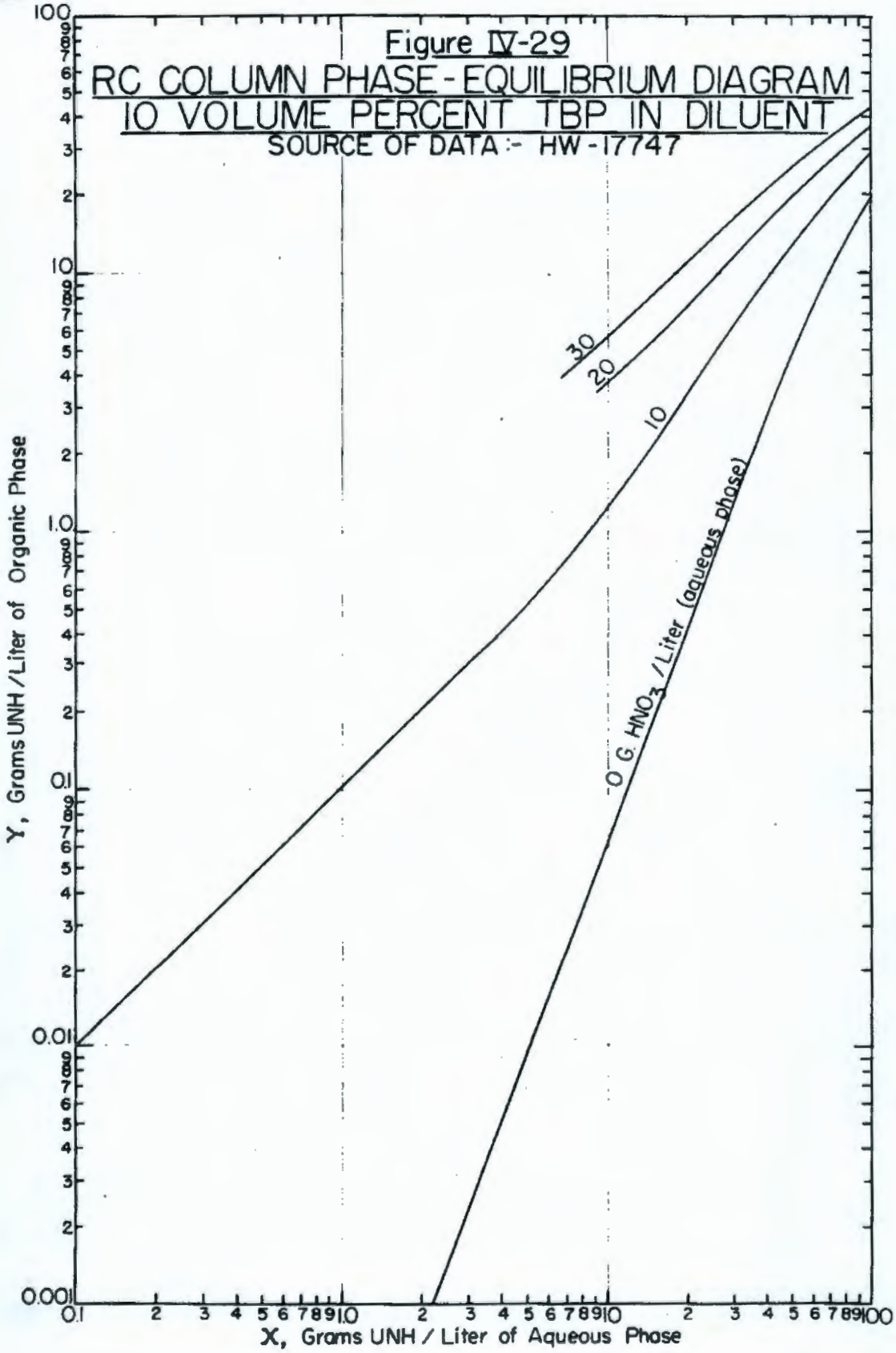
Figure IV-29

RC COLUMN PHASE-EQUILIBRIUM DIAGRAM
10 VOLUME PERCENT TBP IN DILUENT

SOURCE OF DATA :- HW-17747



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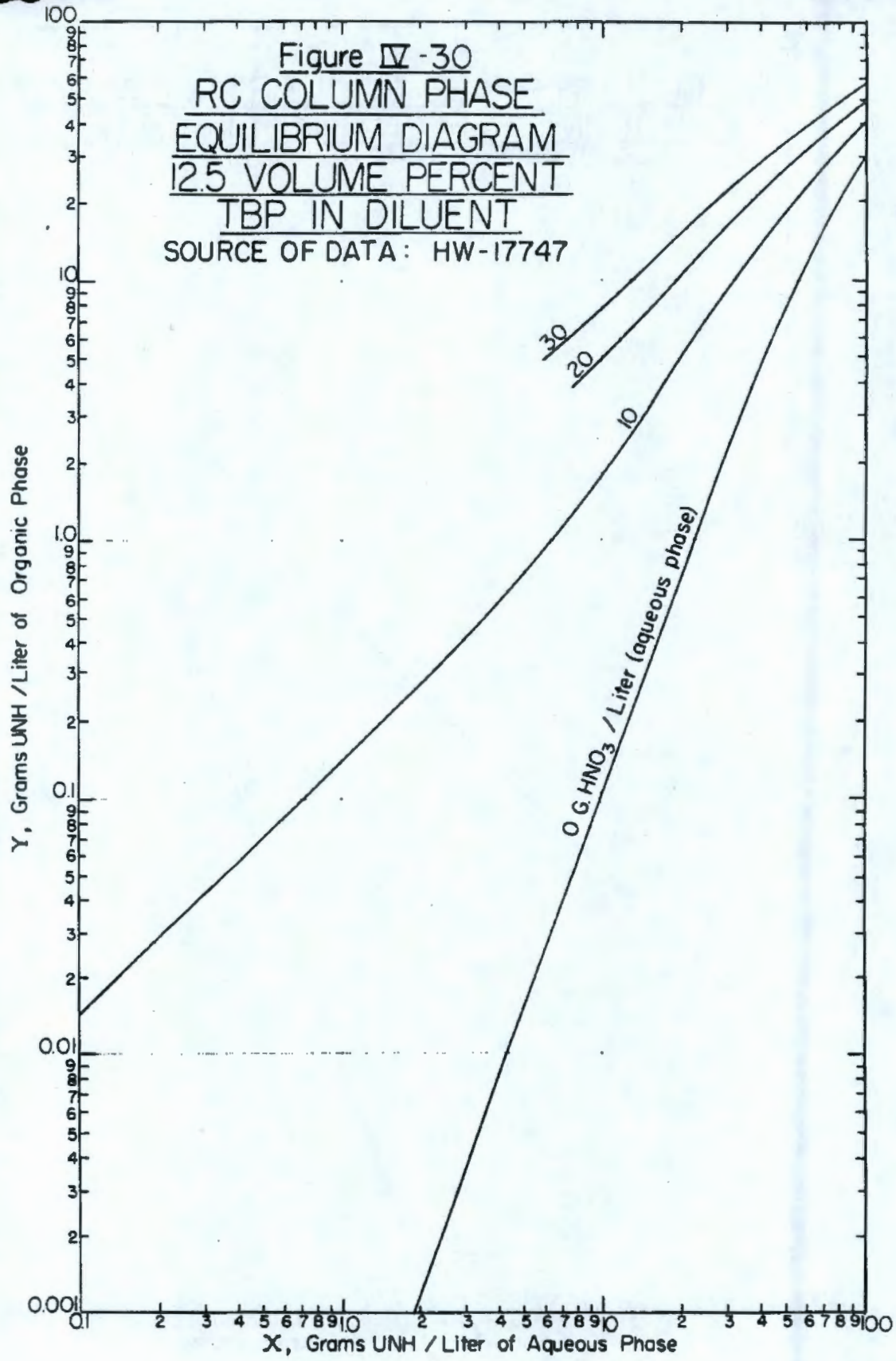

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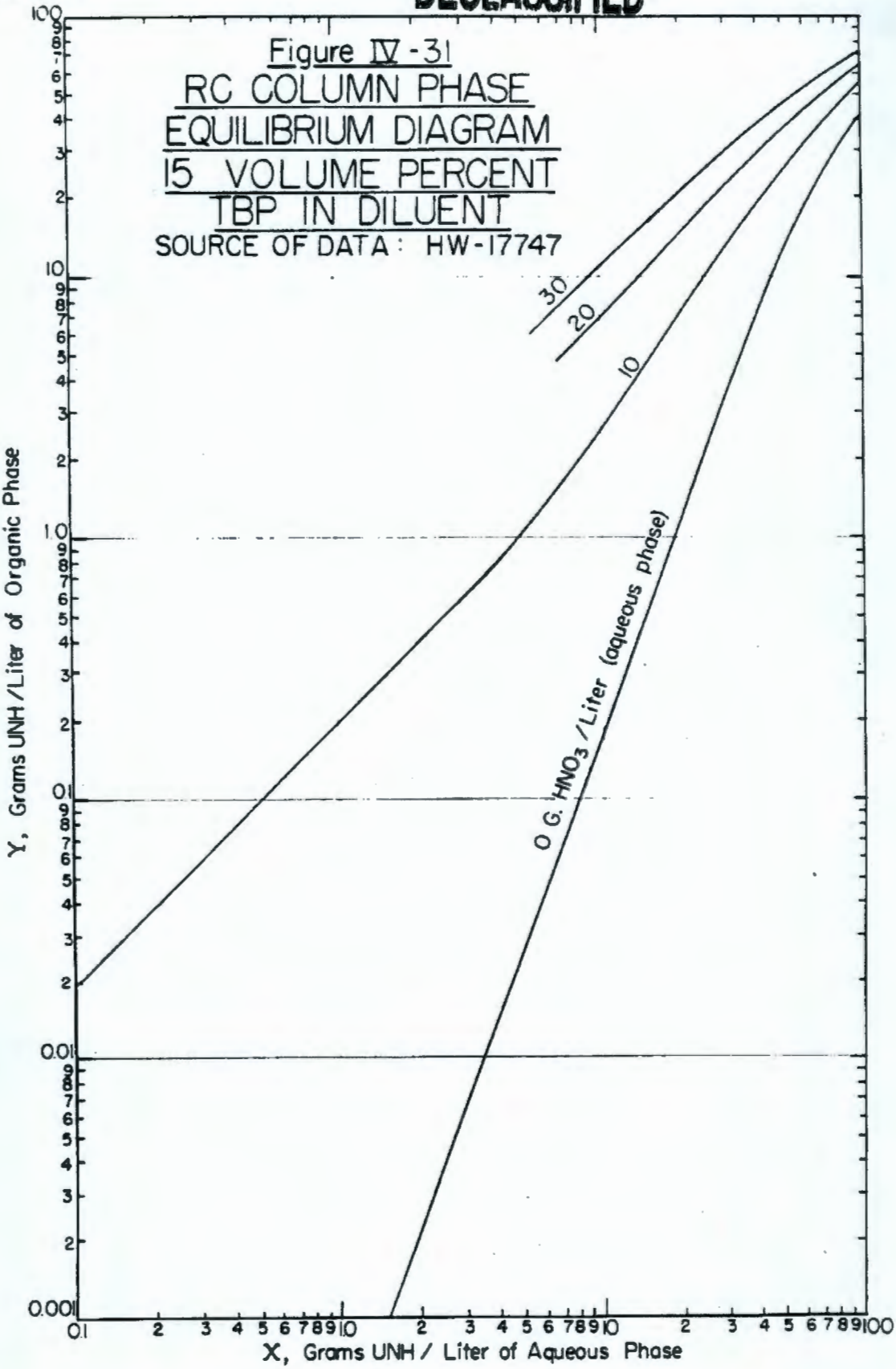

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Figure IV-32
PLUTONIUM DISTRIBUTION
EFFECT OF HNO_3 CONCENTRATION
& OXIDATION STATE

SOURCE OF DATA: ORNL-557

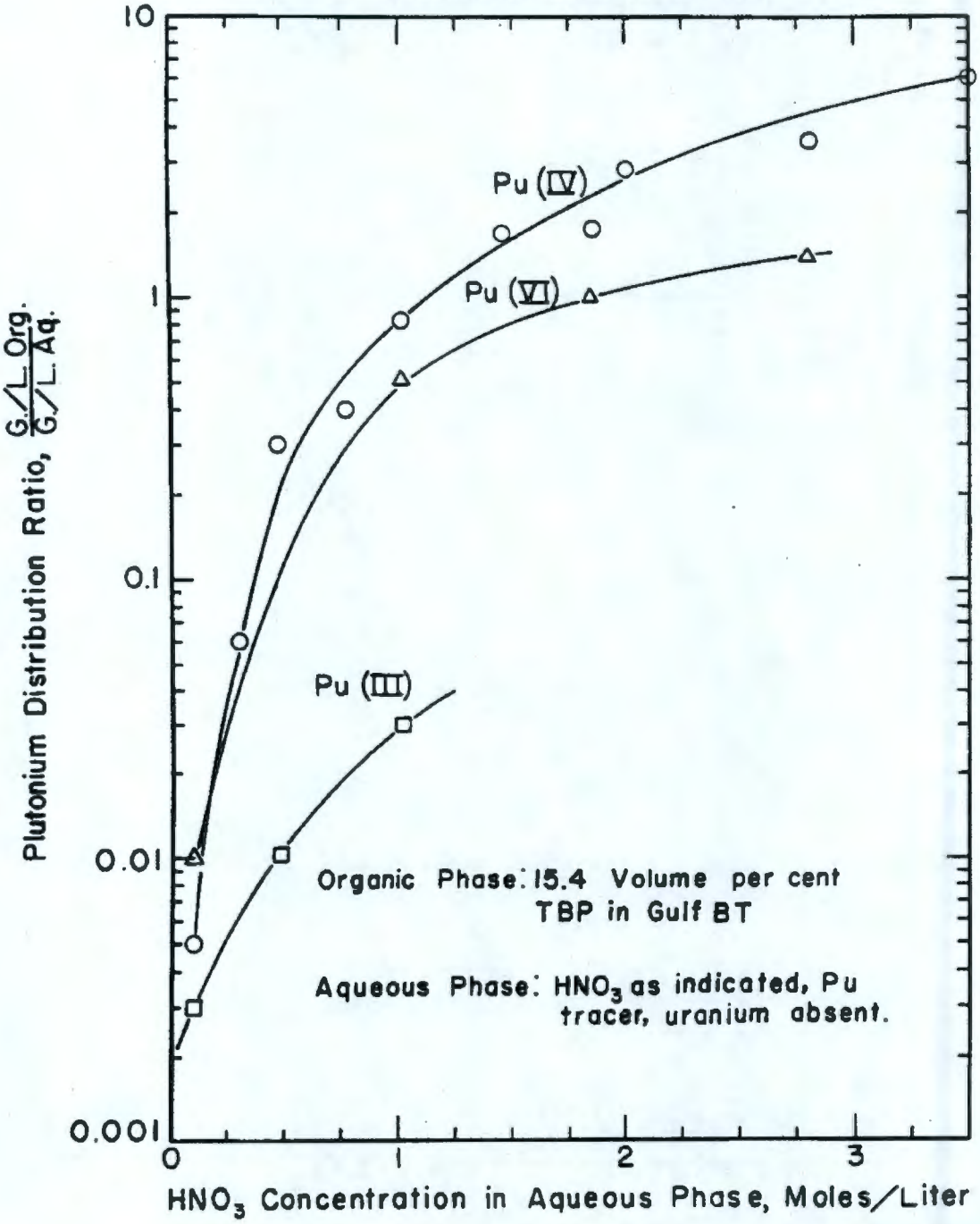

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Figure IV-33

PLUTONIUM (IV) DISTRIBUTION

EFFECT OF DEGREE OF URANIUM SATURATION OF TBP

SOURCE OF DATA: ORNL-717

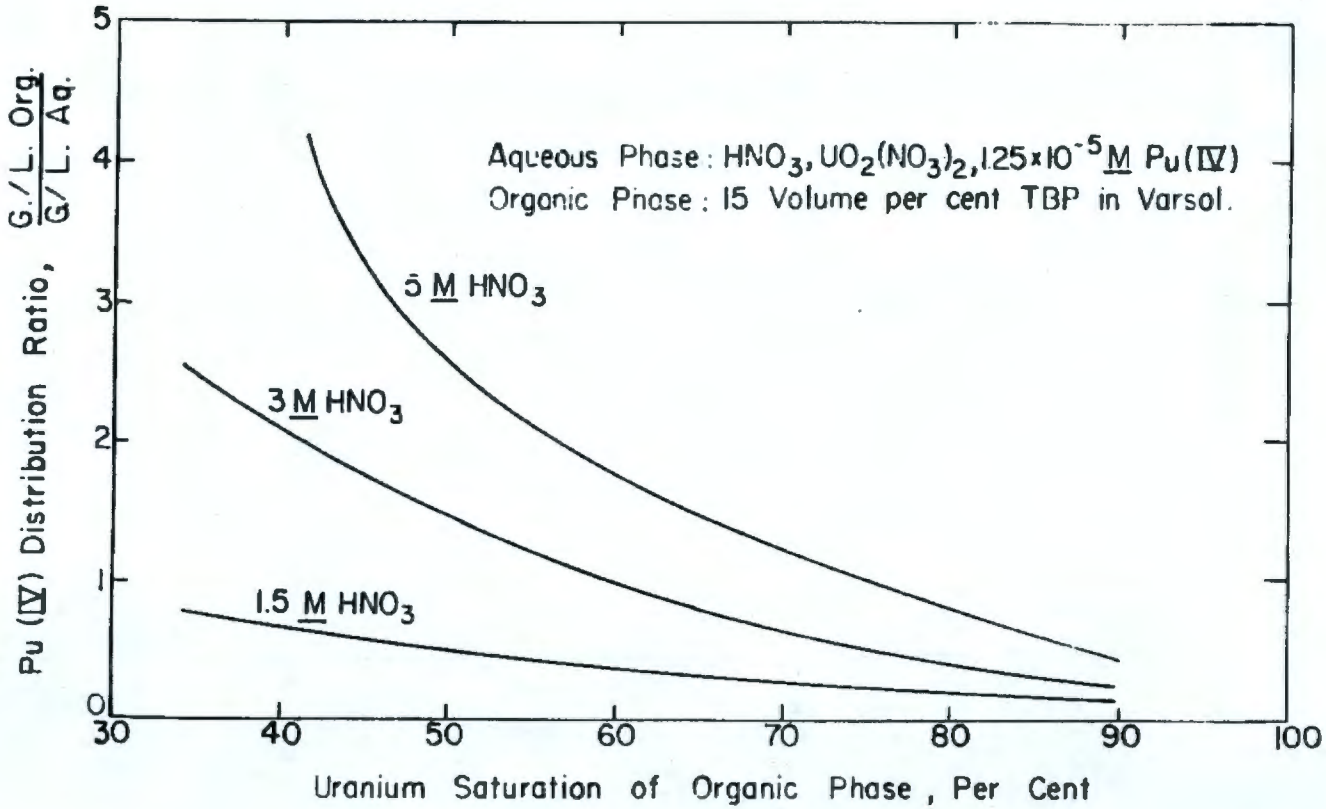

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Figure IV-34

ZIRCONIUM, RUTHENIUM AND GROSS FISSION-PRODUCT DISTRIBUTION EFFECT OF PER CENT URANIUM SATURATION OF TBP

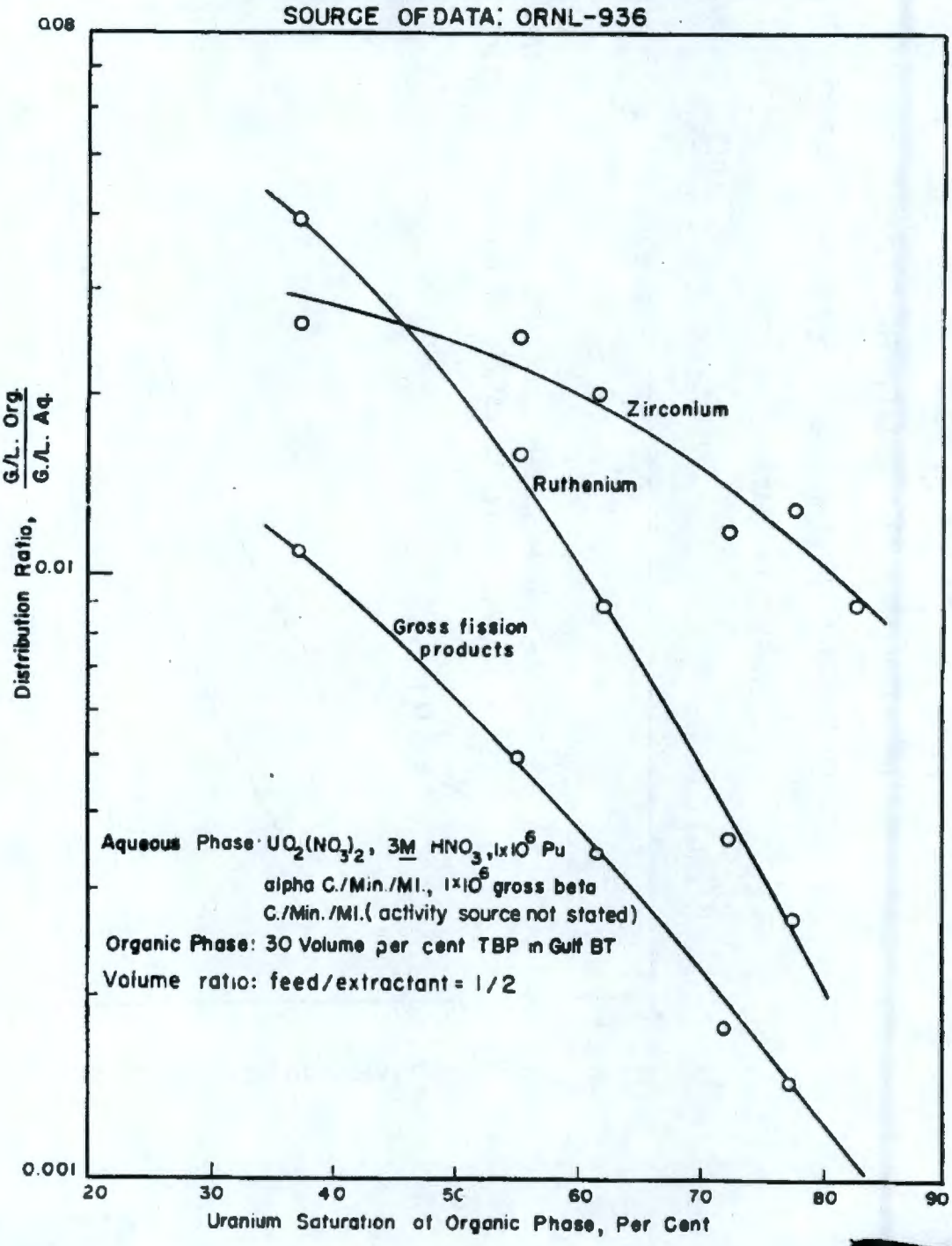

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Figure IV-35

GROSS BETA AND GAMMA-EMITTING FISSION-PRODUCT DISTRIBUTION
EFFECT OF URANIUM AND HNO_3 CONCENTRATION

SOURCE OF DATA: ANL-4530

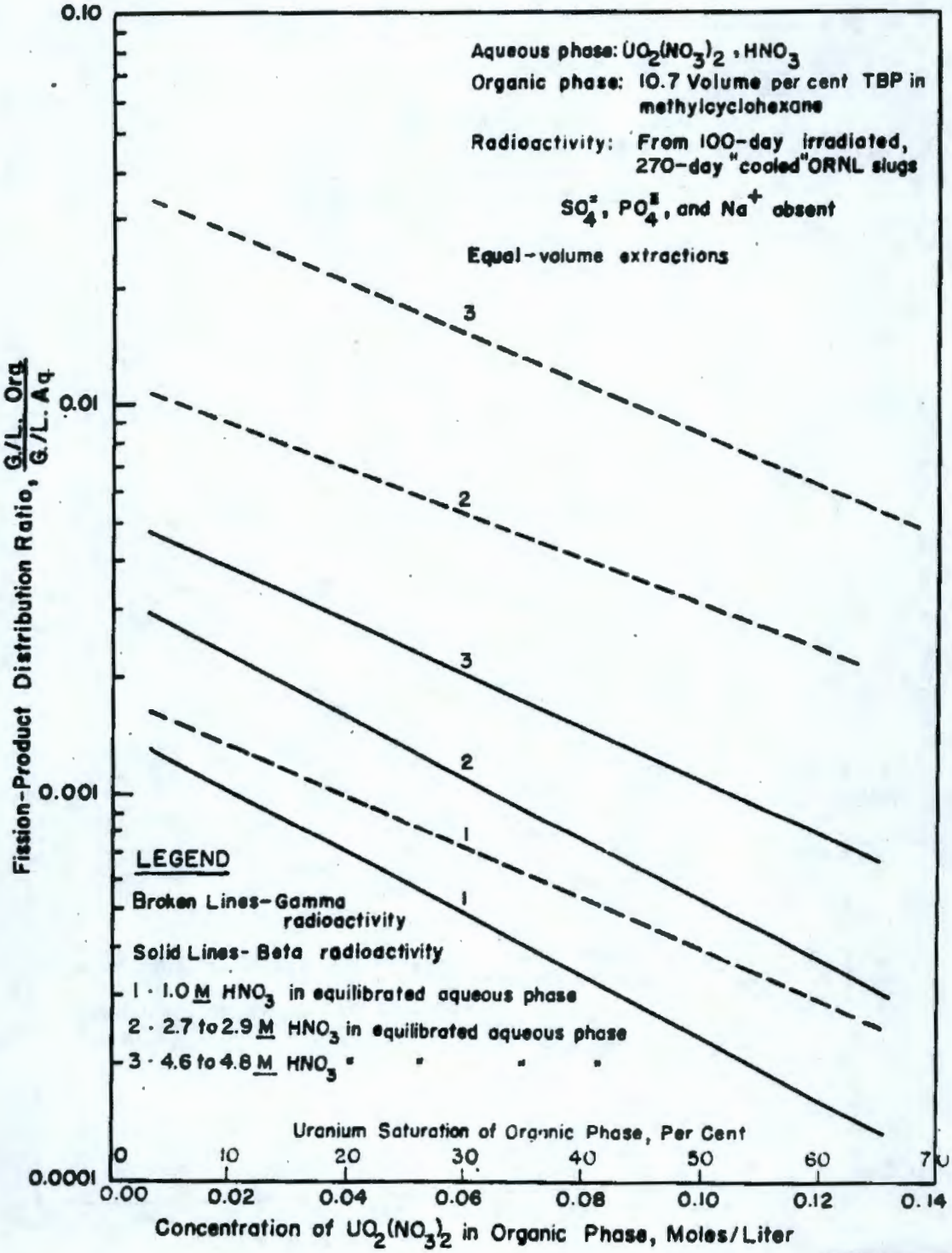

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Figure IV - 36

FISSION-PRODUCT DISTRIBUTION
EFFECT OF TBP AND HNO_3 CONCENTRATION

SOURCE OF DATA: ANL 4530

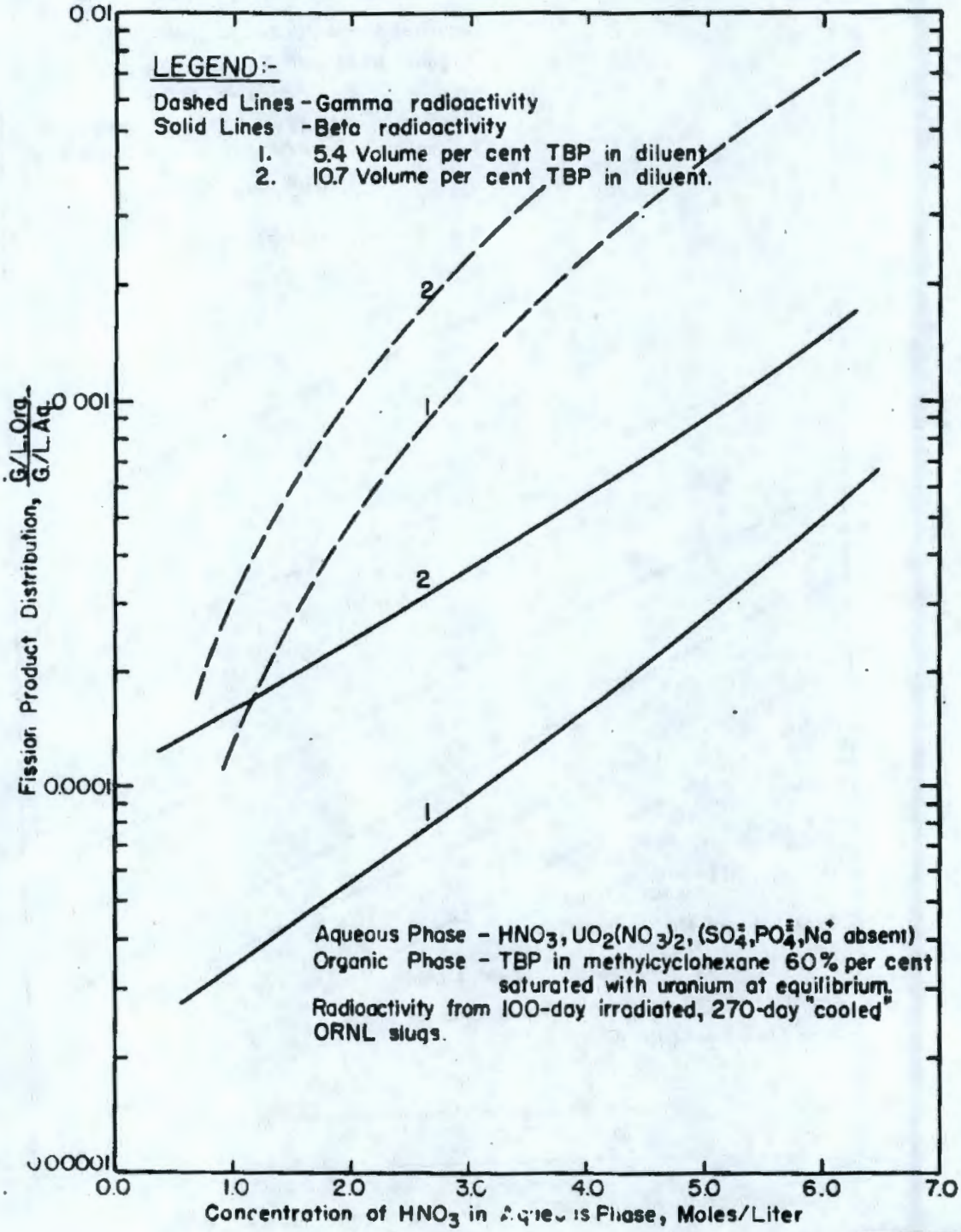

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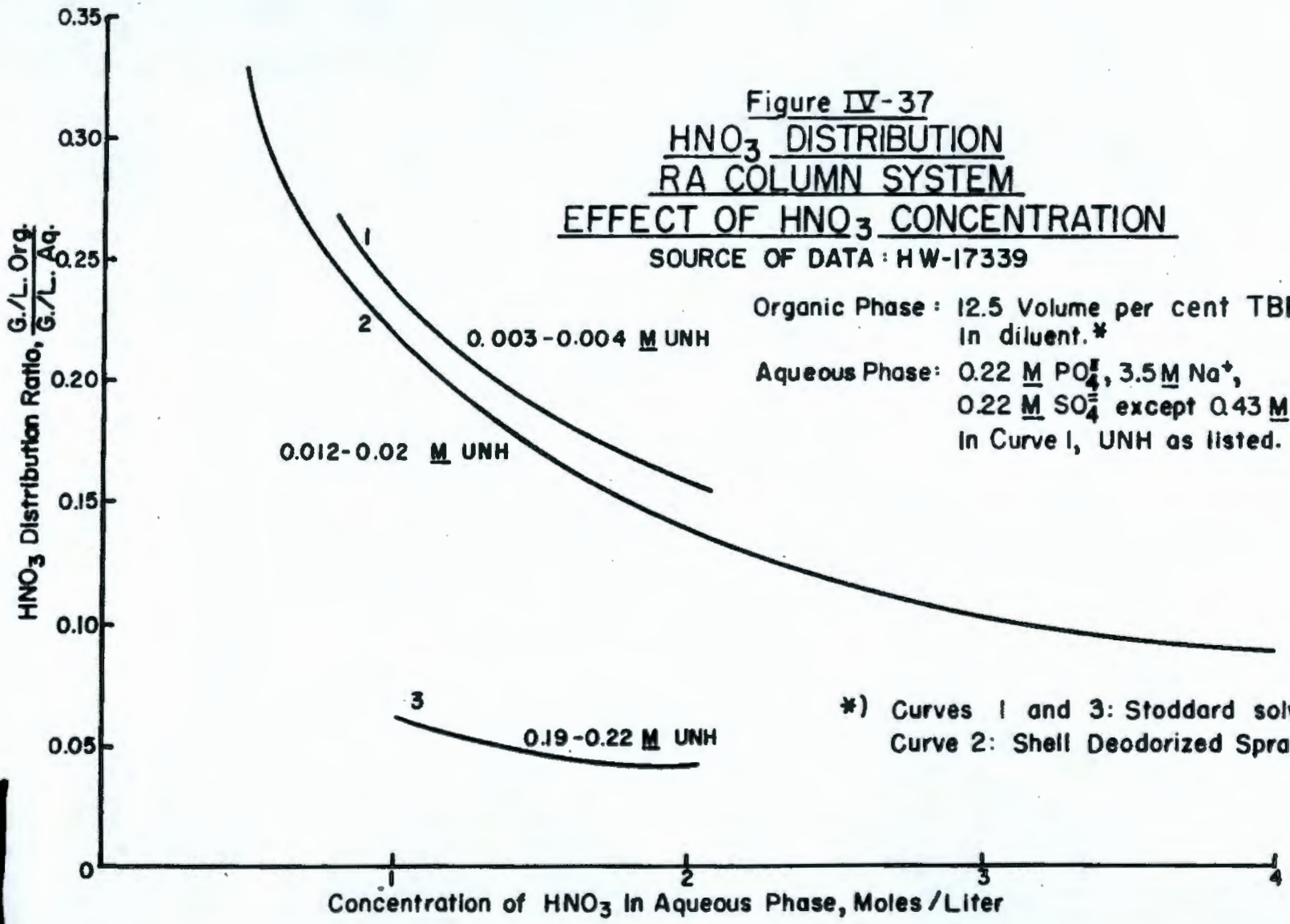
Figure IV-37

HNO$_3$ DISTRIBUTION

RA COLUMN SYSTEM

EFFECT OF HNO$_3$ CONCENTRATION

SOURCE OF DATA: HW-17339



Organic Phase: 12.5 Volume per cent TBP in diluent.*

Aqueous Phase: 0.22 M $PO_4^{\equiv}$, 3.5 M Na^+, 0.22 M $SO_4^{=}$ except 0.43 M in Curve 1, UNH as listed.

