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Section 2 of 5

Document Information

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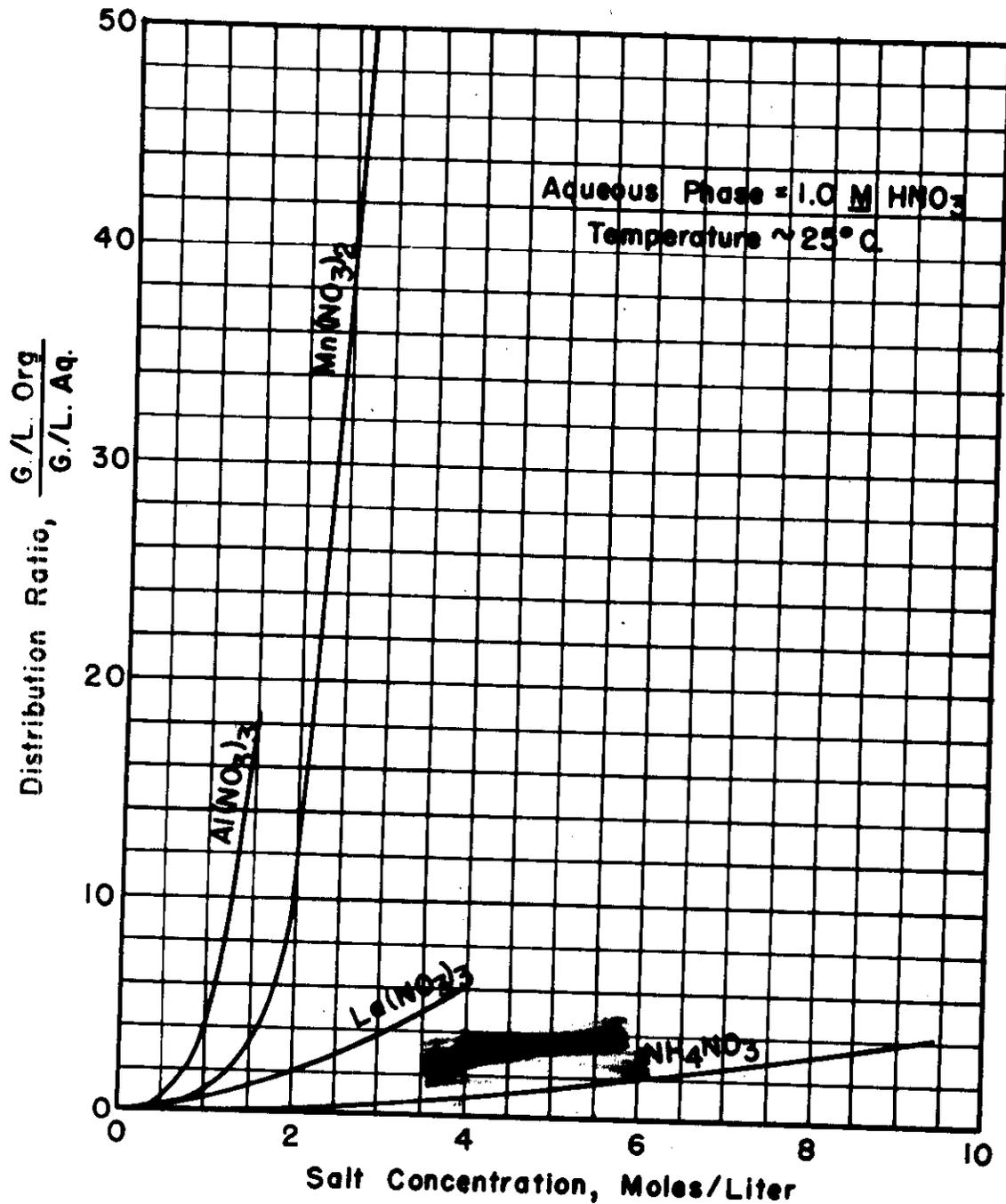
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FIGURE IV - 43

PLUTONIUM (IV) DISTRIBUTION
EFFECT OF SALTING AGENT

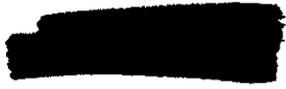
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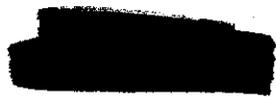
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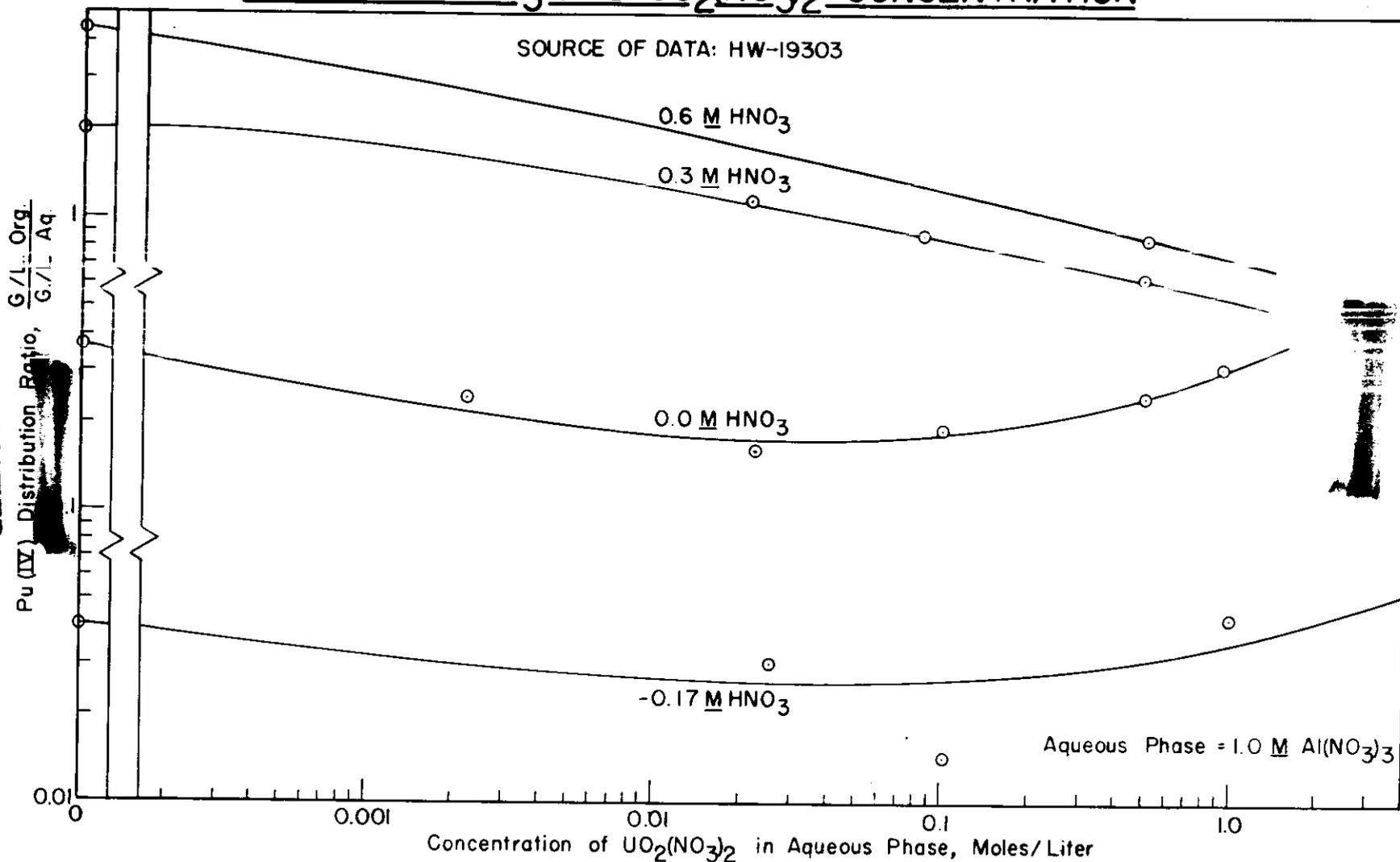
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FIGURE IV - 44
PLUTONIUM (IV) DISTRIBUTION
EFFECT OF HNO₃ AND UO₂(NO₃)₂ CONCENTRATION



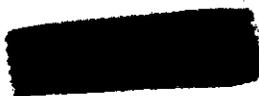
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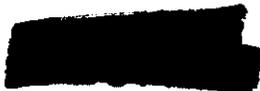


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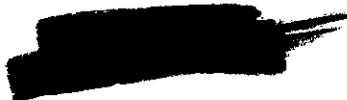
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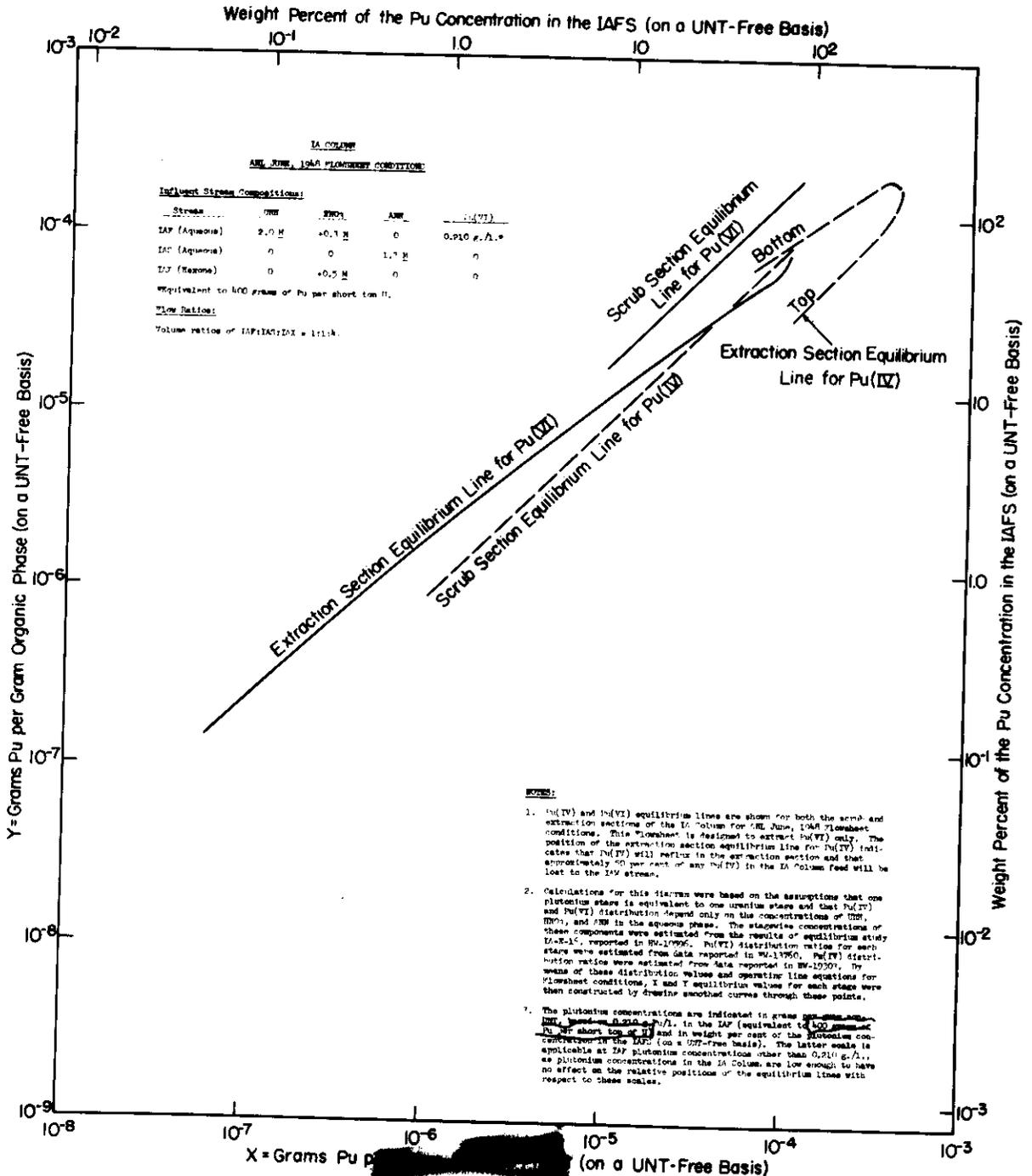
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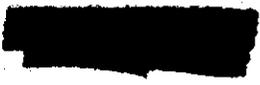
FIGURE IV-46
PLUTONIUM EQUILIBRIUM
IA COLUMN SYSTEM
ANL JUNE, 1948 FLOWSHEET



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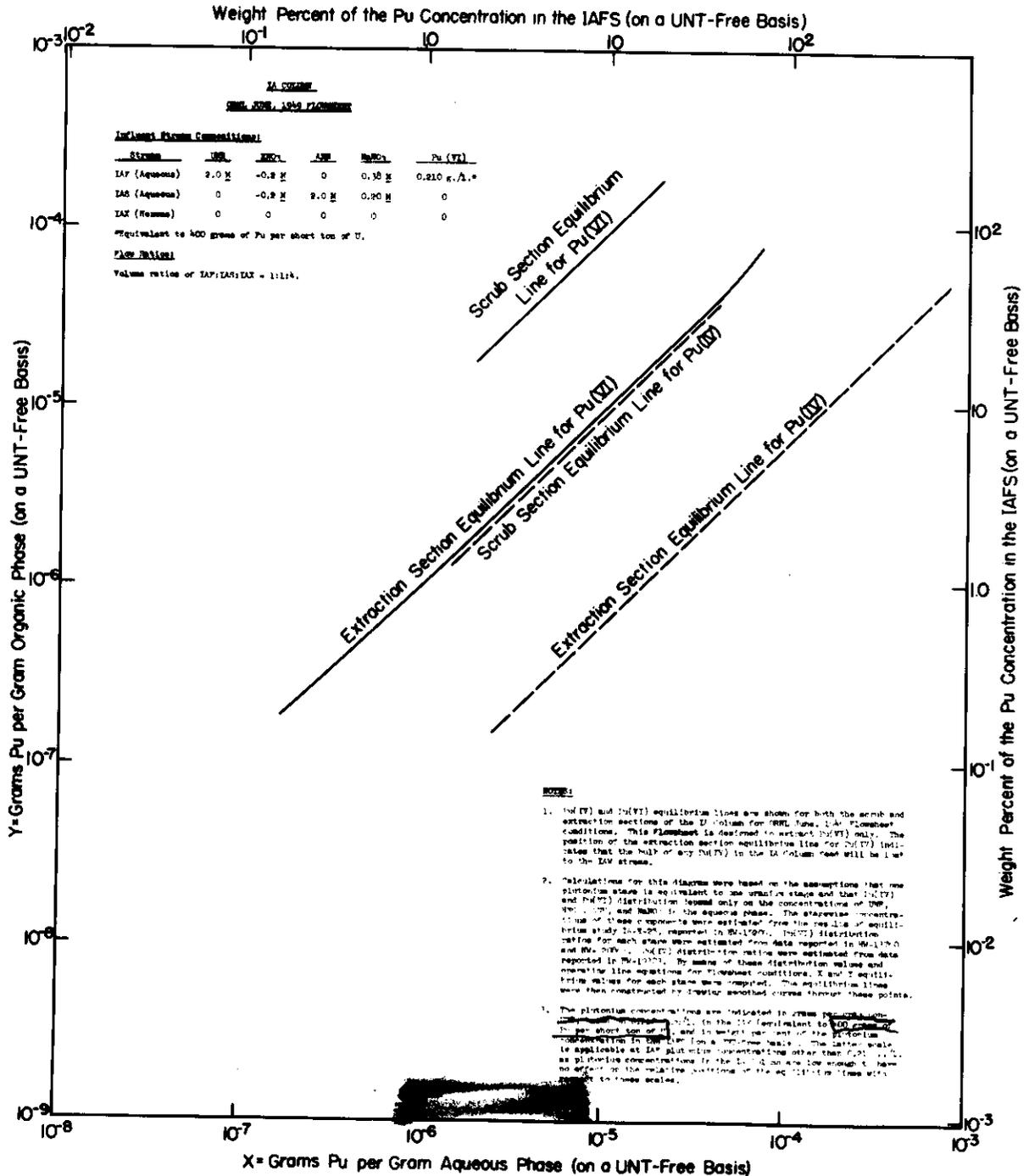
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PLUTONIUM EQUILIBRIUM
IA COLUMN SYSTEM
ORNL JUNE, 1949 FLOWSHEET



NOTES:

- Pu(IV) and Pu(VI) equilibrium lines are shown for both the scrub and extraction sections of the U column for ORNL June, 1949 flowsheet conditions. This flowsheet is designed to extract Pu(VI) only. The position of the extraction section equilibrium line for Pu(VI) indicates that the bulk of any Pu(VI) in the IAFS column feed will be lost to the IAP stream.
- Calculations for this diagram were based on the assumption that the plutonium state is equivalent to the organic stage and that Pu(IV) and Pu(VI) distribution depend only on the concentrations of UO₂, UO₂, and HNO₃ in the aqueous phase. The stepwise concentration of these components were estimated from the results of equilibrium study 10-4-50, reported in ORNL-1001. Pu(IV) distribution ratios for each stage were estimated from data reported in ORNL-1001 and the Pu(VI) distribution ratios were estimated from data reported in ORNL-1001. By means of these distribution values and operating line equations for flowsheet conditions, X and Y equilibrium values for each stage were computed. The equilibrium lines were then reconstructed by linear smoothed curves through these points.
- The plutonium concentrations are indicated in grams per short ton of U, and in weight percent of the plutonium concentration in the IAFS column feed. The latter scale is applicable at IAP plutonium concentrations other than 0.210 g./l. as plutonium concentrations in the IAFS are low enough to have no effect on the relative positions of the equilibrium lines with respect to these scales.

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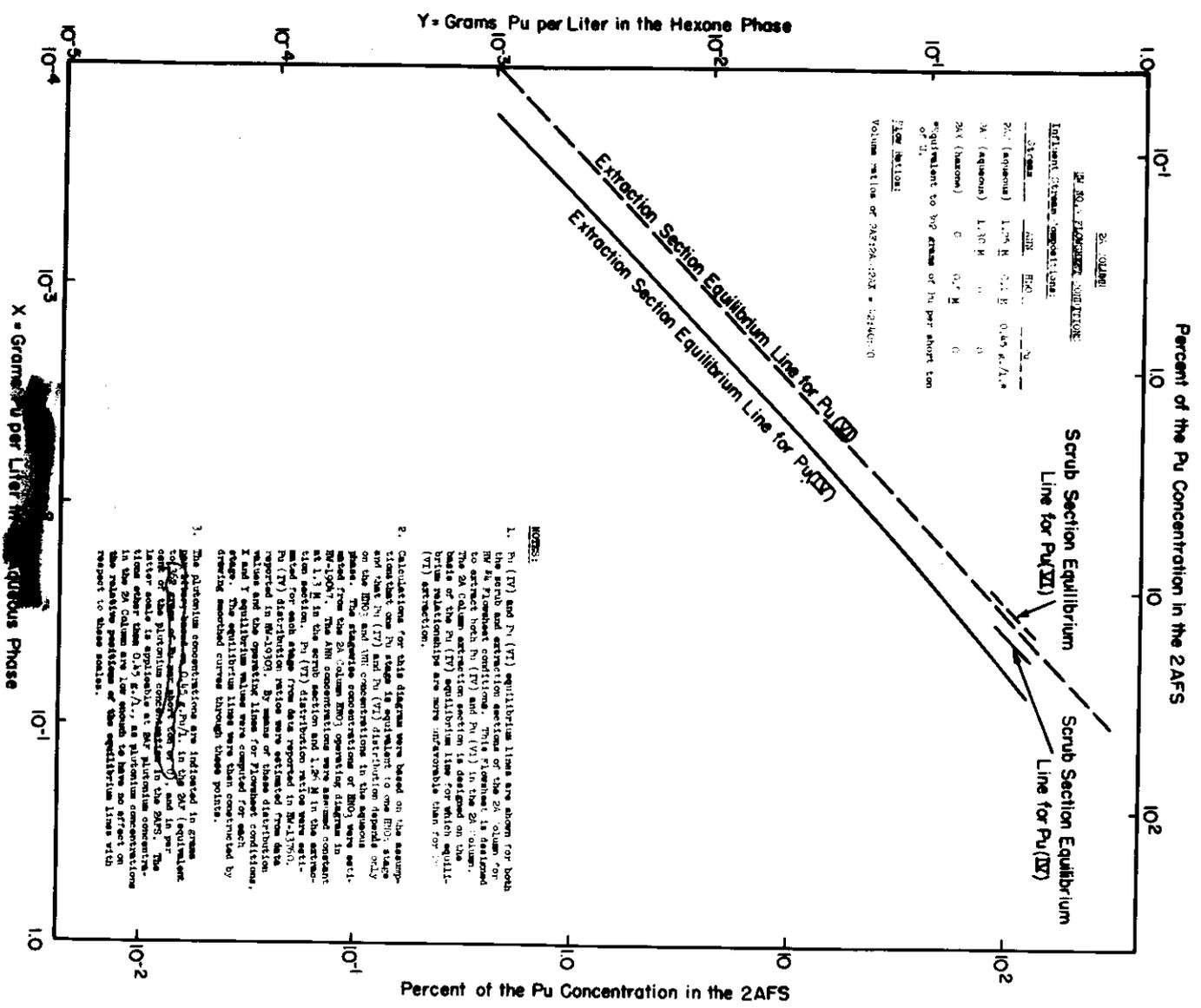
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FIGURE IV-48
PLUTONIUM EQUILIBRIUM
2A COLUMN SYSTEM
HW NO. 4 FLOWSHEET



- NOTES:
1. Pu (IV) and Pu (VI) equilibrium lines are shown for both the scrub and extraction sections of the 2A column for HW No. 4 Flowsheet conditions. This placement is designed to extract both Pu (IV) and Pu (VI) in the 2A column. The 2A column extraction section is designed on the basis of Pu (IV) equilibrium line for which equilibrium values are more unfavorable than for Pu (VI) extraction.
 2. Calculations for this diagram were based on the assumption that one Pu stage is equivalent to one H₂O stage for Pu (IV) and Pu (VI) distribution depends only on the H₂O and UH₄ concentrations in the aqueous phase and the UH₄ concentrations of H₂O were withheld from the 2A column H₂O. The AMU concentrations were assumed constant at 1.15 M in the scrub section and 1.20 M in the extraction section. Pu (VI) distribution ratios were withheld for each stage from data reported in HW-13760. Pu (IV) distribution ratios were estimated from data reported in HW-13760. Equilibrium values and the operating conditions for each X and Y equilibrium lines were computed for conditions shown in the diagram. The equilibrium lines were then connected by drawing smoothed curves through these points.
 3. The plutonium concentrations are indicated in grams per liter in the 2AFS phase. In the 207 (aqueous) cell of the plutonium concentration diagram the latter scale is applicable at 207 plutonium concentrations other than 0.45 g./l., as plutonium concentrations in the 2A column are low enough to have no effect on the relative positions of the equilibrium lines with respect to these scales.

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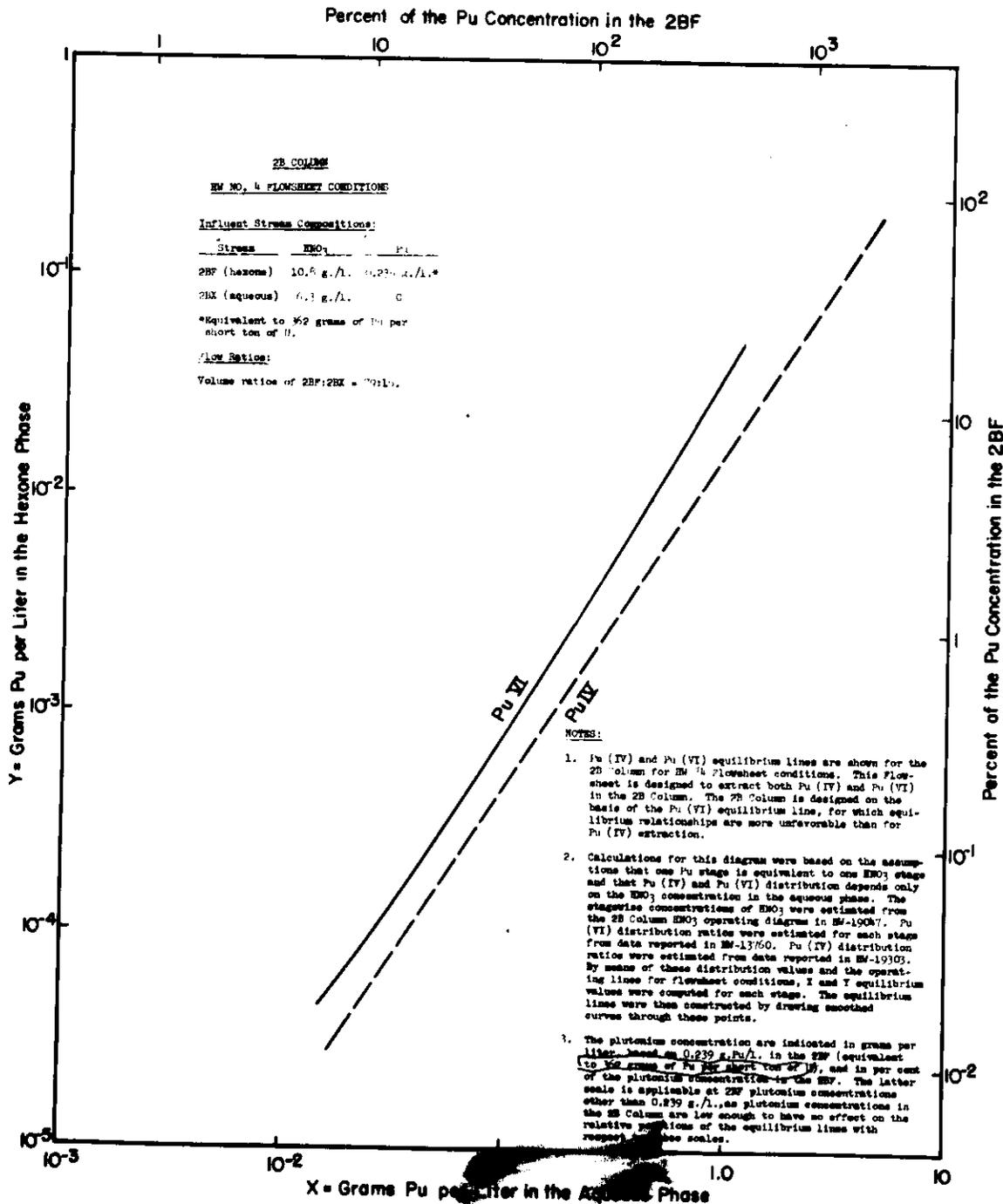
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FIGURE IV-49
PLUTONIUM EQUILIBRIUM
2B COLUMN SYSTEM
HW NO. 4 FLOWSHEET



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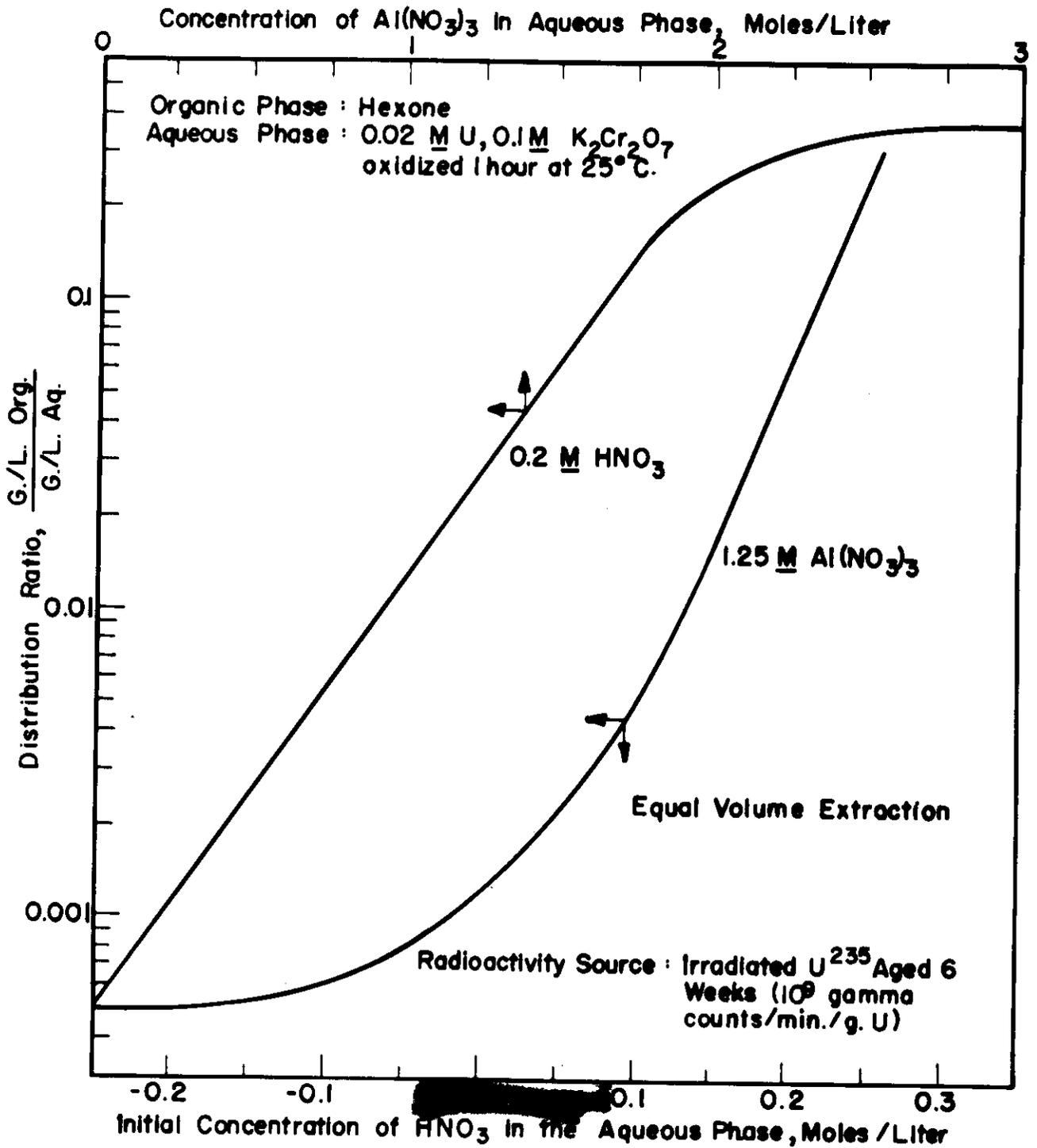
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FIGURE IV-50

GAMMA EMITTING FISSION PRODUCT DISTRIBUTION
EFFECT OF HNO₃ AND Al(NO₃)₃ CONCENTRATION

SOURCE OF DATA: MonN-319



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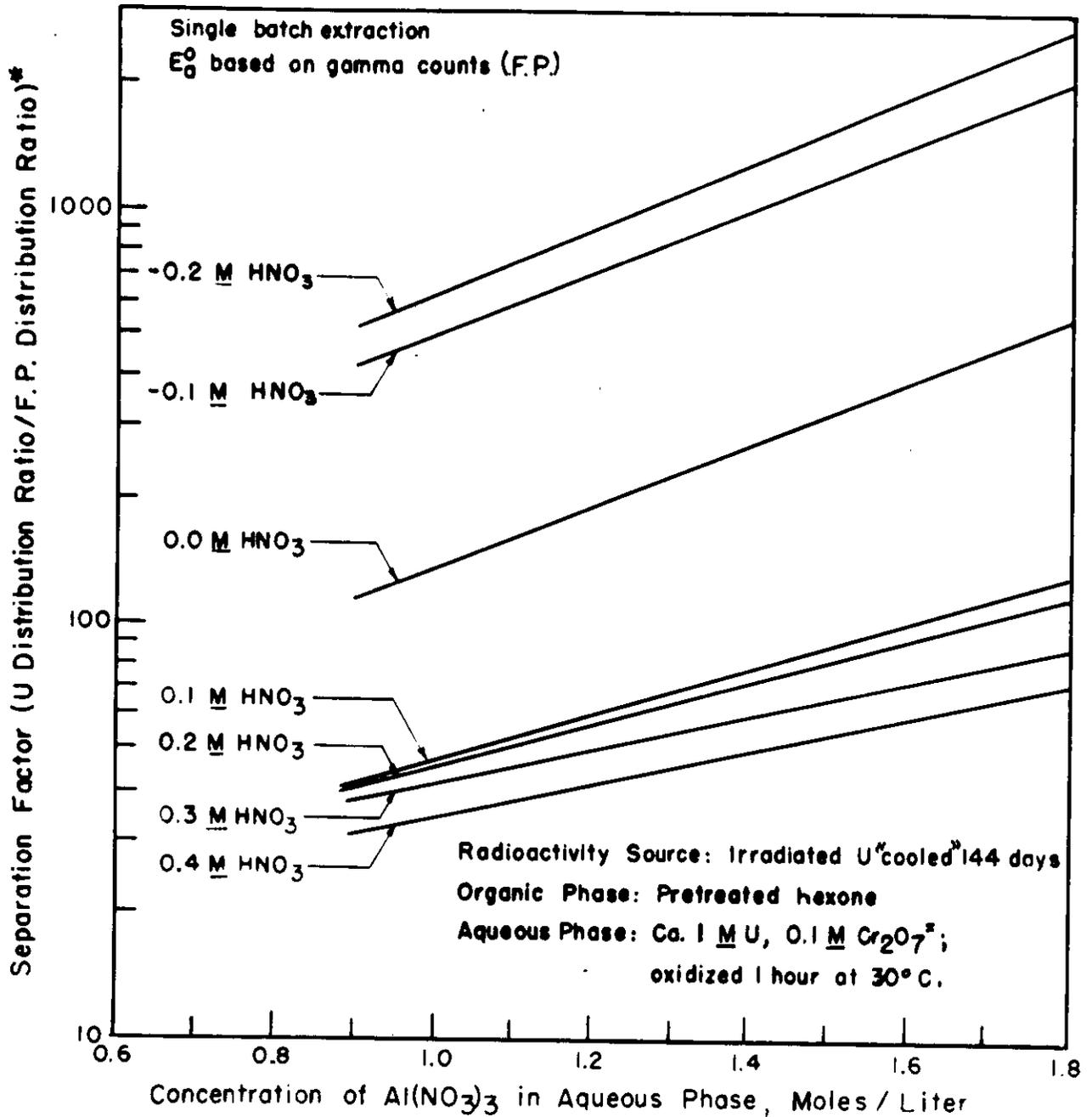


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FIGURE IV-51

**URANIUM-FISSION PRODUCT SEPARATION FACTOR
EFFECT OF $\text{Al}(\text{NO}_3)_3$ AND HNO_3 CONCENTRATION**

SOURCE OF DATA: ORNL-343



* Distribution Ratio, $\frac{\text{G./L. Org.}}{\text{G./L. Aq.}}$

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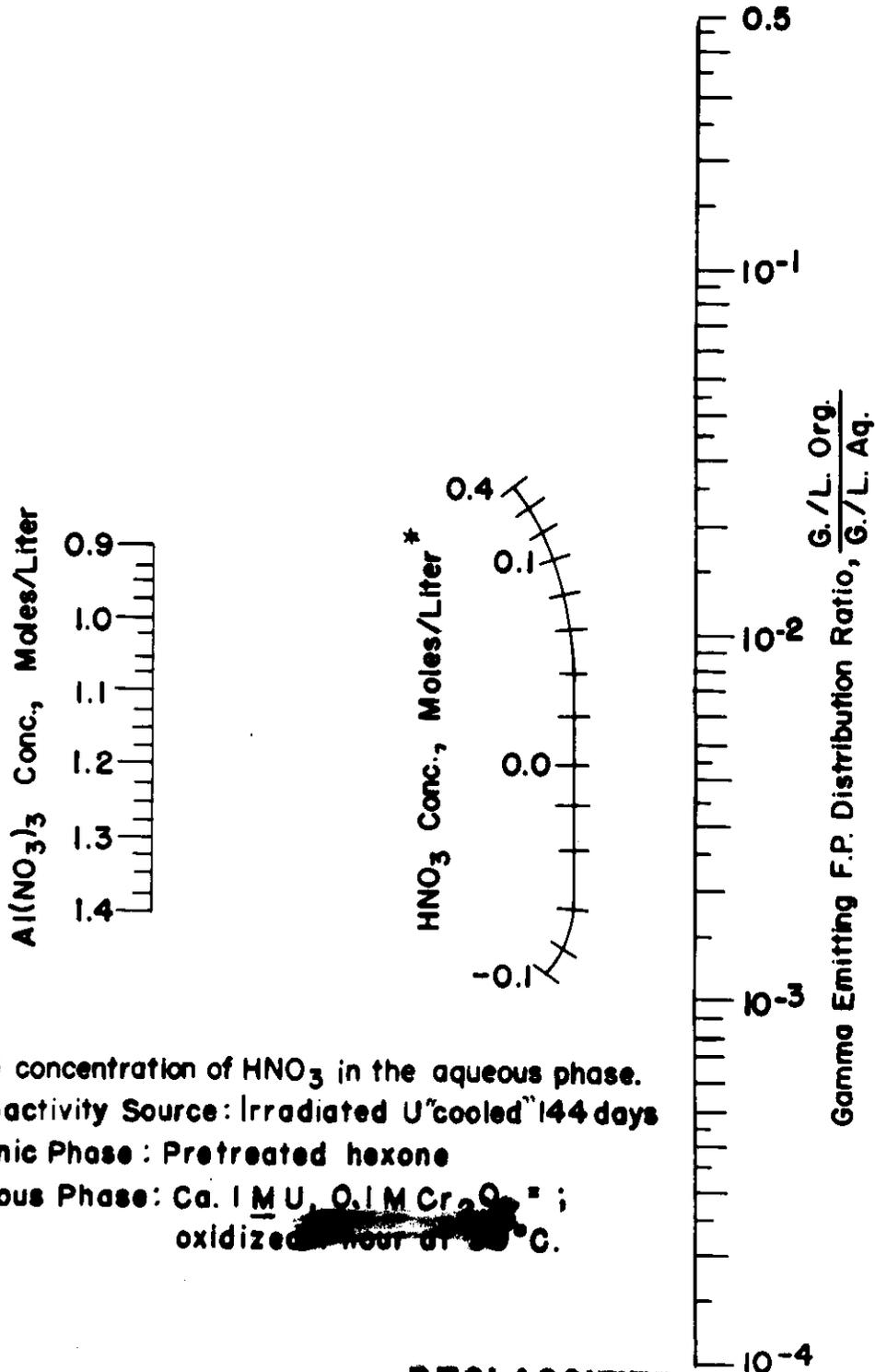
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FIGURE IV-52

GAMMA EMITTING FISSION PRODUCT DISTRIBUTION
EFFECT OF $Al(NO_3)_3$ AND HNO_3 CONCENTRATION

SOURCE OF DATA: ORNL - 37



* Initial concentration of HNO₃ in the aqueous phase.
 Radioactivity Source: Irradiated U²³⁵ "cooled" 144 days
 Organic Phase: Pretreated hexone
 Aqueous Phase: Ca. 1 M U, 0.1 M Cr₂O₇²⁻ ;
 oxidized for 24 hours at 50°C.

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TABLE IV-53

RUTHENIUM DISTRIBUTION
SPECIES PRESENT IN PROCESS SOLUTIONS

A. Hanford Works Laboratory Data (HW-10415):

Species Present in Dissolver Solution	Percent of Total Ru in Dissolver Solution Aged About 10 Days	Volatilization Rate % Ozone at 95°C., Percent/Minute	Distribution Ratio, ^c $\frac{G./L. Org.}{G./L. Aq.}$
Total Ru	100	(95% in 6 hrs.)	0.006
A1	45	10	0.015
A2	50	1.0	0.004
B	5 ^a	0.1 ^b	0.0018

- a. The fraction of ruthenium species B is quite low in fresh dissolver solution (1 per cent or less). However, the fraction increases markedly upon standing to 10 or 20 per cent species B after 30 days.
- b. After 6 hours using 2% ozone, practically all of the Ru remaining is species B.
- c. ORNL June, 1949 Flowsheet.

Note: After a head-end treatment consisting of air sparging dissolver solution, containing initially 0.02M $KMnO_4$, for 6 hours at 95°C., the initial ruthenium distribution ratio, R_D , is about 10^{-3} under ORNL June, 1949 Flowsheet conditions. (208)

B. ORNL Laboratory Data (ANL-51-43):

Form	Distribution Ratio, $\frac{G./L. Org.}{G./L. Aq.}$
Ru A	7.4 ± 30%
Ru B	0.05 ± 20%
Ru C	ca. 0.001
Ru D	> 1'

Notes:

1. Conditions:
 Aqueous phase: 1 M $Al(NO_3)_3$, 0.79 M HNO_3
 Set'd with hexone
 Ruthenium: Ru tracer, distilled as RuO_4
 Organic phase: 0.7 M HNO_3
 Set'd with H_2O
2. An equilibrium mixture of Ru A and Ru B is obtained when Ru tracer is introduced into the aqueous phase and allowed to remain in contact with hexone for several days. The equilibrium constants of the reaction $Ru B \rightleftharpoons Ru A$, $k = \frac{Ru A}{Ru B}$, are as follows: in the organic phase, $20 \pm 50\%$; in the aqueous phase, ca. 0.2 (calculated). Half time for the establishment of the equilibrium is ca. 1 hour.
3. Ru C is obtained when the tracer is allowed to stand in dilute HNO_3 for several months. In contact with hexone Ru C is fairly rapidly converted to a mixture of Ru A and Ru B. Nitrite accelerates the conversion. Strong oxidation converts Ru C to Ru D.
4. Ru D obtained when the tracer is allowed to stand in $KMnO_4$ for several months. Ru D changes fairly rapidly to a mixture of Ru A and Ru B when it is in contact with hexone.

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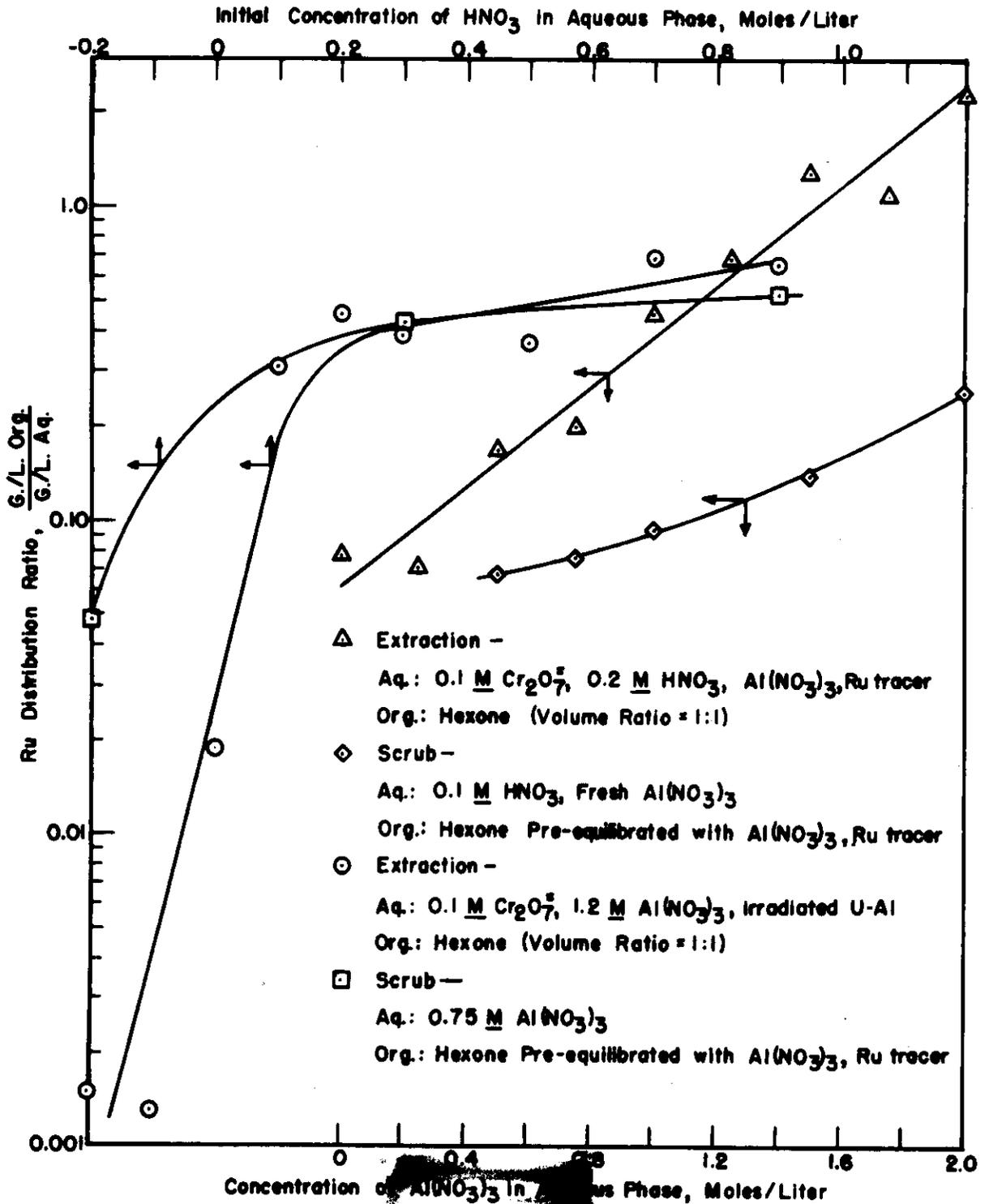
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FIG. [REDACTED]
RUTHENIUM DISTRIBUTION
EFFECT OF $Al(NO_3)_3$ AND HNO_3 CONCENTRATION

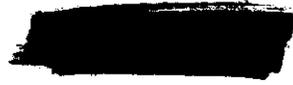
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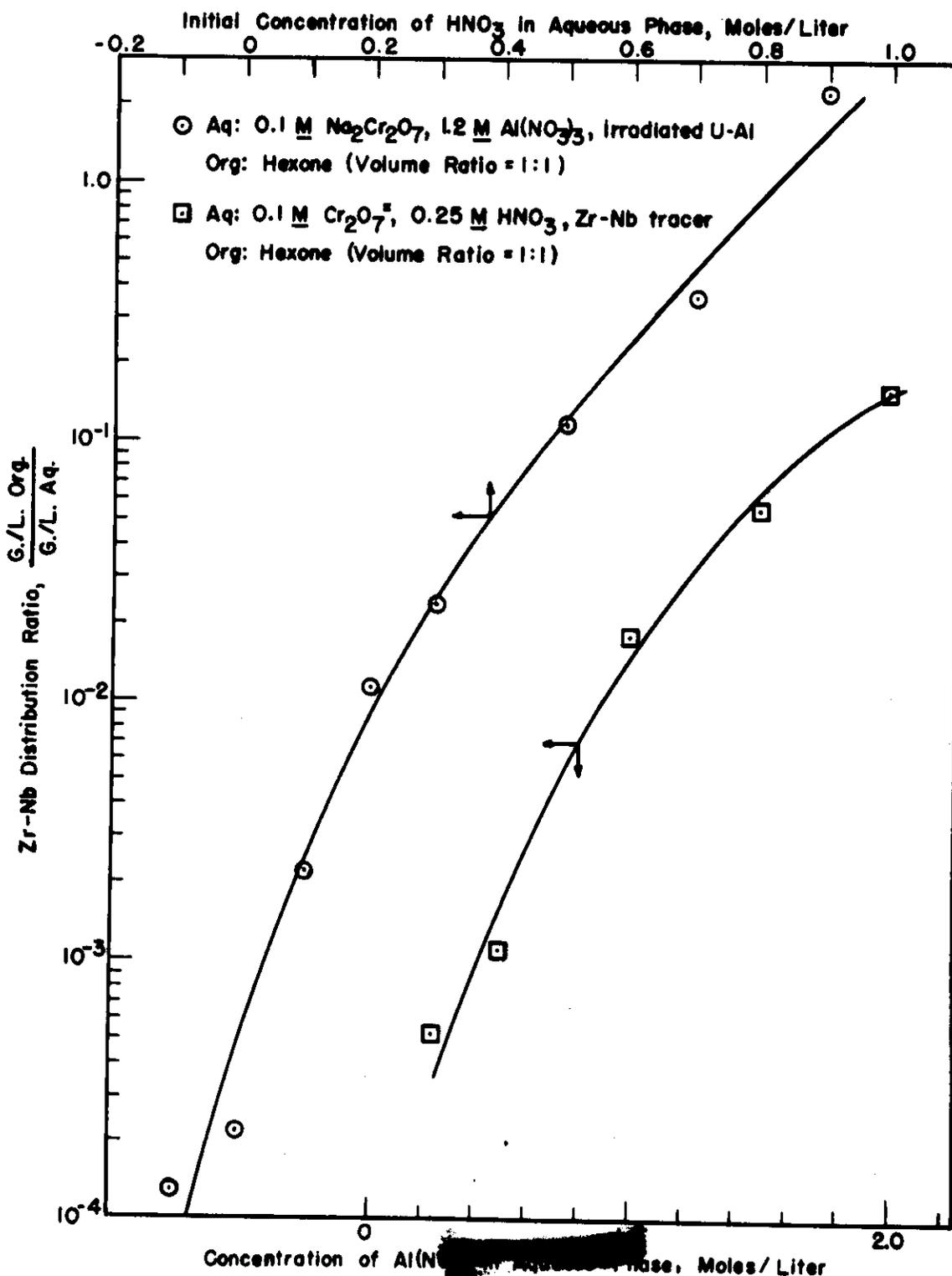
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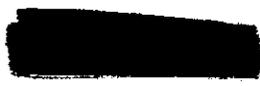
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FIGURE IV-55
ZIRCONIUM-NIOBIUM DISTRIBUTION
EFFECT OF $Al(NO_3)_3$ AND HNO_3 CONCENTRATION

SOURCE OF DATA: ORNL-343



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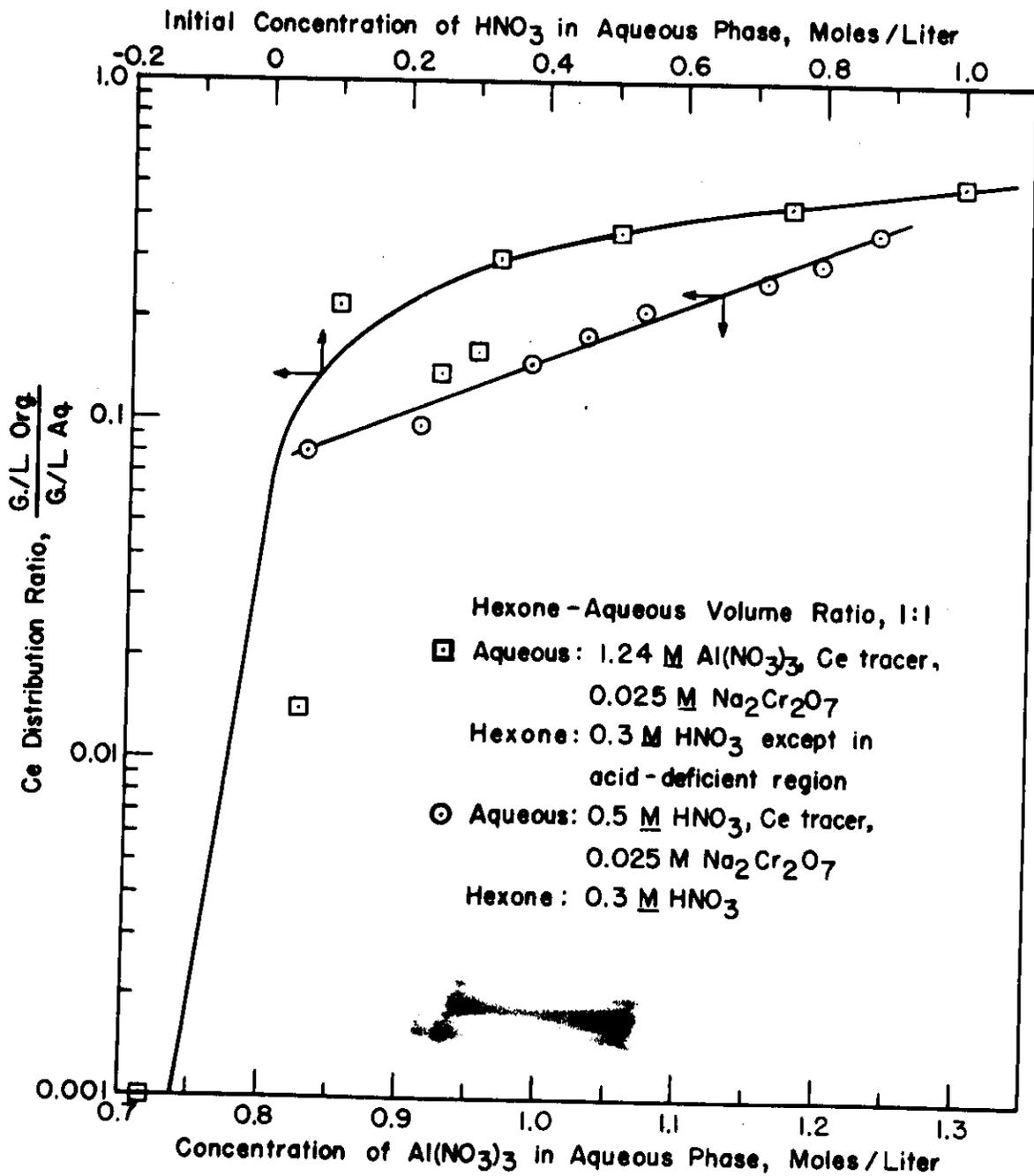
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FIGURE IV-56

CERIUM DISTRIBUTION

EFFECT OF $Al(NO_3)_3$ AND HNO_3 CONCENTRATION

SOURCE OF DATA: KAPL-223



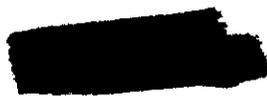
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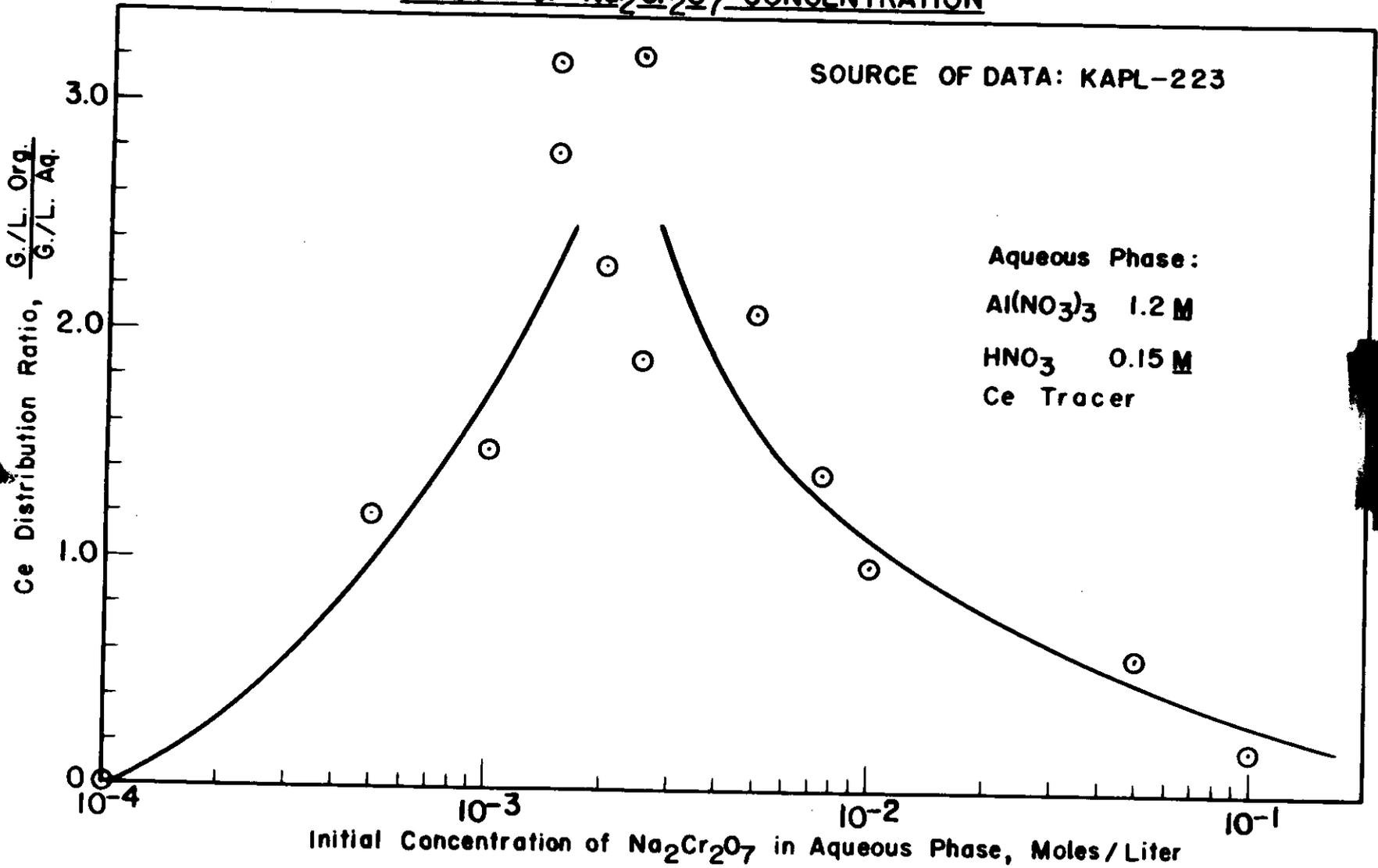


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FIGURE IV-57
CERIUM DISTRIBUTION
EFFECT OF $\text{Na}_2\text{Cr}_2\text{O}_7$ CONCENTRATION



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FIGURE IV-57

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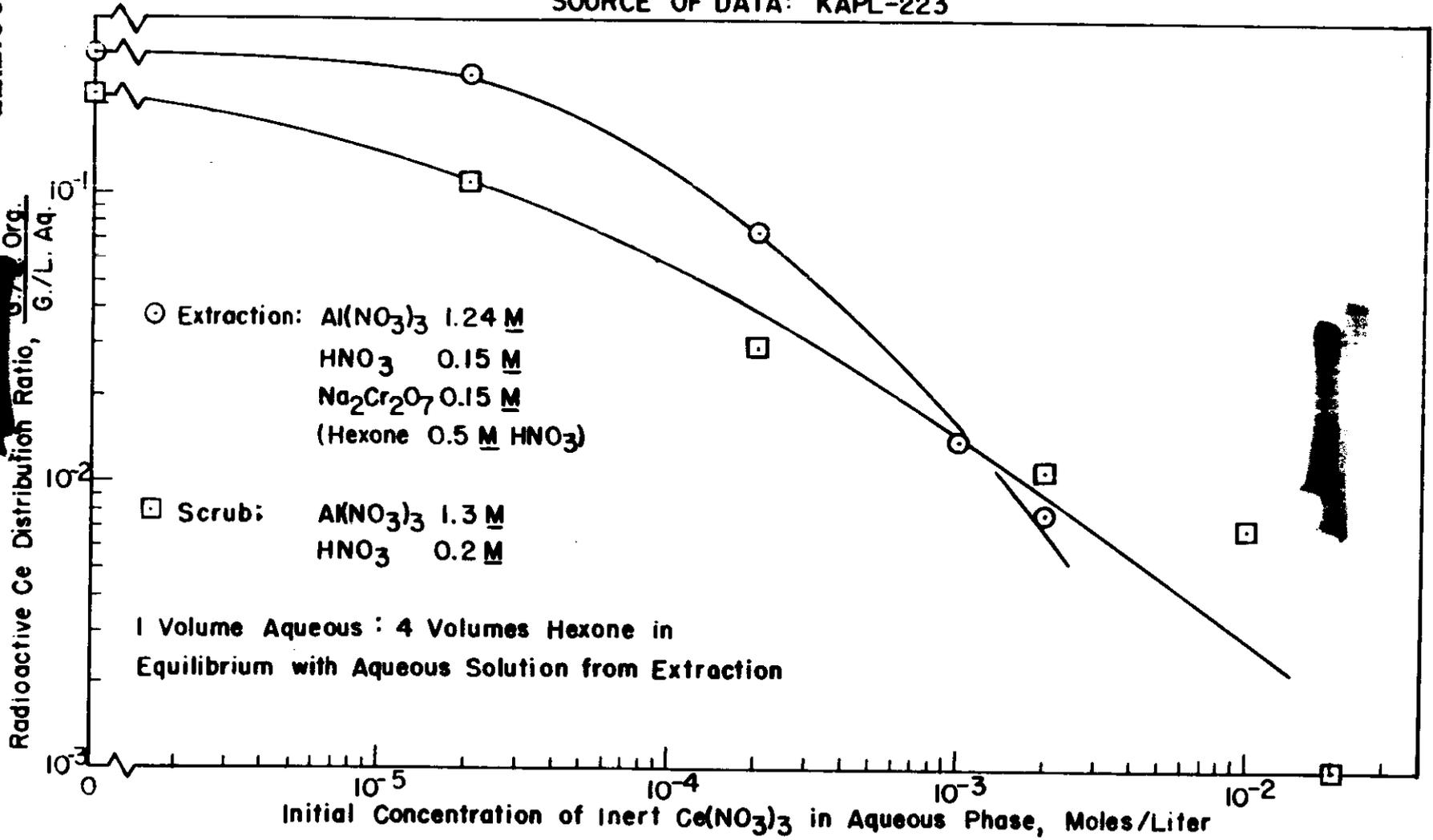