*) Curves 1 and 3: Stoddard solvent.
Curve 2: Shell Deodorized Spray Base.

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Fig. IV-37

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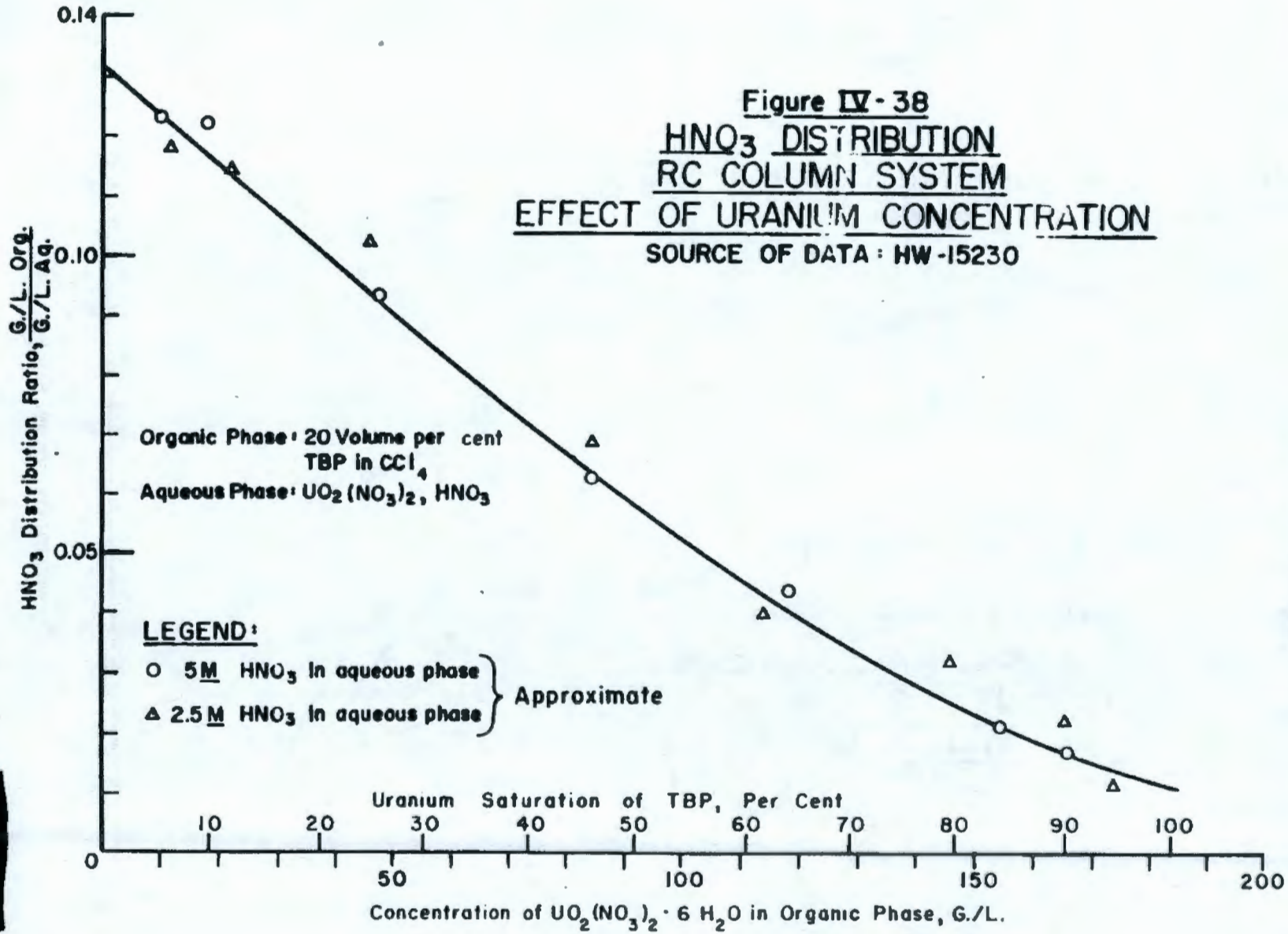

Figure IV-38
HNO_3 DISTRIBUTION
RC COLUMN SYSTEM
EFFECT OF URANIUM CONCENTRATION
SOURCE OF DATA: HW-15230

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PART II: PROCESS, continued

CHAPTER V. PROCESS ENGINEERING (SOLVENT-EXTRACTION)

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CHAPTER V. PROCESS ENGINEERING (SOLVENT-EXTRACTION)

A. BASIC PRINCIPLES

1. Introduction

Solvent-extraction operations are defined in the Chemical Engineers' Handbook[4] as "those in which separation of mixtures of different substances is accomplished by treatment with a selective liquid solvent". Although solvent-extraction operations may include leaching and washing of solids, the term as employed in this manual refers to liquid-liquid extraction. In liquid-liquid extraction the mixture treated is liquid and the two phases or layers resulting from the solvent treatment are both liquids. In the TBP-process RA Column, for example, uranyl nitrate dissolved in an aqueous phase is selectively extracted into an organic phase when the two liquids are brought into contact. The effectiveness of the extraction is dependent on the chemical composition and physical properties of the two phases as well as the type of extraction equipment.

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2. Solvent-Extraction Equipment

2.1 General

The physical construction of liquid-liquid extraction equipment may assume many different forms.[1][14][29] However, an extraction process consists of three operations, as follows: (a) mixing and bringing the material to be extracted into intimate contact with the solvent, (b) allowing the solute to diffuse, and (c) separating the resulting phases or layers. In addition, equipment is usually provided to recover and purify the solvent. The contact in the extraction equipment may be either of a stage-wise or of a differential nature. In a stage-wise system, the two phases are intimately contacted, causing the transfer of solute to the solvent phase to reach or at least approach equilibrium. The two phases are then separated and the process is repeated with fresh solvent. Each stage-wise contact which attains equilibrium is called a theoretical stage. In differential operation, a large number of short contacts between the solute-rich feed phase and the only sparingly miscible solvent phase is achieved by subdividing one phase and passing it countercurrently through the other, continuous phase. Settling or disengaging zones are provided to separate the phases after the required extent of countercurrent contact. Among the many types of equipment available, those which have been investigated for uranium and plutonium recovery systems are (a) the multiple-vessel mixer-settler, (b) the S.O.D. (Standard Oil Development) mixer-settler, (c) the pump mixer-settler (Separations Process Research Unit type), (d) the horizontal extractor, (e) packed columns, and (f) pulse columns. A more complete description of solvent-extraction equipment and a discussion of the advantages and disadvantages of the several types may be found in the Redox Technical Manual[14] and elsewhere.[3][4][29]

2.2 Pulse columns

In a pulse column, the liquid contents of the column are pulsed up

and down through a series of spaced horizontal perforated plates. This pulsing movement is superimposed on the net countercurrent flow. The upward and downward pulsing movement of the column contents through the plate perforations causes the perforated plates to provide agitation resulting in more or less intimate mixing of the two countercurrently flowing phases. The functioning of pulse columns under various conditions of flow rate and pulse frequency and amplitude is described in more detail in Subsection C2, below.

The pulsing operation also performs another important and necessary function in that it provides the means for countercurrent flow of the aqueous and organic phases. Experience indicates that the specific gravity difference between the two phases is usually not sufficient to cause an appreciable countercurrent flow through the small holes in the perforated plates. Consequently, the net flow of the lighter phase up and the heavier phase down the column is caused almost entirely by the actions of the pulse generator and stream pumps.

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Based on identical extraction duty, pulse columns have the advantage that they are shorter(7)(16) than packed columns and the disadvantage that they are mechanically more complex and therefore would be expected to require more maintenance.

Pulse columns have been selected as the solvent-extraction contactors for the Uranium Recovery Plant primarily because they could be fitted into the short cells in the TBP Plant Building (221-U). The height requirement for packed columns would have necessitated up to 35-ft. deep excavations to be made in four of the existing 221-U Building cells. It was realized that these excavations would be costly and might prove structurally hazardous.

The over-all heights of packed and pulse RA and RC Columns required for equally good performance are compared below:

Column	Extraction Column Total Height, Ft. Packed	Pulse
RA	50	21
RC	38	17

3. Special Terms

The terms defined in this subsection are those frequently used in discussing the operation or evaluating the performance of solvent-extraction columns. Examples, including colloquial terms which have come into use for the TBP process, are included in the following discussion.

3.1 Extraction, stripping, scrubbing

In connection with solvent-extraction in the TBP process, the term extraction is used to describe mass transfer, notably of uranium, from

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the aqueous to the organic phase, as in the lower section of the RA Column. (See the chemical flowsheet in Chapter I.)

The term stripping is used to describe mass transfer of uranium from the organic to the aqueous phase. Thus, in the RC Column uranium is said to be stripped from the organic feed to the aqueous effluent stream.

The removal of fission products from a uranium-bearing organic stream by contacting it with an aqueous stream is referred to as scrubbing. Thus, in the TBP process scrubbing is carried out in the upper plate section of the RA Column, above the RAF feed point.

3.2 Pulse amplitude and frequency

The term pulse amplitude is used to define the magnitude of the up-and-down motion of the pulse column liquid contents. Amplitude as used in this manual is defined as the distance between extreme positions that would be reached by the liquid during each pulse cycle if there were no net flow through the column. (The amplitude defined in this manner is twice the distance between one extreme position and the mean position.)

The pulse frequency is the time rate of pulsing. It is usually expressed in cycles per minute.

3.3 Simple and dual-purpose columns

As the name implies, a simple column is designed to carry out a single solvent-extraction function (either extraction, or stripping, or scrubbing). The TBP-process RC Column is a simple column performing only uranium stripping. The RA Column is designed to carry out two separate solvent-extraction functions and is therefore referred to as a dual-purpose or compound column. In the lower portion of the RA Column, uranium and some fission products are extracted, while in the upper section fission products are scrubbed from the organic phase.

3.4 Flooding

Flooding (or complete flooding) in a liquid-liquid extraction pulse column designates a typical behavior of the two liquid phases when flow rates are so high that the two phases cannot pass countercurrently and the dispersed phase leaves through the continuous-phase exit line at the dispersed-phase entry end of the column. Flooding also occurs if the continuous phase leaves the column through the exit line intended for the dispersed phase (e.g., RAS accompanies the RAU in the TBP-process RA Column). The flooding capacity is the throughput level (i.e., flow rates) at which an infinitesimal increase in flow rates results in flooding.

Local flooding in the column consists in an unusually large accumulation of dispersed phase at some location in the two-phase zone. It may appear as an accumulation of closely-packed dispersed-phase globules or as a single large globule filling the space between two or more plates. If a local flood maintains a given size (i.e., the increased effective "head" of the dispersed phase is sufficient to cause the dispersed phase

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to flow from the local-flood zone at a rate equal to the dispersed-phase flow rate entering the zone), the column may be operated indefinitely and give satisfactory performance as an extraction unit.

Cyclic local flooding consists in the formation and dissipation of local floods on a fairly frequent schedule.

3.5 Reflux (external and internal)

In solvent-extraction, as in other diffusional processes, external reflux may be returned to the solvent-extraction column to enrich the extract concentration. For example, the TBP-process RAU stream could be increased in uranium concentration by using a concentrated aqueous uranium solution in place of an aqueous-nitric acid mixture for the RAS stream.

In a dual-purpose column a portion of the solute may be extracted in one part of a column and stripped in the other. This phenomenon is referred to as internal reflux. For example, in the upper section of the RA Column a portion of the uranium in the organic phase is refluxed internally, some uranium being stripped from the organic phase by the RAS and carried back down the column where it is again extracted.

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3.6 Equilibrium and operating lines

As used in this manual, equilibrium lines refer to graphical representations of the equilibrium solute distribution between the phases for the chemical conditions expected in the countercurrent solvent-extraction contactors. Phase equilibrium lines for all the TBP columns have been determined from either simple batch or countercurrent batch laboratory studies conducted to approximate closely the chemical conditions expected in the extraction columns. These studies are discussed in Chapter IV.

An operating line is a locus of points depicting the actual solute concentrations of the aqueous and organic phases at various heights within the column. The operating-line equation is developed from a solute material balance made around either end of a packed or plate section. Typical operating and equilibrium lines and a discussion of their use in evaluating column performance are presented in Section B of this chapter.

3.7 Height equivalent to a theoretical stage -- (H.E.T.S.)

The mass-transfer effectiveness of solvent-extraction columns may be evaluated in terms of the height of contractor which is required to perform the same extraction as a single theoretical stage. A theoretical stage is achieved in a column when two influent streams (not at equilibrium), entering a section of the column, mix and produce effluent streams which are in equilibrium with one another. For solvent-extraction columns containing several theoretical stages the H.E.T.S. may be obtained by dividing the height of the contacting section by the number of theoretical stages required to accomplish the same extraction being carried out by the column.

Although the number of theoretical stages is generally obtained for the TBP-process columns by the graphical or semi-graphical methods discussed in Subsection 33 of this chapter, when the operating and equilibrium lines are both straight the number of stages (N_s) may be calculated from the following equation which is similar to a form presented by Colburn[2]:

$$N_s = \frac{\log \left[(1-P)\,M + P\right]}{\log (1/P)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where P = the extraction factor, L/mV for extraction and mV/L for stripping:

L/V = slope of the operating line, (volume of aqueous phase per unit time)/(volume of organic phase per unit time);

m = slope of the equilibrium line, (concentration, g./l., in the organic phase)/(concentration, g./l., in the aqueous phase);

M = X_1/X_2 for extraction and Y_1/Y_2 for stripping -- (if the extractant contains solute, the values of M become $(X_1 - Y_x/m)/(X_2 - Y_x/m)$ and $(Y_1 - X_x m)/(Y_2 - X_x m)$ for extraction and stripping, respectively;

X = the solute aqueous-phase concentration, g./l. -- subscript 1 designates inlet (feed) concentration, subscript 2 designates raffinate concentration, and subscript x designates extractant concentration;

Y = the solute organic-phase concentration, g./l. -- subscript 1 designates the organic feed concentration, subscript 2 designates the organic effluent concentration, subscript x designates the organic extractant concentration.

For the phase-equilibrium relationships involved in the TBP process (see Figs. V-1 and V-2) the equilibrium lines are curved. Therefore, the slope is not constant and the value of P varies. However, a close approximation of the number of stages may be obtained from the above equation by using an appropriate mean value for the slope of the equilibrium line.

3.8 Height of a transfer unit -- (H.T.U.)

The H.T.U. (height of a transfer unit), like the H.E.T.S. defined above, is a measure of the mass-transfer effectiveness of a solvent-extraction column. As compared with the H.E.T.S., it has certain

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correlation advantages, notably in that in TBP-process systems as in Redox process systems, it is less sensitive to variations in the numerical value of the extraction factor P.

The number of transfer units in the perforated plate sections of TBP-process columns may be expressed by the integrals:

$$N_{ow} = \int_{X_2}^{X_1} \frac{dX}{X - X^*}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

or

$$N_{oo} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where N_{ow} = the number of "over-all water-film" transfer units for transfer from the aqueous to the organic phase;

N_{oo} = the number of "over-all organic-film" transfer units for transfer from the organic to the aqueous phase;

X = the concentration of the diffusing component in the aqueous phase;

X^* = the concentration of the diffusing component in the aqueous phase in equilibrium with an organic phase of composition Y;

Y = the concentration of the diffusing component in the organic phase;

Y^* = the concentration of the diffusing component in the organic phase in equilibrium with an aqueous phase of composition X.

Thus, the number of transfer units is an integrated ratio of the change to diffusing-component concentration to the concentration driving force which causes the transfer between phases.

The H.T.U. (height of a transfer unit) is calculated by dividing the packed height by the number of transfer units calculated from one of the above integrals.

When the equilibrium and operating lines are both straight, the number of transfer units (N_t) may be calculated from the following equation, developed by Colburn:

$$N_t = \frac{2.3 \log \left[(1-P)\,M + P\right]}{1-P} \quad \ldots\ldots\ldots\ldots\ldots(4)$$

If the extraction values for M and P given under 3.7, above, are substituted

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in the above equation, N_t becomes N_{ow}. Similarly, if stripping values are substituted for M and P, N_t becomes N_{oo}. The equation is not rigorous unless the operating and equilibrium lines are both straight (constant P). However, approximate N_t values may be obtained by using an appropriate mean value of P.

The "over-all" number of transfer units, N_{ow} and N_{oo}, include contributions of both the individual aqueous and organic-film number of transfer units which are related by the following equations:

$$1/N_{ow} = 1/N_w + (L/mV)\ 1/N_o \quad \cdots\cdots\cdots\cdots\cdots\cdots (5)$$

$$1/N_{oo} = 1/N_o + (mV/L)\ 1/N_w \quad \cdots\cdots\cdots\cdots\cdots\cdots (6)$$

where N_w is the number of transfer units required for transfer across the aqueous film and N_o is the number of transfer units required for transfer across the organic film. It is seen from these equations that if the individual-film transfer-unit values are largely independent of P, as is often believed to be the case, the over-all values will be likewise independent whenever the terms $(L/mV)1/N_o$ and $(mV/L)1/N_w$ in Equations (5) and (6), respectively, are negligible, viz., when P (i.e., L/mV for Equation (5) or mV/L for Equation (6)) is less than about 0.1. As P increases from 0.1 to 1, the terms $(L/mV)1/N_o$ and $(mV/L)1/N_w$ become increasingly significant, so that more significant variation of over-all transfer-unit values with P might be expected in this region.

3.9 Relation between H.T.U. and H.E.T.S.

By combining the integrated expressions for N_t (number of transfer units) and N_s (number of theoretical stages) presented under A3.7 and 3.8, above, it is found that the H.E.T.S. and H.T.U. are theoretically related by the equation below, which is rigorously correct only for straight operating and equilibrium lines:

$$\frac{\text{H.E.T.S.}}{\text{H.T.U.}} = \frac{-2.3 \log P}{1-P},$$

where the extraction factor P is, as explained under A3.7, the slope of the operating line divided by the slope of the equilibrium line for extraction operations and the reciprocal for stripping operations. For operating and equilibrium lines which are both straight and parallel, the value of P is unity and, although the above equation reduces to an indeterminate form, it may be demonstrated that the H.E.T.S. equals the H.T.U. As the relative slopes of the operating and equilibrium lines are changed so that these lines diverge more and more, the numerical value of P becomes progressively smaller than unity and the H.E.T.S. becomes progressively larger than the H.T.U. For curved operating and/or equilibrium lines, the equation applies as an approximation provided appropriate mean values of the slopes of these lines are chosen.

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B. THE OPERATING DIAGRAM (H.E.T.S. AND H.T.U. CALCULATIONS)

1. Introduction

The purpose of this section is to discuss the calculation procedures and operating diagrams used in evaluating the solvent-extraction performance of the RA and RC Columns. Examples of H.E.T.S. and H.T.U. calculations are given in Subsection B3. A summary of the expected H.T.U. values for the plant RA and RC Columns under TBP-HW No. 4 and No. 5 Flowsheet conditions is given in Subsection C3.

The operating diagrams discussed in this chapter are X-Y plots (somewhat similar to the McCabe-Thiele diagram used in distillation) with X and Y axis values depicting aqueous and organic phase concentrations, respectively. Each of the diagrams includes an X-Y equilibrium line for the diffusing uranium (see the equilibrium data in Chapter IV and HW-17747) and an operating line derived from a material balance around the column. The operating diagrams are used for calculating the number of equivalent theoretical stages and/or the number of transfer units required for the desired extraction.

From the operating diagram, quantitative or qualitative analysis may be made of the effects which changing operating variables have on the extraction efficiency of the separation. On Figures V-1 and V-2 parameters which show the effect of nitrate ion concentration upon phase equilibrium are included.

2. Operating Line Equations

The units used for constructing the RA and RC Column operating diagrams were chosen as grams of UNH (uranyl nitrate hexahydrate) per liter of solution. By neglecting the change in the volume of solution flowing (L and V) due to the slight mutual solubility of the organic and water phases and the transfer of uranyl nitrate and HNO_3, a material balance around the bottom end of the column produces a straight operating line, represented by the equation below, employing the usual nomenclature (defined in Table V-1).

$$L(X - X_w) = V(Y - Y_x) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (7)$$

or

$$Y = (L/V)X + Y_x - (L/V)X_w \quad \cdots\cdots\cdots\cdots\cdots \quad (8)$$

A similar balance may be made around the scrub section (top) of the RA Column and leads to the equation

$$Y = (L/V)X + Y_u - (L/V)X_s \quad \cdots\cdots\cdots\cdots\cdots \quad (9)$$

The operating line for the RC Column is developed in an analogous manner by a material balance around the top of the column, yielding the equation:

$$Y = (L/V)X + Y_w - (L/V)X_x \quad \cdots\cdots\cdots\cdots \quad (10)$$

The use of the operating lines presented above is illustrated in Subsection B3 and Figures V-1 and V-2. For a derivation of the operating line equation reference is made to Chapter V of the Redox Technical Manual.(14)

3. Example H.E.T.S. and H.T.U. Calculations

3.1 Example H.E.T.S. calculation -- RA extraction section

Outlined below is an evaluation of the uranium mass transfer performance of the extraction section of a TBP RA Column as indicated by a graphical stage step-off computation of H.E.T.S. A discussion of the theory of the method may be found in Perry(4). In this example the column is operating under conditions approximating those shown on the TBP-HW No. 4 Flowsheet, presented in Chapter I.

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The following data were obtained during the steady-state period of a typical pilot-plant run, 16"-17-RAU, in a 16-inch-diameter column with a 12.1-foot-high perforated-plate section.

Stream	Volume, Liters	UNH Concentration, G./L.
RAF	4,650	134.5
RAS	2,910	0
RAX	11,750	0.0045
RAU	11,860	53.9
RAW	7,700	0.16

Substituting these data in Equations (8) and (9) presented in Subsection B2 leads to the following operating line equations:

For the Scrub Section: $Y = 0.245X + 53.9$ ..... (11)

For the Extraction Section: $Y = 0.655X - 0.1003$ .....(12)

These equations are graphically presented on Figure V-1 together with the appropriate equilibrium line, selected in accordance with the uranium mass-transfer equilibrium information in Chapter IV.

Before the number of stages in the extraction section can be calculated, the composition of the aqueous and organic phases at the top of this section must be determined. It should be recalled that because of the mechanical construction of the RA Column, which is a dual-purpose column, the organic effluent from the extraction section is the influent to the scrub section and the aqueous effluent from the scrub section mixed with the RAF (feed) is the influent to the extraction section. For calculation purposes it has been assumed that sufficient stages are present in the scrub section so that the organic and aqueous phases at the bottom of the scrub section are in equlibrium, i.e., the organic phase composition at the bottom of the scrub section (or top of the extraction section) is

found at the intersection of the scrub section operating and equilibrium lines. After the organic composition is determined, the stage step-off procedure can either start or terminate at this value of Y. In Figure V-1, the step-off is started at the waste composition, X_w (0.16 g./l.), using the RAW total NO_3^- concentration to determine the correct equilibrium line. The HNO_3 concentration in the organic stream leaving the bottom stage is assumed to be negligibly small. (Experimental calculations have indicated that the total number of stages is relatively independent of this value.) It may be noted that a total of 3.21 stages are needed, yielding an H.E.T.S. value of 12.1/3.21 = 3.8 feet.

3.2 Example H.T.U. calculation -- RA extraction section

The operating and equilibrium lines developed and shown in Figure V-1 for the above H.E.T.S. calculation (Run 16"-17-RAU) will be used for the following H.T.U. example calculation.

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The number of transfer units ("over-all aqueous-film" basis) in the RA Column may be obtained by utilizing the expression

$$N_{ow} = \int_{X_2}^{X_1} \frac{dX}{X - X^*} \quad \text{.....(13)}$$

If both the operating and equilibrium lines are straight, analytical integration leads to the expression

$$N_{ow} = \left(\frac{1}{1 - P}\right) \ln \left[(1-P) \left(\frac{X_1 - Y_x/m}{X_2 - Y_x/m}\right) + P \right] \quad \text{..... (14)}$$

(See Table V-1, for nomenclature.)

Since the UNH equilibrium line (Fig. V-1) has considerable curvature at the concentrated end when plotted on linear coordinates, it would be difficult to determine an appropriate mean value for the extraction factor, P, to be used in Colburn's equation. Therefore, the calculation is broken into two parts with the number of transfer units in the concentrated region, from X = 2.5 g. UNH/l., to X = 89.8 g. UNH/l., calculated by graphical integration of Equation (13) and the number of transfer units in the dilute region, from X = 0.16 g./l. to X = 2.5 g./l. calculated by Colburn's equation (Equation 14).

(a) Concentrated-region transfer units by graphical integration In graphically integrating Equation (13), values of X and X^* are obtained by drawing constant Y lines on the operating diagram (Fig. V-1) and reading X and X^* values at the intersections of the constant Y lines with the operating and equilibrium lines, respectively. These data are tabulated below.

X	X*	1/(X - X*)
2.5	0.2	0.4347
3.5	0.3	0.3125
4.5	0.4	0.2439
6.5	0.5	0.1667
8.5	0.6	0.1266
12.5	1.0	0.0870
16.5	1.4	0.0662
24.5	2.5	0.0453
32.5	3.8	0.0348
48.5	7.4	0.0243
64.5	12.3	0.0192
75.5	16.7	0.0120
89.8	20.4	0.0144

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The graphical integration may be performed by plotting $1/(X - X^*)$ versus X and finding the area under the curve by conventional methods[5][14] such as counting squares. For this particular example,

$$N_{ow}\Big]_{2.5}^{89.8} = \int_{2.5}^{89.8} \frac{dX}{X - X^*} = 4.04$$

(b) Dilute region transfer units by Colburn's equation Equation (14) above is utilized for the dilute region transfer-unit calculations:

$$N_{ow} = \frac{2.3 \log}{1-P} \left[(1-P) \frac{(X_1 - Y_x/m)}{(X_2 - Y_x/m)} + P \right]$$

$$N_{ow}\Big]_{0.16}^{2.5} = \frac{2.3 \log}{1-0.08187} \left[(1-0.08187) \frac{(2.5 - 0.000562)}{(0.16 - 0.000562)} + 0.08187 \right] = 2.90$$

(c) H.T.U. The total number of transfer units in the RA Column extraction section is found by addition of the result obtained under (a) and (b), above:

$$N_{ow} = N_{ow}\Big]_{2.5}^{89.8} + N_{ow}\Big]_{0.16}^{2.5} = 4.04 + 2.90 = 6.94$$

The H.T.U. is obtained by dividing the 12.1-ft. perforated-plate section height by the number of transfer units:

$$\text{H.T.U.} = 12.1/6.94 = 1.75 \text{ feet.}$$

3.3 Example H.E.T.S. calculation -- RC Column

Outlined below is the graphical stage step-off H.E.T.S. method used for evaluating the uranium stripping performance of the packed section of a TBP RC Column operating at conditions closely approximating HW No. 4

Flowsheet conditions. The following data were obtained during the steady-state period of a typical pilot-plant run, 16"-18-RCU, made in a 16-inch-diameter column with a 12.1-ft.-high perforated-plate section.

Stream	Volume, Liters	UNH Concentration, G./L.
RCF	7690	50.2
RCX	8050	0.0030
RCU	8210	48.2
RCW	7440	0.23

The X and Y values used on the uranium operating diagram (Fig. V-3) are expressed as g.UNH/liter of solution. These units were selected so that a straight operating line (Equation (10), Subsection B2) results. Substituting the above data in Equation (10) leads to the expression

$$Y = 1.082\,X + 0.227$$

This operating line is plotted on Figure V-2 with the appropriate equilibrium line determined by the concentration of HNO_3 present. The variation of HNO_3 concentration as the aqueous stream flows through the column affects the uranium equilibrium value for each stage. Investigations of HNO_3 acid transfer indicate that about 90 per cent of the HNO_3 introduced in the organic feed (RCF) to the column is transferred in the first theoretical stage. The remaining 10 per cent is assumed to be transferred in the second stage.

Based on these premises, the stage step-off is started at $Y_f = 50.2$, $X_u = 48.2$, using the equilibrium line corresponding to the aqueous concentration of 8.43 g./l. For the second stage, the equilibrium line corresponding to a nitric acid concentration of 10 per cent of this value (0.843 g./l.) is used. Since 2.03 extraction stages have been stepped off on Figure V-2 and the extraction section height is 12.1 feet, the H.E.T.S. is 12.1/2.03 = 6.0 feet. (The equilibrium line corresponding to no nitric acid in the aqueous phase was extrapolated in estimating the fractional stage.)

3.4 Example H.T.U. calculation -- RC Column

The number of uranium transfer units ("over-all organic-film" basis) in the RC Column may be obtained by using a suitable method for integrating the basic equation

$$N_{oo} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*}$$

discussed under A3.8, above.

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In determining the number of uranium transfer units obtained in the column for Run 15"-17-RCU, the equilibrium and operating lines developed under B3.3, above, and plotted on Figure V-2 are used.

Since the UNH equilibrium line (Figure V-2) has considerable curvature at the concentrated end when plotted on arithmetic coordinates, it would be difficult to determine an appropriate value for the extraction factor, P, to be used in Colburn's equation. Therefore, the calculation is broken into two parts, with the number of transfer units in the concentrated region (Y = 6 to 50.2 g.UNH/l.) calculated by graphical integration, and the number of transfer units from Y = 0.23 g./l. to Y = 6 g./l. calculated by classical integration.

(a) Concentrated-region transfer units by graphical integration In evaluating the integral

$$N_{oo}\Big]_{6}^{50.2} = \int_{6}^{50.2} \frac{dY}{Y - Y^*},$$

values of Y and Y* are found from Figure V-2 at the intersection of appropriate constant X lines with the operating and equilibrium lines, respectively. These data are tabulated below.

Y	Y*	1/(Y - Y*)
6	0.02	0.1672
8	0.05	0.1258
10	0.09	0.1009
15	0.30	0.0680
20	0.75	0.0519
25	1.50	0.0426
30	2.60	0.0365
40	6.60	0.0299
50	14.0	0.0278
50.2	15.0	0.0284

The graphical integration may be performed by plotting 1/(Y - Y*) versus Y and finding the area under the curve by conventional methods(5)(14) such as counting squares. For this particular example,

$$N_{oo}\Big]_{6}^{50.2} = \int_{6}^{50.2} \frac{dY}{Y - Y^*} = 2.27$$

(b) Dilute region transfer units by classical integration For smaller values of Y (Y = 0.23 to 6) the value of Y* becomes negligible in comparison with Y. Thus,

$$N_{oo}\Big]_{0.23}^{6.0} = \int_{0.23}^{6.0} \frac{dY}{Y - Y^*} \cong \int_{0.23}^{6.0} \frac{dY}{Y} = \ln \frac{6.0}{0.23} = 3.25$$

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(c) H.T.U.

$$\text{Total } N_{oo} = 2.27 + 3.25 = 5.52$$

The H.T.U. is therefore 12.1/5.52 = 2.2 feet.

C. VARIABLES AFFECTING COLUMN EXTRACTION PERFORMANCE AND FLOODING CAPACITY

1. Introduction

The purpose of this section is to discuss the influence of the various process variables on the design and operation of the solvent-extraction columns in the TBP Plant. The effects of these variables on waste losses, flooding capacity, and column rangeability will be described. For clarity in presentation, a line of demarcation has been drawn between the variables whose values have been fixed by mechanical factors during plant design (design variables) and those variables whose values can be changed by operating conditions (operating variables).

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Based on data more fully explained later in this section, a summary table giving the expected performance of the TBP-process RA and RC Columns at the indicated processing rates, under the conditions of the TBP-HW No. 4 Flowsheet, follows. Details on the column and perforated plate geometry are presented under C4 and in Chapter XV.

RA Column Extraction Section (Diam. 20 In.; "Packed" Height 12 Ft.)[a]

Short Tons U/Day	Volume Velocity, Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	% U Loss In Waste	H.E.T.S., Ft.	No. of U Transfer Units	H.T.U.,[e] Ft.
2.5	700	0.1	3.4	7.5[c]	1.6
5.0	1400	0.4	4.3	6.0[c]	2.0
6.0	1700	0.8	5.0	5.2[c]	2.3
	RC Column (Diam. 30 In.; "Packed" Height 12 Ft.)[b]				
2.5	360	0.1	3.8	7.0[d]	1.7
5.0	720	0.05	4.2	8.0[d]	1.5
6.0	870	0.05	4.2	8.0[d]	1.5

Notes: (a) Values selected at pulse amplitude of 1.28 in. and a pulse frequency of 50 cycles per minute. Flooding volume velocity of column is about 3500 gal./(hr.)(sq.ft.), sum of both phases.

(b) Values selected at pulse amplitude of 0.57 in. and a pulse frequency of 90 cycles per minute. Flooding volume velocity of column is about 1000 gal./(hr.)(sq.ft.), sum of both phases.

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(c) "Over-all water-film" transfer units.

(d) "Over-all organic-film" transfer units.

(e) On the basis of available data, RA Column H.T.U. values under TBP-HW No. 5 Flowsheet conditions are only slightly (up to 10%) higher than No. 4 Flowsheet RA Column H.T.U.'s at the same uranium processing rates.

With the exception of the RA Column waste loss at 6 tons U/day (20% above design capacity) the estimated uranium losses cited above are at or below the 0.5 per cent loss per column used as the basis of design for the TBP Plant.

The numbers of transfer units or theoretical stages required in the RA Column extraction section and in the RC Column under TBP-HW No. 4 Flowsheet conditions to limit uranium losses to 0.5% per column are as follows:

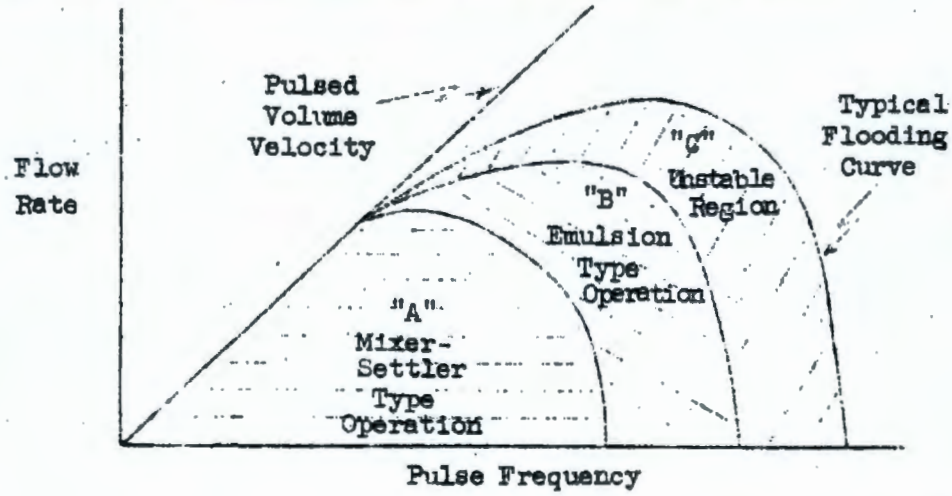
Column	Required No. of Stages	Required No. of Transfer Units
RA extraction section	3.5	6(a)
RC	3.5	6(b)

Notes: (a) "Over-all water-film" transfer units.

(b) "Over-all organic-film" transfer units.

2. The Three Types of Pulse-Column Operation

Observations of a 3-inch I.D. glass pulse column in operation have revealed a correlation between certain types of phase dispersion, the range of pulse frequency at any given amplitude, and the effectiveness of uranium transfer. Changes in the type of phase dispersion resulting from changes in the operating variables (flow rate and pulse frequency at any fixed amplitude) are indicated in the figure below.



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This figure applies qualitatively to both the RA and the RC Column.

The changes in column appearance accompanying changes of frequency or flow rate involve gradual blending of one type of operation into another. Operation in the region labeled "A" (see graph) has been designated as "mixer-settler" type, and operation in the intermediate region, "B", "emulsion" type. The name "unstable region" applied to the right-hand section, "C", is derived from the characteristics of the column when operated near the flooding point. The "mixer-settler" operation (for 1/8-in.-diameter plate perforations) is characterized by large drop size, clear aqueous layers between plates at intermediate points in the pulse cycle, clear organic-phase layers under the plates during portions of the downward pulse, high stability, and high values of H.T.U.

The "emulsion" region is characterized by small drop size, uniform dispersion of phases, and low H.T.U. The "unstable region" is characterized by mixtures of fine and coarse organic drops, formation of large drops of organic phase by coalescence, infrequent sudden reversals of continuous phase (local flooding) in short sections of column, build-up of one to two feet of continuous organic phase under the bottom plate of the cartridge, and generally somewhat higher H.T.U. values than for emulsion-type operation.

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3. Effects of Operating Variables on Extraction and Capacity

This subsection is designed to indicate the effects of the several operating variables on the extraction effectiveness and throughput capacity of the TBP-process solvent-extraction columns. For the most part the data presented were extrapolated from pilot-plant data obtained with 3, 5, 8, and 16-inch-diameter pulse columns. For this reason, the values of the variables shown are only approximate, but the validity of the trends indicated is well established.

3.1 Effect of pulse frequency

In the range of operating variables investigated in pilot-plant studies it was found that changes caused by variation in pulse amplitude and/or pulse frequency may be correlated by the use of the arithmetic product of the pulse amplitude and pulse frequency. Since the pulse amplitudes in the plant columns have been fixed by the design of the pulse generators, the amplitude-frequency product can be divided by the fixed pulse amplitude (1.28 and 0.57 in. in the RA and RC Columns, respectively) and the correlation presented with frequency as the independent variable.

Figures V-3 and V-4 indicate the effect of pulse frequency variations in the RA and RC Columns operating at the fixed pulse amplitudes and at volume velocities corresponding to instantaneous uranium processing rates of 2.5, 5.0, and 6.0 tons per day. The plots presented were obtained by extrapolating data from pilot-plant studies in 3, 5, 8, and 16-inch-diameter pulse columns. These data indicate that H.T.U. values decrease with increasing pulse frequency over the range studied. For example,

under the conditions of the TBP-HW No. 4 Flowsheet, at a volume velocity of 1400 gal./(hr.)(sq.ft.), sum of both phases, corresponding to a uranium processing rate of 5 tons/day, the plant-size (20-in. diam.) RA Column H.T.U. decreases from 2.4 ft. at 25 cycles/minute to 2.0 ft. at 55 cycles/minute. The H.T.U. of the RC Column (30-in. diam.) at a volume velocity of 720 gal./(hr.)(sq.ft.), sum of both phases, (corresponding to 5 tons U/day) decreases from about 2.6 feet at 55 cycles/minute to 1.5 feet at 90 cycles/minute.

Figures V-5 and V-6 illustrate the effect of frequency on the flooding capacity of the column. As indicated by these figures, the operation of a pulse column differs markedly from that of a packed column, in that no measurable countercurrent flow can be obtained in a pulse column unless the column contents are pulsed. At low frequencies (up to about 30 and 35 cycles/min., respectively, for the RA and RC Columns at the respective plant amplitudes of 1.28 and 0.57 in.) the capacity of the columns is equal to the pulsed volume velocity and thus increases in proportion to the frequency. Accordingly, at low frequencies the pulsed volume velocity may be computed from the relation

$$VV = 74.81\ af,$$

where

VV = volume velocity, gal./(hr.)(sq.ft.),

a = pulse amplitude, inches,

f = pulse frequency, cycles/min.

The number 74.81 appearing in the above equation is a conversion factor for the units, (gal./(hr.)(sq.ft.))/(in./min.). As the frequency increases further, the flooding capacity becomes increasingly lower than the pulsed volume velocity. After passing through a maximum in the neighborhood of 50 and 55 cycles/min. for RA and RC, respectively, (at the plant amplitudes) the flooding capacity decreases with further increases in the frequency, until, above a certain limiting frequency, no countercurrent flow through the column is possible. At the plant amplitudes, these limiting frequencies for the RA and RC Columns are in the neighborhood of 75 and 105 cycles/min., respectively.

The ranges of frequencies permitting plant column capacities corresponding to instantaneous uranium processing rates of 2.5, 5.0, and 6.0 tons per day are tabulated below.

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Flooding Frequencies

U Processing Rate, Tons/Day	Volume Velocity, Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Flooding Frequencies, Cycles/Min. Upper	Lower
RA Column:			
2.5	700	72	7
5.0	1400	71	14
6.0	1700	70	17
RC Column:			
2.5	360	99	9
5.0	720	94	17
6.0	870	92	20

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These data, extrapolated from pilot-plant data from 3, 5, 8, and 16-inch pulse columns, apply to the plant-size columns (20-in.-diam. RA, 30-in.-diam. RC). (It should be noted, however, that the frequency of the plant pulse generators may be varied only between 25 and 90 cyc./min., so that some of the flooding frequencies tabulated above cannot actually be attained in the TBP Plant.)

3.2 Effect of volume velocity

The effect of volume velocity on H.T.U. values in the RA and RC Columns at selected pulse frequencies is plotted in Figures V-7 and V-8. These data indicate a gradual increase in RA Column H.T.U. values as the volume velocity increases. This effect becomes more pronounced at volume velocities above 1400 gal./(hr.)(sq.ft.), sum of both phases. Typical values for the RA Column at a pulse frequency of 55 cycles/minute are listed below.

H.T.U. vs. Volume Velocity - RA Column Extraction Section
Pulse frequency = 55 cyc./min.

U Processing Rate, Tons/Day	Volume Velocity, Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	H.T.U., Ft.
1.4	400	1.4
2.5	700	1.5
5.0	1400	2.0
6.0	1700	2.2
7.1	2000	2.5

RC Column H.T.U. values go through a minimum with increasing volume velocity. This minimum point occurs at about 800 gal./(hr.)(sq.ft.), sum of both phases. Typical values for the RC Column at a pulse frequency of 90 cycles/minute are listed below.

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H.T.U. vs. Volume Velocity - RC Column Extraction Section
Pulse frequency = 90 cyc./min.

U Processing Rate, Tons/Day	Volume Velocity, Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	H.T.U., Ft.
2.1	300	1.8
2.5	360	1.7
5.0	720	1.5
6.0	870	1.5
6.9	1000	1.6

3.3 Effect of alternative flowsheets

Pilot-plant runs indicate no significant differences between the TBP-HW No. 3 and No. 4 Flowsheet H.T.U. values for either the RA or the RC Column. Although only two pilot-plant RA Column runs were made under TBP-HW No. 5 Flowsheet conditions it is expected that the increased aqueous flow rate and the increased aqueous-to-organic flow ratio would result in only a slight (up to 10%) increase in the RA Column H.T.U. values (for a given uranium production rate) over the TBP-HW No. 4 Flowsheet H.T.U.'s. With the exception of the RAF stream, all column influent stream compositions and flows are the same in the TBP-HW No. 4 and No. 5 Flowsheets. (See Figures I-2 and I-3). In the TBP-HW No. 5 Flowsheet, which involves no feed concentration step, each ton of uranium is contained in a 47% greater RAF volume than under the conditions of the TBP-HW No. 4 Flowsheet.

Operational changes from nominal TBP-HW No. 4 Flowsheet conditions to flowsheets employing feeds prepared from supernate or sludge alone do affect the RA Column H.T.U. values. The H.T.U. values increase about 100 per cent when supernate feed is used. A decrease in H.T.U. values of approximately 15 per cent accompanies a change to a sludge feed. The major portion of the fluctuation in H.T.U. values is thought to be attributable to changes in the aqueous-to-organic flow ratios plus a small effect caused by concentration changes.

3.4 Effect of aqueous-to-organic flow ratio

Redox-process packed-column experiments indicate an increase in H.T.U. values with increasing aqueous-to-organic volume flow ratios (L/V). A 2 to 2.5-fold increase in H.T.U. values was noted with an increase in L/V from 0.2 to 5.0. It is believed that in a qualitative sense such a trend prevails also with TBP-process pulse columns.

3.5 Effect of physical properties

The physical properties of most importance in solvent-extraction column performance are (a) the density difference between the aqueous and organic phases, (b) the viscosities of the phases, (c) interfacial tension between the phases, and (d) the diffusivities of the diffusing components.

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These physical properties of the solutions in all TBP-process columns are sufficiently favorable, as evidenced by the adequately low H.T.U. values and adequately high flooding capacities of the TBP columns, though not quite as favorable as in the Redox process. Although not too well understood quantitatively, the following semiquantitative statements illustrate the general importance of the above physical properties on packed solvent-extraction column performance.

3.51 Density difference between phases

For given column and plate geometry and materials of construction, the flooding capacity increases as approximately the first power of the density difference between the phases. This density difference is generally 0.2 to 0.35 g./ml. for the TBP-process columns -- whereas column operation is feasible (generally with lower flooding capacities, however) in systems with a density difference as low as 0.05 g./ml.

3.52 Viscosity

Low viscosity of the continuous phase generally favors high flooding capacity, the flooding capacity being proportional to about the minus 0.2 power of the viscosity. Viscosities in the TBP streams are relatively low, ranging from 1.0 to 1.5 centipoises in aqueous streams, and from 1.8 to 2.5 centipoises in organic streams.

3.53 Interfacial tension

Low interfacial tension generally favors high flooding capacity. (The flooding capacity is proportional to about the minus 0.1 power of the interfacial tension.) Interfacial tensions between organic and aqueous phases of the TBP-process systems are low, about 16 dynes/cm., though not as unusually low (5 to 10 dynes/cm.) as the interfacial tensions in the Redox-process systems.

3.54 Diffusivity

Individual-film H.T.U. values are generally believed to vary directly with the value of the dimensionless Schmidt number raised to approximately the 0.5 power,

$$\left(\frac{\mu}{\rho D}\right)^{0.6}$$

where any set of consistent units may be used, such as:

μ = viscosity, lb./(hr.)(ft.);

ρ = density, lb./cu.ft.;

D = diffusivity of the diffusing component, sq.ft./hr.

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Hence individual aqueous-film or organic-film H.T.U. values should be smaller for lower viscosity and higher diffusivity values. Smaller values of the Schmidt number undoubtedly account, in part, for the lower H.T.U. values obtained in Redox columns than in the TBP uranium recovery or Purex-process columns.

3.6 Effect of diluent

Transfer unit heights and flooding capacities may vary somewhat with the physical properties imparted by the diluent to the solvent phase, as discussed under 3.5, above.

Scouting runs in a 3-inch pilot-plant column indicate that H.T.U. values obtained with Amsco 125-90W as diluent are about the same as those obtained with Shell Deodorized Spray Base. (For the properties of these diluents reference is made to Chapter IV.)

3.7 Effect of column temperature

Three-inch-diameter pulse-column, pilot-plant runs indicated no significant difference between the uranium losses at 77°F. and at 110°F. for either the RA or the RC Column.

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4. Effects of Design Variables on Extraction and Capacity

The studies of pulse column variables in nominal 3, 5, 8, and 16-inch-diameter columns led to the following cartridge and column geometry specifications for the TBP-process RA and RC Pulse Columns.

Column Geometry

	RA Column	RC Column
Inside diameter	20 in.	30 in.
Over-all height, including disengaging sections but not connectors	21 ft.	17 ft.
Perforated-plate section height	3.17 ft. (scrub) 12 ft. (extn.)	12 ft.

RA and RC Column Perforated-Plate Cartridge Geometry

Plate spacing	2 in. (center line to center line)
Hole size	0.125-in. diameter
Perforated area	23%
Plate material	Stainless steel (Type 347)
Plate thickness	0.0625 in.
Diametric clearance (plate to wall)	0.125 in. maximum

Cartridges of the geometry specified in the above table were also used in the major portion of the pilot-plant TBP-process pulse-column studies. A cartridge of this geometry is often referred to as a "standard cartridge."

The following table summarizes the approximate magnitude of the effects on column H.T.U. and capacity of those variables which are fixed by the design of the columns and cannot be changed in the course of regular operation. These effects were considered in arriving at the design specifications of the plant columns. The selected values of the variables are generally near optimum.

Effect of Design Variables on Column Extraction and Capacity

Variable	Relative Importance*	General Effect
Pulse amplitude	First-order effect on both extraction and capacity (in the range 0.25 to 1.5 in.).	As amplitude increases H.T.U. values are reduced to a minimum and then increase. The capacity increases with amplitude to a maximum then decreases.
Plate hole diameter	First-order effect on capacity; second-order effect on extraction (in the range 0.04-in. to 3/16-in. diameter).	1/8-in.-diameter holes give good all-around performance. H.T.U. and capacity increase with hole diameter.
Plate free (perforated) area	Second-order effects on both extraction and capacity in the range 10 to 40% free area.	H.T.U. and flooding capacity increase with increase in free area in the 10 to 40% range.
Plate spacing	Second-order effects on both extraction and capacity in the range 1 in. to 4 in.	H.T.U. and flooding capacity increase with increase in plate spacing.
Column diameter	Second-order effect on extraction in the RA Column in the range 3 to 20 in.; third-order effect on extraction in the RC Column in the range 3 to 30 in. Third-order effects on column capacities.	H.T.U. increases with column diameter. Superficial throughput capacity not significantly affected by diameter.
Plate surfacing	Third-order effect.	The best performance in stainless steel plates is comparable to the best in plastic-faced plates.

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Variable	Relative Importance*	General Effect
Wall clearance (between plates and column wall)	Third-order effect for clearance up to 1/8-in. on the diameter in a 3-in.-diameter column.	The H.T.U. increases with increasing wall clearance.
Disengagement section	Third-order effect on capacity.	The capacity is not significantly affected by disengagement section design if the residence time to separate the mixed phases is above about 5 minutes.
Influent stream distributors	Third-order effect on extraction and capacity.	Column performance with simple distributors is equal to that with multi-hole type.
Continuous phase	Second or third-order effect.	Limited data indicate superior performance with the aqueous phase continuous for both RA and RC Columns.

*) The above comparisons reflect approximately the following differences:

First order -- greater than 3-fold effects on H.T.U. and/or capacity.
Second order -- less than 2-fold effects.
Third order -- effects less than approximately ± 30%.

The comparisons in the table are mainly based on data obtained in a 3-inch-diameter pulse column and a few runs in 8 and 16-inch-diameter columns. Because of the limited number of pilot-plant runs made to study these effects and the omission of numerous qualifying details, the comparisons are only approximate. Reference is made to Document HW-19170 for complete details of the pilot-plant studies which are the basis for these comparisons.

D. DECONTAMINATION OF URANIUM FROM FISSION PRODUCTS AND PLUTONIUM

1. Introduction

This section deals with the decontamination performance of the TBP Plant solvent-extraction battery. The function of this battery is to reduce the concentrations of the fission products and plutonium associated with the uranium recovered from underground storage to levels low enough to permit further processing of the uranium at Hanford and at off-site facilities with no more elaborate radiation protection procedures than are needed in handling natural uranium.

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Virtually all of the decontamination is achieved in the RA Column, where the product uranium is purified by extracting it into the organic (TBP plus diluent) phase while the bulk of the fission products and plutonium remain in the aqueous phase. A small additional amount of decontamination is also effected in the RC Column (over-all D.F.'s in the range of 3) when "irreversibly extracted" fission products (see below) are present.

The bulk of the RA Column decontamination is effected at the top of the extraction section, where less than 1 per cent of the fission products and 10 per cent of the plutonium (reduced to the relatively inextractable (III) valence state by ferrous ion in the aqueous phase) are extracted into the organic stream along with the uranium. This organic stream then passes into the scrub section where additional decontamination is carried out by scrubbing the ascending organic stream with a highly salted (2 M nitric acid) aqueous stream which also contains the ferrous ammonium sulfate and sulfamic acid required for the reduction of plutonium. The scrub stream is highly salted to minimize stripping (and hence internal refluxing in the column) of uranium.

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The radioactive fission-product constituents associated with the uranium feed are discussed in Chapter II. The chemistry of these fission products and plutonium, and their phase distribution ratios at TBP-process conditions are discussed in Chapter IV. The relative inextractability into the organic phase of plutonium (III) and the fission products (organic/aqueous distribution ratios below 0.1 for most species) is the fundamental property which enables their almost quantitative separation from uranium in the RA Column.

Decontamination of uranium from plutonium and fission products by the TBP solvent-extraction process has been successfully demonstrated by many experimental studies, including (a) laboratory batch-extraction studies conducted at Hanford and Oak Ridge and (b) "hot" pilot-plant packed-column studies at Oak Ridge (processing approximately 3-1/2 year old Hanford sludge and supernate). In addition, decontamination of uranium on a pilot-plant scale has been successfully demonstrated in mixer-settlers, packed columns, and pulse columns for other processes (Purex and "25") utilizing diluted TBP as the solvent. These studies were conducted at the Argonne and Oak Ridge National Laboratories and at Knolls Atomic Power Laboratory. Salient performance data from TBP-process decontamination studies and the Purex-process decontamination studies utilizing pulse columns are presented in Subsection D4, below.

2. Design Basis for Decontamination

At the time of the expected start-up of the Uranium Recovery Plant (January 1952) the radioactivity levels of the combined sludges and supernates from underground storage will range from approximately 8×10^{-4} to 7×10^{-2} "countable" beta curies and from 2×10^{-4} to 3×10^{-2} "countable" gamma curies per gram of uranium. The actual combined radioactivity level in each series of cascade tanks is dependent upon the irradiation and "cooling" history of the uranium. Tentative specifications for the recovered uranium allow a radioactivity level of 1×10^{-7} beta curies and

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5×10^{-8} gamma curies per gram of uranium (approximately 30% and 300% of the radioactivity of natural uranium, respectively). The TBP process has been designed to recover uranium aged at least two years or longer. The 2-year, or longer, "cooling" time is necessary to allow the fission-product radioactivities (notably Ru and Zr) to decay to lower levels. The decontamination factors required to meet the tentative specifications when processing two-year-old waste containing uranium which has received an integrated exposure of 400 Mw.-days/ton over 360 days are 7.5×10^4 and 2×10^4 for beta and gamma respectively (countable curie basis). The required D.F.'s are smaller for wastes aged over a longer period.

The underground storage tanks also contain up to approximately 4×10^{-6} grams of plutonium per gram of uranium. Since the maximum permissible concentration of plutonium in recovered uranium is tentatively set at 1×10^{-7} grams per gram of uranium, the over-all plutonium decontamination factor must be approximately 40.

Experimental studies have shown that uranium may be decontaminated from fission products by as high as 10^4 to 10^5 and from plutonium by a factor of at least 40 in one TBP solvent-extraction cycle[25].

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3. Mass Transfer (Scrubbing) of Fission Products and Plutonium

Normal mass-transfer concepts may be used to explain the functioning of the RA Column in the removal of plutonium and fission products with known, reproducible distribution coefficients. Principles of mass transfer may also be used to calculate the number of equivalent stages or transfer units required to attain any desired D.F. for a fission product, group of fission products, or plutonium.

Laboratory and pilot-plant decontamination performance data show that such an idealized approach is actually applicable to nearly all of the fission products. Thus, as would be predicted on the basis of mass-transfer theory, decontamination factors for the RA Column are of the order of 10^4 to 10^5 (99.99 to 99.999% removal) for fission products and 50 for plutonium. Hence, behavior of fission products and plutonium in accordance with classical mass-transfer concepts is the rule rather than the exception. From 0.001 to 0.1% of the fission products in the RAF remain in the RAU because of:

(a) insufficient height of the scrub section;

(b) distribution coefficient values unfavorable for stripping (E_a^o in the range from 0.2 to 0.4); and

(c) the so-called "inextractable" (or, more correctly, "unstrippable" or "unscrubbable") behavior of certain fission products, due to complexing in the organic phase or formation of organic-favoring forms. In these cases, E_a^o values for the fission products are greater than 0.5.

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Although the fraction of the total fission products in the RAF which exhibits "inextractable" performance is small (generally 0.1% or less), it is nonetheless highly important because D.F.'s for recovered U (from fission products) must be on the order of 10^4.

3.1 D.F. as a function of the distribution ratio and the number of scrub stages or transfer units

The Colburn equations,

$$N_s = \log \left[(1 - P) M + P\right] / \log(1/P)$$

and

$$N_t = 2.3 \log \left[(1 - P) M + P\right] / (1 - P),$$

(discussed in Section A, above) may be used to estimate the stage and transfer unit requirements for fission product and plutonium removal. Figure V-9, which is a graph of the number of "over-all organic-film" transfer units in the RA Column scrub section versus decontamination factor, has been constructed on the basis of the Colburn equations and the assumption that the distribution ratios of the fission products and the plutonium remain constant throughout the scrub section and at the top of the extraction section. This assumption is approximately correct for most individual fission products and for plutonium. Thus, Figure V-9 may be used to estimate the number of RA Column scrub-section stages or transfer units for an individual fission product or plutonium if the distribution ratio is known. Conversely, the graph may be employed to calculate the decontamination factor for an individual fission product or plutonium in the RA Column if the distribution ratio and number of stages or transfer units are known. The assumption required for the use of Fig. V-9 (that the distribution ratios of the fission products remain constant at the top of the extraction section and throughout the scrub section) is not correct for groups of fission products and individual "inextractable" fission products whose apparent distribution ratios increase at each stage in the scrub section. Figure V-10 contains two graphs, also based on the Colburn equations, which are plots of the extraction-section and scrub-section D.F.'s versus the distribution ratios for an RA Column with a scrub section equivalent to one theoretical stage or three "over-all organic-film" transfer units. These graphs may be used to estimate the over-all RA Column decontamination factor for individual "inextractable" fission products or groups of fission products whose apparent distribution ratios are known for both the extraction section and for one scrub stage or three scrub transfer units. Sample calculations for both Figures V-9 and V-10 are given below.

It will be noted that some decontamination occurs with no stages or transfer units in the scrub section. This initial decontamination is a consequence of the fact that the organic feed to the scrub section has been contacted with an aqueous phase, RAFS, containing approximately two thirds of the RAF concentrations of fission products and plutonium. The organic feed to the scrub section has therefore already undergone considerable decontamination due to the highly aqueous-favoring distribution coefficients

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of the fission products and plutonium (most of the fission products and plutonium remain in the aqueous phase) in this part of the extraction section.

The use of Figure V-9 may be illustrated with two calculations showing the determination of (a) the number of "over-all organic-film" transfer units or stages required to attain a given D.F. for an individual fission product of known distribution ratio (E_a^o), and (b) the D.F. attained with a set number of transfer units for a given fission product with a known E_a^o.

(a) Let it be assumed that the fission product has an E_a^o of 0.01, the required D.F. is 2×10^4, and it is desired to determine both the number of stages and number of transfer units required. Reading on the left-hand vertical scale (Fig. V-9) up to D.F. = 2×10^4 and across to $E_a^o = 0.01$ (radial parameter line), it is found (on the abscissa) that approximately 6 transfer units are required. As may be read from the theoretical stage parameter line, this corresponds to about 2 theoretical stages.

(b) Let it be assumed that the fission product has an E_a^o of 0.01, there are 5 transfer units in the scrub section, and it is desired to determine the D.F. attained. Reading on the lower horizontal scale over to 5 transfer units and following the vertical line at 5 up to its intercept with the $E_a^o = 0.01$ line, one finds the intercept to be 7×10^3 (D.F. scale). The D.F. attained is therefore 7×10^3. Similar calculations may also be made when the number of stages is known.

The use of Figure V-10 may be illustrated with a calculation showing the determination of the D.F. attained with one theoretical stage for a group of beta-emitting fission products whose extraction section and scrub section apparent distribution ratios (E_a^o) are known.

Let it be assumed that this group of beta-emitting fission products has an apparent E_a^o of 8×10^{-4} in the extraction section and 7×10^{-3} in the scrub section and it is desired to determine the D.F. attained. Reading up from $E_a^o = 8 \times 10^{-4}$ on the extraction-section graph, one finds the intercept on the extraction section D.F. scale to be 750. Reading up from $E_a^o = 7 \times 10^{-3}$ on the scrub-section graph to its intercept with the one theoretical stage line, one finds the intercept to be 29 (scrub-section D.F. scale). The over-all RA Column D.F., as determined by the equation given on the Figure, is then $(750)(29) - 29 + 1 = 2.2 \times 10^4$. The last two terms of this equation, which correct for fission-product reflux from the scrub section, were negligible in this case. Similar calculations may also be made for three scrub-section transfer units.

3.2 <u>The "irreversible" extraction of some fission products</u>

It has been observed in laboratory and pilot-plant studies that certain fission products, or -- as is more often the case -- small fractions

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of certain fission products, under some conditions extract initially into the organic phase and cannot be subsequently scrubbed back into an aqueous stream. Such "irreversible" extraction behavior has been explained in terms of two mechanisms, both of which undoubtedly occur to some extent in the TBP process.

One of the possible mechanisms is the formation of an organic-favoring complex compound of the fission product in question with some other solute. Zirconium may be thus complexed by DBP (dibutyl phosphate), formed by the hydrolysis of TBP. Other complexes may be attributable to unknown impurities. Because of the extremely low concentrations in which the individual fission products are present (on the order of 10^{-5} to 10^{-7} M in the RAF stream) a very low concentration of complexing agent could be effective.

Another possible mechanism is the presence of certain fission products in more than one chemical form, some with low and some with high distribution ratios. While it has not been proven that this is the reason why a small fraction of ruthenium is "irreversibly" extracted under TBP process conditions, it has been found in the Redox process that ruthenium exists in several solute species, at least one of which has a distribution ratio greater than 1 and thus is extracted into the organic phase with uranium.

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Analytical results from Oak Ridge pilot-plant runs (see Table V-2) indicate that small fractions of both the Ru and Zr present undergo "irreversible" extraction in the TBP process. Solvent treatment procedures used in the TBP Plant should, however, help to minimize this phenomenon.

4. Laboratory and Pilot-Plant Decontamination Performance

4.1 Laboratory batch studies

"Hot" laboratory-scale batch experiments, under conditions simulating those of the process, have been extensively used in the study of the decontamination performance of the TBP process. Laboratory countercurrent batch studies have given good checks of column performance and thus have provided a useful means of obtaining quantitative indications of the effects of various independently controlled factors on process decontamination performance. Some illustrative laboratory countercurrent batch dF's for simulated RA-RC Column conditions are tabulated below:

Source of Feed	Approx. Age of Feed	No. of Stages			dF		
		Extn.	Scrub	Strip.	Beta	Gamma	Pu
Sludge[22]	4.5 yr.	4	1	--	4.5[a]	>3.3[a]	1.4[a]
Sludge[24]	3.5 yr.	5	4	5	5.5	4.8	0.3[b]
Simulated current waste[24]	90 days	5	4	5	4.3	4.0	1.0[b]
Supernate[24]	3.5 yr.	5	4	5	4.5	(c)	(c)

Notes: (a) RAU dF's. (All other dF's in above table are for RCU.)

(b) No plutonium reductant was used in these experiments.

(c) Not reported.

In all cases the product streams from the above extractions met the tentative specifications for beta and gamma radioactivity.

4.2 Pilot-plant studies

Pilot-plant studies of the decontamination performance of the TBP process were carried out in packed columns at Oak Ridge National Laboratory. No pilot-plant data on the decontamination performance of pulse columns operating under TBP process conditions have been obtained. However, "hot" pulse column runs have been made at Oak Ridge on the Purex process. The Purex process is designed to recover both uranium and plutonium from pile-irradiated uranium and, like the TBP process, utilizes a TBP-and-diluent extractant. TBP process decontamination performance may be expected to be roughly equivalent to that of the Purex first cycle. Equipment sizes for these studies were as follows:

Process	Type of Column	Runs	Column	Diam., In.	Packed[a] Height, Ft.
TBP	Packed	HS-3, 5	RA scrub	1.6	10
			extn.	1.6	12.5
			RC	2.5	18
TBP	Packed	HS-8, 11	RA scrub	1.6	5
		HW-1, 2	extn.	1.6	17.5
			RC	2.5	18
TBP	Packed	HS-16	RA scrub	1.6	0
			extn.	1.6	22.5
			RC	2.5	18
Purex	Pulse	IHP-5	IA scrub	2	12.5
			extn.	2	7.5
			IB extn.	2.5	11.5
			scrub	2	6
			IC	4	12
Purex	Pulse	IHP-8, 9	IA scrub	2	18
			extn.	2	12
			IB extn.	2.5	18
			scrub	2	8
			IC	4	12

Note: (a) TBP process pilot-plant columns packed with 1/4 by 3/8-in. split Raschig rings. Purex pulse columns "packed" with perforated plates with 1/8-in.-diam. holes, 23% free area, 2-in. spacing.

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The decontamination factors obtained in some of these studies are summarized briefly below. A somewhat more detailed summary is presented in Table V-2. Table V-2 includes some dF's for those individual fission products (Ru, Zr, Nb, Sr, and Cs) which are important because one or more of them generally control the gross fission-product decontamination factors obtained.

TBP Process Pilot-Plant dF's
(Age of feed approximately 3.5 years)

Run	Type of Feed	RA Column Scrub Sect. Packed Height, Ft.	Initial Feed Radioactivity(c) Beta Co./Min. / Mg. U_5 ($\times 10^{-5}$)	Initial Feed Radioactivity(c) Gamma Mv. / Mg. U	RCU Stream dF's Beta	RCU Stream dF's Gamma	Product Uranium Radioactivity, % of the Radioactivity of Natural Uranium Beta	Product Uranium Radioactivity, % of the Radioactivity of Natural Uranium Gamma
HS-3	HW Supernate	10	3.5	145	4.5	4.7	10	50
HS-8	HW Supernate	5	2.2	100	4.5	4.5	10	50
HS-5	Simulated Sludge and Supernate	10	1.3	59	4.5	5.0	5	10
HS-11	Simulated Sludge and Supernate	5	1.2	52	4.4	4.4	5	40
HS-16	Simulated Sludge and Supernate	0	1.1	61	3.5	4.0	40	120
HW-1	HW Sludge and Supernate	5	8.5	49	5.0(b)	4.0	10(b)	230
HW-2	HW Sludge and Supernate	5	6.4	57	4.5(b)	3.6	30(b)	90

Purex Process Pilot-Plant dF's
(Age of feed approximately 0.4 years)

Run	Source of Feed	IA Column Scrub Sect. "Packed" Height, Ft.	Initial Feed Radioactivity(c) Beta Co./Min. / Mg. U ($\times 10^{-5}$)	Initial Feed Radioactivity(c) Gamma Mv. / Mg. U	RCU Stream dF's Beta	RCU Stream dF's Gamma	RCU Radioactivity, % of Radioactivity of Natural Uranium Beta	RCU Radioactivity, % of Radioactivity of Natural Uranium Gamma
IHP-5	ORNL Slugs	12.5	8.1	685	4.4	3.5	35	3.5×10^3
IHP-8	HW Slugs	18	140	1.25×10^4	4.4	3.8	700	3.5×10^4
IHP-9	HW Slugs	18	162	1.5×10^4	4.6	3.9	500	4×10^4

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Notes: (a) Pu dF's ranged from 1.6 to 2.4 for all runs in which a Pu reducing agent was added to the RA Column scrub or feed streams.

(b) The beta radioactivity level of the RCU stream was higher than for the RAU stream during runs HW-1 and HW-2. This is believed to have resulted from entrainment of aqueous phase along with the RAU. Beta dF and product uranium beta radioactivity figures are based on the RAU instead of the RCU.

(c) Beta counting geometry was approximately 11%. The radioactivity of natural uranium under these counting conditions is approximately 80 beta co./(min.)(mg. U) and 0.005 gamma mv./mg. U.

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Results of the TBP-process packed-column runs tabulated above indicate little advantage in increasing the RA Column scrub section packed height over 5 ft.

It is believed that the Purex process gamma dF's are lower than for the TBP process because the feed contained higher concentrations of difficultly-extractable short half-life gamma-emitting fission products (such as 45-day Ru^{103}), due to the much shorter feed "cooling" time.

The Purex process IA Column requires a greater scrub section height than the TBP process RA Column mainly because of the higher TBP content of the extractant stream (30% TBP for Purex as compared to approximately 12.5% TBP for the TBP process). This increase in TBP content of the extractant effectively raises the fission-product distribution ratios to a degree where a much greater scrub-section height is required for the Purex process to achieve a decontamination performance equal to the TBP process.

The uranium product (RCU stream) from the TBP process runs was within the tentative specifications for beta and gamma activity, except for Runs HW-1, HW-2, and HS-16. The RAU streams were within the specifications for both Runs HW-1 and HW-2, and it is believed the RCU was contaminated with entrained aqueous phase. Run HS-16 demonstrated that adequate decontamination is not quite attainable without a scrub section. The tentative allowable plutonium content specifications were met in all runs listed, except for Run HS-3, where no reducing agent (to reduce plutonium to the relatively inextractable (III) valence state) was added.

RAU dF's for the TBP runs, as tabulated on Table V-2, increase with an increase in feed activity. This is believed due to the facts that the radioactivity of the RAU from the low-activity runs was close to background levels and that there is an apparent difficulty of removing the last traces of radioactivity regardless of starting activity.

It may be noted from Table V-2 that RA Column Zr dF's for the TBP runs range in the neighborhood of 1.7, while Purex process IA Column dF's are in the range of 3.2 to 3.5. The higher Zr dF's for the Purex runs

are believed due to employment of a sodium carbonate solvent-washing procedure during the Purex runs (i.e., it is believed that Zr was complexed by a solvent impurity during TBP process runs). These data emphasize the importance of maintaining effective solvent treatment procedures in the TBP Plant.