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FIGURE IV-58
CERIUM DISTRIBUTION
EFFECT OF INERT $Ce(NO_3)_3$ CONCENTRATION

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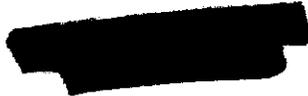
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FIGURE IV-58

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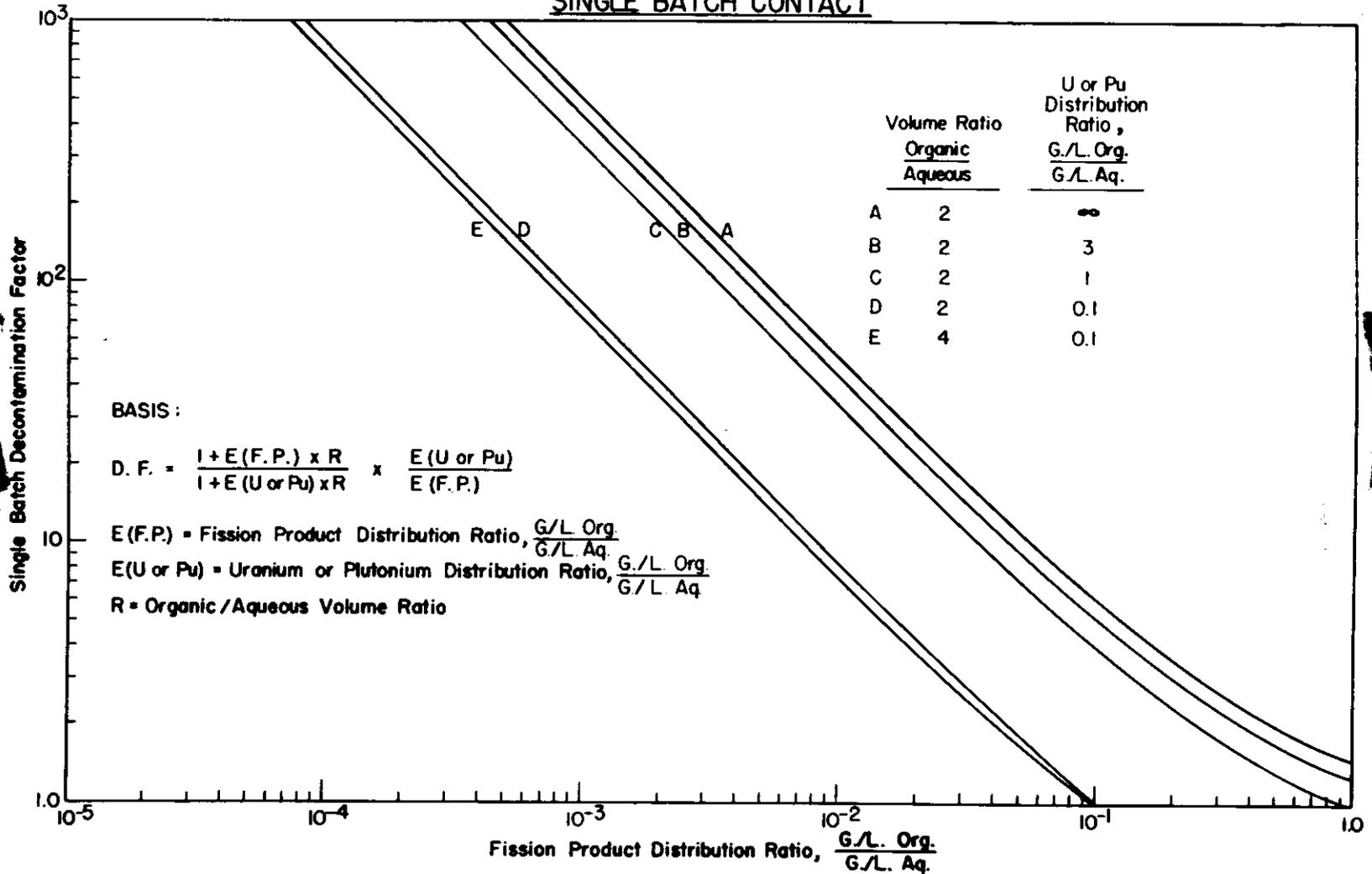
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FIGURE IV-59
URANIUM OR PLUTONIUM DECONTAMINATION FACTOR
AS A FUNCTION OF FISSION PRODUCT DISTRIBUTION RATIO
SINGLE BATCH CONTACT



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FIGURE IV-59

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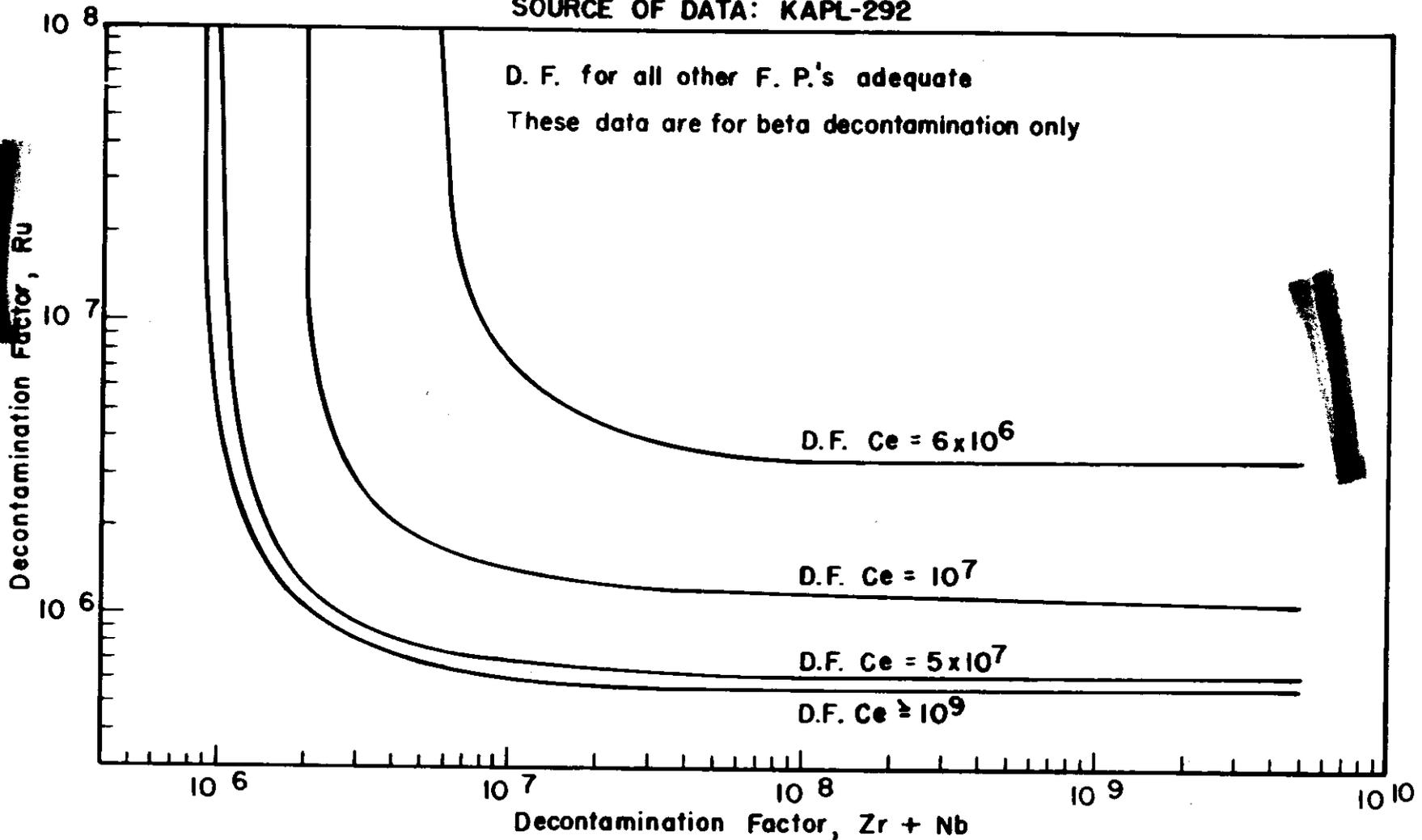


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FIGURE IV-60
RELATIONSHIP AMONG Ce, Ru, AND Zr+Nb
DECONTAMINATION FACTORS
OVER-ALL Pu D.F. = 10^7

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FIGURE IV-60

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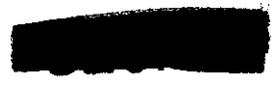
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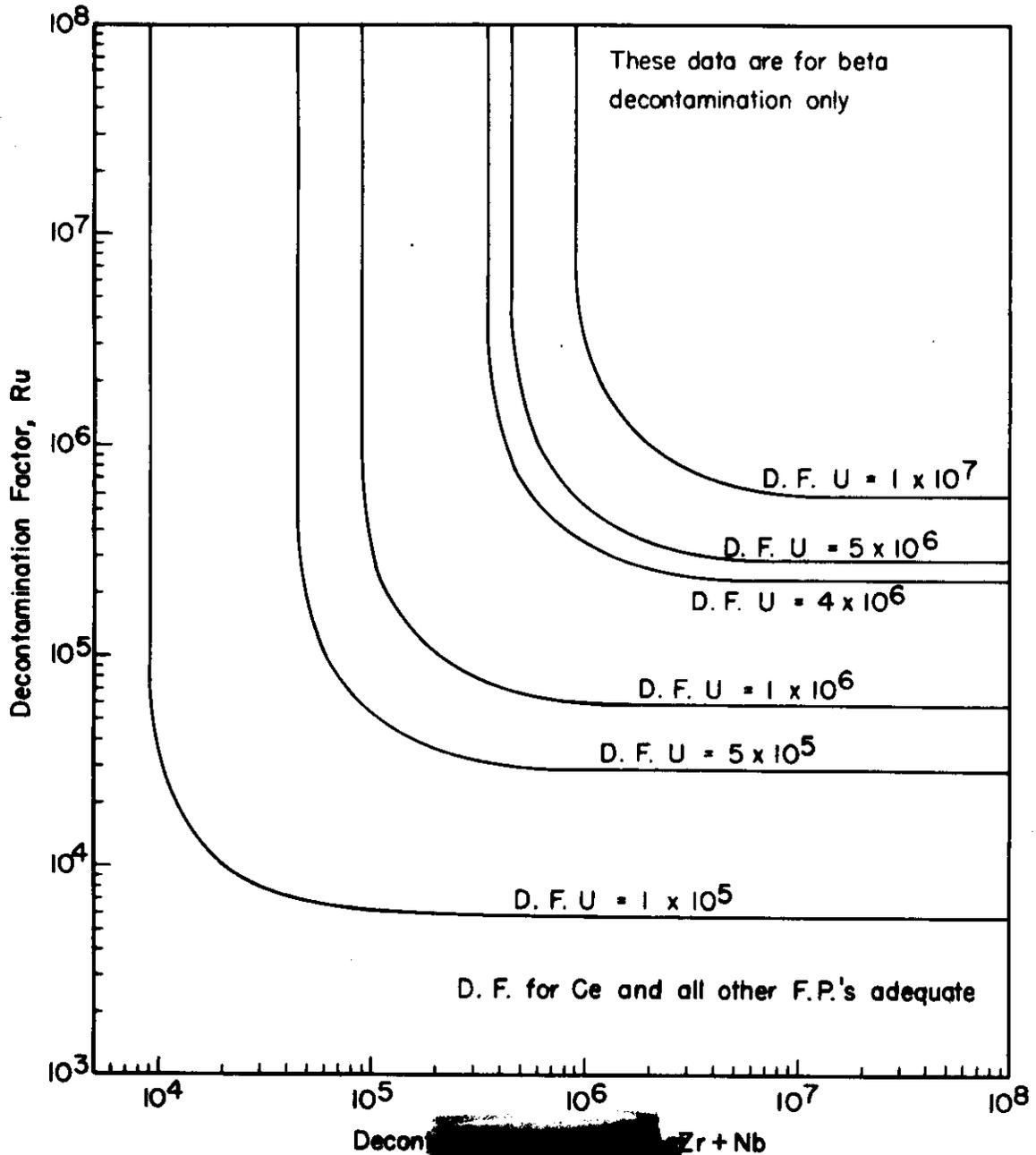


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FIGURE IV-61
RELATIONSHIP AM [REDACTED] Zr+Nb
DECONTAMINATION FACTORS FOR VARIOUS
OVER-ALL URANIUM D.F.'S

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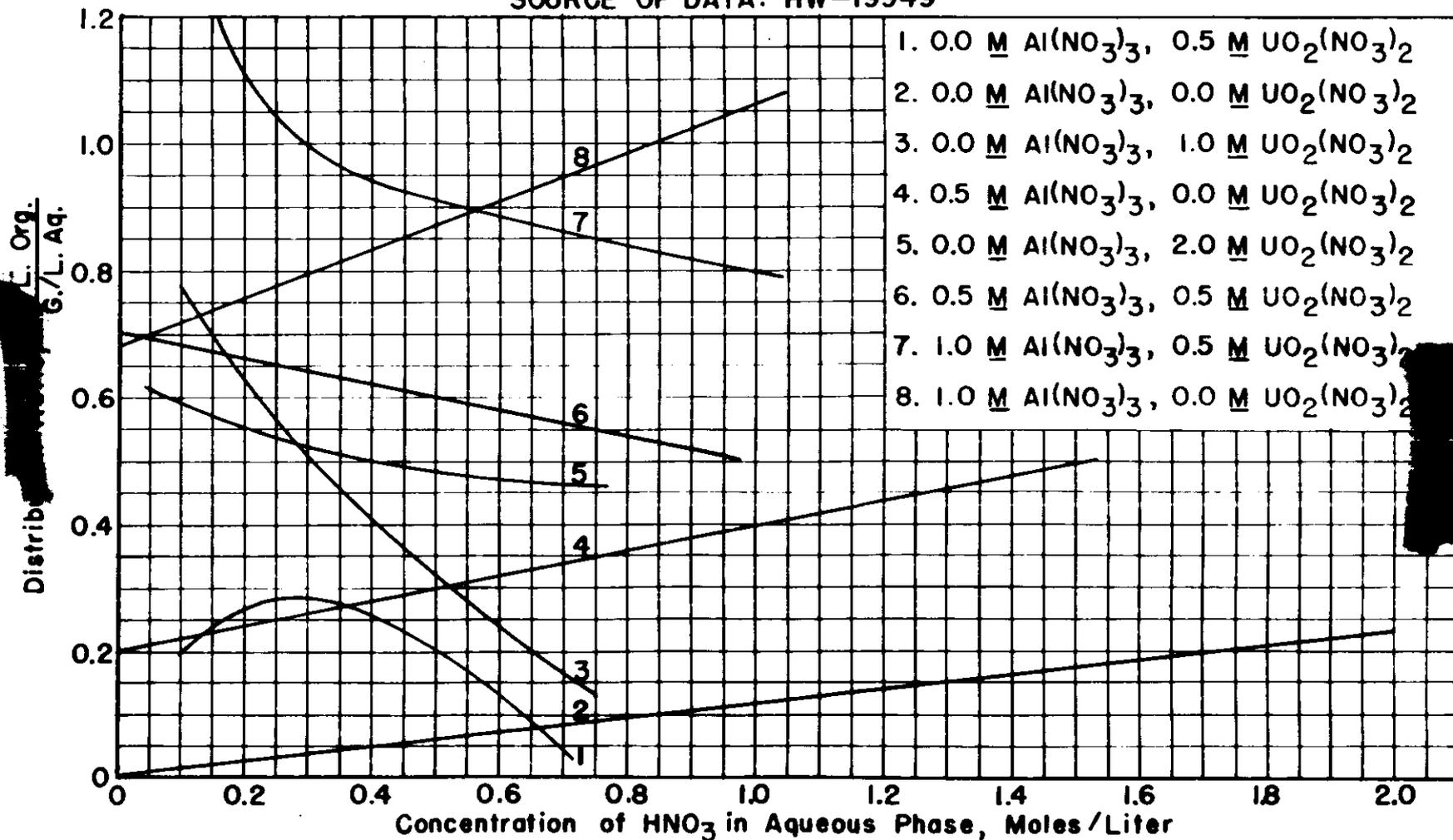
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FIGURE IV-62
HNO₃ DISTRIBUTION IN THE SYSTEM UO₂(NO₃)₂ - Al(NO₃)₃
EFFECT OF HNO₃ CONCENTRATION

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FIGURE IV-62

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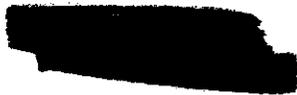
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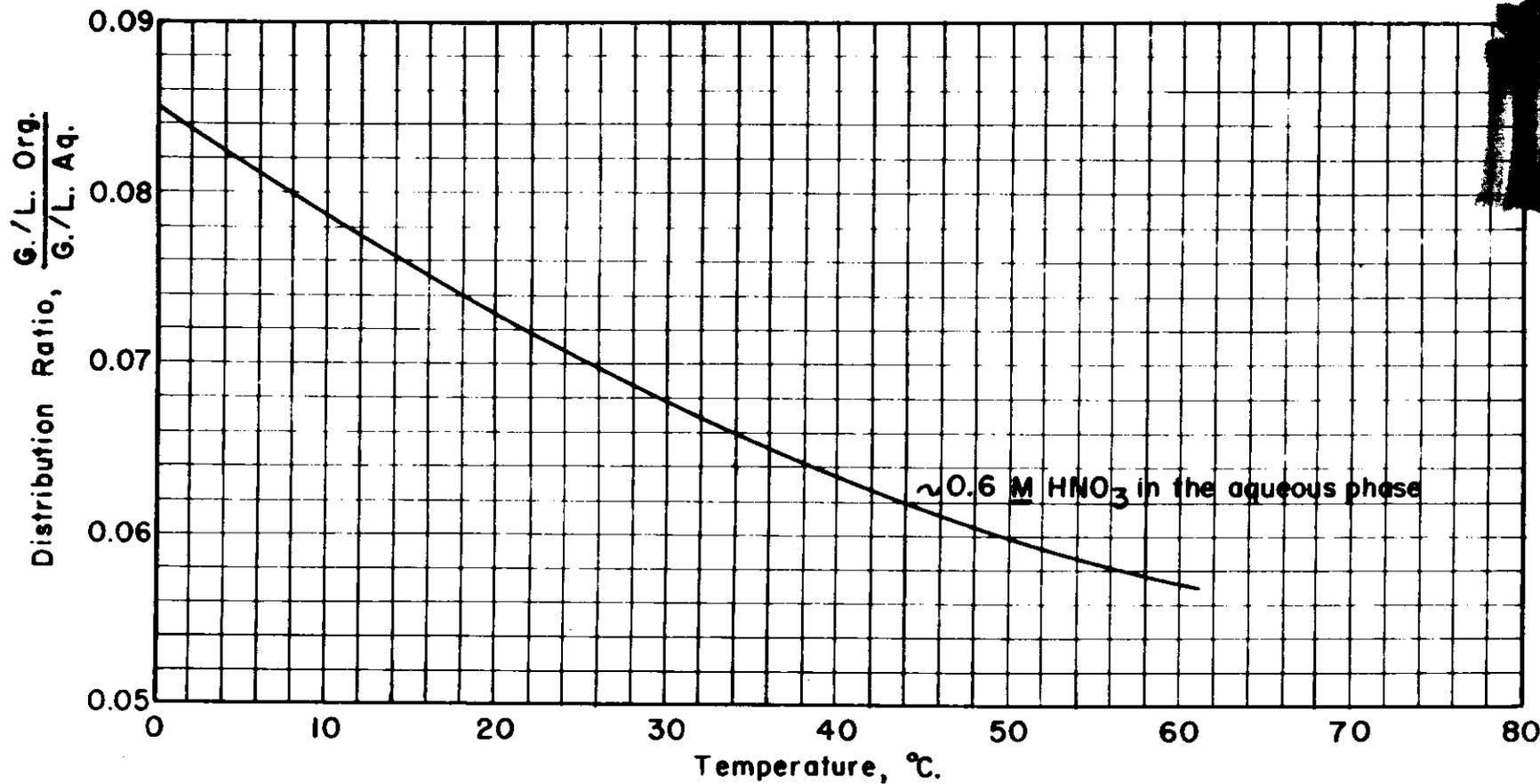
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FIGURE IV-63
HNO₃ DISTRIBUTION AS A FUNCTION OF TEMPERATURE

SYSTEM: HNO₃-H₂O-HEXONE

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FIGURE IV-63

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PART II: PROCESS, continued

CHAPTER V: PROCESS ENGINEERING (SOLVENT-EXTRACTION)

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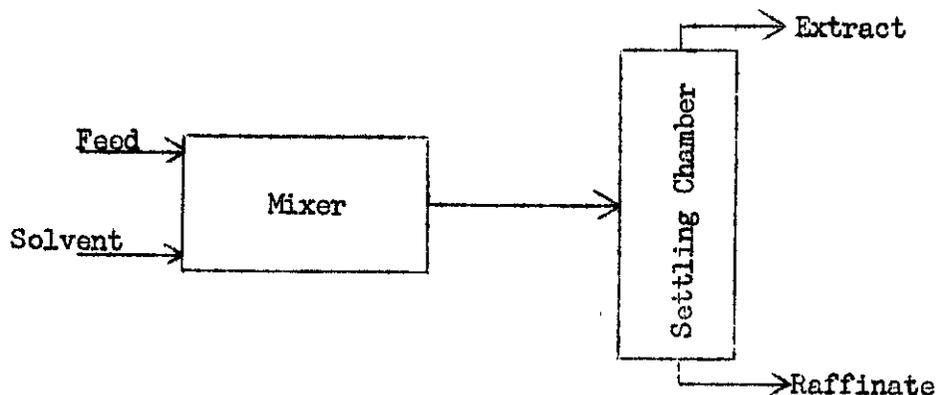
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CHAPTER V. PROCESS ENGINEERING (SOLVENT-EXTRACTION)A. BASIC PRINCIPLES1. Principles of Solvent-Extraction

Solvent-extraction operations are defined in the Chemical Engineers' Handbook⁽²⁾ as "those in which the separation of mixtures of different substances is accomplished by treatment with a selective liquid solvent". Although solvent-extraction operations may include leaching and washing, solvent-extraction as used in this manual refers to liquid-liquid extraction. In liquid-liquid extraction the mixture treated is liquid and the two phases resulting from the solvent treatment are both liquids. In the Redox IA Column, for example, plutonium and uranium are selectively extracted into an organic phase when the aqueous feed originally containing all the U and Pu is treated with hexone solvent. Naturally, the extraction obtained is dependent upon the chemical composition of the phases involved as well as the type of extraction equipment. For a discussion of the chemical considerations involved in the various solvent-extraction contactors of the Redox Plant the reader is referred to Chapter IV. In practice, there are actually many different solvent-extraction methods available for obtaining the liquid-liquid extraction performance desired. A few of these methods are discussed briefly below.

1.1 Simple contact

The simplest method and the one most common on a laboratory scale is the simple contact in which solvent and feed to be extracted are brought together, mixed, and the two phases are allowed to settle. The operation may be either batch (beaker experiment) or continuous as shown in the schematic flow diagram below:

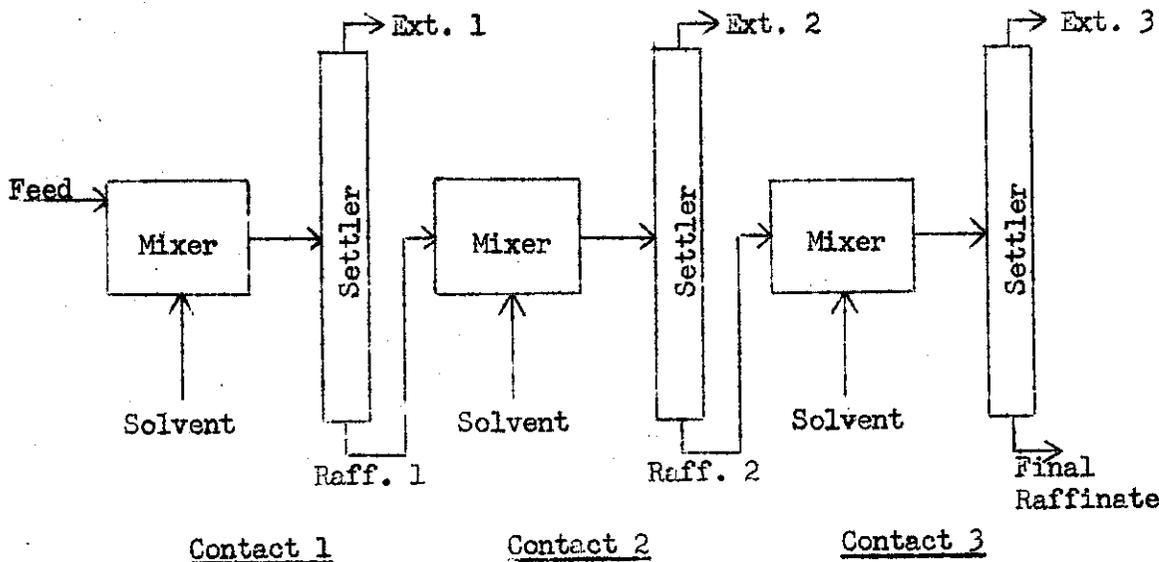
Single Contact Extraction

For any given ratio of solvent to feed, the amount of solute which may be extracted is fixed solely by equilibrium considerations (assuming the phases have reached equilibrium during contacting).

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1.2 Simple multistage (cocurrent) contact

In a simple contact the extract solute concentration and raffinate solute concentration are limited by the equilibrium distribution coefficient. If a raffinate with a lower concentration of solute is desired, the raffinate from the first simple contact may be mixed with fresh solvent as shown in the schematic diagram below:

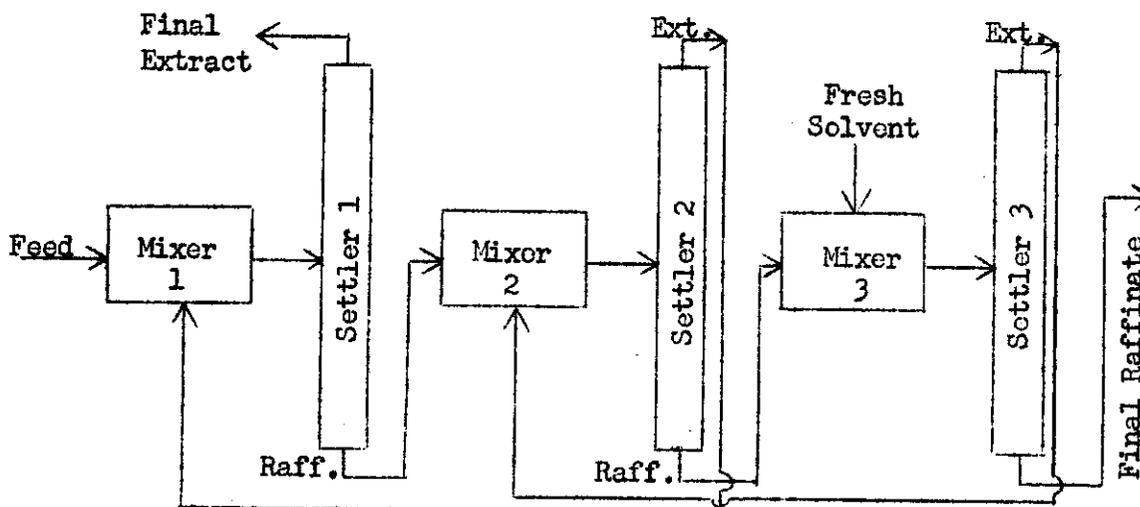


Simple Multistage Extraction (3 Contacts)

If a sufficient number of contacts are made and a sufficiently large volume of solvent is used, the concentration of the extracted component in the final raffinate can be reduced to almost any desired low value.

1.3 Countercurrent multicontact extraction

In countercurrent multicontact extraction (also called countercurrent batch extraction), feed and solvent enter the system at opposite terminals of a series of contacts and flow countercurrently through the system. Fresh extractant first contacts low solute concentration raffinate and then contacts more concentrated raffinate as its own solute concentration increases.



Countercurrent Multicontact Extraction

1.4 Continuous countercurrent differential contact

In continuous countercurrent differential contact operations a very large number of infinitesimally small contacts are achieved by subdividing one phase and passing it countercurrently through the other continuous phase. Either of the phases may be made continuous or dispersed (i.e., either the solvent or the liquid to be extracted may be subdivided and allowed to pass through the other). If the lighter liquid is to be continuous, the dispersed heavier phase is introduced at the top and allowed to fall by gravity through the continuous phase. Conversely, if the heavier liquid is to be continuous (as is the case for all of the Redox solvent-extraction columns) the dispersed lighter phase is introduced below the surface of the continuous phase and allowed to rise by gravity through the heavier continuous phase.

In practice, continuous countercurrent differential contacting is achieved in solvent-extraction columns.

2. Solvent-Extraction Equipment

Many different types of equipment are available and could conceivably be used to accomplish the required Pu and U separation and purification in the Redox Plant. The limitations, advantages, and disadvantages of the important equipment types are mentioned in the following discussion.

2.1 Batch equipment

Although batch equipment may be used for any number of industrial applications, it has been little used in Redox except in the countercurrent multistage laboratory equilibrium studies made to simulate equilibrium conditions in the various column contactors. These studies are discussed in Chapter IV.

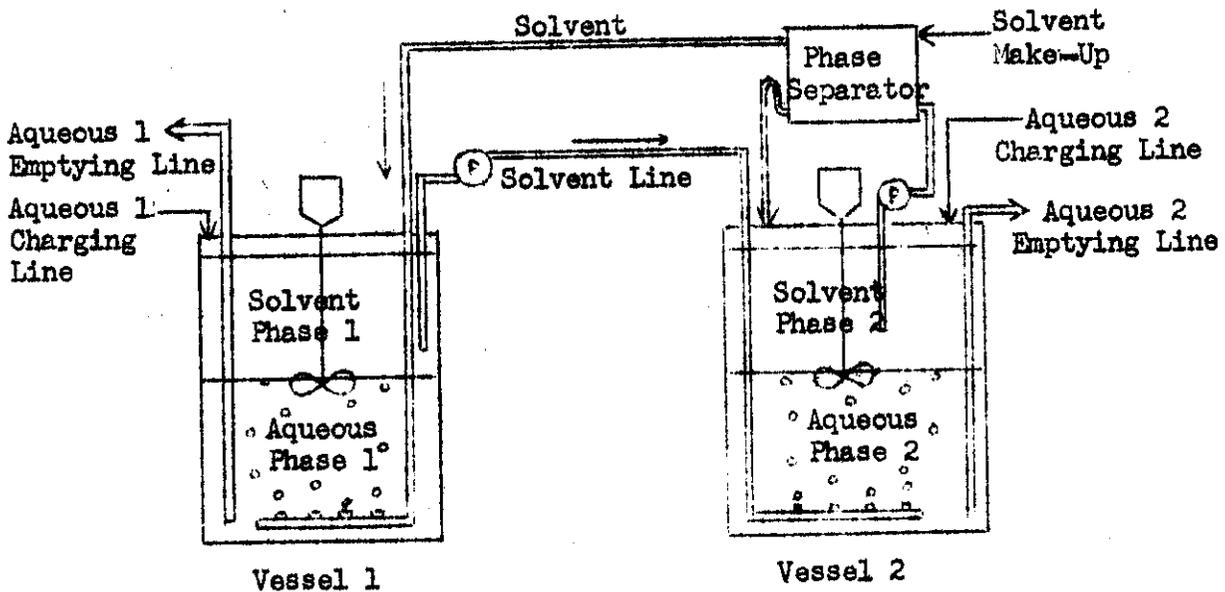
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In batch equipment a high stage efficiency may be attained in each contact. In the Redox process, however, numerous contacts are required to achieve the desired extraction. These contacts present design and operating problems, discussed under 2.2, below, which render the use of continuous equipment for the Redox Plant much more advantageous.

2.11 Closed-cycle extractor

An interesting application of batch equipment is the closed-cycle extractor (sometimes colloquially called a "mouse-trap") shown in the schematic diagram below.

Although such a system is not used in the present Redox Plant it has been considered for the reworking of off-standard plutonium product streams (e.g., concentrated 3BP containing excessively high concentrations of uranium or fission products), and has been used to a limited extent in Redox studies at Oak Ridge National Laboratory.



Closed-Cycle Extractor

When operation of the system is started, Vessel 1 is charged with the aqueous phase containing the solute to be extracted (e.g., above-uranium-specification 3BP treated to reduce Pu to the non-extractable, trivalent state) and Vessel 2 is charged with a second aqueous phase (e.g., water) which, because of its chemical composition, is capable of removing the solute (e.g., uranium) from solvent phase 1. Solvent (e.g., hexone or some other appropriate organic solvent) is next added to each of the tanks above the aqueous phase and the solvent recirculation system and agitators are started.

In Vessel 1, the solvent picks up solute (e.g., uranium) as it passes up through aqueous phase 1. The enriched solvent collecting at the top of the vessel is then pumped into the aqueous phase at the bottom of Vessel 2 where the solute is extracted from the solvent into aqueous phase 2. The solvent phase collected at the top of Vessel 2 is then sent back to Vessel 1. With continued solvent recycling, the system eventually approaches equilibrium and must be emptied and recharged.

2.2 Continuous mixer-settlers

Continuous mixer-settler equipment can be designed to conduct simple, cocurrent multiple, or countercurrent multiple-contact operations. Of these three methods, only the variations of the countercurrent multiple-contact method are discussed below since the simple contact method and the cocurrent multiple-contact method involve a comparatively inefficient use of solvent.

Pilot-plant and small-scale laboratory Redox studies using several types of contactors capable of continuous countercurrent multicontact extraction have been conducted at a number of A.E.C. sites. Various mixer-settler arrangements, each employing different refinements of the same basic principle, have been examined. Among those considered and briefly discussed below are the multiple-vessel mixer-settler, the S.O.D. (Standard Oil Development) mixer-settler, the pump mixer-settler (S.P.R.U. type), and the horizontal extractor.

Since the continuous mixer-settler variations all embody the same basic operating principles, the advantages and disadvantages of the group as a whole are considered.

Among the advantages of mixer-settler equipment are the following:

- (a) High stage efficiencies (i.e., 80 per cent or greater) may be obtained at carefully controlled operating conditions. Therefore, for a solvent-extraction process known from laboratory equilibrium studies to require a given number of stages, mixer-settler equipment may be designed with a fairly high degree of certainty that a sufficient number of stages have been provided.
- (b) Mixer-settler equipment generally requires less plant height (hence a less expensive plant structure) than solvent-extraction columns (see Chapter XIV for solvent-extraction column heights).

A few of the disadvantages of mixer-settler equipment which led to the selection of solvent-extraction columns as the contactor for the Redox Plant are enumerated below:

- (a) Agitators are required for each stage to mix the phases adequately. Careful agitator-speed measurement and control may be required to obtain agitator speeds at which high stage efficiency is not accompanied by emulsion formation.

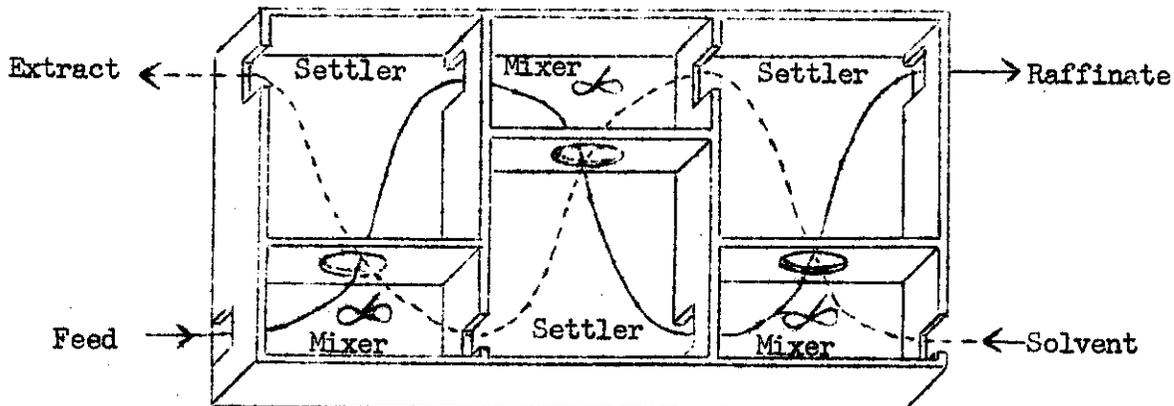
- (b) Either pumps and liquid-level controllers are required to maintain proper interstage flow or, if gravity flow is employed between stages, adequate means must be supplied to maintain the correct hydraulic balance within each system.
- (c) Stuffing boxes and seals for the pumps and agitators are possible leakage sources from which contamination may be spread.
- (d) Complex, costly piping is required to operate and service the pumps, liquid-level controllers, and agitators of some types of mixer-settler units.
- (e) Since mixer-settler units incorporate many agitators and/or pumps, each dependent upon the other for maintaining solvent-extraction performance, it is expected that shutdown periods would be more frequent and greater maintenance effort would be required in a plant incorporating mixer-settlers in place of solvent-extraction columns.
- (f) Although high stage efficiencies have been demonstrated in small-scale mixer-settler units, little is known about scaling-up to plant size units or about the performance of such units over a wide range of processing rates.

2.21 Multiple-vessel mixer-settler

A multiple-vessel mixer-settler is used to perform the countercurrent multicontact extraction discussed under 1.3, above. The mixed phases from the mixer are pumped (or flow by gravity) to the settler, where the phases disengage. The heavy phase in the settler is then transferred (either by pump or by gravity) to the next mixer while the light phase continues its countercurrent path.

2.22 S.O.D. mixer-settler

The mixer-settler developed by the Standard Oil Development Company is an interesting variation of the conventional design. In the compact box-like unit the mixers and settlers are separated by partitions. The differential head required to induce countercurrent flow is produced by the angle of tilt of the box unit (solvent- raffinate end low). Openings or ports are suitably placed in the partitions between the mixers and settlers to permit the proper flow of the phases between stages.



Schematic Diagram (Top Removed)
Showing Flow Through S.O.D. Mixer-Settler

2.23 Pump mixer-settler (S.P.R.U. type)

The pump-type mixer-settler developed by S.P.R.U. (Separations Process Research Unit of the Knolls Atomic Power Laboratory) uses the basic flow pattern shown in the schematic diagram for the S.O.D. mixer-settler in 2.22, above. However, the agitators of the S.P.R.U. unit are designed to give a centrifugal pumping action which mixes the two phases and discharges them into the settling zone. Since the hydraulic head required for stage-to-stage flow is produced by the pump-agitators, the unit is not tilted, as the S.O.D. mixer-settler and horizontal extractor must be, to produce flow.

2.24 Horizontal extractor

In the horizontal extractor the piping between the mixers and settlers is eliminated. Essentially, a multistage unit consists of a slightly inclined tube having agitators located at suitable intervals to provide intimate two-phase contact. Phase separation and counter-current flow take place in the space between the mixing units. The flow of the phases from mixer to mixer is controlled by the angle of tilt.

2.3 Solvent-extraction columns

Columns are used to accomplish solvent-extraction by the counter-current differential extraction method discussed in 1.4, above. Among the advantages of solvent-extraction columns, on which their selection as the type of solvent-extraction equipment to be used in the Redox Plant is based, are the following:

- (a) Packed extraction columns incorporate no moving parts in their design and therefore require a minimum of maintenance on radio-actively "hot" equipment.
- (b) They make effective use of solvent by virtue of their counter-current method of contacting the phases.
- (c) As indicated in Section D, solvent-extraction columns may be operated over adequately large flow ranges with little change in extraction efficiency.

The simplest type of extraction column is the spray column. The dispersed phase is introduced through a suitable nozzle and rises (or falls) through the continuous phase in the column to the phase interface.

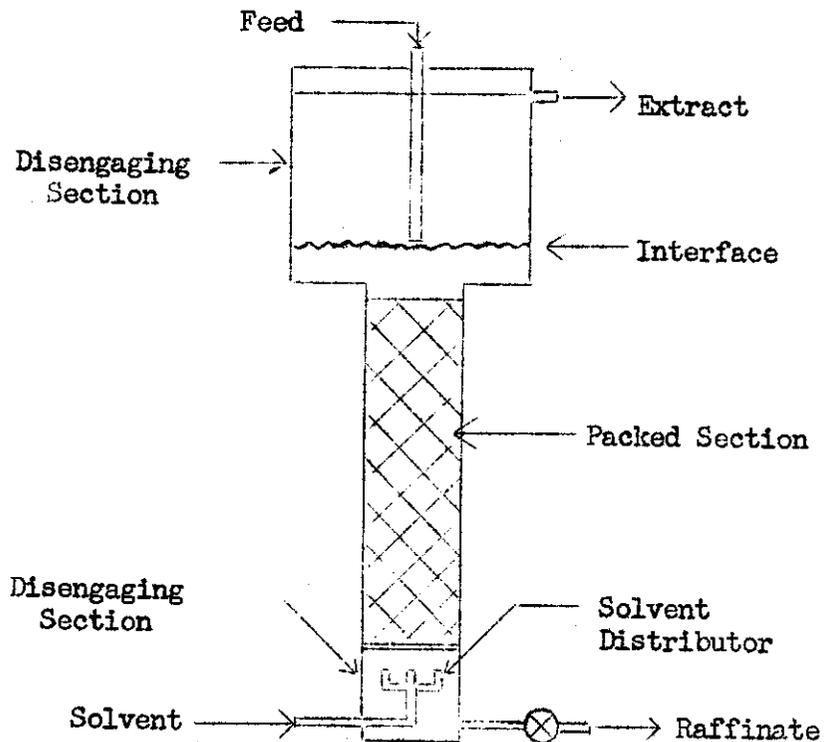
In a packed column more effective extraction may generally be obtained than in an open spray column of the same height. In a packed column the dispersed phase is broken up and forced to follow a tortuous path. The type of packing used for a given application is dependent upon the chemical nature of the system and the processing requirements, while packing depth (packed height) is dependent upon the degree of separation required. The diameter chosen is dependent upon the system and the required processing rate.

The packing is held in position by packing supports. These supports (spirals or gratings) should generally be designed to take up no more column cross section than the packing itself. They also prevent plugging of the influent or effluent lines with packing.

To minimize channeling in packed columns, some method of distributing the dispersed phase is generally used. For the Redox columns it was found that fine dispersion of the organic phase by "shower-head" distributors is not required since subdivision is quickly accomplished in the packing. Therefore, the single tube, three-hole "spider" and seven-hole ring distributors illustrated in Chapter XIV have been specified for the Redox Plant.

The design of both ends of solvent-extraction columns generally incorporates settling zones in which phase disengagement takes place. In the Redox columns the required phase disengagement is accomplished in an enlarged, disengagement section at the top of the column (see the schematic diagram below), and in a section (not enlarged) void of packing at the bottom of the column.

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Schematic Diagram
Packed Solvent-Extraction Column

Packed columns may be designed to operate with either phase continuous by controlling the position of the phase interface in the column. In the Redox Plant columns, the aqueous phase is made continuous because interface-control instrumentation is simpler with the interface at the top of the column, and because, in the Redox columns, the extraction performance with the organic phase dispersed is at least as good as, if not better than, with the aqueous phase dispersed.

Column design details are determined by the nature of the chemical system, the solvent-extraction effectiveness required, and the desired throughput. The considerations which led to the design of the various packed columns used in the Redox Plant are discussed in Section D.

The extraction height required in packed columns may be reduced by using a pulse column. In pulse columns the packing is replaced with a number of spaced perforated plates. In operation the column contents are pulsed up and down through the perforated plates with a net flow of the lighter phase up (and heavier phase down) the column. Although pulse columns are generally shorter than packed columns capable of the same solvent-extraction performance, they are mechanically more complex and therefore require more maintenance.

Pulse columns have been selected as the solvent-extraction contactors for the Metal Waste Recovery (TBP) process. It was possible to fit the pulse columns into the 22-ft. deep cells of the existing 221-U Building.

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This would not have been possible with packed columns without deepening the cells by about 30 ft. At the time of the basic phases of the design of the Redox Plant, pulse columns were in an early, pioneering stage of development. Their appraisal as an alternative to packed columns in the Redox Plant would have to be based on an economic balance of lower building cost vs. the added initial cost of pulse generators and a probably higher maintenance cost.

3. Special Terms

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

3.1 Extraction, stripping, scrubbing

In connection with solvent-extraction in the Redox process, the term extraction is used to describe mass transfer, notably of uranium and/or plutonium, from the aqueous to the organic phase, as, for instance, in the lower section of the IA Column. (See the chemical flowsheet in Chapter I.)

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

The removal of fission products from a uranium or plutonium-bearing organic stream by contacting it with an aqueous stream is referred to as scrubbing. Scrubbing is, for example, carried out in the upper packed section of the IA Column. The removal of small residual amounts of uranium from the plutonium-bearing aqueous stream in the IB Column by contacting with an organic stream is also referred to as scrubbing.

3.2 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 Redox IC Column is a simple column performing only uranium stripping. Other columns are designed to carry out two separate solvent-extraction functions and are therefore referred to as dual-purpose, or compound, columns. The IA and IB Columns are examples of dual-purpose Redox columns. In the lower portion of the IA Column, uranium, plutonium, and some fission products are extracted, while in the upper section fission products are scrubbed from the organic phase. Similarly, in the lower section of the IB Column, uranium is scrubbed from the plutonium-bearing aqueous phase, while in the upper section plutonium is reduced and extracted from the organic phase into the aqueous phase.

3.3 Flooding

Flooding (or complete flooding) in a packed liquid-liquid extraction

column designates a typical behavior of the two liquid phases when flow rates are so high that the two phases cannot pass countercurrently through the column, with the result that dispersed phase leaves the column 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., IAS accompanies the IAP in the Redox IA 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. The local flood may occur in the packed section or below an obstruction, such as a packing support. It may appear as an accumulation of closely packed dispersed-phase globules or as a single large globule forming a phase interface across the column. 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 to flow through the constriction at a rate equal to the dispersed-phase flow rate entering the local-flood 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.

3.4 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 Redox IAP stream could be increased in uranium concentration by using a concentrated aqueous uranium solution in place of aqueous aluminum nitrate for the IAS 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 IA Column a portion of the uranium in the organic phase is refluxed internally, some uranium being stripped from the organic phase by the IAS and carried back down the column where it is again extracted.

3.5 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 Redox 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

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solute material balance made around either end of a packed section. Typical operating and equilibrium lines and their use in evaluating column performance are presented in Section B of this chapter.

3.6 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 contactor 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 Redox columns by the graphical methods described in Subsection B3 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 as presented by Colburn(1):

$$N_s = \frac{\log [(1-P)M + P]}{\log 1/P}, \dots \dots \dots (1)$$

- where P = the extraction factor, L/mV for extraction and mV/L for stripping;
- L/V = slope of the operating line, (weight of aqueous phase per unit time)/(weight of organic phase per unit time) on a solute-free basis;
- m = slope of the equilibrium line, (concentration in the organic phase)/(concentration in the aqueous phase);
- M = X_1/X_2 for extraction and Y_1/Y_2 for stripping -- (if the extractant contains sufficient solute, the values of M become $\frac{X_1 - Y_x/m}{X_2 - Y_x/m}$ and $\frac{Y_1 - X_x m}{Y_2 - X_x m}$ for extraction and stripping, respectively);
- X = the solute aqueous-phase concentration -- subscript 1 designates inlet (feed) concentration, subscript 2 designates raffinate concentration, and subscript x designates extractant concentration;
- Y = the solute organic-phase concentration -- subscript 1 designates the organic feed concentration, subscript 2 designates the organic effluent concentration, subscript x designates the organic extractant concentration.

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For the phase-equilibrium relationships involved in the Redox process (see Figs. V-1, V-3, and V-4), as in the general case, 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.

3.7 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 advantages which are discussed under Subsections C10 and D4 in this chapter.

The number of transfer units in the packed sections of Redox columns may be expressed by the integrals:

$$N_{ow} = \int_{X_2}^{X_1} \frac{dX}{X - X^*}, \dots \dots \dots (2)$$

or

$$N_{oh} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*}, \dots \dots \dots (3)$$

where N_{ow} = the number of "overall water-film" transfer units for transfer from the aqueous to the hexone phase;

N_{oh} = the number of "overall hexone-film" transfer units for transfer from the hexone 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 in diffusing-component concentration to the concentration driving force which causes the transfer between phases.

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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:

$$N_t = \frac{2.3 \log \left[\frac{(1-P)M + P}{1-P} \right]}{(1-P)} \dots \dots \dots (4)$$

If the extraction values for M and P given in Subsection A3.6, above, are substituted in the above equation, N_t becomes N_{ow} . Similarly, if stripping values are substituted for M and P, N_t becomes N_{oh} . 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 "overall" number of transfer units, N_{ow} and N_{oh} , include contributions of both the individual aqueous and hexone-film number of transfer units, which are related by the following equations:

$$1/N_{ow} = 1/N_w + (L/mV) 1/N_h, \dots \dots \dots (5)$$

$$1/N_{oh} = 1/N_h + (mV/L) 1/N_w, \dots \dots \dots (6)$$

where N_w is the number of transfer units required for transfer across the aqueous film and N_h is the number of transfer units required for transfer across the hexone 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 overall values will be likewise independent whenever the terms $(L/mV)1/N_h$ 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 $(L/mV)1/N_h$ and $(mV/L)1/N_w$ become increasingly significant, so that more significant variation of overall transfer-unit values with P might be expected in this region.

3.8 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 A3.6 and A3.7, 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:

$$\frac{H.E.T.S.}{H.T.U.} = \frac{-2.3 \log P}{1-P},$$

where the extraction factor P is, as explained under A3.6, 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.

B. THE OPERATING DIAGRAM (H.E.T.S. AND H.T.U. CALCULATIONS)

1. Introduction

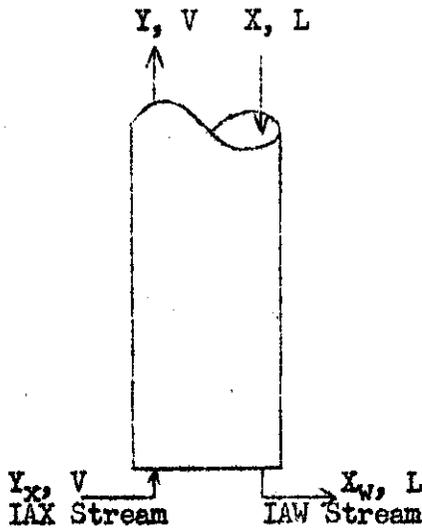
Included in this section is a discussion of the development and use of the uranium operating diagrams in evaluating the solvent-extraction performance of the Redox IA and IC Columns. Examples of the H.E.T.S. and H.T.U. calculation methods used in typical IA and IC Column runs are demonstrated in Subsection B3. Although sample calculations have not been included for all Redox columns, typical Pu and U (and in some cases HNO₃) operating diagrams tabulating the number of transfer units and stages required for flowsheet conditions are included for all Redox columns on Fig. V-6 through V-12 inclusive.

The operating diagrams discussed in this chapter are X - Y plots (similar to the McCabe-Thiele diagrams used in distillation) with X and Y axis values depicting aqueous and organic-phase concentrations, respectively. Each of the diagrams includes an X - Y phase equilibrium line for the diffusing component, and an operating line with influent and effluent compositions labelled. The operating diagrams are used for calculating the number of equivalent theoretical stages or the number of transfer units required for the desired extraction. From the operating diagrams a quantitative or qualitative analysis may be made of the effect which changing phase flow ratios may have upon the difficulty (change in number of stages or transfer units) of the separation. On some of the operating diagrams are included parameters which show the effects of composition changes (e.g., salting strength parameters of Fig. V-1) upon phase equilibrium.

2. Derivation of the Operating Line (IA Extraction Section)

The concentration units used for constructing the IA Column operating diagram were chosen as grams of UNT (uranyl nitrate trihydrate) per gram of non-UNT. By neglecting the change in the grams of non-UNT for either phase (L and V, expressed as grams of non-UNT) due to (a) the slight mutual solubility of hexone and water, (b) the transfer of HNO₃, and (c) the transfer of salts other than UNT (i.e., ANN, Na₂Cr₂O₇, NaNO₃), a linear operating line may be obtained. For the IA Column extraction section, the uranium operating line may be derived from a UNT balance around the bottom end of the column as indicated by the schematic diagram and equations below:

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Values of X and Y, expressed as g. UNT/g. non-UNT, indicate the compositions of the aqueous and hexone phases, respectively.

Values of L and V, expressed as g. non-UNT per unit of time, indicate the weight flow of the aqueous and hexone phases, respectively.

At steady-state operating conditions, the weight of UNT entering the above section of column (over a given time period) via the influent organic and aqueous streams must equal the weight of UNT leaving via the effluent organic and aqueous streams. The weight of UNT carried by each of the four flowing streams in unit time is the product of the flow rate times the UNT concentration: $Y_x V$, $X_w L$, YV , and XL , respectively. Thus a material balance equation for UNT may be written by equating the influent flow of UNT to the effluent flow of UNT, as follows:

$$X(L) + Y_x(V) = Y(V) + X_w(L) \dots \dots \dots (7)$$

Solving Equation (7) for Y gives the following equation, which represents a straight line in terms of Y and X if (L/V) , Y_x , and X_w are constants:

$$Y = (L/V) X + Y_x - X_w(L/V) \dots \dots \dots (8)$$

The use of the above operating line is illustrated under B3.1, below, and on Figure V-1.

Operating diagrams for the other Redox columns are developed in an analogous manner. For the 2A and 2B Columns, however, the volume change of the phases is negligible (less than 1 to 2%), and straight operating lines may be developed on operating diagrams with concentrations expressed as g./l.

3. Example H₂E.T.S. and H₂T.U. Calculations

3.1 Example H₂E.T.S. calculation - IA extraction section

Outlined below is the graphical "stage step-off" method used for

calculating the number of equivalent stages (and the H.E.T.S.) for uranium transfer in the IA Column extraction section. Operating conditions approximate those shown on the HW No. 4 Flowsheet (Figure I-2). A discussion of the stage concept may be found in the preceding section of this chapter while a theoretical discussion of the graphical method may be found in Perry's Chemical Engineers' Handbook⁽²⁾. The following data were obtained during the steady-state period (5 hours) of a typical pilot-plant run, Run 8"-20-U, in an 8-in. diameter column with a 13.9-ft. packed extraction section.

<u>Stream</u>	<u>Volume, Liters</u>	<u>Density, Kg./L.</u>	<u>Weight, Kg.</u>	<u>UNT* Conc., Kg./L.</u>	<u>UNT Weight, Kg.</u>	<u>Non-UNT Weight, Kg.</u>
IAF	1245	1.644	2047	0.898	1118	929
IAS	1249	1.264	1579	0	0	1579
IAX	4558	0.810	4016	0	0	4016
IAP	5121	0.968	4957	0.220	1127	3830
IAW	2214	1.170	2590	0.0012	2.6	2587

*) UNT (uranyl nitrate trihydrate), rather than UNH, is used in the H.E.T.S. determination since an average of only 3 to 3.5 molecules of water accompany one molecule of uranium in transferring between phases.

The scrub-section and extraction-section operating-line equations used below were developed from material balance expressions about the top and bottom of the IA Column, respectively, as discussed in Subsection B2, above. These equations have been plotted on the equilibrium diagram, Figure V-1, which applies for the IA Column operating at HW No. 4 Flowsheet chemical conditions. For definition of the terms used in the equations below the reader is referred to Table V-24, Nomenclature.

$$\begin{aligned}
 \text{Scrub Section: } Y &= (L/V)_{\text{Scrub}} X + Y_p - (L/V)_{\text{Scrub}} X_s \\
 &= (1579/3830) X + (1127/3830) - 0 \\
 &= 0.412 X + 0.294
 \end{aligned}$$

$$\begin{aligned}
 \text{Extraction Section: } Y &= (L/V)_{\text{Extn.}} X - (L/V)_{\text{Extn.}} X_w + Y_x \\
 &= (2587/4016) X - (2587/4016)(2.6/2587) + 0 \\
 &= 0.644 X - 0.000647
 \end{aligned}$$

The equilibrium line chosen from the family of curves on Figure V-1 is dependent upon the aqueous-phase (IAW) total salting strength. For Run 8"-20-U, the IAW total salting strength (sum of the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ concentration and the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salting-equivalent of the NaNO_3 present) was determined to be 377 g./l.

The organic-phase composition at the bottom of the scrub section is found at the intersection of the scrub section operating and equilibrium lines. Since this organic concentration is also the organic-phase concentration at the top of the extraction section, this Y value must also appear at the concentrated end of the extraction-section operating line. Therefore, the extraction-section stage step-off is begun at the point X_{fS} , which is the aqueous-phase concentration at the top of the extraction section. Stages are stepped off in the manner demonstrated on Figure V-1 until the waste composition X_w (which equals 0.001 for this case) is reached. Since 7.8 extraction stages have been stepped off on Figure V-1, and the extraction-section packed height is 13.9 feet, the H.E.T.S. is $13.9/7.8 = 1.8$ feet.

3.2 Example H.T.U. calculation -- IA extraction section

The number of transfer units in the IA Column may be obtained by suitable methods for integrating the expression

$$N_{OW} = \int_{X_2}^{X_1} \frac{dX}{X - X^*}$$

as explained under A3.7, above.

For the IA Column the equilibrium line is of irregular curvature with a point of inflection near the dilute end. Therefore, formal integration of the above equation is not easily accomplished and methods must be used which closely account for the equilibrium-line curvature. A close approximation of the number of transfer units may be obtained using either the graphical integration method illustrated in the example below or a computation method employing Simpson's Rule(2).

The operating and equilibrium lines developed for the H.E.T.S. calculations under B3.1, above, and shown on Fig. V-1 may be used in the example IA extraction-section H.T.U. calculations for Run 8ⁿ-20-U. From the extraction-section equilibrium and operating lines on Fig. V-1, the following values of X and X*, from $X_{fS} = 0.47$ to $X_w = 0.001$, were obtained. (To obtain the value of X* for a given value of X, a constant Y line is drawn through X. The intersection of the constant Y line with the equilibrium line -- read on the X axis -- is the X* value.)

<u>X</u>	<u>X*</u>	<u>1/(X - X*)</u>
0.47	0.218	3.97
0.3	0.153	6.8
0.20	0.113	11.5
0.10	0.067	30.3
0.06	0.041	52.5
0.05	0.028	45.5
0.04	0.017	43.5
0.03	0.011	52.6
0.02	0.0084	86.2
0.01	0.0024	132
0.005	0.0009	244
0.001	0	1000

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The values of X and $1/(X - X^*)$ are plotted as shown on Figure V-2 and the number of transfer units beneath the curve from $X = 0.47$ to $X = 0.001$ is determined by graphical integration to be 10.6. Dividing the 13.9-ft. packed height (Z) by the number of transfer units, the H.T.U. is $13.9/10.6 = 1.3$ ft.

3.3 Example H.E.T.S. calculation -- IC 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 Redox IC Column operating at conditions closely approximating HW No. 4 Flowsheet conditions (see Fig. I-2). The following data were obtained during the steady-state period (approximately 6 hours) of a typical pilot-plant run, Run 5ⁿ-55-CU, made in a 5-in. diameter column packed with 19.6 ft. of 1/2-in. by 1/2-in. stainless steel Raschig rings:

Stream	Liters	Concentrations, Kg./L.			Weight, Kg.				
		Density	UNT	HNO ₃	Total	UNT	HNO ₃	Non-UNT	Non-UNT
							UNT	Non-HNO ₃	
ICF	897	0.916	0.145	0.0013	821	129	1.15	692	691
ICX	291	0.998	5.9×10^{-6}	0	290	0.0015	0	290	290
ICU	356	1.248	0.358	0.0032	444	128	1.13	316	315
ICW	814	0.801	3.0×10^{-6}	0	652	0.0025	0	652	652

The X and Y values used on the HNO₃ operating diagram (Fig. V-4) are expressed as g.HNO₃/g.non-UNT non-HNO₃. These units have been chosen so that straight operating lines may be obtained in cases where appreciable HNO₃ transfer occurs in the column. In the particular example shown, little HNO₃ transfer occurs and g.UNT/g.non-UNT units could be used without introducing a significant error.

The following equation was derived from a UNT balance around the dilute end of the column, and plotted as the operating line on the IC Column uranium operating diagram (Fig. V-3). (For the derivation of a typical IA Column extraction-section operating line, see B3.1, above.)

$$\begin{aligned}
 Y &= (L/V)X - (L/V)X_x + Y_w \\
 &= \left(\frac{290}{652}\right)X - \left(\frac{290}{652}\right)\left(\frac{0.0015}{290}\right) + \left(\frac{0.0025}{652}\right) \\
 &= 0.445X + 1.54 \times 10^{-6}
 \end{aligned}$$

Although the operating line for use on the nitric acid operating diagram (Fig. V-4) may be calculated in a similar manner, a satisfactory nitric acid operating line may be obtained by drawing a straight line through the two points which represent column end conditions (i.e., X_x , Y_w , and X_u , Y_f) on Fig. V-4. The subscripts x, w, u, and f refer, respectively, to the ICX, ICW, ICU and ICF streams.

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$$X_x' = 0$$

$$Y_w' = 0$$

$$X_u' = (1.13/315) = 0.00359$$

$$Y_f' = (1.15/691) = 0.00167$$

In the IC Column both nitric acid and UNT transfer, with both concentrations affecting the equilibrium for each stage. Therefore, the equilibrium concentrations for the various stages in the column do not fall on any given parameter on Figures V-3 and V-4, but must be calculated from stage to stage in the manner described below. It is noted that under HW No. 4 Flowsheet conditions the UNT equilibrium curve is close to the 0 HNO₃-parameter curve. The higher HNO₃ concentration parameters shown on Figure V-3 are of use in connection with the ANL (acid) Flowsheet.

- (a) The first stage on both the UNT and HNO₃ operating diagrams is stepped off at the concentrated end. The first stage on the UNT diagram is drawn, as indicated, from the concentrated-end terminal point (X_u, Y_f) to a point on the nitric acid parameters which corresponds to the concentrated end aqueous-phase nitric acid concentration ($X_u = 128/316 = 0.405$; $Y_f = 129/692 = 0.187$). The corresponding first stage on the nitric acid diagram is drawn from the nitric acid concentrated-end conditions (X_u, Y_f) to a point on the UNT parameters which corresponds to the concentrated-end aqueous-phase UNT concentration.
- (b) Successive stages are stepped off in a similar manner, the aqueous-phase HNO₃ (or UNT) concentration at the end of the preceding stage being used to determine the parameter used for the next stage on the UNT (or HNO₃) operating diagram. Stages are stepped off until the Y_w value is attained or surpassed in the last stage. ($Y_w = 0.0025/652 = 3.84 \times 10^{-6}$.)
- (c) The equilibrium lines on each diagram may be obtained by drawing a smooth curve through the points representing the equilibrium conditions of each stage.
- (d) Because of the wide divergence in slope between the equilibrium and operating lines in the dilute region, linear interpolation on a rectilinear plot does not give a correct value for the last fraction of a stage in the IC Column. Linear interpolation on a logarithmic plot would be more accurate in this case, but the best procedure is to use the equation developed by Colburn, as indicated below:

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$$N_s = \frac{\log [(1-P)M+P]}{\log 1/P}$$

From $Y_i = 1.4 \times 10^{-3}$ to $Y_w = 3.84 \times 10^{-6}$:

$$P = m(V/L) = 4.6 \times 10^{-4} (652/290) = 1.03 \times 10^{-3}$$

$$M = \frac{Y_i}{Y_w} = \frac{1.4 \times 10^{-3}}{3.84 \times 10^{-6}} = 3.65 \times 10^2$$

$$N_s = \frac{\log (0.999)(365) + 0.001}{\log 1/0.00103} = 0.86$$

The total number of stages is therefore the sum of the two stages stepped off on the diagram plus the 0.86 stage calculated above. The H.E.T.S. for the 19.6-ft. packed section is $19.6/2.86 = 6.85$ ft.

3.4 Example H.T.U. calculation -- IC Column

The number of transfer units for uranium in the IC Column may be obtained by suitable methods for integrating the basic expression

$$N_{oh} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*}$$

as discussed under A3.7.

For determining the number of uranium transfer units obtained in the column for Run 5^a-55-CU, the equilibrium and operating lines developed under B3.3, above, and plotted on Fig. V-3 are used.

Since the UNT equilibrium line (Fig. V-3) has considerable curvature at the concentrated end (when plotted on a linear plot), 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 (from $Y_f = 0.187$ to $Y_i = 0.02$) calculated by graphical integration, and the number of transfer units from $Y_i = 0.02$ to $Y_w = 3.84 \times 10^{-6}$ calculated from Colburn's equation(1).

(a) Concentrated-region transfer units by graphical integration

The data (from $Y_f = 0.187$ to $Y_i = 0.02$), used in the graphical integration, have been obtained from the equilibrium and operating lines on Figure V-3. The Y^* value corresponding to a given value of Y may be found by reading the Y -axis value of the intersection of the equilibrium line and a vertical line through the given value of Y . This data is tabulated below:

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<u>Y</u>	<u>Y*</u>	<u>1/(Y - Y*)</u>
0.187	0.059	7.8
0.14	0.024	8.6
0.100	0.0078	10.9
0.08	0.0038	13.1
0.06	0.0015	17.1
0.04	0.00048	25.3
0.02	0.00009	50.2

The above values of Y and 1/(Y - Y*) are plotted on Figure V-5 and the number of transfer units from Y_f = 0.187 to Y₁ = 0.02 is calculated to be 2.40.

(b) Dilute region transfer units by Colburn's equation The following equation, explained in A3.7, is used for the dilute-region transfer unit calculation:

$$N_{oh} = \frac{2.3 \log [(1-P)M + P]}{(1-P)}$$

From Y₁ = 0.02 to Y_w = 3.84 x 10⁻⁶;

P = m(V/L) = (4.6 x 10⁻⁴)(652/290) = 1.03 x 10⁻³

M = Y₁/Y_w = 0.02/3.84 x 10⁻⁶ = 5220

N_{oh} = $\frac{2.3 \log [(0.999)(5220) + 0.001]}{0.999}$ = 8.5

From the calculations in (a) and (b) above, the total number of transfer units from Y_f to Y_w is 10.9, the H.T.U. for the 19.6-ft. packed section is 19.6/10.9, i.e., 1.8 ft.

4. Operating Diagrams for All Redox Columns

In Subsection B3 the use of IA uranium and IC uranium and nitric acid operating diagrams for evaluating the mass-transfer performance of IA and IC Columns during typical HW No. 4 Flowsheet pilot-plant runs is demonstrated. Methods similar to those shown for the example calculations may be used to determine the actual number of stages and transfer units required to obtain flowsheet waste losses. Operating diagrams for typical Redox columns, showing the required number of plutonium and uranium stages and transfer units at various Redox flowsheet conditions, are included in this chapter as Figures V-6 through V-12, inclusive.

4.1 IA Column uranium and nitric acid operating diagrams (Fig. V-6)

Uranium operating diagrams for IA Columns operating at HW No. 4, ORNL June 1949, and ANL June 1948 Flowsheet conditions are shown on Fig. V-6.

Although the required number of uranium stages or transfer units is approximately the same for each of the indicated flowsheet conditions, the shapes of the equilibrium lines used are considerably different. The HW No. 4 Flowsheet line, for example, has a point of inflection at about $X = 0.05$. Hence, with slight changes in operating conditions (higher aqueous-to-organic flow ratio or decreased aqueous-phase salting strength) the operating and equilibrium lines would be closer together and a significantly increased number of stages or transfer units would be required to obtain waste losses below the point of inflection. From the three IA Column uranium diagrams of Fig. V-6 it may be noted that the scrub solution (IAS) quickly approaches its maximum uranium concentration (i.e., approaches the scrub equilibrium and operating line "pinch"). Hence, the proportion of internal reflux of uranium resulting from two or three stages in the scrub section of the IA Column would not be significantly increased by additional scrub stages.

Also shown on Fig. V-6 is the HW No. 4 Flowsheet nitric acid operating diagram. Negative values of X are shown on the plot. This means that the aqueous phase is acid deficient; that is, caustic has been added beyond the amount required to neutralize any free nitric acid in a solution containing aluminum nitrate, uranyl nitrate, and free nitric acid. There are 4 to 5 equivalent stages indicated on the positive acid side on Fig. V-6. The number of positive acid stages can be decreased considerably (from 6 to as little as one equivalent stage) by decreasing the salting strength, or increasing the aqueous-to-organic flow ratio. The number of positive acid stages is also affected by non-flowsheet influent-stream HNO_3 concentrations. The position of the HNO_3 equilibrium line in the dilute range (below $Y' = 0.005$) may possibly be slightly in error since analytical difficulties are encountered in the dilute range.

4.2 IA Column plutonium operating diagram (Fig. V-7)

On Figure V-7 are presented Pu(VI) operating diagrams for IA Columns processing IAF prepared from uranium slugs containing 400 g. Pu/short ton U. This corresponds to a plutonium concentration of 0.21 g. Pu/l. at HW No. 4, ANL June 1948, and ORNL June 1949 Flowsheet conditions. The equilibrium lines are based upon calculations using Chemical Research Section Pu(VI) distribution ratio data and data obtained during countercurrent batch equilibrium studies made for each of the flowsheets with IA-system process solutions containing "cold" uranium. For calculation of the plutonium equilibrium line it was assumed that one Pu(VI) stage is equivalent to one uranium stage; i.e., phase distribution ratio calculations were made for Pu(VI) using the aqueous-phase chemical compositions present in each of the stages of the uranium countercurrent batch studies.

The HW No. 4 Flowsheet Pu(VI) diagram exhibits a point of inflection as does the uranium diagram. Therefore, Pu(VI) waste losses may be appreciably affected by slight changes in column operating conditions.

As indicated on Fig. V-7, a considerably greater number of plutonium (VI) stages and transfer units is required for a column operating at ORNL June 1949 Flowsheet conditions than one operating at HW No. 4 or ANL June 1948 Flowsheet conditions, since the equilibrium and operating lines

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are closer together for the ORNL Flowsheet. The number of stages required may be reduced from 11.9 to 6.5 by increasing the aluminum nitrate concentration of the ORNL Flowsheet IAS from 2.0 to 2.18 M as indicated by the lower right-hand corner diagram in Fig. V-7. A similar reduction in the required number of stages may be made by increasing the IAS to IAF ratio from 1 to approximately 1.3.

4.3 IB Column uranium and plutonium operating diagrams (Fig. V-8)

Uranium and plutonium operating diagrams for the IB Column processing IBF containing 100 g. Pu/short ton U at HW No. 4 Flowsheet conditions are presented on Fig. V-8.

Successful operation of the IB Column is dependent upon the reduction of Pu(VI) or (IV) to Pu(III) by ferrous ion.

On Figure V-8 the operating diagram for plutonium mass transfer in the IB Column is shown. The position of the equilibrium line is dependent upon the aqueous-phase ferrous-ferric ratio and is developed from the distribution ratio equations presented in Chapter IV.

In addition to the mass-transfer phenomenon depicted on the operating diagram, the performance of the IB Column is dependent upon reaction rate, i.e., the reduction of Pu(VI) or (IV) to the aqueous-favoring Pu(III) state (E_a values of roughly 5×10^{-4}) when the Pu and ferrous ion come into contact in the top packed section of the IB Column. Chemical Research Section data(22) have indicated that Pu(VI) is rapidly (in less than 20 seconds) converted to Pu(III) in simulated aqueous IB Column solutions. Also, successful operation of the ORNL pilot-plant IB Column has demonstrated the rapid Pu reduction.

As indicated by the slight change in the scrub-section aqueous-phase plutonium concentration, little plutonium(III) refluxes in the bottom (scrub) section of the IB Column.

4.4 IC Column uranium and nitric acid diagrams (Fig. V-9)

On Figure V-9 are shown the uranium and nitric acid operating diagrams for a IC Column operating at either HW No. 4 or ANL Flowsheet conditions. The operating diagrams were developed using the "stage-to-stage" calculation method explained under B3.3.

The "loop" in the ANL Flowsheet nitric acid diagram is caused by the reflux of nitric acid in the lower (or concentrated) portion of the IC Column. The position of the HNO₃-equilibrium line at the concentrated end is not easily determined. Hence the loop, shown by the dotted line, is, at best, an approximation. Nitric acid does not reflux at HW No. 4 Flowsheet conditions. However, with a slight increase in the ICF (or ICX) nitric acid concentration or a higher ICF to ICX ratio, acid would reflux giving an equilibrium curve of the same general shape as the ANL Flowsheet nitric acid equilibrium line.

4.5 2D and 3D Column uranium and nitric acid operating diagrams

The operating diagrams for the 2D and 3D Columns are very similar to those for the IA Column, discussed under B4.1, above, and are not presented separately.

4.6 2E and 3E Column uranium and nitric acid operating diagrams

Operating diagrams are not shown for the HW No. 4 Flowsheet 2E or 3E Columns. Although these columns operate with different chemical compositions and flow ratios, their operating diagrams are developed in the same manner as the IC diagram. The number of stages and transfer units required for the 2E and 3E Columns have been listed on the table in Subsection B5, below.

4.7 2A and 3A Column plutonium and nitric operating diagrams (Fig. V-10)

The 2A Column plutonium operating diagram for HW No. 4 Flowsheet, shown on Figure V-10, is based upon the mass transfer of Pu(IV). Fewer stages or transfer units are required to obtain flowsheet waste losses if plutonium is present in the 2A Column in the Pu(VI) state. By employing cross-over oxidation techniques (i.e., hot crossover) which insure quantitative conversion of plutonium to Pu(VI), a given plutonium yield in the 2A Column is more easily attained. However, conversion of all Pu to Pu(VI) in the 2A Column makes Pu stripping in the 2B Column more difficult.

Operating diagrams have not been indicated for the 3A Column. Its operating diagram is quite similar to the 2A Column diagram. Since the 3AX flow rate is only 7/8 of that of 2AX, the slope of the operating line is correspondingly greater for the 3A Column. In addition, the salting strength and nitric acid concentration of the 3AF (0.36 M HNO₃) is higher than the 2AF (0.10 M HNO₃), thereby raising the position of the 3A extraction-section equilibrium line. Since the equilibrium and operating lines for the 3A Column are both raised above the 2A lines by about the same amount, there is little difference in the stage or transfer-unit requirements for the 2A and 3A Columns.

4.8 2B and 3B Column plutonium and nitric acid operating diagrams (Fig. V-11)

The plutonium operating diagram for a 2B Column operating at HW No. 4 Flowsheet conditions (shown on Fig. V-11) is based upon the mass transfer of Pu(VI). Since the equilibrium relationships for Pu(IV) stripping are more favorable than for Pu(VI) stripping, fewer stages and transfer units are required to obtain flowsheet waste losses if the 2BF contains Pu(IV).

Operating diagrams have not been shown for stripping in the 3B Column. The 3B diagram is of the same general type as the 2B diagram. However, since the nitric acid concentration of the 3BF (0.26 M HNO₃) is higher than that of 2BF (0.17 M HNO₃), and since the organic flow is lower in the 3B Column (about 7/8 of that in the 2B Column), the positions of both the

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operating and equilibrium lines are raised slightly with a net increase in the number of stages or transfer units required in the 3B Column. As indicated in Subsection B5, 3.2 stages or 8.2 transfer units are required to attain the flowsheet 0.05 per cent Pu loss in the 3B Column while 2.9 stages or 7.9 transfer units are required to attain the same loss in the 2B Column.

4.9 Operating diagrams for the IS Column (Fig. V-12)

The IS Column may be required for recovery of excessive uranium and/or plutonium losses from off-standard waste streams under a variety of circumstances. In each case when the need for reworking an off-standard stream arises the selection of the operating conditions is considered a separate problem. In the selection of conditions for adequate recovery and decontamination, special attention must be paid to the nitric acid operating diagram. The operating conditions should not result in sufficient internal reflux of nitric acid to permit the build-up of hazardous concentrations of nitric acid in the bottom of the scrub section and top of the extraction section (the part of the system most susceptible to HNO₃ build-up). If the build-up of organic-phase nitric acid concentrations above 1.0 M anywhere in the system is avoided, the formation of potentially reactive HNO₃-hexone mixtures will be precluded by an adequate margin. For further discussion of the selection of IS rework operating conditions, reference is made to Document HW-14756(17).

Shown on Fig. V-12 are plutonium and uranium operating diagrams for the IS Column operating at a set of typical rework (HW No. 3 Flowsheet) conditions. The waste losses used on the diagrams are 2% of the uranium and plutonium present in the ISF instead of the approximately 0.5% losses shown on HW No. 3 Flowsheet. The allowable losses in the IS Column are subject to considerable variation with the frequency of rework. For example, if the frequency of rework is less than the design basis, the allowable losses in the ISW may possibly be increased, depending, of course, upon economic considerations.

As indicated on the plutonium operating diagram of Fig. V-12, the plutonium extraction attained in the IS Column is dependent upon the valence state of the plutonium in the ISF. Considerably fewer than the 3.8 stages or 5.0 transfer units shown for Pu(IV) transfer are required if the plutonium is in the six valence state. Since an H.T.U. value of 5 ft. is not unlikely in the IS Column (optimum H.T.U. values of 3.5 to 4 ft. obtained in a 3-in. diameter pilot-plant IS Column) most of the 28-ft. extraction-section packed height would be used to attain flowsheet losses if plutonium is processed as Pu(IV). Additional extraction safety factor may be obtained by converting ISF plutonium to Pu(VI).

5. Equivalent-Stage and Transfer-Unit Requirements for All Redox Columns

As discussed earlier in this chapter (under A3.6 and A3.7), the number of stages and transfer units are measures of the difficulty of the extraction duty performed by a solvent-extraction contactor. The number of stages or transfer units required to attain flowsheet waste losses for uranium and plutonium extraction in the various Redox columns have been

determined from operating diagrams similar to Figures V-6 through V-12, inclusive, discussed in Subsection B4. The number of stages and transfer units required for all Redox columns operating under the conditions of various Redox flowsheets are summarized in the following table:

Number of Equivalent Stages and Transfer Units
for All Redox Solvent-Extraction Columns

Column	Redox Flowsheet	Waste Loss, % of U or Pu in IAF		No. of Equiv. Stages		No. of Transfer Units	
		Pu	U	Pu	U	Pu	U
IA Extn. Sect. (a)	HW No. 4	0.2	0.2	8.5	8.3	11.4(b)	11.3(b)
IA Extn. Sect. (a)	ORNL June '49	0.2	0.2	11.9	8.8	14.9(b)	12.1(b)
IA Extn. Sect. (a)	ANL June '48	0.2	0.2	9.5	11.2	12.4(b)	14.0(b)
IB Scrub Sect. (d)	HW No. 4 or ORNL	—	3×10^{-5}	—	4.5	—	11.6(b)
IC	HW No. 4	—	0.05	—	2.4	—	7.8(c)
IC	ORNL	—	0.05	—	2.4	—	7.8(c)
IC	ANL	—	0.05	—	4.1	—	8.4(c)
2E and 3E	HW No. 4 or ORNL	—	0.05	—	2.1	—	7.6(c)
2A (Based on PuIV)	All three	0.2	—	3.7	—	7.5(b)	—
2B (Based on PuVI)	All three	0.05	—	2.9	—	7.9(c)	—
3A (Based on PuIV)	All three	0.2	—	3.6	—	7.5(b)	—
3B (Based on PuVI)	All three	0.05	—	3.2	—	8.2	—
IS Rework (Extn. Sect.)	HW No. 3	0.1(d)	0.1(d)	3.8	3.0	5.0	5.0

- Notes: (a) Also applies for uranium in the 2D and 3D Columns.
 (b) "Overall aqueous-film" basis.
 (c) "Overall organic-film" basis.
 (d) % of the U and Pu content of ISF.

The numbers of equivalent stages and transfer units listed in the above table are for the nominal flowsheet conditions and may vary by as much as $\pm 30\%$ with relatively minor changes in salting strength and flow ratio. For example, a 20 g./l. increase in the total ANN salting strength present in the extraction section of a IA Column operating at HW No. 4 Flowsheet conditions decreases the required number of theoretical uranium stages from 8.3 to 6.1.

From the required number of stages or transfer units, as tabulated in the above table, the packed height required to attain the desired U or Pu losses in each column may be calculated if values of H.E.T.S. or H.T.U. are known which are applicable to the operating conditions for each column. Values of the H.E.T.S. or H.T.U. are affected by a number of variables as discussed in the following section (Section C). Experimentally determined H.E.T.S. and H.T.U. values for uranium transfer in the Redox columns appear in Section D.

C. REDOX EXTRACTION COLUMNS; VARIABLES AFFECTING EXTRACTION AND CAPACITY

The performance of a packed column may be evaluated in terms of its mass-transfer effectiveness and its processing capacity. The variables affecting column performance may be divided into two categories, physical and chemical, with the former pertaining to the physical structure of the column, packing size, flow rates, and temperature, and the latter referring to the chemical composition of the process solutions. The chemical variables for all Redox columns and their effects on phase-equilibrium relationships are discussed in Chapter IV. The important physical variables and the general trends of their effects are discussed below. More detailed information concerning specific columns may be found in subsequent sections of this chapter.

1. Variation with Packing Size

The flooding capacities of Redox columns increase considerably with packing size. Under HW No. 4 Flowsheet conditions, the complete flooding capacities of the IA Column extraction section, IB Column scrub section, and IC Column are approximately 2.0, 1.5, and 1.7 times greater, respectively, when packed with 1-in. Raschig rings than the same columns packed with 1/2-in. rings.

Optimum H.T.U. values in columns packed with 1-in. rings are only slightly (about 0 to 30 per cent) higher than those with 1/2-in. rings. However, at higher processing rates, i.e., at rates above about 70% of the flooding capacity of 1/2-in. rings (sum of aqueous and hexone flow rate equal to approximately 1200 gal./(hr.)(sq.ft.)), lower H.T.U. values are obtained in IA, 2D, and 3D Columns packed with 1-in. rings instead of 1/2-in. rings.

2. Variation with Flow Rate

Plots of H.T.U. as the ordinate vs. flow rate as the abscissa are convex downward for all Redox columns. The curves become flatter with increased packing size, and for plant-size Redox columns packed with 1/2-in. or 1-in. Raschig rings, the minimum H.T.U. generally occurs at approximately 30 to 60 per cent of the complete flooding capacity. H.T.U. plots for all Redox columns are attached as Figures V-14 to V-21, and are discussed in Section D, below.

3. Variation with Column Diameter

In pilot-plant studies in 5.05-in. and 8.42-in. columns there was no appreciable difference either in complete flooding capacity or in H.T.U. which could be attributed to the difference in column diameter. However, small H.T.U. scale-up factors (about 0 to 25 per cent) were noted in going from 3-in. to 8-in. I.D. columns, both packed with 1/2-in. by 1/2-in. stainless steel Raschig rings.

4. Variation with Packed Height

Experimental studies in pilot-plant IA, IB, and IC Columns with packed heights varying from 11 to 20 ft. indicated a definite increase of H.T.U. with packed height. The H.T.U. for a 20-ft. packed height was approximately 10 to 25 per cent higher than for a 14-ft. height. This might have been due to the fact that, as packed height increased, a greater portion of the total packed height operated on very dilute uranium or it may have been due, at least in part, to poorer distribution of the phases (channeling) as the packed height increased. No effect on the flooding capacity attributable to packed height has been noted.

5. Phase-Disengaging Sections

In the Redox columns it has been found necessary, particularly at column volume velocities (sum of both phases) exceeding about 900 gal./ (hr.)(sq.ft.), to incorporate enlarged top sections in the column design to minimize the entrainment of aqueous phase in the organic effluent.

The arbitrarily chosen Redox column enlarged top section — a 5-ft. section (approx. 3 ft. of organic phase above the interface) with double the nominal packed-section diameter — has proven satisfactory for minimizing entrainment in experimental column studies at flow rates expected to exceed those used in the Redox Plant columns. At column flow rates (sum of both phases) from 300 to 2500 gal./ (hr.)(sq.ft.), residence times for organic in the enlarged top sections range from 25 to 3 minutes, respectively.

Enlarged disengaging sections at the base of the columns have been found unnecessary. Disengagement of organic droplets from the aqueous phase is accomplished satisfactorily in an unpacked 15 to 21-in. high section at the base of the column. (See Chapter XIV for dimensions of specific columns.) Residence times for aqueous phase in the bottom disengaging sections of the columns, for flow rates (sum of both phases) of 300 and 2500 gal./ (hr.)(sq.ft.), range from approximately 10 to 0.5 min., respectively.

Since entrainment from the Redox Plant Columns is, for most operating conditions, expected to be less than 0.1 per cent, the upper processing capacities of the columns are limited by the flooding capacities of the packing rather than by entrainment.

6. Influent-Stream Distributors

Development studies have shown that plant-size Redox columns packed

with 1/2-in. or 1-in. Raschig rings do not require elaborate influent-stream distributing devices. Extraction performance is as good using simple three-hole organic-stream distributors (see details in Chapter XIV) as with multi-hole "shower head" distributors. The hexone velocity emerging from the three-hole distributors is not critical, satisfactory performance having been realized over a range from 0.05 to 5 ft./sec. Single pipe distributors are adequate for the aqueous influent streams. An enlargement of the column diameter at the IAF feed inlet point was found to offer no improvement either in extraction or column throughput capacity.

As a precaution, a hollow-cone hexone-phase mixing device is provided at the IBF feed point (see Chapter XIV), but this device is of unproved value since development studies in plant-size columns were conducted with plutonium absent.

7. Effects 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. Data for these physical properties of the solutions in all Redox columns are generally quite favorable, as evidenced by the lower H.T.U. values and higher flooding capacities of the Redox columns as compared with the tributyl phosphate-hydrocarbon diluent systems, for example. 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.

7.1 Density difference between phases

For a given size and type of tower packing, 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 all Redox 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.

7.2 Viscosity

Low viscosity of the continuous phase generally favors high flooding capacity, the flooding capacity being proportional to about the -0.2 power of the viscosity. Viscosities in the Redox streams are relatively low, ranging from ca. 0.9 to 3.5 centipoises in aqueous streams, and from 0.56 to 1.0 centipoise in hexone streams.

7.3 Interfacial tension

Low interfacial tension generally favors high flooding capacity. (The flooding capacity is proportional to about the -0.1 power of the interfacial tension.) Interfacial tensions between hexone and aqueous

phases of the Redox systems are unusually low, ranging from approximately 5 to 10 dynes/cm., compared with approximately 16 dynes/cm. for the TBP Waste Metal Recovery system.

7.4 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 0.6 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.

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 Waste Metal Recovery or Purex process columns.

8. Effects of Alternative Flowsheets

Differences between ANL, ORNL, and HW Flowsheets actually have very minor effects on the flooding capacity and the optimum H.T.U. values obtained. No significant differences in the flooding capacity are noted for any given Redox column operating under the conditions of the various flowsheets. As indicated in the tabulation below, the optimum H.T.U. values are practically the same (within experimental error) for the various flowsheets.

Optimum H.T.U. Values for Various Flowsheets

(Data obtained in 5.05 and 8.42-in. I.D. Columns packed with 1/2-in. Raschig rings.)

Flowsheet	Optimum H.T.U., Ft.	
	IA Column	IC Column
ANL June 1948	1.1	1.8
ORNL June 1949	1.2	1.7
HW No. 4	1.2	1.7

Although the optimum H.T.U. values are much the same, there are slight differences in the positions of the H.T.U. vs. flow rate curves for the ANL and the acid-deficient flowsheets (see Figure V-14 and V-17).

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The number of transfer units required to obtain the same uranium waste loss for any particular Redox column operating at ANL, ORNL, and HW No. 4 Flowsheet conditions varies only about $\pm 10\%$ as indicated in Subsection B5.

The number of stages required to obtain the same uranium waste loss for a particular column varies considerably with the flowsheet. This is particularly true for the IC, 2E, and 3E Columns. For a IC Column operating at ANL Flowsheet conditions approximately 4.1 stages are required to attain 0.05% U waste loss, while 2.4 stages are required to attain the same loss in an ORNL or HW Flowsheet IC Column. This difference in the required number of stages is due to the higher nitric acid concentration in an ANL IC Column; the higher concentration raises the position of the uranium equilibrium line (higher uranium distribution ratios, E_d) producing a higher value of the extraction factor, P (see Subsection 10, below).

9. Effect of Aqueous-to-Organic Flow Ratio

H.T.U. values for Redox columns are lower when the volume flow of the continuous aqueous phase, L, is less than the volume flow of the dispersed hexone phase, V. This is illustrated by the following H.T.U. values which represent approximate optimum values for 1/2-in. rings in each column:

<u>Redox Column</u>	<u>Volume Flow Ratio, L/V</u>	<u>H.T.U., Ft. (a)</u>
IB (Scrub Section)	0.2	1.5
IC	0.3	1.7
IA (Extraction Section)	0.5	1.2(b)
2A (Extraction Section)	1.0	2.6
IS Rework (Extraction Section)	5.0	3.5

Notes: (a) "Overall aqueous-film" H.T.U. values for all except the IC Column which is an "overall hexone-film" H.T.U. value.

(b) Extraction in IA is better than in other Redox columns, apparently due to fortuitous physical properties.

This trend to lower H.T.U. values as the dispersed-phase flow becomes relatively greater than the continuous-phase flow is believed to be associated with the presence of more dispersed-phase globules (and hence more interfacial area for mass transfer) at the higher dispersed-phase flow rate. One of the requirements for the best extraction performance, however, is that the packing must be preferentially wet by the continuous rather than the dispersed phase.

10. Effect of the Extraction Factor on the H.E.T.S.

The extraction factor, P , has been defined under A3.6, above, as L/mV for extraction and mV/L for stripping (i.e., the slope of the operating line divided by the slope of the equilibrium line for extraction, and the reciprocal of this value for stripping). A table of nomenclature appears at the end of this chapter. H.T.U. values for all Redox extraction columns have been found not to vary significantly with changes in the value of the extraction factor. However, since the H.E.T.S. and the H.T.U. are related directly through the value of the extraction factor, the H.E.T.S. varies as much as four-fold among various Redox columns due to changes in extraction factor. This is illustrated by the following data:

<u>Redox Column</u>	<u>Average Extraction Factor, P</u>	<u>H.T.U., Ft.</u>	<u>H.E.T.S., Ft.</u>
IA (Extraction Section)	0.5	1.2	1.8
IB (Scrub Section)	0.05	1.5	4.9
IC	0.01 to 0.05	1.7	6.6

The H.E.T.S./H.T.U. ratios, above, agree closely with ratios predicted by the theoretical equation, given under A3.8, indicating that the 3.7-fold variation in H.E.T.S. between the IA and IC Columns is due to the much smaller average extraction factor in the IC Column.

11. Effect of Temperature on Extraction

Distribution ratio data (see Chapter IV) for plutonium and uranium indicate that the phase-equilibrium relationships for stripping from the organic to the aqueous phase are favored by an increase in temperature. Also, as the temperature is increased the Schmidt number decreases (see C7.4, above) and it might be expected that the H.T.U. in the IC Column would be decreased with increased temperature. However, studies in an 8.42-in. diameter IC Column showed no significant difference in H.T.U. when the temperature of the feeds was increased from 19°C. to 33°C.

12. Effect of Packing Surface Conditioning

H.T.U. values approximately double the normal values have been observed for a IA Column packed with 1/4-in. by 1/4-in. stainless steel Raschig rings which had been degreased and pickled in 60 per cent nitric acid for 3 hours at 50°C. The H.T.U. gradually decreased to normal after the packing was exposed to the IA system for 2 to 4 days (19). No such surface effects have been observed in Redox studies using 1/2-in. or 1-in. Raschig ring packing which had been pickled as above.

D. REDOX H.T.U., H.E.T.S., AND FLOODING DATA; DEVELOPMENT OF PLANT COLUMN SPECIFICATIONS

1. Introduction

As discussed above in Section C, the extraction performance of a packed column is conveniently measured in terms of either the Height Equivalent to a Theoretical Stage (H.E.T.S.) or the Height of a Transfer Unit (H.T.U.). Numerical values of the H.E.T.S. or the H.T.U. are a function of the system employed, the geometry of the packed column, and a number of operating variables as discussed in general terms in Section C.

Knowing the number of theoretical stages or transfer units required in each Redox column based on the operating diagrams presented in Section B, the packed height required for recovery of uranium and plutonium in each Redox column may be calculated by multiplying the number of transfer units (or equivalent stages) by the H.T.U. (or H.E.T.S.) values applicable for each column. The purpose of this section is to present H.T.U. data obtained experimentally in Redox plant-size columns based on studies made with unirradiated uranium. Also presented are flooding capacity data for each column and the methods of employing the H.T.U. and flooding data in establishing column diameters and packed heights for uranium and plutonium recovery in all Redox columns.

Since the H.T.U., rather than the H.E.T.S., concept was actually used in establishing design specifications for the Redox columns, the bulk of the experimental data presented in this section, and the methods of establishing packed heights, are based on transfer units rather than equivalent stages. H.E.T.S. data for the IA extraction section and the IC Column are presented for comparison in Subsection 4, below.

Design criteria for the scrub sections of decontamination columns are presented in Section E.

2. H.T.U. and Flooding Capacity Data

Total flooding capacities (designated on the plots simply as "flooding") and H.T.U. data for uranium transfer in Redox plant-size columns packed with both 1/2-in. by 1/2-in. by 1/32-in. wall and 1-in. by 1-in. by 1/32-in. wall stainless steel Raschig rings are presented graphically on Figures V-14 through V-21. These data were obtained in solvent-extraction studies (using unirradiated uranium) carried out at chemical conditions closely simulating those of the various Redox flowsheets. For additional information the reader is referred to references (11), (14), (15), (19), (20), and (21), listed at the end of this chapter.

Physical properties, phase-equilibrium relationships, and phase flow ratios are fairly well fixed for each Redox column by the chemical flowsheet conditions. Consequently, if the column geometry is fixed, as in solvent-extraction studies in a given diameter column with a given size and height of packing, the remaining primary variable which affects the

extraction performance is the sum of the phase flows through the column. This is expressed in this chapter as volume velocity in gal./hr. (sq.ft. of column cross-sectional area), the flow being the sum of both the aqueous and organic phases.

Figures V-14 through V-21 are plots, for the various Redox columns, of the H.T.U. as ordinate vs. the volume velocity (sum of both phases) as the abscissa. Reference to the above plots for plant-size Redox columns packed with 1/2-in. or 1-in. stainless steel Raschig rings reveals that all of the curves are convex downward, and that the minimum H.T.U. generally occurs somewhere in the range from 30 to 60 per cent of the complete flooding capacity for the packing. The H.T.U. vs. volume velocity curves for 1-in. packing are generally somewhat flatter than corresponding curves for 1/2-in. packing, and the minimum H.T.U. for 1-in. rings is generally about 10 to 20 per cent higher than the minimum value for 1/2-in. rings. Likewise, the minimum for the larger packing occurs at a higher volume velocity. Minimum H.T.U. values (based on uranium transfer) for all Redox columns are summarized below for the various Redox flowsheets, and for different sizes of packing:

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H.T.U. AND FLOODING CAPACITY DATA

Based on uranium transfer in 5.05-in. and 8.42-in. diameter columns packed with 19 to 20 ft. of Raschig rings of the sizes indicated below.

Redox Column	Flowsheet	Packing Size, In.	Minimum H.T.U., Ft.	% of Flooding At Min. H.T.U.	Complete Flooding Capacity, Gal./ (Hr.) (Sq. Ft.), Sum of Both Phases
IA (Extn. Sect.)	HW No. 4	1/2	1.3	40	1850 ± 200
	HW No. 4	3/4(a)	1.4	50	2700
	HW No. 4	1	1.5	50	3550 ± 150
	ORNL(b)	1/2	1.2	ca. 30	>1650
	ANL(b)	1/2	1.1	60	1900 ± 50
IB (Scrub Sect.)	(All)(c)	1/2	1.5	65	2000 ± 200
	(All)(c)	3/4(a)	1.5	55	2700
	(All)(c)	1	1.6	55	ca. 3500
IC	(d)	1/2	1.7	40	1800 ± 200
	(d)	3/4(a)	1.9	30	2400
	(d)	1	2.1	15	3000 ± 100
	ANL(b)	1/2	1.8	60	1500 ± 50
2D and 3D(e) (Extn. Sect.)	HW No. 4	1/2	1.3	45	1850 ± 200
	HW No. 4	3/4(a)	1.4	50	2700
	HW No. 4	1	1.5	50	3500
2E and 3E(e)	(d)	1/2	1.4	35	1800
	(d)	3/4(a)	1.6	35	2600
	(d)	1	1.7	40	>3500
2A and 3A (Extn. Sect.)	(All)	1/2	2.6	30	1800 ± 100
	(ALL)	3/4(a)	2.8	45	2600
2B and 3B	(All)	1/2	2.4	50	1550 ± 50
	(all)	3/4(a)	2.6	55	2100
IS Rework (Extn. Sect.)	HW No. 3	1/2(f)	4.2	80	2450 ± 50
	HW No. 3	3/4(a)	5.0	80	3000
IO	(All)	1	2.1	35	3050 ± 100

- Notes: (a) Since 3/4-in. rings were not tested, these values have been estimated by interpolation.
- (b) The ORNL June 1949 Flowsheet is referred to simply as ORNL and the ANL June 1948 Flowsheet as ANL.
- (c) Chemical and flow conditions for the IB Column scrub section are almost identical in the ANL, ORNL, and HW No. 4 Flowsheets.
- (d) Data apply to the ORNL or HW No. 4 Flowsheets.
- (e) Limited data for the 2D and 2E Columns are extended by the analogy of these columns to the IA and IC Columns, respectively.
- (f) IS Column data are based on studies made in a 3-in. diameter column.

As shown in the table above, minimum H.T.U. values range from 1.1 ft. for the IA Column extraction section to 5.0 ft. for the IS Column extraction section operating at rework conditions. The trend is from low to high H.T.U. values with increase in the aqueous-to-organic volume flow ratio, as discussed in Subsection C9, above. Most of the H.T.U. values lie in the narrow band from 1.5 to 2.5 ft.

For each column, the optimum H.T.U. values obtained under the conditions of the three flowsheets are approximately equal.

The optimum H.T.U. values for 1-in. Raschig rings are usually less than 20% higher than those for 1/2-in. rings and occur at higher values of volume velocity. H.T.U. values for 3/4-in. rings have been estimated, by linear interpolation, between those for 1/2-in. and 1-in. rings.

Flooding capacities, expressed as gal./(hr.)(sq.ft.), range from approximately 1700 to 2400 for 1/2-in. rings, from approximately 2200 to 3000 for 3/4-in. rings, and from approximately 3000 to 3700 for 1-in. rings. The increase in ring size from 1/2 to 1 in. is thus accompanied by a 70 to 100 per cent increase in flooding capacity.

As indicated by the flowsheet, all other Redox columns bear a close resemblance to one of the first extraction cycle columns (IA, IB, or IC). The resemblances are reflected in the flooding capacities of the IB Column scrub section and 2A Column extraction section as well as in the flooding capacities of other pairs of similar columns.

IB Column scrub-section studies made with "shower head" (multi-hole) type scrub introduction devices indicated that the presence of ferrous sulfamate reduced flooding capacities to approximately 75 per cent of the values obtained in the absence of ferrous sulfamate (Figure V-16). The presence of ferrous sulfamate or of ferrous ammonium sulfate and sulfamic acid was without significant effect on the flooding capacity of the 2D Column extraction section.

3. Development of Plant Column Specifications

H.T.U. data presented on the attached Figures V-14 through V-21 provided the experimental background for specifying the diameters and packed heights for uranium and plutonium recovery in the various Redox solvent-extraction columns. Detailed dimensions of all Redox solvent-extraction columns appear in Chapter XIV.

Column diameters and packing sizes were selected so that each column would operate in the range of optimum performance (i.e., lowest H.T.U. values) over the range of processing rates specified as the design basis. As discussed in Chapter XIV, this design basis specified a sustained production rate of from 1 to 2.5 short tons of irradiated uranium per day at an 80 per cent operating efficiency (giving instantaneous rates ranging from 1.25 to 3.1 tons per day). Approximately 20 per cent additional capacity for handling rework streams is provided in most columns, as discussed further below.

On the basis of solvent-extraction studies in most of the Redox columns using both 1/2-in. by 1/2-in. by 1/32-in. wall and 1-in. by 1-in. by 1/32-in. wall stainless steel Raschig rings, 1/2-in. rings were originally specified for Columns IA, IS, IB, 2D, 3D, 2A, 3A, 2B, and 3B, while 1-in. rings were specified for Columns IC, 2E, 3E, and IO. However, because of a subsequent interest in increasing the uranium-processing capacity of the Redox Plant to an as-yet-unspecified rate above the original sustained production capacity of 2.5 tons/day (3.1 tons/day, instantaneous rate), 3/4-in. by 3/4-in. stainless steel Raschig rings are being procured at the time of this writing for installation in all columns which would limit the plant capacity if packed with 1/2-in. rings. For these reasons, estimated performance data for 3/4-in. Raschig rings are listed below along with experimental data for 1/2-in. and 1-in. rings.

The following subsections present data on the expected rangeabilities and complete flooding capacities for various sizes of Raschig rings in each of the Redox extraction columns and illustrate how the respective packed heights were selected to attain the uranium and plutonium waste losses shown for each column on the chemical flowsheets in Chapter I. Similar design bases for the scrub sections of the decontamination columns (IA, 2D, 3D, 2A, 3A, IS) are presented in Section E of this chapter. To provide a convenient comparison of the capacities of the various Redox extraction columns with alternative sizes of packing, Table V-13 summarizes the rangeability for most of the columns (at HW No. 4 Flowsheet conditions) using 1/2-in., 3/4-in., and 1-in. stainless steel Raschig rings. Since the 4-in. diameter 2A and 3A Columns and the 3-in. diameter 2B and 3B Columns are considered too small for 1-in. rings, the above table does not include the use of 1-in. rings in Columns 2A, 3A, 2B, and 3B. As pointed out above, the rangeabilities of the various columns using 3/4-in. rings are not based on experimental data, but on interpolations between data for 1/2-in. and 1-in. rings (and extrapolations in the bases of Columns 2A, 3A, 2B, 3B, and IS).

3.01 The IA Column extraction section

Since both plutonium and uranium are to be extracted in the IA Column extraction section, with losses in the IAW (waste) stream not exceeding 0.2 per cent of either the plutonium or the uranium in the IAF (feed) stream, the packed height in this section must be adequate for recovery of whichever of these two materials is the more difficult to extract. Although the simultaneous extraction of uranium and plutonium has been demonstrated in pilot-plant columns at Argonne and Oak Ridge National Laboratories (as well as in the mixer-settler banks at Knolls Atomic Power Laboratory), plutonium was not present during "cold" solvent-extraction studies in small-scale and plant-scale columns at Hanford Works. Consequently, H.T.U. data for plutonium extraction in plant-size columns are not available. However, because of similarities in the chemical nature and solvent-extraction behavior of plutonium to these properties for uranium, it is assumed that column geometries and operating rates which result in optimum solvent-extraction performance for uranium will also be at least near optimum for plutonium. It is further assumed that scale-up factors for plutonium extraction (i.e., the increase in H.T.U. with increasing column diameter) will be of a similar magnitude to those found for uranium extraction.

The following uranium extraction data, appropriate to the plant IA extraction section (6.5-in. I.D., 28-ft. packed height), are taken from experimental studies in 5.05-in. and 8.42-in. diameter columns, data from which are plotted on Figures V-14 and V-15;

Flowsheet	Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 2 Feet(a)		
		Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Short Tons U/Day	
			Instantaneous	Sustained
ANL	1/2	500 to 1700	0.91 to 3.1	0.73 to 2.5
ORNL	1/2	500 to 1700(b)	0.91 to 3.1(b)	0.73 to 2.5(b)
HW No. 4	1/2	300 to 1700	0.55 to 3.1	0.44 to 2.5
HW No. 4	3/4	(350 to 2400)(c)	(0.64 to 4.4)(c)	(0.51 to 3.5)(c)
HW No. 4	1	600 to 3000	1.1 to 5.5	0.88 to 4.4

- Notes: (a) "Overall water-film" basis.
 (b) Estimated by extrapolation.
 (c) Estimated by interpolation.

The calculated number of transfer units required for plutonium and uranium recovery in the IA extraction section are as follows:

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<u>Flowsheet</u>	<u>No. of Transfer Units Required^(a)</u>	
	<u>For 0.2% Pu Loss</u>	<u>For 0.2% U Loss</u>
ANL	12.4	14.0
ORNL	14.9	12.1
HW No. 4	11.4	11.3

Note: (a) "Overall water-film" basis. Increasing the concentration of aluminum nitrate salting strength in the extraction section by 0.1 M above the flowsheet value decreases the number of transfer units required (to obtain the specified uranium and plutonium losses) by approximately 15 to 30 per cent.

Since the 28-ft. packed height provides a minimum of 14 transfer units (for uranium H.T.U. values equal to or less than 2 ft.), uranium lost to the IAW stream should be less than 0.2 per cent of the feed uranium when the IA Column is operated within the above ranges at conditions of any of the three flowsheets.

Transfer-unit requirements for uranium and plutonium extraction are nearly equal under the conditions of HW No. 4 Flowsheet, whereas more plutonium than uranium transfer units are needed under ~~HW No. 4~~ ORNL Flowsheet conditions.

If, as expected, the H.T.U. for plutonium transfer is 2 ft. or less over the ranges of production given above for good uranium transfer, the 28-ft. packed height provides a 23 per cent safety factor (when operating under the HW No. 4 Flowsheet) for attaining the flowsheet plutonium loss of 0.2 per cent in the IAW stream. In the event that high plutonium losses in the IAW are experienced due to higher-than-expected H.T.U. values for plutonium, the number of transfer units required for plutonium recovery may be reduced (thus reducing the plutonium loss) by either increasing the aluminum nitrate concentration in the IA extraction section by 0.1 to 0.2 M, or increasing the IAX flow rate, or both.

3.02 The IB Column plutonium scrub section

This portion of the IB Column below the center feed point removes essentially all of the uranium from the plutonium, reducing the uranium content of the plutonium metal to 0.1 per cent or less. At an irradiation level of 400 g. Pu/short ton of U, this permits only 4.4×10^{-5} per cent of the IAF feed uranium to accompany the plutonium in the IBP stream.

The following uranium extraction data appropriate to the Redox Plant IB scrub section (5-in. I.D. column, 25-ft. packed height) are taken from experimental studies in a 5.05-in. diameter column packed with 19 ft. of 1/2-in. or 1-in. stainless steel Raschig rings. Data from these studies are plotted on Figure V-16.

Flowsheet	Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 1.8 Feet(a)		
		Gal./ (Hr.)(Sq.Ft.), Sum of Both Phases	Short Tons U/Day	
			Instantaneous	Sustained
All three	1/2	400 to 1800	1.1 to 4.9	0.87 to 3.9
All three	3/4	(600 to 2400) (c)	(1.6 to 6.5) (c)	(1.3 to 5.2) (c)
All three	1	800 to 2800	2.2 to 7.6	1.7 to 6.1

- Notes: (a) "Overall water-film" basis.
 (b) Chemical differences among the three flowsheets (ANL, ORNL, and HW No. 4) are insignificant for the IB Column.
 (c) Estimated by interpolation.

Approximately 12 transfer units ("overall water-film" basis) are required in the IB scrub section to reduce the uranium accompanying the plutonium to 4.4×10^{-5} per cent of the IAF feed uranium. The 25-ft. packed height in the plant IB scrub section provides 14 transfer units or more over the above ranges of processing rates, based on an H.T.U. equal to or less than 1.8 ft.

3.03 The IB Column plutonium extraction section

This portion of the IB Column above the center feed point extracts 99.8 per cent, or more, of the IBF plutonium from this hexone feed stream back into the aqueous phase. As discussed in Chapter IV and elsewhere, this is accomplished in the IB extraction section by reducing the oxidation state of the plutonium to the +3 level (using ferrous sulfamate reducing agent in the IBX stream), in which form the plutonium distribution ratio in favor of the aqueous phase is on the order of 500.

Because of the 2.7-fold higher total flow rate through the IB extraction section than through the IB scrub section, the plant IB extraction section is 9 in. inside diameter and the scrub section is 5 in. inside diameter. Since plutonium was not present in plant-size IB Column studies made at Hanford Works, the 15-ft. packed height of the plant IB extraction section was based on the performance of pilot-plant IB Column studies made at Argonne and Oak Ridge National Laboratories, as summarized below:

Source	IB Extraction Section Dimensions			Pu Loss in IBU, %
	Diameter, In.	Packed Height, Ft.	Packing	
ANL	1	6.3	Fenske helices(a)	0.2
ORNL	3	10	Raschig rings(b)	0.05 to 0.09

- Notes: (a) 3/16-in. O.D. stainless steel helices.
 (b) 1/4-in. by 3/8-in. stainless steel Raschig rings.

The 15-ft. height of 1/2-in. by 1/2-in. stainless steel Raschig rings in the 9-in. diameter Redox Plant IB extraction section allows for approximately a 50 per cent scale-up factor over the performance of the 3-in. ORNL column. The loss of plutonium accompanying the uranium in the IBU stream is expected to be equal to or less than 0.2 per cent of the plutonium in the IAF (feed) stream.

3.04 The IC Column

The IC Column strips 99.95 per cent, or more, of the ICF uranium from the hexone feed stream back into an aqueous phase. As discussed in Chapter IV, this is accomplished by means of an aqueous extractant (ICX) containing no ANN salting agent. The uranium-bearing aqueous effluent (ICU) is ready for concentration and chemical adjustment to the required composition of the feed for the 2D Column.

The following uranium extraction data appropriate to the Redox Plant IC Column (10-in., I.D. 25-ft. packed height) are taken from experimental studies in a 5.05-in. I.D. column packed with 20 ft. of 1/2-in. or 1-in. stainless steel Raschig rings. Data from these studies are plotted on Figure V-17.

Flowsheet	Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 2.5 Feet (a)		
		Gal./Hr. (Sq. Ft.), Sum of Both Phases	Short Tons U/Day	
			Instantaneous	Sustained
ANL	1/2	600 to 1420	1.9 to 4.5	1.5 to 3.6
ORNL or HW No. 4	1/2	300 to 1600	0.95 to 5.1	0.76 to 4.1
ORNL or HW No. 4	3/4	(300 to 2000)(b)	(0.95 to 6.4)(b)	(0.76 to 5.1)(b)
ORNL or HW No. 4	1	300 to 2500	0.95 to 7.9	0.76 to 6.4

Notes: (a) "Overall hexone-film" basis.

(b) Estimated by interpolation.

The calculated numbers of transfer units required for uranium recovery in the IC Column are as follows:

Flowsheet	No. of Transfer Units (a) for 0.05% U Loss
ANL	8.4
ORNL or HW No. 4	8

(a) "Overall hexone-film" basis.

Since the 25-ft. height of 1-in. by 1-in. stainless steel Raschig rings in the plant IC Column provides a minimum of 10 transfer units (for H.T.U. values equal to or less than 2.5 ft.), uranium lost in the ICW should be equal to or less than 0.05 per cent of the IAF feed uranium over the range of processing rates given above for 1-in. Raschig rings.

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3.05 Columns 2D and 3D

The specified 99.8% uranium recovery from these columns is the same as the percentage recovery from the IA Column. The packed heights in the 2D and 3D Columns are, therefore, the same as in the IA Column (described above, under 3.1). The 2D and 3D Column diameters are 7.5 in., as compared with 6.5 in. for IA, because of the additional capacity allowed for rework.

The following uranium extraction data applicable to the Redox Plant 2D and 3D Columns (7.5 in. I.D., 28-ft. packed height) are based on scouting 2D and IA Column studies in 5.05-in. and 8.42-in. I.D. columns, data from which are plotted on Figures V-18 and V-15.

<u>Flowsheet</u>	<u>Raschig Ring Size, In.</u>	<u>Rangeability for H.T.U.</u>		
		<u>Equal to or Less than 2 Feet(a)</u>		
		<u>Gal./(Hr.)(Sq.Ft.), Sum of Both Phases</u>	<u>Short Tons U/Day</u>	
<u>Instantaneous</u>	<u>Sustained</u>			
ORNL or HW No.4	1/2	300 to 1700	0.73 to 4.1	0.59 to 3.3
ORNL or HW No.4	3/4	(350 to 2400)(b)	(0.85 to 5.9)(b)	(0.68 to 4.7)(b)
ORNL or HW No.4	1	600 to 3000	1.5 to 7.3	1.2 to 5.9

Notes: (a) "Overall water-film" basis.

(b) Estimated by interpolation.

3.06 Columns 2E and 3E

The functions of the 2E and 3E Columns are similar to those of the IC Column, described in Subsection 3.04, above. Although the allowable uranium losses are the same for all three columns, the differences in chemical flowsheet conditions for the columns are reflected in the column dimensions. Thus, the diameter of the 2E and 3E Columns is 9 in. (compared to the 10-in. I.D. IC Column) and the packed length, 30 ft. (compared to 25 ft. for the IC Column). The packed length of the 2E and 3E Columns allows for successful operation under acidic (ANL) flowsheet conditions as well as under the conditions of the acid-deficient flowsheets.

The following data applicable to the Redox Plant 2E and 3E Columns are based on scouting 2E Column studies in an 8.42-in. I.D. column packed with 18 ft. of 1-in. Raschig rings:(19)

<u>Flowsheet</u>	<u>Raschig Ring Size, In.</u>	<u>Rangeability for H.T.U.</u>		
		<u>Equal to or Less than 2.5 Feet(a)</u>		
		<u>Gal./(Hr.)(Sq.Ft.), Sum of Both Phases</u>	<u>Short Tons U/Day</u>	
<u>Instantaneous</u>	<u>Sustained</u>			
HW No. 4	1	300 to 2500	1.0 to 8.5	0.8 to 6.8

Note: (a) "Overall hexone-film" basis.

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3.07 The 2A Column extraction section

Plutonium decontamination is to be accomplished in the 2A Column with a permissible waste loss of 0.2%, which establishes the mass-transfer requirements of the extraction section.

As stated above, in Subsection 3.01, the H.T.U. data available for the plutonium-cycle columns are based on studies using "cold" (unirradiated) uranium to simulate plutonium. The following data (which are plotted in Figure V-19) applicable to the plant 2A Column extraction section (4-in. I.D., 28.5-ft. packed height) are taken from experimental studies in a 5.05-in. I.D. column packed with 16 ft. of 1/2-in. Raschig rings:

Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 3 Feet(a)		Instantaneous Production Rates(b)	
	Gal./(Hr.)(Sq.Ft.), Sum of Both Phases		Equiv. Tons U/Day	Grams Pu/Day(c)
1/2	350 to 1350		0.90 to 3.5	340 to 1300
3/4	(350 to 2000)(d)		(0.90 to 5.1)(d)	(340 to 1930)(d)

- Notes:
- (a) "Overall water-film" basis.
 - (b) To calculate "sustained" rates, the instantaneous rates are multiplied by the 0.8 fractional operating-time efficiency.
 - (c) Based on 376 grams Pu/short ton of U enrichment level.
 - (d) Estimated by extrapolation and by analogy with IA Column studies using 1/2-in. and 1-in. rings.

Except for slight differences in acidity and a lower 3AX flow in the HW No. 4 than in the other flowsheets, the three flowsheets (ANL, ORNL, and HW No. 4) are essentially identical for the plutonium cycles.

The 28.5-ft. packed height in the plant 2A Column extraction section provides a minimum of 9.5 transfer units ("overall water-film" basis) over the above operating ranges for which the H.T.U. is 3.0 ft. or less. With only 7.5 transfer units required to attain the flowsheet 0.2 per cent plutonium loss in the 2AW waste stream, this provides a packed height approximately 27 per cent in excess of the bare minimum. This extra height is expected to ensure satisfactory plutonium recovery in spite of minor deviations in plant operation from the flowsheet salting strength and phase flow ratio, and provides some margin of safety in the event that H.T.U. values for plutonium are somewhat higher than those determined using uranium as a stand-in for plutonium.

3.08 The 2B Column

The 2B Column strips all but 0.05% of the 2BF plutonium into an aqueous phase, which is subsequently butted with ANV salting-agent solution to serve as feed for the 3A Column. Chemical conditions and flow ratios for the column are virtually identical under the conditions of all three flowsheets.

The following data applicable to the Redox Plant 2B Column (3-in. I.D., 25-ft. packed height) are taken from experimental studies using uranium to simulate plutonium in a 5.05-in. I.D. column packed with 20 ft. of 1/2-in. stainless steel Raschig rings (data from these studies are plotted on Figure V-20):

Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 2.6 Ft. (a)		
	Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Instantaneous Production Rates (b)	
		Equiv. Tons U/Day	Grams Pu/Day (c)
1/2	250 to 1500	0.61 to 3.7	230 to 1390
3/4	(400 to 1800)(d)	(1.0 to 4.4)(d)	(370 to 1670)(d)

Notes: (a) "Overall hexone-film" basis.

(b) To calculate "sustained" rates, the instantaneous rates are multiplied by the 0.8 fractional operating-time efficiency.

(c) Based on 376 grams Pu/short ton of U enrichment level.

(d) Estimated by extrapolation and by analogy with IC Column studies using 1/2-in. and 1-in. rings.

The 25-ft. packed height in the plant 2B Column provides a minimum of 9.6 transfer units ("overall hexone-film" basis) over the above operating ranges for which the H.T.U. is 2.6 ft. or less. This is in excess of the 7.9 transfer units required in the 2B Column to attain a 0.05 per cent plutonium loss in the 2EW stream.

3.09 The 3A Column

Except for the differences in feed composition (0.33 M HNO₃ in 3AF compared to 0.1 M in 2AF) and extractant flow (70 3AX flow relative to IAF = 100, compared to 80 2AX flow relative to IAF), the 2A and 3A Columns are almost the same. The decrease in 3AX compared to 2AX flow is to minimize the quantity of HNO₃ carried over into the 3B Column, where HNO₃ is detrimental to plutonium stripping.

Because of the column similarities, the 2A Column experimental studies using uranium to simulate plutonium, mentioned above in Subsection 3.07, are the basis for the following rangeabilities applicable to the Redox Plant 3A Column (4-in. I.D. column, 28.5-ft. packed height):

Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 3 Ft. (a)		
	Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Instantaneous Production Rates (b)	
		Equiv. Tons U/Day	Gram Pu/Day (c)
1/2	350 to 1350	1.0 to 3.7	360 to 1410
3/4	(350 to 2000)(d)	(1.0 to 5.5)(d)	(360 to 2060)(d)

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- Notes:
- (a) "Overall water-film" basis.
 - (b) To calculate "sustained" rates, the instantaneous rates are multiplied by the 0.8 fractional operating-time efficiency.
 - (c) Based on 376 grams Pu/short ton of U enrichment level.
 - (d) Estimated by extrapolation and by analogy with IA Column studies using 1/2-in. and 1-in. rings.

The 28.5-ft. packed height in the plant 3A Column extraction section provides a minimum of 9.5 transfer units ("overall water-film" basis) over the above operating ranges for which the H.T.U. is 3.0 ft. or less. With only 7.5 transfer units required to attain the flowsheet 0.2 per cent plutonium loss in the 3AW waste stream, this provides a packed height approximately 27% in excess of the bare minimum.