For Hanford aged uranium wastes the dF's required in the TBP Plant solvent-extraction battery in order to meet the tentative product radioactivity specifications vary with age and irradiation history as follows:

Age of Waste, Years	Approximate dF's Required in Solvent-Extraction For 200 Mw.-Days/Ton U			For 400 Mw.-Days/Ton U		
	Beta	Gamma	Pu	Beta	Gamma	Pu
0.25 (i.e., 90 days)	--	--	--	5.8	5.8	1.6
1	5.0	4.7	1.3	5.2	4.8	1.6
2	4.6	4.1	1.3	4.9	4.3	1.6
4	4.2	3.7	1.3	4.4	4.0	1.6
8	3.9	3.6	1.3	4.2	3.9	1.6

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The TBP process pilot-plant data summarized above and in Table V-2 indicate that the required dF's can be met in the TBP Plant if the feed solution is at least four years old. It is believed that with adequate solvent treatment procedures and good steady-state operation the decontamination performance of the TBP Plant solvent-extraction battery will be good enough to meet the tentative specifications when processing 400 Mw.-day/ton uranium "cooled" for as little as two years. Possible changes to the TBP process which may help to improve decontamination performance but are not presently planned for plant use are (a) addition of selective fission-product complexing agents, (b) operation with the TBP extractant at a higher per cent uranium saturation, and (c) addition of "head-end" or "tail-end" treatment facilities for Zr and Ru removal.

5. Development of the RA Column Scrub-Section "Packed" Height

The specified plate-section height (3.2 ft.) of the TBP Plant RA Pulse Column scrub-section is based primarily on the 5-ft. packed scrub-section height found satisfactory on the Oak Ridge TBP process pilot-plant RA Column. Scale-up data indicate that the 3.2-ft. scrub-section height in a 20-in.-diameter pulse column should equal or exceed the mass-transfer performance of 5 ft. of Raschig-ring packing in a 1.6-in.-diameter packed column.

Consideration of the stage requirements for representative scrubbing duties employed in conjunction with fission-product H.E.T.S. estimates for the RA Column scrub section supports the adequacy of the 3.2-ft. scrub-section height arrived at as described above. The table below lists distribution ratios for conditions approximating those of the TBP process of the important fission products and plutonium, as estimated

from data in Chapter IV. These values are intended as representative only, because, as indicated in Chapter IV, the values vary considerably with changes in per cent saturation of the solvent with uranium and HNO_3. Also listed in the table are the dF's which can be achieved in an RA Column containing one equivalent stage in the scrub section, as obtained from Figures V-9 and V-10.

Component	Estimated E_n^o Extraction Section	Estimated E_n^o First Scrub Stage	dF for RA Column with One-Stage Scrub Section
Ru	0.00028	0.019	4.4
Zr	0.0029	0.011	3.6
Nb	0.0004	0.0004	5.9
Ce	0.0004	0.0004	5.9
All other fission products	<0.001	<0.001	>5.0
Pu(III)	0.05	0.05	1.7

A TBP-process extraction cycle realizing the dF's listed above would decontaminate 400-Mw.-day/ton uranium wastes aged 2 and 4 years to the following fission-product radioactivity levels and plutonium concentrations:

Age of Feed, Years	"Countable" Curies Per Gram U Beta	"Countable" Curies Per Gram U Gamma	Per Cent of the Radioactivity of Natural Uranium Beta	Per Cent of the Radioactivity of Natural Uranium Gamma	Pu, G./G. U
2	6×10^{-8}	1×10^{-8}	18	60	7×10^{-8}
4	2×10^{-8}	5×10^{-9}	6	30	7×10^{-8}

Values in the above table exceed the tentative specifications for recovered uranium. Purex process studies conducted at Oak Ridge have indicated that the 2-in.-diameter pulse column H.E.T.S. for decontamination from fission products is approximately 2 ft.[28] Thus the 3.2-ft.-high scrub section in the TBP Plant 20-ft.-diam. RA Column should be equivalent to one or more scrub stages provided the scale-up factor for the H.E.T.S. does not exceed 60% as the scrub-section diameter is increased from 2 in. to 20 in.

E. LOCATION AND USE OF EXTRACTION COLUMN STATIC AND DIFFERENTIAL PRESSURE INSTRUMENTS

1. Function of Pressure Instruments

A bubbler-type pressure instrument has been provided on each RA and RC Column for the purpose of measuring the apparent density of the column contents. The dip tubes of a three-tube bubbler-type differential

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pressure instrument are located near the top in each column for measurement and control of the interface position (between the lower pair of tubes) and measurement of the organic effluent stream density (between the upper two tubes).

The static pressure instruments serve to provide an indication of incipient flooding.

Interface measurement and control are treated in Chapter XIX.

The organic effluent density gives, under certain conditions, an indication of the approximate uranium concentration present in the organic effluent, thus providing an indirect clue as to possible high uranium losses without the necessity of awaiting a laboratory analysis. Such continuous detection permits early correction of the offending off-standard operating conditions.

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2. Location of Dip Tubes

The static and differential pressure dip tubes are connected to instrument air by connectors on the tops of the RA and RC Columns (see Chapter XV). From the connector the three differential pressure dip tubes extend through the top of the column to terminate at 6-in. depth intervals at the top of the column. The top dip tubes of the RA and RC Columns terminate 30-5/16 in. and 29-11/16 in., respectively, below the connector nozzle on the top of the column. The static pressure tubes for the RA and RC Columns, which extend from a connector on the top of each column down the outside shell of the column, terminate in the enlarged bottom-end sections. The tubes for the RA and RC Columns terminate 2 in. and 1 in. above the bottom of the enlarged bottom-end sections, respectively.

3. Effect of Flow Rate on Column Apparent Density

Studies have been made in packed Redox pilot-plant solvent-extraction columns to determine the effect of increasing countercurrent flow on the pressure measured at the bottom of the columns. These studies (see Chapter V of the Redox Technical Manual, HW-18700) indicate that the apparent density of the column contents gradually decreases with increases in the column throughput (sum of both phases) until incipient flooding conditions are reached. At this point the apparent density decreases more rapidly with increases in flow rates.

Trends similar to those exhibited by the Redox columns have been exhibited in simple TBP process pulse column studies. In Hanford Works pilot-plant studies on an 8-in. simple RA Pulse Column, the apparent density of the extraction section was found to decrease from an average density of approximately 1.20 g./ml. at a column throughout of 500 gal./(hr.)(sq.ft.), sum of both phases, to an average density of approximately 1.15 at approximately 2000 gal./(hr.)(sq.ft.). For the reported runs the amplitude-frequency product varied from approximately 50 to 70 (in.)(cycles/min.), with amplitudes varying from 0.5 to 1.0 in. In 8-in. and 16-in. pilot-plant RC Pulse Column runs the average apparent density

decreased from approximately 1.0 at 500 gal./(hr.)(sq.ft.) to approximately 0.90 to 0.95 at 1000 gal./(hr.)(sq.ft.). For the reported RC Column runs the amplitude-frequency product varied from 35 to 56 (in.)(cycles/min.) with amplitudes varying from 0.5 to 1.0 inch.

Studies were not made on dual-purpose RA Pulse Columns to determine the effect of increased flow rates on apparent column densities.

4. Detection of Flooding

As indicated in the preceding subsection, a sudden decrease in the apparent density of the Redox packed columns has been demonstrated as the columns approach incipient flooding. In three pilot-plant runs in an 8-in.-diameter RC Pulse Column, the average column apparent density decreased below 0.90 g./ml. when flooding occurred. Direct studies demonstrating the RA Column apparent density-flooding relationship have not been made, but the RC experience is qualitatively applicable.

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5. Effect of Uranium Losses on Organic Effluent Density

The uranium concentration of the organic phase at the top of the columns, measured by the top two differential pressure taps, may be used to detect gross differences in uranium extraction within the columns caused by major changes in operating conditions (e.g., column streams shut off or considerably out of specifications). However, since the minimum detectable change readable on the differential pressure instrument (0.02 in. of water) corresponds to a uranyl nitrate composition change of approximately 0.01 M in the organic effluent, the density diptube readings provide an indication of only very unusually high uranium losses (about 10% or more).

F. SPECIAL PROBLEMS

The expectation of continuous satisfactory performance of the TBP Plant solvent-extraction columns over long periods is based on hundreds of hours of trouble-free operation in pilot-plant studies. This section summarizes experimental information on "inextractable" uranium, "red oil" (an oily residue from solvent decomposition), and emulsification difficulties encountered in early pilot-plant runs. In exceptional circumstances, such effects may give rise to anomalous column behavior. Normally, however, such effects occur only to a harmless extent.

1. "Inextractable" Uranium

"Inextractable" uranium (or more properly, "unstrippable" uranium) is uranium which is retained in the organic phase by complexing agents not present in pure solvent. In the laboratory the presence of "inextractable" uranium in solvent is thus revealed by dilute RC uranium distribution coefficients (E_a^o) as high as about 0.05 or even higher, whereas the distribution coefficient of pure solvent is below 0.002. In the plant operation the presence of "inextractable" uranium would cause higher

waste losses from the RC Column than would be obtained using pure solvent. In addition to this effect, in the RA Column the complexing agents may increase the extraction of plutonium and fission products by factors which, on the evidence of some O.R.N.L. laboratory studies, may be as high as 10 to 20[25].

Such distribution-coefficient and loss effects were noted in the early pilot-plant runs made with solvent which had been contaminated by solvent decomposition products (in the form of "red oil"). The similar adverse effect of "red oil" (discussed under F3, below) and dibutyl phosphate (a decomposition product of tributyl phosphate) on the dilute RC uranium distribution coefficient indicates that this compound is probably the main agent responsible for the formation of "inextractable" uranium.

In the TBP Plant undue losses and low decontamination factors resulting from complexing agents are avoided by the solvent treatment procedures outlined in Chapter XI (washing out solvent impurities which are complexing agents).

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2. Emulsification

An emulsion may result from the intimate intermixing of two phases of low interfacial tension.

In the TBP system emulsifying tendencies have been shown by solvent decomposition products and, in the Redox system, by silicious materials derived from the Al-Si slug-bonding layer. Thus in the early TBP pilot-plant runs it was observed that introduction of solvent decomposition products (as "red oil") into the system was followed by reductions in the column flooding capacities of as much as 30%, which were related to increases in the emulsification tendencies of RA and RC systems. In the Redox system, reduction in the interfacial tension between the phases sufficient to cause emulsification resulted from a IAF silicon concentration of 60 p.p.m. but not from 30 p.p.m. A single TBP pulse column run was carried out with approximately 9 p.p.m. of silicon (from slug coating-removal solution) in the RAFS without any increase in emulsifying tendencies being observed.[20] The results of this test do not exclude the possibility that emulsifying properties would be shown by silicon in the TBP system in concentrations on the order of 60 p.p.m. in the RAF.

The immediate effect of a severe emulsion on column operation is the carry-over of aqueous phase in the organic effluent and erratic operation of the interface control instrument. If sufficiently severe, such conditions could increase fission-product contamination of the organic effluent of the RA Column and could also increase uranium waste losses.

Provision has been made in the TBP Plant to minimize or avoid the effects of the two emulsifying materials mentioned above. Small amounts of silicious material in the form of particles, derived from the Al-Si slug bonding layer or from sand blown into underground tanks, are removed in the feed (RAF) centrifugation step. The solvent treatment procedures outlined in Chapter XI prevent the accumulation of emulsifying impurities.

3. "Red Oil"

"Red oil" is a complex mixture of nitrated organic compounds, uranium butyl-phosphate complexes, organic residues from RAX, and probably monobutyl, dibutyl, and tributyl phosphates. Physically it appears as a brown or red layer of organic material. "Red oil" was formed during concentration procedures peculiar to operations in the pilot-plant studies conducted in the 321 Building, viz., concentrating RAW and RCU solutions to conserve uranium and inorganic salts for re-use in RAFS.

The conditions of the formation of "red oil" exemplify in extreme form the conditions under which solvent decomposition may be expected to take place. Those conditions were temperatures in excess of 105°C. in the presence of relatively large amounts of boiling aqueous phase, relatively highly concentrated in nitric acid (1 to 5 M).

The adverse effects of "red oil" on uranium stripping in the RC Column and emulsions in both columns were mentioned above under F2 and F3. As discussed in Chapter XI, no completely satisfactory method of removing "red oil" from contaminated solvent has been developed to date. However, "red oil" is not expected to be encountered in TBP Plant operations because the solvent is not exposed to the deleterious effects of high acidities at high temperatures.

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TABLE V-1

NOMENCLATURE

RAF = RA Column aqueous feed stream
RAS = RA Column aqueous scrub stream
RAU = RA Column organic effluent stream
RAW = RA Column aqueous effluent stream
RAX = RA Column organic extractant
RCF = RC Column organic feed stream (RAU)
RCU = RC Column aqueous effluent stream
RCW = RC Column organic effluent stream
RCX = RC Column aqueous extractant

a = Pulse amplitude, inches
D = Diffusivity, sq.ft./hr.
D.F. = Decontamination factor ($dF = \log_{10} D.F.$)
E_a^o = Distribution ratio, g./l. solute in organic phase divided by g./l. solute in aqueous phase. E_a^o is equal to m expressed in weight per unit volume units.
f = Pulse frequency, cycles/minute
H.E.T.S. = Height of theoretical stage
H.T.U. = Height of transfer unit
K = Equilibrium constant
L = Volume flow of aqueous phase per unit time
m = Slope of equilibrium line; dY^*/dX
M = X_1/X_2 for extraction and Y_1/Y_2 for stripping. If the extractant contains solute, the values of M become $(X_1-Y_x/m)/(X_2-Y_x/m)$ and $(Y_1-X_xm)/(Y_2-X_xm)$ for the extraction and stripping, respectively.
N_o = Number of transfer units for transfer across the organic film
N_{oo} = Number of "over-all organic-film" transfer units for transfer from the organic to the aqueous phase
N_{ow} = Number of "over-all aqueous-film" transfer units for transfer from the aqueous to the organic phase
N_s = Number of theoretical stages for extraction or stripping
N_t = Number of extraction or stripping transfer units
N_w = Number of transfer units for transfer across the aqueous film
P = The slope of the operating line divided by the slope of the equilibrium line. (L/mV) for extraction (i.e., the transfer from aqueous to organic), and the reciprocal (mV/L) for stripping (i.e., the transfer from organic to aqueous).
T/D = Tons per day
UNH = Uranyl nitrate hexahydrate (M.W. = 502.2)
V = Volume flow of organic phase per unit time
V.V. = Volume velocity in column, gal./(hr.)(sq.ft.), sum of both phases
X = G.UNH/liter aqueous solution
X* = G.UNH/liter aqueous solution in equilibrium with organic phase with composition denoted by Y.
Y = G.UNH/liter organic solution
Y* = G.UNH/liter organic solution in equilibrium with aqueous phase with composition denoted by X.
Z = Length of pulse column "packed" section or cartridge
μ = Viscosity
ρ = Density

Subscripts

1, 2 = Concentrated and dilute-end values, respectively for X and/or Y
i = Intermediate value of X or Y, located between values of X or Y with subscripts 1 or 2
f = Concentration in feed stream
fs = Concentration in combined feed and scrub stream
s = Concentration in scrub stream
u = Concentration in uranium-bearing effluent stream
w = Concentration in waste stream
x = Concentration in extractant stream

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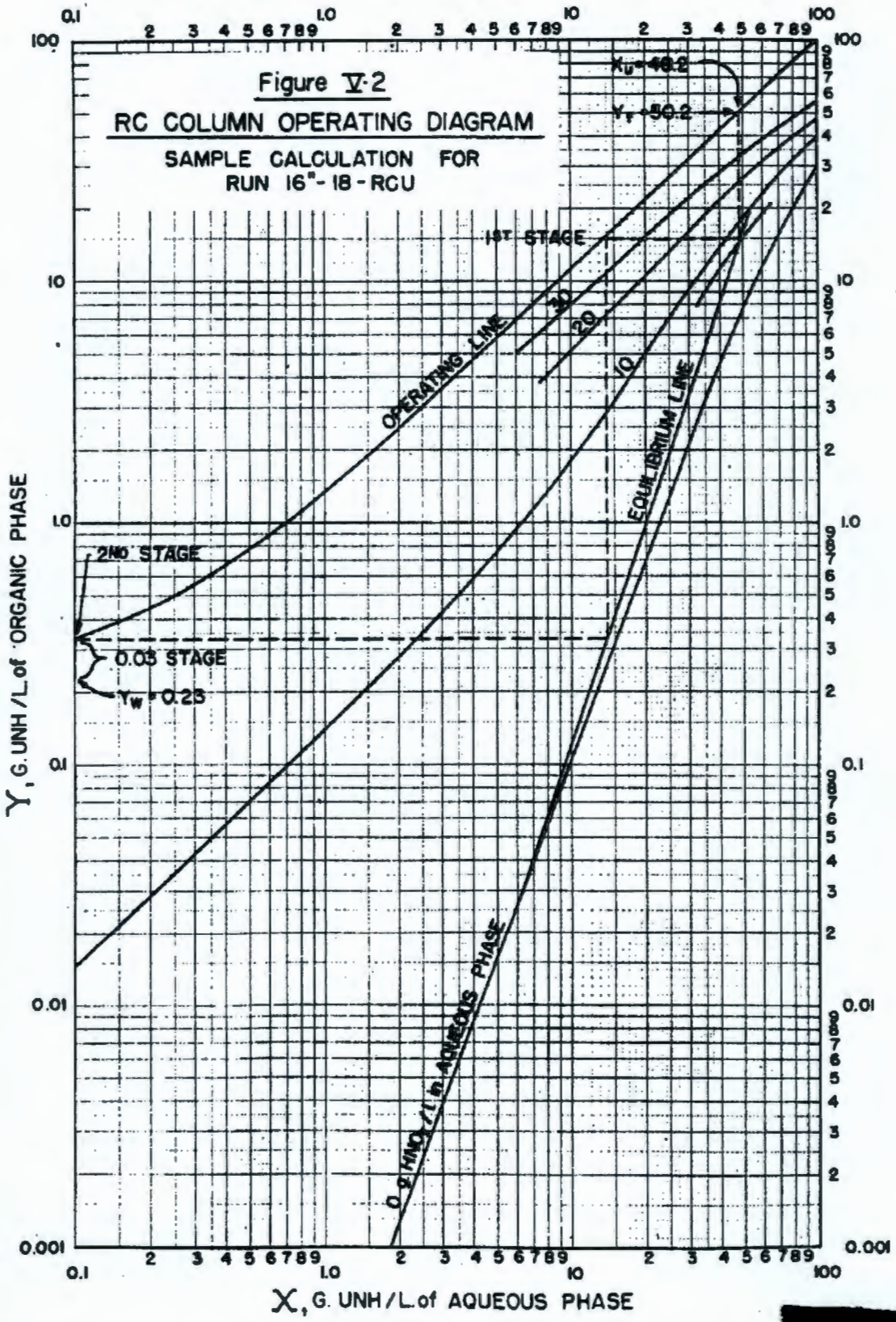

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Figure V-3
H.T.U. vs. PULSE FREQUENCY
RA COLUMN EXTRACTION SECTION

Source of Data:	Extrapolated from HW-19170, Figs. 6,7,8,10.
Diffusing Component:	UNH.
Flowsheet Conditions:	TBP-HW Nº 4.
H.T.U. Calculations:	Over-all Aqueous-Film Basis.
Column Inside Diameter:	20 In
Plate Section:	Plates with 1/8 In Holes, 23% Free Area. Plates Spaced at 2 In. (Face to Face). Height = 12 Ft.
Pulse Amplitude:	1.28 In.
Legend:	V V = Volume Velocity, Gal./(Hr.)(Sq. Ft.), Sum of Both Phases. T./D. = U Production Rate, Short Tons U Per 24 Hr, Per Column.

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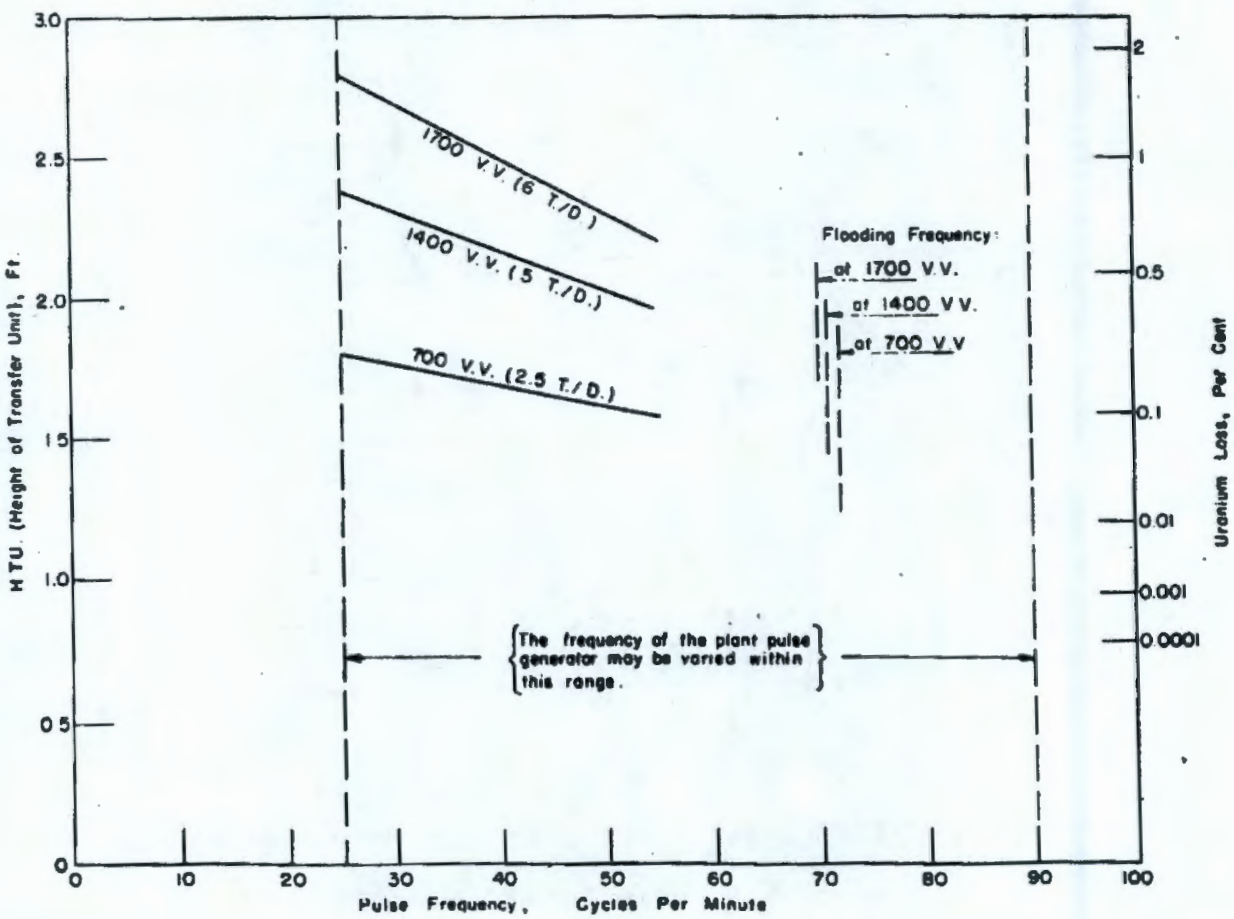

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Figure V-4
H.T.U. vs. PULSE FREQUENCY
RC COLUMN

Source of Data:	Extrapolated from HW-19170, Figs. 11,12,13,15,16.
Diffusing Component:	UNH.
Flowsheet Conditions:	TBP - HW № 4.
H.T.U. Calculations:	Over-all Organic-Film Basis.
Column Inside Diameter:	30 In.
Plate Section:	Plates with 1/8 In. Holes, 23% Free Area.
	Plates Spaced at 2 In. (Face to Face).
	Height = 12 Ft.
Pulse Amplitude:	0.57 In.
Legend:	V.V. = Volume Velocity, Gal./(Hr.)(Sq. Ft.), Sum of Both Phases.
	T/D. = U Production Rate, Short Tons U Per 24 Hr., Per Column.

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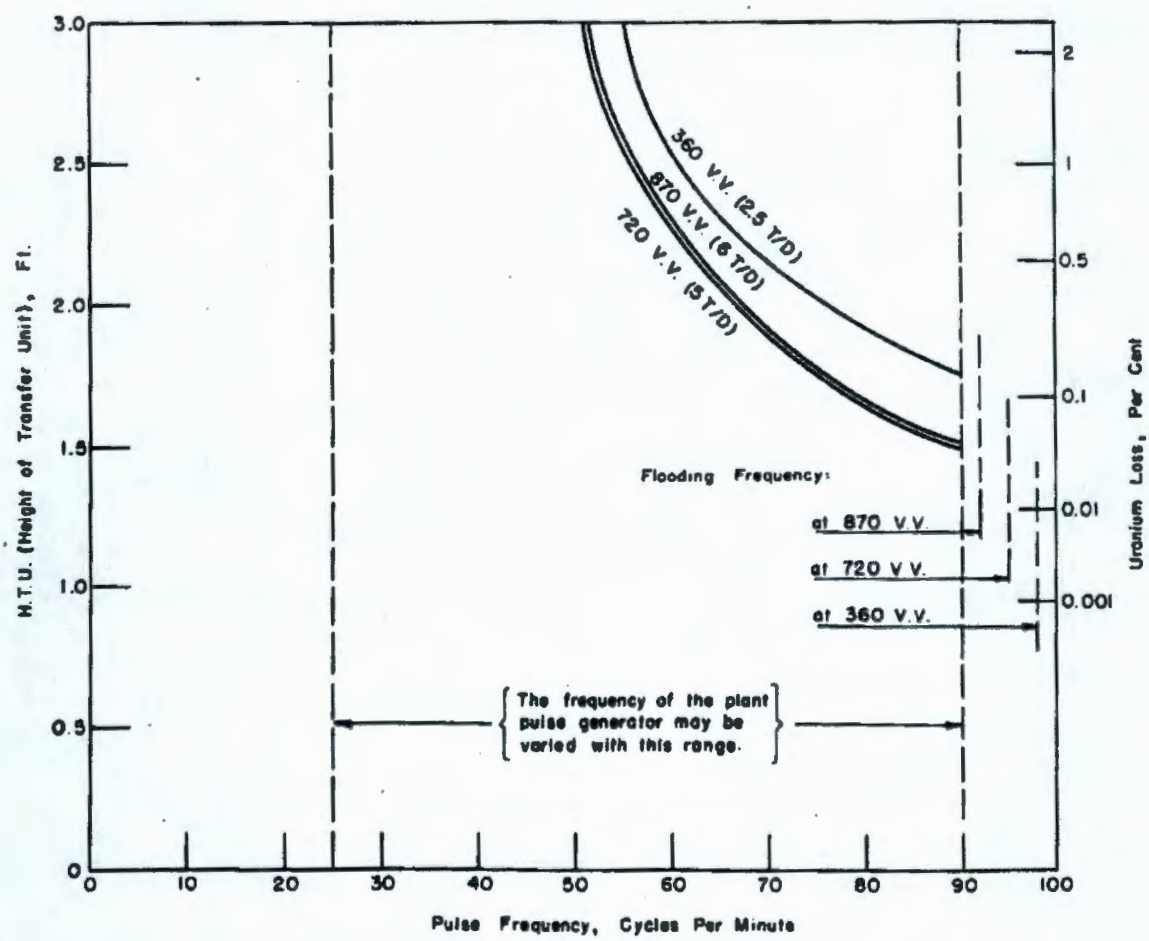

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Figure V-5
FLOODING CAPACITY vs. PULSE FREQUENCY
RA COLUMN

Source of Data:	Interpolated from HW-19170, Fig. 18.
Flowsheet Conditions:	TBP-HW Nº 4.
Column Inside Diameter:	20 In.
Plate Sections:	Plates with 1/8 In Holes, 23% Free Area. Plates Spaced at 2 In. (Face to Face). Height = 3.17 Ft. in Scrub, 12 Ft in Extraction Section.
Pulse Amplitude:	1.28 In

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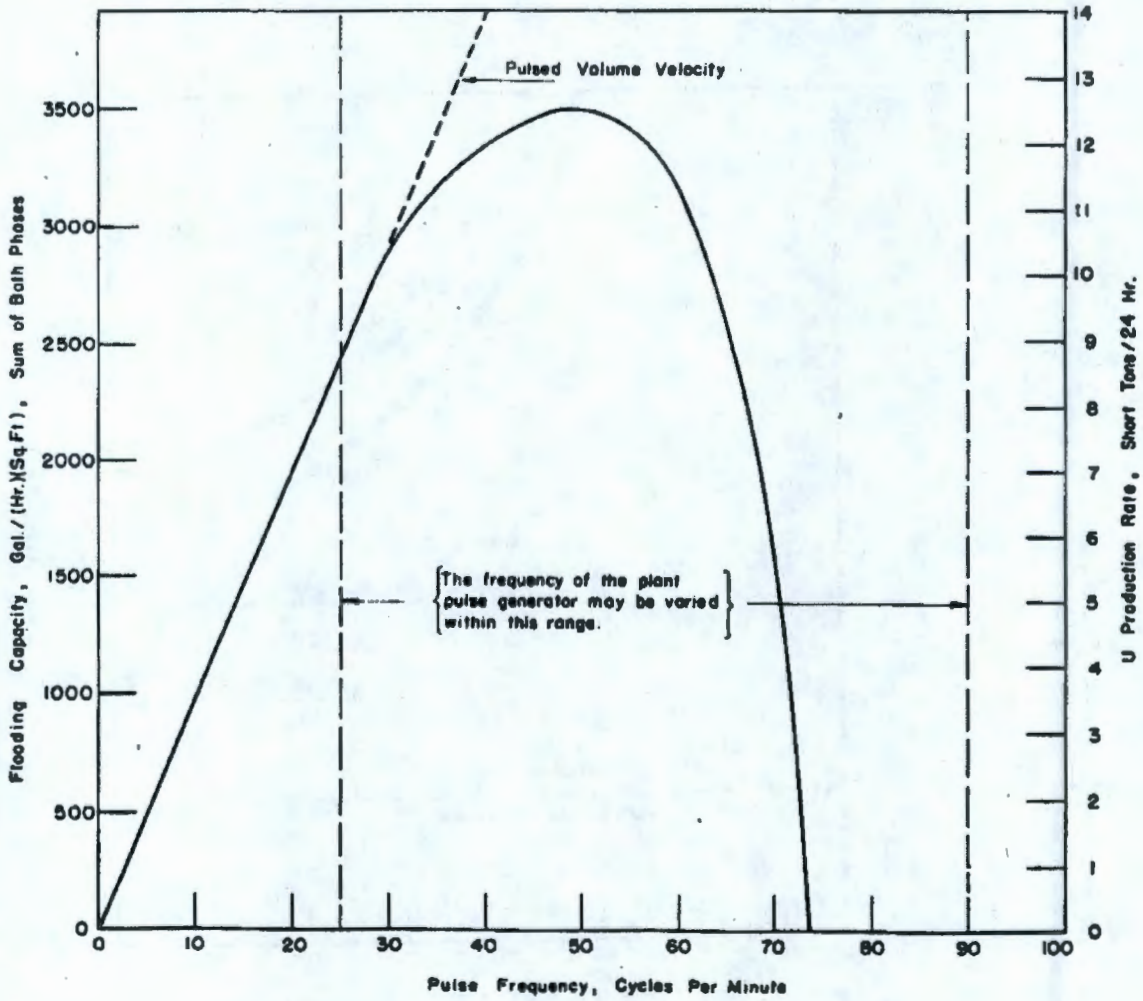

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Figure V-6
FLOODING CAPACITY vs. PULSE FREQUENCY
RC COLUMN

Source of Data:	Interpolated from HW-19170, Fig. 21.
Flowsheet Conditions:	TBP-HW Nº 4.
Column Inside Diameter:	30 In.
Plate Section:	Plates with 1/8 In Holes, 23% Free Area.
	Plates Spaced at 2 In. (Face to Face).
	Height = 12 Ft.
Pulse Amplitude:	0.57 In.