3.10 The 3B Column

The flowsheet conditions of the 2B and 3B Columns are almost the same except for the differences in feed composition (0.26 M HNO₃ in 3BF compared to 0.17 M HNO₃ in 2BF) and flow rate (69 3BF flow relative to IAF = 100, compared to 79 2BF flow relative to IAF).

Because of the column similarities, the 2B Column experimental studies with uranium simulating plutonium, mentioned above in Subsection 3.08, are the basis for the following rangeabilities applicable to the Redox Plant 3B Column (3-in. I.D. column, 25-ft. packed height):

Raschig Ring Size, In.	Rangeability for H.T.U. Equal to or Less than 2.6 Ft. (a)		
	Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Instantaneous Production Rates (b) Equiv. Tons U/Day	Grams Pu/Day(c)
1/2	• 250 to 1500	0.69 to 4.1	250 to 1500
3/4	(400 to 1800)(d)	(1.1 to 4.9)(d)	(410 to 1860)(d)

- Notes:
- (a) "Overall hexone-film" basis.
 - (b) To calculate "sustained" rates, the instantaneous rates are multiplied by the 0.8 fractional operating-time efficiency.
 - (c) Based on 376 grams Pu/short ton of U enrichment level.
 - (d) Estimated by extrapolation and by analogy with IC Column studies using 1/2-in. and 1-in. rings.

The 25-ft. packed height in the plant 3B Column provides a minimum of 9.6 transfer units ("overall hexone-film" basis) over the above operating ranges for which the H.T.U. is 2.6 ft. or less. This is in excess of the 8.2 transfer units required in the 3B Column to attain a 0.05 per cent plutonium loss in the 3BW stream.

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3.11 The IS (rework) Column

The function of the IS Column is to recover uranium and plutonium from off-standard Redox aqueous waste streams. Because of adoption of the TBP process, its functions no longer include recovery of uranium from underground (Bismuth Phosphate process) wastes. These rework operating conditions will have to be set on the basis of the composition of the particular off-standard waste to be reworked. The chemical and phase volume-ratio conditions must be chosen so as to prevent refluxing of HNO_3 in the column and high HNO_3 in the ISP. (17)

The use of the IS Column in rework of waste high in uranium content is illustrated by the nominal conditions of IS Column operation given in the HW No. 3 Flowsheet. (17a) The routing of streams and preparation of IS Column feeds are discussed in Chapters VI, X, and XII. Operating diagrams for typical uranium and plutonium rework operation are discussed above, in Subsection B4.

Studies with unirradiated uranium in a 3-in. I.D. column having an extraction section packed with 15 ft. of 1/2-in. Raschig rings are the main basis for the H.T.U.-volume velocity curves for the extraction section of the plant-size IS Column. These curves for the plant-size column (5-in. I.D., 28-ft. packed height in extraction section) are presented on Figure V-21 and indicate typical performance only.

The experimental studies reveal that the H.T.U. for the IS extraction section operating at rework conditions decreases continuously as the volume velocity increases up to about 85 per cent of the flooding capacity. As discussed above in Subsection C9, the generally high H.T.U. values for the IS (rework) Column are believed due to the high value of the aqueous-to-organic volume flow ratio.

The following rangeabilities applicable to a plant-size column are based upon the IS experimental studies mentioned above:

Raschig Ring Size, In.	Rates for Best Extraction (85% of Flooding)		H.T.U., Ft. (b)	Approx. Waste Losses	
	Gal./ (Hr.)(Sq.Ft.), Sum of Both Phases	Equiv. Tons/Day (a)		U, %	Pu, %
1/2	2100	0.50	4.2	1.0	1.0
3/4	(2600)(c)	(0.62)(c)	(5)(c)	(2.0)(c)	(2.1)(c)

Notes: (a) Instantaneous uranium tonnage rates (for the 5-in. IS Column) equivalent to the ISP volume if ISP were 0.48 M in uranium, as for flowsheet IAP and relative flow rates were the same as in HW No. 3 Flowsheet. (ISF:ISX:ISS = 10:2:1)

(b) "Overall water-film" basis; estimated for the 5-in. plant IS Column assuming a 20 per cent scale-up factor from the 3-in. column experimental data.

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(c) Estimated by extrapolation and by analogy with IA Column studies using 1/2-in. and 1-in. rings.

As stated above, operating conditions for the IS Column will vary with the composition of the stream to be reworked so that the above performance data are presented as typical only.

3.12 The IO Column

The primary purpose of this hexone-washing column is to remove residual plutonium and uranium from the combined hexone waste streams (i.e., ICW, 2EW, 3EW, 2BW, and 3BW) before this spent hexone is treated with caustic and distilled in the Hexone Distillation Column, G-3 (see Chapter IX). Plutonium and uranium stripped from the spent solvent (into water or approximately 2 wt. per cent Na₂CO₃) in the IO Column may be recovered by recycling the batches of concentrated salt waste (of which the IOW becomes a part) to the Rework Adjustment Tank, D-7, thence to the IS Feed Tank, F-8, and back to the IS (rework) Column.

Using water as the IOX stream, the IO Column conditions are similar to the dilute end of the IC Column (for uranium) or the 2B Column (for plutonium), except that the aqueous-to-organic flow ratio may be as low as 1/20 during normal plant operation with uranium and plutonium losses at or below the flowsheet concentration in the IOF (0.10 g. UNH/l.; 0.000014 g. Pu/l.). The following performance data applicable to the 12-in. I.D. Redox Plant IO Column (packed with 15-ft. of 1-in. by 1-in. stainless steel Raschig rings) are based on IO Column studies and analogy with the IC and 2B Columns.

Rangeability for H.T.U.'s (a) Equal to or Less than
3 Ft. (for Uranium) and 4 Ft. (for Plutonium)

Gal./(Hr.)(Sq.Ft.) sum of both phases	300 to 2500
Gal. hexone processed/24 hr.	5400 to 45,000
Equiv. tons uranium/24 hr. (Redox Plant)	0.7 to 5.9

Note: (a) "Overall hexone-film" basis.

A minimum of approximately 5 transfer units for uranium and 3.75 for plutonium should ensure removal of over 90 per cent of the uranium and plutonium from the hexone in the IO Column.

4. H.E.T.S. versus H.T.U. Data

Although H.T.U. data were employed, above, to illustrate the development of solvent-extraction column specifications for the Redox Plant, essentially the same column design specifications could have been arrived at using H.E.T.S. data rather than H.T.U. data. As explained in Subsection C10, above, the H.E.T.S. is influenced markedly by the numerical value of the extraction factor, while the H.T.U. is relatively insensitive to this variable. This difference between H.E.T.S. and H.T.U. values is shown on Figure V-22 by experimental H.E.T.S. and H.T.U. data for both the IA extraction section and the IC Column.

H.T.U. values for both columns fall in the range from 1 to 2 ft. H.E.T.S. values for the IA extraction section average approximately 2 ft. vs. 1.3 ft. for the corresponding H.T.U. values, whereas H.E.T.S. values for the IC Column range from 5.4 to 6.4 ft. As explained in Subsection C10, these high H.E.T.S. values for the IC Column are due to the relatively small average value of the extraction factor (0.01 to 0.05 vs. approximately 0.5 in the IA extraction section).

The H.E.T.S. varies with the numerical value of the extraction factor as well as with all of the factors which affect the H.T.U., H.E.T.S. values of 5 to 10 ft. being commonly observed in packed solvent-extraction columns when the extraction factor is 0.05 or less. Thus, an abnormally high H.E.T.S. value does not necessarily indicate a difficult mass-transfer operation, but may be due to a small extraction factor. The mass-transfer performance of a packed solvent-extraction column is, therefore, considered to be better revealed by H.T.U. than by H.E.T.S. data.

E. FISSION-PRODUCT DECONTAMINATION; DEVELOPMENT OF SCRUB-SECTION HEIGHTS

1. Introduction

This section is devoted to the performance (required and expected) of the scrub sections of the decontamination columns, namely Columns IA, 2D, 3D, 2A, 3A, and the IS (rework) Column. The function of these decontamination-column scrub sections is to remove as much of the fission products as possible from the ascending hexone streams (which carry uranium and/or plutonium) by scrubbing the hexone phase with a highly salted 1.3 M to 2 M aqueous aluminum nitrate stream. The scrub streams are highly salted to minimize stripping (and hence internal refluxing in the columns) of uranium and/or plutonium. (The IB Column scrub section performs a different function and is discussed in Section D, above).

The more important radioactive fission products of process significance are discussed in Chapter II. The chemistry of these fission products, and their phase-distribution ratios at Redox process conditions are discussed in Chapter IV. The relative inextractability into the hexone phase of these fission products (hexone/aqueous distribution ratios below 0.1 for most species) is the fundamental property which enables their almost quantitative separation from uranium and plutonium in the Redox solvent-extraction columns.

Because some species of radioactive ruthenium, zirconium, and niobium (columbium) present in the dissolved, irradiated slugs decontaminate less readily than the bulk of the fission products, special provisions are made in the Redox Plant to remove 90 per cent or more of these three fission products in the "head-end" IAF feed preparation steps prior to solvent-extraction. These head-end treatments, which involve volatilizing ruthenium in the feed-oxidation step and adsorbing zirconium and niobium on a solid scavenger (MnO₂ or Super Filtrol) are discussed in Chapter III.

Decontamination of uranium and plutonium from fission products in the Redox solvent-extraction process has been successfully demonstrated by many independent experimental studies at various A.E.C. sites, including

the following: (a) laboratory batch-extraction studies conducted at at least four sites, (b) "hot" pilot-plant packed-column studies at Argonne and Oak Ridge National Laboratories (including operation at full Hanford radioactivity level at ORNL), and "hot" countercurrent mixer-settler studies at Knolls Atomic Power Laboratory. High-spot performance data from the above decontamination studies and scale-up factors allowed in arriving at design specifications for the decontamination-column scrub sections for the Redox Plant columns are presented in Subsections 5 and 6, below.

2. Design Basis for Decontamination

For slugs irradiated at energy levels as high as 600 megawatt-days per ton and "cooled" for 90 days, beta and gamma radioactivity in the dissolver solution will be approximately 0.23 and 0.16 (theoretical) curies per gram of uranium, respectively. Since the permissible radioactivity levels in the product uranium are tentatively set at a maximum of 1×10^{-7} beta curies and 5×10^{-8} gamma curies per gram, the overall uranium decontamination factors for the Redox process should be at least 2×10^6 for beta and 3×10^6 for gamma activity. The allowable total activity (beta plus gamma) in the product plutonium is tentatively set at 8×10^{-5} theoretical curies per gram and thus the decontamination factor for the combined activity in plutonium should be approximately 8×10^6 at a concentration of 530 grams of plutonium per ton of uranium in the dissolver solution.

Experimental studies have shown that uranium and plutonium decontamination factors of more than 10^4 may be expected for the combination of head-end and first-solvent-extraction-cycle treatment under acid-deficient flowsheet conditions.⁽⁷⁾ A reduction in the column feed concentrations of Ru, Zr, and Nb by a factor of approximately 10 is effected in the head-end treatment with the remaining decontamination to the 10^4 value attained in the first-cycle columns. Most of the decontamination in the first-cycle columns is effected in the IA Column. Fission products in the IAP stream are divided approximately equally between the IBP and the IBU, and only on the order of 10% of the fission-product radioactivity in the ICF is carried by the ICW.

Second-plutonium-cycle decontamination factors are expected to be approximately 100 for beta and 300 to 500 for gamma; second-uranium-cycle decontamination factors, approximately 20 to 50 for beta and approximately 40 to 65 for gamma. The second-cycle decontamination factors will be substantially lower than those for the first cycle because the fission products which are most susceptible to removal by solvent-extraction are removed in the first-cycle columns.

3. Mass Transfer (Scrubbing) of Fission Products

Normal mass-transfer concepts may be used to explain the functioning of the scrub sections of the decontamination columns in the removal of 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 or group of fission products.

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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 IA Column are of the order of 10^4 (99.99% removal of fission products). Hence, behavior of fission products in accordance with classical mass-transfer concepts is the rule rather than the exception. From 0.01 to 0.1% of the fission products in the IAF remain in the IAF because of:

- (a) insufficient height of the scrub section;
- (b) distribution coefficient (E_a^0) values unfavorable for stripping (i.e., E_a^0 in the range from 0.2 to 0.4); and
- (c) the so-called "inextractable" (or, more rightfully, "unstrippable" or "unscrubbable") behavior of certain fission products, due to complexing in the organic phase or formation of organic-favoring forms of some fission products (notably Ru). In these cases, E_a^0 values for the fission products are greater than 0.5.

Although the fraction of the total fission products in the IAF which exhibits "inextractable" performance is small (generally 0.1% or less), it is nonetheless highly important because D.F.'s for recovered U and Pu (from fission products) must be on the order of 10^6 to 10^7 .

This subsection deals with the mass-transfer behavior of the bulk of the fission products (99 per cent or more) which exhibit normal mass-transfer behavior. Subsection E4 discusses the phenomenon of "irreversible" extraction of some of the fission products.

3.1 Fission-product operating diagrams

The basic principles for the construction of operating diagrams are discussed above, in Section B. As indicated in Section B, equilibrium data are an essential element in the diagrams. The following equilibrium data (distribution coefficients) for fission products are intended as representative only, because, as indicated in Chapter IV, the values vary considerably with changes in HNO_3 or $\text{Al}(\text{NO}_3)_3$ concentration:

<u>Fission Product</u>	<u>Distribution Coefficient, E_a^0</u>
Ca	0.01
Nb	0.02
Ru	0.01 to 0.2
Zr	0.02

Values are estimated for the scrub section of the IA Column operating under HW No. 4 Flowsheet conditions. It is estimated that distribution coefficients for the remaining fission products are on the order of 0.01 or less.

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The listed values for distribution coefficients were used in constructing four of the operating diagrams (for Ce, Nb, Ru, Zr) presented on Figure IV-23. (The diagram for "inextractable" Ru is discussed in Subsection 4, below.) Because of the wide range of concentrations involved, it was more convenient to construct the diagrams on logarithmic-scale coordinates. With the exception of Nb, Ru, and Zr, decontamination factors of over 10^4 are indicated for each of the fission products in a IA Column scrub section with 2 to 2.5 equivalent stages (e.g., 2.4×10^5 for Ce).

3.2 D.F. as a function of the number of scrub stages or transfer units

The straight operating and equilibrium lines suggest application of the Colburn equations (see under A3.6 and A3.7, above) to the calculation of stages and transfer-unit requirements in fission-product removal. Figure V-24, which is a graph of transfer units in the IA Column scrub section versus decontamination factor has been constructed on the basis of the Colburn equations and the assumption stated on the figure. With the aid of the graph it is possible to determine the number of IA Column scrub-section stages or transfer units required to attain a specified D.F. for a fission product of known distribution coefficient. Conversely, the graph may be employed to calculate the decontamination factor for a fission product of known distribution coefficient in a column with a known number of stages or transfer units in the scrub section. Sample calculations are given below.

It will be noted that Figure V-24 indicates 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, IAFS, containing approximately one-half the IAF fission-product concentration. The organic feed to the scrub section has therefore already undergone considerable decontamination due to the highly aqueous-favoring distribution coefficient of the fission products (most of the fission product remains in the aqueous phase) in this part of the extraction section. Further reduction in the concentration of fission products in the organic phase is effected in the scrub section by scrubbing the ascending organic stream with an aqueous phase in which the fission products are relatively very soluble. For each transfer unit in the scrub section, the decontamination factor is increased by a factor of approximately 2.5 for fission products with distribution ratios (E_a^0) below 0.05. As E_a^0 values increase, the effect of each transfer unit on the decontamination factor becomes less pronounced so that, for values of E_a^0 above 0.35, increases in the height of the scrub section have little effect on the decontamination factor.

The use of Figure V-24 may be illustrated with two calculations showing the determination of (a) the number of "overall hexone-film" transfer units required to attain a given D.F. for a fission product of known E_a^0 , and (b) the D.F. attained with a set number of transfer units for a given fission product with a known E_a^0 .

- (a) Let it be assumed that the fission product has an E_a^0 of 0.05, the required D.F. is 3×10^5 , and it is desired to determine the number of transfer units required. Reading on the left-hand vertical scale (Fig. V-24) up to D.F. = 3×10^5 and across to $E_a^0 = 0.05$ (radial parameter line), it is found (on the

abscissa) that approximately 10 transfer units are required. (As may be read from the theoretical-stage parameter line at D.F. = 3×10^3 and $E_a^0 = 0.05$, this corresponds to about 5 theoretical stages.)

- (b) Let it be assumed that the fission product has an E_a^0 of 0.20, there are 5 transfer units in the scrub section, and it is desired to determine the D.F. attainable. Reading on the lower horizontal scale over to 5 transfer units and following the vertical line at 5 up to its intercept with the $E_a^0 = 0.20$ line, one finds the intercept to be 1.3×10^3 (D.F. scale). The D.F. attainable is therefore 1.3×10^3 . The influence of E_a^0 on the D.F. is shown by taking a second example, assuming 5 transfer units and an E_a^0 of 0.005. For this latter case, the indicated D.F. is 1.2×10^4 . The forty-fold decrease in E_a^0 is therefore accompanied by a one-hundred-fold increase in the D.F.
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Figure V-24 may also be used in calculations involving the number of theoretical stages in the IA Column scrub section by using the sloping (stage) parameter lines instead of the vertical (transfer-unit) lines.

4. The "Irreversible" Extraction of Some Fission Products

It has been observed in laboratory and pilot-plant studies that certain fission products, or -- as is more often the case -- small fractions of certain fission products, under some conditions extract initially into the hexone 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 Redox 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 MIBC (methyl isobutyl carbinol) or MO (mesityl oxide) under acid-flowsheet conditions; and cerium, by dichromate. Other complexes may be attributable to unknown impurities. Because of the extremely low concentrations in which individual fission products are present (on the order of 10^{-5} to 10^{-4} M in the IAF stream) a very low concentration of complexing agent would be effective.

Another possible mechanism is the presence of certain fission products, notably ruthenium, in more than one chemical form, some with low and some with high distribution ratios. While the solvent-extraction behavior of ruthenium is only partially understood, it is fairly well established that ruthenium exists in several solute species, of which two, designated by the Oak Ridge nomenclature as RuA and RuB, both believed to be nitroso complexes, predominate in nitrate-salted hexone-aqueous systems. The distribution ratio (org./aq.) of RuA in IA-type systems is generally in the range of 1 to 10. That of RuB is about 0.1 or less. In any one system an equilibrium proportion of RuA:RuB tends to become established at a slow rate (half-time of the order of 1 hr.). The equilibrium ratio of RuA to RuB under Redox IA Column conditions is not known, but is believed to be in the range 0.01 to 0.1.

The effect of the presence of significant amounts of RuA on decontamination from ruthenium is adverse. As apparent from Figure V-23, the

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concentration of a ruthenium species with a distribution ratio (E_a^0) of 2 is not significantly reduced by processing in the IA Column. Thus if 5% of the total ruthenium is present in a form with a distribution ratio (E_a^0) of 2, a total Ru (arithmetic) decontamination factor of 20 cannot be exceeded.

The bearing of ruthenium volatilization on the "inextractable" ruthenium problem is complex and not entirely clear. On the one hand, laboratory data obtained at Hanford indicate that the initial gross Ru distribution ratio (E_a^0) is about 3 to 6 times as high for untreated dissolver solution as for the 5% residue from volatilization (E_a^0 of 0.008 as compared with 0.0018 in a typical instance). On the other hand, in SPRU (mixer-settler pilot plant) runs under ORNL flowsheet conditions, Ru D.F.'s across the IA battery were only 30 to 400 after head-end treatment (volatilization of ruthenium and MnO_2 scavenging) as compared with 500 without head-end treatment.

For further data on the chemical species of ruthenium in solution and their distribution ratios and conversion rates, reference is made to Chapter IV.

5. Laboratory and Pilot-Plant Decontamination Performance

5.1 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 Redox process. The quantitative prediction of column performance with more than order-of-magnitude accuracy from laboratory countercurrent batch studies has not been possible, because of the complexities and uncertainties of individual fission-product extraction-stage and transfer-unit heights, and because of such anomalies as the "irreversible" extraction behavior of some fission products, discussed in Subsection E4, above. However, simple, multiple, and countercurrent batch laboratory results often provide a valuable qualitative and order-of-magnitude quantitative indication of the effects of various independently controlled factors on process decontamination performance. Some illustrative laboratory countercurrent batch dF's are tabulated below.

Column Simulated	Flowsheet	Radio-activity Approx. % HW Level	No. of Stages		dF	
			Extn.	Scrub	Beta	Gamma
IA(8)	ANL	5	6	4	1.6	1.4
IA(8)	ORNL No. 1	5	6	4	3.8	(a)
IA(6)	HW No. 4	(a)	10	6	3.4	2.7
IA(6)	ORNL No. 1	(a)	10	6	3.9	3.1
IA(16)	ORNL No. 1	100	1	2	2.9	2.7
IA(16)	ORNL No. 1	100	1	2	3.8(b)	3.7(b)
2D(8)	ANL	30	6	4	0.3	0.3
2D(8)	ORNL No. 1	30	6	4	2.5	2.5

Notes: (a) Not reported.

(b) Including dF in head-end treatment, in which ca. 90% of the Ru was removed by ozonolysis and ca. 70% of the Zr and Nb by Filtrol scavenging. (All other dF's in the above table were obtained without head-end treatment.)

5.2 Pilot-plant studies

Pilot-plant studies of the decontamination performance of the Redox process were carried out in packed columns at Argonne and Oak Ridge National Laboratories and in mixer-settlers in the Separations Process Research Unit at Knolls Atomic Power Laboratory. The pilot-plant equipment sizes were as follows:

Column or Mixer-Settler Battery	ANL Columns(a)		ORNL Columns(b)		SPRU
	Diam., In.	Packed Height, Ft.	Diam., In.	Packed Height, Ft.	Mixer Settlers(c) No. of Stages
IA, extn. scrub	1	10.7	3	26.0	12
	1	10.0	3	13.8	8
IB, extn. scrub	1	6.3	3	10.0	10
	1	6.3	3	14.0	10
IC	1.5	8.4	3	14.3	10
2A, extn. scrub	1	8.9	--	--	--
	1	8.3	--	--	--
2B	1	7.8	--	--	--
2D, extn. scrub	--	--	2	25.8	12
	--	--	2	12.5	8
2E	--	--	2	14.7	10

Notes: (a) Packed with 1/4-in. Raschig rings. (Fenske helix packing was used in early runs and summarized here.)

(b) Packed with 1/4-in. diam by 3/8-in. long Raschig rings.

(c) 600 ml./stage.

The decontamination factors obtained in these studies are summarized briefly below. A somewhat more detailed summary is presented in Table V-25. Table V-25 includes dF's for those individual fission products (Ru, Zr, Nb, and Ce) which are important because they generally control the gross fission-product decontamination factors obtained.

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Pilot-Plant First-Cycle dF's

<u>Equipment</u>	<u>Flowsheet</u>	<u>Radioactivity, Approx. % HW Level</u>	<u>Gamma dF Based on Radio- activity in Dissolver Solution</u>	
			<u>Pu (IBP Stream)</u>	<u>U (ICU Stream)</u>
ANL packed columns	ANL	5	3.1	2.9
	ORNL No. 1	5	3.8	3.6
	HW No. 4	5	3.7	3.8
ORNL packed columns	ANL	5 to 30	3.2	2.0
	ORNL No. 1	30 to 100	3.9	3.7
SPRU mixer- settlers	ORNL No. 1	5	4.1	3.9
	HW No. 4	5	4.3	4.0
	ORNL No. 1*	5	5.0*	4.9*

*) Including dF in head-end treatment (Ru volatilization with $KMnO_4$ and Zr-Nb scavenging with co-formed MnO_2). (All other dF's in the above table were obtained without head-end treatment.)

Pilot-Plant Second-Cycle dF's

<u>Equipment</u>	<u>Flowsheet</u>	<u>Radioactivity, Approx. % HW Level</u>	<u>Gamma dF Based on Radio- activity in 2AF or 2DF</u>	
			<u>Pu (2BP stream)</u>	<u>U (2EU Stream)</u>
ANL packed columns	ANL	100	2.6	--
ORNL packed columns	ANL	30	--	1.0
	ORNL No. 1	30	--	1.8

Pilot-Plant Two-Cycle dF's

<u>Equipment</u>	<u>Flowsheet</u>	<u>Radioactivity, Approx. % HW Level</u>	<u>Gamma dF Based on Radio- activity in Dissolver Solution</u>	
			<u>Pu (2BP Stream)</u>	<u>U (2BU Stream)</u>
ANL packed columns	ANL	100	5.7	--
ORNL packed columns	ANL	30	--	3.0
	ORNL No. 1	30	--	5.6

It may be noted from Table V-25 and from the above summary that second-cycle dF's are generally substantially lower than those for the first cycle. This is due in large measure to the fact that the fission products in second-cycle feeds contain a lower proportion of those chemical species which are easy to decontaminate from and hence were very largely removed by the first cycle.

With 600 Mw.-day/ton, 90-day "cooled" slugs the dF's required to be achieved in the solvent-extraction battery in order to meet the tentative product radioactivity specifications are as follows:

	dF Required in Solvent-Extraction	
	If no Head-End Treatment is Used	If Head-End Treatment is Used
U beta	6.3	ca. 5.1
U gamma	6.5	ca. 5.3
Pu beta	6.9	ca. 5.9
Pu gamma	6.9	ca. 5.9

The pilot-plant data summarized above and in Table V-25 indicate that, with head-end treatment (discussed in Chapter III), the required dF's for both uranium and plutonium will be met in the Redox Plant in two solvent-extraction cycles under acid-deficient flowsheet conditions. Under acid (ANL) flowsheet conditions two cycles may be inadequate. If two solvent-extraction cycles should suffice for achievement of the required dF's, the third cycles can be by-passed and held as stand-by.

6. Development of Redox Plant Scrub-Section Packed Heights

The specified packed heights (20 ft.) of the scrub sections of the Redox Plant decontamination columns (IA; 2A, 3A; 2D, 3D; IS) are based primarily on the 12.5 and 13.8-ft. heights found satisfactory in the ORNL pilot-plant studies discussed under 5.2, above. A height allowance of about 50% was made for the scale-up factor on going from the 2-in. and 3-in. columns packed with 1/4-in. by 3/8-in. Raschig rings to 4-in. to 7.5-in. columns packed with 1/2-in. by 1/2-in. rings. Since the original design, the packing size has been changed to 1-in. by 1-in. in IA, and 3/4-in. by 3/4-in. in Columns 2A, 3A, 2D, 3D, and IS.

Consideration of the transfer-unit requirements, for representative scrubbing duties (see Subsection E3, above) employed in conjunction with fission-product H.T.U. estimates for the decontamination-column scrub sections, supports the adequacy of the 20-ft. scrub-section heights arrived at as described above. Thus, as read from Figure V-24, the attainment of a IA Column D.F. of 10^4 for a fission-product species with a distribution ratio (E_a) of 0.01 requires about 6 transfer units. With an estimated H.T.U. of 2.5 to 3 ft., a D.F. of 10^4 would be achieved by 6 times 2.5 to 3, i.e., 15 to 18 ft. of scrub-section packed height, as compared with 20 ft. available.

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F. LOCATION AND USE OF EXTRACTION COLUMN PRESSURE TAPS

1. Function of Pressure Taps

In the Redox Plant a lag of several hours may occur from the time that a column effluent line sample is taken until the analysis is known. Furthermore, line samples will not be taken routinely. It is desirable to have a method of detecting any off-standard operation as soon as it starts so that immediate corrections in operating conditions can be made and appropriate line samples may be taken as an aid in determining the causes and extent of the off-standard operation. Studies of the solvent-extraction of uranium in plant-size packed columns at Hanford Works have demonstrated that static or differential pressure, measured at connections along the side of the column, gives a reliable indication of flooding in the packing, and that differential pressure reflects the apparent density of the liquid in the column as influenced by the concentration of the uranium salt (and of aluminum nitrate salting agent) in solution.

2. Location of Pressure Taps

The pressure taps on the several solvent-extraction columns have been located so as to provide the maximum useful information for control purposes. The locations are based upon an appraisal of the solution density gradient through the column and of important variables which affect this density gradient for anticipated operating conditions. The types of pressure instruments used on each of the solvent-extraction columns and the locations of the pressure taps are summarized in the table below. The technical basis for the tabulated information will be apparent from the discussion which follows. For a functional description of these instruments and data on their ranges and accuracy, reference is made to Chapter XIX.

Types and Location of Extraction Column Pressure Taps

<u>Column</u>	<u>Type of Taps</u>	<u>Location of Taps</u>	<u>Spacing of Taps, Ft.</u>
IA, IS, 2D, 3D	Differential	6 ft. below top of extn. section ^(a)	4
IB	Static	5 in. below bottom of packing	--
IC, 2E, 3E	Differential	15 ft. below top of packed section ^(a)	4
2A, 3A	Static	5 in. below bottom of packing	--
2B, 3B	Static	6 in. below bottom of packing	--
IO	Static	6 in. below bottom of packing	--

Note: (a) Position of center line between two taps.

3. Effect of Uranium Losses on Density

3.1 IA, IS, 2D, and 3D Columns

Figure V-26 shows the estimated aqueous-phase (i.e., continuous-phase) density as a function of packed height for the extraction section of IA-type columns (i.e., Columns IA, IS, 2D, and 3D). Below a level approximately 10 feet down from the top of the extraction section, the aqueous-phase density is mainly dependent on the ANN concentration in the aqueous waste stream (determined by the scrub-stream ANN concentration and the scrub-to-feed ratio). The principal dissolved constituent contributing to the aqueous-phase density just below the feed point is the uranium in the feed, which is to be maintained substantially constant in plant operation. The aqueous-phase density changes the greatest amount as a result of aqueous-phase uranium concentration changes in the zone from approximately 3 ft. to 9 ft. below the top of the extraction-section packing (if it is assumed that the top 2 ft. are used up in achieving effective mixing of the phases). The differential pressure taps for these columns are located in this region because it is in this region that variations in column performance entail the most pronounced changes in aqueous-phase uranium concentrations -- and hence density. For example, with the IA Column extraction section operating under HW No. 4 Flowsheet conditions, an increase in H.T.U. from 2 to 3 ft. (corresponding to an increase in uranium loss from approximately 0.08% to 0.65%) would result in an increase in the aqueous-phase density between the pressure taps located as shown in the table above from 1.234 to 1.275 g./ml. (a change corresponding to about 8% of instrument scale). It is noted however that a change in differential pressure reading for the IA Column may also be due to a change in ANN concentration or changes in flow rate (or ratio).

Since high Pu(VI) losses are generally accompanied by high uranium losses, the IA Column differential pressure readings provide an indirect indication of Pu(VI) losses also. However, since the plutonium in the column is too dilute to affect the differential pressure readings directly, Pu(IV) losses are not indicated by the readings.

3.2 IB Column

In the IB Column the uranium concentration in the aqueous phase never exceeds approximately 100 g. UNH/l., and uranium is always a minor contributor to the density of the aqueous phase. For example, a tenfold change in the uranium concentration in the IBP stream exerts a negligible effect on the aqueous-phase density gradient through the column. Consequently, static or differential pressure taps on the IB Column are not suited to indicating off-standard uranium extraction. However, the static pressure tap at the base of the column is useful as an approximate indication of the ANN salting strength in the aqueous phase. It may also be used to indicate flooding, as discussed below.

3.3 IC, 2E, and 3E Columns

Since uranium is by far the major dissolved constituent contributing to the aqueous-phase density in the IC, 2E, and 3E Columns, these columns

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are ideally suited to be monitored for changes in uranium transfer by means of differential pressure taps along the side of the column. While the following discussion deals specifically with the IC Column, it is also applicable to the 2E and 3E Columns.

In order to provide a sensitive indication of high uranium content in the ICW stream, the differential pressure taps have been located as close as possible to the top (i.e., ICW) end of the IC Column, but sufficiently far down the column so that the differential pressure instrument is capable of registering changes in aqueous-phase density as uranium extraction changes.

If the IC Column is operating at a given waste loss (e.g., 0.05% of the feed uranium), the UNH concentration and its contribution to density can be computed as a function of packed height. This calculation has been made for several representative IC Column operating conditions and three resulting curves are plotted on Figure V-27. As indicated on this figure, at a point 10 ft. above the bottom (or 15 ft. below the top) of the packed section of the column, the calculated aqueous-phase density changes from 1.01 to 1.03 g./ml. (a change corresponding to about 1% of instrument scale) when the uranium waste loss changes from 0.05% to 0.5%. Density changes of this magnitude are sufficiently large to be registered by the differential pressure instrument.

Curves for the 2E or 3E Columns are similar to those shown for the IC Column although they are displaced slightly to the right because of an increased uranium concentration.

3.4 2A, 2B, 3A, and 3B Columns

Since no uranium is present in these columns and plutonium concentrations are too small to affect the aqueous-phase density significantly, differential pressure instruments would not be capable of responding to changes in plutonium transfer. However, as in the case of the IB Column, the static pressure tap at the base of each of the second and third plutonium-cycle columns is useful in indicating when flooding occurs and, for the 2A and 3A Columns, also indicates the approximate ANN concentration in the aqueous phase.

3.5 IO Column

A static pressure tap on the IO Column provides a method of detecting flooding conditions in the column. A macro build-up of uranium in the aqueous phase is indicated by an increase in apparent density for the solution in the column.

4. Effect of Flow Rate on Apparent Density

Figure V-28 shows the effect of flow rate on apparent density as obtained in experimental runs. It is not known to what relative extents the decrease in apparent density with increasing flow rate is (a) due to fluid friction of the phases flowing countercurrently or (b) to the

sometimes-postulated effect of the rising hexone-phase globules averaging in with the aqueous phase to give a weighted-average density for the two-phase system.

The absolute values of the experimental apparent densities as plotted may be in error because of improper functioning of the instruments used (relaxed-diaphragm pressure transmitters). However, the trend of decrease of apparent density with increasing flow rate in any one column appears to be well established from the data on which Figure V-28 is based.

5. Detection of Flooding

As shown in Figure V-28, there is a decrease in apparent density with increase in flow rate for any one column. This decrease in density is related to a gradual increase in the relative percentage of organic phase (as compared to the aqueous phase) in the column as the flow rate is increased. At flooding, portions of the column are completely filled with organic phase and the pressure tap readings for a column will show a more or less sharp decrease in apparent density.

G. SPECIAL PROBLEMS

The expectation of continuous satisfactory performance of the Redox Plant solvent-extraction columns over long periods is based on thousands of hours of trouble-free operation in pilot-plant studies. This section summarizes experimental information on "crud" formation, emulsification in the columns, and some trace-impurity effects. In exceptional circumstances, such effects may give rise to anomalous column behavior. Normally, however, if such effects (like crud formation) occur at all, they do so to only a harmless extent.

1. Crud Formation

The formation of a dark brown-to-black precipitate, which built up on the interface, was observed in almost all IA, IC, and 2D Column runs and in about 10 per cent of the IB runs made in "cold" pilot-plant columns at Hanford Works. This observation was generally borne out by "hot" and "cold" pilot studies at other sites. In the Hanford experiments with 1/2-in. and 1-in. Raschig-ring packing, the "cruds" did not give rise to maloperation of the columns or accessories. The cruds were swept out by the effluent organic stream at sufficient rates to prevent excessive accumulation at the interface.

Crud formation has been attributed to diverse causes, but the specific origins of cruds observed in pilot-plant runs are only partially understood. A crud formed in the 2D Column under acid-deficient conditions is sometimes attributed to precipitation of iron (from the reductant in 2DS) at the relatively low hydrogen ion concentration of the system (pH about 2). In a pilot-plant run at Oak Ridge under acid-deficient conditions (18), the 2DU (2D organic effluent) line was plugged by a crud with an Fe:Al atomic ratio of approximately 6:1. Attempts to reproduce such a crud

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at Hanford succeeded only qualitatively: a crud did form, but its Fe:Al ratio was 40 times lower and it did not accumulate in sufficient quantity to result in line plugging or other mechanical trouble.

Suspended solids in column influent streams may contribute to crud formation. This effect is expected to be minimized in the Redox Plant by passing all "cold" column influents through strainers which remove all particles larger than 0.005 in., and by the feed clarification step discussed in Chapter III.

Analyses of interface crud from Hanford IA Column ("cold") runs indicated that compounds of tin and silicon were important factors in the crud formation⁽¹²⁾. The origin of these materials and the methods for their removal are discussed in Chapter III.

There is evidence to indicate that some crud formation may be related to impurities in the hexone⁽⁴⁾. The sources of impurities in the hexone and the methods for their removal are described in Chapter IX.

Crud accumulations may sometimes be removed by temporary operation of the affected column at increased acidity. To remove cruds resisting such treatment, mechanical flushing of the column may be required.

2. Emulsification

An emulsion may result from the intimate intermixing of two phases of low interfacial tension.

In pilot-plant experiments at Hanford, 2 to 3 ft. of emulsion was observed at the interface in ORNL June 1949 Flowsheet, 5-in. diameter IB Column runs in which a "shower-head" organic distributor was used. The distributor plate contained 121 holes 0.04 in. in diameter.

Surface-active impurities, notably some silicious materials derived from the Al-Si slug-bonding layer, may reduce the interfacial tension between the phases sufficiently to cause emulsification. In Hanford pilot-plant experiments, emulsion resulted from a IAF silicon concentration of 60 p.p.m., but not from 30 p.p.m.^(3, 12).

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. Such conditions of operation, if due to silicious materials, may be reflected in an increase in the silicon content of uranium or plutonium product streams.

3. Trace-Impurity Effects

The effects of trace impurities derived from slugs on column performance were investigated to a very limited extent on the laboratory scale. These investigations were carried out with IAF made from crystalline UNH. Ammonium nitrate was used as salting agent. The column was packed with 3/16-in. stainless steel Fenske helices. The results indicate

that traces of Si, Sn, Fe, and Cu may have significant effects on H.E.T.S., but they can by no means be regarded as conclusive. The following are IA Column results obtained under conditions designed to be comparable: (9,10)

<u>Trace Impurity Added</u>	<u>H.E.T.S., Ft.</u>
None	1.75
Si	2.21
Sn	1.30
Sn and Si	1.23
Fe, Al, and Cu	1.19

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FIGURE V-1
EXAMPLE HETS DETERMINATION FOR URANIUM MASS TRANSFER IN THE EXTRACTION SECTION OF A REDOX IA COLUMN
(OPERATING AT HW-No. 4 (SEE FIG. I-2) FLOWSHEET CONDITIONS)

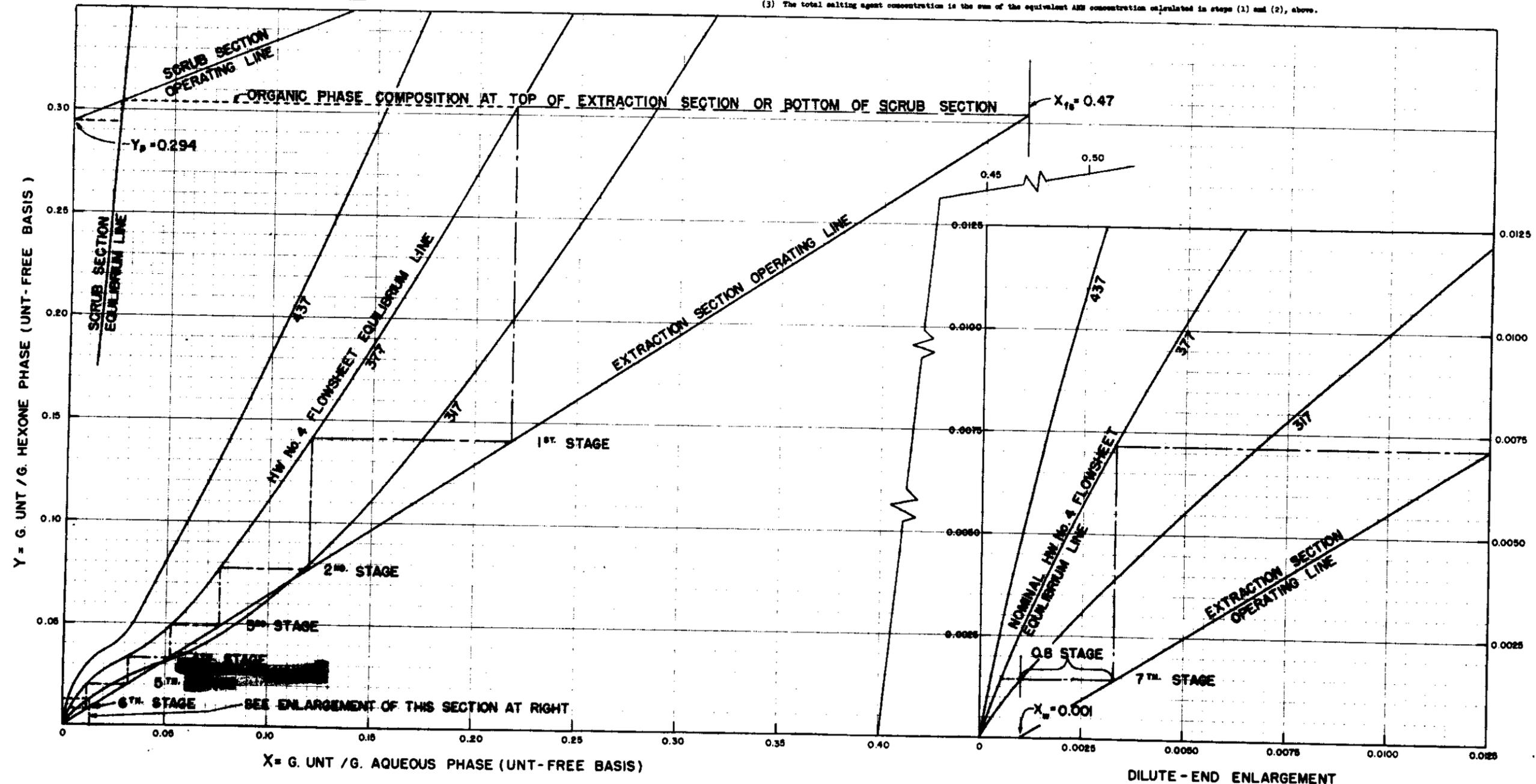
DATA FROM HW

Run No. 87-80-3. Date: 6-20-59. Calculation based on 2 hr. period from 2045 to 0145.
Average $Al(NO_3)_3 \cdot 9H_2O$ concentration in IAW = 363 g./l.
Additional salting agent conc. (From H_2NO_2) = $19 \times 0.735 = 14$ g./l.
Total equivalent salting agent conc. = 377 g./l. ANH.
ANH conc. in IAW calculated from the following equation (conc. in g./l.):
 $g^{ANH} = 0.9987 + 0.000997(ANH) + 0.000509(HNO_3) + 0.000613(H_2NO_2) + 0.000416(ANH) + 0.000659 (Ba_2Cr_2O_7 \cdot 2H_2O)$
 $Y_p = g\text{-ANH/g. non UAN in IAW stream}$
 $Y_{p'} = g\text{-ANH/g. non UAN in aqueous phase below feed point}$
 $Y_o = g\text{-ANH/g. non UAN in IAW stream}$
Number of stages, N , extraction section = 7.60
Feed height (extraction section, feet) = 11.30
H.S.T.S., extraction section, feet = 1.70

CALCULATION METHOD

The equilibrium lines represent the uranium phase equilibrium data to be used in determining uranium mass-transfer performance of Redox IA Columns operating at approximately 25°C. at HW No. 4 Flowsheet conditions. The "377" line and the scrub section equilibrium line have been developed from data obtained during Hanford Works equilibrium study IA-E-27 in which a series of counter-current batch separator funnels were operated to simulate a Redox IA Column having a scrub and 10 extraction stages (no plutonium). The curve designated "377" applies for a total equivalent salting agent concentration of 377 g.ANH/liter in the IAW. This concentration includes the equivalent salting agent concentration of the hypothetical H_2NO_2 formed when obtaining "acid-deficient" feed solutions by neutralizing with NaOH (see (2) below). The family of extraction section lines represents deviations from a total equivalent salting agent concentration of 377 g.ANH/liter of as much as ± 60 g. ANH/liter. The stepwise procedure for choosing the appropriate extraction equilibrium line is as follows: -

- (1) Calculate the concentration of ANH in IAW stream using the density equation (see equation at left), the measured concentration of UAN and HNO_3 (negative), and the "hypothetical" computed H_2NO_2 concentration. The hypothetical H_2NO_2 concentration can be calculated from the amount of NaOH added during preparation of feed solutions and flow ratio data or obtained by direct laboratory analysis for the sodium ion. If no NaOH has been added to produce the acid-deficient condition, the H_2NO_2 term of the equation can be ignored.
- (2) If H_2NO_2 is present in the IAW it must be included in the total equivalent salting agent concentration. In determining the positions of the equilibrium lines it is assumed that one gram of H_2NO_2 is equivalent in salting strength to 0.735 grams of ANH.
- (3) The total salting agent concentration is the sum of the equivalent ANH concentration calculated in steps (1) and (2), above.



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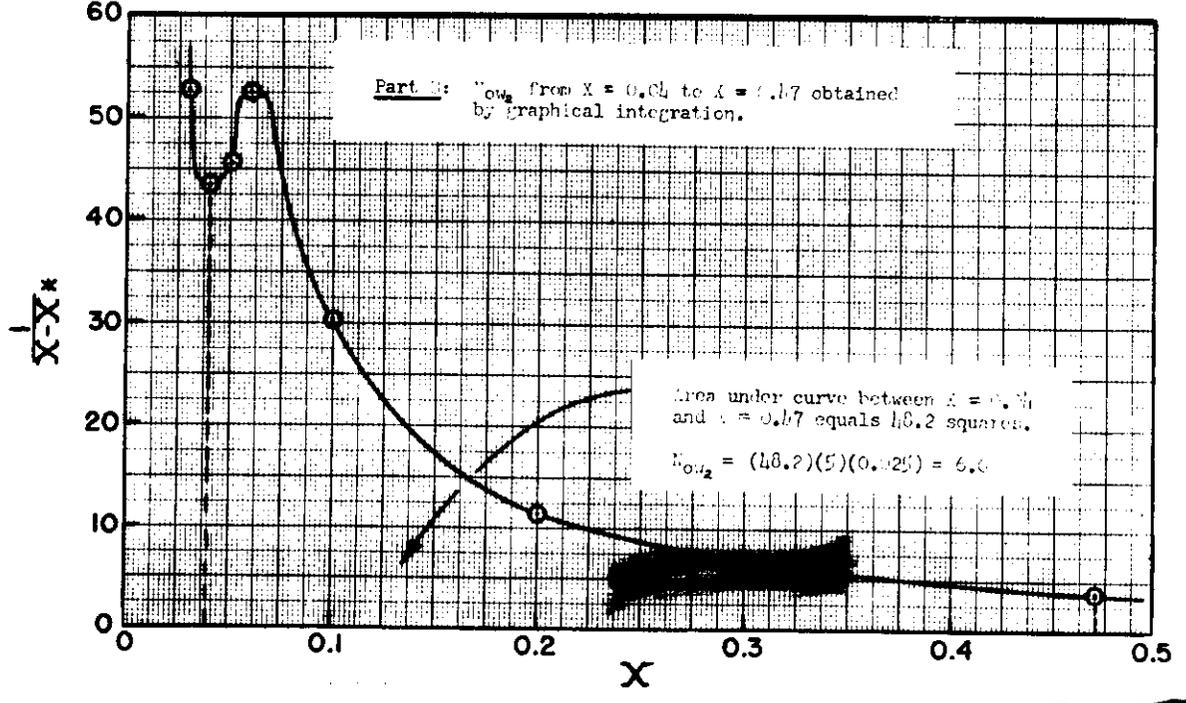
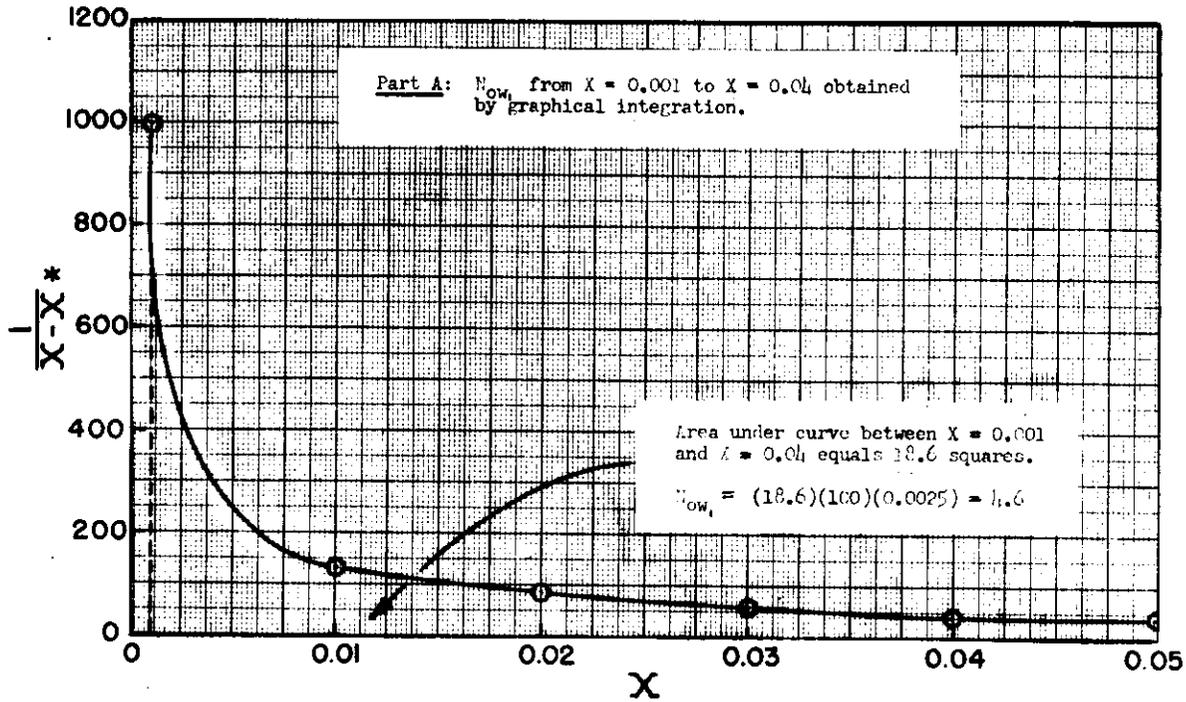
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FIGURE
GRAPHICAL INTEGRATION METHOD FOR THE NUMBER OF TRANSFER UNITS OBTAINED DURING RUN 8"-20-U

$$N_{ow} = N_{ow_1} + N_{ow_2} = 4.6 + 6.0 = 10.6$$

$$H.T.U. = \frac{z}{N_{ow}} = \frac{13.92 \text{ ft.}}{10.6} = 1.31 \text{ ft.}$$



412



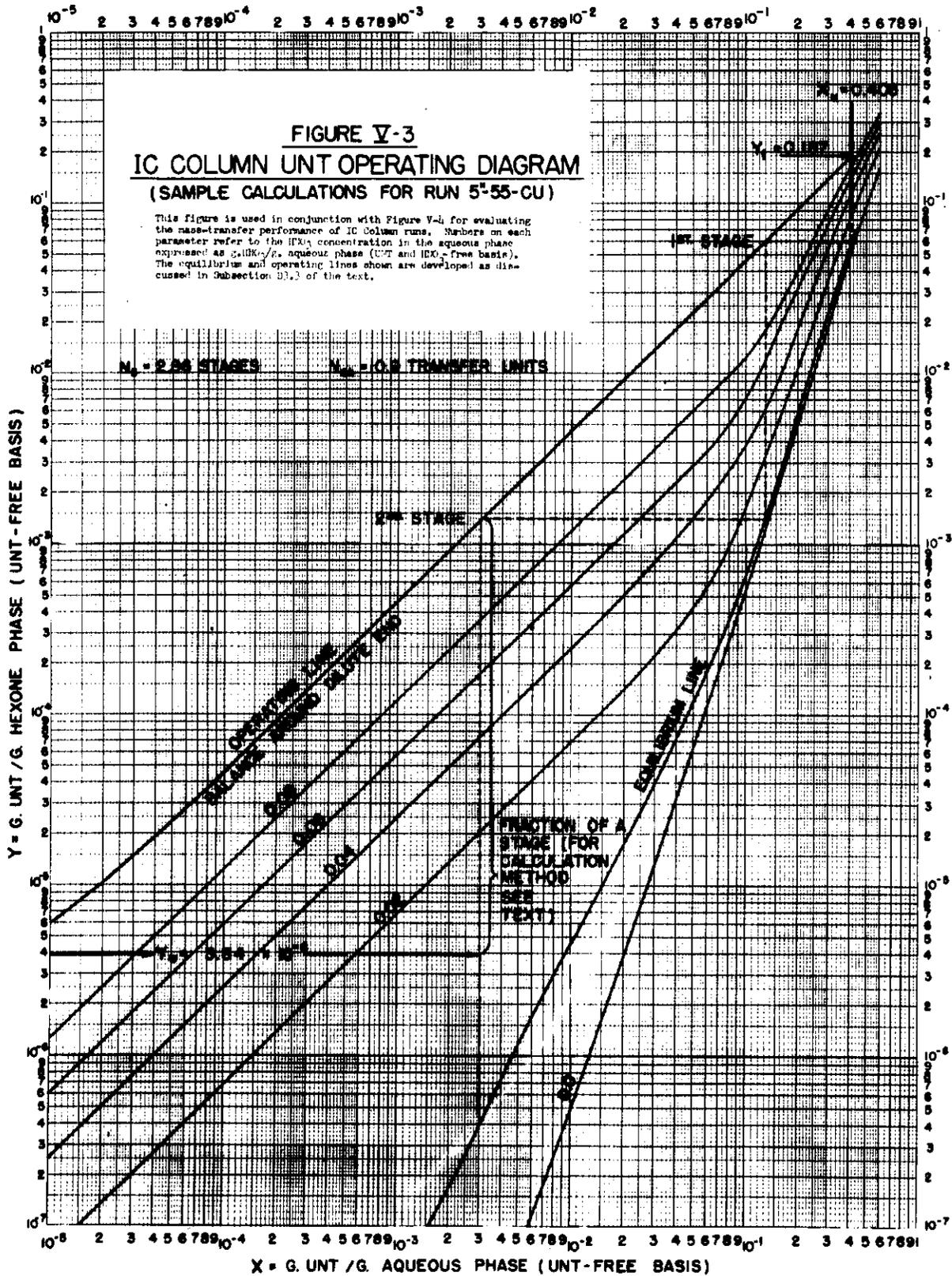
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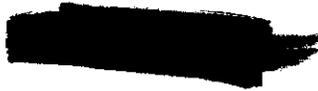
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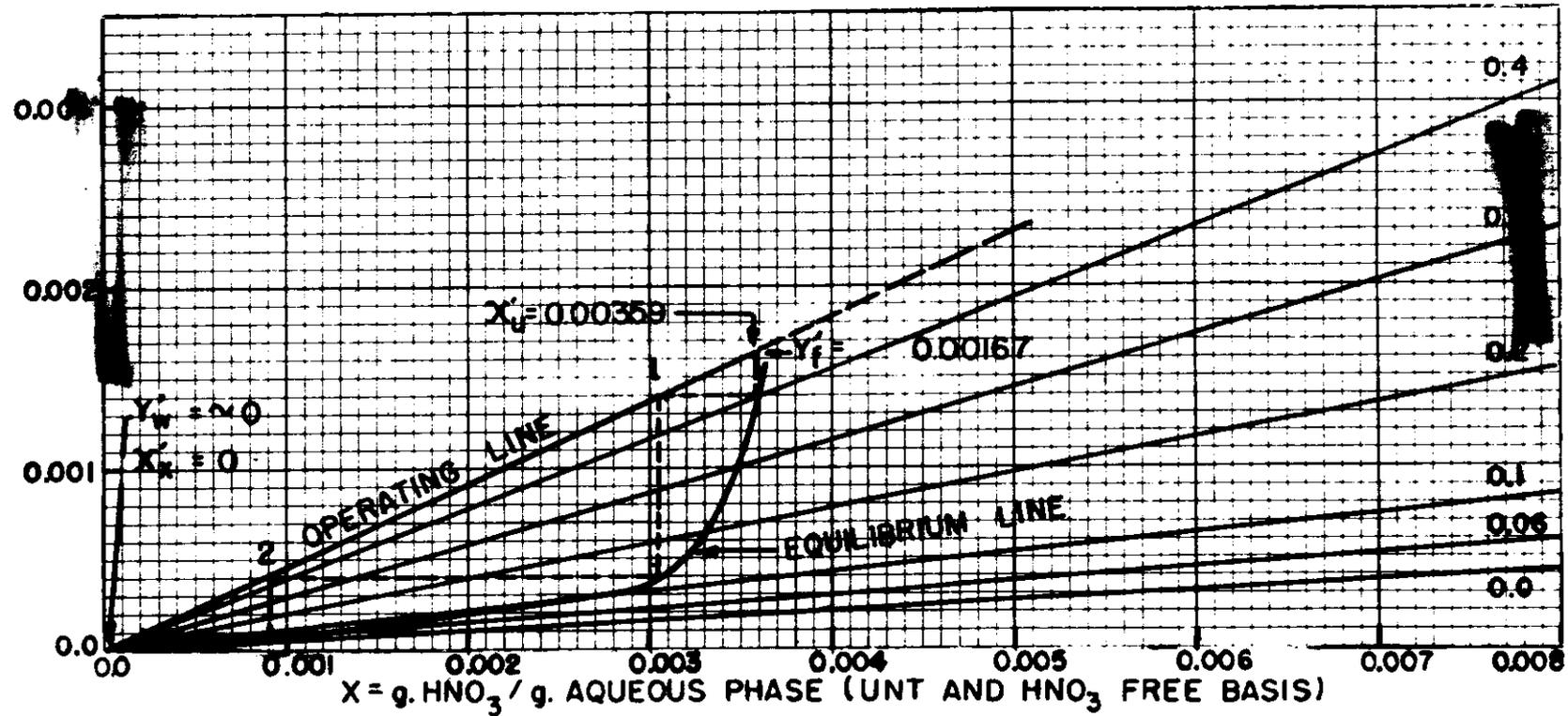


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FIGURE V-4 IC COLUMN HNO₃ OPERATING DIAGRAM (CALCULATIONS FOR RUN 5"-55-CU)

This figure is used in conjunction with Figure V-3 for evaluating the mass-transfer performance of IC Column runs. Numbers on each parameter refer to the UNT concentration in the aqueous phase expressed as g.UNT/g. aqueous phase(UNT-free basis). The equilibrium and operating lines shown are developed as discussed in Subsection B3.3 of the text.