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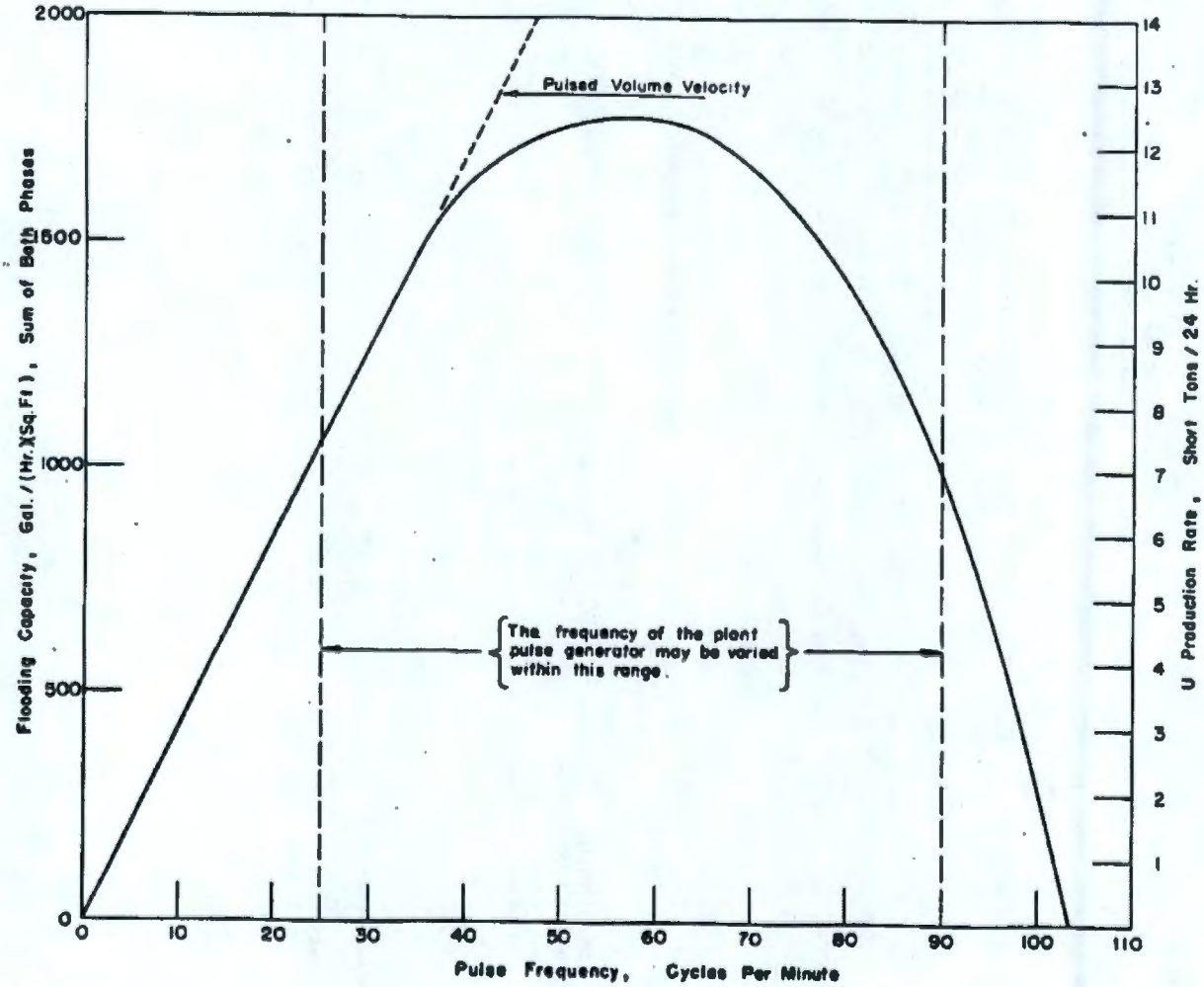

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Table V-2

DECONTAMINATION FA Test [illegible] in [illegible] TBP 4X Pulsed Flowsheet [illegible] Equipment

TBP Process Pulsed-Column df's Based on Radioactivity in AAF
(Age of Feed Approximately 3.[illegible] Years, References [illegible])

Run	Source of Feed	Packed Height in Scrub Sections, Ft.(a)	Feed Stream Radioactivity (h) Beta (c.p.m./mg.U) (x 10^-5)	Feed Stream Radioactivity (h) Gamma (mr/mg.U)	AAU Stream df's Beta	Ru	Nb	Zr	Ce	Ce	TRE(b)	Pu	HCU Stream df's Beta	Gamma	Ru	Nb	Zr	Ce	Ce	TRE(b)	Pu	Product Uranium Radioactivity, % of the Radioactivity of Natural Uranium Beta	Gamma	Relative Flow Ratios AAF:SA:TBA:AAU:HCU	Feed Stream Compositions AAF U, g/l	HNO3, N	PO4^-3, M	SO4^-2, M	NO3^-, M	Na^+, M	HAU Fe^+2, M	Th^+4, M	HAC Al, M	Nitrant	HCU
MS-3	HW Supernate	10	3.5	145.0	4.0	4.0	3.8	---	1.7	5.4	5.3	---	4.6	4.7	4.1	2.7	4.2	1.4	5.2	5.2	5.4(e)	10	50	1:0.5:1.5:1.5	21.2	4.0	---	---	---	---	2.1	0.0	10	Gulf HT	H_2O
MS-6	HW Supernate	5	2.2	100	3.9	3.2	---	---	---	---	---	---	4.5	4.6	4.0	---	---	---	---	---	1.6	10	50	1:0.5:1.5:1.5	24.0	4.0	---	---	---	---	2.05	0.05	10	Gulf HT	H_2O
MS-9	Simulated Sludge and Supernate(d)	10	1.26	59.1	4.1	3.7	3.3	---	1.8	---	---	---	4.6	5.0	4.5	3.0	---	2.0	---	---	1.8	5	10	1:0.5:1.5:2.0	57.7	3.0	---	---	---	---	3.3	0.05	13	Gulf HT	H_2O
MS-11	Simulated Sludge and Supernate(d)	5	1.19	52.0	3.0	3.2	---	---	---	---	---	---	4.4	4.4	4.0	---	---	---	---	---	1.7	5	40	1:0.5:1.5:2.0	61.2	2.55	0.275	0.13	4.2	---	3.1	0.05	13	Gulf HT	H_2O
MS-16	Simulated Sludge and Supernate(d)	0	1.39	61.4	3.6	3.1	---	---	---	---	---	---	3.5	4.0	3.3	---	---	---	---	---	2.1	40	120	1:0.5:1.5:1.25	55.9	2.9	0.12	0.32	4.4	---	---	(e)	14	Gulf HT	H_2O
HS-1	HW Sludge and Supernate(f)	5	4.47	49.4	5.0	4.0	3.0	>5.8	1.7	---	5.5	2.4	4.0	3.5	3.1	---	---	---	---	---	1.7	10(g)	230	1:0.55:2.2:1.67	60.5	4.1	0.15	0.10	5.9	2.1	4.95	(e)	12.3	Decbase	H_2O
HS-2	HW Sludge and Supernate	5	6.4	56.6	4.5	3.8	3.3	5.6	1.7	5.3	4.5	---	4.3	4.1	4.2	---	---	---	---	---	2.1	30(g)	90	1:0.5:2.0:1.6	57.5	3.7	0.20	0.22	6.6	3.4	5.1	(e)	12.5	Decbase	H_2O

Purex Process Pulsed-Column df's (Based on Radioactivity in AAF)
(All Runs at O.R.N.L. Purex Flowsheet No. 1 Conditions)

Run	Source of Feed	Age of Feed, Days	Packed Height in Scrub Sections, Ft.(a)	Feed Stream Radioactivity (h) Beta (c./m./mg.U) (x 10^-5)	Feed Stream Radioactivity (h) Gamma (mr/mg.U)	IAF Stream df's Beta	Gamma	Ru	Zr	Ce	TRE(b)	ICU Stream df's Beta	Gamma	Ru	Nb	Zr	Ce	TRE(b)	ICU Activity, % of Activity Of Natural U Beta	Gamma	References	Column Operating Conditions Column	Pulse Frequency, Cycles/Min.	Pulse Amplitude, Inches
IMP-5	O.R.N.L. Slugs	> 70 days	12.5	8.1	685	3.5	2.8	2.2	3.2	3.5	5.3	4.4	3.6	3.0	3.3	5.1	6.5	35	3.5×10^3	ORNL-1045	IA Extraction	58	0.42
																					IA Scrub	58	0.92
IMP-8	HW Slugs	160 days	18	14.3	1.2×10^4	3.6	2.7	2.7	3.3	3.2	5.0	4.4	3.8	3.2	4.1	4.3	7.4	700	3.5×10^4	CF-51-8-46	IB Extraction	58	0.75
																					IB Scrub	58	1.38
IMP-9	HW Slugs	120 days	18	162	1.5×10^4	3.9	2.3	2.7	4.9	3.4	5.8	4.6	4.6	3.7	3.7	4.8	8.0	900	4×10^4	CF-51-8-46	IC	73	0.36

O.R.N.L. Purex Flowsheet No. 1

Stream	Composition	Relative Volume
IAF	1.39 M UNH, 2.0 M HNO_3, 0.32 M $NaNO_2$	100
IAS	3 M HNO_3	67
IAI	30% TBP in Amsco 123-15	333
IBS	30% TBP in Amsco 123-15	89
IBI	0.03 M $Fe(NH_4SO_3)_2$, 0.6 M HNO_3	89
ICI	Demineralized H_2O	665

NOTES:

(a) For other equipment details, see text.

(b) TRE = total rare earths.

(c) No plutonium reductant was added to the scrub or feed streams during run MS-3.

(d) Feed for runs MS-9, MS-11, and MS-16 was made up from HW supernate with UNH, Na_3PO_4 and H_2SO_4 added to simulated sludge and supernate.

(e) 0.4 M ferrous sulfamate for plutonium reduction was added to the HAF stream at a relative flow ratio of approximately 0.38 during runs MS-16, MS-1, and MS-2.

(f) Entrained aqueous carried with the HAU during run MS-1 resulted in contamination of the HCU; thus the df's for the HAU are lower than for the HCU.

(g) Per cent of natural uranium radioactivity based on the HCU stream. All other per cent of natural uranium radioactivity figures are based on the HAU stream.

(h) Beta counting at approximately 11% geometry. The radioactivity of natural uranium under equivalent counting conditions is approximately 80 beta cp./min./mg.U and 0.205 mr./mg.U.

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Figure V-7
H.T.U. vs. VOLUME VELOCITY
RA COLUMN EXTRACTION SECTION

Source of Data:	Extrapolated from HW-19170, Figs. 6, 7, 10.
Diffusing Component:	UNH
Flowsheet Conditions:	TBP-HW Nº 4.
H.T.U. Calculations:	Over-all Aqueous-Film Basis
Column Inside Diameter:	20 In.
Plate Section:	Plates with 1/8 In. Holes, 23% Free Area. Plates Spaced at 2 In. (Face to Face). Height = 12 Ft.
Pulse Amplitude:	1.28 In

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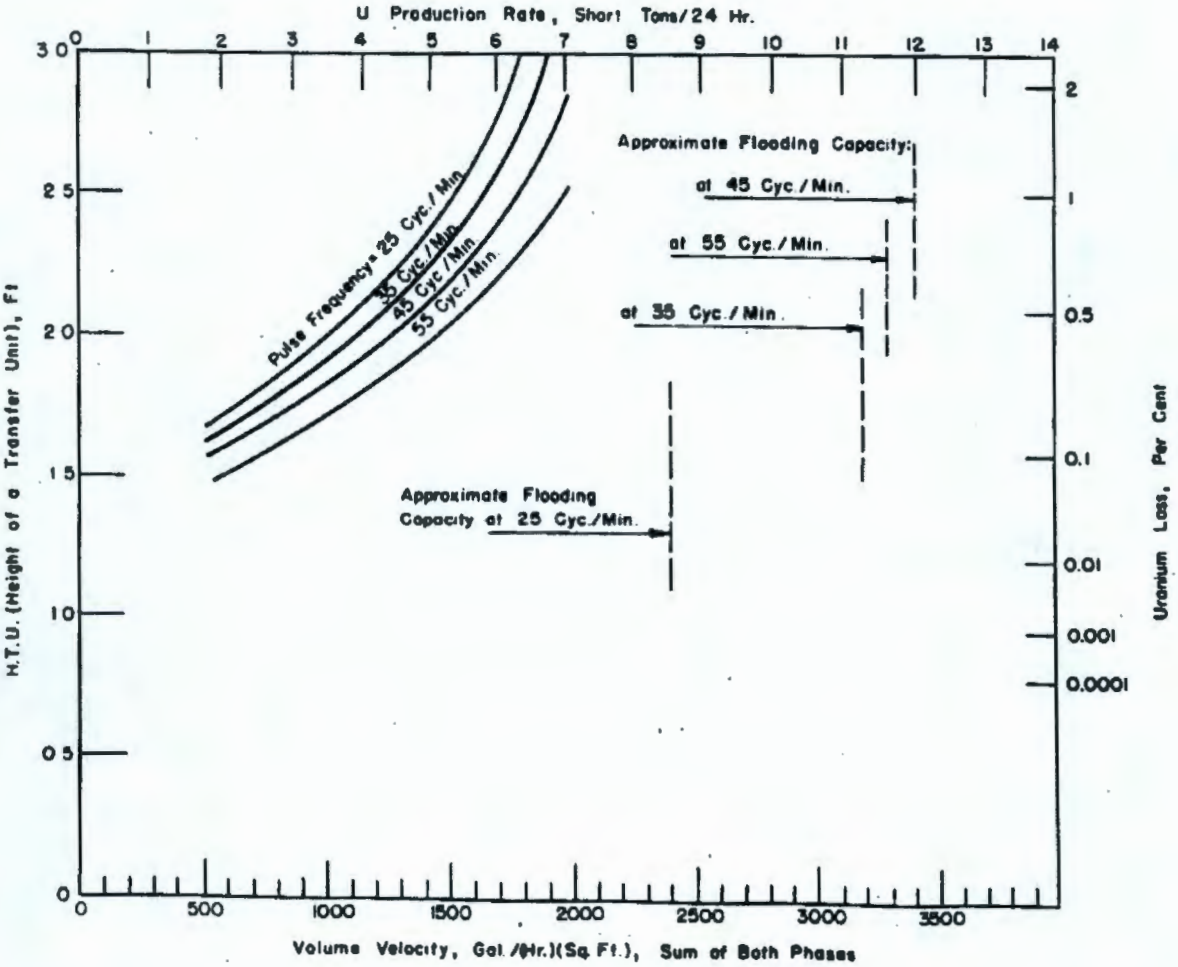

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Figure V-1
OPERATING DIAGRAM FOR RA COLUMN

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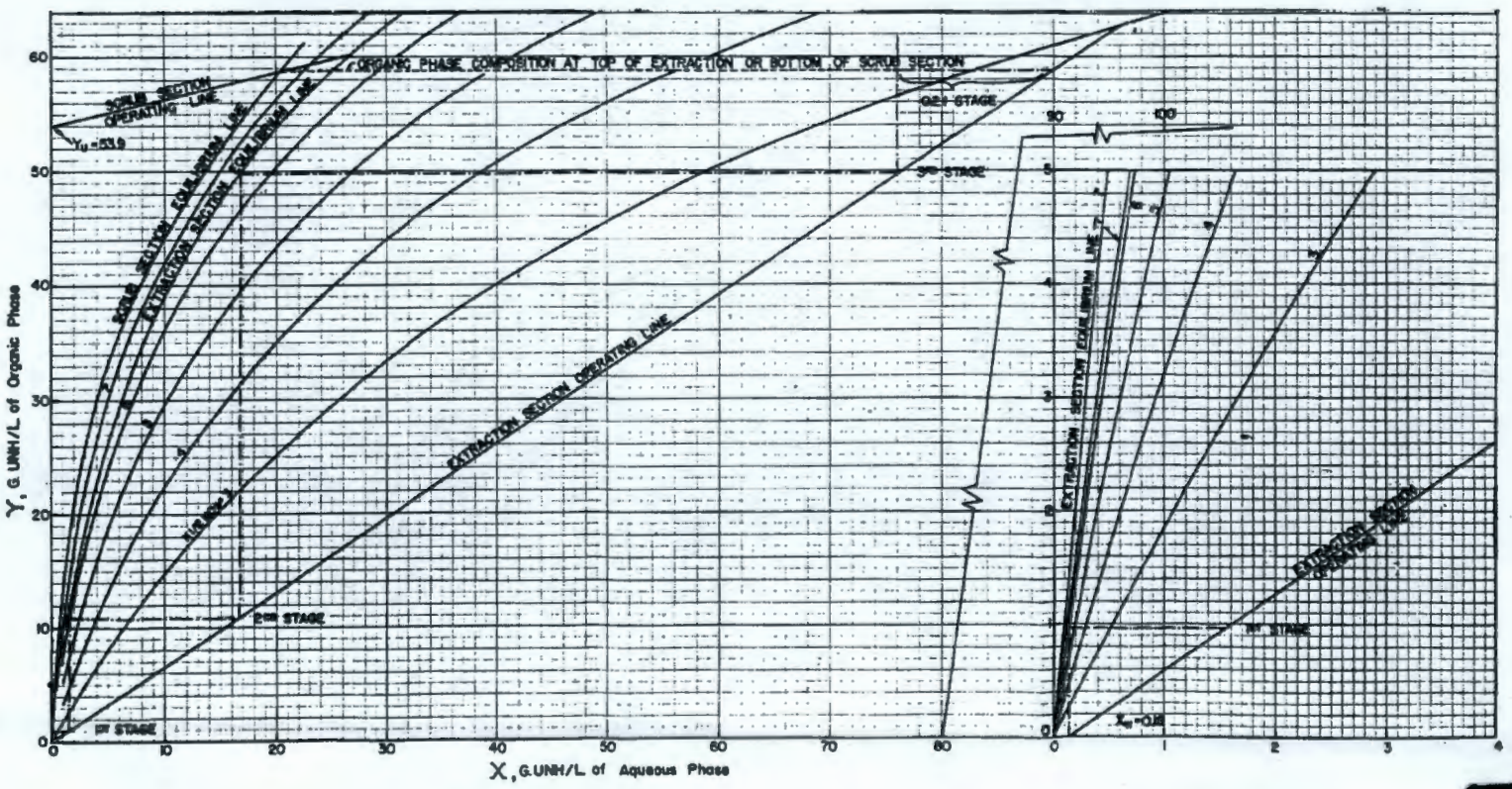

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Figure V-8
H.T.U. vs VOLUME VELOCITY
RC COLUMN

Source of Data:	Extrapolated from HW-19170, Figs. 11, 12, 13, 16.
Diffusing Component:	UNH
Flowsheet Conditions:	TBP-HW Nº 4
H.T.U. Calculations:	Over-all Organic-Film Basis
Column Inside Diameter:	30 in.
Plate Section	Plates with 1/8 in. Holes, 23% Free Area.
	Plates Spaced at 2 in (Face to Face)
	Height = 12 Ft
Pulse Amplitude:	0.57 in

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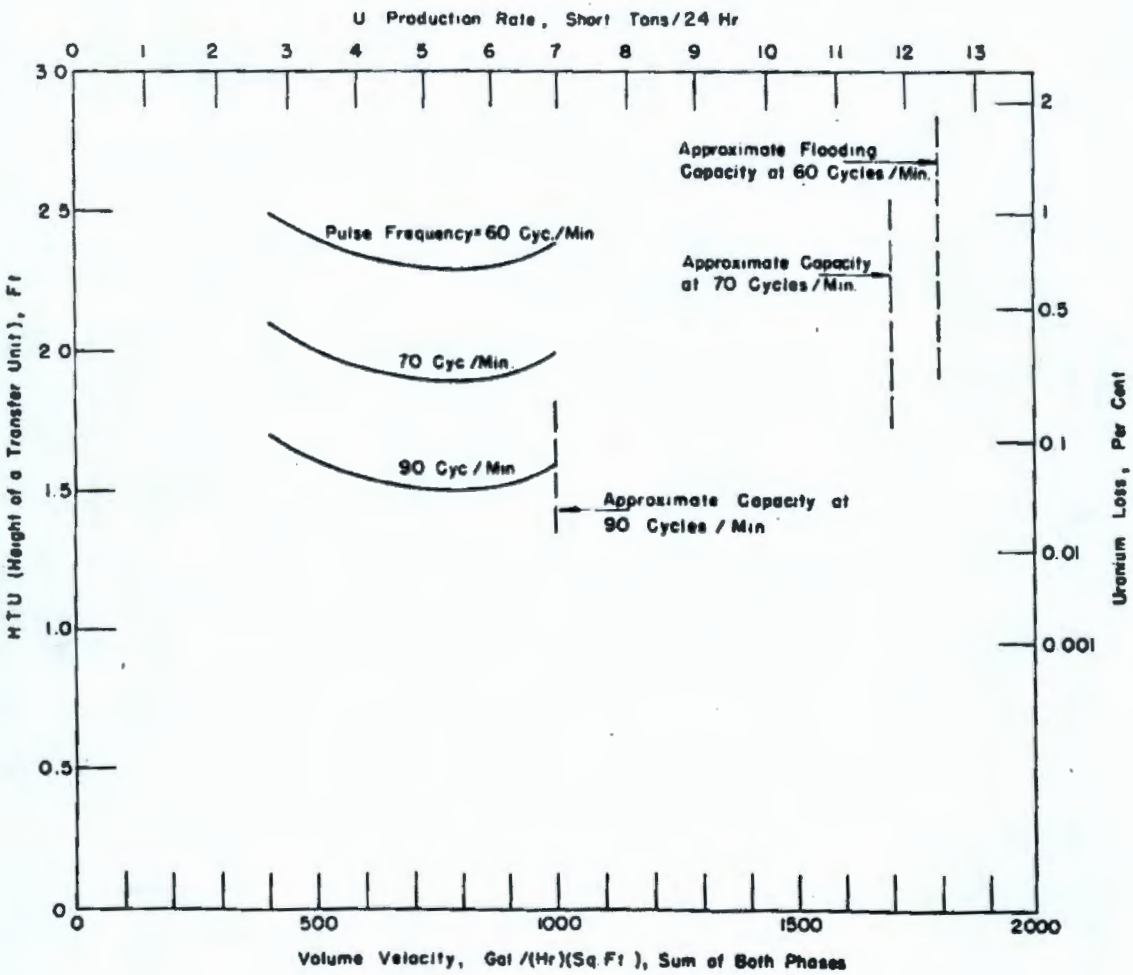

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FIGURE V-9
DECONTAMINATION IN THE RA COLUMN

Effect of Fission—Product Distribution Ratio

Basis: (a) Feed: scrub: extractant volume flow ratios = 1 : 0.5 : 2.5. (b) Fission-product distribution ratios in the portion of the extraction section just below the feed tee equal to those in the scrub section. (c) "Over-all organic-film" transfer units in the scrub section.

Nomenclature: E_s^* = Distribution ratio in the scrub section, g. of f.p. per liter of organic phase divided by g. of f.p. per liter of aqueous phase.
V = Organic phase flow rate, volume per unit time
L = Aqueous phase flow rate in the scrub section, volume per unit time.
P = extraction factor = $E_s^* V/L$.

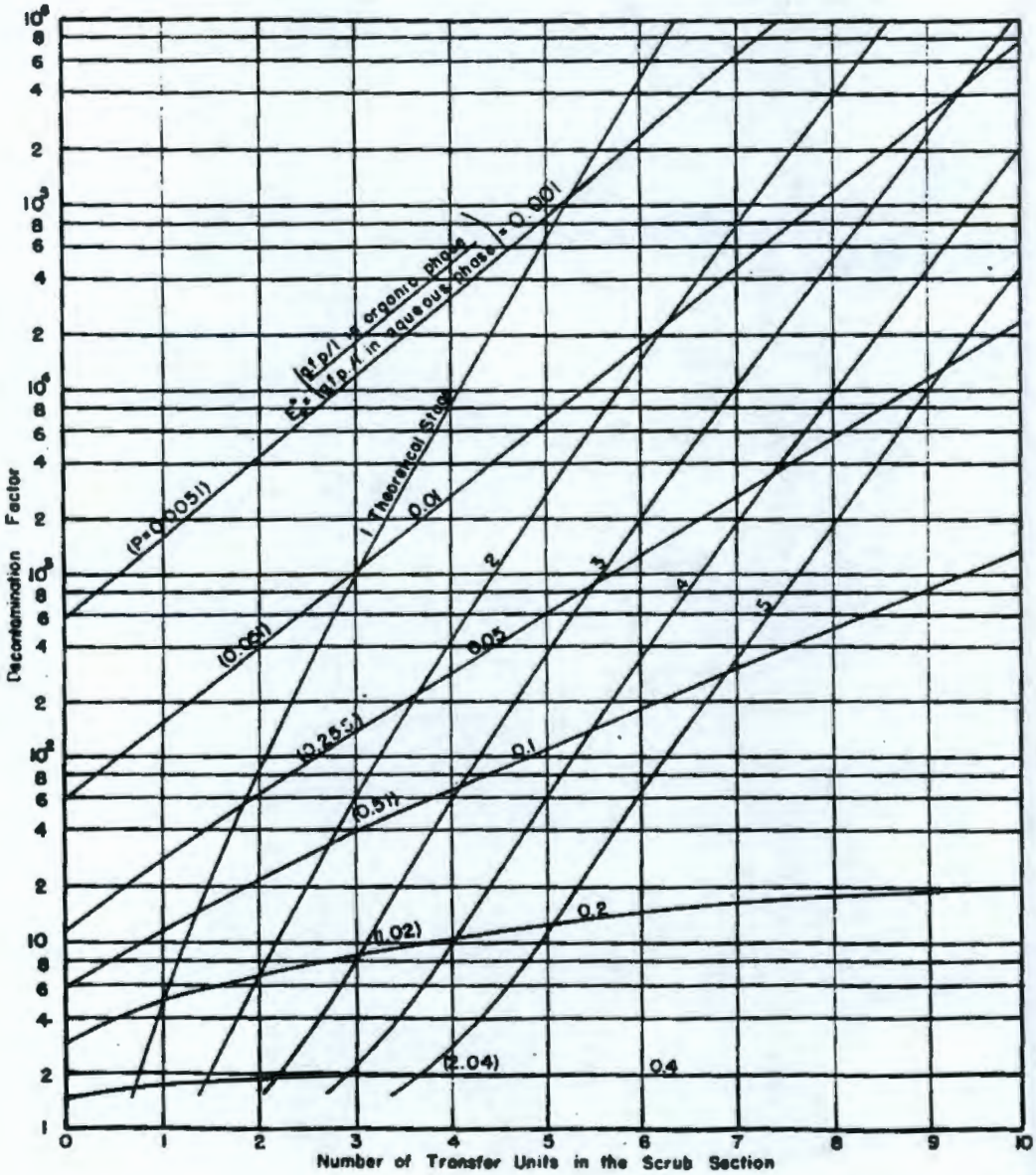

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FIGURE V-10

DECONTAMINATION IN THE RA COLUMN

Effect of Fission - Product Distribution Ratio

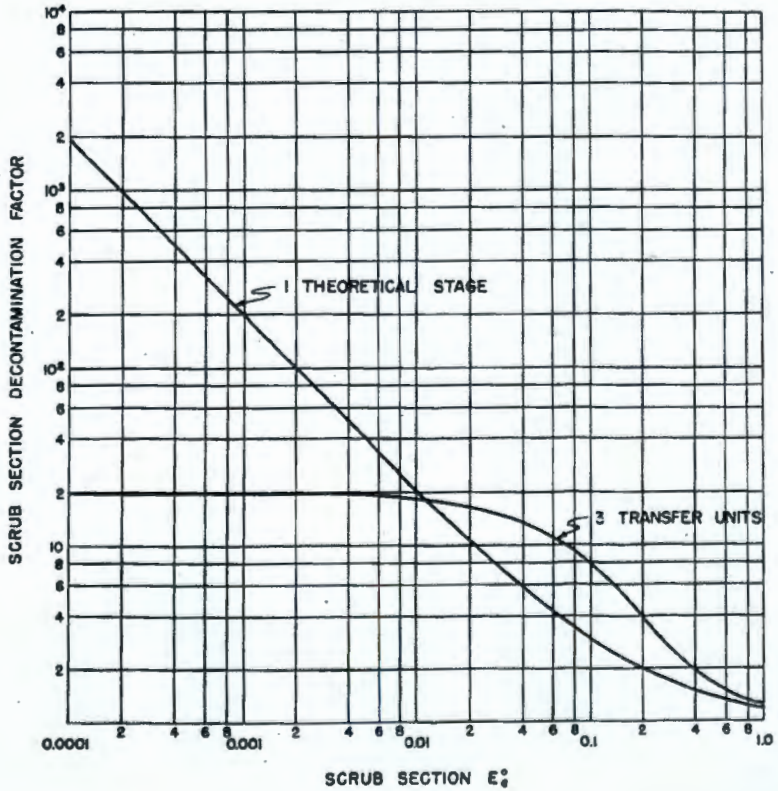
Basis: (a) Feed:scrub:extractant volume flow ratios = 1:0.5:2.5.

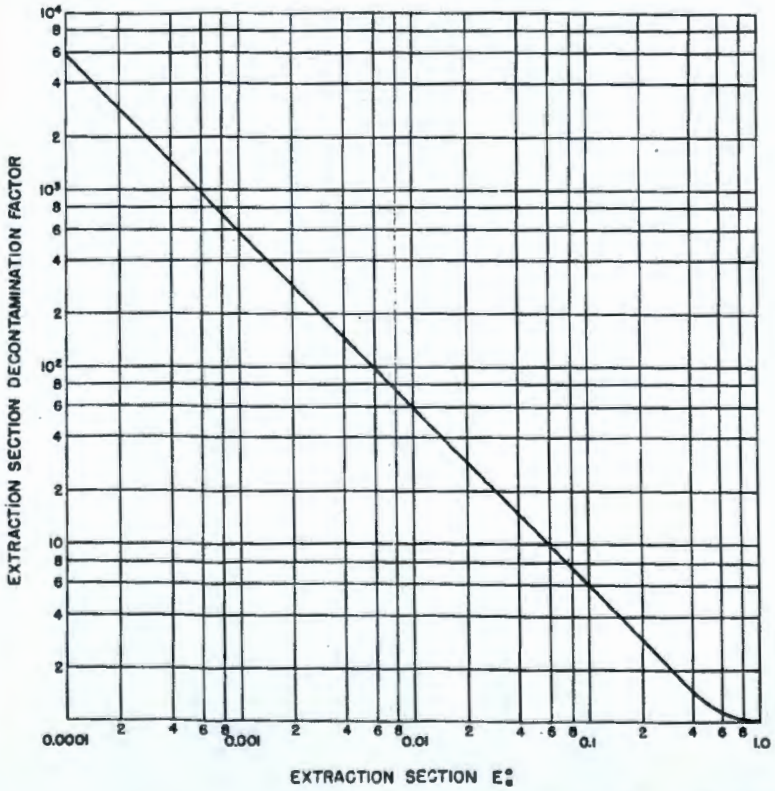
Nomenclature: E_d^o = Fission-product distribution ratio, g. of f.p. per liter of organic phase divided by g. of f.p. per liter of aqueous phase.

Use: The over-all uranium D.F. from fission-products or groups of fission-products whose apparent distribution ratios vary between the scrub and extraction sections may be determined from these figures for an RA Column containing 1 scrub stage or 3 scrub "over-all organic-film" transfer units. The over-all D.F. is related to the individual scrub and extraction section D.F.s, as read from the figures, by the following equation:

Over-all RA Column D.F. = (Scrub Section D.F.) (Extraction Section D.F.) - Scrub Section D.F. + 1

The last two terms of this equation correct for the effect of fission-product reflux from the scrub section.





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PART II: PROCESS, continued

CHAPTER VI. SOLVENT-EXTRACTION PROCEDURE

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CHAPTER VI. SOLVENT-EXTRACTION PROCEDURE

A. ENGINEER'S FLOW SKETCH

1. Introduction

A brief over-all description of the uranium recovery process is presented in Chapter I in connection with the discussion of the chemical flowsheets. The purpose of this chapter is to describe normal and off-standard operating procedures for the solvent-extraction portion of the process. An engineer's flow sketch will be utilized in this description, as well as to indicate the process streams and equipment employed. The reader is referred to Chapters IV, V, XV, and XVI for detailed background information on solvent-extraction process chemistry, process engineering, and equipment.

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2. Interpretation of the Flow Sketch

The engineer's flow sketch presented as Figure VI-1 schematically shows the process streams and equipment for the solvent-extraction portion of the uranium recovery process. This figure indicates more of the details of the process than the chemical block diagrams of Chapter I, but less detail than the engineering flow diagrams of Chapter XIV. In order to indicate the connections between the feed concentration, solvent-extraction, and waste concentration steps, the equipment associated with all three steps is shown in the engineer's flow sketch. It will be noted that the flow pattern is such that two parallel streams (each nominally handling 5 tons of uranium per day) proceed through the feed concentration and solvent-extraction equipment. The streams then join and are processed through one of three alternative waste concentration batteries. The tanks, columns, control equipment, and stream flow rates necessary to process 10 tons per day of uranium are noted. Additional information covering such items as lubrication lines, electrical lines, connectors, and spare connectors may be obtained from the engineering flow diagrams in Chapter XIV. Exact dimensions of process equipment may be found in the detailed mechanical design drawings for the specific equipment pieces.

B. NORMAL PROCEDURE

1. Introduction

The principal equipment items of the solvent-extraction cycle are two parallel pairs of pulse columns, RA and RC, for countercurrent liquid-liquid extraction. The compositions and flow rates shown on Figure VI-1 correspond very closely to those presented in the TBP-HW No. 4 Chemical Flowsheet (see Chapter 1) at a uranium production rate of 5 tons per day in each of the two parallel processing lines. The satisfactory operating range of the installed equipment, however, covers a much broader range of conditions as a result of the flexibility designed into the plant. Thus it is possible to operate the various processing units, including the pulse solvent-extraction columns, over a range of uranium production rates

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from 2 to 5 tons per day without exceeding the allowable uranium waste losses.

2. Steady-State Operation

The first (RA) extraction column is a compound column consisting of an extraction and a scrub section. In the extraction (lower) section of the column, uranium and some fission products and plutonium are extracted from the continuous aqueous phase into the rising, dispersed organic phase (RAX). In the scrub (upper) section of the column, the rising uranium-laden extractant is countercurrently contacted by a scrub solution (RAS), which scrubs the bulk of the fission products and plutonium from the dispersed extractant. The influent and effluent streams involved in column operation are as follows:

The aqueous uranium-bearing feed (RAF) is pumped through a recording and controlling rotameter from the RAF Feed Tank, TK-19-6, to an intermediate feed point, between the scrub and extraction sections, of the RA Column, ET-19-8. The aqueous scrub stream (RAS), containing ferrous ammonium sulfate as a reductant, sulfamic acid as a holding agent for the reductant, and nitric acid as a salting agent, is fed through a recording and controlling rotameter to the top of the RA Column. The aqueous waste effluent from the RA Column (RAW) should contain not more than 0.5% of the entering uranium. The rate at which this stream leaves the column is controlled by the interface dip tubes located at the top of the column. After being collected in the RAW Receiver Tank, TK-19-7, the aqueous waste is pumped under liquid-level control to the Pooled RAW-RCW Receiver Tank, TK-13-6.

The organic extractant (RAX), TBP-hydrocarbon mixture, is pumped from the RAX Feed Tank, TK-20-6, through a recording and controlling rotameter to the bottom inlet of the RA Column. The organic effluent, RAU, leaves the top of the column and contains the bulk of the uranium from the RAF, together with a small fraction of the original quantity of fission products. It flows by gravity to the bottom of the RC Column, ET-19-2.

The function of the RC Column is to strip the uranium from the organic into an aqueous phase. This is accomplished by contacting the dispersed organic phase (RCF) with a slightly acidified aqueous stream (RCX) introduced at the top of the column through a recording-controlling rotameter. The effluent TBP-hydrocarbon organic phase (RCW) leaving the top of the RC Column should contain not more than 0.5% of the uranium contained in the RAF.

The RCW stream, after leaving the column, flows to the RCW Receiver Tank, TK-9-1, and is then processed in the RO Column. The flow rate of the effluent aqueous stream (RCU) from the RC Column is controlled by the column interface dip tubes located at the top of the column. This stream flows by gravity (through a flooded jet, which may be used to empty the column) to the RCU Pump-Out Tank, TK-19-3, and is then pumped under liquid-level control to the RCU Receiver Tank, TK-16-1.

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All non-radioactive aqueous influent streams to the solvent-extraction battery are gravity fed from tanks situated in the "cold" section of the TBP Plant (Building 221-U). The "cold" organic influent stream to the solvent-extraction column is fed directly from the RAX Feed Tank, TK-20-6 (located in Cell 20 in the canyon).

It will be noted that flow rates of the RAF, RAS, RAX, and RCX streams are controlled by recording-controlling rotameters. The flowrates of the RAW and RCU streams are controlled by interface dip tubes located at the top of each column. All these instruments are automatic, but can be operated manually when required, e.g., when the equipment is started up or shut down. Differential and static pressure recorders are also provided on each column as a means of detecting flooding conditions in the columns and as an aid in the early determination of any excessive uranium losses. A functional description of the instruments is given in Chapter XIX.

Auxiliary equipment shown on the sketches, such as strainers, samplers, jets, and pumps, is described in Chapters XVI and XVII.

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3. Startup

The preceding discussion has dealt with steady-state operation of the columns. In order to avoid unnecessary waste losses or an off-standard uranium stream in establishing steady-state operation, a startup procedure similar to the following is employed:

(a) The TBP-hydrocarbon organic extractant (RAX) flow to the RA Column is started.

(b) As soon as the RA Column is filled with the organic extractant, the pulse generator is started, and the "cold" aqueous flow (RAS) is established.

(c) The organic overflow from the RA Column fills the RC Column while correct interface conditions are being reached in the RA Column.

(d) When the RC Column is filled with the organic phase, the RC pulse generator is started, and the "cold" aqueous flow (RCX) is established.

(e) After the interfaces in the two columns have been established, the introduction of the radioactive feed (RAF) to the RA Column is started.

The control instruments are manually operated while flows are being increased or decreased, but when flows become steady the instruments are shifted to automatic control.

4. Shutdown

When the TBP Plant solvent-extraction columns are to be shut down, a

reversal of the above-mentioned startup procedure, as outlined below, is followed.

(a) The feed (RAF) to the RA Column is shut off.

(b) Stripping uranium from the columns is then carried out for a period of about 10 to 15 minutes. It is estimated that about 300 gallons of organic extractant will be required to extract the uranium from the aqueous phase in the plant-size RA Column. With the flow rates shown on Figure VI-1, approximately 300 to 500 gallons of RAX will be used if stripping is carried on for 10 to 15 minutes. Increasing stripping time will therefore be required if the solvent-extraction battery is operating at a uranium production rate lower than 5 tons per day (or, alternatively, the RAX flow may be increased at the beginning of the stripping operation).

(c) After the column stripping is completed, the RAX flow is discontinued, but pulsing and the addition of RAS is continued. When the RAX flow ceases, the organic phase normally dispersed in the column gradually rises to the top. This is accompanied by a temporary decrease in the aqueous effluent (RAW) flow rate as the aqueous feed takes up the volume previously occupied by the dispersed organic globules. As soon as the displaced organic phase is replaced, the interface level returns to its normal position and the RAW flow rate resumes a value equal to the RAS flow rate.

(d) The organic phase above the interface in the RA Column is displaced by the continued addition of RAS. This requires manual operation of the interface controller in order to allow the aqueous level to rise above the normal control point. Top phase disengaging section specific gravity readings, based on the differential pressure between the top two of the three differential-pressure dip tubes, provides an indication of when essentially all of the organic phase has been displaced from the column.

(e) RA Column pulsing and the addition of RAS are discontinued.

(f) Normal operation of the RC Column is continued until the flow of RCF(RAU) ceases. The sequence of events in the RC Column during this period is very similar to the operation of the RA Column when the organic feed was shut off. That is, the organic material normally present in the column gradually rises to the top. Simultaneously, the organic phase is replaced by the aqueous influent (RCX). During this period the interface level drops and the flow of aqueous effluent (RCU) decreases. After the organic replacement has been completed, the organic-aqueous interface level resumes its normal position. The nearly-normal RCU flow, equal to RCX flow, is then reestablished by the automatic controller.

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(g), The organic phase above the interface in the RC Column is displaced by continued addition of RCX. This is accomplished by manual operation of the interface controller in the same manner as described under (d), above.

(h) Pulsing of the RC Column and the addition of RCX are discontinued.

(i) At this stage, both the RA and RC Columns contain only "cold" aqueous solutions. These solutions may be drained into the RAW or RCU Receivers, respectively, by manual manipulation of the automatic interface controllers.

If direct maintenance is required in the column cell areas, it is possible to introduce special decontamination solutions into the head tanks for decontaminating the inside of a particular column or other "hot" equipment piece. Wall sprays are also available for cleaning the cell and the outer surfaces of the equipment.

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C. REMEDY OF OFF-STANDARD CONDITIONS

1. Specifications

Purity specifications for the product of the TBP Plant and the permissible losses to waste streams have not been firmly established and probably will not be until operation of the plant has made it possible to determine the performance under normal running conditions. Firm product specifications and the decisions as to when an off-standard stream is to be reworked will be based on a balance among several considerations. The possible deleterious effects of the off-specification material on subsequent processing, the value of the uranium in off-standard waste streams, and the cost of meeting the specifications by normal operation or by rework will be major factors in the decision.

At this writing, tentative specifications for decontaminated uranium (RCU) are:

Impurity	Maximum Concentration
Beta radioactivity from fission products	1×10^{-7} absolute curie/g.U
Gamma radioactivity from fission products	5×10^{-8} absolute curie/g.U
Plutonium	1 part/10^7 parts of U (0.1 p.p.m.)
Iron	1 part/10^3 parts of U (1000 p.p.m.)
Sodium	1 part/10^3 parts of U (1000 p.p.m.)
$PO_4^{\equiv}$	2 parts/10^3 parts of U (2000 p.p.m.)
Ni, S, Mo, Cr, W, Si, B [redacted]	1 part of each/10^4 parts of U (100 p.p.m.)

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The maximum permissible total uranium losses to the solvent-extraction battery waste streams will be finally set after the plant is in operation, but will probably not exceed about 2.0% of the uranium in the RAF feed.

2. Detection of Off-Standard Conditions

During routine plant operation, it is expected that only three streams leaving the solvent-extraction cycle will be monitored by analysis for off-standard conditions. These streams are the uranium effluent stream from the RC Column (RCU), the fission-product-laden waste stream from the RA Column (RAW), and the organic effluent (RCW) from the RC Column. After detection of off-standard conditions in an effluent stream, it will be necessary to check systematically back through the possible sources of error until the specific cause is discovered and corrected.

Generally, detection of an off-standard uranium or waste effluent stream calls for an immediate check of readings supplied by the instruments for each column. These readings include:

(a) flow rates of all influent streams;

(b) pressure readings from the differential and static pressure taps (to detect possible flooding, or in some cases, high uranium loss);

(c) specific gravities of influent streams;

(d) radiation recorder readings (if required).

Flow rates of all influent process streams to the TBP columns are controlled by Hammel-Dahl diaphragm-operated motor valves positioned by Foxboro recorder-controllers. Normal control of flow rates is automatic except during periods of startup and shutdown. If the flow rate of a particular stream, as indicated by the recorder, is suspected of being incorrect, it is possible to obtain a cross-check by the use of feed tank weight-factor readings.

The flow control, static and differential pressure, and radiation instruments are described in Chapter XIX. There are four dip tubes on each of the RA and RC Columns for indicating static and differential pressures. One of the dip tubes (the static pressure tap) is located below the perforated-plate cartridge. The other three tubes in each column are located in a cluster (6-inch vertical spacing between the top and center tubes and 6-inch vertical spacing between the center and bottom tubes) just above the perforated-plate cartridge. The differential pressure measured across the top two of the three dip tubes is influenced primarily by the density of the organic effluent from the particular column in question. During normal operation the aqueous-organic interface level in the column is between the bottom two of the three dip tubes. Thus, variations in the differential pressure across these two tubes will indicate a change in the interface level. The location of the static and differential pressure taps on the solvent-

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extraction columns and the technical basis of their use are discussed in Chapter V.

3. Use of Column Static and Differential Pressure Readings

3.1 Detection and remedy of flooding

Flooding in the solvent-extraction columns is detected by the use of remote instruments, because of the high radiation level of the process solutions. Chief reliance for the detection of flooding is placed on the static pressure readings for the column under consideration. At flooding, there will be a drop in the static pressure reading as the lighter organic (dispersed) phase tends to fill the columns. A secondary effect will be erratic changes in aqueous effluent rate as the controller attempts to steady a changing interface by regulating the aqueous effluent flow rate. The normal readings of the instruments will be known from calibration during initial column operation.

Generally, a flood in a column is dissipated by reducing the influent stream flow rates and/ or the pulse frequency and then waiting until the operation of the column is restored to normal. It should be noted in this connection that if the pulse frequency is reduced too far (i.e., to a point at which the pulsed volume velocity is less than the volume velocity of the combined column influent streams) the flood will not be dissipated. After normal operation is established, the flow rates and/or pulse frequency may be returned to operating levels. If non-standard conditions (such as emulsification or plugging of the packing) are the cause of flooding, it may be necessary to shut the plant down until these conditions are remedied.

3.2 Detection of high uranium loss

The organic phase effluent density, as determined by pressure measurements, gives an indication of gross uranium losses from the columns. In the RA Column, a decrease in the organic effluent (RAU) phase density will usually indicate that excessive losses are occurring. In the RC Column an increase in the organic effluent (RCW) phase density, or an increase in the static pressure at the base of the column, may give warning that excessive uranium losses are occurring. It should be borne in mind, that these pressure measurements also reflect changes in other variables, such as uranium concentration in feeds, flow rates, HNO_3 concentrations, and salt concentrations. However, under normal steady-state operating conditions, a fluctuation in the above pressures may give warning that uranium losses have markedly increased. A normal or special sample from the pooled RAW-RCW streams will provide a check on column operation. A more detailed discussion of the technical background for interpretation of column differential pressure measurements is contained in Chapter V.

4. Rework of Off-Standard Process Streams

Any required rework of off-standard process streams in the TBP Plant will normally involve one of the following two streams:

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(a) the pooled RAW-ROW waste stream--to recover excessive uranium losses; or

(b) the final uranium product stream (RCU)--to decontaminate the uranium from an excessive plutonium and/or fission-product content.

Methods of reworking these off-standard streams are discussed below.

4.1 Off-standard waste streams

Excessive uranium losses in the waste streams of either the RA or the RC Columns are ultimately detected and corrected in the same manner. Due to the process flow involved in the TBP Plant, uranium lost in the columns is combined in the Pooled RAW-ROW Receiver, TK-13-6 . Uranium in the RAW waste stream flows through an RAW Receiver to this Tank. Faulty operation of the RC Column causes a uranium buildup in the RCW (organic waste) stream. The uranium is thence transferred in the RO Column to the ROW (aqueous waste) stream. The ROW stream flows through an ROW Receiver to the Pooled RAW-ROW Receiver. The combined RAW-ROW stream flows to one of four Waste Sampler Tanks (TK-11-1, 12-1, 12-6, or 13-1). The RAW Receiver, ROW Receiver, Pooled RAW-ROW and Waste Sampler Tanks are all provided with samplers. Under normal operating conditions, the following uranium determinations will be made.

Sample	Frequency
RAW Receiver	2 per week
ROW Receiver	4 per week
Pooled RAW-ROW Receiver	21 per week
Waste Sampler Tank	Uranium determinations made only if Pooled RAW-ROW Receiver analyses indicate high losses

If the samples indicate an excessive quantity of uranium in the Waste Sampler Tanks, the waste is routed to the Waste Utility Holdup Tank, TK-4-6 , and thence is reworked via the solvent-extraction cycle Feed Tanks. The RAW and ROW streams cannot be reworked separately.

No rework provisions are made directly for excessive quantities of uranium in the RCW. Should this situation develop, the uranium is stripped from the organic phase in the RO Column, and the waste stream (ROW) is reworked, if desirable, in the waste rework system described above.

4.2 Off-standard uranium product (RCU)

Off-standard uranium streams that do not meet specifications with respect to plutonium content or decontamination from fission products are detected in either the RCU Receiver, TK-16-1, or the RCU Sampler, TK-15-1. Disposition of this material is made to the Feed Utility Holdup Tank, TK-4-1, from which the off-standard batch may be reworked through the extraction cycle by blending with normal feed.

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PART II: PROCESS, continued

CHAPTER VII. CONCENTRATION OF RECOVERED URANIUM

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CHAPTER VII. CONCENTRATION OF RECOVERED URANIUM

A. PROCESS DESCRIPTION

1. General

It has been specified that the uranium end-product of both the Redox and TBP processes (3EU and RCU, respectively) be transformed to the uranium trioxide (UO_3) state for off-plant shipment.(3) The concentration of these mixed uranyl nitrate (UNH) solutions to a degree satisfactory for charging to the UNH Calcination Pots (see Chapter VIII) is described in this chapter.

Redox 3EU is normally concentrated to about 60% UNH by weight before leaving the Redox Plant. In order to avoid confusion between concentration states during discussion of the additional concentration applied before this UNH solution is suitable for charging to the Calcination Pots, the partially concentrated 3EU solution leaving the Redox Plant is designated in this chapter as 3EU (concentrated to 60% UNH).

RCU and 3EU (concentrated to 60% UNH) are mixed and concentrated to a uranyl nitrate concentration corresponding to about 80 to 100% UNH. As discussed in Chapter VIII, the concentrated product stream is fed to the Calcination Pots, where the UNH is calcined to UO_3.

In this chapter uranyl nitrate concentrations in solution are expressed as per cent uranyl nitrate hexahydrate (UNH). This method is merely a convenient convention and implies that if the solution were cooled to its freezing point, UNH would separate from solution as a solid phase.

2. Concentration

The UNH concentration of RCU will probably range from about 5 to 7% UNH, reflecting variations in uranium concentration in the solvent-extraction battery feed and the manipulation of other Column influent stream flow rates to compensate partially for these variations. The design of the concentration system is based upon a 5% UNH RCU since this represents the more conservative approach. The UNH concentration of incoming 3EU, which mixes with the RCU, is about 60%.

The final UNH concentration reached in the system is about 100% UNH (exact figure to be determined during operation). During such a large volume change the physical properties of the solution change markedly. Reference is made to Chapter IV for data on the uranyl nitrate phase diagram and and on density, viscosity, specific heat, and other properties, as a function of temperature and UNH concentration.

The Product Evaporators (E-B-1, E-D-1, and E-D-2) are long-tube, vertical, natural circulation type concentration units. They are described in detail in Chapter XVI. A schematic drawing of one of the Evaporators is presented on Figure VII-1 and may be referred to for additional clarity in the following

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description. Briefly, dilute UNH solution entering the Evaporator mixes with recirculated, more concentrated solution and rises through the vertical tubes as heat is transferred to the solution from condensing steam on the outside of the tube walls. The effective liquid level in a downcomer exerts a static pressure on the liquid at the bottom of the tubes. As the liquid rises in the tubes some is vaporized, thus reducing the density of a unit volume of liquid-vapor mixture. As long as the total pressure (due to the weight of the contents of a tube and the velocity pressure drop of the mixture rising through the tube) does not exceed the static pressure available at the base of the tubes, the vapor-liquid mass jets upward into the vapor space of the Evaporator. The vapor is separated from the concentrated liquid, which returns to the base of the Evaporator through a downcomer for recycle by blending with dilute feed or for withdrawal as product.

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Liquid deentrainment from vapor is accomplished both by interception of the liquid particles on an impingement plate (which also acts as a foam breaker) and by reduction of vapor velocity, due to vapor expansion, to a point where settling of some of the liquid droplets can take place. Additional deentrainment is gained by the abrupt changes of direction of the vapor as it passes through a Peerless Mist Separator (which consists of a series of "Z" plate baffles) in order to reach the vapor exit line of the Evaporator.

3. Nitric Acid Fractionation

The total amount of deentrained water vapor from the Product Evaporators (E-B-1, E-D-1, and E-D-2) contains approximately 1.5 to 2 weight per cent nitric acid. Evaporators E-B-1 and E-D-1 normally contribute about 96% of the total vapor volume, but only about 50% of the total vaporized nitric acid. Evaporator E-D-2 contributes the remaining 50% of the nitric acid in only about 4% of the total vapor volume. Two Nitric Acid Fractionators (T-B-4 and T-D-4) are provided for separating the two chief components of the vapor mixture (nitric acid and water vapor). The Fractionators are described in detail in Chapter XVI.

The Fractionators may be operated with several variations in the methods of feeding them. Normally, however, the entire amount of vapor produced in Evaporator E-D-2 will be routed to Fractionator T-D-4 (through a connection into the vapor space of Evaporator E-D-1), and all of the 40% nitric acid produced by the absorption of nitrogen oxides evolved in the UNH calcination reaction (See Chapter VIII) will be routed to either fractionator unit. As described in B1, below, the vapor from Evaporators E-B-1 and E-D-1 will be apportioned about 38% to the factionator unit receiving the 40% acid and about 62% to the remaining unit in order to maintain approximately the same heat loading on the reboiler of each fractionator unit.

Each Fractionator consists of two sections, an upper 8-1/2 ft. diameter section and a lower 5-ft. diameter section, each of which contains bubble-cap trays.

A typical operating diagram for one of the Nitric Acid Fractionators is presented in Figure VII-2. The operating conditions illustrated by Figure VII-2 differ from those presently conceived of as "normal" in the discussion above; however, an operating diagram similar to that illustrated may be constructed for any desired method of Fractionator operation.

Specifically, the operating diagram of Figure VII-2 illustrates the following:

(a) vapor feed to the Fractionator at a rate of about 21,700 pound moles per day consisting of 1.7 weight per cent nitric acid (vapor feed rate corresponds to processing the vapor evolved when 5 tons of uranium per day in the form of a dilute 5% UNH solution are concentrated to 100% UNH), and

(b) liquid feed to the Fractionator at a rate of about 1350 pound moles per day consisting of 40 weight per cent nitric acid (liquid feed rate corresponds to processing the 40% acid formed by absorption of all of the nitrogen oxides evolved during the calcination of UNH at a rate of 13-1/8 tons of uranium per day).

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Referring to Figure VII-2, the vapor composition (y), expressed as moles of HNO_3 per mole of vapor, and the liquid composition (x), expressed as moles of HNO_3 per mole of liquid are plotted on logarithmic scales. The equilibrium line for the HNO_3-H_2O system is shown as curve A-B.

The descriptive legend on Figure VII-2 illustrates that vapor feed (y_f, 0.0049 mole fraction HNO_3) enters the Fractionator at the juncture between the two sections (between the 8th and 9th plates from the bottom) and that liquid feed (x_f, 0.16 mole fraction HNO_3) enters on the 4th plate from the bottom. (However, under the specific conditions illustrated by the operating diagram it is apparent that plate 2 is the optimum plate for introduction of liquid feed.) Vapor rising through bubble caps of the 9th plate comes into contact with the liquid on this plate and partially condenses with the liberation of enough heat to vaporize an HNO_3-H_2O mixture richer in H_2O than the vapor condensed on the plate. The same phenomenon occurs on every plate, i.e., vapor passing up through the bubble caps of a plate contacts liquid which is richer in the more volatile component (water) than is the liquid on the plate below it, and a new vapor, correspondingly richer in H_2O, is evolved from the plate.

Condensed overhead vapor (x_1) is used as reflux to the top (17th) plate of the Fractionator. The design of the Fractionator is such that the overheads are substantially free of nitric acid (vapor overhead composition, y_o,= 0.00018 mole fraction HNO_3, corresponding to a pH of 2 or about 0.06 weight per cent HNO_3).

A reboiler in the base of the Fractionator furnishes the heat required to attain the desired fractionation in the lower section of the unit and to vaporize the reflux liquid. The nominal composition of the bottom liquid product (x_p = 0.30 mole fraction HNO_3) is 60% nitric acid.

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The operating line on Figure VII-2 consists of three distinct portions. The portion of the Fractionator between the vapor feed inlet point and the vapor product outlet is represented by curve y_o-C, the operating line with the equation

$$y = 0.168\ x + 0.00015$$

The portion between vapor feed inlet and liquid feed inlet is represented by curve C-D, the operating line with the equation

$$y = 0.92\ x - 0.022$$

The portion between liquid feed inlet and product outlet is represented by curve D-x_p, the operating line with the equation

$$y = 1.21\ x - 0.063$$

The slope of the "q" line y_f-C which locates point C, the intersection point between the operating lines above and below the vapor feed inlet point, is slightly less than zero (although not discernible from zero) since the vapor feed is somewhat superheated. The slope of "q" line x_f-D which locates point D, the intersection point between the operating lines above and below the liquid feed inlet point, is about 11 since the incoming liquid feed is cold. (For exact methods of determining the location and slope of operating lines and "q" lines see reference 2).

The theoretical plate requirements for each section of the Fractionator are indicated in the conventional stepwise manner for McCabe-Thiele diagrams on Figure VII-2. The figure indicates a theoretical plate requirement of between 1 and 2 for each of the three sections of the Fractionator. However, there are actually 4 bubble-cap trays plus the reboiler below the liquid feed inlet point, 4 trays between liquid and vapor feed inlets, and 9 trays above the vapor feed inlet. A possible actual operating condition is illustrated by steps drawn in solid lines (which represent the actual bubble-cap trays) with the following assumed tray efficiencies:

(a) 50% Murphree vapor efficiency for plates in the section below liquid feed inlet and for the reboiler,

(b) 45% Murphree vapor plate efficiency in the section between liquid and vapor feed inlet, and

(c) 35% Murphree vapor plate efficiency in the section above vapor feed inlet.

It is noted that with the assumed tray efficiencies neither point C nor point D corresponds exactly to the specific plate where feed material is actually added. The condition where the actual feed plate does not correspond to that calculated to be the optimum (in this case plate 2) is not unusual and means that instead of shifting from one operating line to

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another at point D or C, the old operating line is followed until the actual feed plate is reached. At the actual feed plate location (plates 4 and 8), the operating line for the section above the feed plate is followed. Since the feed to plate 4 is liquid, the vapor rising from plate 4 has a composition corresponding to line E-F. Since the feed between plates 8 and 9 is vapor, the liquid on plate 9 has a composition corresponding to line G-H. It may be noted that with the arbitrarily assumed efficiencies a somewhat greater than required nitric acid separation from the overheads is attained(i.e., the mole fraction HNO_3 in the overheads is less than the y_o of 0.00018).

Trace quantities (about 0.002 to 0.008 g./l.) of chloride ion may enter the organic phase of the RA Column and eventually appear in the Nitric Acid Fractionator. Since the chloride ion favors a solution consisting of about 25% HNO_3 [1], it is expected that bubble-cap trays containing liquid of approximately this composition (about the 6th tray from the bottom) will contain this ion and will, in fact, tend to accumulate it. Since HCl is more volatile than HNO_3 it is boiled up from the concentrated solution, and since it is very soluble in water, it is dissolved in the reflux liquid in the top of the Fractionator. Because the chloride does not tend to pass out of the Fractionator in the overhead vapors or concentrated acid bottoms, most of it accumulates in the Fractionator until purged as a side stream.

As discussed in Chapter III, corrosion of stainless steel by strong nitric acid solutions containing chloride ion concentrations greater than about 200 to 500 p.p.m. may be excessive.[5] A remedy for this condition, should it occur, is discussed in Subsection B2, below.

B. PROCEDURE

1. Normal Procedure

1.1 General

The facilities for concentration of recovered uranium are designed on the basis of the ability to process the maximum instantaneous capacities of both the Redox Plant (at 3-1/8 short tons U/day) and the Uranium Recovery Plant (at 10 short tons U/day) to a form suitable for charging to the UNH Calcination Pots. The succeeding discussion is based upon these capacities. Reference is made to the Engineer's Flow Sketch presented as Figure VII-3 for a functional schematic presentation of the processing facilities provided. A portion of Figure VIII-2 presents a Material Balance Flowsheet for the concentration operation.

1.2 Concentration

The RCU stream is received from the 221-U Building in either Feed Tank X-1 or X-2, where it mixes with 3EU (concentrated to 60% UNH) from the Redox process. Each vessel has a holdup capacity of about one day. The mixed UNH solution is pumped from either TK-X-1 or TK-X-2 by manifolded

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centrifugal pumps to the Feed Preheater, E-B-6. Two pumps in parallel are provided. Normally, they are used alternately. The total flow rate through the pump is about 66.5 gal./min. This flow rate corresponds to a 5%-UNH-RCU and a 60%-UNH-3EU (concentrated to 60% UNH) mixed solution and, as discussed under A2, above, probably represents a slightly greater flow rate than average. During passage through the Feed Preheater the solution temperature is raised from about 70°F. to about 150°F.

Two identical, parallel concentration lines are provided for concentrating the dilute UNH solution. Each line has been designed for a capacity of about 6 to 8 tons of uranium per day if the solution is concentrated from 6.4 to about 55 to 65% UNH. Because of the expected increased rate of evaporator corrosion at higher UNH concentrations and elevated temperatures, a separate, small, more-conveniently-replaceable Evaporator, E-D-2, is provided to concentrate the solution from 55 to 65% UNH up to about 100% UNH. Normally, feed will be apportioned between the two lines so that the heating load on the HNO_3 Fractionator reboilers is approximately equal. If all the 40% nitric acid from the gas absorbing system (note flow sketch, Figure IX-1) enters one Fractionator, as is the normal case, the uranium-bearing Concentrator feed will be distributed approximately 38% to the line receiving the 40% acid and approximately 62% to the remaining line. The concentration-fractionation system receiving the 40% acid is described below.

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Dilute feed (at a nominal rate of 25 gal./min., 38% of total feed rate) enters the base of the Evaporator, E-B-1, and mixes with recycle material. (The inlet point is baffled from the concentrate outlet, which is also in the base of the unit.) The solution passes up the inside of the vertical tubes, absorbing heat and partially vaporizing as it rises, and jets up from the open ends of the tubes. The vapor-liquid mixture strikes impingement baffles, which aid in separating the phases. The vapors expand into a low velocity zone and are then directed through a path requiring abrupt changes in direction before finally reaching the vapor exit line. Liquid separated from the vapor returns to the base of the Evaporator through a downcomer line (which is separate from the heat transfer portion of the unit) and is either mixed and recycled with fresh, dilute feed or withdrawn as partially-concentrated product to the UN Tank, TK-C-1.

The partially-concentrated solution (55 to 65% UNH) in TK-C-1 is pumped to the feed inlet of Evaporator E-D-2. The operation of E-D-2 is similar to that of E-B-1. Vapor from E-D-2 is normally routed to the vapor exit line from Evaporator E-D-1. The concentrated (approximately 100% UNH) bottoms from E-D-2 flow by gravity into Storage Tank X-19. A weight-factor controller for each Evaporator maintains a constant head in the down-comer (and a more or less uniform effective liquid level in the Evaporators) by actuating a control valve in the concentrated product line.

A pressure indicator-controller regulates steam pressure (hence temperature) in each Evaporator steam chest. The entire unit is comparitively insensitive to variations in feed composition and feed rate.

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A 10% concentration or flow rate variation of the feed results in only about a 1% variation in the composition of the product stream.

1.3 Nitric acid fractionation

Approximately 4000 std. cu. ft./min. of water vapor containing about 0.9 weight percent HNO_3 passes from Evaporator E-B-1 into Nitric Acid Fractionator T-B-4. These figures are based upon the aforementioned basis of 38% of total RCU feed flow to Evaporator E-B-1. As described in Subsection A3, above, the vapors are depleted in nitric acid as they rise through the bubble-cap plates, and the liquid is enriched in nitric acid as it overflows from plate to plate. Practically acid-free water vapor issuing from the Fractionator at about 5000 std.cu.ft./min. is condensed in Condenser E-D-3 and routed to the Condensate Tank, TK-C-5. A portion of the condensate is returned as reflux (by flow control from a pressurized header) to the top plate of the Fractionator at a rate of about 5 gal./min. Condensate not used as reflux is pumped at a rate of about 65 gal./min. (total from both Fractionators) to cribs via the 241-WR Diversion Station and Condensate Tanks, TK-007, 008, and 009.

Steam flow rate to the reboiler in the base of the Fractionator is controlled through measurement of the specific gravity of Fractionator bottoms and may be adjusted to produce the desired degree of product acid concentration (normally 60%). The 40% HNO_3 from the 40% HNO_3 Receiver, TK-C-3, is added to the 4th tray up from the bottom of the Fractionator at a nominal rate of about 2.3 gal./min. Normally, all of the 40% acid is routed to one of the two identical Fractionators (in this case T-B-4); however, lines are available to each unit.

The 60% acid product overflows from the reboiler of the Fractionator through a heat exchanger and into the 60% HNO_3 Receiver, TK-C-4. The acid is pumped continuously (at a rate governed by weight-factor control instrumentation in the tank) from TK-C-4 to the Nitric Acid Storage Tank, TK-006, in the 241-WR Diversion Station for eventual reuse in sludge dissolution.

1.4 Steam use

Because of the very large concentration load of Evaporators E-B-1, E-D-1, and E-D-2 (together with lesser heating duties of various other equipment pieces), the greatest possible steam economy is required in order not to exceed the steam production capacity of the 200 West Area Boiler House. Excessive steam demand on the boiler house may necessitate curtailment of the uranium recovery program (rather than to curtail production). Thus the total plant operating period required for uranium recovery might be lengthened, raising unit recovery costs of uranium out of proportion to the value of the steam causing the curtailment.

As an aid in conserving steam, a thermo-compressor system (see Figure VII-3) extracts usable heat from Evaporator and Fractionator steam condensates, and the temperature gradient between effluent condensate (at about 212°F.) from the thermo-compressor system and incoming dilute feed (at about

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70°F.) is utilized in the Feed Preheater, E-B-6, to increase feed temperature to about 150°F.

During peak capacity operation, steam pressure in the steam chest of the Evaporator is about 60 lb./sq. in. ga.(307°F.). Fractionator reboiler steam is at about 100 lb./sq. in. ga. (338°F.). Steam condensate from both sources passes through steam traps connected to Flash Tank B-2, which is maintained at about 30 lb./sq. in. ga. A portion of the condensate flashes to steam as it passes its trap; the remainder collects in B-2 and is discharged through a steam trap to Flash Tank B-2-A, which is maintained at about 5 lb./sq. in. ga. Again, part of the 30-lb./sq. in. ga. condensate flashes to steam at 5 lb./sq. in. ga. as it passes the trap; the remainder collects in B-2-A and is discharged through a steam trap to Flash Tank B-3, which operates at atmospheric pressure. Condensate from B-3 is discharged through a steam trap to the Feed Preheater for extraction of part of its sensible heat by incoming cold feed before eventually finding its way to the Retention Basin.

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Steam in Flash Tank B-2-A (at about 5 lb./sq. in. ga.) is compressed to about 30 lb./sq. in. ga. by a thermo-compressor jet fed by 225-lb./sq. in. ga. steam. The jet discharges into the vapor space of Flash Tank B-2. Steam in Flash Tank B-2 (at about 30 lb./sq. in.ga.) is compressed to about 60 lb./sq. in. ga. by a second thermo-compressor jet. This jet discharges into the steam chest of Evaporator E-B-1. A pressure indicator-controller on the discharge line from each thermo-compressor jet regulates high pressure steam flow to the jet in order to maintain a constant-pressure discharge. Flash Tank B-3 is vented to the atmosphere.

The overall steam saving attainable by use of the thermo-compressor and feed preheating systems is estimated to be 10 to 15% of the total steam that would be required for Evaporators E-B-1, E-D-1, and E-D-2 if these heat-saving systems were not used.

2. Remedy of Off-Standard Conditions

2.1 Fouling of Evaporator tubes

Partial loss of evaporation capacity, as evidenced by a more-dilute-than-normal product or increased steam pressure required to maintain a given product composition, may be an indication of reduced overall heat transfer coefficients due to scale formation in the tubes. If this condition proceeds to the point where it cannot be compensated for by increasing the steam pressure, the offending Evaporator may be shut down slowly, drained, flushed, and scale-dissolving nitric acid solution (nominally 60%) may be sprayed into the top of the unit and recirculated by boiling. After heat transfer rates have been reestablished, feed is readmitted to the Evaporator without removing the acid solution.

Depending upon the processing rate at the time, part or all of the load may be thrust upon the other Evaporators during the shutdown. Whenever possible, the inventory in Feed Tanks X-1 and X-2 should be reduced

prior to shutdown, to provide additional dilute feed surge capacity during the period when one Evaporator is off the line.

2.2 Failure of feed supply to Evaporators

This condition may be detected by an alarm light from the pressure switch, which valves in condensate to replace the interrupted feed supply, or by a drop in temperature in the Evaporator overheads (reflecting the entrance of condensate into the unit).

As indicated above, when feed supply fails, a pressure switch in the feed line automatically opens a valve which admits condensate from Roof Tank X-14 to the Evaporator. The Evaporator boils off the condensate fed to it without excessively diluting the concentrated product until such time as restoration of the feed supply can be made or the unit can be slowly shut down. Supply of condensate to Roof Tank X-14 is maintained by connection of this vessel to the pressurized condensate header system.

2.3 Too high differential pressure across Fractionator

This condition may be detected (a) by differential pressure instrumentation across the Fractionator, (b) to some degree by the pressure indicator on the vapor feed line to the Fractionator, or (c) by the blowing of the Seal Pot, B-4 (or D-4). The phenomenon is usually indicative of too high a vapor velocity in the Fractionator (most likely to occur when starting up). This off-standard condition may be remedied, at least temporarily, by reducing feed flow to the Evaporator or steam flow to the Fractionator reboiler in order to reduce vapor velocity.

2.4 Dropping of effective liquid level in Evaporator

The Evaporator is designed to operate with an effective liquid level which would half-fill the tubes if concentration were not being accomplished. If the effective liquid level falls markedly due to a faulty discharge valve, which passes solution at too rapid a rate, or due to partially plugged instrument dip tubes, which have the effect of opening the control valve further, the reduced head at the base of the tubes may not be great enough to induce a natural circulation through the unit, and the desired product concentration may not be attained. The off-standard condition may be detected by (a) weight-factor instrumentation in Receiver Tank C-1, (b) the flow recorder on the condensed Fractionator overheads line which indicates a less-than-normal quantity of condensate, or (c) the weight-factor indicator for the Evaporator (if a faulty discharge valve is causing the unusual condition). The off-standard condition may also be pointed out by a material balance around the Evaporator-Fractionator unit. Such a material balance may be derived from weight-factor readings in the Evaporator Product Receiver, and from the readings of flow recorders indicating (a) the dilute feed to the Evaporator, (b) condensed overheads from the Fractionator, (c) acid bottoms from the Fractionator, (d) liquid acid feed to the Fractionator, and (e) reflux to the Fractionator. As a first step in attempting to remedy the situation, the Evaporator liquid effluent control

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valve should be opened and closed rapidly several times (in case valve stickiness or sluggishness is causing the difficulty) and the weight-factor instrument air supply should be checked and the air pressure increased rapidly several times within the limitations of the instrument (in case blowing out of any small obstructions in the dip tubes may eliminate the difficulty). If both of these potential remedies fail, the Evaporator may be shut down slowly in order to replace the control valve or unplug the dip tubes.

2.5 Overconcentration of UNH

If the UNH feed rate to an Evaporator is reduced considerably from a normal flow without a compensating reduction of steam chest pressure, overconcentration (uranium concentration greater than 100% UNH) may take place and, if not corrected for, might ultimately result in "freezing" of the Evaporator contents. Overconcentration may be detected by an increasing vapor temperature as indicated by the temperature recorder in the Evaporator or by a reduction in the feed flow rate as indicated by the feed flow recorder-controller. The condition may be corrected, if it has not proceeded too far, by reducing steam pressure or increasing feed flow. If overconcentration has proceeded to the point where scaling of the tubes or freezing of the solution has taken place, the unit must be cleaned out as described under B2.1, above. A preventive measure for the condition would be to inter-connect the vapor temperature recorder and the steam pressure indicator-controller.

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2.6 Reduction of condensate header pressure

The cut-in of the duplicate, parallel pump which pressurizes the condensate header indicates not only that the above condition has occurred, but also that it has been corrected. The spare pump is activated by a pressure switch set to start the pump when header pressure drops below some predetermined value. The off-standard condition may be caused by check valve failure as well as pump failure.

2.7 Increase in acidity of condensate

This occurrence may be detected by means of the pH indicator in the Sample Cooler (E-C7) line. Normally a portion of the combined condensates from both Fractionators is routed through the Sample Cooler. However, by appropriate valving, the condensates may be routed through the Cooler separately in order to determine which is the offending Fractionator. Increase in the supply of reflux condensate to that Fractionator may remedy the off-standard condition. The degree of correction of the condition by increasing reflux has as its limitation the attainment in the Fractionator of a vapor velocity that may be high enough to blow the Seal Pot (due to boil-off of the additional reflux liquor). If condensates with a pH equal to 2 or higher cannot be produced, it may still be feasible to crib the liquid. An alternative procedure would be the neutralization of condensates before cribbing.