Y = g. HNO₃ / g. HEXONE PHASE (UNT AND HNO₃ FREE BASIS)



HW-18700
FIG. V-4

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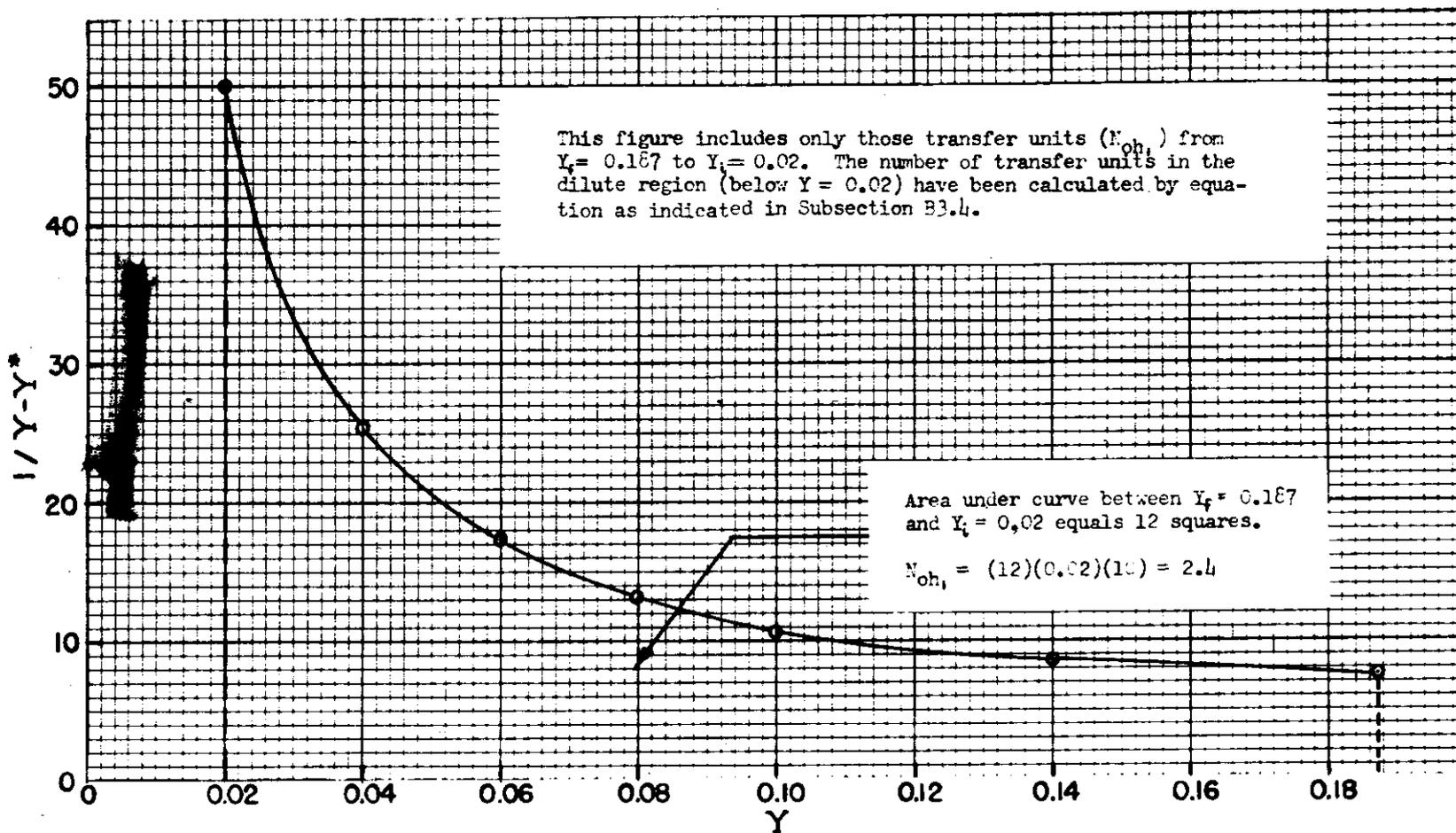
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FIGURE V-5

DETERMINATION OF THE NUMBER OF TRANSFER UNITS OBTAINED DURING RUN 5"-55-CU
BY GRAPHICAL INTEGRATION



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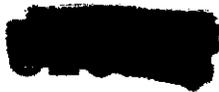
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HW-18700
FIG. V-5

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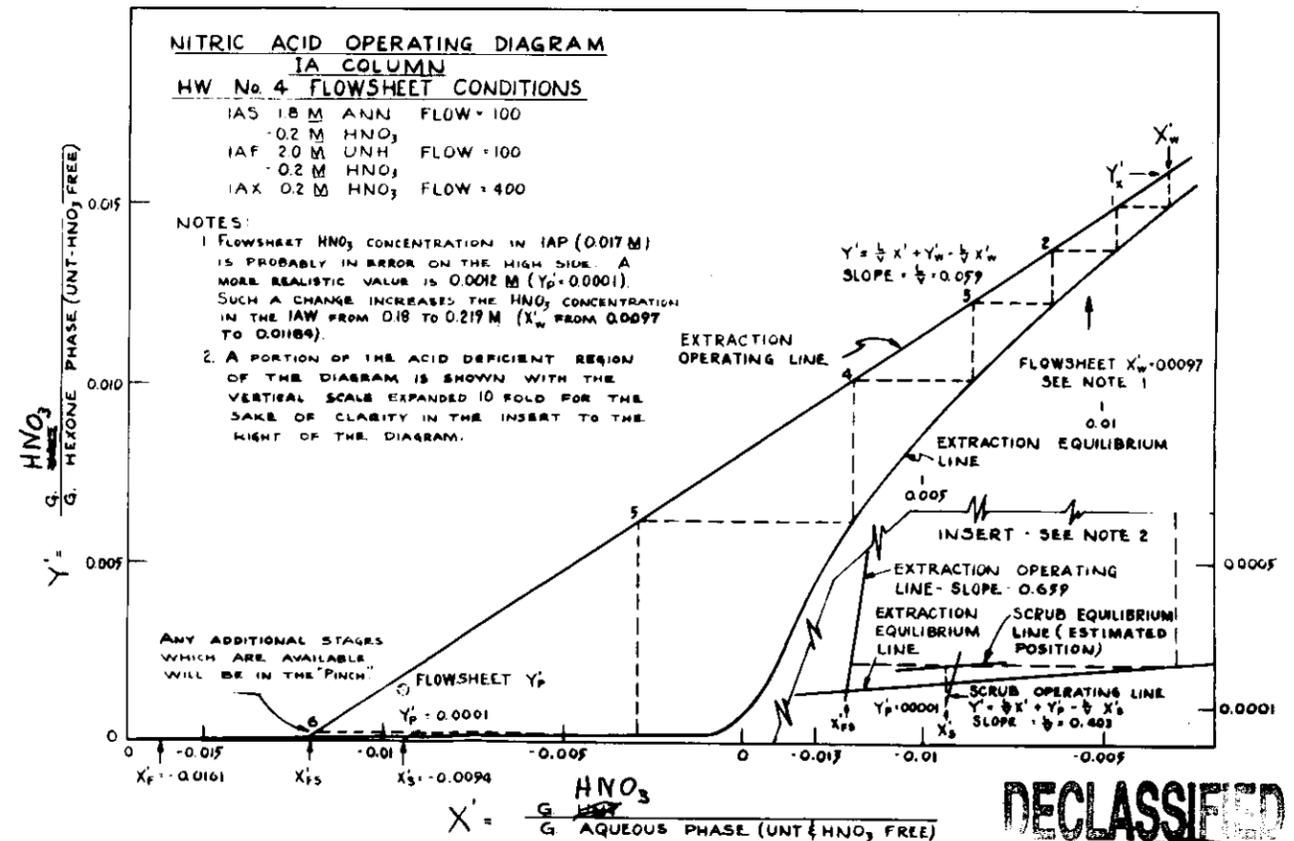
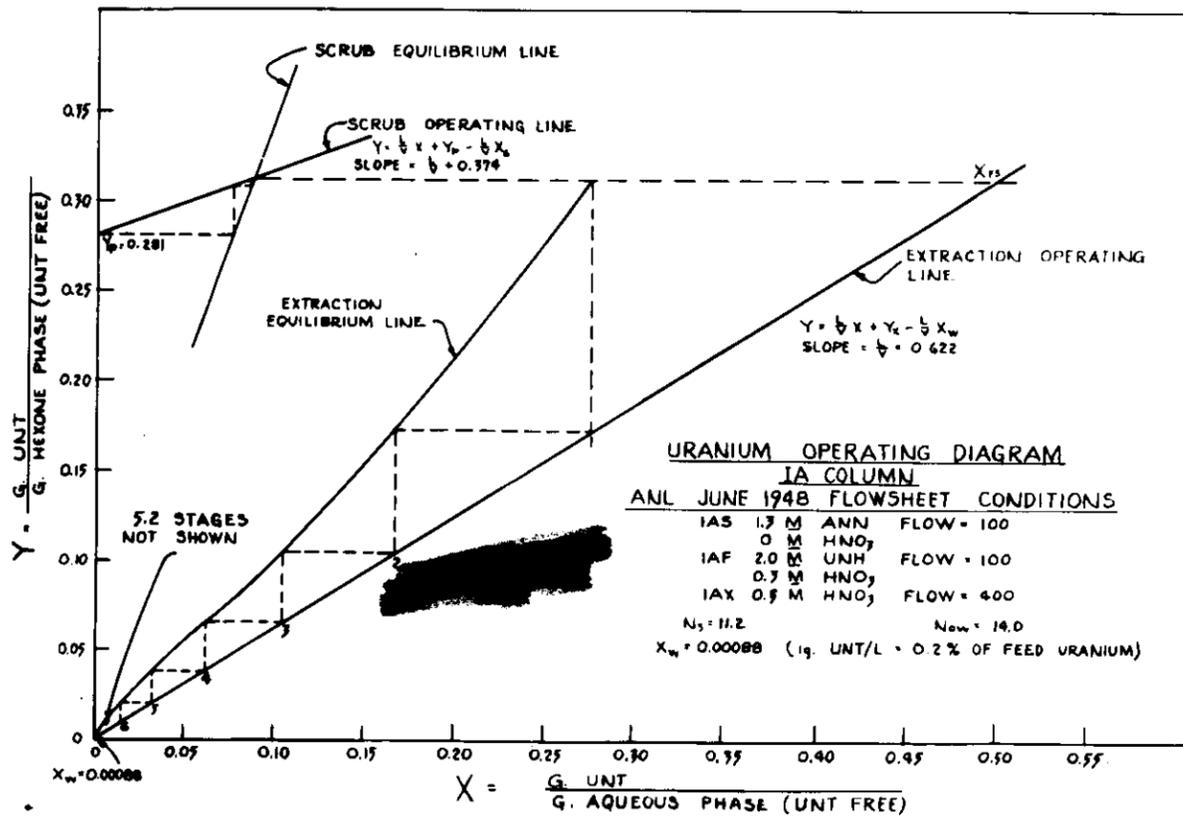
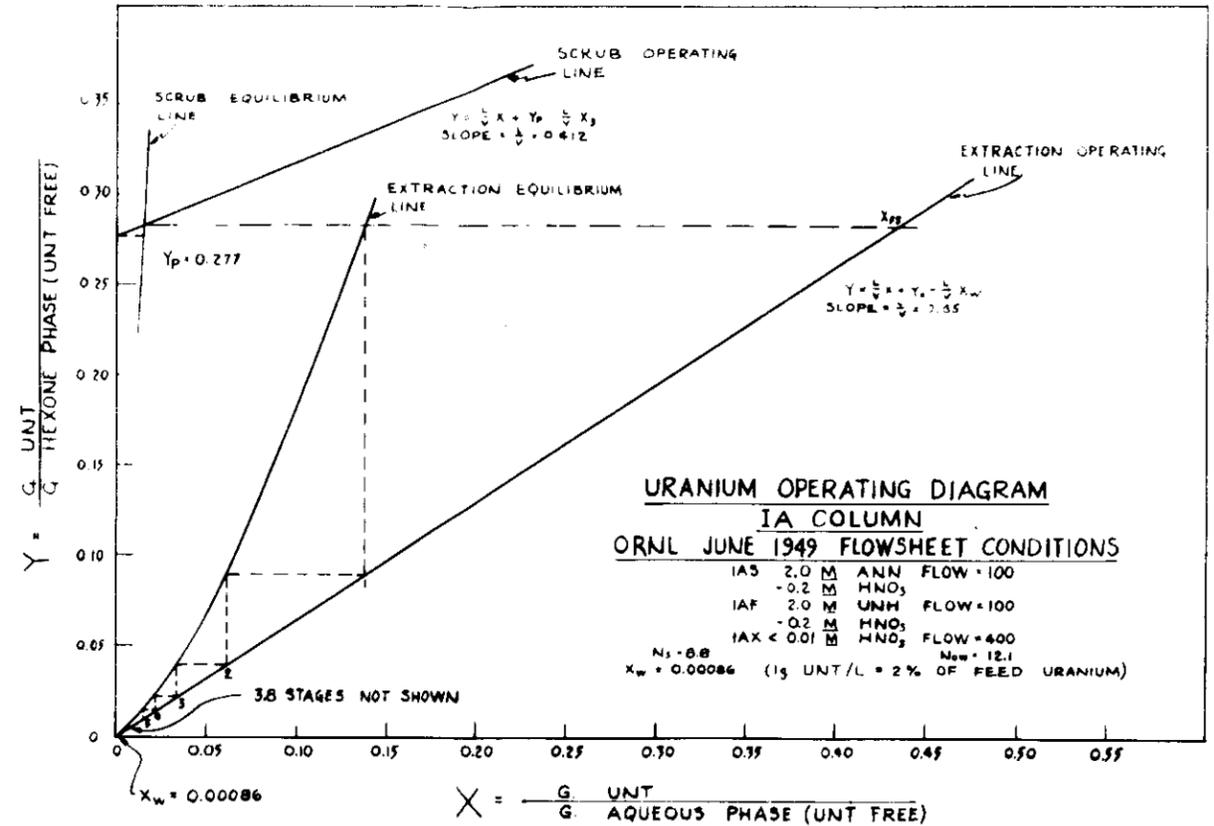
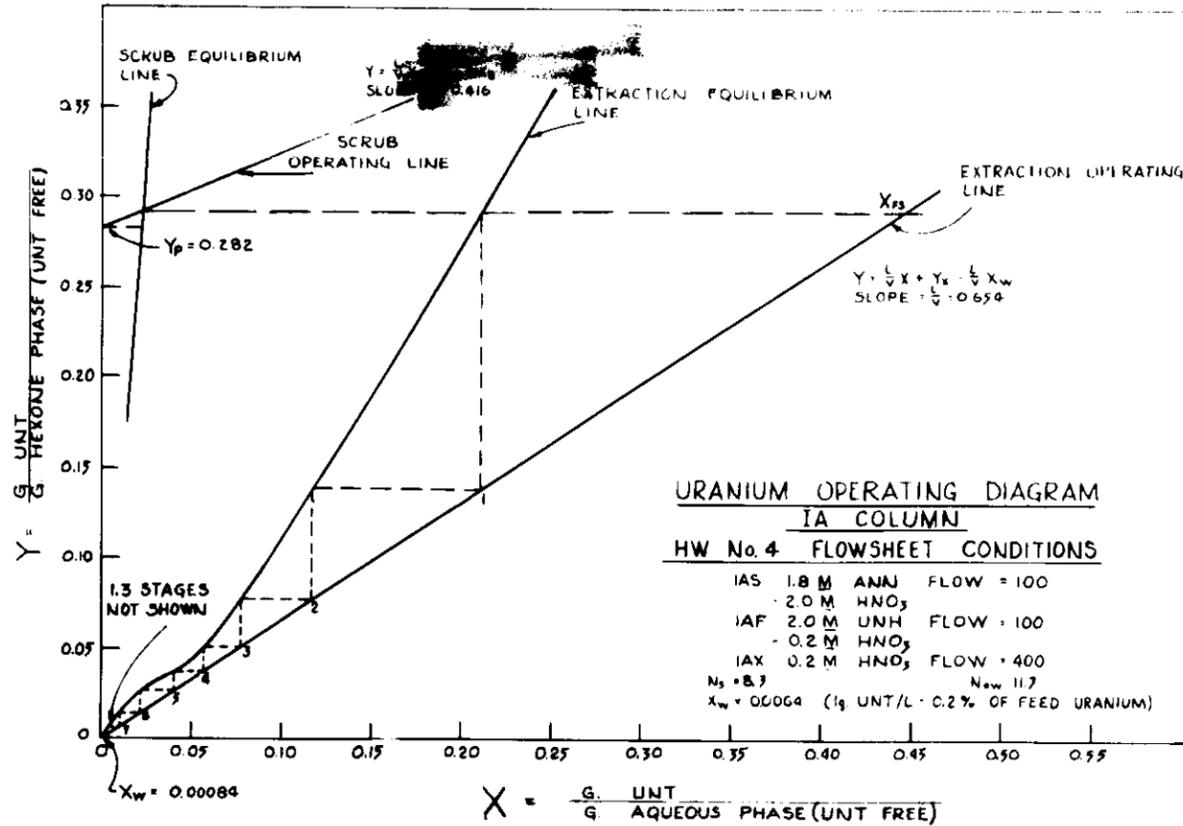


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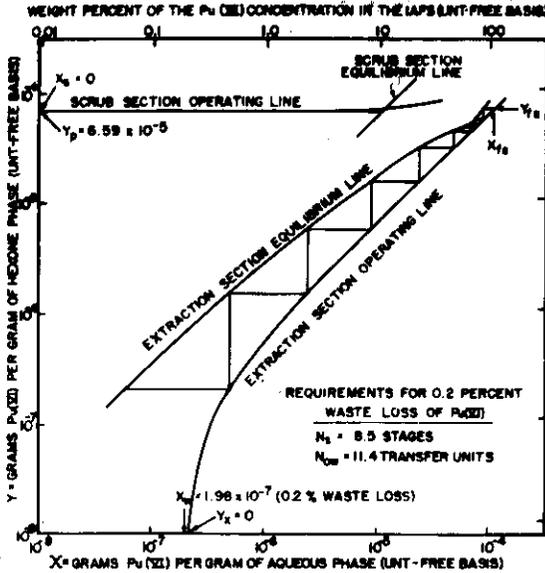
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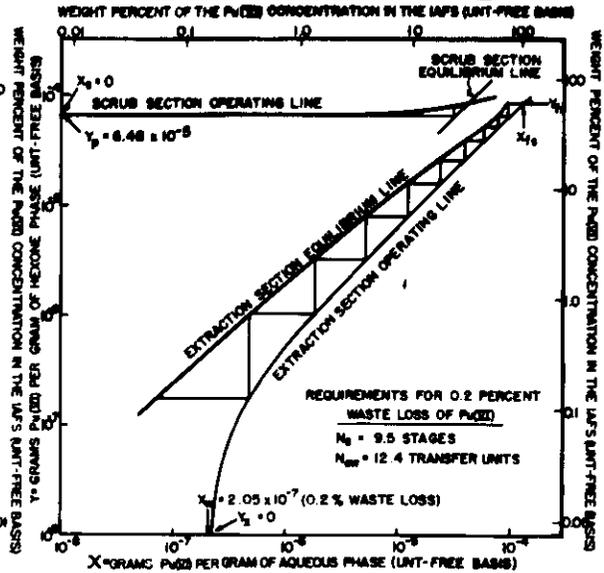
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FIGURE 7-7
IA COLUMN Pu(VI) OPERATING DIAGRAMS

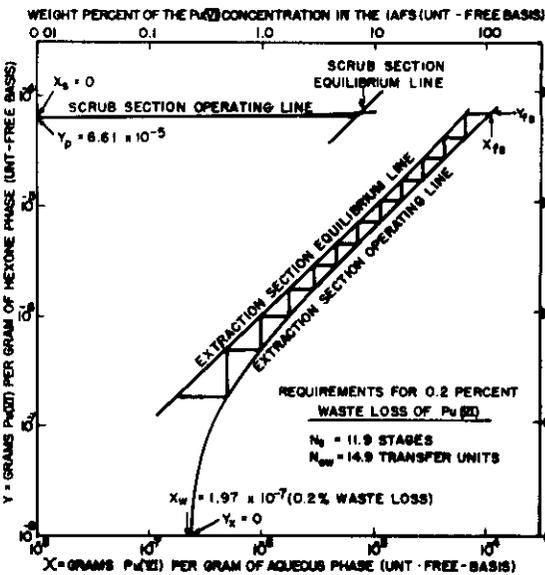
H.W. N° 4 FLOWSHEET



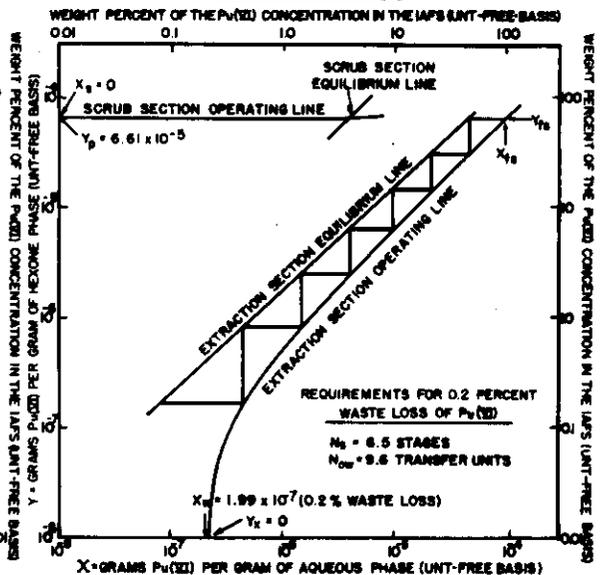
A.N.L. JUNE, 1948 FLOWSHEET



O.R.N.L. JUNE, 1949 FLOWSHEET



O.R.N.L. JUNE, 1949 FLOWSHEET WITH SALTING STRENGTH INCREASED 0.1M IN THE EXTRACTION SECTION



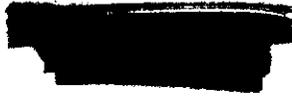
NOTES:

- Influent stream compositions and flow ratios for the three flowsheet diagrams are as specified for the HW N° 4, ANL June, 1948, and ORNL June, 1949 Flowsheets (Figs. 1-2, 1-3, and 1-4). The diagram for the ORNL June, 1949 Flowsheet with increased salting strength shows the effect of increasing the IAS AM concentration from 2.0M to 2.1M, with influent stream flow ratios and other concentrations remaining the same. Approximately the same effect could be obtained by increasing the relative flow of the IAS 25%, leaving the IAS AM concentration at 2.0M.
- Plutonium concentrations are indicated in grams per gram of non-UHT, based on 0.210 g./l. in the IAF (equivalent to 600 grams of Pu per short ton of U), and in per cent of the plutonium concentration in the IAFS (on a UHT-free basis). The latter scale may be applied to any other plutonium concentration, as the plutonium concentration range in the IA Column is low enough to have no effect on the position of the Pu(VI) equilibrium line.

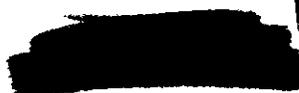
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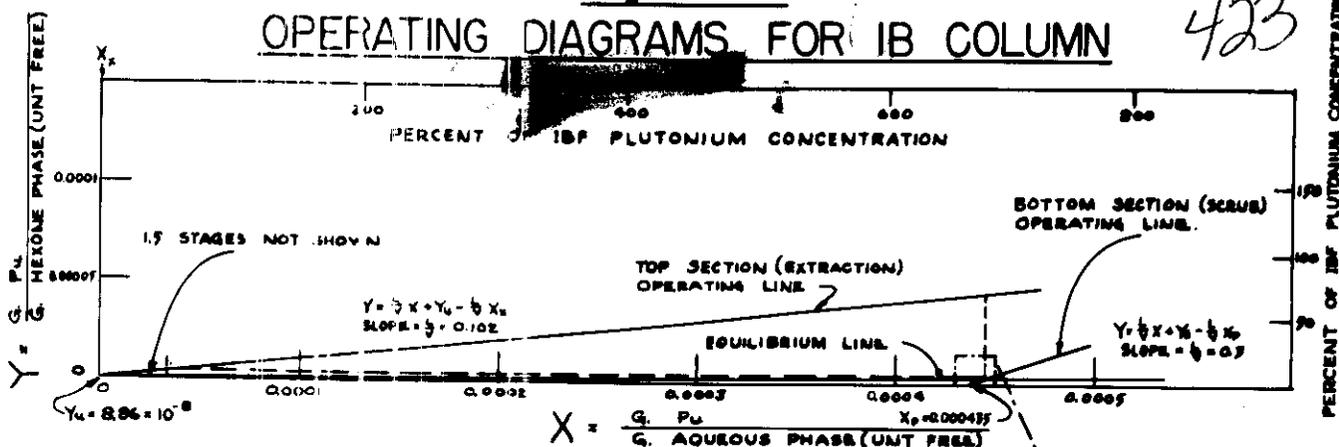
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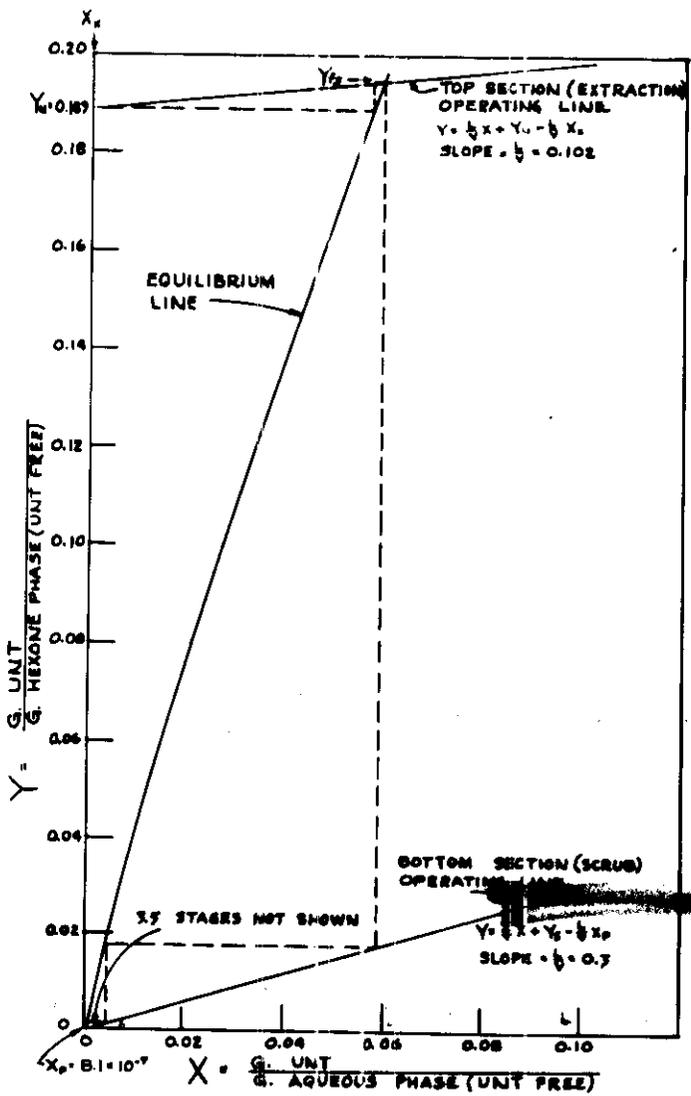
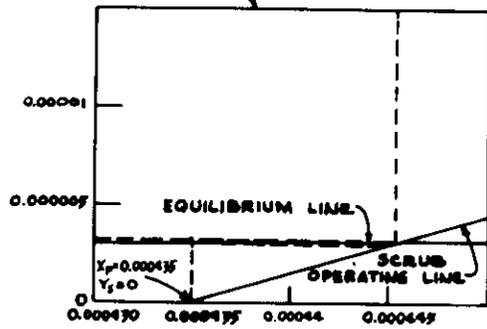
Figure V-8

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PLUTONIUM OPERATING DIAGRAM
 IB COLUMN
 HW No 4 FLOWSHEET CONDITIONS

IBX 1.3 M ANN IBF 0.476 M UHM IBS 0.05 M HNO₃
 0.05 M HNO₃ 0.017 M HNO₃
 0.05 M Fe(H₂NSO₃)₂ 2.1 · 10⁻⁴ M Pu
 N₂ = 2.5 (EXTRACTION) N_{scrub} = 6.6 (EXTRACTION)
 $Y_0 = 8.86 \cdot 10^{-8}$ (6.8 · 10⁻⁸ g. Pu/L = 0.2 % OF FEED PLUTONIUM AT A
 FEED CONCENTRATION OF 400 G. Pu / TON U)
 IBF FLOW : IBX : IBS :: 420 : 40 : 200



URANIUM OPERATING DIAGRAM
 IB COLUMN
 HW No.4 FLOWSHEET CONDITIONS

IBX 1.3 M ANN IBF 0.476 M UHM IBS 0.05 M HNO₃
 0.05 M HNO₃ 0.017 M HNO₃
 0.05 M Fe(H₂NSO₃)₂ 2.1 · 10⁻⁴ M Pu
 N₂ = 4.5 (SCRUB) N_{scrub} = 11.6 (SCRUB)
 $X_0 = 8.1 \cdot 10^{-7}$ (8.7 · 10⁻⁶ g. UNT/L = 1 PART URANIUM PER
 1000 OF PLUTONIUM AT A FEED CONCENTRATION OF
 400 G. Pu / TON U)
 IBF FLOW : IBX : IBS :: 420 : 40 : 200

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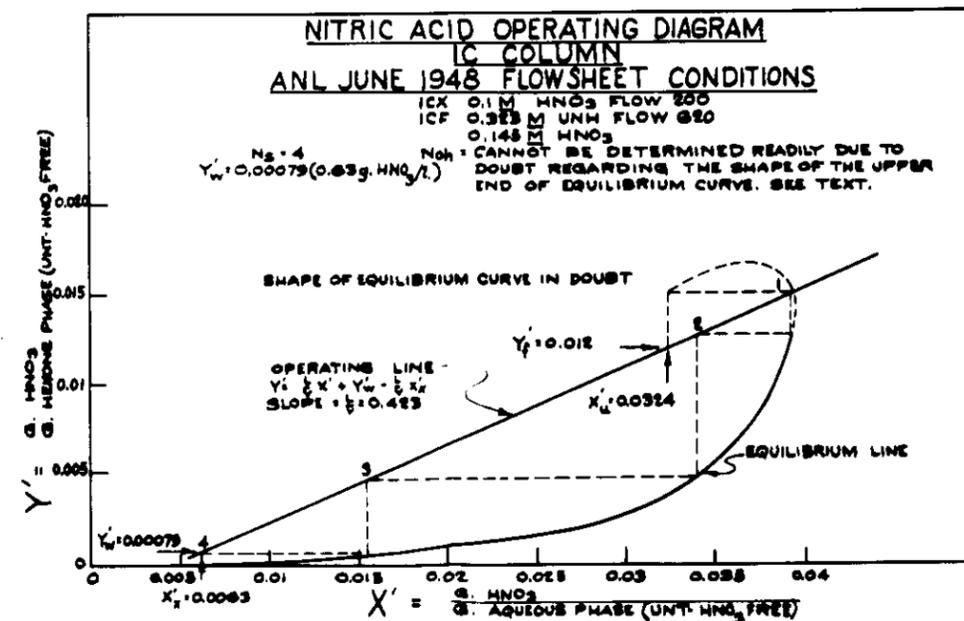
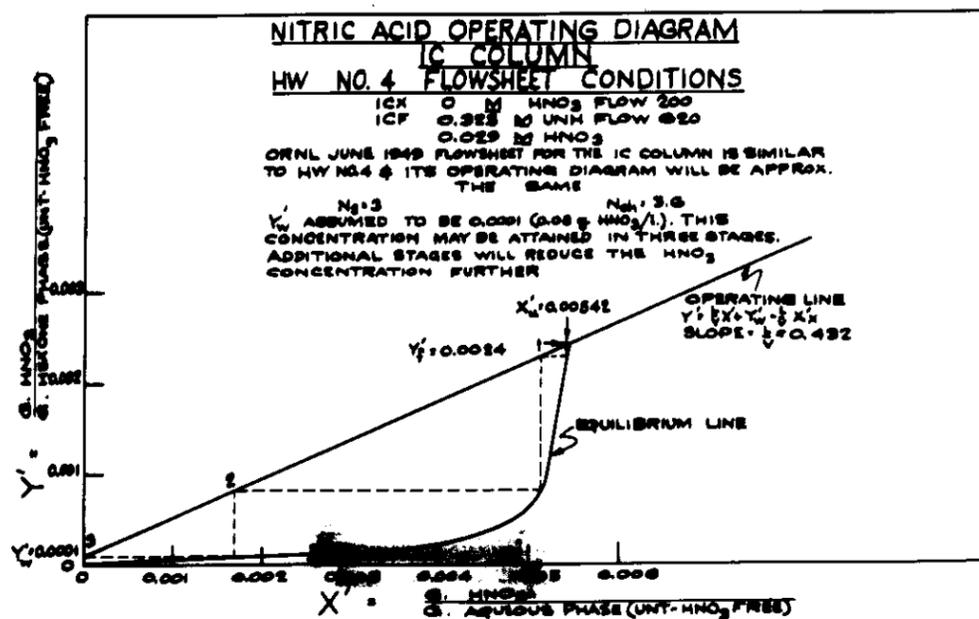
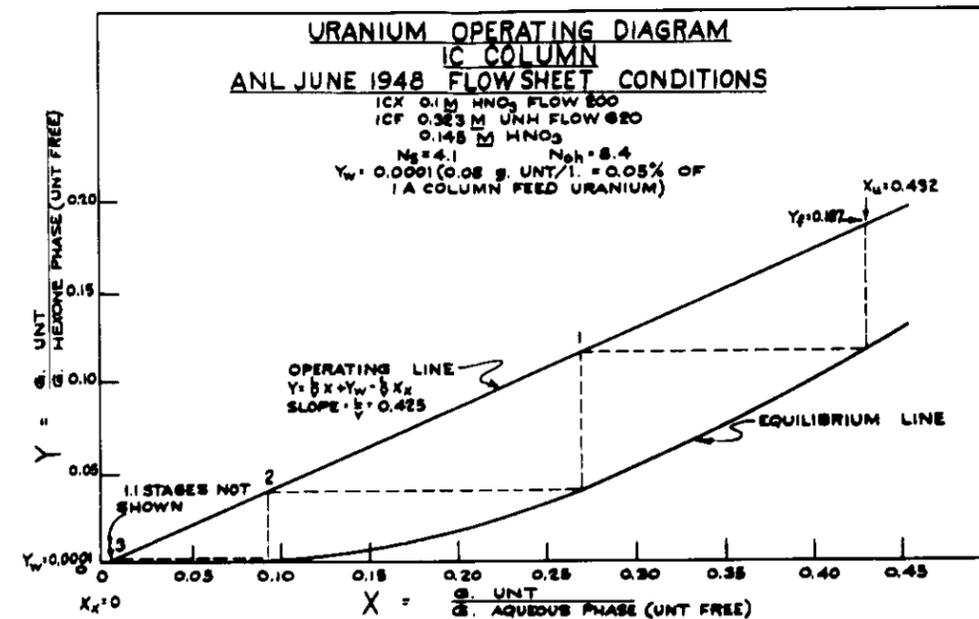
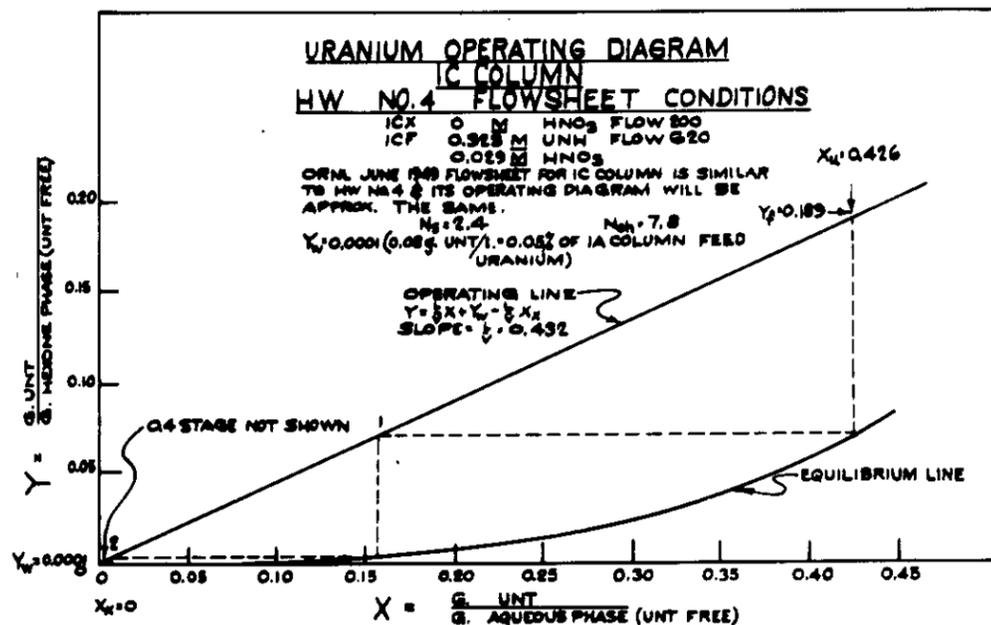
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Figure V-9
OPERATING DIAGRAMS FOR IC COLUMN



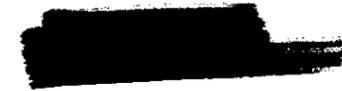
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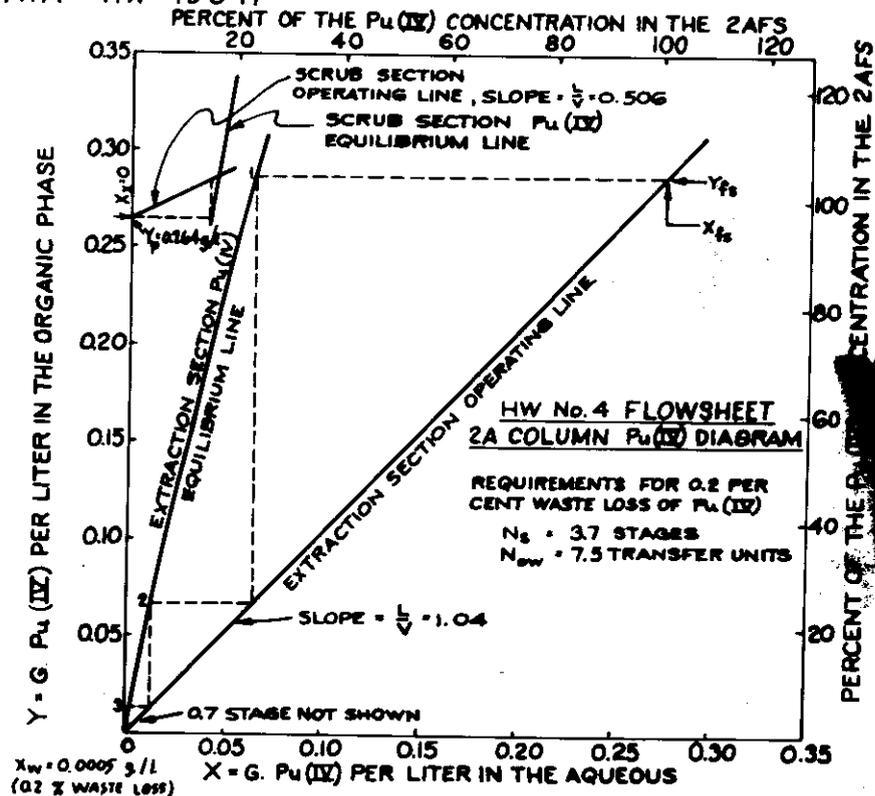
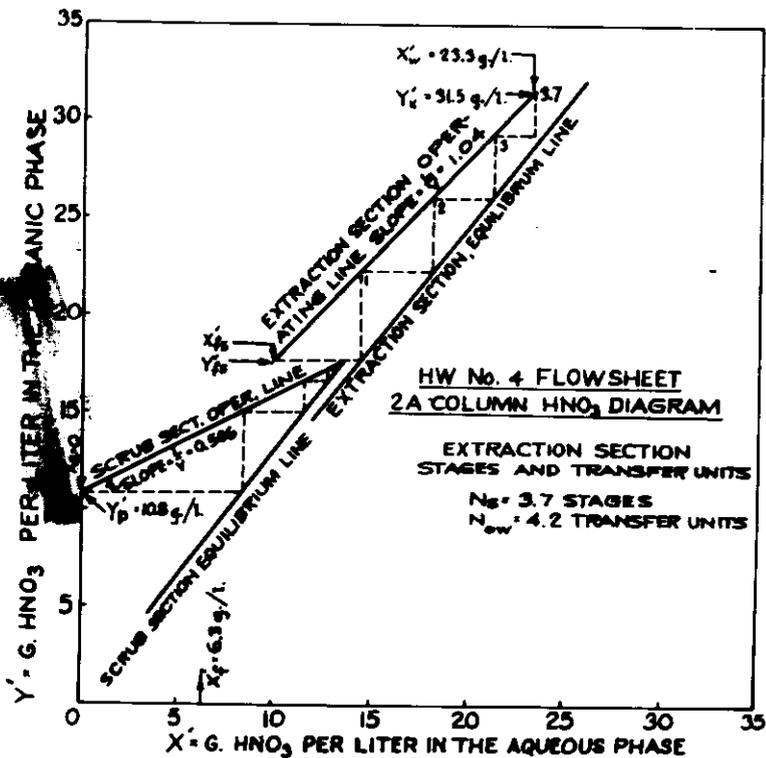
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FIGURE V-10 OPERATING DIAGRAMS FOR THE 2A COLUMN

SOURCE OF DATA : HW-19047



NOTES:

1. Stream compositions and flow ratios are as specified on the HW#4 Flowsheet (Fig. I-2).
2. The number of stages and "overall water-film" transfer units required in the 2A Column extraction section for a Waste Loss of 0.2 per cent of the 2AF Pu(IV) to the 2AV are shown on the plutonium (IV) diagram.
3. The 2A Column is designed to extract both Pu(IV) and Pu(VI). As Pu(IV) is the more difficult of the two valence states to extract, the stage and transfer unit requirements for a 0.2 per cent waste loss of plutonium will be reduced if the 2AF contains Pu(VI).
4. It was assumed in constructing these diagrams that the number of extraction section stages for nitric acid extraction was equal to the number of extraction section stages for Pu(IV) extraction. Thus both diagrams have the same number of extraction section stages.
5. The Pu(IV) diagram plutonium concentrations are indicated in grams per liter, based on 0.50 grams per liter in the 2AF (equivalent to 500 grams Pu per short ton of U) and in per cent of the Pu(IV) concentration in the 2AFs. The latter may be applied to any other 2AF plutonium concentration, as the plutonium concentration range in the 2A Column is low enough to have no effect on the position of the Pu(IV) equilibrium line.

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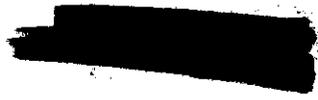
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HW-18700
FIG. V-10

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FIGURE V-11
2B COLUMN OPERATING DIAGRAMS FOR THE HW No. 4 FLOWSHEET

SOURCE OF DATA : HW-19047

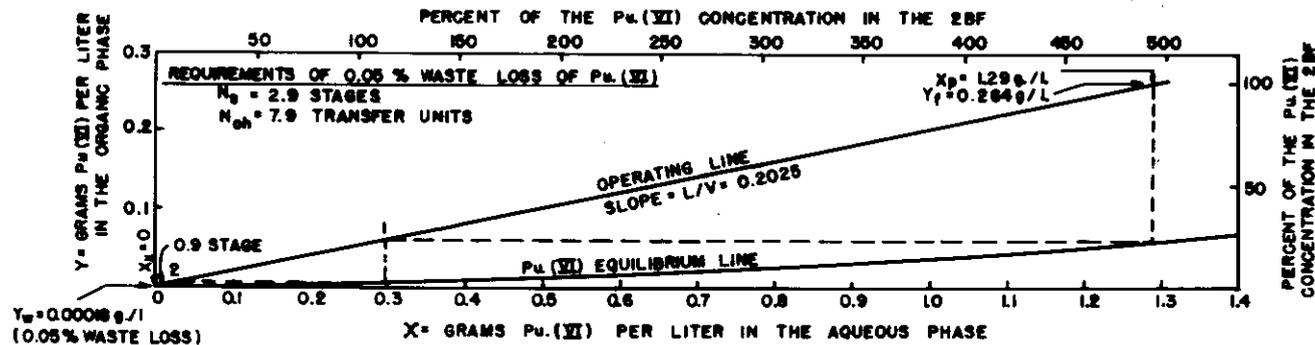
Stream compositions and flow ratios are as specified on the HW#4 Flowsheet (Fig. I-2).

Calculations for these diagrams were based on the assumption that the number of Pu(VI) stages and number of HNO₃ stages are equal. Thus the same number of stages is shown on each diagram.

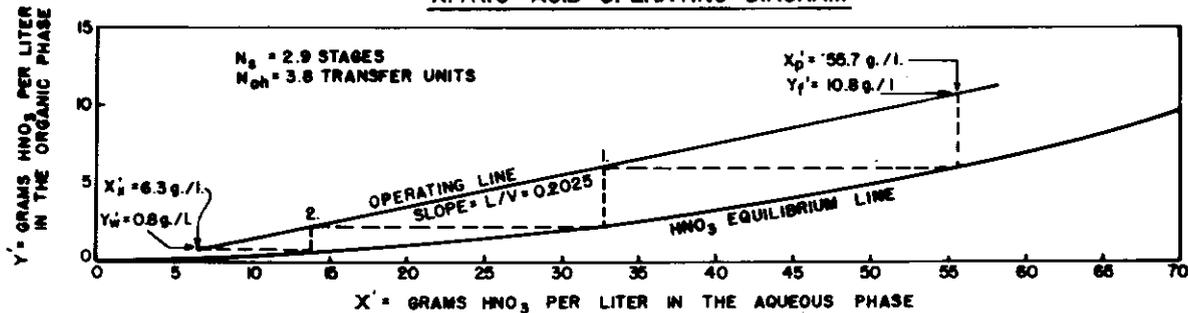
Pu (VI) OPERATING DIAGRAM

The 2B Column is designed to strip both Pu(IV) and Pu(VI). Equilibrium relationships for Pu(IV) stripping are more favorable than for Pu(VI) stripping, thus the number of stages and transfer units for a 0.05 per cent waste loss of plutonium will be reduced if the 2HF contains Pu(IV).

Plutonium concentrations are indicated in grams per liter, based on 0.264 grams per liter in the 2HF (equivalent to 600 grams Pu per short ton of U), and in per cent of the 2HF plutonium concentration. The latter scale may be applied to any other 2HF plutonium concentration, as the plutonium concentration range in the 2B Column is low enough to have no effect on the position of the Pu(VI) equilibrium line.



NITRIC ACID OPERATING DIAGRAM



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 FIG V-11

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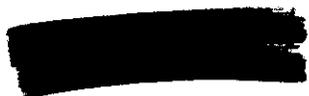
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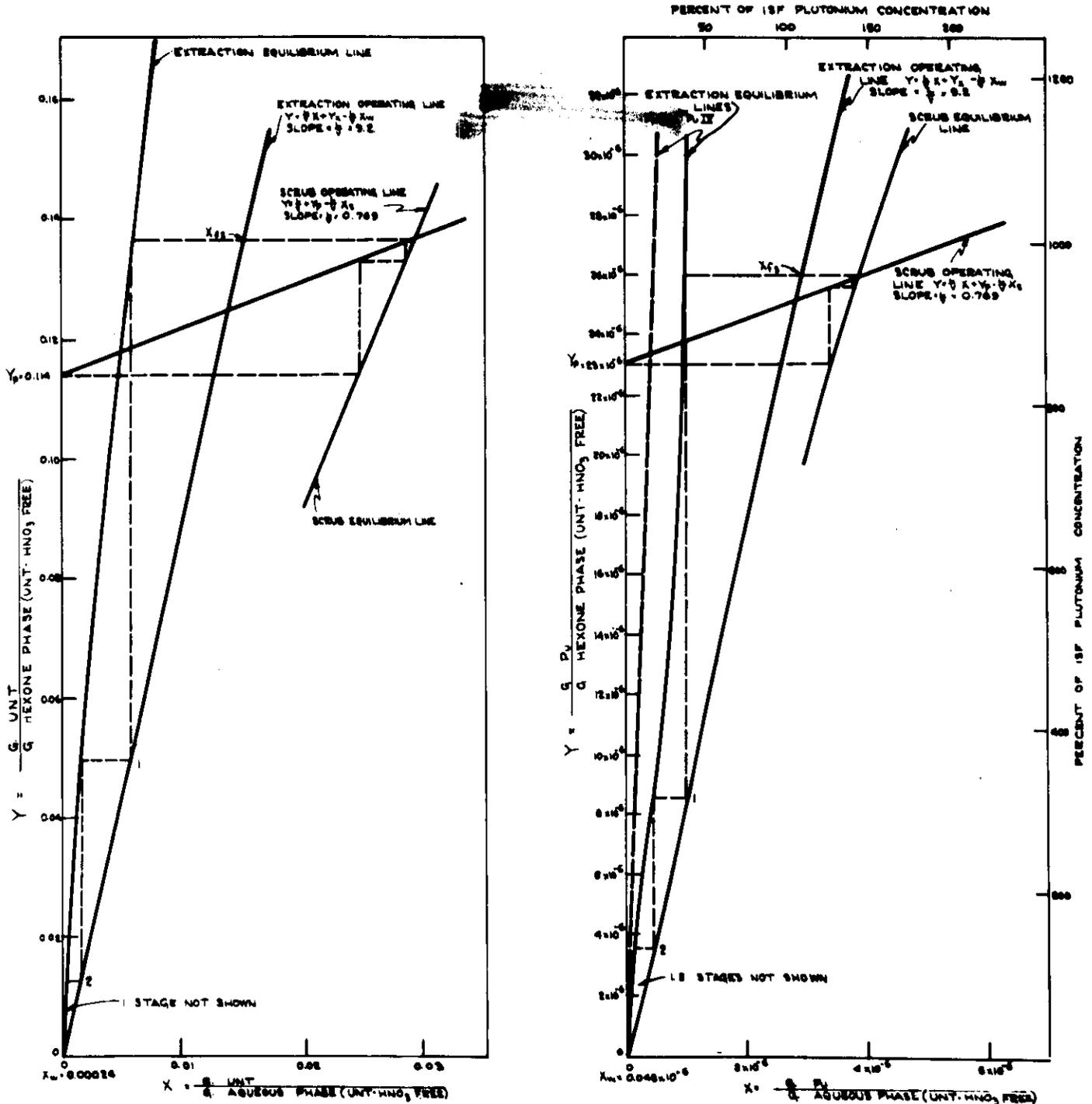
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FIGURE V-12
OPERATING DIAGRAM FOR IS REWORK COLUMN



URANIUM OPERATING DIAGRAM
IS COLUMN

HW N53 FLOWSHEET CONDITIONS FOR REWORK OF OFF-STANDARD STREAMS (HW-18700) EXCEPT THAT URANIUM WASTE LOSS IS ASSUMED 2% OF ISF FEED URANIUM (A 0.1% URANIUM LOSS BASED UPON IAP)

ISU	13 M ANN	FLOW = 277
ISF	0.15 M HNO ₃	FLOW = 277
	0.05 M ANN	
	0.05 M UHM	
	0.15 M HNO ₃	
ISX	0.2 M HNO ₃	FLOW = 554
	0.2 M HNO ₃	

N₅ = 2.0
X_W = 0.00024 (0.25 G. UNIT/L. 1% OF ISF URANIUM)
(NOTE UNEQUAL SCALES)

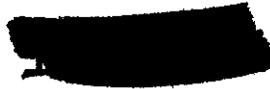
PLUTONIUM OPERATING DIAGRAM
IS COLUMN

HW N53 FLOWSHEET CONDITIONS FOR REWORK OF OFF-STANDARD STREAMS (HW-18700) EXCEPT THAT PLUTONIUM WASTE LOSS IS ASSUMED 2% OF ISF FEED PLUTONIUM (A 0.1% PLUTONIUM LOSS BASED UPON IAP)

ISU	13 M ANN	FLOW = 277
ISF	0.15 M HNO ₃	FLOW = 277
	0.05 M ANN	
	0.05 M UHM	
	0.15 M HNO ₃	
ISX	0.2 M HNO ₃	FLOW = 554
	0.2 M HNO ₃	

N₅ = 2.0
X_W = 0.046 x 10⁻⁶ (0.25 G. P_U/L. 1% OF PLUTONIUM AT A PLUTONIUM CONCENTRATION IN URANIUM IN THE ISF OF 100 G. P_U/TON U)
(NOTE UNEQUAL SCALES)

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Table V-13

RANGEABILITIES OF THE REDOX PLANT COLUMNS

Basis: HW #4 Flowsheet

Refer to Figures V-12 to V-21 for Experimental Data

Operating Rangeabilities For Good Extraction Performance

Column	Column I.D., In.	Raschig Ring Size, In.	Gal./Hr. (Sq.Ft.), Sum of Both Phases	Pu Production Rate, G.Pu/Day, Instantaneous ^(b)	Equivalent Short Tons U/Day Instantaneous Rate
1A	6.5	1/2	300 to 1700	---	0.55 to 3.1
		3/4	350 to 2400	---	0.64 to 4.4
		1	600 to 3000	---	1.1 to 5.5
1B	5.0 (Scrub Section)	1/2	400 to 1800	---	1.1 to 4.9
		3/4	600 to 2400	---	1.6 to 6.5
		1	800 to 2800	---	2.2 to 7.6
1C	10.0	1/2	300 to 1600	---	0.95 to 5.1
		1	300 to 2500	---	0.95 to 7.9
2D and 3D	7.5	1/2	300 to 1700	---	0.73 to 4.1
		3/4	350 to 2400	---	0.85 to 5.9
		1	600 to 3000	---	1.5 to 7.3
2E and 3E	9.0	1/2	300 to 1700	---	1.0 to 5.8
		1	300 to 2500	---	1.0 to 8.5
2A	4.0	1/2	350 to 1350	340 to 1300	0.90 to 3.5
		3/4	350 to 2000	340 to 1930	0.90 to 5.1
2B	3.0	1/2	250 to 1500	230 to 1390	0.61 to 3.7
		3/4	400 to 1800	370 to 1670	0.96 to 4.4
3A	4.0	1/2	350 to 1350	360 to 1410	0.97 to 3.7
		3/4	350 to 2000	360 to 2060	0.97 to 5.5
3B	3.0	1/2	250 to 1500	250 to 1550	0.69 to 4.1
		3/4	400 to 1800	410 to 1860	1.1 to 4.9
1B	5.0	1/2	2100 ^(a)	---	0.50 ^(a)
		3/4	2600 ^(a)	---	0.62 ^(a)
10	12.0	1	300 to 2500 (Processing 5,400 to 45,000 gal. hexone/24 hr.)		0.7 to 5.9

Notes:

(a) Stated values are for optimum performance conditions predicted for the 1B Column on the basis of typical uranium rework runs in 3-in. I.D. column. Stated uranium processing rate is based on a ISP which is 0.476 M in uranium and a flow ratio in the column (ISP:HX:ISS) of 10:2:1 (i.e., HW #3 Flowsheet conditions).

(b) Based on 376 grams Pu/short ton of uranium enrichment level.

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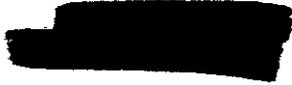
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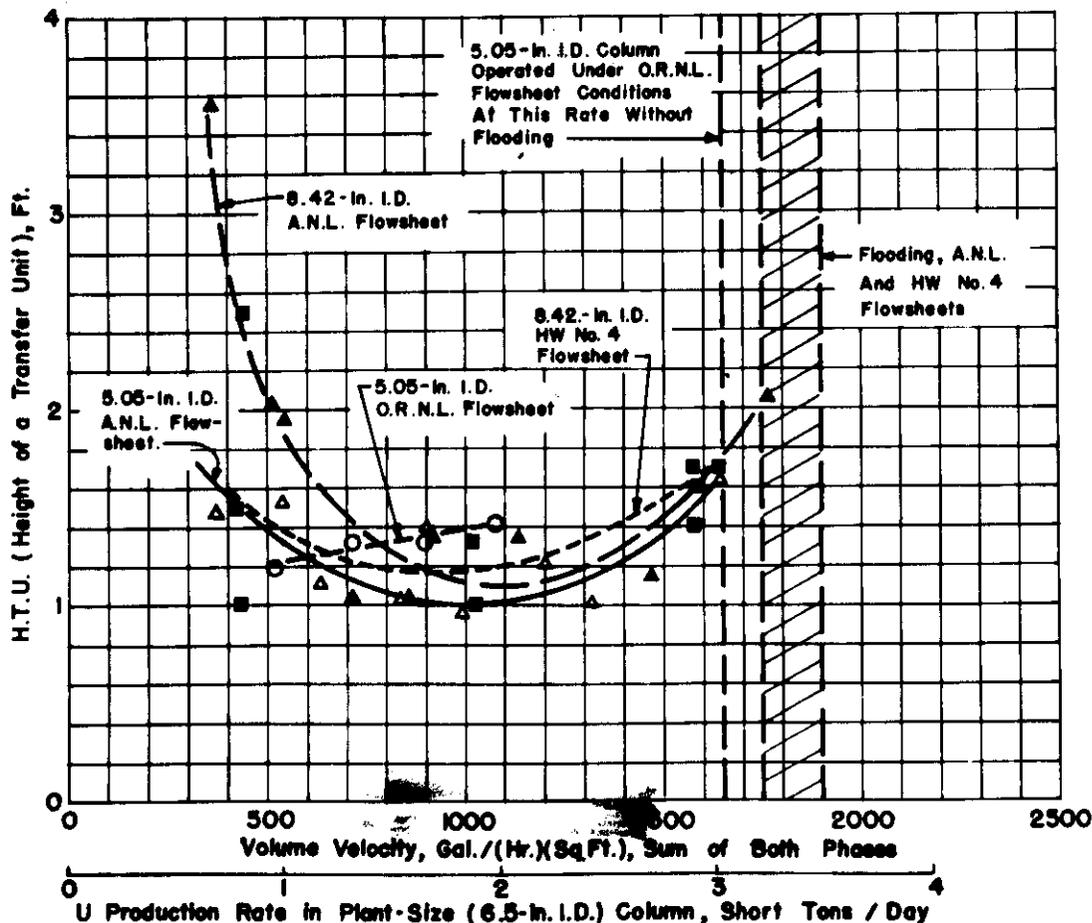


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Figure X-14
H.T.U. vs. VOLUME VELOCITY - 1A COLUMN EXTRACTION SECTION
Comparison of Flowsheets

Diffusing Component : $UO_2(NO_3)_2$ (Unirradiated U)
 Packing : $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall Stainless-Steel Raschig Rings.
 H.T.U. Calculations : "Overall Aqueous - Film" Basis
 Legend :

Symbol	Flowsheet	Column I.D., in.	Packed Length, Ft.
△	A.N.L.	5.05	19.6
▲	A.N.L.	8.42	19.1
■	HW No. 4	8.42	13.9 or 14.7
○	O.R.N.L.	5.05	19.6



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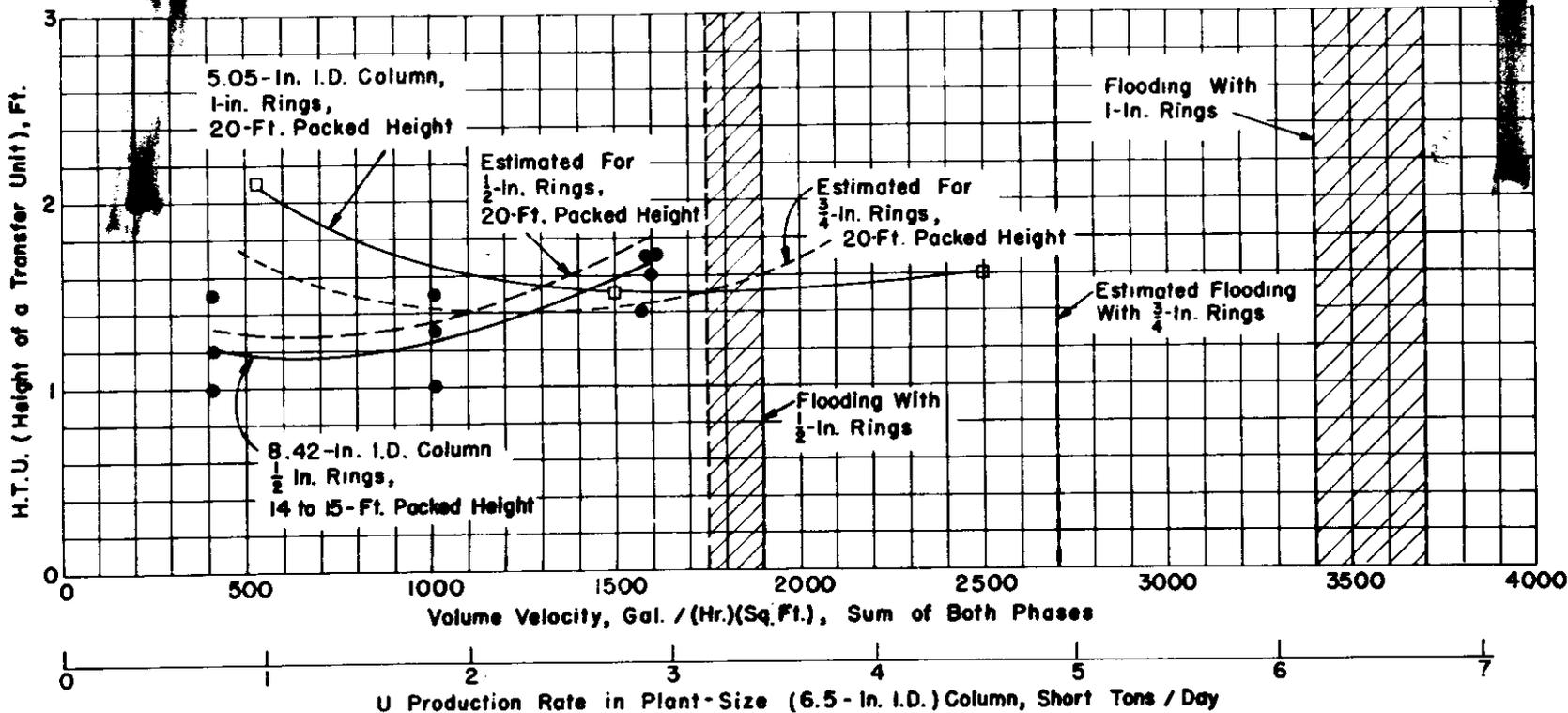
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Figure V-15
H.T.U. vs. VOLUME VELOCITY - IA COLUMN EXTRACTION SECTION
Comparison of $\frac{1}{2}$ -Inch and 1-Inch Raschig Rings.

Diffusing Component: $UO_2(NO_3)_2$ (Unirradiated U)
 Chemical Flowsheet: HW No. 4
 Packing: $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall or
 1-in. x 1-in. x $\frac{1}{32}$ -in. Wall
 Stainless Steel Raschig Rings.
 H.T.U. Calculations: "Overall Aqueous-Film" Basis

Legend:

Symbol	Raschig Ring Size, in.	Column I.D., in.	Packed Length, Ft.
●	$\frac{1}{2}$	8.42	13.9 or 14.7
□	1	5.05	19.8



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HW-18700
 Fig. V-15

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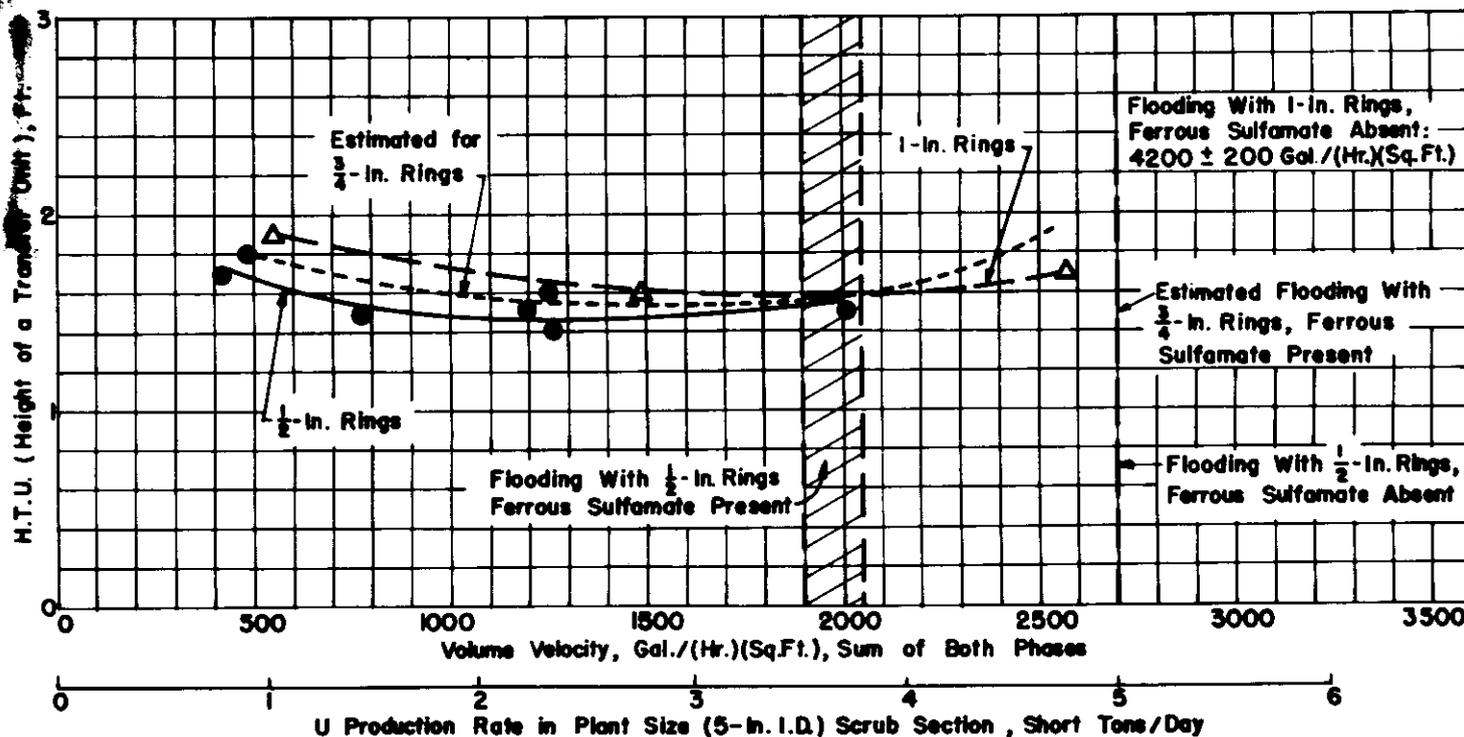
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Figure V-16
H.T.U. vs. VOLUME VELOCITY - IB COLUMN SCRUB SECTION

Diffusing Component: $UO_2(NO_3)_2$ (Unirradiated U)
 Flowsheet: HW No. 4
 Column Diameter: 5.05 in.
 Packed Height: 19.6 to 19.8 Ft.
 Pecking: $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall or 1-in. x 1-in. x $\frac{1}{32}$ -in. Wall
 Stainless-Steel Raschig Rings, as Indicated.
 H.T.U. Calculations: "Overall Aqueous-Film" Basis

Legend:

Symbol	Raschig Ring Size, in.
●	$\frac{1}{2}$
△	1



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 Fig. V-16

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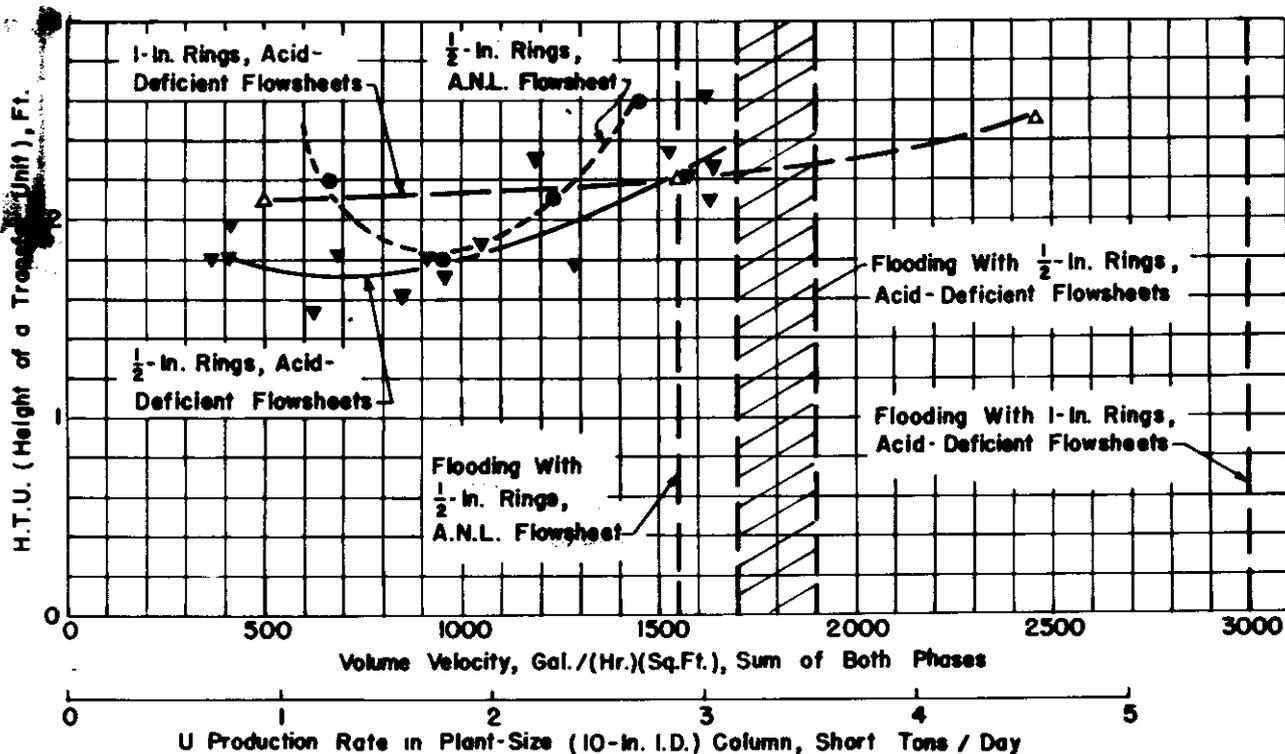
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Figure V-17
H.T.U. vs. VOLUME VELOCITY-IC COLUMN

Diffusing Component: $UO_2(NO_3)_2$ (Unirradiated U)
 Column Diameter: 5.05 in.
 Packed Height: 19.6 to 19.8 Ft.
 Packing: $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall or
 1-in. x 1-in. x $\frac{1}{32}$ -in. Wall Stainless-
 Steel Raschig Rings.
 H.T.U. Calculations: "Overall Organic-Film" Basis:

Legend:

Symbol	Raschig Ring Size, in.	Flowsheet
●	$\frac{1}{2}$	A.N.L.
△	1	HW No. 4
▼	$\frac{1}{2}$	HW No. 4 or O.R.N.L.



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 Fig. V-17

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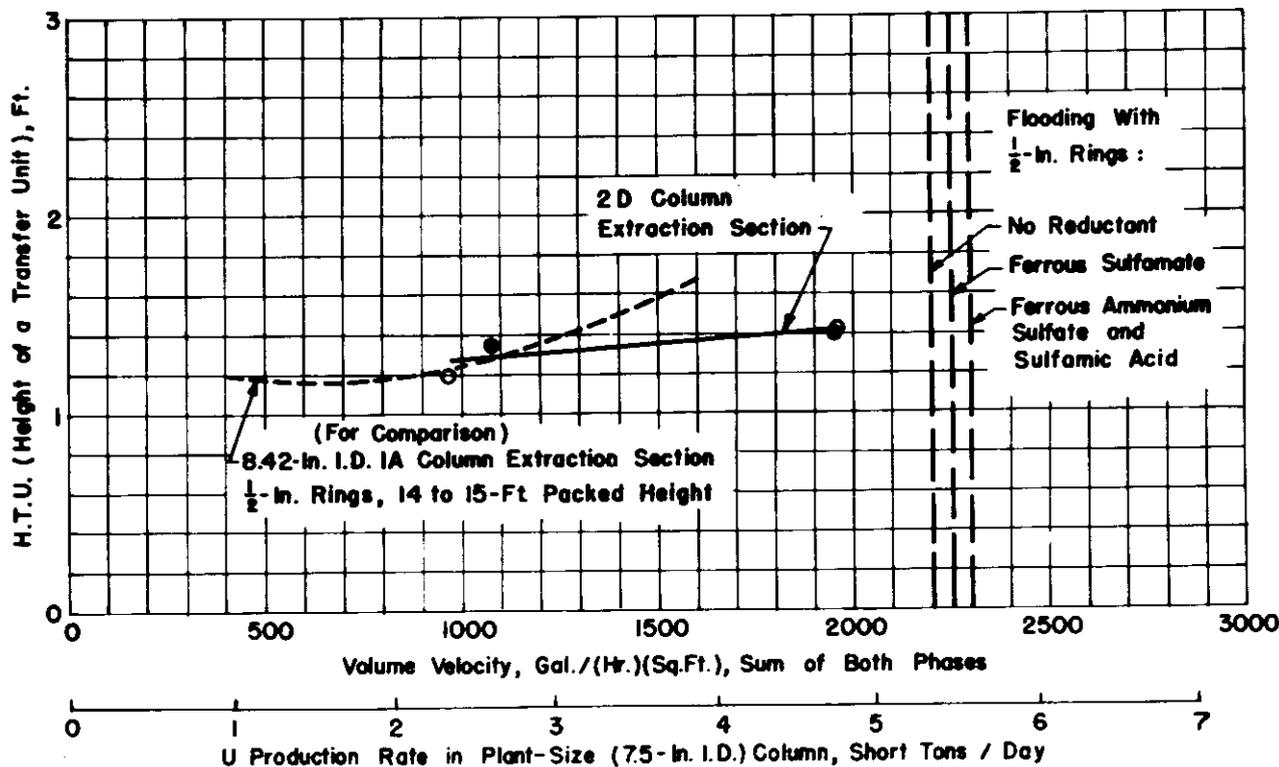
Figure V-18

H.T.U. vs. VOLUME VELOCITY - 2D COLUMN EXTRACTION SECTION

Diffusing Component: $UO_2(NO_3)_2$ (Unirradiated U)
 Chemical Flowsheet: HW No. 4, With Reductant Modified as Shown.
 Column Diameter: 5.05 in.
 Packed Height: 15 Ft.
 Packing: $\frac{1}{8}$ -in. x $\frac{1}{8}$ -in. x $\frac{1}{16}$ -in. Wall Stainless -
 Steel Raschig Rings.
 H.T.U. Calculations: "Overall Aqueous-Film" Basis

Legend:

Symbol	Reductant
○	Ferrous Sulfamate
●	Ferrous Ammonium Sulfate and Sulfamic Acid.



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 Fig. V-18

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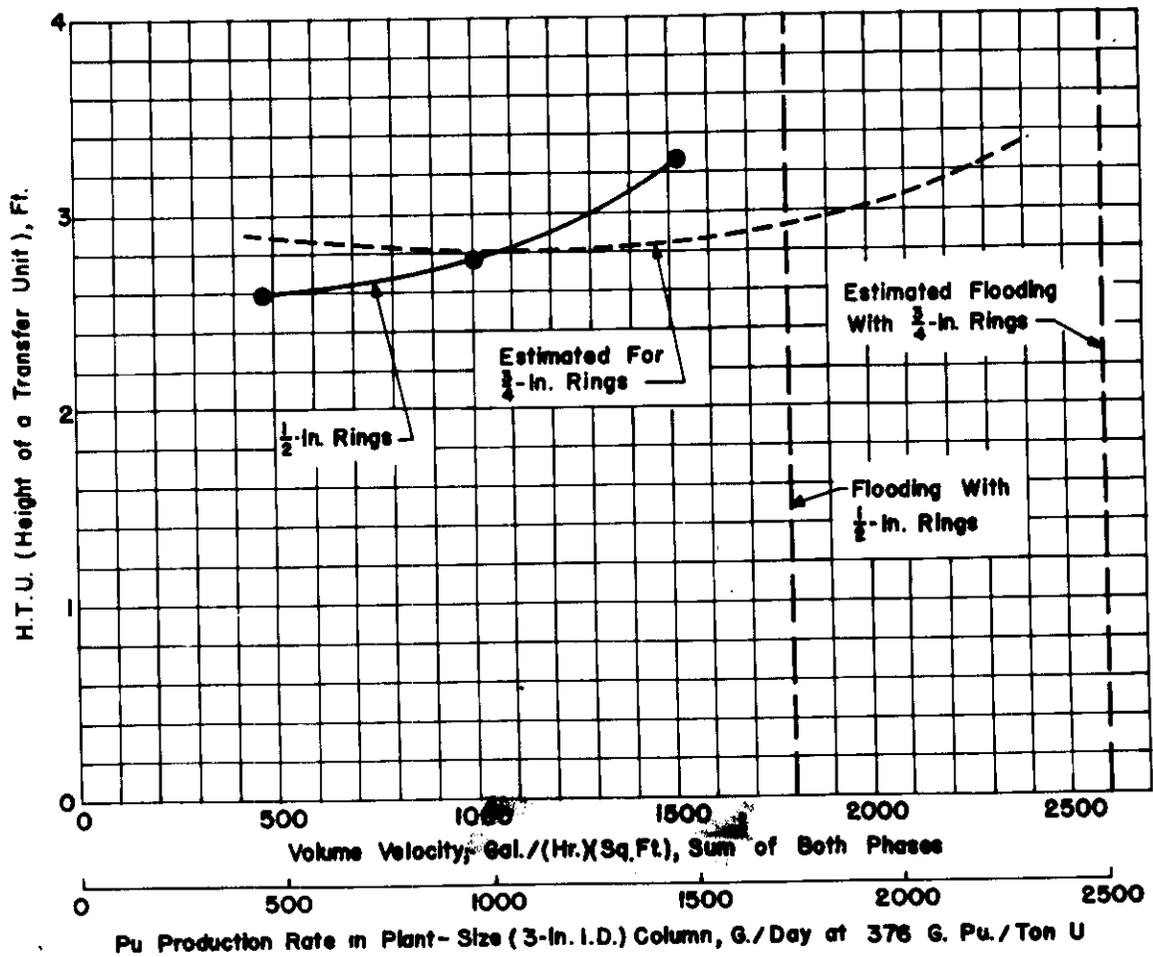
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Figure V-19

H.T.U. vs. VOLUME VELOCITY - 2A COLUMN EXTRACTION SECTION

Diffusing Component: Unirradiated U (UNH) Used as a "Stand-in" for Pu.
 Flowsheet: HW No. 4
 Column Diameter: 5.05 in.
 Packed Height: 16.0 Ft.
 Packing: $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall Stainless-Steel Raschig Rings.
 H.T.U. Calculations: "Overall Aqueous-Film" Basis



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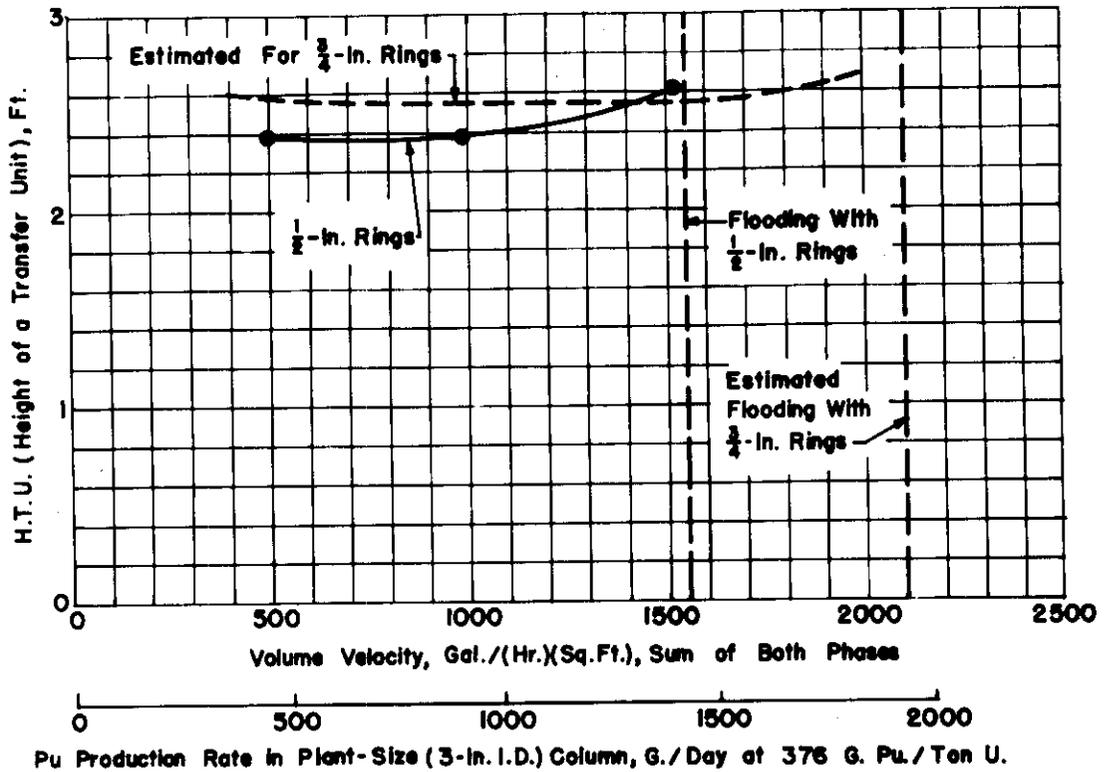


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Figure V-20

H.T.U. vs. VOLUME VELOCITY - 2B COLUMN

Diffusing Component: Unirradiated U (UNH) Used as a "Stand-In" for Pu.
 Flowsheet: HW No. 4
 Column Diameter: 5.05 in.
 Packed Height: 19.9 Ft.
 Packing: $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall Stainless-Steel Raschig Rings.
 H.T.U. Calculations: "Overall Organic-Film" Basis



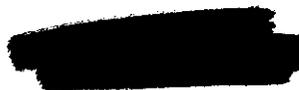
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Figure X-21

HT.U. VS. VOLUME VELOCITY, 1/2 IN. COLUMN EXTRACTION SECTION

Diffusing Component: $UO_2(NO_3)_2$ (Unirradiated U)

Flowsheet:		Concentrations of Constituents, Moles / Liter
Stream	Relative Flow Volumes	
ISF	10	0.04 UNH, 2.0 ANN, 0.085 to 0.15 HNO ₃ , 0.54 to 0.69 NaNO ₃ , 0.025 Na ₂ Cr ₂ O ₇ ·2H ₂ O, 0.0085 Cr ⁺⁺⁺ , 0.0225 Fe ⁺⁺⁺ , 0.065 to 0.13 SO ₄ ⁻ , 0.004 to 0.008 PO ₄ ⁻
ISS	1	1.3 ANN, -0.2 HNO ₃ (Acid-Deficient)
ISX	2	(Neutral Hexane)

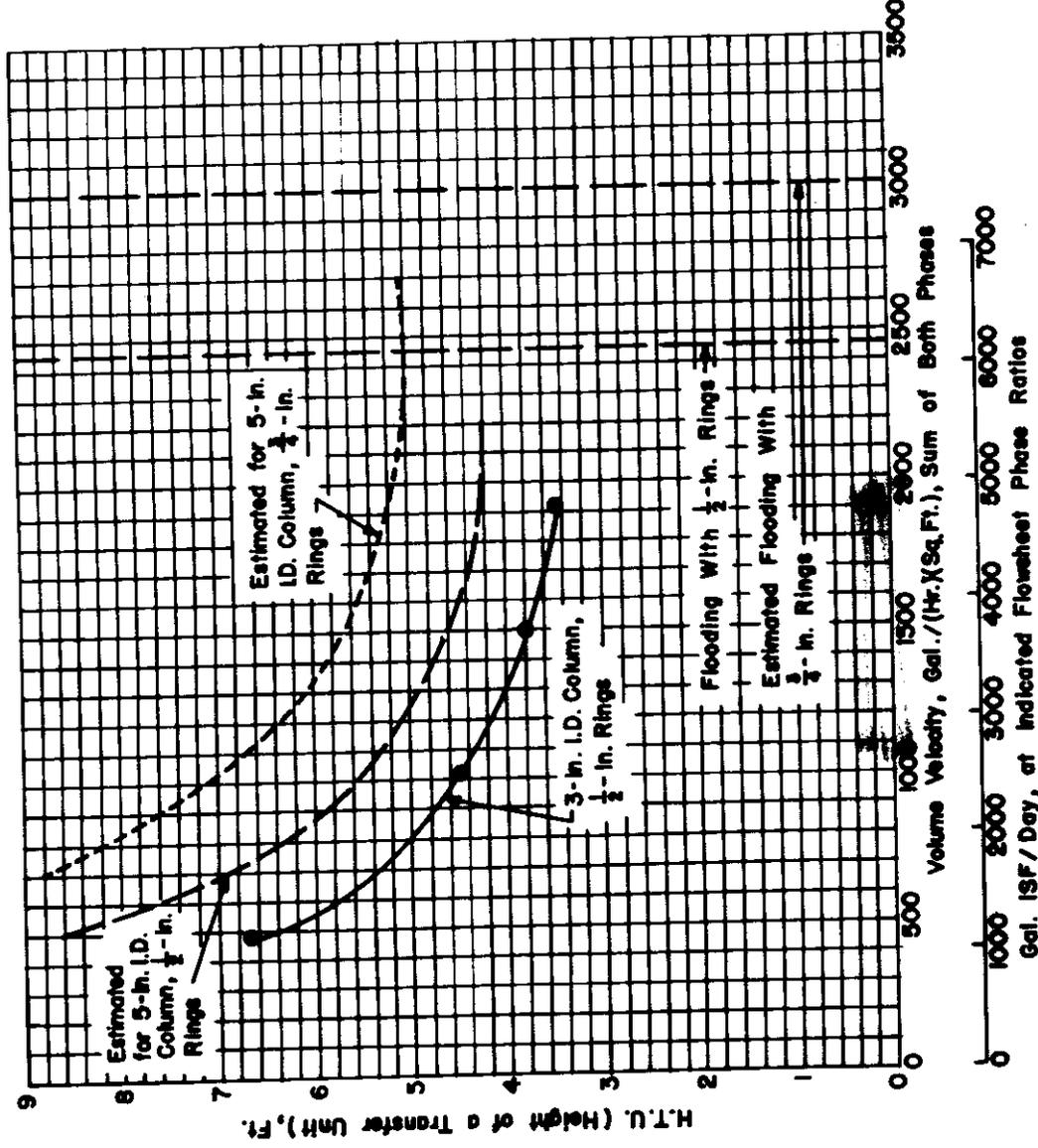
Column Diameter: 3 in.

Packed Height: 15.3 Ft.

Packing: 1/2-in. x 1/8-in. x 1/16-in. Wall Stainless-Steel Raschig Rings

Pecking:

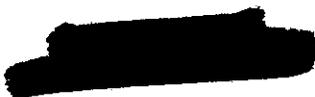
H.T.U. Calculations: "Overall Aqueous-Film" Basis



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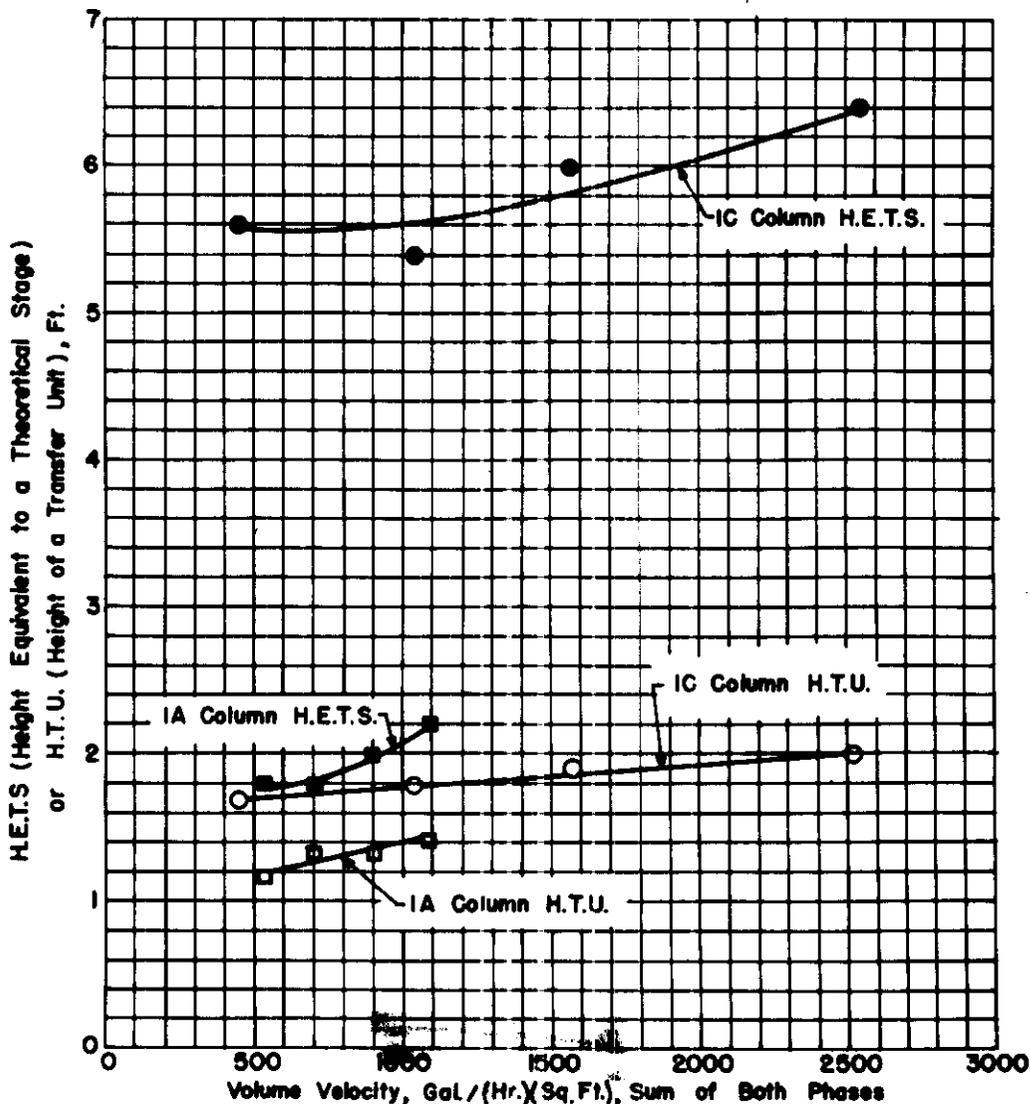
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Figure 22
COMPARISON OF H.E.T.S. WITH H.T.U.
Typical IA and IC Column Runs

Diffusing Component : $UO_2(NO_3)_2$ (Unirradiated U)
 Flowsheet : HW No. 4
 Column Diameters : 5.05-in. I.D. IA Column (Extraction Section)
 8.42-in. I.D. IC Column
 Packing : $\frac{1}{2}$ -in. x $\frac{1}{2}$ -in. x $\frac{1}{32}$ -in. Wall Stainless-Steel Raschig Rings (IA)
 1-in. x 1-in. x $\frac{1}{32}$ -in. Wall Stainless-Steel Raschig Rings (IC)
 H.T.U. Calculations : "Overall Aqueous Film" Basis For IA Column
 "Overall Organic Film" Basis For IC Column



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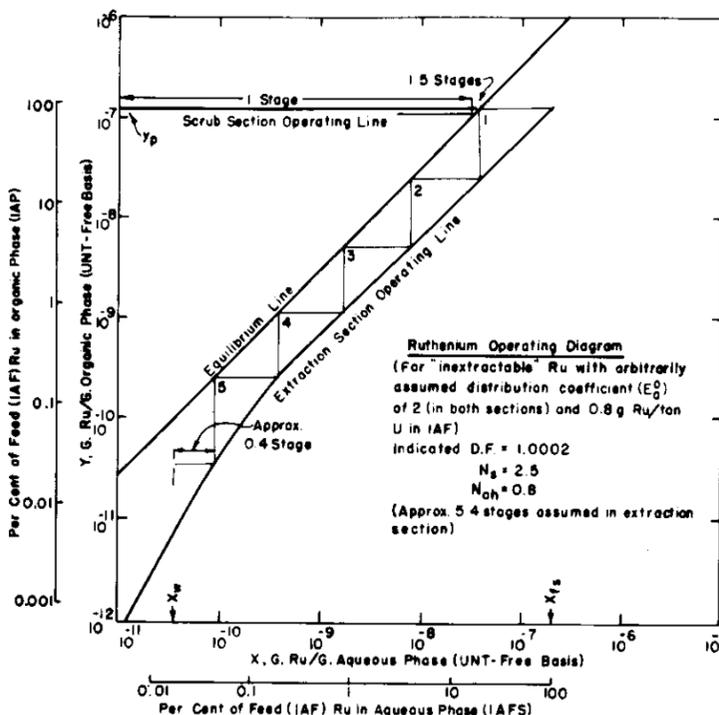
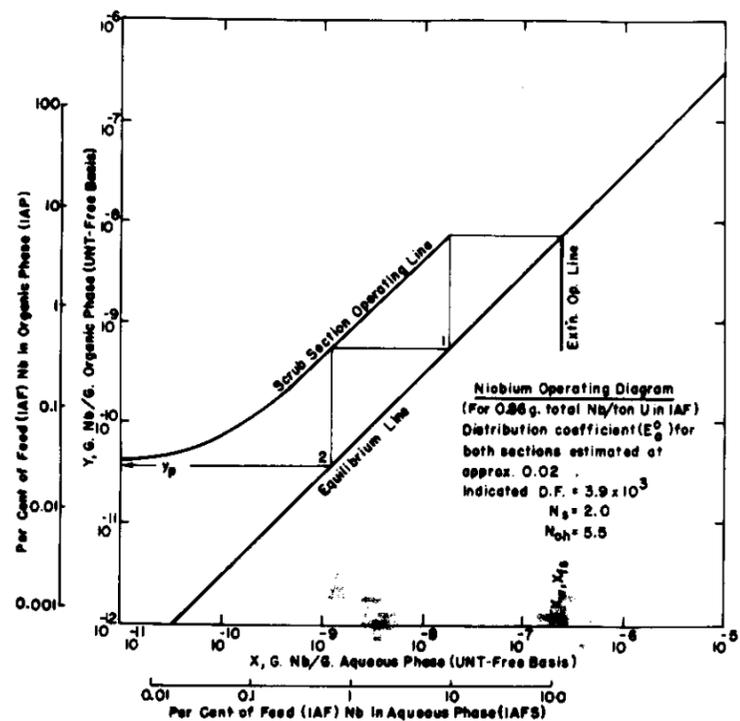
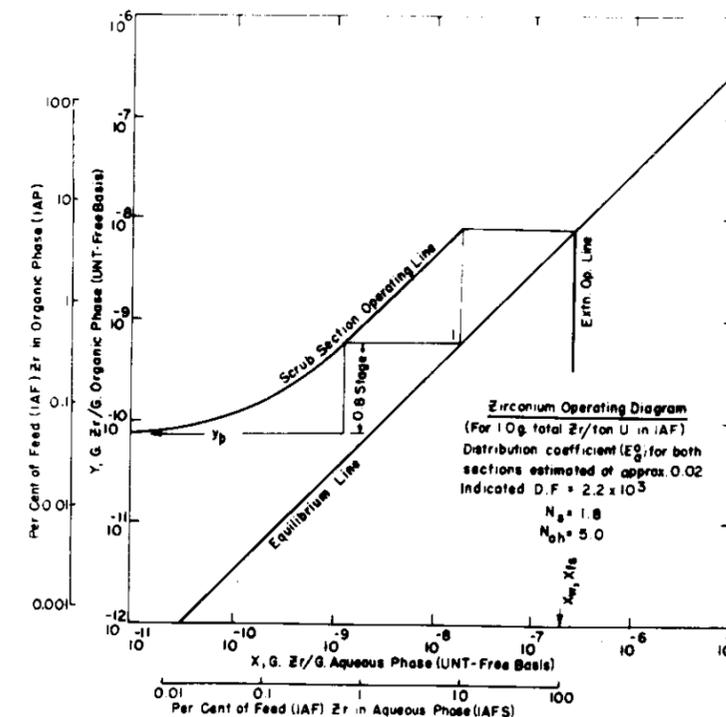
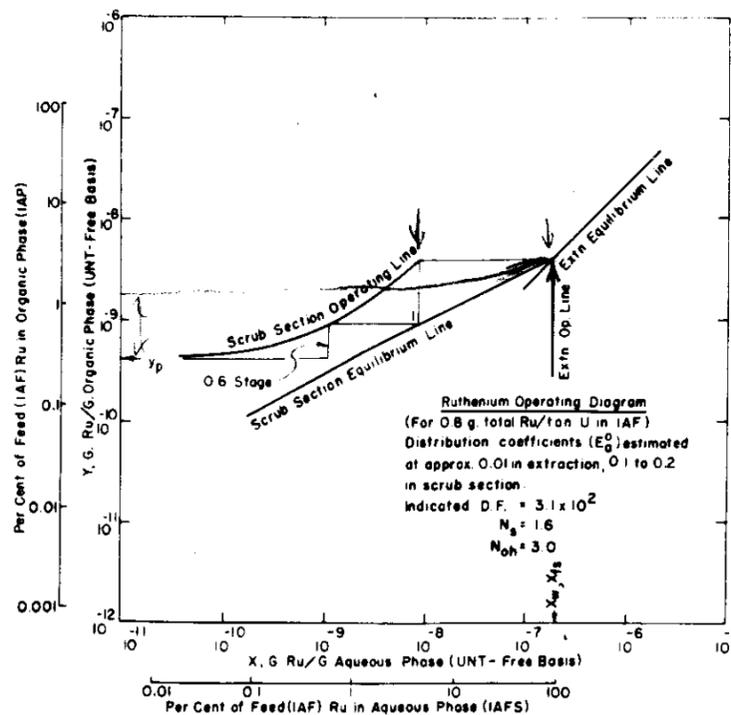
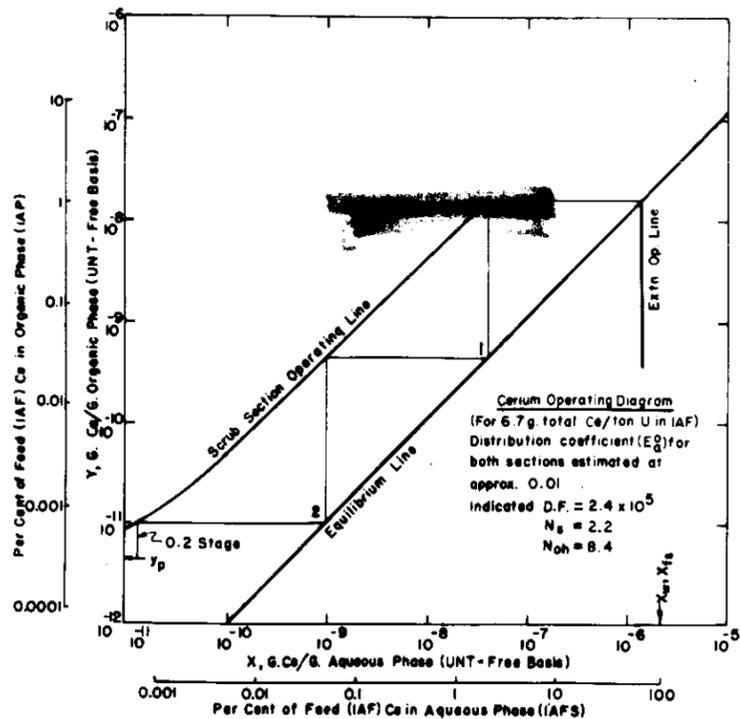


Figure V-23
IDEALIZED FISSION-PRODUCT OPERATING DIAGRAMS - IA COLUMN

- Basis:
- (1) Decontamination factors and fission-product concentrations from HW-14261
 - (2) Integrated 400 megawatt-days exposure over 360 days, followed by 90 days "cooling"
 - (3) Distribution coefficients estimated from data in ORNL-343 and KAPL-223
 - (4) Phase volume ratios as in HW No.4 Flowsheet.
 - (5) Concentrations of fission products in scrub (X_s) and extractant (Y_x) are zero in every case.

Symbols: X_{fs} , concentration of the f.p. in IAFS.
 X_w , concentration of the f.p. in IAW.
 y_p , concentration of the f.p. in IAP.
 N_s , number of stages in scrub section.
 N_{oh} , number of transfer units in scrub section, "overall organic-film" basis.

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Figure V-24

DECONTAMINATION IN THE IA COLUMN
Effect of Fission-Product Distribution Ratio

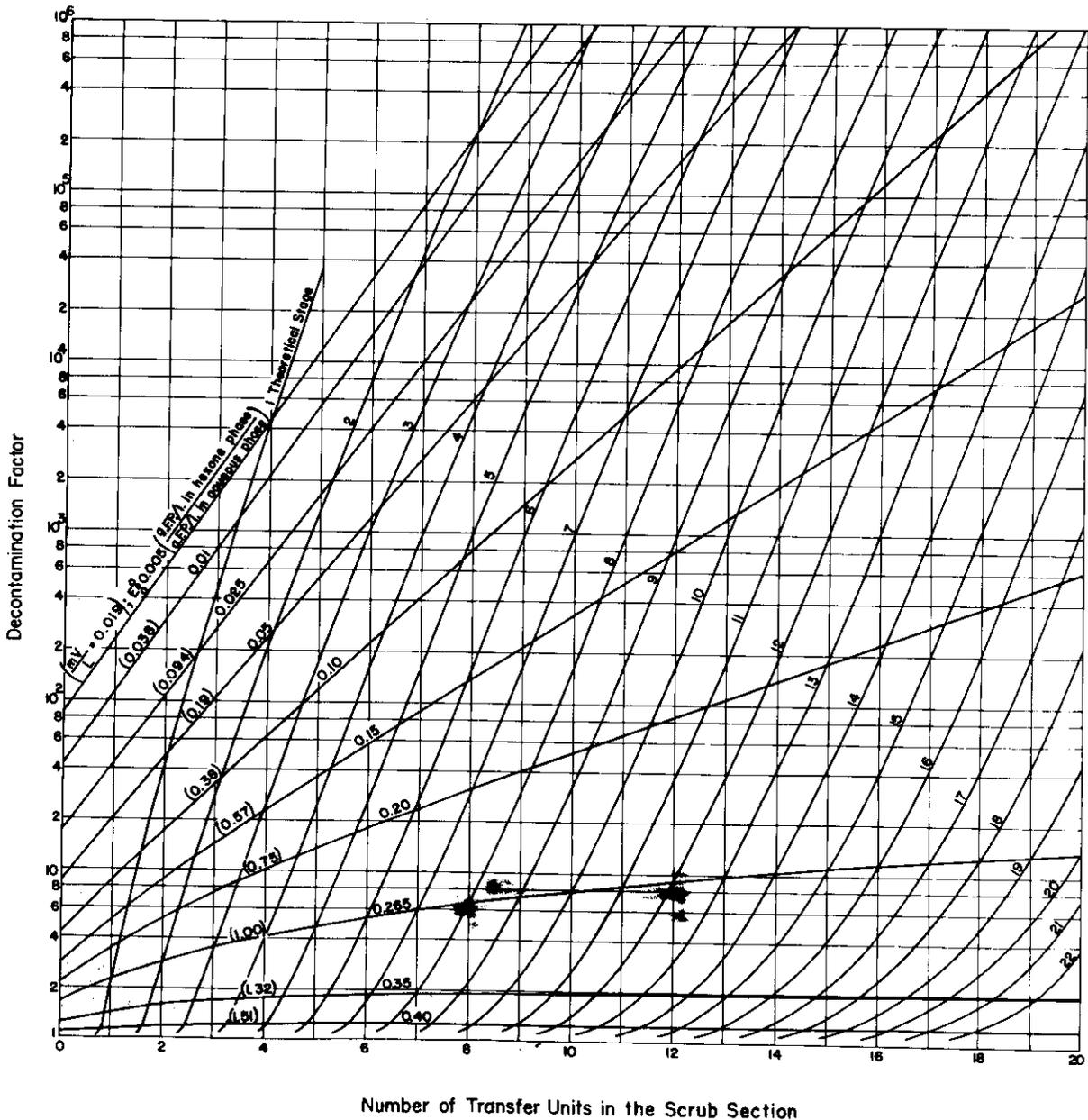
Basis: (a) Feed: scrub: extractant volume flow ratios = 1:1:4. (b) Fission-product distribution ratios in the portion of the extraction section just below the feed tee equal to those in the scrub section. (c) "Overall organic film" transfer units in the scrub section.

Nomenclature: m = Slope of the scrub section equilibrium line; i.e., g. of f.p. per g. UNT-free organic phase divided by the g. of f.p. per g. UNT-free aqueous phase.

V = Organic phase flow rate (UNT free), wt. per unit time.

L = Aqueous phase flow rate (UNT free) in the scrub section, wt. per unit time.

E_0^O = 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.



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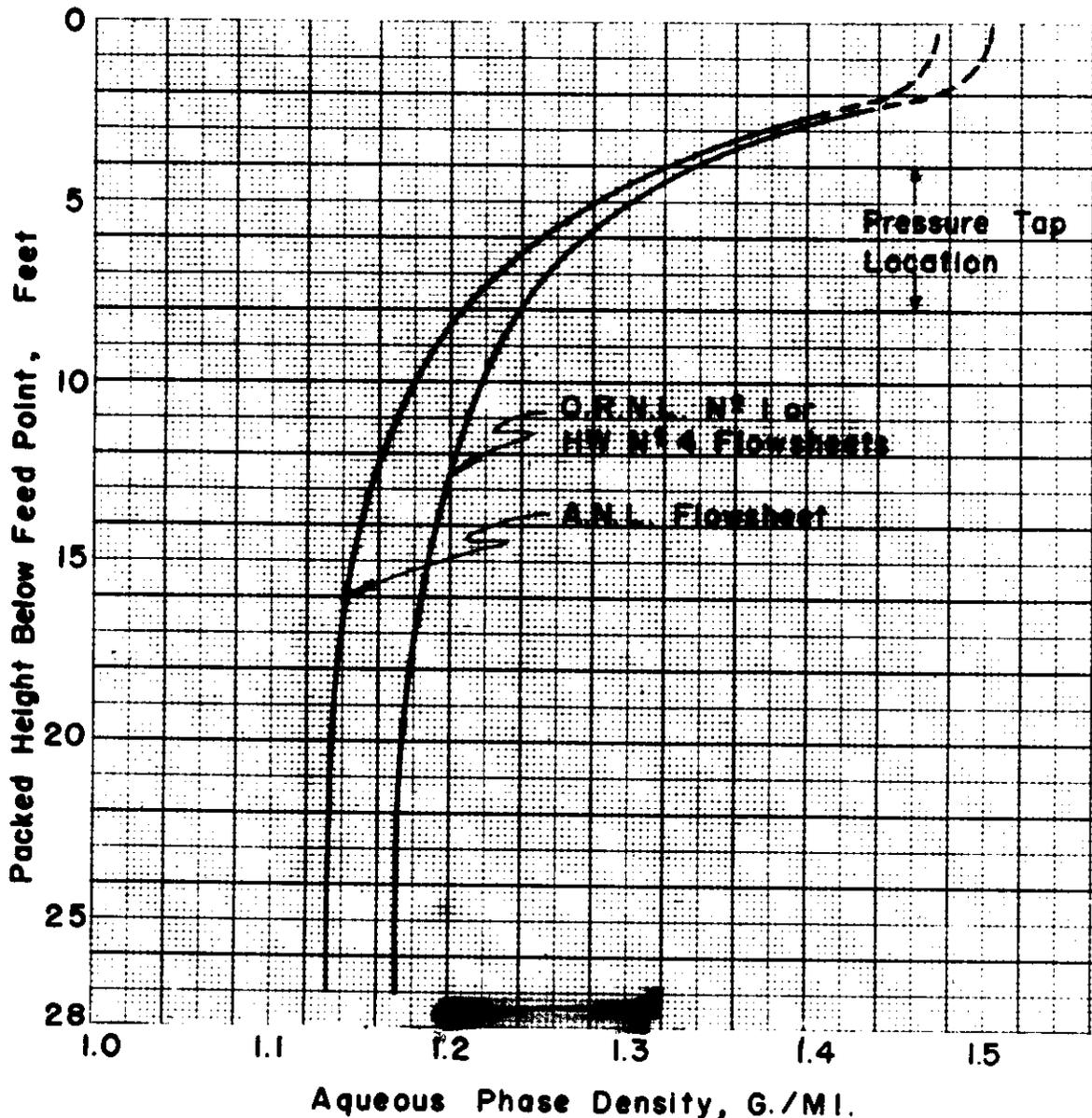


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Figure V-26

AQUEOUS PHASE DENSITY vs. PACKED HEIGHT
IA COLUMN EXTRACTION SECTION

These curves indicate the approximate aqueous-phase density in the IA Column as a function of height for the ANL, ORNL #1 or HW #4 Flowsheets. No allowance has been made for the effect of flow rate on apparent density. The curves have been calculated on the basis of an assumed H.E.T.S. of 1.8-ft. for the ANL Flowsheet, and 2.5-ft. for the ORNL #1 or HW #4 Flowsheets. The top 2 ft. of extraction section packed height were assumed effectively lost to extraction, to allow for the mixing of the IAF and IAS.



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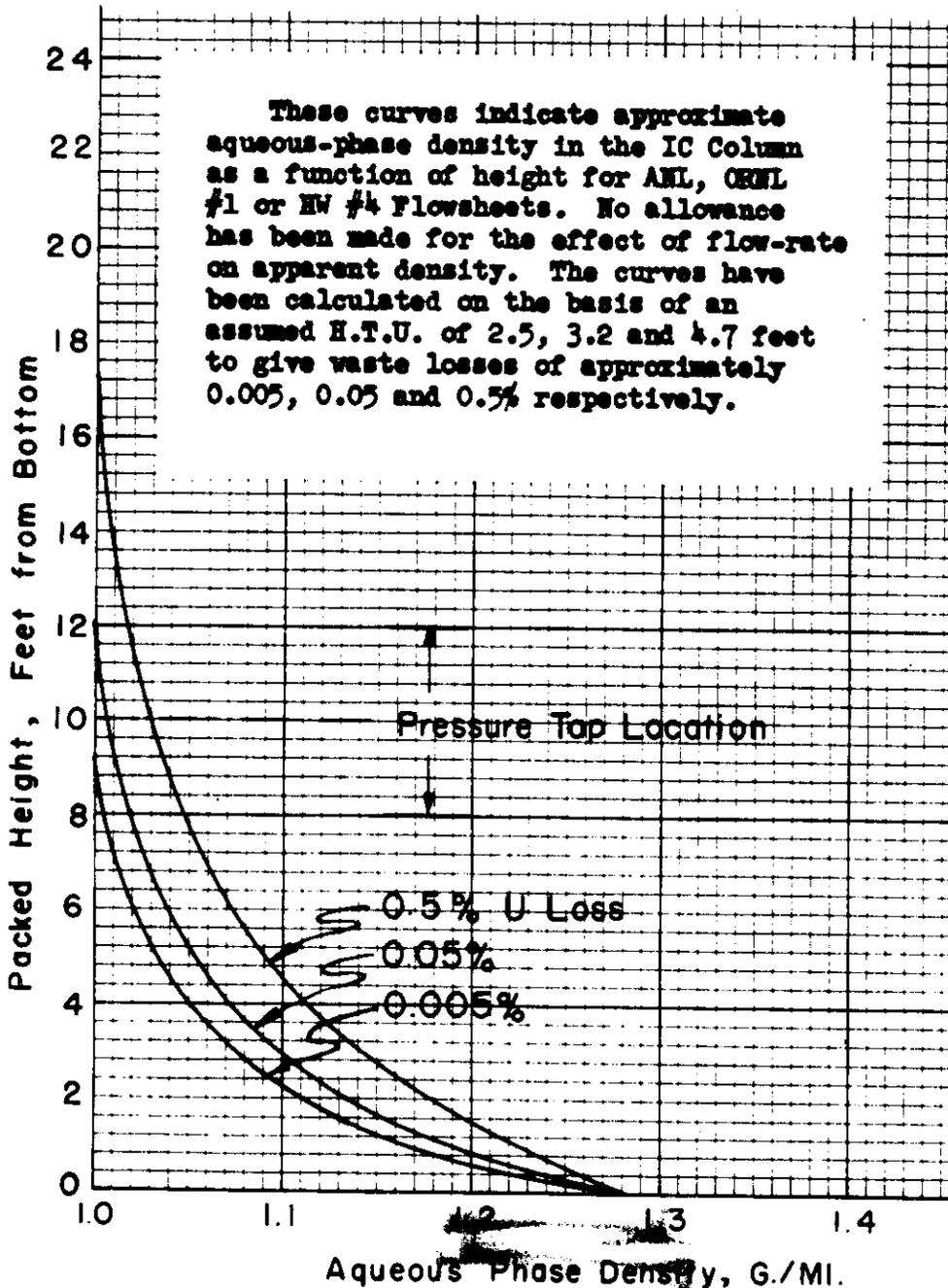


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Figure V-27
AQUEOUS PHASE DENSITY vs. PACKED HEIGHT
IC COLUMN



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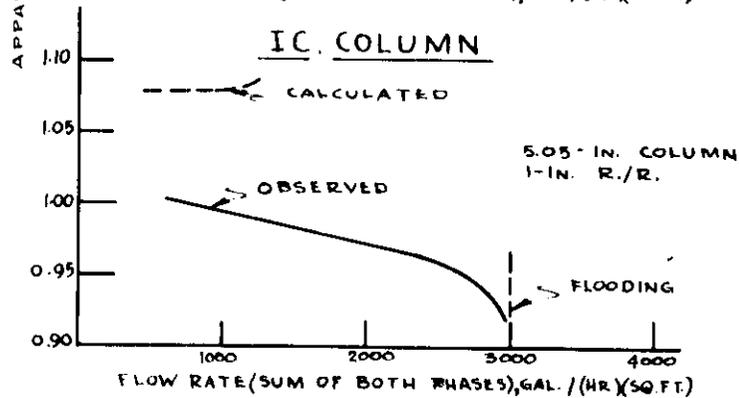
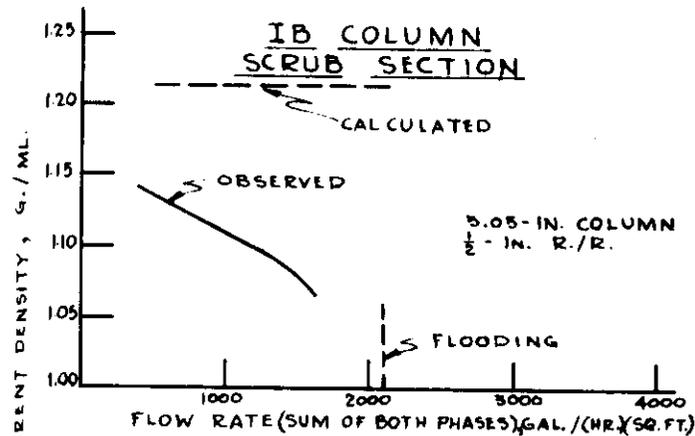
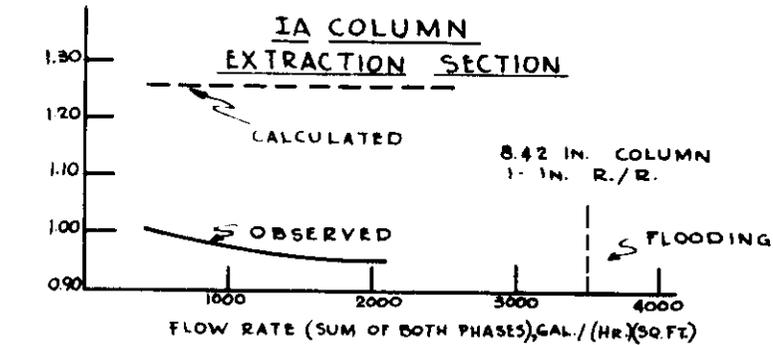
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EFFECT OF FLOW RATE ON APPARENT DENSITY
REDOX IA, IB, & IC COLUMNS



Calculated average column densities are for a stationary aqueous phase which has a concentration gradient similar to that existing in a column running at HW Flowsheet conditions. Experimental data were obtained under HW Flowsheet conditions.

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TABLE V-29

NOMENCLATURE

- I_{AF} = IA Column aqueous feed stream.
- I_{AS} = IA Column aqueous scrub stream.
- I_{AP} = IA Column organic effluent stream.
- I_{AW} = IA Column aqueous effluent stream.
- I_{AX} = IA Column organic extractant.
- I_{CF} = IC Column organic feed stream.
- I_{CU} = IC Column aqueous effluent stream.
- I_{CW} = IC Column organic effluent stream.
- I_{EX} = IC Column aqueous extractant.
- L = Mass flow of aqueous phase on a UNT-free basis (weight/unit time). L/V represents the slope of the operating line.
- m = Slope of the equilibrium line; dY^*/dX or Y^*/X if m is constant.
- M = X_1/X_2 for extraction and Y_1/Y_2 for stripping. If the extractant contains sufficient solute the values of M become $(X_1 - Y_2/m)/(X_2 - Y_2m)$ and $(Y_1 - X_2m)/(Y_2 - X_2m)$ for extraction and stripping, respectively.
- P = The slope of the operating line divided by the slope of the equilibrium line. (L/mW) for extraction (i.e., transfer from aqueous to organic), and the reciprocal (mW/L) for stripping (i.e., transfer from organic to aqueous).
- U_{6H} = Uranyl nitrate hexahydrate (Mol.wt. = 502).
- U_{3H} = Uranyl nitrate trihydrate (Mol.wt. = 448).
- V = Mass flow of organic phase on a UNT-free basis (weight/unit time).
- X = Weight ratio; g. UNT/g. aqueous phase on a UNT-free basis. Also, in connection with plutonium operating diagrams, g. Pu/l. of aqueous phase on a UNT-free basis.

- X' = Weight ratio; g. HNO₃/g. aqueous phase on a UNT and HNO₃-free basis. Also, in connection with plutonium-cycle operating diagrams, g. HNO₃/l., aqueous phase.
- X* = Concentration in an aqueous phase in equilibrium with an organic phase of concentration Y. (Same units as X.)
- Y = Weight ratio; g. UNT/g. organic phase on a UNT-free basis. Also, in connection with plutonium operating diagrams, g. Pu/l. of organic phase on a UNT-free basis.
- Y' = Weight ratio; g. HNO₃/g. organic phase on a UNT and HNO₃-free basis. Also, in connection with plutonium-cycle operating diagrams, g. HNO₃/l. organic phase.
- Y* = Concentration in an organic phase in equilibrium with an aqueous phase of concentration X. (Same units as Y.)
- Z = Length of packed section, feet.

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 streams.
- p = Concentration in plutonium-bearing effluent 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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PART II: PROCESS, continued

CHAPTER VI. SOLVENT-EXTRACTION PROCEDURE

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CHAPTER VI. SOLVENT-EXTRACTION PROCEDURE

A. ENGINEER'S FLOW SKETCHES

1. Introduction

A brief overall description of the Redox process is presented in Chapter I, in connection with the discussion of the chemical flowsheets. The reader is also referred to Chapter IV for background material which involves the chemistry of solvent-extraction operation.

Embodiment of the above-mentioned chemical process principles in the Redox Plant is set forth in the engineer's flow sketches (Figures VI-1, VI-2, and VI-3), which, with a description of solvent-extraction procedures, form the basis of the present chapter.

2. Interpretation of the Flow Sketches

The engineer's flow sketches presented as Figures VI-1, VI-2, and VI-3 schematically show the process streams and equipment for the First Solvent-Extraction Cycle, Second and Third Uranium Cycles, and the Second and Third Plutonium Cycles, respectively. The schematic symbols employed for all of the diagrams are explained on Figure VI-1.

The stream volumes shown on the sketches are based on a uranium processing rate of 3-1/8 tons per day. Tank volumes are shown as working volumes and generally represent about 70 to 80% of full capacity for the tanks.

Additional information covering such items as lubrication lines, electrical lines, connectors, and spare connectors may be obtained from the engineering flow diagrams in Chapter XII. Exact dimensions of process equipment may be found in the detailed mechanical design drawings for the specific equipment pieces.

Plutonium concentration (included on Figure VI-3) is treated separately, in Chapter VII.

B. NORMAL PROCEDURE

The compositions and flow rates shown on Figures VI-1, VI-2, and VI-3 correspond very closely to those presented in the HW #4 Redox Chemical Flowsheet at a throughput of 3-1/8 tons of uranium metal per day. The satisfactory operating range of the installed equipment, however, covers a much broader range of conditions as a result of the "built-in" flexibility of the plant. It is possible to operate the Redox Plant with the O.R.N.L., A.N.L., or modifications of the H.W. Flowsheets as presented in Chapter I. In addition, the continuous uranium processing capacity may be varied by a factor of about 3, from 1.2 to 3.9 tons per day (instantaneous rates), without exceeding the allowable plutonium and uranium waste losses. It is also possible to by-pass certain solvent-extraction cycles, as discussed later in this chapter, if adequate decontamination of uranium and/or plutonium can be achieved in fewer than the three cycles available for each.

1. First Solvent-Extraction Cycle

1.1 General

The principal steps of the First Solvent-Extraction Cycle are performed in three countercurrent liquid-liquid extraction columns and an evaporator for concentration of the uranium-laden effluent from the third extraction (IC) column. The daily charge to the IA Column (first extraction column) at a uranium processing rate of $3\text{-}1/8$ tons/day is 1576 gallons of feed solution (IAF) containing from 1150 to 1630 grams of plutonium. (This corresponds to 240 to 522 g. Pu/short ton of U.) See Appendix A for a tabulation of Pu concentration vs. pile-irradiation level of uranium.) The beta radioactivity will be on the order of 300 (absolute) curies/gal. and gamma activity will be about 200 curies/gal. These nominal numbers for radioactivity may vary by a factor of about three, depending upon (a) irradiation in the piles, (b) "cooling" time, and (c) decontamination effected in head-end treatment.