2.8 Chloride accumulation in HNO_3 Fractionator

As discussed in Subsection A3, above, there is a possibility of an accumulation of chloride ion on one or more of the bubble-cap trays. This condition, should it occur, will be detected by routine sampling of the various plates below the vapor inlet point to the Fractionator. If chloride accumulation is detected, the contents of the plate or plates involved will be purged (either completely and periodically or by small continuous withdrawal of liquid) from the system through the sample ports. The frequency and extent of such purging will be determined on the basis of experience.

2.9 Excessive corrosion in Evaporator E-D-2

Evaporator E-D-2 is designed to concentrate uranyl nitrate solution from about 55 to 65% UNH up to about 100% UNH. As mentioned in Subsection B1.3, above, it is expected that practically all Evaporator corrosion will occur in E-D-2. If E-D-2 fails due to excessive corrosion, it is planned to replace the unit. During the period when replacement is being made, either or both Product Evaporators, E-B-1 or E-D-1, can be adjusted to produce temporarily a 100% UNH product in order to maintain production capacity.

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Figure VII-1
SCHEMATIC DRAWING
UNH PRODUCT EVAPORATOR, E-B-1 AND E-D-1

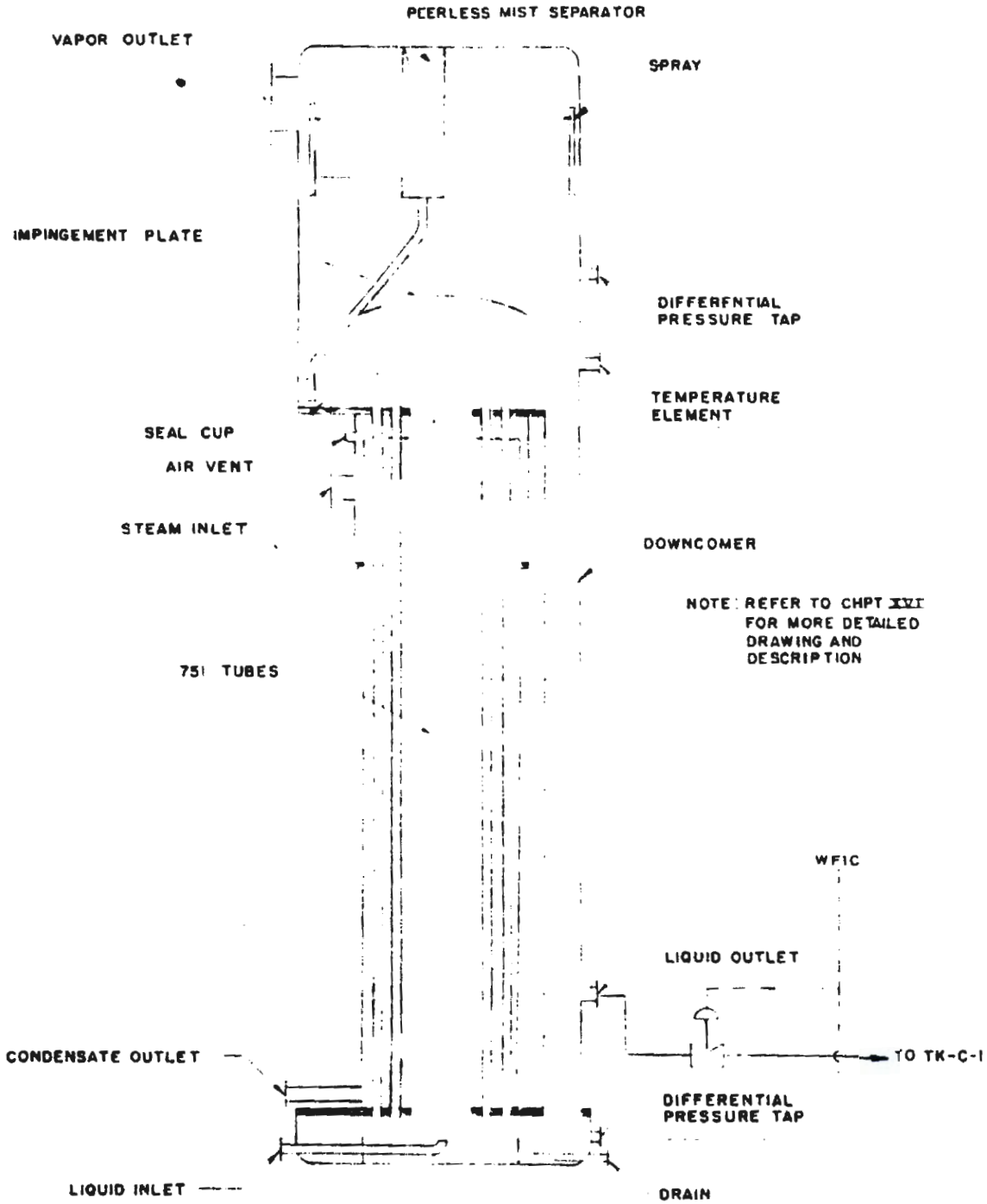

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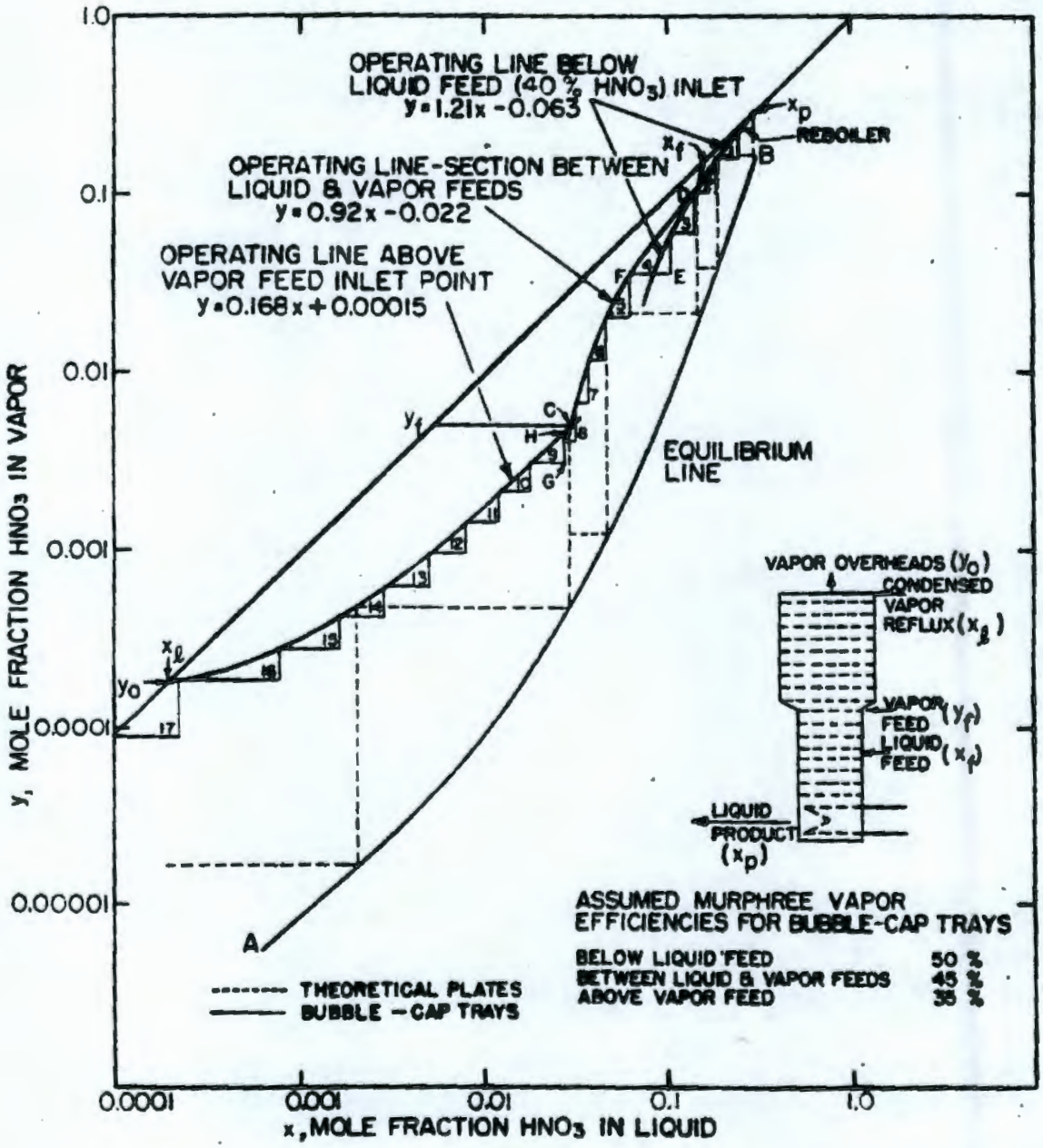
Figure VII - 2
OPERATING DIAGRAM-HNO_3 FRACTIONATOR
McCABE-THIELE TYPE



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PART II: PROCESS, continued

CHAPTER VIII. CALCINATION

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CHAPTER VIII. CALCINATION

A. PRODUCT SPECIFICATIONS

1. General

Uranium trioxide produced at Hanford is shipped to the K-25 site at Oak Ridge, Tennessee, for further processing. Because of the singular nature of both the Hanford and K-25 operations (involving aspects affecting UO_3 specifications that may be determined only upon full-scale operation), it is impossible at the time of writing to list more than tentative UO_3 product specifications. Operational or equipment modifications made at a future date by either site may modify the following tentative specifications.

Although at the time of writing it is contemplated that all UO_3 produced at Hanford will be converted to UF_6 at K-25, it is also possible to convert UO_3 into uranium metal.

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2. Chemical and Radioactivity Specifications of UO_3 (21)(23)(24)

Tentative chemical specifications for UO_3 are presented in the following table. For purposes of comparison, the corresponding expected composition or property of UO_3 produced at Hanford is also included in the table.

Constituent or Property	Tentative Specification	Expected UO_3 Composition (a)
Beta activity from fission products	Not more than 30% of the beta activity of natural uranium.	25% (b) (8.3×10^{-8} curies/g.)
Gamma activity from fission products	Not more than 300% of the gamma activity of natural uranium.	250% (b) (4×10^{-8} curies/g.)
Plutonium	100 p.p.b.	<80 p.p.b.
UO_3 (purity)	97% min.	97% min.
Na^+	Not more than 1000 p.p.m.	200 p.p.m.
$PO_4^{\equiv}$	Not more than 2000 p.p.m.	150 p.p.m.
Iron	Not more than 1000 p.p.m.	1000 p.p.m.
Ni, S, Mo, Cr, W, Si, B	Not more than 100 p.p.m. each	100 p.p.m each
H_2O	Not more than 0.1%	0.1% (c)
HNO_3	Not more than 0.6%	--
U_3O_8	--	0.1 to 0.3% (d)

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(a) The expected UO_3 composition is based upon the assumption that 3-1/8 tons (23.7%) out of a total instantaneous processing rate of 13-1/8 tons of uranium per day is from current metal production (Redox process). As the proportion of uranium in UO_3 from current metal production increases toward 100%, the beta activity, gamma activity, plutonium content, sodium content, and phosphate content change toward 10%, 100%, 10 p.p.b., 500 p.p.m., and zero, respectively. As the proportion of uranium in UO_3 from aged metal wastes (TBP process) increases toward 100%, these figures become 30%, 300%, < 100 p.p.b., 100 p.p.m., and 200 p.p.m., respectively.

(b) The contribution of U-237 (6.7-day half-life) to the total radioactivity of the uranium product is discussed under A2.1, below.

(c) Mallinckrodt process results.

(d) Mallinckrodt process results. (HCl-insoluble matter is taken to be U_3O_8.) If the UNH decomposition time cycle is shortened by increasing operating temperatures, the proportion of U_3O_8 may rise to 1 to 5%.

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2.1 U-237 radioactivity in the product

In addition to fission products, the uranium product of the Redox Plant may contain significant amounts of another radioactive constituent formed in the pile -- 6.7-day half-life uranium isotope U-237. U-237 is formed in the piles predominantly by the nuclear reaction:

$$\text{U-238} + \text{neutron} \longrightarrow \text{U-237} + 2\ \text{neutrons}$$

Since U-237 is chemically identical with the rest of the uranium, it is not removed in the Redox process or in calcination. Its concentration in the uranium product is thus entirely a function of the irradiation history and "age" (since pile discharge of the material processed). After uranium has been irradiated for approximately 70 days (about 10 U-237 half-lives), the radioactivity due to U-237 reaches essentially a saturation value, i.e., continued irradiation does not appreciably increase U-237 activity. The saturation activity of U-237 at any point in the pile is a function of the neutron flux at that point, and neutron flux is, in turn, proportional to the pile power level. Thus a particular neutron flux may be attained through the centrally-located tubes in a pile operating at a specified total power level or through "fringe" tubes in a pile operating at a somewhat higher total power level.

The U-237 radioactivity of Redox process uranium under some selected conditions is as follows:

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[redacted]

[redacted]

Power Level, Megawatts/Ton Uranium	"Age" (Since Pile Discharge), Days	Beta Radioactivity Due to U-237, % of Natural Uranium Beta, ± About 30%[a]
1	0	200,000[b]
	74	100
	96	10
2	0	400,000[b]
	81	100
	103	10
3	0	600,000[b]
	84	100
	106	10
4	0	800,000[b]
	88	100
	110	10

(a) Activities measured with G-M tube allowing 10 mg./sq.cm. for window, air, and Scotch tape. (b) Saturation activity, calculated.

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The distinction between the beta radioactivity due to U-237 and that due to fission products in Redox process uranium product less than about 100 to 115 days "old" constitutes an analytical problem. Presumably, if the activity is due to U-237, the UNH can be converted into UO_3, packaged, and shipped since the U-237 activity will have decayed to negligible values by the time the UO_3 is reanalyzed at K-25. On the other hand, confirmation of excessive beta activity as due to fission products would be cause for rework of the uranium. At the time of this writing analytical methods are being developed for determining the radioactivity due to fission products alone. One method being considered involves "counting" of product solution from which all isotopes of uranium have first been removed by chromatographic techniques.

3. Physical Specifications of UO_3[21][23][24]

The following table lists tentative physical property specifications for UO_3 and, for purposes of comparison, the corresponding expected value for Hanford produced UO_3.

Property	Tentative Specification	Expected Value For Hanford UO_3
Particle size	80% through 80 mesh	More than 80% through 80 mesh[a]
Bulk density	3.2 g./ml. (200 lb./cu.ft.) min.	3.5 to 4 g./ml. (220 to 250 lb./cu.ft.)[b]
Surface area	1.6 sq. m./gm. (nitrogen adsorption) min.	---

(a) Because of security restrictions, the UO_3 Mikro-Pulverizer was ordered on the basis of grinding a heavy, dry, alumina clay-like material to 100% through 80 mesh. There is no assurance that the mill will produce an identical size reduction with UO_3. (Actually, the screen to be supplied with the Mikro-Pulverizer has 1/16-in. perforations.) The approximate size analysis of UO_3 milled by the Mallinckrodt Chemical Company on a No. 158 Mikro-Pulverizer fitted with a 3/64-in. Herringbone screen (4200 rev./min.) is:

Mesh No.	Per Cent Retained	
20	0.05	
30	0.5	
40	1.7	15.75% retained
50	3.5	on 80 mesh
70	6.1	
80	3.9	
100	6.6	
140	10.2	
200	9.2	
325	15.1	
through 325	42.8	

(b) Mallinckrodt process results.

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B. PROCESS CHEMISTRY

1. Process Description

Concentrated uranyl nitrate hexahydrate (UNH) solution is converted to uranium trioxide (UO_3) by thermal decomposition of the UNH solution in batch-charged, externally heated Calcination Pots. As discussed in Chapter VII, feed solution concentration will correspond in composition to 80 to 100% UNH. The chemical reaction occurring during the conversion of UNH to UO_3 (under the operating conditions contemplated) may be summarized as:

$$UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 + 1.86NO_2 + 0.14NO + 0.57O_2 + 6H_2O$$

The exact proportions of the gases evolved during the decomposition step are dependent upon the operating conditions employed, the operating temperature being the most important determining factor. The degree of agitation is also an important variable. The interaction of the various nitrogen oxides from the UNH decomposition reaction with water and oxygen or air is treated in Chapter IX.

The design temperature of the decomposition reaction is 400 to 450°F. The reaction rate increases with increasing pot temperature. However, the important influences of other variables (notably, type and degree of agitation and feed composition and temperature) have prevented any adequate correlation of reaction rate with pot temperature.

The total heat requirement for the UNH conversion is dependent upon the feed solution composition. The theoretical amount of heat required to form UO_3 from an 80% UNH feed solution is about 1700 B.t.u./lb. uranium, while for a 100% UNH feed it amounts to about 1100 B.t.u./lb. (decomposition reaction carried out at about 450°F.). The heat requirement for calcination is needed both to supply sensible heat to bring the reactants to the desired temperature and maintain them there, and to provide for the heat absorbed in the calcination reaction.

Data on the specific heat of uranyl nitrate solutions at 25°C. as a function of weight per cent uranyl nitrate are found in the literature.(12) Based upon the data available, the specific heat of a 100% UNH solution at its freezing point, 60°C. (140°F.), is estimated to be 0.31 B.t.u./(lb.)(°F.). (See Chapter IV.) The average specific heat of a 100% UNH solution between 230°F. (pot charge temperature) and 260°F. (the approximate boiling temperature of the solution) is estimated to be about 0.32 B.t.u./(lb.)(°F.). From 260°F to 400°F. the solution loses water and the specific heat drops rapidly, approaching that of UO_3 (0.08 B.t.u./(lb.)(°F.)) at about 400°F. It is noted that, from an operational standpoint, use of as highly concentrated a feed solution as possible may offer a process advantage through the reduction of the quantity of heat to be transferred through the walls of the reaction vessel. However, due to the complex nature of the solution and its corrosion properties, a complete economic balance cannot be arrived at without additional experimental information.

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At temperatures on the order of 850°F. or higher, some U_3O_8 (a greater amount than 0.1%) may be formed either by reduction of UO_3 or directly from UNH. Thus, temperature control of the conversion reaction is essential if the U_3O_8 content of the UO_3 product is not to exceed a specified value. The reactions producing U_3O_8 at elevated temperatures may be summarized as:

$$3UO_2(NO_3)_2 \xrightarrow{>850°F.} U_3O_8 + 6NO_2 + 2O_2$$

$$6UO_3 \xrightarrow{>850°F.} 2U_3O_8 + O_2$$

These reactions are essentially complete at 1000 to 1500°F.(5)(20) At a UNH decomposition temperature of 400 to 450°F. (as measured in the center of the reacting mass), the production of U_3O_8 is hindered so effectively that only on the order of 0.02% of the product consists of U_3O_8.

Several of the properties of UO_3 depend to some extent upon the rate of UNH reduction to UO_3. Uranium trioxide produced in a rapid UNH calcination (such as UNH spray drying) is considerably less dense (bulk density of 50 to 150 lb./cu.ft.) than UO_3 formed by the slower, Mallinckrodt calcination (bulk density of 200 to 250 lb./cu.ft.). It appears also that a slower UNH decomposition favors larger crystal agglomeration of the UO_3.(7

When the calcination reaction is carried out on a batch scale, the physical state of the mixture in the reaction vessel passes through several stages. The liquid uranyl nitrate solution first charged remains clear until the evolution of brown nitrogen oxides can be detected. There is a

rather definite appearance change of the solution at this point, a change from a clear to a turbid solution. As decomposition proceeds, as evidenced by continued evolution of nitrogen oxides, the solution first becomes increasingly viscous and finally a plastic, doughlike state is reached just before the transition to the solid, powdery state. The evolution of nitrogen oxides practically ceases with the formation of the solid phase.(5)(7)

It has been demonstrated that the extremely viscous, plastic state may be by-passed by continuous or semicontinuous decomposition methods. Spray decomposition techniques, wherein a concentrated UNH solution is atomized in a heated chamber with a resulting flash decomposition to UO_3, have entirely eliminated intermediate physical states between UNH and UO_3.(10)(11) A semicontinuous process, wherein concentrated UNH solution is added into a heated reaction vessel containing a preponderance of UO_3 powder, has by-passed at least the extremely plastic state.(15)(21)

The spray decomposition techniques, by virtue of the relatively high chamber temperature required to flash-decompose the UNH solution, inherently convert more of the uranium to the U_3O_8 state than does a batch process.(11) Since the operations of producing UF_6 or uranium metal from UO_3 both manufacture UO_2 as an intermediate step, it appears that the presence of U_3O_8 ($2UO_3 \cdot UO_2$) would not be objectionable for these operations.

Usually a UO_3 product drying period is required in order to meet specifications on residual moisture and nitrate in the powder. Such a drying involves heating at an elevated temperature, with sufficient agitation, until the moisture or nitrate content is reduced to the specified values.

2. Properties of UO_3

2.1 Chemical properties

Uranium trioxide (UO_3) is a powdery solid ranging in color from bright yellow through orange-yellow, orange-brown, and even red. The product of the Hanford UO_3 Plant is orange-yellow. Unlike elements of low atomic weight, which form a limited number of oxides, uranium can form a series of oxides in which the oxygen content varies in a continuous fashion.(18) Several allotropic varieties of UO_3 exist. An amorphous form seems usually to have an orange-red color. In addition to the amorphous form, a number of crystal modifications exist. At least one of these crystalline modifications has been identified as having a hexagonal crystal structure. Differences in allotropic form probably account for the appearance differences noted above.

Decomposition of uranyl nitrate to UO_3 gives a product that has been observed to be microcrystalline, whereas UO_3 prepared by thermal decomposition of the hydrated uranyl peroxide in air is predominantly the amorphous variety.(19) The heat of formation of either the amorphous or crystalline varieties is 1840 B.t.u./lb.(17)

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Uranium trioxide shows amphoteric characteristics and will react with mineral acids to produce uranyl salts and with metallic oxides to form uranates.(12)

The UO_3 powder is very hygroscopic and tends to crust over upon exposure to air. It hydrates rapidly to $UO_3 \cdot H_2O$, the rate increasing with temperature.(4)(20) Data are only qualitative but UO_3 exposed to air at room temperature gains weight at the rate of about 0.1% per hour according to data taken at the Mallinckrodt Chemical Company plant in St. Louis (relative humidity of air not given).(20)

At a temperature of between 850 to 1300°F. noticeable thermal decomposition toward the compound U_3O_8 begins in air at atmospheric pressure. The reaction is, for practical purposes, irreversible, but it is possible to convert U_3O_8 to UO_3 by heating in about 30 atmospheres of oxygen.(18)(19) Both the thermal stability and ease of reduction of UO_3 depend upon the crystal structure of the material.(18)

Gaseous UO_3 may exist under certain conditions. However, the volatility of the solid is very small, and, in general, high temperature (above 1150°C.) and reduced oxygen partial pressure (about 4×10^{-4} atmospheres) is required for gaseous UO_3 formation.(17)

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2.2 Physical properties

Uranium trioxide is a powdery solid with an absolute density of about 450 lb./cu.ft. (7.2 g./ml.). The bulk density of the powder depends upon a number of factors, the most important of which is particle size. The bulk density may range from about 50 lb./cu.ft. for the very fine and fluffy product of uranyl nitrate spray decomposition techniques, up to about 250 lb./cu.ft. for powder produced by batch decomposition of uranyl nitrate in externally heated reaction pots (Mallinckrodt process).(7)(11)

The particle size of UO_3 grains depends upon preparation methods. Spray decomposition methods have produced grains which have a diameter o the order of 0.02 to 2 microns.(11) The Mallinckrodt process produces particles of UO_3 generally 1 micron and larger in diameter. The Hanford product is generally similar in particle size to Mallinckrodt UO_3. (See Subsection A3, above.) The Mallinckrodt product has a surface area of approximately 4400 sq.ft./lb., while the spray decomposition product has a surface area about 5 to 10 times this figure.(10)

The hardness of UO_3 is about 3.0 on Mohs' scale (comparable in hardness to calcite).(8)

The specific heat of UO_3 powder is approximately 0.072 B.t.u./(lb.) (°F.) over the temperature range 70 to 210°F. It increases slowly to about 0.083 B.t.u./(lb.) (°F.) at 1100°F.(12)

No noticeable electrical conductivity is shown by UO_3 up to about 570°F. Above this temperature the conductivity increases slowly; it is

presumed to be due to slight reduction of UO_3 toward U_3O_8. The specific conductivity of UO_3 at 750°F. is less than 5×10^{-8} mho cm.(4) The conductivity of UO_3 often detected at ordinary temperatures (which disappears at 200 to 300°F.) is attributed to absorption of water from the air.(4)

Finely powdered UO_3 caught up by a vigorous air blast carries a positive electrical charge.(4)

3. Properties of U_3O_8

3.1 Chemical properties

Triuranium octoxide (U_3O_8) is a solid ranging in color from olive green to dark green to black. It is found in nature as the mineral pitchblende and in other uranium minerals. The color of the compound seems to be influenced by the bulk density, temperature of preparation, and small deviations in the oxygen content.(4)

Among other methods, U_3O_8 may be prepared by thermal reduction of UO_3.

The crystal structure of U_3O_8 is orthorhombic.(19)

The decomposition temperature of U_3O_8 is about 3100°F. under one atmosphere of oxygen. It decomposes to $UO_{2.25}$ solid and 10^{-3} atmospheres of UO_3 gas.(7) The heat of formation of U_3O_8 is 1810 B.t.u./lb. at 65°F.(12)

The compound is not hygroscopic. The observations that the green oxide prepared at low temperature slowly hydrates in air without changing outwardly, whereas the black modification prepared at high temperature does not, is probably due to the presence of UO_3 in the green oxide.(4) The lower the temperature of preparation, the higher the proportion of UO_3 present in the mixture.

3.2 Physical properties

The absolute density of U_3O_8 is about 480 lb./cu.ft. (7.7 g./ml.). The bulk density of U_3O_8 powder depends upon particle size and methods of preparation, but it is in the range of 150 lb./cu.ft.(12)

The hardness of U_3O_8 is about 3.5 on Mohs' scale (between calcite and fluorite -- about the same as aluminum).(8)

The specific heat of U_3O_8 is approximately 0.075 B.t.u./(lb.) (°F.) over the temperature range 70 to 210°F.(6)

The compound is an electrical non-conductor at ordinary temperatures. However, the specific conductivity slowly increases with temperature and

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is considerably greater than the specific conductivity of UO_3 powder at higher temperatures. For example, at 400°C. the specific conductivity of U_3O_8 is 7×10^{-4} mho cm., while for UO_3 it is less than 5×10^{-8}. At 100°C. the specific conductivity of U_3O_8 is 9.0×10^{-7} mho cm. (Data are lacking for the conductivity of UO_3 at this temperature.)

The thermal conductivity of U_3O_8 ranges from 0.14 to 0.31 B.t.u./(hr.)(sq. ft.)(°F./ft.) depending upon the physical state of the solid.(12)

C. PROCESS ENGINEERING

1. General

A UO_3 product may be obtained from several types of uranyl nitrate decomposition processes (batch, semicontinuous, or continuous) and with the employment of a wide variety of types of calcination or drying equipment. Batch decomposition of uranyl nitrate in calcining pots has been chosen as the method of UO_3 production because of the successful, long-term experience of the Mallinckrodt Chemical Company with similar types of equipment and methods of operation. Although other processes have been developed on a laboratory scale (and in some instances on a semiworks scale), their full-scale practicability has not yet been demonstrated.

The tentative chemical and physical form of the UO_3 product has been specified in Section A. In general, chemical and physical properties may be altered by the manipulation of several process variables, among them being decomposition temperature and time, speed of agitation, concentration of feed, and the length and type of a drying period.

2. Batch Calcination Pot Process

2.1 Design basis

The uranyl nitrate calcination process is designed to produce a UO_3 product at a maximum instantaneous rate of 13-1/8 tons of uranium per day. (This figure reflects the combined maximum instantaneous design capacities of the Redox and THP Plants.) The average production rate over a long period is expected to be about 10-1/2 tons of uranium per day.

Eighteen Calcination Pots are provided for the uranyl nitrate thermal decomposition reaction. The nominal batch size per pot is 58 gal., representing 462 lb. of UO_3 per pot at a feed solution concentration corresponding to 80% UNH; or 50 gal., representing 600 lb. of UO_3 per pot at a feed solution concentration corresponding to 100% UNH.

The approximate pot cycle (for design purposes) is:(16)

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Charging pot	15 minutes
Preheating to 390 to 400°F.	143 minutes
Decomposition of the charge	180 minutes
Cooling and unloading	105 minutes
Total	7 hours 23 minutes

This cycle has been demonstrated by Mallinckrodt operations and represents a conservative operational cycle. The design cycle is approximately the same for either 80% or 100% UNH feed, since the 80% UNH batch size is slightly larger than the 100% UNH batch size although containing less uranium. It is anticipated that the decomposition and cooling and unloading operations can be shortened considerably.

It may be economically advantageous to reduce the concentration of feed to less than 100% UNH (perhaps 90 or 95% UNH); the lower salt concentration would reduce corrosion and, thereby, prolong Feed Concentrator life. The probability of reducing the time cycle and the ability of the Calcination Pots to process a less concentrated uranium feed solution favor this plan.

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2.2 General description of pot and furnace

Reference is made to Chapter XVI for a detailed description of calcination equipment. Each of the eighteen Calcination Pots is a covered, 1-inch thick cylindrical stainless steel vessel with a hemispherical bottom. The pots are 30 in. in diameter by 32 in. deep. An individual electric furnace surrounds each pot and furnishes the heat necessary to accomplish the calcination reaction. Each furnace (55 kw. at 220 volts, 2-phase, 60-cycle) is designed to produce a maximum chamber temperature of 1600°F. measured 1/4 in. from the exterior surface of the pot.(3) Based upon experience in a similar installation at the Mallinckrodt Chemical Works, a design heat-transfer coefficient of 12 through the walls of the pot during the uranyl nitrate decomposition portion of the cycle has been assumed.

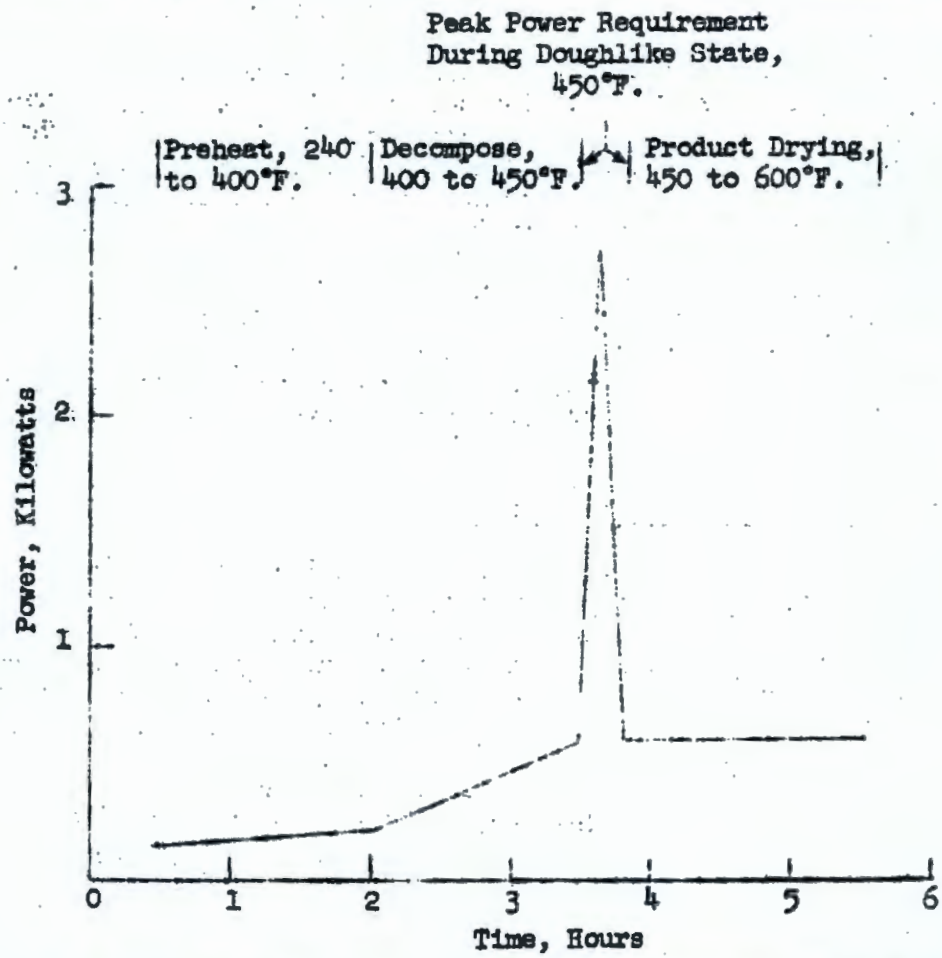
2.3 Agitation

Agitation during uranyl nitrate decomposition is required in order to maintain efficient heat transfer to the reacting mass, to aid in the formation of a uniform-sized product, and to minimize high local heat concentrations at the wall of the pot.

A sweep-type agitator (illustrated in Chapter XVI) maintains a clearance between the blade and the walls and hemispherical bottom of the pot of about 1/8 inch. The blades of the agitator are positioned so that the reacting mass is displaced from the edges toward the center of the pot. With a relatively small pot-to-agitator clearance, the magnitude of the UO_3 scaling or caking problem on the walls of the pot is reduced (although not eliminated).

Load requirements of the agitator vary considerably during the Calcination Pot cycle (reflecting physical state changes in the reacting mass --

see Subsection B1). The agitator for each Calcination Pot in the UO_3 Plant is powered by a 7-1/2 hp. (5.6 kw.) electric motor. The agitator power requirement for a Mallinckrodt-type batch decomposition (charge equivalent to 600 lb. UO_3) is represented schematically by the following figure:



The speed of agitation has an important effect on the properties of the UO_3 product. The design speed of agitator rotation is 40 rev./min. Laboratory experiments in which a semicontinuous process was employed indicate a correlation of fineness and uniformity of product with agitation speed. At speeds of 100 to 150 rev./min., generally a finer and more uniform product was obtained (other variables remaining constant) than at 40 rev./min.(21) (The plant agitators will have a tip speed of about 5.3 ft./sec. which is about 2-fold greater than the laboratory agitator tip speed when the laboratory agitator operates at 150 rev./min.) Although quantitative data are lacking, it is clear that with higher agitation speeds a more uniform temperature exists throughout the reaction mass.

2.4 Product removal(1)

The UO_3 product of the calcination reaction consists, preponderantly, of very fine powder (about 80% or more through 80 mesh). However, caked

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or encrusted UO_3 may adhere to the sides of the pot or to the agitator, and some lumps may exist in the powdery mass.

The product is removed by a vacuum suction system which draws the powder through a flexible stainless steel hose attached to a pipe which is inserted into the pot. The vacuum unloading system discharges through a pneumatic unloading Cyclone Separator and Bag Filter into a Mikro-Pulverizer. (Refer to Chapter XVII.)

The Mallinckrodt Company has removed encrusted UO_3 in their pots by mechanical means such as chipping out the crust. In the Hanford operations, such methods will always be available, but, in addition, facilities are provided for adding nitric acid to the pots to dissolve residual encrustation and to dispose of the solution.(16) It is expected that acid dissolution of UO_3 encrustation will be required non-routinely.

The vacuum unloading system is designed on the basis of handling 3200 lb. of UO_3 per hour (total figure for all pots). To accomplish this end, about 500 standard cu.ft./min. of air are pulled through the vacuum unloading header.

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2.5 Calcination Pot vent system

Air from in-leakage, nitrogen oxides, and water vapor are evolved at a fairly uniform rate (about 250 standard cu.ft./min. total from all pots at 13-1/8 tons/day) during the decomposition period. Since pot operating schedules overlap, the overall vapor evolution rate remains essentially constant.

The Calcination Pots are each designed with a valved vent line which is opened during the decomposition cycle so that vapors may be routed to the gas absorption system. (See Chapter IX.) The vent is valved closed during pot charging or unloading operations (when the pot lid is removed) in order to avoid air loading of the gas absorption system. The pots are designed to operate at a vacuum of 10 inches of water as maintained by a pressure-controlled bleed-in valve which admits air to the vent line to maintain the 10-inch vacuum. The vent system is designed to maintain 10 inches of water negative pressure with air in-leakage to the pot of up to 40 standard cu.ft./min.

2.6 Methods for confining UO_3 dust(1)

One of the important design considerations for the UO_3 process is the elimination of the dust hazard in breathing air to as great a degree as practicable. A special system for maintaining clean air is provided for those UO_3-handling areas where air contamination would otherwise be likely. The system consists of providing a limiting air velocity that will prevent passage of UO_3 dust from the normal containing vessel or equipment piece into the air of the operating area.

The physical aspects of the ventilation supply and exhausting system are described in detail in Chapter XVII. The design bases for the system are:

(a) Removal of UO_3 to a degree such that operating-area air shall not contain more than 1.4×10^{-6} grams of uranium per cu.ft.;

(b) Removal from the air of all particles of UO_3 1 micron or larger in diameter.

The method of attaining the above aims is to sweep air at high velocity (400 linear ft./min.) across the location of the source of the potential contamination followed by passage of this contaminated air through Bag Filters before discharging it from a local stack.

During the decomposition reaction the pots are totally enclosed, and any slight air leakage which may occur (through the agitator shaft seal or under the pot lid) will be inward. (See under C2.5, above.) During the pot charging or unloading operations, on the other hand, the pot lid is off and the possibility of UO_3 dust entering the air of the operating area would exist except that at this time the special 400-ft./min. air sweep is drawn across the top of the pot.

In like manner, the Drum Filling Assembly Hood, E-19, is provided with an air sweep system which can be dampered into operation when the shipping drums are charged with UO_3 powder.

A standard commercial-type vacuum cleaner system has been provided for use in the case of powder spills. This system will be used as required for clean-up in the Pot Room and around product-handling facilities. (See Chapter XVII.)

It is expected that the quantity of UO_3 dust passing per day to the Bag Filters will range from 1 to 10 lb. The only justification for recovery of such a small amount of UO_3 is the elimination of the health hazard due to UO_3 in the breathing air. Since only 2 or 3 drums of recovered UO_3 are expected to be collected per year, storage for eventual recovery will present no problem.

2.7 Size adjustment of product(1)

The UO_3 product removed from the pots by the vacuum unloading system is preponderantly a very fine powder, but some particle agglomeration into small lumps makes necessary a size adjustment operation to meet the particle size requirement of about 80% or more through 80 mesh. Maximum lump size is about 1/16 inch when the Mikro-Pulverizer screen with 1/16-inch perforations is used. The expected particle size analysis, before the sizing operation, is approximately the following:

20 to 30% through 325 mesh sieve
80 to 90% through 80 mesh sieve
95 to 99% through 40 mesh sieve
100% less than 1/2 inch in diameter.

Although the entire sizing operation is obscured by the lack of reliable data, it would seem that the chief purpose of the operation is to reduce the size of the relatively few large particles (greater in size than about 40 mesh) so that a more uniformly sized product is obtained

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although the proportion of the total solids passing 80 mesh may not be changed appreciably.

A Mikro-Pulverizer is provided for the sizing operation. It is described in detail in Chapter XVII. The larger particles of UO_3 entering the Pulverizer are reduced in size by impact (and by attrition with each other) with a series of hammers attached to a shaft rotating at high speed (about 3500 rev./min.). Close clearance is maintained between the hammers and a screen through which the milled particles must pass to leave the Pulverizer. The entire product-milling system is totally enclosed to minimize the UO_3 dust hazard from this source.

2.8 Product-packaging system(1)

The physical aspects of the product-packaging system are described in detail in Chapter XVII. The method of packaging, briefly, is to receive UO_3 in tared 30-gal. drums from a batch-type weigh hopper. The drums are located on a scale having an accuracy of ±0.1 lb. and the final weight is recorded. Facilities are provided for sampling material as it enters the drum. A special hood is located above the packaging station and is designed to sweep potential contamination. The contaminated air passes through Bag Filters before discharging from a local stack.

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3. Other UO_3 Production Processes

3.1 Spray decomposition of UNH(10)(11)

Spray decomposition of UNH, a continuous means of UO_3 production, has been demonstrated on a small scale. The process consists of atomizing a concentrated uranyl nitrate solution into a heated decomposition chamber maintained at such a temperature that water and nitrogen oxides almost instantaneously flash from the radiantly heated UNH solution, leaving UO_3. The UO_3 drops to the bottom of the reaction vessel and is continuously removed by a screw conveyer.

3.2 Drum drying of UNH(9)

Conventional drum drying techniques for converting UNH to UO_3 have also been demonstrated on a small scale. The process consists of forming UO_3 on the outer surface of a steam-heated drum which dips into a concentrated uranyl nitrate solution as it rotates. A blade scrapes UO_3 from the surface before that section of the drum rotates into the UNH solution again. The speed of drum rotation is such that enough time is available for the complete decomposition of UNH to UO_3 before the product is scraped off.

3.3 Hanford semicontinuous process(21)

A semicontinuous UNH decomposition process, wherein uranyl nitrate is added continuously to a Calcination Pot containing UO_3 until the pot is completely charged, has been demonstrated on a laboratory scale at

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Hanford(21) and on a production scale by the Mallinckrodt Company.(15) By maintaining a preponderance of UO_3 in the reaction pot at all times, it has been demonstrated that the extremely viscous stage encountered in the straight batch Calcination Pot process can be by-passed.

As mentioned in C1 above, none of the above-mentioned continuous or semicontinuous processes have been chosen as the production process since none were in a sufficient state of development at the time final design effort was required.

D. PROCEDURE(13)(14)(16)

1. Normal Procedure

1.1 General

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In the following discussion of operating procedure, reference is made to Figure VIII-1, a schematic and functional presentation of the uranyl nitrate decomposition and UO_3 product-handling facilities. A Material Balance Flowsheet for the calcination procedure and other related operations is shown in Figure VIII-2. As indicated under C2.1, the nominal instantaneous production rate of the calcination facility is 13-1/8 short tons of uranium per day.

1.2 Concentrated feed storage

Concentrated UNH feed solution for the Calcination Pots is received in the UNH Melt Storage Tank, TK-X-19 (working volume about 4200 gal.), from Product Evaporator E-D-2. As discussed in Chapter VII, Evaporator E-D-2 is normally fed with about 60% UNH solution by pump from the UNH Receiver Tank, TK-C-1 (working volume about 3000 gal.). However, the process piping of TK-C-1 is such that it may also be used as a feed vessel for the Calcination Pots if so desired.

The Calcination Pots are supplied with feed from a loop header which receives feed, via pump, from TK-X-19 (or TK-C-1). The header discharges back into the vessel feeding it; it is sloped so that it drains into the feed vessel when feed flow is discontinued.

Since the UNH feed to the Calcination Pots has a high freezing point, both TK-X-19 (by means of a tank coil) and TK-C-1 (by means of a tank jacket) are equipped to maintain the solution at an elevated temperature. The loop header is steam traced or jacketed.

1.3 Uranyl nitrate decomposition

The loop header supplying the pots is pump-fed at about 20 gal./min. from TK-X-19. The pot schedules are overlapped so that a pot is charged from the feed loop header about every 25 minutes.

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The lid is opened (pot vent valve closed and special dust vent opened) so that the level of liquid charged to the pot may be observed. After approximately 50 gal. (liquid height about 10 in. below the pot edge) of solution are added, feed flow from the loop header is valved off, the pot lid replaced, the dust vent dampered off, and the pot vent valved into operation. The temperature of the incoming feed solution is about 230°F. It should be emphasized that the exact batch size specified is in doubt due to uncertainty as to the most desirable uranium feed concentration.

Two controlling thermocouples are used in the electric-furnace Calcination Pot cycle. The first is located at the outer wall of the pot (between pot and furnace) and measures pot "skin" temperature. The second is located within the hollow agitator shaft and more nearly measures the temperature of the reaction mass at the center of the pot. During operation, the pot skin thermocouple is set at 1400°F. and automatically maintains this temperature (by switching the furnace full on or full off) until the temperature measured by the agitator thermocouple reaches 400°F. At this point both thermocouples are automatically reset: the pot skin temperature thermocouple to 800°F., and the agitator shaft thermocouple to 600°F. An intermediate cooling period (as measured by the pot skin thermocouple) occurs after the reset, during which the temperature drops from 1400°F. to 800°F. Again, the 800°F. temperature is maintained at the pot wall until the agitator thermocouple measures 600°F. The furnace is automatically turned off by the agitator thermocouple at this point of the cycle.

From a physical point of view, the period during which the reacting mass is being heated from feed temperature to about 400°F. represents the preheating of the charge. The uranyl nitrate decomposition itself is substantially accomplished between 400 and 450°F. in a maximum of three hours (the pot wall temperature is maintained at about 800°F. during this period). After decomposition, the powder temperature slowly rises until the shaft thermocouple registers 600°F., the temperature which represents the end of the drying period and the end of the heating cycle. It may be possible to operate at higher temperature levels than those indicated above. If so, the overall time cycle may be shortened appreciably below the 7-1/2 hour period indicated under C2.1, above. Agitation at about 40 rev./min. is provided during the entire preheating, decomposition, and drying period for the charge.

After the heating cycle is complete and the furnace has been turned off, the pot walls are cooled by drawing room-temperature air through the annular space between the furnace heating element and the pot by appropriate dampering of the 8-in. ventilation duct. The special dust vent is opened, the pot lid removed, and the unloading pipe inserted into the powder mass. Opening of the slide valve between the unloading pipe and the negative pressure in the product removal header allows the powder to be drawn into the product handling system via the header. As much cake material as possible is knocked or chipped loose and removed via the header. The total time requirement for the cooling and unloading portion of the pot cycle is estimated to be about 60 to 105 minutes.

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If usual methods of removing powder prove inadequate, a small amount of nitric acid may be added to the pot via a flexible tubing line from an acid header in order that the accumulated UO_3 encrustation may be dissolved and removed as completely as desirable. However, it is expected that acid dissolution of the encrustation will not be required routinely. (See under C2.4, above.) The uranyl nitrate solution produced is jetted to Tank TK-X-20 through the same flexible tubing line which, after appropriate valving, serves as the suction leg for a steam jet.

1.4 Product handling and packaging

About 31,000 lb./day of UO_3 at a density of about 250 lb./cu.ft. are received from the vacuum unloading header in the Pneumatic Unloading Cyclone and Bag Filter, X-3. An electric-motor-driven shaking mechanism is provided for the Bag Filter and is actuated automatically for a short period each time Exhauster X-4 is stopped. A rotary valve discharges a maximum flow of 3000 lb./hr. of UO_3 powder from the Cyclone into a Mikro-Pulverizer, X-6. (The normal flow will be about 1300 lb./hour.)

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The Mikro-Pulverizer discharges powder directly into Storage Bin X-7. The Storage Bin has a 3-day capacity; its bottom is cone shaped with 60 degree sides (measured from the horizontal) to minimize the bridging action of powder. The bin discharges into Screw Conveyer X-8 which transports the powder to the Drum Filling Assembly, E-19. Powder is added to tared 30-gal. capacity drums, which rest on a scale while being filled (about 1000 lb. of UO_3 per drum). After being filled, drums are transferred to another scale which makes a permanent record of the weight of the drum. The upward sweep of ventilation air past the filling mechanism and into a hood minimizes the UO_3 dust hazard.

The product in the sealed 30-gal. drums is conveyed by Gravity Roller Conveyer E-20 to a loading dock. There the drums are arranged on pallets (4 to a pallet) and are conveyed to a storage warehouse by a fork-lift truck.

1.5 Uranium oxide dust-handling methods

The special exhausting system (for the Calcination Pots and drum-filling assembly), designed to prevent passage of large quantities of UO_3 dust into the breathing air, is actuated by Exhaust Fan X-13. The dust-containing air is passed into Continuous Ventilation Bag Filter X-11 at a rate of about 7000 standard cu.ft./min. The Bag Filter is of the two-compartment type to permit replacement of bags in one compartment while the adjacent compartment is operating. Filtered air is drawn through Glass Wool Filter X-12 before being discharged from a local stack.

Each compartment of the Bag Filter has its own dust collection hopper. The dust can be discharged through rotary valves to special containers, analyzed, and disposed of accordingly.

2. Remedy of Off-Standard Conditions

2.1 Excessively high concentrations of U_3O_8 in product

The maximum permissible concentration of U_3O_8 in UO_3 has not been established positively. Any such off-standard condition will be detected by routine sampling of each drum before shipment. Above-tolerance amounts of U_3O_8 indicate too high a reaction or product-drying temperature in the Calcination Pots. (Conversely, below-tolerance amounts indicate that reaction temperatures and, hence, reaction rates may be increased if desired.)

If the U_3O_8 content of the powder is too high, the Calcination Pot operational cycles must be adjusted to operate at lower temperatures. There is no convenient remedy for lowering the U_3O_8 content of batches already processed. High-U_3O_8-content material may be (a) dissolved in nitric acid and the resulting uranyl nitrate solution redecomposed at a lower temperature or (b) blended with material having a low U_3O_8 concentration to yield a mixture that meets specifications. Both of these methods are inconvenient to employ, especially if appreciable quantities of powder are involved.

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2.2 Excessively high nitrate or moisture content in product

These conditions will be detected by routine sampling of each drum before off-plant shipment. Too high a proportion of nitrate or moisture indicates an inadequate product-drying cycle after the decomposition reaction. Drying temperature may not be high enough or drying time may not be long enough.

The condition may be remedied by increasing the drying temperature or the length of the drying period. Batches already processed may be recycled to the Calcination Pots for another drying cycle, or they may be dissolved in nitric acid and routed back to Storage Tank X-19 for eventual reprocessing.

2.3 Failure of Mikro-Pulverizer screen

This condition may be detected by occasional determination of particle size during the routine analysis of the Mikro-Pulverizer product as it is loaded into drums. The condition may be corrected by replacement of the Mikro-Pulverizer screen. Batches already processed, if far out of specifications, may be recycled to the Mikro-Pulverizer after the screen has been replaced.

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PART II: PROCESS, continued

CHAPTER IX. ACID RECOVERY

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CHAPTER IX. ACID RECOVERY

A. PROCESS DESCRIPTION

1. General

The uranyl nitrate calcination process, previously described in Chapter VIII, is accompanied by the evolution of large quantities of nitrogen oxides. Calcination of Redox and TBP Plant uranium product streams at a rate equivalent to 13 tons of metal per day will evolve about 58,000 cubic feet per day (STP) of nitrogen oxides which are recoverable. Cooling of these oxides and absorption in water results in a recovery of 17 tons per day of 40 to 45% nitric acid. This weak acid is introduced into the nitric acid fractionators (Chapter VII) and concentrated to about 60 to 61% HNO_3 for eventual reuse in waste metal dissolution. This recovery of nitrogen oxides as nitric acid results in a raw material cost saving of approximately $150,000 per year (300 days) at current acid prices of about $48/ ton (60% HNO_3). This chapter covers the description and operating procedure of the acid-recovery process. Equipment details are described in Chapter XVII.

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2. Nitric Oxide Oxidation

Recovery of the nitric acid is accomplished in the Gas Cooler, E-A-2, and the Nitric Absorber, T-A-1, which are located in A Cell of 224-U Building. (See Figure IX-1.) The gases handled by the acid-recovery system are liberated during the thermal decomposition of uranyl nitrate to uranium trioxide, which proceeds according to the equation:

$$UO_2(NO_3)_2 \xrightarrow{275°-500°F} UO_3 + 1.86NO_2\uparrow + 0.14NO\uparrow + 0.57O_2\uparrow \quad \ldots\ldots(1)$$

As the gaseous products are cooled, nitric oxide (NO) begins to react with excess oxygen (from reaction plus pot leakage) to form the peroxide.

$$2NO + O_2 \longrightarrow 2NO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Reaction (2) is not sensibly reversible at temperatures under 150°C. The rate of reaction between nitric oxide and oxygen is unusual in its temperature dependence in that it has a negative temperature coefficient; i.e., the cooler the gases the faster they react.[1,2] This reaction rate is expressed mathematically by the equation.

$$-\frac{d\,(NO)}{dt} = k\,(NO)^2\,(O_2),$$

in which k is a constant at any fixed temperature. The equation states that the rate of conversion of nitric oxide to nitrogen peroxide is proportional to the square of the nitric oxide concentration and the first power of the oxygen concentration. As stated above, the rate increases with decrease of temperature. The value of the reaction rate constant, k, increases about 10 per cent for each 10°C. drop in temperature.[6]

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The following table lists several approximate values of k at typical temperatures: (8)

Temperature, °C.	k, $(Mm.Hg)^{-2}(Min.)^{-1}$
25	26
50	17
86	13

Nitrogen peroxide formed by the oxidation of nitric oxide exists as two molecular species, NO_2 and N_2O_4. These two species come to practically instantaneous equilibrium, as expressed:

$$2NO_2 \rightleftharpoons N_2O_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The equilibrium constant, K_4, is a function of the temperature.

$$K_4 = \frac{N_2O_4}{(NO_2)^2}$$

The following table lists several approximate values of K_4 at typical temperatures: (3)

Temperature, °C.	K_4, $(Atmospheres)^{-1}$
10	26.5
25	7.8
50	1.3
75	0.28

3. Nitrogen Peroxide Absorption

The reaction

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \ldots\ldots\ldots\ldots (4)$$

between nitrogen peroxide and water to form nitric acid assumes that the active species is NO_2 and the N_2O_4 is inert. N_2O_4 dissociates to restore equilibrium (Reaction (3)) as NO_2 disappears by reaction to form HNO_3. Reaction (4) is reversible and the equilibrium may be expressed as

$$K = \frac{(HNO_3)^2\ (NO)}{(NO_2)^3\ (H_2O)}.$$

This expression may be considered the product of the two partial constants (6)

$$K_1 = \frac{(NO)}{(NO_2)^3} \quad \text{and} \quad K_2 = \frac{(HNO_3)^2}{(H_2O)}.$$

For any one temperature and composition of the liquid phase, the partial

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pressures of nitric acid and water vapor are obviously constant, so that the equilibrium between nitrogen oxides and nitric acid solution may be expressed by the partial constant [3]

$$K_3 = \frac{(NO)}{(NO_2)^3} .$$

The values of K_3 are such that the lower the temperature the more the equilibrium is displaced toward HNO_3. The values of K_3 also decrease with extreme rapidity as the concentration of nitric acid in the liquid phase increases. The following table, listing a few K_3 values as a function of temperature and acid concentration, illustrates both of these points: [3]

Weight % HNO_3	Temperature, °C.	K_3, (Atmospheres)$^{-2}$
5	25	79,500,000
5	50	7,950,000
5	75	851,000
25	25	178,000
25	50	12,300
25	75	1,070
50	25	456
50	50	40
50	75	5.1

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At ordinary temperatures the partial pressure of nitric oxide in equilibrium with nitric acid much above 40 to 50 per cent strength is so small that Reaction (4) practically stops unless a high partial pressure of oxygen is maintained and a long time allowed for the reactions. The rate of NO_2 absorption to form HNO_3 is so rapid that the nitrous gases are at all times substantially in equilibrium with the liquid, and the absorption may proceed only as the nitric oxide present in the gas reoxidizes. The $NO \longrightarrow NO_2$ oxidation proceeds at a rate of about 1270 mm. Hg/min. (at 40°C. and an oxygen partial pressure of 150 mm. Hg) if the initial NO partial pressure is about 65 mm. Hg., and at only about 0.3 mm. Hg/min. at an initial NO partial pressure of 1 mm. Hg. By use of the equilibrium constants K_3 and K_4 for Reactions (4) and (3) and the rate constant, k, for Reaction (2) it is possible to calculate equipment sizes required for absorption of a known quantity of nitrogen oxides per unit of time. [5,7] Values of K_3 have been determined for all acid strengths up to 65 percent HNO_3 and temperatures from 10° to 75°C. [3]

4. Equipment Design Considerations

Theoretical considerations show that at atmospheric pressure a long residence time for the gas volume is required to produce high strength acid; i.e., Reaction (2) is controlling instead of Reaction (4). The equipment must be designed, therefore, to allow time for the reoxidation of the nitric oxide liberated during the absorption of the nitrogen peroxide. Early absorption practice made use of as many as eight,

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or more, packed ceramic acid circulation towers in series in order to achieve the desired gas holdup time required for this reaction. Modern absorption methods however, use bubble-cap columns made from acid-resistant stainless steels. The bubble-cap unit provides a series of graded acid strengths essential for efficient absorption. In addition, cooling can be applied on each plate and sufficient volume holdup between plates can be designed into the column to suit the conditions of time and temperature required for the nitric oxide reoxidation.

The plant Nitric Absorber, T-A-1, is a 20-bubble-cap tray, 4-1/2 ft. diameter tower with plates spaced on 18-in. centers. The unit is described in more detail in Chapter XVI. The Nitric Absorber is designed so that the gaseous-phase residence time between plates is about 8 seconds, under the conditions illustrated by Figure IX-1. If a 35% contacting efficiency per plate is assumed, the proportion of nitrogen oxides in the gases leaving the absorber is about 0.2 weight per cent.

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The liquid holdup time per plate at design flow rate of condensate to the Absorber (1.25 gal./min.) is about 10 minutes per plate.

The total heat evolved in the absorption of NO_2 in water to form nitric acid is about 18,000 B.t.u./mole of NO_2 (about 104,000 B.t.u./hr. on a 13-1/8 tons of uranium/day basis). The heat is removed by cooling coils provided for some of the plates. The coils pass through the liquid held up on the plates. Water enters the coils at about 75°F. and leaves at about 85°F. Sufficient coil area is provided so that the temperature of the liquid on any tray does not exceed 100°F. (Actually, tray liquid temperature varies from about 75°F. at the topmost tray to 100°F. on the bottom trays.)

The rate of NO_2 absorption in the Nitric Absorber under flowsheet conditions, or illustrated in Figure IX-1 (except that no NO_2 is assumed to be removed in the Gas Cooler, E-A-2), is summarized, approximately, in the following table:

Plate Number	Per Cent of Total Acid Formed in Nitric Absorber
1 (Bottom)	About 30
2	20
3	15
4	10
5	7
10	1
15	0.1
20	0.05

5. Gas Cooling

Before the gaseous products from the calcination process enter the bubble-cap column they are cooled from a temperature which may range as high as 500°F. to about 85°F. in the Gas Cooler, E-A-2. The hot entering gases consist of about 55 volume % water vapor, 17% NO_2, 1.3% NO, 5.2% O_2,

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20% air, and 1.3% HNO_3. During the cooling operation most of the water is condensed and some nitrogen peroxide is absorbed in the condensed moisture. The condensate consists of about 42% nitric acid. It leaves the Gas Cooler and eventually joins the acid stream issuing from the base of the Nitric Absorber, T-A-1. The exit gases leaving the Cooler consist of about 5 volume % water vapor, 5% NO_2, 16% N_2O_4, 9% O_2, less than 1% NO, and 65% air. The Gas Cooler is a water-cooled, finned-tube heat exchanger with the gases in contact with the external longitudinal fins. External fouling of this type of heat exchanger has less effect on the heat-transfer capacity of the finned surfaces as compared to bare tubes. The fins also provide turbulence to the gas flow in the laminar-flow region and increase the fin-side heat-transfer coefficients.(4)

About 2500 sq. ft. of cooling surface (including the fins) are provided in the Gas Cooler. Estimation of overall heat-transfer coefficients (U) to be expected in the Cooler is difficult because of the many operations (cooling of a gas of varying composition, condensation of some of the gaseous components, and cooling of the condensate) involved. However the U factor for the gas cooling may range from 4 to 10 B.t.u./(hr.)(sq.ft.)(°F.), while for the condensation it may range from 150 to 250 B.t.u./(hr.)(sq.ft.)(°F.).

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B. PROCEDURE

1. Normal Procedure

The gas from the uranyl nitrate decomposition pots is carried through a duct to the acid recovery system by means of a duct-pressure-controlled steam jet located at the top of the Nitric Absorber, T-A-1 (see Figure IX-1). Initial cooling of the gas to about 85°F., before absorption, is accomplished in the Gas Cooler, E-A-2, where water is condensed and removed as dilute nitric acid. The Gas Cooler also provides space and time for the oxidation of nitric oxide to nitrogen peroxide (Reaction (2)) to approach completion. Contraction of the gases in the Gas Cooler under steady-state conditions sweeps the decomposition gases towards the recovery system, and the nitric absorber jet relays the gas volume from the cooler through the absorption column. The cooled gas is introduced at the bottom of the Nitric Absorber and passes upward through the bubble caps located on the plates in the Absorber. Process steam condensate is added at a controlled rate to the top plate of the Absorber and flows downward through the Absorber counter-current to the direction of the gas flow. The nitrogen peroxides are thus absorbed in the water to form dilute nitric acid in the topmost plates, with the concentration increasing incrementally to about 40 to 45% on the bottom plate. Acid flows from the bottom of the Absorber into the Bleacher, T-C-6. The weak acid condensates from the Gas Cooler, which contain traces of uranium nitrate from decomposition pot entrainment, join with the Absorber Acid before entering the Bleacher. Atmospheric air is admitted to the Bleacher to scrub out dissolved nitric oxide in the acid stream. This air may be used to make up any oxygen deficiency required in the Nitric Absorber for nitric oxide oxidation, or by-passed around the Absorber to the stack, should the volume required for bleaching exceed that required for oxidation. The bleached acid flows to the Nitric Cooler, TK-C-3, from

which tank it is pumped at a controlled rate to the nitric acid Fractionators, T-B-4 and T-D-4, for concentration to 60 to 61% strength. This acid is sent to the waste metal removal facilities and used to dissolve metal wastes. Water-cooled coils are located on the bubble-cap plates in the Nitric Absorber to remove the heat of formation of the nitric acid (ca. 18,000 B.t.u. per lb. mole NO_2 absorbed). The water from these coils is reused in the Gas Cooler before being sent to the retention basin.

A material balance flowsheet for the acid recovery operations is shown as part of Figure VIII-2.

A small amount of entrained uranium (about 3 lb./day as UNH) is expected to enter the acid recovery system via the decomposition pot gases. (See Figure VIII-2.) About 2 lb. enters the dilute acid formed in the Gas Cooler; the remaining 1 lb. is found in the dilute acid product from the HNO_3 Absorber. As shown in Figure VIII-2, the UNH content in the 60% acid product (from both product concentration and nitrogen oxide absorption sources) is about 0.12 wt. %. This 60% acid is utilized in dissolving uranium slurry removed from underground.

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2. Remedy of Off-Standard Conditions

2.1 High chloride content in Absorber

The trace quantities of chlorides, introduced to the Nitric Absorber through the condensate feed water or by way of the decomposition pot gases, will accumulate in the Absorber due to a distillation and reabsorption phenomenon which occurs in the nitric acid. These chlorides exist in the system as hydrochloric acid and are usually found at their greatest concentration in nitric acid of a strength between 22.0 and 23.5% HNO_3. A build-up of chlorides in the Absorber will result in serious corrosion to the stainless steel in contact with the nitric acid which contains the high local concentration of chlorides. The recommended practice is to purge the column whenever the chloride concentration reaches 0.05% in nitric acid of the aforementioned concentration. This is accomplished by sampling the Absorber at those plates containing nitric acid of this critical concentration range and determining the chloride content. Should the chloride content indicate a flush to be necessary, the water feed rate may be increased to decrease the make acid strength to about 20% and purge the chlorides out through the bottom of the Absorber. This method results in a momentary surge of weak product acid, but the Absorber can be brought back to normal conditions readily by reducing the water feed until the desired acid strength is attained. An alternate flushing method, which may be used, consists of purging, through the samplers, the individual Absorber plates on which high local concentrations of chloride are found. This method is lengthy and does not give positive assurance of complete chloride removal, since the plates are not completely drainable.

2.2 High nitric oxide content in acid

The presence of dissolved nitric oxide in the Absorber acid is made evident by the orange-yellow or greenish color of the acid. It is desirable to maintain the dissolved oxides at a minimum, since they represent

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a loss and cause subsequent fuming whenever the acid is handled. A dissolved oxide content of 0.5% (below which the acid is substantially colorless) or less is not considered objectionable. The concentration of dissolved oxides is a function of the quantity and temperature of the air entering the Bleacher. This air flow should be regulated, as required, to maintain about 5% excess oxygen in the Absorber exhaust. Should more air be required to effect good bleaching, the bypass line from the Bleacher to the stack may be used so as to prevent overloading of the Absorber with excess Bleacher air.

The HNO_2 content of the 40% acid is small (probably considerably less than 0.1%). The greater portion of the small concentration of HNO_2 passes overhead (either dissolved in condensate or out with non-condensibles in the Fractionator). HNO_2 concentrations up to 0.1% may be tolerated in the recovered acid.

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2.3 High nitric oxide content in stack gas

The presence of excess nitric oxides in the stack gas, as evidenced by orange-red coloration, represents a recovery loss and a hazard to personnel working in the immediate area. The several possible causes and remedies for this condition are discussed below.

(a) Insufficient air admitted to the absorption system, either by way of the decomposition pots or the Bleacher, will result in high stack losses. Since oxygen is required for the efficient absorption of the nitrogen peroxide, an oxygen deficiency will result in nitric oxide being discharged to the stack.

(b) The tower and condensate feed water temperatures influence the stack loss to a large extent. Insufficient cooling water through the plate cooling coils results in an adverse condition for nitric oxide oxidation and absorption. Warm feed water introduced at the top plate of the Absorber will have the same effect.

(c) Insufficient feed water to the column will result in a rise in acid concentration with a corresponding decrease in absorption efficiency and increased stack loss.

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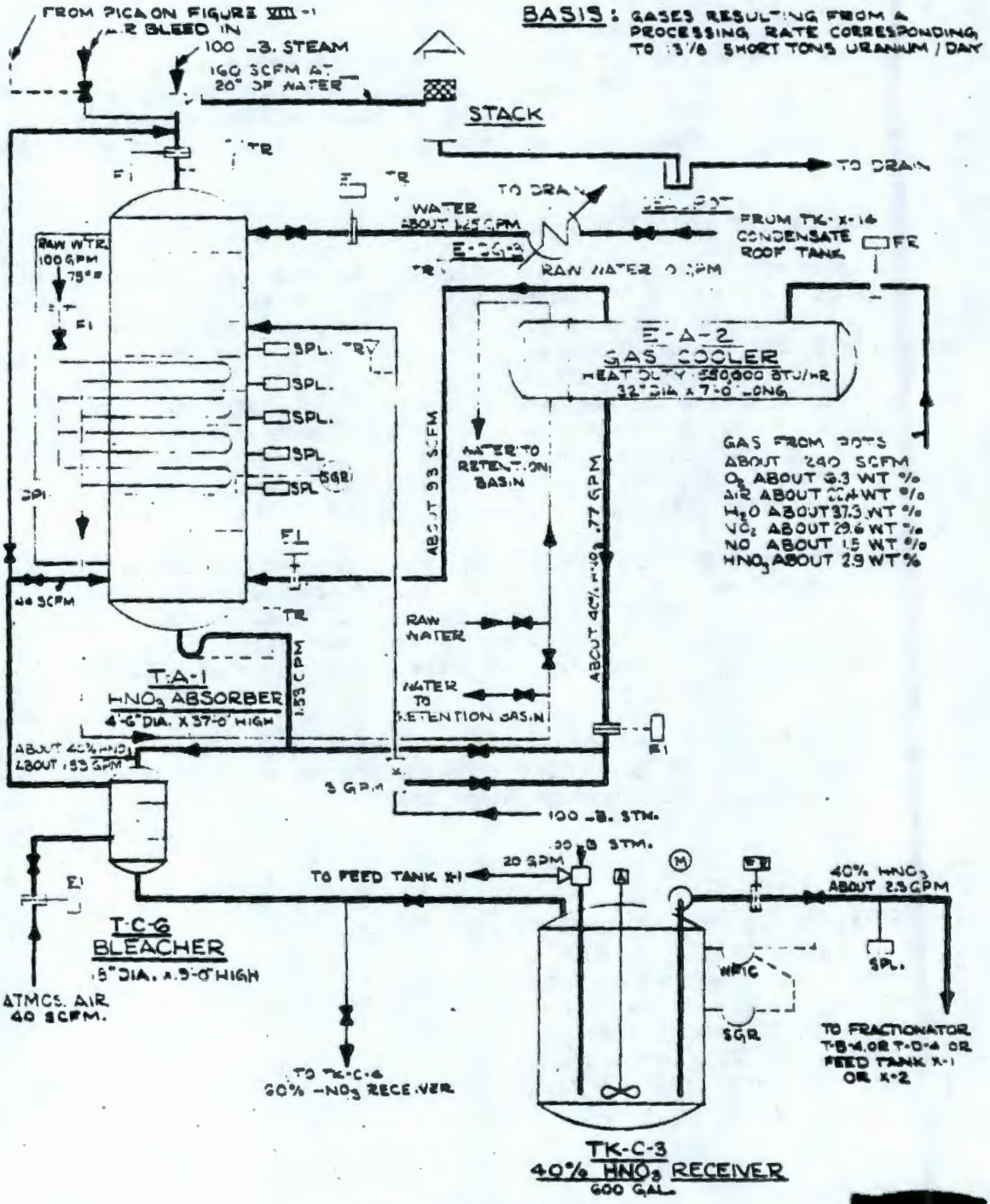
FIGURE IX-1
ENGINEER'S FLOW SKETCH
NITROGEN OXIDES RECOVERY SYSTEM
BASED ON SK-2-6220



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