1.2 Steady-state operation

The uranium and plutonium-bearing feed (IAF) is pumped through a recording and controlling rotameter from the IA Feed Tank, F-7, to the center feed point of the IA Column. This uranium-plutonium solution mixes with the aluminum nitrate-salted (ANN-salted) aqueous scrub (IAS) which is gravity-fed through a recording and controlling rotameter to the top of the column. In the extraction (lower) section of the IA Column uranium, plutonium, and some fission products are extracted into the rising hexone extractant (IAX). In the scrub (top) section of the column the rising uranium-laden hexone is scrubbed by IAS which extracts the bulk of the fission products from the rising hexone globules. Before being gravity-fed to the bottom of the IA Column, the hexone (IAX) stream, from the Organic Header, may be acidified by line-blending with 60% HNO_3 supplied from Tank 701-A. The process involves feeding 60% HNO_3 by means of a piston pump into a mixing tee carrying the hexone stream. The frequency of the pump piston and therefore the volume of nitric acid is changed in direct proportion to the hexone rate by automatic control instruments. A description of this control equipment is contained in Chapter XIX.

The aqueous waste effluent from the IA Column (IAW) should contain not more than 0.2% of the entering uranium and plutonium, in addition to 99.9 per cent or more of the entering fission products. The organic effluent (IAP) contains the bulk of the uranium and plutonium from the IAF, together with a small fraction of the original quantity of fission products.

The IAP stream cascades to the middle (feed point) of the IB Column. It is the function of the IB Column to separate the plutonium from the uranium. A chemical reductant (either ferrous sulfamate or a mixture of ferrous ammonium sulfate and sulfamic acid) and ANN are gravity-fed through a recording-controlling rotameter into the top of the IB Column in an aqueous extractant stream (IBX). The reducing agent contained in the IBX reduces the plutonium to the trivalent state, in which form it is highly distributed to the aqueous phase.

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Uranium is not affected by the chemical reductant and remains in the hexone stream in the hexavalent state. In the scrub (lower) section of the IB Column the aqueous stream is scrubbed by the rising hexone scrub stream (IBS), so that the total uranium content of the aqueous effluent plutonium stream (IBP) is less than 0.1 weight per cent of the plutonium. Of the total gamma curies entering the IB Column, approximately one half (about 50 to 100 curies per 3-1/8 tons of uranium fed to the IA Column) are contained in the IBP stream and are essentially removed in the Second and Third Plutonium Decontamination Cycles. The uranium-laden hexone stream (IBU) leaving the top of the IB Column should contain not more than 0.2% of the plutonium introduced into the IA Column and on the order of 100 gamma curies of radioactivity (on the basis of 3-1/8 tons of U).

The IBU stream cascades to the bottom of the IC Column. An aqueous extractant stream (ICX) is gravity-fed through a recording-controlling rotameter to the top of the IC Column and extracts uranium from the rising hexone phase. The effluent hexone phase (ICW) leaving the IC Column should contain not more than 0.05% of the uranium contained in the IAF. The aqueous uranium stream (ICU) leaving the bottom of the IC Column cascades to the middle of the steam stripping column located on the ICU Concentrator. The small amount of hexone dissolved in the ICU is flashed off in the column (by the water vapor rising from the Concentrator pot) to prevent the formation of undesirable hexone decomposition products during concentration. A 25% caustic solution is added continuously by a metering pump to the Concentrator to adjust the acidity of the concentrate prior to further processing in the Second and Third Uranium Decontamination Cycles.

The IS Column, which is shown on Figure VI-1 in parallel with the IA Column, is normally not used. It serves for the rework of any aqueous waste streams for the recovery of excessive uranium and/or plutonium losses. Its use for this purpose is discussed in Section C, below. The rework operating procedure for the IS Column is similar to that for the IA Column. By means of in-cell jumper changes, the IS Column may be operated as a IA-type column -- either in parallel with, or in place of, the IA Column.

All "cold" aqueous influent streams to the solvent-extraction battery are gravity-fed from tanks situated in the "cold" sections of the Redox Processing Building (202-S). "Cold" organic influent streams to the solvent-extraction columns are fed directly from the Organic Header, with nitric acid line-blended into each stream (if required) as described above.

Flow-control instrumentation on column influent streams (both "cold" and "hot") is automatic but can be operated manually when required, e.g., when the equipment is started up or shut down. Column interface controllers maintain the interface in each column by regulating the flow of aqueous effluent from each column. Differential pressure recorders on the IA, IS, and IC Columns and a static pressure recorder on the IB Column are provided as a means of detecting flooding conditions in the columns and also as an aid in the early determination of any excessive uranium losses. A detailed description of the various instruments shown on the flow sketches is given in Chapter XIX.

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Auxiliary equipment shown on the sketches, such as strainers, samplers, jets, and pumps, is described in detail in Chapters XVI and XVII.

1.3 Start-up

The preceding discussion has dealt with steady-state operation of the columns. A brief outline of the start-up procedure employed for the First Solvent-Extraction Cycle is given below.

- (a) The columns are first filled with "cold" aqueous solutions; i.e., IAS solution in the IA Column, IBX solution in the IB Column, and ICX solution in the IC Column.
- (b) After step (a), above, the "cold" hexone streams are started to the columns; i.e., IAX to the IA Column, IBS to the IB Column. The open steam at the base of the ICU Concentrator column is turned on to strip the hexone from the IC aqueous effluent.
- (c) After the flow rates of the "cold" aqueous and hexone streams become steady, feed (IAF) solution is gradually started to the IA Column. Caustic solution addition to the ICU Concentrator is started in order to neutralize the effluent ICU. When the ICU Concentrator pot is full and its content boiling, the open steam supply to the base of the Concentrator column is turned off.

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.

1.4 Shutdown

When the Redox Plant is to be shut down, a reversal of the above-mentioned procedure for start-up is followed, as outlined below:

- (a) The feed (IAF) to the IA Column is shut off.
- (b) Stripping plutonium and uranium from the columns is then carried on for a period of about 30 minutes, if flow rates are as shown on Figure VI-1, with all streams on except the IAF. About 90 gallons of organic (IAX) are required to strip uranium from the plant-size IA Column. It is possible to turn off both the IAF and the IAS and to strip uranium from the static aqueous phase with only the IAX stream flowing. However, allowing the IAS stream to continue flowing has the advantage of gradually increasing the salting strength in the extraction section of the column and of displacing fission products out the bottom of the column. The flow rates shown on Figure VI-1 provide approximately 130 gallons of organic (or one aqueous displacement) if stripping is carried on for thirty minutes. Increased stripping times are therefore required if flow rates lower than those indicated in Figure VI-1 are used.

- (c) After IA Column stripping is completed, the IAS, IAX, and IAW flows are stopped, leaving the column temporarily filled with its liquid contents. The IB Column is allowed to run for an additional period of approximately thirty minutes to insure complete removal of uranium (and plutonium) from the IB Column. After IB stripping is complete, the IBS flow is stopped. The organic solvent left in the IA, IB, and IC Columns is then displaced successively from the top of each column by introducing IAS to the IA Column, IBX to the IB Column, and ICX to the IC Column.
- (d) Finally, the aqueous contents of the IA and IB Columns are drained to the Salt Waste Header, and the uranium-bearing aqueous solution in the IC Column is drained to the ICU Concentrator, which leaves the columns empty for the next start-up.

If direct maintenance is required in the Silo or Canyon area, 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 Silo and Canyon and the outer surfaces of "hot" equipment.

2. Second and Third Uranium Decontamination Cycles

2.1 General

The engineer's flow sketch for the Second and Third Uranium Decontamination Cycles is presented as Figure VI-2. In general, the process equipment provisions and connections are similar to those of the First Solvent-Extraction Cycle, as described in Subsection 1, above.

As presented in Figure VI-2, the required further decontamination of the uranium effluent stream from the First Solvent-Extraction Cycle (ICU) is accomplished by solvent-extraction with hexone in a battery of four columns used in series. The first two of these (2D and 2E Columns) constitute the Second Uranium Decontamination Cycle; the last two (3D and 3E Columns), the Third Uranium Decontamination Cycle.

Because of uncertainties existing at the time the Redox Plant was designed, 3-cycle operation was provided for, to insure adequate decontamination of uranium and plutonium. Subsequent developments indicate that only two uranium cycles may be required, especially if the Dissolver solution is subjected to head-end treatment as discussed in Chapter III.

After initial start-up, it is expected that the 3DF uranium stream (i.e., concentrated 2EU) will meet final uranium specifications on a continuing basis. The 3DF can then be routinely jetted to the 3EU Concentrate Sampler, E-12, on an 8-hr. basis and thence to decontaminated UNH storage, thus entirely by-passing the Third Uranium Decontamination Cycle. It may prove advantageous to use the by-passed third cycle as a rework facility (discussed in Section C) in the event that only two cycles are routinely required for uranium decontamination.

If one-cycle processing of uranium develops as a feasible operation, it can be accomplished by directing concentrated ICU into the 2DF Tank (which would act as a receiver on an 8-hour basis) and thence jetting to the 3EU Concentrate Sampler, E-12.

2.2 Steady-state operation

Feed for the 2D Column (2DF) overflows from the ICU Concentrator, F-2, where it has been concentrated and adjusted in acidity, to the 2DF Tank, F-1. The uranium feed (2DF) is pumped through a recording and controlling rotameter to the center feed point of the 2D Column. Uranium extraction and decontamination is as in the IA Column. The hexone extractant (2DX) is gravity-fed through a recording-controlling rotameter to the bottom of the 2D Column. An aqueous scrub stream (2DS) containing aluminum nitrate and a reducing agent (either ferrous sulfamate or a mixture of ferrous ammonium sulfate and sulfamic acid) is gravity-fed to the top of the 2D Column. The function of the reducing agent is to reduce residual quantities of plutonium contained in the uranium-laden hexone stream to the aqueous-favoring form (trivalent oxidation state) and thereby effect decontamination of the uranium from plutonium. The hexone stream containing uranium (2DU) leaving the top of the 2D Column cascades into the bottom of the 2E Column, where, like in the IC Column, the uranium is extracted into an aqueous solution (2EX). The aqueous uranium stream (2EU) leaving the 2E Column overflows to the 2EU Concentrator, F-5. Here it is stripped of hexone, neutralized with caustic, and then concentrated to form a feed (3DF) identical in composition with 2DF.

The uranium solution (3DF) thus obtained may be subjected to another solvent-extraction cycle for further decontamination in the 3D and 3E Columns. The operation of this third cycle is identical to that of the second.

The product from these decontamination cycles is an aqueous solution containing about 60 weight per cent uranyl nitrate hexahydrate (UNH) and innocuously small amounts of radioactive fission products and plutonium. Tentative specifications of the final uranium are as follows:

Beta radioactivity from fission products	1×10^{-7} absolute curies/g. U
Gamma radioactivity from fission products	5×10^{-3} absolute curies/g. U
Plutonium	1 part/ 10^7 parts of U
Iron	1 part/ 10^3 parts of U (1000 p.p.m.)
Sodium	1 part/ 10^3 parts of U (1000 p.p.m.)

2.3 Start-up

The start-up procedure for the Second and Third Uranium Decontamination Cycles is identical in principle to that described for the

First Solvent-Extraction Cycle (under 1.3, above). It involves (a) starting the "cold" aqueous streams to fill the columns, (b) starting the hexone stripping streams, and (c) gradually starting the uranium feed after the hexone and "cold" aqueous streams are adjusted to the proper rates. As in the ICU Concentrator, the initial stripping of hexone from the feed to the 2EU Concentrator is accomplished by open steam to the base of the Concentrator column.

2.4 Shutdown

The shutdown procedure for the Second and Third Uranium Decontamination Cycles is also identical in principle to that discussed for the First Solvent-Extraction Cycle (under 1.4, above). It involves (a) turning off the feed stream (2DF or 3DF), (b) stripping the remaining uranium from the columns, (c) overflowing the hexone with a "cold" aqueous solution (i.e., 2DS or 2EX), (d) draining the aqueous contents of the 2D and 3D Columns to the Salt Waste Header, and (e) draining the uranium-bearing aqueous contents of the 2E and 3E Columns to their respective uranium concentrators.

3. Second and Third Plutonium Decontamination Cycles

3.1 General

3.1.1 Introduction

The engineer's flow sketch for the Second and Third Plutonium Decontamination Cycles is presented as Figure VI-3. In general, most of the process equipment provisions and connections are similar to those of the First Solvent-Extraction Cycle, as described in Subsection 1, above.

As presented in Figure VI-3, the required further decontamination of the plutonium effluent stream from the First Solvent-Extraction Cycle (IBP) is accomplished, after re-oxidation of the plutonium, by solvent-extraction with hexone in a battery of four columns in series. The first two of these (2A and 2B Columns) constitute the Second Plutonium Decontamination Cycle; the last two (3A and 3B Columns), the Third Plutonium Decontamination Cycle.

3.1.2 By-passing of cycles

It was mentioned under 2.1, above, that it may be unnecessary to use all three decontamination cycles to secure uranium of sufficient purity. The achievement of adequate plutonium decontamination by the use of only two of the available three cycles may also be possible. However, a one-cycle Redox process for plutonium is not feasible since the plutonium from the IB Column (IBP) must be separated from the aluminum nitrate salting agent.

The third Plutonium Decontamination Cycle may be by-passed by connecting the 2B Column aqueous effluent (2BP) line directly to the 3BP Receiver, E-2. This can be accomplished by a jumper change in the Silo.

3.13 Critical mass control

A general discussion of the size of the critical mass of plutonium and of critical mass control methods is presented in Chapter XXV. The reader is referred to that chapter for a discussion of how the size of the critical mass is affected by such variables as plutonium concentration, nitrate concentration, the number of megawatt-days/ton of pile exposure received by the parent slugs, and the geometric configuration of the plutonium solution.

As explained in Chapter XXV, operational critical mass control in the solvent-extraction cycles is necessary only in the Second and Third Plutonium Decontamination Cycle tanks. The uranium cycles are considered safe by virtue of the invariable co-presence of enough neutron-absorbing U^{238} to render criticality impossible. The plutonium-cycle columns are safe by virtue of their geometries, provided that their plutonium content does not exceed 5 kilograms.

In the plutonium-cycle tanks, critical mass control is achieved by operation in safe batches, each containing approximately 300 g. of plutonium. As discussed in Chapter XXV, the maximum allowable batch plutonium content will be set at a value somewhat in excess of 300 g., to provide reasonable working tolerances in batch size control.

Tanks which receive continuously are subjected to an additional safeguard because they are more liable to accidental overflowing. These tanks, which include IBP Receiver (or 2AF Tank), 3AF Tank, and 3BP Receiver, are designed to overflow before they can collect a volume of solution which will contain over 600 g. of plutonium when the plant is processing slugs with irradiation levels of up to 420 megawatt-days/ton (approximately 380 g. Pu/ton U). At higher slug irradiation levels, in order to maintain this same safeguard, the IBP stream must be diluted with aluminum nitrate solution (from the IBP Butt Tank, E-6 & 7-B) to a higher relative volume than indicated on the HW #4 Flowsheet. By limiting these tanks to contain not over 600 g. of plutonium when the tanks are filled to overflowing, they do not attain the critical mass for plutonium from slugs with 420 megawatt-days/ton or greater pile exposure (i.e., 380 g. Pu/ton U or over).

As discussed in Chapter XXV, the possibility of criticality during plant operation is extremely remote even when sufficient plutonium is present to form a minimum critical mass. For example, the following events must occur simultaneously in a given tank before it will become critical: the plutonium (ca. 600 g.) must (a) totally precipitate, (b) form a 12 to 15-inch sphere surrounded on all sides by at least 4 inches of water reflector, (c) be uniformly suspended in a spherical shape at approximately the optimum Pu concentration (20 to 40 g. Pu/l.), and (d) contain no nitrate or other foreign solutes.

The concentration of plutonium processed determines the maximum volume of solution normally contained in process tanks in order to maintain the batch size within the nominal 300-g. figure. This is illustrated in the table below, which is based on a uranium processing rate of 3-1/8 tons/day.

<u>G. Pu/Ton of U</u>	<u>G. Pu/Gal. of IBP</u>	<u>Gal. IBP Containing 300 G. Pu</u>	<u>Gal. 3BP Containing 300 G. Pu</u>
250	1.24	242	98
275	1.36	220	89
300	1.49	202	82
350	1.74	173	70
400	1.98	151	61
600	2.98	100	40.5

Note: Working volume for IBP Receiver = 215 gal.; for 3BP Receiver = 89 gal.

Contemplated routine analysis for plutonium at steady-state conditions will be only from the 3BP Sampler. The total product plutonium (in 3BP) will be checked against the amount of feed plutonium (in IAF) for purposes of accountability. A small change in the amount of plutonium as accounted for in the 3BP (plus a small amount in the waste stream) as compared with the amount introduced as IAF is normally expected. However, a sudden drop in the amount of plutonium collected as 3BP (on the order of 50 or more g. of Pu) is of immediate concern as it is indicative of a severe off-standard condition, such as precipitation in one of the receiver tanks. For example, if plutonium in the 2AF Tank were to start to precipitate just after the 3BP Receiver is emptied, by the time 300 g. of Pu (one batch) would normally have collected as 3BP only 130 g. of Pu (from solution held up in the second and third cycles) would collect in the 3BP Receiver. In the meantime 600 g. of Pu would have precipitated in the 2AF Tank -- 300 g. from the initial content of the tank and an additional 300 g. from the 2AF solution received in the interval.

At start-up, additional samples of plutonium streams are obtained because a period of about 24 hours is required from introduction of IAF until steady-state conditions are reached at the 3BP Receiver. Because of this significant time delay, it is necessary to obtain grab samples from all tanks which could have accumulated 300 grams of plutonium during the time interval from start-up to the time of sampling.

The discussion above has not made allowances for plutonium introduced as a rework stream. If, as an example, 3BP solution is to be reworked through the 2A Column, it will be about 3 times as concentrated in plutonium (Flow ratio of 2AF:3BP = 42:16) as normal 2AF. It is probably advisable to dilute such a rework stream with ANN solution to the same plutonium concentration as normal 2AF so as to enable maintenance of the nominal 600-g. tank overflow point. When such rework is being done, it is required that exact material balance figures (through an increased sampling schedule) be available in order to keep plutonium batch size within the nominal 300-g. figure.

After shutdown of the plant, it is considered good policy to flush vessels in the plutonium cycles with nitric acid before start-up. A nitric acid flush of the plutonium system will dissolve plutonium salts and tend to remove all the held-up plutonium from the system. This

procedure permits the keeping of accurate plutonium material balances after the plant is again in operation.

3.14 Continuous and batch cross-over oxidation procedures

At the time of writing this chapter, a decision has not been reached as to whether the plutonium cross-over oxidation will be accomplished on a batch or on a continuous basis. Batchwise oxidation was provided for in the original plant design. Subsequent technological improvements have pointed up the feasibility of continuous oxidation, the employment of which simplifies operating procedures and helps relieve a potential bottleneck for increasing the plant plutonium production capacity. A description of both processes is given in this section.

Figure VI-3 shows equipment and process lines as originally scheduled for installation in the Redox Plant. A proposed design change to permit continuous rather than batchwise cross-over oxidation involves the following line changes. The IBP stream cascades directly to the 2AF Tank, E-5. Because the oxidation reaction will then occur in the 2AF Tank, it is necessary that the tank be equipped with a chemical addition line (for $\text{Na}_2\text{Cr}_2\text{O}_7$ addition) and an agitator. In order to handle 3BP solution which requires reworking, a new line is installed from the 3BP Rework Tank, E-4, to the present IBP Receiver, E-6. After chemical adjustment in Tank E-6, the rework plutonium stream is pumped to the Cross-Over Oxidizer, E-7, and then pumped to the 2AF Tank, E-5.

3.2 Steady-state operation

With a batchwise cross-over oxidation of plutonium, the plutonium stream (IBP) is gravity-fed to the IBP Receiver, E-6. From here, it is pumped (in batches) through a recording-controlling rotameter to the Cross-Over Oxidizer, E-7. Feed to the oxidizer may enter directly into the tank, or it may be introduced into the column above the tank, E-7, if it is necessary to strip the dissolved hexone from the solution (required only for hot oxidation of plutonium to the VI valence state). The oxidant ($\text{Na}_2\text{Cr}_2\text{O}_7$) is batched into the Cross-Over Oxidizer from the Cross-Over Addition Tank, E-7-D. Plutonium in the IBP stream leaving the IB Column must be reoxidized from the III to the IV or VI valence state to render the plutonium readily extractable by hexone in the 2A Column. With 0.1 M concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ and HNO_3 , plutonium III is oxidized to plutonium IV in less than a minute at room temperature. Oxidation of plutonium IV to the VI valence state at these same concentrations requires from two to four hours at a temperature of about 80°C. To prevent partial decomposition of the hexone which may cause some plutonium precipitation, the hexone is vapor-stripped from the IBP solution before a hot cross-over oxidation (i.e., oxidation to the Pu(VI) state). If, however, the plutonium is to be oxidized only to the IV valence state, the absence of heating during oxidation renders hexone stripping unnecessary. For a discussion of the chemistry of the cross-over oxidation step, reference is made to Chapter IV. From the Cross-Over Oxidizer the plutonium stream is pumped batchwise to the 2AF Tank, E-5. Thence it is continuously pumped through a recording-controlling rotameter to the 2A column.

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With continuous cross-over oxidation of plutonium, the IBP stream is gravity-fed to a receiver (probably the 2AF Tank, E-5), where it is treated with acid dichromate solution. The resultant oxidized plutonium stream is then continuously pumped through a recording-controlling rotameter to the center feed point of the 2A Column.

Plutonium extraction in the 2A Column is based on the same principle as its extraction in the 1A Column. After extraction in the 2A Column, the plutonium is stripped (transferred from the organic to the aqueous phase) in the 2B Column. The plutonium-bearing effluent (2BP) from the 2B Column is adjusted in salting strength by the continuous addition of aluminum nitrate so that its composition is approximately that of the IBP. The required aluminum nitrate is continuously supplied to the 3AF Tank, E-1, through a recording-controlling rotameter from the ANN Butt Tank, E-1 and 2-A. The adjusted solution (3AF) may be processed in the Third Plutonium Decontamination Cycle (3A and 3B Columns) which is similar to the preceding cycle.

The aqueous effluent from the third cycle is collected in the 3BP Receiver, E-2, sampled for accountability and to check for conformance with specifications, concentrated, and finally received in PR cans. The concentration procedure is described in Chapter VII.

The flow of the "cold" streams follows the general pattern described previously for the First Solvent-Extraction Cycle. Hexone from the Organic Header is blended with 60% HNO₃ from the common HNO₃ head tank, 603, through separate batch feed tanks (702-A, for the 2A Column; 703-A, for the 3A Column). After line blending, the hexone is gravity-fed through recording-controlling rotameters to the bottoms of the two columns. Aluminum nitrate scrub solution for the extraction columns is gravity-fed through recording-controlling rotameters from separate tanks (802-A, for the 2A; 803-A, for the 3A) in order to allow the use of Na₂Cr₂O₇ as an oxidizing agent in the 2A scrub solution if desired. Aqueous extractant for the stripping columns (2B and 3B) is gravity-fed through recording-controlling rotameters from feed tanks (802-B, for 2B; 803-B, for 3B) supplied from a common head tank, 408.

The purity specifications for 3BP have not, at this writing, been definitely established. It is tentatively expected that the specifications will be approximately as follows:

Beta plus gamma radioactivity from fission products	3×10^{-5} absolute curies/g. of Pu
Iron	Approx. 5% by wt. of Pu
Uranium	Specification has not been determined. The Pu in the 3BP solution is expected to be contaminated by approx. 0.1 wt.% of U, based on the weight of Pu.
Aluminum	Specification has not been determined. The Pu in the 3BP solution is expected to be contaminated by approx. 3 wt.% of Al, based on the weight of Pu.

3.3 Start-up

The start-up procedure for the Second and Third Plutonium Decontamination Cycles is identical in principle to that described for the First Solvent-Extraction Cycle (under 1.3, above). It involves (a) starting the "cold" aqueous streams to fill the columns, (b) starting the "cold" organic streams, and (c) gradually starting the plutonium feed after the hexone and "cold" aqueous streams are flowing at the prescribed rates.

It should be noted that critical mass control procedures make it necessary to increase sampling frequency at start-up. (See 3.13, above.) The sampling schedule must be sufficient to keep accountability records for plutonium on individual tanks as they gradually reach steady-state concentrations.

3.4 Shutdown

The shutdown procedure for the Second and Third Plutonium Decontamination Cycles is also identical in principle to that described for the First Solvent-Extraction Cycle (under 1.4, above). It involves (a) turning off the feed stream (2AF or 3AF), (b) stripping the remaining plutonium from the columns, (c) overflowing the hexone with a "cold" aqueous (i.e., 2AS or 2BX) solution, (d) draining the aqueous contents of the 2A and 3A Columns to the Salt Waste Header, and (e) draining the plutonium-bearing aqueous contents of the 2B and 3B Columns to the 2AF Tank and 3BP Receiver, respectively.

C. REMEDY OF OFF-STANDARD CONDITIONS

In Subsections 1 to 4, below, after a recapitulation of uranium and plutonium product specifications, the general methods of detection and remedy of possible off-standard conditions in the solvent-extraction battery are discussed. Specific off-standard conditions, their detection, likely causes, and remedies are dealt with in more detail in Tables VI-4 to VI-7. A brief synoptic discussion of these tables is presented in Subsection 5, below.

1. Purity and Yield Specifications

In general, final specifications for the effluent streams from Redox have not been firmly established, and probably will not be until after operation of the plant has made it possible to determine the performance under normal running conditions. Final decisions on specifications and on when an off-standard stream is to be reworked will be based on a balance between considerations (a) of the adverse behavior of an off-specification material in subsequent processing (or on the value of the U and/or Pu losses in the case of waste streams), and (b) of the cost of meeting the specifications in normal operation or by rework.

At this writing, tentative specifications for decontaminated uranium (3EU) are:

Beta radioactivity from fission products	1×10^{-7} absolute curies/g. U
Gamma radioactivity from fission products	5×10^{-8} absolute curies/g. U
Plutonium	1 part/ 10^7 parts of U
Iron	1 part/ 10^3 parts of U (1000 p.p.m.)
Sodium	1 part/ 10^3 parts of U (1000 p.p.m.)

Tentative specifications for decontaminated plutonium (3BP) are:

Beta plus gamma radioactivity from fission products	8×10^{-5} absolute curies/g. of Pu
Iron	Approx. 5% by wt. of Pu
Uranium	Specification has not been determined. The Pu in the 3BP solution is expected to be contaminated by approx. 0.1 wt.% of U, based on the weight of Pu.
Aluminum	Specification has not been determined. The Pu in the 3BP solution is expected to be contaminated by approx. 3 wt.% of Al, based on the weight of Pu.

The maximum permissible total uranium and plutonium losses to the solvent-extraction battery waste streams will be finally set after the plant is in operation, but will probably not exceed about 1.5% of the uranium and plutonium in the IAF.

2. General Methods of Detection of Off-Standard Conditions

During routine plant operation, it is expected that only the final effluent streams will be checked by frequent analyses. 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, plutonium, 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 (especially solutions in the ANN head tanks); and
- (d) radiation-recorder readings (if required).

Flow rates of all influent process streams to the Redox columns are controlled by Hammel-Dahl valves operated by Foxboro recorder-controllers and Fischer and Porter rotameter-transmitters. Normal control of flow rates is automatic except during periods of start-up and shutdown. If the flow rate of a particular stream, as indicated by the recorder, is suspect, 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. The technical basis of the location of static and differential pressure taps on the solvent-extraction columns is discussed in Chapter V. The exact locations of the several pressure taps are given in Chapter XIV.

3. Use of Column Static and Differential Pressure Readings

3.1 Detection and remedy of flooding

Detection of flooding in the solvent-extraction columns is done 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 differential pressure or static pressure readings for the column under consideration. At flooding, there will be a drop in either of these two pressure readings as the lighter organic phase tends to fill the columns. A secondary effect will be erratic changes in aqueous effluent rate as the controller attempts to maintain a changing interface by regulating the aqueous effluent. The normal readings of the several instruments are established by calibration during initial operation of the columns.

Generally a flood in a column is dissipated by reducing the influent stream rates and then waiting until the operation of the column is restored to normal. The flow rates may then be gradually increased. If non-standard conditions are the cause of flooding (such as emulsification or plugging of the packing), it may be necessary to shut the plant down until these conditions are remedied.

3.2 Detection of high uranium loss

Pilot-plant studies have demonstrated that static or differential pressure measurements give an indication of uranium waste losses from the columns as well as of flooding. A discussion of the technical background of the use of such measurements is contained in Chapter V.

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3.21 IA, 2D, 3D, and IS Columns

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The IA, 2D, 3D, and IS Columns are all equipped with differential pressure taps which are located in that region of the column extraction section in which the density changes attendant upon variations in uranium waste losses are most pronounced. Because of the presence of ANN salting agent in these columns, a rise in the differential pressure reading for a column does not necessarily reflect a high uranium loss but may indicate an increased concentration of ANN. Correction for this effect must be made before a high uranium loss may be reliably inferred.

Since high Pu(VI) losses are generally accompanied by high uranium losses, the IA Column differential pressure readings provide an indirect indication of Pu(VI) losses also. However, since the plutonium in the column is too dilute to affect the differential pressure readings directly, Pu(IV) losses are not indicated by the readings.

3.22 IC, 2E, 3E Columns

Since uranium is by far the major solute contributing to the aqueous-phase density in the IC, 2E, and 3E Columns, these columns are ideally suited to be monitored for changes in uranium transfer by means of differential pressure readings. It is expected that a waste loss increase as small as 0.025% is sufficiently large to be registered on the differential pressure instrument.

3.23 Other columns

Since no uranium is present in the 2A, 2B, 3A, and 3B Columns and since the plutonium concentrations are too low to affect pressure readings, the static pressure taps on the plutonium-cycle columns cannot be used to detect high plutonium losses. Uranium losses in the IB Column are likewise unsuited to be monitored by pressure taps, the uranium concentrations involved being too low. Besides their use to detect flooding, the IB, 2A, and 3A Column static pressure readings provide an indication of the ANN concentration.

4. Rework of Off-Standard Process Streams

Any required rework of off-standard process streams in the Redox process will normally involve one of the following three streams:

- (a) the concentrated salt waste -- to recover excessive uranium and/or plutonium losses;
- (b) the final uranium product stream (3EU, or 2EU if the Third Uranium Decontamination Cycle is not used) -- to decontaminate the uranium from an excessive plutonium and/or fission-product content; and
- (c) the final plutonium product stream (3BP, or 2BP if the Third Plutonium Decontamination Cycle is not used) -- to decontaminate the plutonium from an excessive uranium and/or fission-product content.

Methods of reworking these off-standard streams are discussed below.

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4.1 Off-standard concentrated salt waste

Uranium enters the salt-waste concentrate directly from the IAW, 2DW, and 3DW streams. Plutonium is received directly from the IAW, 2DW, 2AW, and 3AW streams. Uranium and plutonium are also received, indirectly, from the uranium and plutonium stripping columns (ICW, 2EW, and 3EW for U; 2BW and 3BW for Pu), through the hexone-washing column (IO), in the IOW stream. Relatively small amounts of uranium and plutonium may be received in the salt waste by way of the bottoms from the Condensate Evaporator.

If the concentrated salt waste shows uranium and/or plutonium concentrations above the allowed values, it is transferred to the Rework Adjustment Tank, D-7. If the off-standard waste contains excess plutonium, it is necessary to oxidize the solution while in Tank D-7 until the plutonium is converted to the ^{IV}VI valence state. After chemical adjustment, the solution is transferred to the IS Feed Tank, F-8. Uranium or plutonium extracted in the IS Column enters the IB Column as IBF. Depending upon conditions, it may be necessary to reduce IA Column flow rates so as not to exceed IB Column capacity. As shown in Figure VI-1, it is possible to route the ISP stream directly to the IC or 2E Column feed point (by a jumper change made with the remote crane). However, unless plant experience shows that excess plutonium losses are practically never encountered, the routing of ISP may be to the IB Column even though the particular batch treated may not contain plutonium, because of the inconvenience of more or less frequent jumper changes.

4.2 Off-standard uranium product (3EU)

As shown in Figure VI-2, normal rework of off-standard 3EU will be from the 3EU Concentrate Sampler, E-12, to the Rework 2DF Tank, E-13, and thence, after chemical adjustment, to the 2DF Tank, F-1, as feed to the 2D Column.

In the rather unlikely event of the 3EU containing amounts of plutonium too large to throw away (as 2DW) or containing fission products in concentrations above about 100 times the maximum allowed values, it will be necessary to transfer the off-standard 3EU from the Rework 2DF Tank, E-13, back to the Oxidizer, H-4, via the Reoxidation Header. Treatment of the off-standard stream would then follow normal processing procedures as discussed in Section B, above.

If, as it appears likely at the present writing, it is possible to decontaminate uranium in two cycles (and perhaps in only one cycle), advantage may be taken of the unused third cycle for uranium rework. Such a procedure could be accomplished as outlined below. With a two-cycle process, normal uranium routing would be through the first and second uranium cycles as presently outlined. The uranium stream from the 2EU Concentrator, F-5, would flow to the 3DF Tank, F-4, and would then be jetted to the 3EU Concentrate Sampler, E-12, on an 8-hour basis. If adequate uranium decontamination should normally be obtainable in a single cycle, the ICU concentrate could be routed directly (by gravity flow) to the 3DF Tank and thence jetted to the 3EU Concentrate Sampler.

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An off-standard batch would be jettied from the 3EU Concentrate Sampler to the Rework 2DF Tank for chemical adjustment and then directly (via new jumpers) as a 3DF stream to the 3D Column. After being processed in the 3D and 3E Columns, the uranium stream would flow to the 3EU Concentrator and thence to the 3EU Concentrate Receiver, E-11.

4.3 Off-standard plutonium product (3BP)

Normal routing of off-standard plutonium (3BP) will be from the 3BP Sampler, E-3, to the 3BP Rework Tank, E-4. From Tank E-4, the stream is jettied to the Cross-Over Oxidizer, E-7 (via the IBP Receiver, E-6, if continuous cross-over is used). However, if the 3BP contains excess uranium, it must go back to the First Cycle in order to go through the IB Column. In order that the plutonium may be properly extracted in the IA Column, it must be oxidized to the VI valence state. This oxidation is carried out in the Cross-Over Oxidizer, E-7, at near-boiling temperature. To prevent the decomposition of hexone during oxidation, the dissolved hexone is stripped out of the solution in the Cross-Over Oxidizer column before the oxidation is carried out. The oxidized solution is transferred to the IA Feed Tank, F-7. Rework plutonium streams containing only **excess** fission products can be oxidized continuously at room temperature in the 2AF Tank, E-5, with $\text{Na}_2\text{Cr}_2\text{O}_7$ and ANW being added in the Cross-Over Oxidizer.

5. Specific Off-Standard Conditions

5.1 Solvent-extraction columns

Tables VI-4, VI-5, and VI-6 contain a listing of the off-standard conditions which can conceivably occur in the operation of the solvent-extraction columns. Methods of detection, possible causes, and remedies are indicated for the various off-standard conditions in the several columns of the tables. An attempt has been made to list the separate causes in the order of likelihood of their occurrence. For example, on Table VI-4 under Item A, the most frequent cause of high uranium loss to the IAW was judged to be a low salting strength in the extraction section of the IA Column.

The following brief table covers likely causes of off-standard conditions as detected by contemplated routine analyses of effluent streams from the Redox Plant. Cross references to Tables VI-4, VI-5, and VI-6 are made in order to aid in quickly determining which specific condition is at fault and how it may be corrected.

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Solvent-Extraction ColumnsSynopsis of Possible Off-Standard Conditions

<u>First Symptom</u>	<u>Likely Causes</u>	<u>Reference (Table No. and Item)</u>
(a) Excess uranium in salt waste stream	(1) U from IAW, 2DW, 3DW (2) U from ICW, 2EW, 3EW (3) U from U concentrator condensates	Table VI-4,A; Table VI-5,A Table VI-4,F; Table VI-5,B Table VI-7,A
(b) Excess plutonium in salt waste stream	(1) Pu from IAW (2) Pu from 2AW, 3AW (3) Pu from 2DW (4) Pu from 2BW, 3BW	Table VI-4,B Table VI-6,A Table VI-5,B Table VI-6,D
(c) Excess fission-product content in 3EU		Table VI-4,C; Table VI-5,D
(d) Plutonium in 3EU	IB + 2D + 3D Column failure	Table VI-5,C; Table VI-4,E
(e) Excess fission-product content in 3BP		Table VI-4,C; Table VI-6,B
(f) Uranium in 3BP	U in IBP	Table VI-6,C; Table VI-4,D
(g) Aluminum in 3BP	3A Column flooded	Table VI-6,E

Note: Excessive concentrations of impurities such as Fe and Cr are treated as given in items (c) or (e), above. A large amount of these particular ions may indicate an excessive corrosion rate in the process equipment.

5.2 Uranium concentrators

Table VI-7 contains a listing of the off-standard conditions which can conceivably occur in the operation of the uranium concentrators. Methods of detection, possible causes, and remedies are indicated for the various off-standard conditions in the several columns of the table. The off-standard conditions covered in Table VI-7 are (a) uranium in the condensate, (b) excessively dilute product stream, and (c) excessively concentrated product stream.

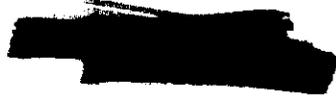
5.3 Excessive plutonium accumulation

Effective critical mass control calls for the immediate splitting of any plutonium-cycle tank batch containing more than the maximum permissible amount of plutonium. For details of the critical mass control methods, reference is made to the discussion under B3.13, above, and to Chapter XXV.

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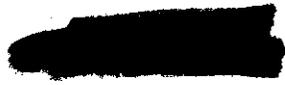
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FORM 104

SECTION 100 INDEX OF OPERATIONAL CONDITIONS
FOR ANALYTICAL PROCEDURE 0018

Operational Condition

Definition

(Listed in operational order of probability)

(The indicated procedure only to agree with the corresponding item number.)

- A. High Reading Low in the IAS Stream**

 - (1) Routinely, by analysis of the total unreacted salt water.
 - (2) Specifically, uranium analysis of a IAS (IAS) sample.
 - (3) High reading low may be compensated by an increase in the differential-pressure reading for the column.
- B. High Reading Low in the IAS Stream**

 - (1) Low saltling strength is the extraction section.
 - (2) Low concentration of IAS in the IASJ detected by a IAS IIS sample (or IAS sample).
 - (3) Low scrub (IAS) ratio detected by PIC or IR reading.
 - (4) High IAS ratio detected by PIC reading.
 - (5) Low uranium concentration in the IASJ detected by SCR or from uranium accountability sample.
 - (6) A low extractant (IAS) ratio detected by PIC reading.
 - (7) Flooding of the column; detected by PIC reading.
 - (8) A low concentration of SO_2 in the extraction section; detected by IAS sample or by IR reading on the IAS SO_2 tank, 701-4.
- C. High Saltling/Reagent Content in IAS Stream**

 - (1) Through (A) as above (Item A) for uranium.
 - (2) Incomplete oxidation of plutonium to the VI valence state in feed preparation; detected by analysis of the IAS IIS sample.
 - (3) Leak of H_2O_2 as a boiling oxidant in the IAS stream; detected by analysis of IAS, or IAS IIS sample.
 - (4) Flooding; detected by low readings.
 - (5) High saltling strength in scrub section; detected by IAS IIS sample (or IAS) for IAS.
 - (6) Wrong SO_2 detected by IR or IAS IIS sample.
 - (7) Inoperative head-amp treatment; detected by strip analysis.
 - (8) Off-standard solvent; detected by analysis of solvent before use.
 - (9) Possibility (failure) of reagent (i.e., impurely oxidant) steps in feed; detected by IR on SO_2 tank, 701-4, or by IAS sample.
- D. High Reading in the IAS Stream**

 - (1) Routinely, high reading (from the IR column) will be detected in routine analysis of the effluent plutonium stream (99%).
 - (2) Specifically, uranium analysis of the IAS (highly necessary, as uranium in the plutonium stream should come only from the fuel in column operation).
 - (3) Low saltling strength; detected by low analysis of the IAS stream.
 - (4) Flooding; detected by low reading for IR column.
 - (5) Low PIC (scrub scrub) or possibly high PIC (scrub section) ratio; detected by PIC reading.
 - (6) Low SO_2 in lower half of column; detected by strip analysis of IAS stream.
- E. High Plutonium in the IAS Stream**

 - (1) Routinely, higher than normal plutonium in the concentrated salt water (plutonium transfer in the 99%).
 - (2) Specifically, by plutonium analysis of the IAS.
 - (3) Perhaps by analysis of the effluent uranium stream 999 (only if 20 and 30 columns did not scrub out Pu).
 - (4) Routinely, by analysis of the concentrated salt water.
 - (5) If the concentrated salt water shows excess B (or Pu), a grab sample of the IAS should be taken to determine if the strip column are not operating correctly. This sample would include leaches from the IAS, 201, and IAS for uranium; the 201 and the 301 for plutonium.
- F. High Uranium Low in the IAS Stream**

 - (1) Specifically, by uranium analysis of the IAS. (Should be made only after a IAS sample shows that a strip column is at fault).
 - (2) If the concentrated salt water shows excess B (or Pu), a grab sample of the IAS should be taken to determine if the strip column are not operating correctly. This sample would include leaches from the IAS, 201, and IAS for uranium; the 201 and the 301 for plutonium.
 - (3) Specifically, by uranium analysis of the IAS. (Should be made only after a IAS sample shows that a strip column is at fault).

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TABLE VI-5
DETECTION AND REMEDY OF OFF-STANDARD CONDITIONS
SECOND AND THIRD URANIUM DECONTAMINATION CYCLES

Off-Standard Condition	Detection	Likely Causes (Listed in approximate order of probability)	Remedies (The indicated remedies apply to causes with the corresponding item number)
A. <u>High Uranium Loss to the ZW (or 3W) Stream</u> See Table VI-4, Item A.			
B. <u>High Plutonium Loss to the ZW</u>	(1) Routinely, by a plutonium analysis of the concentrated salt waste. (2) Specifically, plutonium analysis of a ZW line sample.	(1) Defective IB Column operation. See Table VI-4, Item E.	(1) See Table VI-4, Item E.
C. <u>High Plutonium in the ZEU Stream</u>	(1) Routinely, by plutonium analysis of the effluent uranium (3EU) stream. (2) Routinely, by plutonium analysis of the concentrated salt waste. If plutonium is found in the ZEU because of the omission of reducing agent in the ZDS (and 3DS because common feed tank) it will end in the 3EU stream. If plutonium is found in the ZEU because of a fault such as flooding, it will presumably be scrubbed out in the 3D Column and end in the concentrated salt waste. (3) Specifically, by plutonium analysis of the ZDU stream. If the ZEU (or ZEW) shows a plutonium loss above about 0.5% (of the Pu in IAF) an immediate check should be made of the IB Column.	(1) Leak of reducing agent in the scrub section. (a) Low concentration; detected by analysis of the ZEW stream. (b) Low flow rate; detected by FRC instrument reading. (2) Flooding, detected by DFR reading.	(1) Increase reducing agent in the scrub section. (a) If due to low concentration of reducing agent, drain the scrub tank, 3D2-D, and perform a 3DS Feed Tank. Refill with 3DS of the proper concentration from tank 3D6. (b) If due to low flow, increase rate setting on the FRC. (2) Decrease flow rates. See text, under 3.1.
D. <u>High Fission Product Content in 3EU</u> See Table VI-4, Item C.	If analysis of the 3EU shows larger than usual amounts of Ru, Zr, or Nb, check should be made on the effectiveness of the "head-end" treatment.		
E. <u>High Uranium in the ZW (or 3W) Stream</u> See Table VI-4, Item F.			

Note: Most of the material (with the exception of Items D and E dealing specifically with the IB Column) contained in Table VI-4 is applicable by analogy to the Second and Third Uranium Decontamination Cycles with the proviso that nomenclature changes be taken into account (e.g., ZW or 3W now replaces IAW, etc.). Items of distinction or of difference are noted in the entries above.

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TABLE VI-4

**DETECTION AND REMEDY OF OFF-STANDARD CONDITIONS
SECOND AND THIRD PLUTONIUM DECONTAMINATION CYCLES**

<u>Off-Standard Condition</u>	<u>Detection</u>	<u>Likely Causes</u> (Listed in approximate order of probability)	<u>Remedy</u> (The indicated remedies apply to causes with the corresponding item number).
A. High Plutonium Loss to the 24W (or 34W) Stream	<ol style="list-style-type: none"> (1) Routinely, by analysis of the concentrated salt waste. (2) Specifically, by analysis of the 24W stream. 	<ol style="list-style-type: none"> (1) Through (4) as in Table VI-4, Item E. (2) Improper oxidation of plutonium (III valence to IV or VII); detected by analysis of the 24W for Pu(III). (3) Lack of H_2O_2 in the 24W as a holding oxidant; detected by analysis of 24W. (4) For the 34W stream alone; insufficient 4W concentration in extraction section; detected by 4W analysis of the 34W. 	<ol style="list-style-type: none"> (1) Through (4) as in Table VI-4, Item E. (2) More severe oxidation. The detailed procedure for the cross-over oxidation is not completely defined at this writing. However, increased oxidation can be secured through: <ol style="list-style-type: none"> (a) Increased concentration of oxidant. (b) Higher temperature. (c) Lower hold-up times. <p>If the reoxidation cannot be quickly accomplished in the 24W Feed Tank, the solution can be added to the 32P Recarb Tank for more drastic treatment.</p> (3) Increase oxidant concentration; the 24W Feed Tank, 202-4, may be drained and refilled with scrub solution of the correct concentration from the 24S Make-Up Tank, 570. (4) Increase 4W concentration by use of 22P Butt Tank, E-1 & 24. <ol style="list-style-type: none"> (a) If due to low concentration of 4W in the 22P Butt Tank, drain, and fill with 4W solution of the correct concentration from Tank 501. (b) If due to low flow rate, increase setting on FRC.
B. Excess Plutonium Products in the 24P (or 34P) Stream See also Table VI-4, Item C.	<ol style="list-style-type: none"> (1) Routinely, by analysis of a 3EP sample. (2) Specifically, by analysis of the 24P. (3) An indication of high activity-level streams is furnished by the RR instruments. 	<ol style="list-style-type: none"> (1) Flooding; detected by PR reading. (2) High salting strength in scrub section; detected by 24W line sample for 4W. (3) Feed to the column is at a high level of activity due to improper head-end and first-cycle treatments. Detected by sample of 1BP (or by RR on 1BP Receiver). (4) Off-standard solvent; detected by analysis of solvent before use. 	<ol style="list-style-type: none"> (1) Decrease rates. See text, under C3.1. (2) Decrease salting strength. Drain Feed Tank 202-4, and refill with scrub solution of the correct composition from Tank 450. (3) Check through first-cycle and head-end treatment of feed. See Table VI-4, Item C, for first cycle coverage; Chapter III for head-end preparation. (4) Rework of solvent. See Chapter IX for procedure.
C. High Uranium Content in the 24P (or 34P) Stream	<ol style="list-style-type: none"> (1) Routinely, by uranium analysis of the 3EP. (2) Specifically, by uranium analysis of a 24P line sample. 	<ol style="list-style-type: none"> (1) Faulty IB Column operation. 	<ol style="list-style-type: none"> (1) Correct IB Column operation. See Table VI-4, Item D.
D. High Plutonium Loss to the 25W (or 35W) Stream	<ol style="list-style-type: none"> (1) Routinely, by analysis of the concentrated salt waste. (2) If the concentrated salt waste sample shows excess Pu, a grab sample of the 10W stream should be taken to determine if the strip columns (2B, 3B) are not operating correctly. (3) Specifically, by plutonium analysis of the 25W (or 35W). This analysis should be made only after a 10W sample shows that a strip column is at fault. 	<ol style="list-style-type: none"> (1) Flooding; detected by PR reading. (2) Low strip rate; detected by FRC reading. (3) Off-standard solvent; detected by analysis of solvent before use. 	<ol style="list-style-type: none"> (1) Decrease rates. See text, under C3.1. (2) Increase rate setting on FRC. (3) Rework of solvent. See Chapter IX for procedure.
E. High Aluminum in the 3EP Stream	<ol style="list-style-type: none"> (1) Routine analysis of the 3EP (Sampler). 	<ol style="list-style-type: none"> (1) Flooding in 3A Column. 	<ol style="list-style-type: none"> (1) Decrease rates. See text, under C3.1.

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TABLE VI-7

DETECTION AND REMEDY OF OFF-STANDARD CONDITIONSURANIUM CONCENTRATORS(a)Off-Standard ConditionDetectionLikely Causes

(Listed in approximate order of probability)

Remedies

(The indicated remedies apply to causes with the corresponding item number)

A. Uranium in the Condensate

- (1) Excess uranium in a total salt waste sample. Note however that excess uranium loss is more likely to result from faulty solvent-extraction column operation, as indicated in Tables VI-4 and VI-5.

- (1) Foaming; detected by an increase in differential pressure across packed section. A high rate of foaming may result in a decrease in product overflow from the concentrator pot.
- (2) Entrainment; detected by slight increase in differential pressure across the packed section. This condition should occur only at high rates.

- (1) Decrease rate, perhaps add foam agents.
- (2) Reduce rate, a slight excess feed rate may be accommodated by a corresponding decrease in the reflux rate if operation at minimum rates is required.

B. Excessively Dilute Product Stream

- (1) Specifically, by sample of the ZDF Tank, F-1; ZDF Tank, F-4; or ZEU Concentrate Sampler, E-12.
- (2) Low temperature in concentrator pot.

- (1) Low steam consumption; detected by FSC reading.
 - (a) Low setting on SGRC controlling steam flow.
 - (b) Steam trap jammed shut.
 - (c) Scale on steam coils.
- (2) High feed rate; detected by high steam rate, large pressure drop across the loaded tower.
- (3) Steam trap jammed open; detected by high steam rate.

- (1) Increase steam rate.
 - (a) Increase rate setting on SGRC.
 - (b) Replace trap.
 - (c) Requires shut-down. Boil cleaning solution (HNO₃, caustic, or dilute HF) in tank until the scale is dissolved from the coils.
- (2) Decrease feed rate to the concentrator.
- (3) Replace trap.

C. Excessively Concentrated Product Stream

- (1) Specifically, by sample of the ZDF Tank, F-1; ZDF Tank, F-4; or ZEU Concentrate Sampler, E-12. Note that if the effluent from the concentrator has been over-concentrated, it may solidify in the receiver upon cooling.
- (2) High temperature in concentrator pot.

- (1) High setting of SGRC controlling steam flow.

- (1) Decrease steam rate.

Note: (a) ICU Concentrator, F-2;
ZEU Concentrator, F-5; and
ZEU Concentrator, E-10.

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PART II: PROCESS, continued

CHAPTER VII. PLUTONIUM CONCENTRATION

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CHAPTER VII. PLUTONIUM CONCENTRATIONA. DESCRIPTION OF PROCESS1. General

Decontaminated plutonium solution from the 2B or 3B Columns must be evaporated to a volume suitable for shipment to the (231 or) 234-5 processes. In order to conduct the operation with a maximum of operating convenience and to minimize the problem of exposed coil scaling at low liquid levels, the required volume reduction is carried out in two concentrator vessels: the Plutonium Pre-Concentrator, E-16, and the Plutonium Concentrator, E-17. Approximately a three-fold volume reduction is obtained in the Pre-Concentrator following steam-stripping of the dissolved hexone in the Pre-Concentrator stripping-deentrainment column. The final volume reduction is carried out in the Concentrator. The concentrated plutonium product is removed in critically safe 30-liter batches, containing approximately 300 grams Pu, via the PR Can.

The following table summarizes a number of the important process and operating variables in the plutonium concentration steps as a function of the enrichment level of the parent slugs. The tabulation illustrates a range over which these operations may be conducted. The bases for this table include the assumption that the second and third plutonium cycles can deliver those quantities listed above the 376 g./ton level without resorting to dilution of the IBP stream with ANN solution as an additional aid in maintaining critically safe batch sizes in the IBP Receiver, 3AF Feed, and 3BP Receiver Tank. Hence the conditions indicated for enrichment levels above 376 grams of plutonium/ton of uranium would not be applicable at plant start-up, but only upon incorporation of certain equipment changes⁽¹⁾ as an alternative to the above mentioned dilution required at enrichment levels above 376 g./ton. Because of critical mass limitations throughout the cross-over step and the plutonium decontamination cycles which require the above batch dilution at enrichment levels above 376 grams of plutonium/ton of uranium, the plant at start-up will be limited to a maximum instantaneous production of about 1.5 Kg./day of plutonium (1.2 Kg./day, or 36 Kg./mo. sustained production rate). Relatively minor equipment revisions⁽¹⁾ should permit operation up to the 600 g./ton level shown in the table below without the requirement that the IBP stream be diluted with ANN solution for critical mass control.

PLUTONIUM CONCENTRATION AND PROCESSING RATE
VERSUS ENRICHMENT LEVEL

Bases: Uranium Capacity (Maximum Instantaneous)^(b) = 3.125 Short Tons/Day
(255 Gal. 3BP/Day).

Average Batch Size = 300 Grams Plutonium

Volumetric Basis: Redox Production Plant Chemical Flowsheet
(HW-No. 4). No Dilution of IBP, 2BP, or 3BP
for Critical Mass Control.

Final Pu Concentration = 10 G./L. in 30 L. (7.95 Gal.).
One PR Cage.

Enrichment Level, Grams Pu/Short Ton of U	Pu Rate Grams/Day (Maximum Instantaneous) ^(b)	Batch Volume Gal. 3BP/300-Gram Batch	Average Pu Conc. in 3BP G. Pu/L. ^(a)	Overall Volume Reduction	Number of 300-G. Batch/Day (Maximum Instantaneous) ^(b)
250	781	98	0.81	12.3/1	2.6
300	938	82	0.97	10.3/1	3.1
350	1094	70	1.13	8.8/1	3.6
376	1176	65	1.22	8.2/1	3.9
400	1250	61	1.30	7.7/1	4.2
450	1406	54	1.46	6.8/1	4.7
500	1563	49	1.62	6.2/1	5.2
600	1875	41	1.94	5.2/1	6.3

(a) Uncorrected for losses earlier in process.

(b) Average production rates may be determined by multiplying the maximum instantaneous rates by 0.8.

It is emphasized that the above processing conditions apply to an assumed uranium capacity of 3.125 short tons per day. Uranium production may vary, but values for the last column above may, with the capacity limitations discussed below, be readily computed by multiplying the batches/day figure by the ratio of the new uranium rate to 3.125.

The capacity of the plutonium concentrators is limited by the time required for transferring the solutions to and from the individual concentrators, and the heat transfer limitations of the concentrators. A maximum of six to seven 300-gram Pu batches per day may be processed through the present concentration equipment (a maximum instantaneous rate of from 1800 to 2100 grams Pu per day) if no reflux is added to the concentrator columns. Use of reflux at a rate equal to 25 per cent of the total overhead rate will reduce the maximum capacity to 5 to 6 batches per day. These capacities can be maintained so long as the

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uranium processing rate does not exceed 4.3 tons per day with no reflux or 3.7 tons per day with 25 per cent reflux when operating under HW No. 4 Flowsheet conditions. These capacities may be maintained during higher uranium processing rates if operating conditions are adjusted to give a smaller volume of 3BP per ton of uranium processed. If the plutonium capacity of the Redox Plant is to be increased above this maximum rate, revisions to the present concentrators or the installation of a second set of concentrators will be necessary. These capacity considerations apply to the plutonium concentration equipment alone and do not imply that the plant as a whole is capable of meeting these capacities. Further minor changes at early parts of the process may be required before the plant can exceed an instantaneous plutonium production rate of over five 300-gram batches per day.

To process the maximum number of batches per day, the time cycles of the two concentrators must be as nearly equal as possible. This is necessary in order that one concentrator will not be standing idle for a portion of the time when the other is in operation. The time cycles may be made equal except in cases where the final Pre-Concentrator volume would be less than 20 gal., as this volume is necessary to cover the Pre-Concentrator coil. The volume to which a batch should be concentrated in the Pre-Concentrator for optimum time cycle operation and the estimated time cycle per concentrator, as determined by the initial volume of 3BP collected for the batch in the 3BP Receiver, may be determined from Figures VII-1 and VII-2.

The Plutonium Pre-Concentrator and the Plutonium Concentrator are located in the Plutonium Cage in the North Sample Gallery. These vessels and their auxiliaries are shown on the Engineer's Flow Sketch for the Second and Third Plutonium Cycles, contained in Chapter VI and a general description of the plutonium cage is contained in Chapter XI. The Pre-Concentrator, Concentrator, and PR Can are discussed from a functional point of view in Subsections A3, A4, and A5, below.

2. Properties and Compositions of Solutions

2.1 Physical properties and compositions

Tabulated below are the important components and physical properties of the 3BP solution before and after concentration. Normal flowsheet variations, caused by slight variations in column flow ratios, compositions of feed streams, and operating temperatures, are to be expected during operation and are reflected in the range of values indicated.

Bases: Operation at 400 g./ton level at 3.125 ton/day U processing rate (maximum instantaneous) under HW No. 4 Flowsheet conditions. Volume reduction in Pre-Concentrator to 23 gal.

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Component	Stream		
	3BP	Pre-Concentrate	Concentrate
Pu, g./l. (a)	1.2 to 1.4	3.2 to 3.7	9.2 to 10.7
HNO ₃ , M	1.0 to 1.2	2.6 to 3.2	7.7 to 9.2
Al ⁺⁺⁺ , g./g. Pu(b)	0.03	0.03	0.03
Fe ⁺⁺⁺ , g./g. Pu(c)	<0.05	<0.05	<0.05
Cr ⁺⁺⁺ , g./g. Pu(b)	<3 x 10 ⁻³	<3 x 10 ⁻³	<3 x 10 ⁻³
Na ⁺ , g./g. Pu(b)	2 x 10 ⁻³	2 x 10 ⁻³	2 x 10 ⁻³
SO ₄ ⁼ , g./g. Pu(b)	1 x 10 ⁻³	1 x 10 ⁻³	1 x 10 ⁻³
Silica (as SiO ₂), g./g. Pu(b)	4 x 10 ⁻³	4 x 10 ⁻³	4 x 10 ⁻³
Ca ⁺⁺ , g./g. Pu(b)	1 x 10 ⁻³	1 x 10 ⁻³	1 x 10 ⁻³
Mg ⁺⁺ , g./g. Pu(b)	1 x 10 ⁻³	1 x 10 ⁻³	1 x 10 ⁻³
Cl ⁻ , g./g. Pu(b)	1 x 10 ⁻³	1 x 10 ⁻³	1 x 10 ⁻³
Hexone, Wt. % of Soln.	1.7 to 2.0	0	0
UNH, g./g. Pu(b)	0.001	0.001	0.001

Properties

Specific gravity at 25°C.	1.03 to 1.04	1.08 to 1.10	1.25 to 1.29
Boiling point, °C.	100 to 101	101 to 103	114 to 117
Freezing point, °C.	-3 to -5	-11 to -15	-24 to -31
Viscosity at 25°C., cp.	1.0	1.1	1.5 to 1.7

Radioactivity from Fission Products

Gross beta plus gamma curies/g. Pu(c)	8 x 10 ⁻⁵	8 x 10 ⁻⁵	8 x 10 ⁻⁵
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- (a) The plutonium is present mostly (ca. 80%) in the IV valence state. The remainder is in the VI state.
- (b) Specifications for the allowable concentrations of these components were not available at the time of this writing. Values given are order-of-magnitude estimates of the expected impurity concentrations, based on available solubility data and demineralized water specifications. (Demineralized water enters the plutonium product stream because it is used for 2BX and 3BX make-up.)
- (c) Probable specification value.

Nitric acid concentrations and physical properties will differ slightly from those values listed above if 2BP solution is being processed, since the 2BP stream contains a lower concentration (0.8 to 1.0 M) of nitric acid. Different plutonium concentrations in the irradiated slugs, variations in uranium processing rates, and changes from HW No. 4 Flowsheet operating conditions may cause deviations from the figures tabulated above. The physical properties of concentrator solutions depend almost entirely on the nitric acid concentration, as even the final

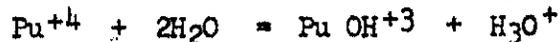
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plutonium concentrations are relatively low. This is illustrated by the freezing points listed in the table above. The original 3BP freezing point is only 3 to 5 degrees lower than pure water, as the nitric acid concentration is relatively low. The final freezing point of the concentrate is 20 to 28 degrees lower because the concentration steps have increased the acid concentration eight-fold to a concentration which depresses the freezing point substantially. The plutonium concentration, while also increased eight-fold, is still low enough to have no appreciable effect. (This is an opposite condition from that encountered in the uranium concentrators where the final concentrate contains sufficient uranium to raise the freezing point substantially.)

2.2 Chemical behavior

Plutonium is present in the concentrators in the form of the IV and VI ions (Pu^{+4} and PuO_2^{++} ions. Pu^{+4} may be associated in ionic complexes with up to six NO_3^- ions, PuO_2^{++} with up to two NO_3^- ions). The plutonium nitrates are very soluble in high concentrations of nitric acid. Pu(IV) nitrate concentrations as high as 1200 g./l. in 1.7 M nitric acid have been reported. (2)

In plutonium solutions with nitric acid concentrations below 0.5 M, there is a possibility of partial hydrolysis or the formation of the polymerized form of plutonium(IV). Nitric acid is normally present in the concentrator solutions at concentrations (see table above) where this cannot occur. The plutonium(IV) hydrolysis reaction is rapid and reversible and takes place according to the following equation: (4)



Plutonium hydroxide will precipitate if the solution pH is 2.5 or greater. (2) Plutonium polymer is a complex mixture of high molecular weight, hydrolyzed Pu(IV) stable in low (about 0.1 M or less) acid solutions. (4) As long as the acidity of the solution is on the order of 0.1 M, polymerization takes place relatively slowly at elevated temperatures.* When the acidity is of the order of 0.01 M, however, polymerization occurs very rapidly and is complete in a matter of minutes. (3) This polymer will partially precipitate when the nitric acid concentration is increased to approximately 1 M, and redissolves on further increase in acid concentration to 6 M. (3) Depolymerization rates are slow, unless the solution is heated. Polymer may be rapidly dissolved and depolymerized by increasing the nitric acid concentration to 6 M and heating at 90°C. for one hour. (3) As pointed out above, the range of acid concentrations in the concentrators are sufficiently high that no difficulties due to polymer formation or hydrolysis are anticipated.

Occasional precipitation of plutonium from hexone-saturated 2BP solutions, which had been stored for several weeks, was observed at Argonne National Laboratory and traced to hexone or its decomposition products. (5)(6)

*It was reported that polymer can be produced by heating Pu(IV) for one hour in low (0.1-0.3 M) acid solutions, but that polymerization is not complete as some Pu(IV) is oxidized to Pu(VI) by the acid. Temperature was not given but is believed to be between 70 and 100°C.

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Analysis of the supernate revealed that generally over 90 per cent of the plutonium had precipitated. It is believed that methylisopropyl diketone, a hexone decomposition product, is the material responsible for the formation of the precipitate, which is believed to be an impure plutonium (IV) oxalate. Stability experiments at Hanford Works (7) have shown that 2BP or 3BP solutions saturated with diketone (20 g./l.) yield a precipitate when heated to 80°C. for from three to four hours, and in eight to ten hours when pure hexone is substituted for the diketone. Concentrations of either hexone or diketone of 3 g./l. (approximately 15% of the saturation value) gave no precipitate when heated to 75 to 80°C. for 48 hours. No plutonium precipitation was observed in hexone-saturated aqueous Redox solutions after standing for six weeks at room temperature. It was concluded that plutonium will not precipitate in normal IBP, 2BP, or 3BP streams at room temperature and that any step requiring the heating of these solutions should be entirely safe if preceded by a hexone-stripping operation to remove 90 to 95% of the dissolved hexone.

Decomposition products are regularly removed from the hexone used in the Redox Plant in the solvent treatment facilities and the bulk of the dissolved hexone is removed from the 3BP stream by live-steam stripping before it is heated in the concentrators. These preventative measures should eliminate the possibility of a hexone-plutonium precipitation.

It has been experimentally demonstrated that the hexone-plutonium precipitate may be dissolved, (5)(6) if the remaining dissolved solvent is first removed from the solution, in excess concentrated nitric acid (16 M) at room temperature or in a solution of 0.65 M HNO₃, 0.1 M Na₂Cr₂O₇, and 1.3 M Al(NO₃)₃ at 75°C. Attempts to dissolve it in 6 M and 10 M HNO₃ at 75°C. failed. No dissolution attempts have been made at boiling temperatures.

3. Plutonium Pre-Concentrator

3.1 Description

The Plutonium Pre-Concentrator, E-16, in which the initial concentration of the plutonium product stream is carried out, consists of a vertical tank equipped with jacket and coil and mounted with a column. The function of the column is two-fold: it serves both for stripping hexone from the entering feed, and deentraining plutonium solution droplets from the overhead vapor.

The tank (180-gal. volume) is supplied with 100-lb./sq.in. steam, water, and air through a single line to the coil (9.4 sq.ft.) and jacket (8.1 sq.ft.) and with 15-lb./sq.in. steam to a sparger which discharges into the top of the tank. The column (12 in. inside diameter) contains two sections packed with one-inch Raschig rings (lower section 4 ft. 9 in. high, upper section 21 in. high), a weir-type inlet feed distributor located between the two packed sections, and three demineralized water spray nozzles at the top of the column for intermittent flushing and to provide liquid reflux, if necessary. Flow indicators are provided on the steam line to the coil and jacket, the steam line to the sparger,

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and the water line to the spray nozzles. Column differential pressure, tank-to-cell differential pressure, and tank weight factor indicators are also provided. A vapor condenser, E-15, containing 22 sq.ft. of condensing surface is connected to the vapor outlet at the top of the column. A more complete description of the Pre-Concentrator is contained in Chapter XV.

3.2 Hexone stripping

Hexone is steam stripped from the entering plutonium feed solution as it flows down through the lower packed section into the tank. Live steam for the stripping operation may be supplied through the sparger or by boiling a heel of demineralized water in the tank. The latter method is preferred, as it provides an additional "perfect plate" for the stripping operation. It may be desirable to use the former method, however, to reduce the time required for the stripping operation.

The transfer unit height for hexone stripping in the lower packed section is expected to be on the order of 1-1/2 ft.; thus the 4-3/4 ft. of packing provide approximately three transfer units and will reduce the hexone concentration in the Pre-Concentrator feed to approximately 0.1 weight per cent (95% hexone removal). Additional hexone removal is accomplished in the tank if the stripping steam is supplied by boiling the tank liquid.

3.3 Concentration

Following the stripping operation, the plutonium solution is concentrated by boiling with coil and jacket steam to a volume suitable for processing in the Concentrator. The bulk of any remaining hexone is distilled from the solution at this time. The Pre-Concentrator is designed to operate at a boil-up rate of 29.5 lb./hr. (sq.ft. of liquid surface), which corresponds to a total rate of 175 lb./hr. Vapor velocity through the column when operating at this boil-up rate is 1.7 ft./sec.

3.4 Deentrainment

Entrained droplets of plutonium solution must be removed from the overhead vapors during the stripping and concentration operations in order to minimize plutonium contamination of the condensate stream. The upper packed section acts to deentrain these droplets during the stripping operation and both packed sections perform this function during the concentration operation. During both operations a condensate deentrainment factor of 10^4 is required. This corresponds to a plutonium loss to the condensate of approximately 0.0001 g./l. At the normal operating rates it is expected that this requirement can easily be met without the use of reflux. If it should become necessary to improve deentrainment, reflux may be added from the water spray nozzles. Under these circumstances, a reflux rate equal to one-fourth of the total overhead rate is recommended.

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4. Plutonium Concentrator

4.1 Description

The Plutonium Concentrator, E-17, in which the final concentration of the plutonium product stream is carried out, consists of a vertical tank equipped with jacket and coil and mounted with a column. The column serves to deentrain plutonium solution droplets from the overhead vapor stream.

The tank (48 gal. volume) is supplied with 100-lb./sq.in. steam, water, and air through a single line to the coil (2.8 sq.ft.) and jacket (2.9 sq.ft.). The column (6 in. inside diameter) is packed with 4 ft. 8 in. of graded packing consisting principally of 1/2-inch Raschig rings. A cold-finger reflux condenser (2.4 sq.ft.) is contained in the top of the column to provide liquid reflux intermittently for flushing or continuously, if required. A vapor condenser, E-18, containing 9.8 sq.ft. of condensing surface is connected to the column vapor outlet. Flow indicators are provided on the steam line to the coil and jacket and on the water line to the reflux condenser. Column differential pressure, tank-to-cell differential pressure, and tank weight factor indicators are also provided. A more complete description of the Concentrator is contained in Chapter XV.

4.2 Concentration

The plutonium solution is concentrated by boiling with coil and jacket steam to the final PR Can volume in the Concentrator. The Concentrator is designed for a boil-up rate of 41 lb./(hr.)(sq.ft. of liquid surface), which corresponds to a total rate of 72 lb./hr. Vapor velocity through the column at this boil-up rate is 2.7 ft./sec.

4.3 Deentrainment

A condensate deentrainment factor of 10^4 is required during the concentration operation. This corresponds to a plutonium loss to the condensate of approximately 0.0001 g./l. At the normal operating rate it is expected that this requirement can easily be met. If it should become necessary to improve deentrainment, a portion of the vapor stream can be refluxed with the reflux condenser. Under these circumstances, a reflux rate equal to one-fourth of the total overhead rate is recommended.

5. PR Can

The PR Can (15 gal. capacity, 30 l. working volume) is a stainless-steel vessel used to transport the concentrated plutonium solution to the (231 or) 234-5 Building. A complete description of the PR Can is contained in Chapter XVI. When being stored or transported inside the building, the PR Can is contained in an outer carrier vessel. For transportation between buildings, both of these vessels are contained in a special truck-mounted carrier. The PR Can is filled through a hole in the top. This hole is closed with a clamp-operated metal plug during

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transportation. The hole and the area over which the plug travels are enclosed within a well which limits the spread of leakage and allows any leakage to be flushed into the can. Both the PR Can and its carrier vessel are equipped with eyes for engaging hoist hooks.

The PR Can is filled through the PR Can Stopper, which is located inside the east end of the Plutonium Cage. This stopper is a metal plug, fitted with a teflon gasket to provide a vacuum-tight seal, which contains the filling line from the Plutonium Concentrator, E-17, and a vacuum line from the Plutonium Transfer Trap, E-21.

B. PROCEDURE

1. Normal Procedure

The procedure described below applies to 2BP or 3BP material resulting from the processing of 3.125 short tons of uranium per day at a plutonium level of about 400 grams per ton. For other enrichment levels, batch volumes are selected in accordance with paragraph A-1, above, and the extent of volume reduction in each concentrator is determined from Fig. VII-1 to give maximum operating convenience and optimum time cycles. In all cases, batch volumes contain approximately 300 grams of plutonium as specified for critical mass control and at higher plutonium levels a greater number of batches of smaller initial volumes must be processed through the equipment per day.

1.1 Receiving and sampling

The 3BP solution is received in the 3BP Receiver, E-2, in the canyon until the batch volume of 6l gal. is collected. The batch is jetted from the 3BP Receiver to the 3BP Sampler, E-3, also in the canyon, where it is sampled. The batch is held here until it is determined from the sample that it meets specifications. If the sample shows that the batch contains more than the proper amount of plutonium it is split in half at this point by jetting only one-half of it to the Pre-Concentrator and holding the other half for processing as a separate batch.

1.2 Pre-Concentration

The sampled batch is jetted from the 3BP Sampler through a 3 gal./min. steam jet into the Pre-Concentrator, located in the Plutonium Cage. The feed enters the Pre-Concentrator column through the feed inlet. Live steam is fed through the column during the period when feed is being admitted. This steam is supplied, either from the sparger or from boiling demineralized water in the tank, at the rate of 300 lb./hr. to strip the hexone from the entering feed. The time required for the stripping operation is approximately 30 minutes. At the completion of the stripping operation, steam is fed to the coil and jacket at the approximate rate of 200 lb./hr. and the solution is concentrated by boiling to a volume of 23 gal. It is then cooled to 35°C. for transfer to the Plutonium Concentrator, E-17. The times required for concentration and cooling are approximately 150 minutes and 15 minutes, respectively. The

overhead vapor streams from the stripping and concentration operations are condensed in Condenser E-15, and collected in the Pre-Concentrator Condensate Receiver, E-14. Condensate is jettted periodically from this receiver to the waste condensate treatment system, where it is subjected to an additional distillation before disposal to the cribs.

1.3 Concentration

The cooled concentrate in the Plutonium Pre-Concentrator, E-16, is transferred to the Plutonium Concentrator, E-17, by drawing a vacuum on the Concentrator with the vacuum jet via the Plutonium Transfer Trap, E-21. The valve between the Pre-Concentrator and the Concentrator is then opened and the batch is drawn into the Concentrator. Approximately 30 minutes are required for the transfer operation. Steam is admitted to the coil and jacket at the approximate rate of 90 lb./hr. and the solution is heated to boiling. Boiling is continued at this steam rate until the batch has been evaporated to the final PR Can volume of about 8 gal. The solution is then cooled with coil and jacket water to 25°C. before final transfer into the PR Can. The times required for heating, evaporation, and cooling are approximately 20 min., 110 min., and 50 min., respectively. Overhead vapor from the Concentrator is condensed in condenser E-18 and collected in the Concentrator Condensate Receiver, E-19. This waste condensate is periodically jettted to the waste treatment system.

1.4 Packaging and removal

The PR Can and its carrier vessel are brought up to the east end of the Plutonium Cage. The PR Can is lifted from the carrier vessel by a traveling chain hoist and carried into the Cage. It is then raised in place under the PR Can Stopper. A vacuum is drawn on the PR Can with the vacuum line from the Plutonium Transfer Trap. The valve between the Concentrator and the PR Can is then opened and the concentrated plutonium solution is drawn into the PR Can. The final sample, for accountability, critical mass control, and product purity, is taken from the line sampler during this transfer. At the completion of the transfer, the PR Can is removed from the Stopper and cleaned of any outside contamination. It is then closed and put into the outer carrying container for shipment. It is estimated that the time required for the packaging and removal operation will be at least one hour, although the actual solution transfer time is only about ten minutes.

1.5 Critical mass control

Specifications for critical mass control (see Chapter XXV) allow the handling of batches with an average plutonium content of 300 grams in the concentrators and PR Can. Batch size is controlled in the 3BP Sampler so that the average size of batches fed to the Pre-Concentrator will be approximately 300 grams. Slight upward deviations from this figure will be allowed in order to avoid the necessity of frequently splitting batches in the 3BP Sampler. The maximum allowable batchsize will be determined after the plant goes into operation, as discussed in Chapter XXV.

The only possible circumstances that would result in the accumulation of over a safe batch of plutonium in the concentrators are an accidental mixing of two batches or a holdup of plutonium, caused by accidental precipitation or crystallization, which would mix with the next batch. If two batches are accidentally mixed, they must be split immediately. It will be normal procedure to make material balances, based on the 3BP Sampler Tank and PR Can samples, for each batch processed. Plutonium holdups large enough to cause a criticality hazard will thus be detected and must be immediately removed by the methods outlined under 2.6 below.

2. Remedy of Off-Standard Conditions

2.1 Off-standard plutonium product solutions

Off-standard plutonium product solutions (those failing to meet the specifications for uranium and fission-product decontamination or product purity) should be detected in the 3BP Sampler and recycled as outlined in Chapter VI. Any off-standard condition which should escape detection in the 3BP Sampler will be detected from the PR Can line sample after the solution has been loaded. It is considered unlikely that this will ever happen, and thus no facilities for recycling PR Can solutions have been installed. However, if it does become necessary to rework PR Can solutions, a spare flange has been left on the Plutonium Transfer Trap, E-21, to which a suitable connection for adding recycle solutions can be added. Solutions added to the Transfer Trap are recycled as outlined under 2.2, below.

2.2 Rework of Plutonium Transfer Trap solutions

All solutions from the Plutonium Cage in need of reprocessing are routed back to the process through the Plutonium Transfer Trap, E-21. Plutonium solutions may be added to the Transfer Trap from PR Cans (as outlined in 2.1, above), from the Plutonium Cage sump through the sump jet, or, if the PR Can is accidentally overfilled, through the vacuum line from the PR Can. These solutions are sampled in the Transfer Trap to determine the type of rework necessary and are then jettted to the 3BP Sampler, E-3. They are then reworked through the process as outlined in Chapter VI, or, if otherwise within shipping specifications, concentrated for shipment. It must be noted that the 3BP Sampler is regularly in use, and thus the routing of rework solutions through it must be carefully scheduled. Contaminated rework solutions routed through the 3BP Sampler must be followed by a demineralized water flush, in order to avoid cross-contamination of main-line product solutions.

2.3 Insufficient condensate decontamination

A condensate deentrainment (decontamination) factor of 10^4 , which corresponds to a plutonium concentration in the condensate of approximately 0.0001 g./l., is required in order that the condensate may be disposed of to underground cribs after one additional evaporation. (See Chapter X for a discussion of waste condensate treatment and cribbing tolerances.) Under normal operating conditions it is expected that the

actual condensate deentrainment factor will be greater than 10^5 . (See Chapter XV.) Excessive contamination of the condensate streams is possible only if the concentrators are operated with (a) an excessively high boil-up rate, (b) too large a volume of reflux, or (c) the column packing partially plugged with solids. All three of these conditions may cause high entrainment losses and, sometimes, flooding and will be indicated by high differential pressure drops across the columns. Pressure drops should never be allowed to exceed 7 inches of water across the Pre-Concentrator column and 5 inches of water across the Concentrator column. If differential pressure readings show that these allowable pressure drops are being exceeded in either column, the boil-up rate should immediately be lowered and, when stripping hexone or using reflux, the feed or reflux rate cut back. If contamination of the condensate (caused by entrainment) exceeds 0.0001 g. Pu/l. and the columns are operating well within their allowable pressure drop range, reflux should be added at a rate equal to 25 per cent of the total overhead rate to improve deentrainment.

No provisions are made for returning plutonium-contaminated condensate to the concentrators, as the plutonium will be recovered in the waste treatment system if enough is present to make recovery economical.

2.4 Plugging of column packing

Plugging of the packing in either column is very unlikely, as the concentrator solutions are normally far from the saturation point and thus any solution in contact with the packing will have little tendency to deposit solids upon it. Periodic wash-downs will tend to remove any solids that deposit before they can plug the packing. Should the packing become plugged, the solids can be removed by a water wash-down of the packing. This is done with the water spray in the Pre-Concentrator column and by operating with reflux in the Concentrator column. If this method is unsuccessful the column must be removed and the packing dumped and cleaned or replaced with new packing.

2.5 Over-concentration

Over-concentration in either concentrator will be evident from weight factor instrument readings on both the concentrator and condensate receiver vessels. In cases of over-concentration where the volume is still greater than 4 gal., the solution should be diluted to the final concentration volume (20 gal. in the Pre-Concentrator, 8 gal. in the Concentrator) with demineralized water. If the volume is less than 4 gal., a volume of 60% nitric acid sufficient to bring the volume to 4 gallons should be added and water then added to bring the volume up to the final concentration volume. After dilution the solution should be heated to 90°C. and circulated through the recirculating jet spray for one hour. The processing of the solution may then be continued following normal procedure. This dilution procedure should remove any plutonium that has crystallized out because of the over-concentration. It is possible, however, that it will not, and this holdup of plutonium will be detected and removed as outlined in 2.6 below.

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2.6 Plutonium holdup in vessels

A plutonium holdup in the concentrator vessels could result from an accidental precipitation or crystallization of the plutonium from the concentrator solutions. Off-standard conditions which may result in precipitation or crystallization are: (a) nitric acid concentration less than 0.5 M in the Pre-Concentrator (3BP) feed stream; (b) incomplete hexone removal from the Pre-Concentrator feed stream, or (c) extreme over-concentration. Nitric acid concentrations less than 0.5 M are extremely unlikely, as the bulk of the acid contained in the 3B Column feed streams leaves this column in the 3BP stream. Incomplete hexone removal will result only if the stripping steam rate to the Pre-Concentrator column is too low and would be obvious because of the resultant low condensate collection rate in the Pre-Concentrator Condensate Receiver, E-14. There is only a slight possibility that the incomplete removal of hexone would cause a precipitation, as it would be distilled off in the Pre-Concentrator before it was in contact with the plutonium solution long enough to result in precipitation. It is unlikely that over-concentration will result in a plutonium holdup if handled as outlined under 2.5, above.

Any holdup of plutonium caused by these or other reasons, will be detected by the plutonium critical-mass and accountability material balance, which is made on the basis of the 3BP Sampler and PR Can samples for each batch.

Plutonium holdups are removed by adding 25 gal. of 6 M nitric acid solution to the Pre-Concentrator, heating to boiling, and circulating for one hour with the recirculating jet spray. During this period reflux is added to the Pre-Concentrator column, at a rate equal to the boil-up rate, to flush the column. The solution is then cooled and transferred to the Concentrator. It is again heated to boiling and circulated with the recirculating jet spray for one hour. During this period the column is operated under conditions of total reflux to flush the packing. The refluxing is then stopped and the solution concentrated to 8 gal. for shipment. If this treatment fails to remove the held-up plutonium, use may be made of the following expedient, which is based on limited information and may not be optimum. An oxidizing solution (25 gal.) containing 0.7 M nitric acid, 0.1 M sodium dichromate, and 1.3 M aluminum nitrate is added to the Pre-Concentrator, heated to 75°C., and recirculated for eight hours. This solution is then transferred to the Concentrator, heated to 75°C., and recirculated for another eight hours. It must then be transferred batch-wise through the PR Can to the Plutonium Transfer Trap, as outlined under 2.1 above, from where it is reworked through the plutonium cycles for removal of the sodium dichromate and aluminum nitrate and then processed through the concentrators as a normal batch.

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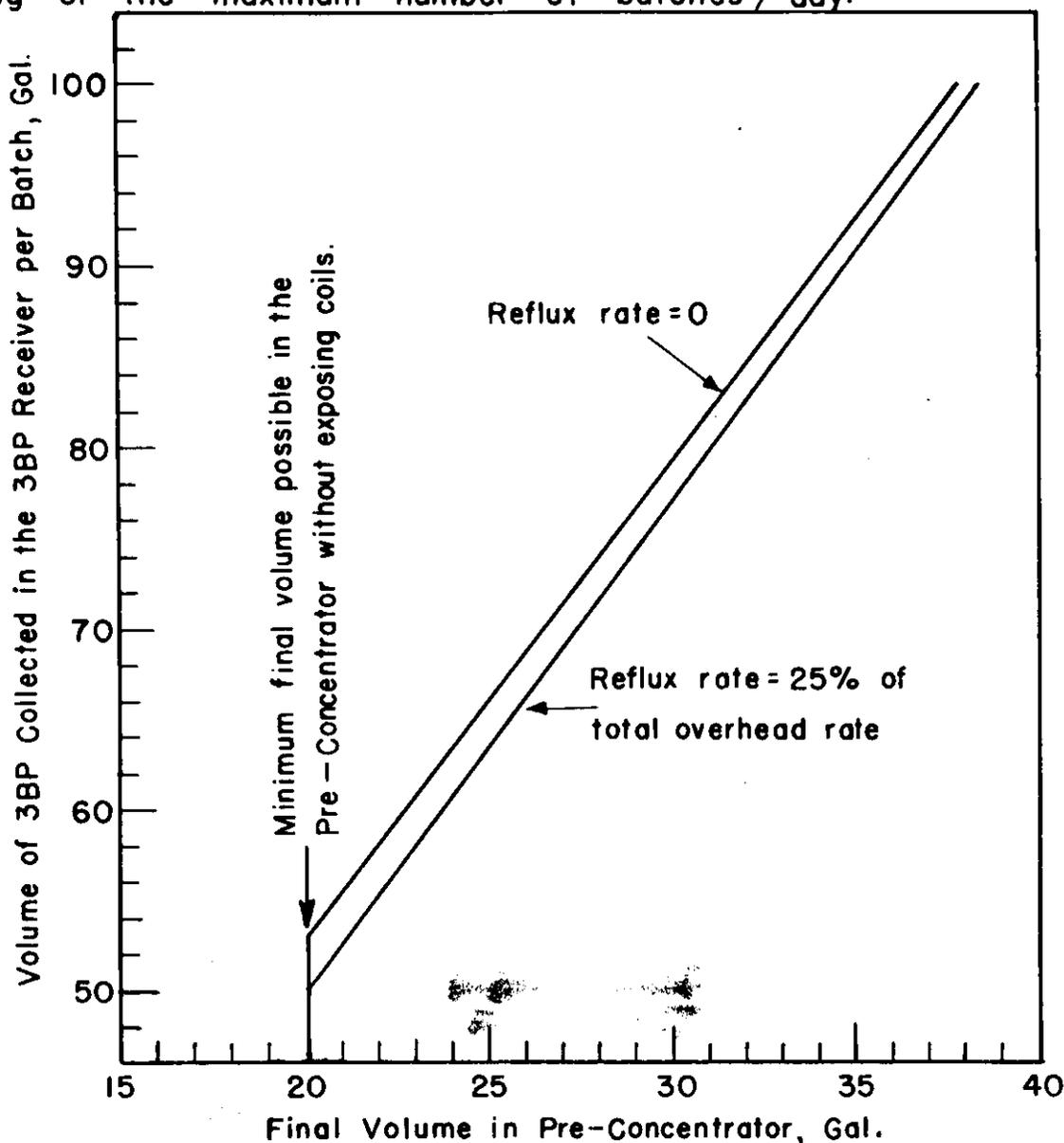
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FIGURE VII-1

VOLUME REDUCTION IN PRE-CONCENTRATOR
FOR MAXIMUM NUMBER OF BATCHES/DAY

Basis: Flow and Heat Transfer Rates Shown on Fig. VI-3

The final Pre-Concentrator volumes plotted on this figure will result in equal batch processing times for the Pre-Concentrator and Concentrator, which permits the processing of the maximum number of batches / day.



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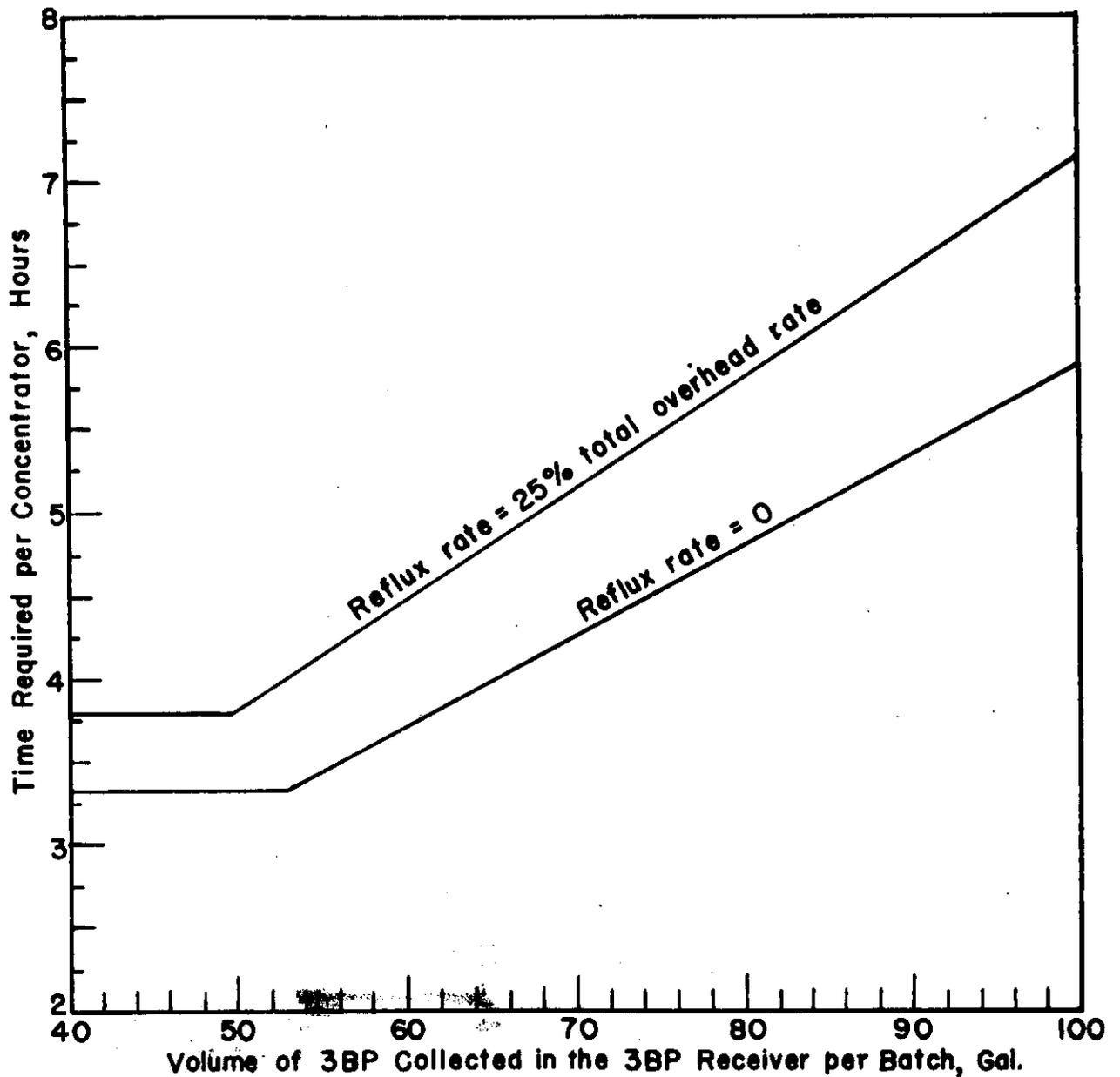
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FIGURE VII-2

OPTIMUM TIME CYCLES IN THE PLUTONIUM CONCENTRATORS

Basis : Flow and Heat Transfer Rates Shown on Fig. VI- 3.

The time required per concentrator is based on an assumed volume reduction in the Pre-Concentrator as indicated by Fig. VII-1.



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PART II: PROCESS, continued

CHAPTER VIII. AQUEOUS MAKE-UP

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CHAPTER VIII. AQUEOUS MAKE-UP

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A. DESCRIPTION OF PROCESS

The function of the Aqueous Make-Up System is the preparation and distribution of aqueous chemical solutions (except dissolver solution) having proper specifications for use throughout the Redox Plant. Figure VIII-1 is a schematic presentation of the entire chemical make-up system. The stream data and chemical requirements shown on this sketch are based on an instantaneous plant capacity of 3-1/8 tons of uranium per day. Compositions of column feed solutions made in the Aqueous Make-Up System are tabulated below:

Feed Stream	Components									
	Al(NO ₃) ₃ ·9H ₂ O		NaOH		Fe(NH ₂ SO ₃) ₂		HNO ₃		Na ₂ Cr ₂ O ₇ ·2H ₂ O	
	Wt. %	M	Wt. %	M	Wt. %	M	Wt. %	M	Wt. %	M
IAS	52.3	1.8	0.62	0.20	--	--	--	--	0.23	0.01
IBX	40.1	1.3	--	--	1.0	0.05	0.27	0.05	--	--
ICX)										
2EX)	--	--	--	--	--	--	0.25	0.04	--	--
3EX)										
2DS)	51.9	1.8	0.62	0.20	1.0	0.05	--	--	--	--
3DS)										
2BX)	--	--	--	--	--	--	0.63	0.1	--	--
3BX)										
2AS	40.3	1.3	--	--	--	--	--	--	0.25	0.01
3AS	40.6	1.3	--	--	--	--	--	--	--	--

The specifications of the chemicals used may be found in Reference (4).

Demineralized water is used in the preparation of all solutions that enter the solvent-extraction columns. Two demineralizing units (on the second level of the silo) are supplied with 200-W Area filtered water, and each has a maximum throughput of 1250 gallons per hour. They discharge into the Demineralized Water Storage Tank, SW-131 (15,000-gallon capacity), located in Building 211-S, the Chemical Tank Farm. Distribution of this water is handled through a head tank, 602 (2400-gallon capacity; three-hour holdup), which supplies the various make-up vessels by gravity flow from the fifth level of the silo.

Aluminum nitrate is delivered by the vendor in the form of 70 to 75 weight per cent (as Al(NO₃)₃·9H₂O) solution and stored in three 149,000-gallon storage tanks, SS-111, 112, and 113, in Building 211-S. The stock solution is adjusted to 61.7 weight per cent in the Aluminum Nitrate Ad-

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justment Tank, 202 (3500-gallon capacity), before it is routed to the head supply tank, 601 (2300-gallon capacity; holdup time of ten hours). Fifty weight per cent sodium hydroxide solution is stored in two 99,000-gallon tanks, SQ-101 and 102 (located in Building 211-S), and delivered to a head supply tank, 604 (1800-gallon capacity; holdup time of twelve hours), on the fifth level of the silo. Similarly, sixty per cent nitric acid solution is stored in three tanks, SA-121 (15,000-gallon capacity) and SA-122 and 123 (41,000-gallon capacity), and delivered to a head supply tank, 603 (1800-gallon capacity; holdup time of 23 hours), on the same level of the silo. Sodium nitrate, used in the coating-removal solution, is purchased as the dry chemical and made up to the desired composition with water in Tank 509 (1100-gallon capacity; holdup time of 54 hours) before being routed to the Dissolver operating gallery tanks. Also, sodium dichromate, an oxidizing agent in some process streams (e.g., IAS, IAF, 2AS, 2AF, ISS, and ISF), and sodium carbonate, used in IOX, are purchased as the dry chemicals and made up into the desired solutions in Tank 506 (400-gallon capacity; holdup time of 110 hours) and Tank 501 (1100-gallon capacity, holdup time of 22 hours), respectively.

Ferrous sulfamate, the plutonium-reducing agent in IB, 2D, and 3D Columns, is prepared in Tank 504 (400-gallon capacity) by reaction of powdered iron with sulfamic acid solution. The completed charge is filtered to Tank 503 (400-gallon capacity) and adjusted to 30 weight per cent ferrous sulfamate before delivery to Tank 405 (130-gallon capacity) for use in the make-up of IBX, 2DS, and 3DS. Ferrous sulfamate may be added also to the ISS Make-Up Tank, 403 (600-gallon capacity), for use when the IS Column is used as a rework column. The use of ferrous ammonium sulfate and sulfamic acid is being considered at the time of this writing as a replacement for the preparation of ferrous sulfamate by the reaction of iron powder and sulfamic acid.

Aqueous wash solutions for decontamination purposes are made and stored in Tank 505 (1100-gallon capacity). Water, nitric acid, and caustic are piped to this tank; other washing aids may be added to the tank manually.

B. PROCEDURES

1. General Procedures

Portable scales and weigh tanks are used for the measurement of small quantities of make-up chemicals such as sodium dichromate, 50 per cent caustic, 60 per cent nitric acid, 30 per cent ferrous sulfamate solution, iron powder, and sulfamic acid. Weight-factor manometers are used for the measurement of large quantities of water, caustic, and nitric acid added to the tanks.

All aqueous solutions are made up batchwise in agitated tanks equipped with heating and cooling coils as shown in Figure VIII-1. Salted feed streams such as IAS, 2AS, 3AS, and IBX are prepared in individual tanks. Since 2DS and 3DS are identical in composition, they are made in the same tank. Similarly, dilute nitric acid streams of like composition (e.g., ICX, 2EX, and 3EX; or 2BX and 3BX) are prepared in a single agitated tank.

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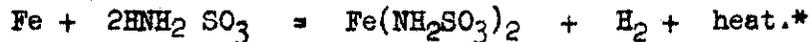
Completed solutions are pumped through Cuno filters to the various gallery tanks from which they are fed to the columns.

2. Preparation of Acid-Deficient Aluminum Nitrate Solutions

The aluminum nitrate solutions, IAS, 2DS, and 3DS, have a specification of minus 0.2 M nitric acid and are, therefore, termed "acid deficient". These solutions become stoichiometrically neutral upon addition of 0.2 moles of nitric acid per liter of solution. The pH of these solutions, however, is on the acid side (pH approximately 2). This "acid deficiency" in IAS, 2DS, and 3DS is produced by the addition of caustic, approximately 0.2 moles per liter of solution. In order that the formation of insoluble oxides of aluminum may be prevented, the caustic is added slowly to the solution at room temperature and in the presence of good agitation. Even when agitation is adequate, local precipitation occurs at the point of caustic addition, but this precipitate redissolves readily.

3. Preparation of Ferrous Sulfamate Solution

Ferrous sulfamate may be prepared by the reaction of sulfamic acid with ferrous hydroxide, ferrous carbonate, or metallic iron. Due largely to the availability of the required materials, the metallic iron method is used. An equation showing the reaction is presented below:



Baker and Adamson U.S.P., or equal, hydrogen-reduced iron powder and technical-grade sulfamic acid are used. Evolution of hydrogen during the reaction necessitates inert-gas blanketing to avoid a fire and explosion hazard.

Solutions of ferrous sulfamate are to be made about 2.3 M in ferrous ion. Since two solids, metallic iron and excess sulfamic acid, are present in the make-up vessel throughout most of the reaction time, vigorous agitation is required. The solubility of ferrous sulfamate (see Chapter IV) is much greater than that of sulfamic acid. An excess (two to three per cent of the stoichiometric quantity) of sulfamic acid is required so that the pH of the final solution is less than 2.2, a pH below which ferrous ion is more stable.

As indicated by the equation, the reaction between metallic iron and sulfamic acid is exothermic. Using hydrogen-reduced iron powder, the reaction should take place without additional heating; in fact, a temperature rise of approximately 20°F. should occur. Although the reaction would be faster at a higher temperature, the temperature should be maintained below

*)This heat of reaction has not been reported. However, sulfamic acid is similar to hydrochloric acid in respect to its reaction with iron; thus, the heat evolved would be approximately equal to the heat of reaction for iron and hydrochloric acid, 20.7 kilocalories per gram mole of iron.

120°F. to minimize hydrolysis of the sulfamate ion to the sulfate ion. Due to the long reaction time required at 120°F. or below, perhaps as long as a full day, a three days' supply is made up per batch.

The Ferrous Sulfamate Preparation Tank, 504, is equipped with heating and cooling coils, temperature and weight-factor indicators, and an agitator. In addition, a nitrogen blanketing and vent system is provided for the elimination of oxygen and removal of the hydrogen evolved in the reaction.

In the preparation of a batch of ferrous sulfamate, 1890 pounds of water are measured into Tank 504, the agitator is turned on, and 1182 pounds of sulfamic acid are added. The nitrogen purge is turned on, and 330 pounds of iron powder are added slowly to the acid slurry. Heating will accelerate the reaction, but the temperature should be controlled below 120°F. When the specific gravity of the solution at 80°F. reaches 1.42, the reaction is considered complete, and the charge is cooled and sampled. Ferrous ion concentration and pH are the criteria of a completed reaction. The desired concentration of ferrous ion is 130 grams per liter in a solution with a pH less than 2.2. If the pH is above 2.2, additional sulfamic acid is dissolved until the desired pH is attained. Then agitation is stopped so that unreacted iron (approximately 65 pounds) can settle out of the solution. After a one-hour settling period, the supernatant is pumped from Tank 504 through a Cuno pressure filter and into the Ferrous Sulfamate Solution Adjustment Tank, 503. A slurry heel (containing approximately 65 pounds of unreacted iron and 190 pounds of sulfamic acid) is left in Tank 504 for use in the next make-up. The solution in the adjustment tank, 503, is diluted with demineralized water to a 30 weight per cent ferrous sulfamate solution.

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REFERENCES

- (1) Harmon, M. K., Memorandum to F. W. Woodfield, Separation Technology Division, October 3, 1949.
- (2) HDC-1293 Preliminary Engineer's Flow Sketch and Process Description. Redox Aqueous Make-Up System. J. M. Frame. 6-22-49.
- (3) HW-13697 Preparation of Ferrous Sulfamate. P. Clagett. 6-10-49.
- (4) HW-19156 Specifications for Acceptance and Sampling Procedures for Essential Materials. Analytical Section, Technical Services Division. May, 1951.

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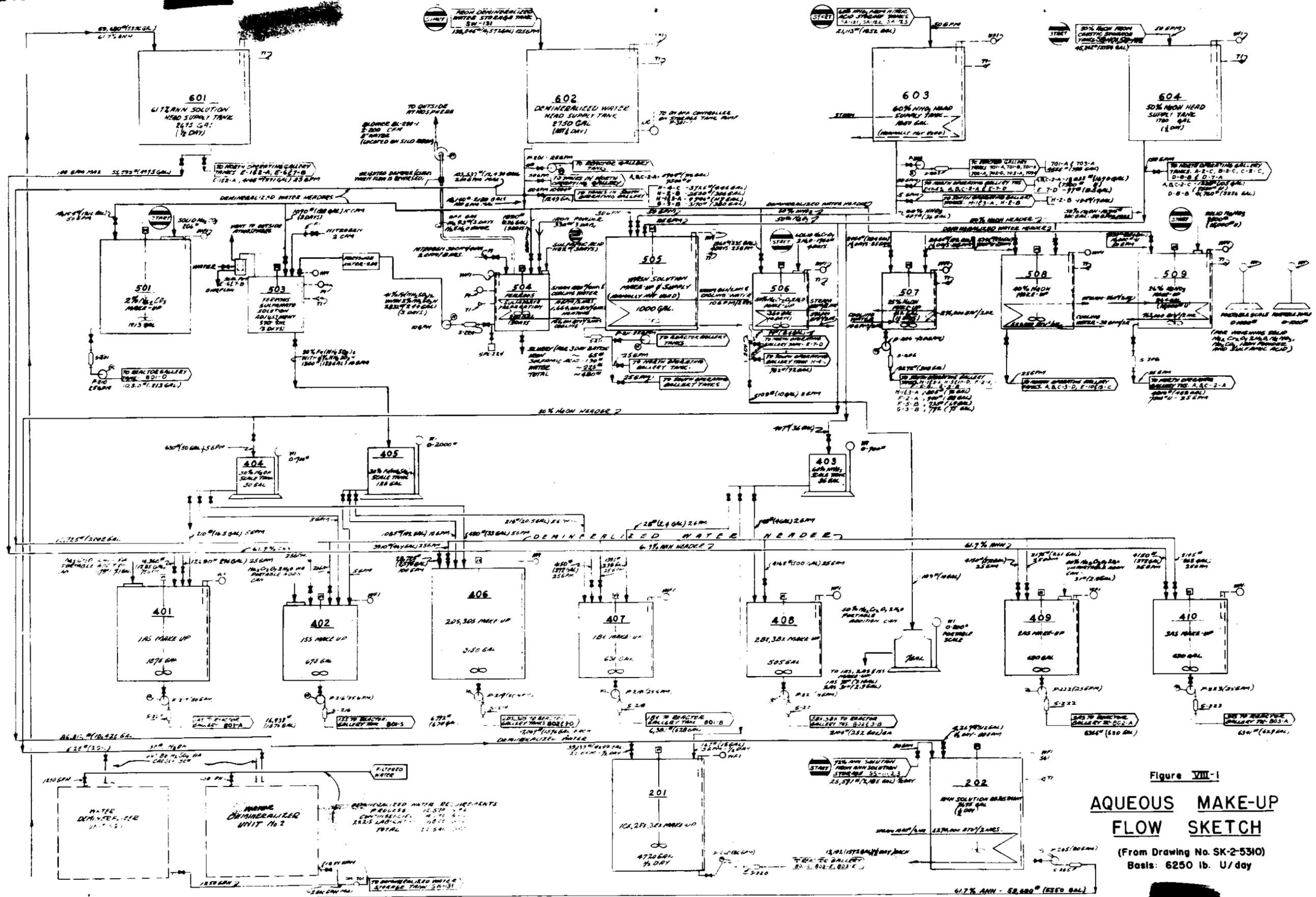


Figure VIII-1

AQUEOUS MAKE-UP FLOW SKETCH

(From Drawing No. SK-2-5310)
Basis: 6250 lb. U/day

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PART II: PROCESS, continued

CHAPTER IX. SOLVENT TREATMENT

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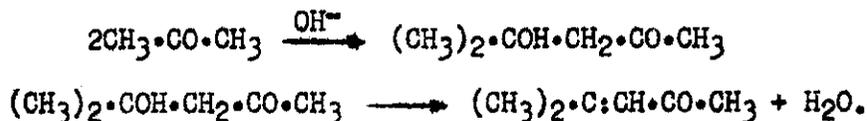
CHAPTER IX. SOLVENT TREATMENTA. INTRODUCTION

The solvent used in the Redox process is methyl isobutyl ketone (MIBK), otherwise known as "hexone". "Hexone" is a trade name employed by the Carbide and Carbon Chemicals Corporation for methyl isobutyl ketone, and, strictly speaking, should not be used for this product when supplied by any other manufacturer. However, the word "hexone" (uncapitalized), representing methyl isobutyl ketone regardless of the manufacturer, has come into common usage during the development period of the Redox process.

Hexone, as received from the manufacturer, contains impurities formed during its synthesis. In addition to these impurities, several oxidation products are formed while hexone is in contact with Redox solutions containing nitric acid. The important impurities are listed in the following table:

<u>Impurity</u>	<u>Chemical Formula</u>	<u>Origin</u>
Methyl isobutyl carbinol (MIBC)	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3$	Synthesis
Mesityl oxide (MO)	$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	Synthesis
Methyl isopropyl diketone	$(\text{CH}_3)_2\text{CH}\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3$	Oxidation product
1,1-dinitroisobutane	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{NO}_2)_2$	Oxidation product
Organic acids, e.g.,		Oxidation products
Acetic acid	CH_3COOH	
Isobutyric acid	$(\text{CH}_3)_2\text{CH}\cdot\text{COOH}$	
Isovaleric acid	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$	

In the synthesis of hexone, (2) a condensation of acetone forms mesityl oxide:



Hydrogenation of the oxide produces hexone:



Small quantities of methyl isobutyl carbinol (MIBC) are formed during the hydrogenation, and small amounts of mesityl oxide (MO) remain; thus, both MIBC and mesityl oxide are present in low concentrations in raw hexone. The other impurities listed are the main products formed from oxidation of hexone by nitric and nitrous acids. The reactions of hexone with nitric and nitrous acids are explained in Chapter IV and also in Reference (12).

For use in the Redox process, hexone as received from the manufacturer must meet the specifications tabulated below(13):

Purity	not less than 99.0% by volume hexone
Distillation	114 to 117°C. (A.S.T.M. D268-46)
Refractive index	$n_D^{20°C} = 1.3953 \pm 0.004$
Color	maximum 15 platinum cobalt (Hazen) standard
Acidity	less than 0.05% by volume as acetic acid
Oxidizing normality	less than 0.001 N
MIBC (methyl isobutyl carbinol)	shall not exceed 0.6% by volume
Mesityl oxide	shall not exceed 0.3% by volume

As is discussed below, procedures must be employed to reduce the MIBC concentration to 0.05 per cent or less before the hexone is suitable for the Redox process.(7) The deleterious effects of hexone impurities on the extraction and decontamination of plutonium and uranium are discussed in greater detail in Chapter IV. Hence, only a brief resume of the problem is presented here.

Both of the two main impurities present in hexone as a result of its synthesis, MIBC and mesityl oxide (MO), can possibly be deleterious to process performance. The removal of zirconium, niobium (i.e., columbium), and cerium from the product streams is believed to be affected adversely by small concentrations (greater than 0.05 per cent) of MIBC in hexone under acid flowsheet conditions,(4) though possibly not under acid-deficient flowsheet conditions. Variations in the plutonium (IBP) and uranium (ICU) decontamination factors of as much as 50- to 100-fold, encountered during O.R.N.L. pilot plant development with the A.N.L. acid flowsheet, were attributed to the high MIBC content of hexone which was approximately 0.1 to 0.3 per cent. Laboratory experiments(14) have indicated that concentrations of MO as low as about 0.25% in the hexone IAP stream will reduce Pu(VI) to a hexone-insoluble state, probably Pu(V). This occurs fairly rapidly, with a half-time of one-half to one hour. A second, slower reduction to Pu(IV) and/or Pu(III) follows, with a half-time of several hours. Thus MO may adversely affect plutonium losses to the IAW, 2AW, and 3AW streams. Only a small amount of data on the effect of hexone impurities were obtained during the pilot plant development of the O.R.N.L. acid-deficient flowsheet. Results of one run at S.P.R.U. under O.R.N.L. Flowsheet conditions have indicated that substituting raw Carbide and Carbon hexone, containing 0.6 per cent MIBC and 0.3 per cent MO, for high-purity, pretreated hexone had no adverse effect on either IBP or ICU decontamination(14), but may have been the cause of about 3 times higher than normal plutonium losses to the IAW (waste) stream.

The effect of other specific impurities have not been as extensively studied. In general, however, low concentrations (less than 0.001 N) of oxidation products in hexone produce no detrimental effect on the distribution coefficients for U(VI), Pu(VI), or Pu(IV). However, based on laboratory studies, oxidizing impurities in hexone in concentrations

exceeding 0.001 N may affect IB Column performance by oxidizing the ferrous ion to ferric ion, thus affecting the Pu(III):Pu(IV) ratio and, hence, the distribution coefficient of plutonium.⁽⁶⁾ Methyl isopropyl diketone should be prevented from accumulating in the hexone because this hexone impurity may, in the plutonium concentration step, decompose to the oxalate ion, and form a precipitate of plutonium oxalate.

Hexone impurities may play a part in the formation of "crud", an insoluble matter which on occasion accumulates at the organic-aqueous interface in the solvent-extraction columns, particularly the IA Column. An occasional tendency for the columns to plug on account of an emulsion at the interface has been noted during the solvent extraction of uranium. Some experimental evidence, described in Chapter IV, indicates that hexone impurities possibly have an effect on "crud" formation in the column⁽¹⁾⁽²⁾⁽³⁾, but no direct correlation has been reported. An expedient which has been used to a limited extent during the development period for the Redox process involved the washing of hexone with aluminum nitrate solution just before it was used.⁽¹⁾ No justification for this method has been reported, except that it seemed to remove (by a process of "crud" formation) those materials which would cause the formation of "crud" with the aluminum nitrate-uranium nitrate solutions in the extraction columns.

Solvent treatment, necessary for removal of hexone impurities, is performed in two separate portions of the Redox Plant. Facilities for batch treatment (Figure IX-1) are provided in the Organic Treatment Building (276-S), located west of the Redox Production Plant (202-S). Equipment for continuous recovery of hexone (Figure IX-2) consists of the IO Column, the lowest column in the Solvent Extraction Column Cascade in the silo, and the Organic Distillation Column, G-3, located in the Organic Cell G of the canyon.

B. PRETREATMENT

Raw hexone is pretreated batchwise according to the procedures outlined later in this chapter (Subsection D1). The facilities provided in the 276-S Building for pretreatment of hexone are shown schematically in Figure IX-1. Essentially, this pretreatment consists of a nitric acid-dichromate wash of the hexone followed by water and caustic washes. This acid-dichromate wash, 1M each in HNO₃ and Na₂Cr₂O₇·2H₂O, oxidizes MIBC to hexone.⁽⁴⁾ Acid concentration has a pronounced effect on the oxidation, the optimum range being 1.0 to 1.4 M. Raw hexone having an MIBC content less than 0.2 per cent is readily purified to 0.02 per cent or less in a 1-1/2 hour, single-stage agitation. At an initial MIBC content of 0.4 per cent, some advantage is gained by increasing the treatment time to 2-1/2 hours. When the initial MIBC considerably exceeds 0.4 per cent, single-stage operation does not yield a product of desired purity. Two-stage treatment with intermediate water washing produces the desired results when the MIBC concentration is as high as 0.67 per cent. In addition to the oxidation of MIBC, mesityl oxide (MO) is oxidized by Na₂Cr₂O₇·2H₂O to organic acids.

Following the acid-dichromate wash, a stoichiometric quantity of

caustic (50 weight per cent) is added to neutralize the acid solution before the wash is pumped to the 276-S Building Crib. Solutions which are "cribbed" should have a pH in the range of 5-8. Acidic solutions (pH below 3) leach the alkaline soil and cause channeling with the resultant decrease in absorption of radioactive contaminants. Retention of plutonium is thought to be favored when the pH is 5-7 and retention of fission products, when the pH is about 8. (The problems of waste disposal are discussed in more detail in Chapter X.) After the neutralized dichromate wash is decanted, two water washes remove residual salts (primarily NaNO_3). A 0.5 per cent (0.13 M) caustic wash neutralizes organic acids formed by oxidation of MO and adjusts the pH of the hexone to approximately 7. Any residual caustic is removed by a final water wash of the hexone.

In the washing operations, adequate time and good agitation are both essential for sufficient contact of the hexone with the washing agent. Occasional emulsification is encountered during washing operations, but a few pounds of nitric acid added to the emulsion ordinarily breaks it. The settling time for the final wash (sixty minutes) is longer than the time (twenty minutes) allotted for the initial and intermediate washes. Following the initial and intermediate washes, a twenty-minute settling period is adequate because a small residual aqueous heel from one wash does not decrease the effectiveness of the following wash appreciably. However, after the final wash, a sixty-minute settling period is allotted so that essentially complete disengagement is achieved and no aqueous heel enters the organic feed system. If more than a few gallons of water were transferred to the Organic Head Tank and entered the extraction columns, the operation of the columns would be adversely affected (resulting in increased plutonium and/or uranium losses). In addition to the longer settling period, the final washing is performed at a temperature less than 77°F., the normal operating temperature in the solvent-extraction columns, so that water of saturation does not separate out of the hexone after it leaves the treatment tank. Data indicating the effect of temperature on the mutual solubilities of water and hexone are presented in the following table: (5)

<u>Solubility of Hexone in Water</u>		<u>Solubility of Water in Hexone</u>	
<u>Temperature,</u> <u>OF.</u>	<u>Weight %</u> <u>Hexone</u>	<u>Temperature,</u> <u>OF.</u>	<u>Weight %</u> <u>Water</u>
45.7	2.62	35.6	1.44
70.3	1.94	77.7	1.94
104.9	1.53	101.7	2.35
130 - 140	1.45 (Min.)	123.6	2.92
165.2	1.53	165.2	3.63
202.1	1.93	201.2	4.73

Additional data are presented in Chapter IV.

C. SOLVENT RECOVERY

The purpose of the Solvent Recovery System is two fold: (a) to remove the residual plutonium, uranium, and fission products from hexone which is recycled to the Redox process and (b) to remove oxidation products (and any condensation products which might be formed) from hexone. This purpose is accomplished by continuous washing and distillation of the hexone. The facilities in the 202-S Building for hexone recovery are shown schematically in Figure IX-2.

1. IO Column Wash

Hexone from the extraction cycles (i.e., ICW, 2BW, 2EW, 3BW, and 3EW) is continuously and countercurrently washed in the IO Column. The wash solution, demineralized water or 2 per cent (0.192 M) sodium carbonate, is used in a ratio of one volume of wash to twenty volumes of solvent. Water does not extract the plutonium, uranium, and fission products quite as readily as carbonate, nor does it neutralize any organic acids. However, water does dissolve the water-soluble organic acids, and it has the advantage over carbonate that it does not add solids to the waste to be stored underground. Dilute sodium hydroxide might be used as the extractant, but it would precipitate residual ions of uranium and plutonium in the column rather than allow them to flow to the waste receiver.

When the plant operates at an instantaneous uranium processing rate of 3-1/8 tons/day, the IO Column (twelve inches in diameter) is operated at a volume velocity of approximately 1300 gal./hr.(sq.ft.), sum of both phases. This volume velocity is about fifty per cent of the flooding capacity of the column when packed with one-inch Raschig rings. At these operating conditions the H.T.U. (see Chapter V) obtained during uranium extraction studies in the IO Column using water as extractant is about 2.5 feet.⁽¹⁰⁾ Although the H.T.U. has not been determined for a column using sodium carbonate extractant under similar operating conditions, a conservative estimate is approximately three feet. Therefore, the fifteen-foot packed section (see Chapter XIV for additional specifications for the IO Column) is equivalent to about five transfer units when dilute sodium carbonate is used as extractant. The diffusing components (Pu, U, and F.P.'s) are present in the column in extremely low concentrations. Their distribution ratios (organic/aqueous) at these low concentrations are very low. However, even though the distribution ratios may be taken as essentially zero, the minimum concentration of diffusing components in the organic effluent is about 1/150 of that in the organic feed to the IO Column. This factor is calculated assuming that 5 transfer units ("overall organic-film" basis) are available, and that the distribution ratios (organic/aqueous) are effectively zero.

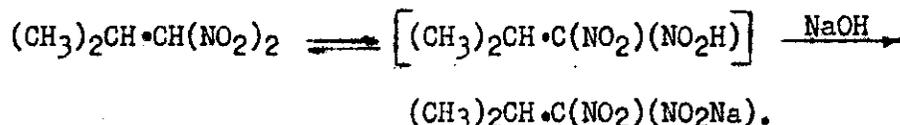
2. Distillation

The organic effluent from the IO Column is treated in the Organic Distillation Column, G-3, by simultaneous distillation and caustic scrubbing (5 weight per cent aqueous NaOH, 1.3 M). The purpose of this treatment is to remove the remaining hexone oxidation products (i.e., methyl isopropyl diketone, 1,1-dinitroisobutane, and organic acids) from the

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hexone so that it may be recycled to the Redox process. Although the mechanics of removal are not clearly understood, methyl isopropyl diketone in concentrations up to 20 grams/liter (approximately 100 times the concentration anticipated during operation) is removed (approximately 90 per cent) by a caustic wash with the hexone in either the liquid or vapor phase.⁽⁸⁾ As illustrated in the following equation, caustic also removes 1,1-dinitroisobutane to a similar degree by forming a water-soluble salt of the tautomer of 1,1-dinitroisobutane:



The organic acids (e.g., acetic acid) are neutralized by the caustic as shown in the equation below:



In addition to the hexone oxidation products, any residual (trace amounts) of uranium, plutonium, and fission products are removed by precipitation of complex sodium salts.

A McCabe-Thiele-type operating diagram for the Organic Distillation Column is plotted in Figure IX-3. The vapor composition (Y), expressed as moles of hexone per mole of vapor, is plotted on a logarithmic scale versus the liquid composition (X), expressed as moles of hexone per mole of liquid, also on a logarithmic scale. The equilibrium data shown are for the hexone-water system although the aqueous phase in the column is a dilute (5 per cent) caustic solution. This approximation is justified because the vapor pressure over the dilute caustic solution is approximately the same as that over water at the same temperature. The horizontal section of the equilibrium line represents the azeotropic composition (36.2 mole per cent hexone) of the hexone-water vapor which is distilled from the immiscible liquid phases at 740 mm. Hg total pressure (the average operating pressure in the column). The compositions and boiling points of the hexone-water azeotropes at different pressures are shown in the following table.⁽⁵⁾

<u>Pressure, mm. Hg</u>	<u>Temperature, °F.</u>	<u>Wt. % Hexone</u>	<u>Mole % Hexone</u>
27	67.6	81.2	43.7
45	78.6	81.0	43.4
89	101.1	79.3	40.8
108	108.1	79.6	41.2
207	132.8	78.5	39.6
382	158.5	77.7	38.5
752	189.5	75.9	36.1
760	190.2	75.7	35.9

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The operating diagram in Figure IX-3 is divided into three sections, each having a separate operating line: (a) hexone feed plate (Plate 5 on Figure IX-2), (b) hexone stripping section (Plates 6 and 7 and the Reboiler), and (c) caustic treatment section (Plates 1, 2, 3, and 4). The hexone feed (0.84 mole fraction hexone) entering the column is mixed on Plate 5 with the hexone-saturated caustic scrub solution (0.0032 mole fraction hexone) overflowing from Plate 4 as shown on Figure IX-3 by the dotted horizontal line starting at X_f . The curved portion at the upper end of the Feed Plate Operating Line represents the changes in composition occurring on the plate as the hexone feed is heated to the boiling point (diluted by condensation of steam used for heating). Thus, X_f (0.84 mole fraction hexone) is diluted to X_{fc} (0.58 mole fraction hexone) by condensed steam and caustic. The straight portion of the operating line for Plate 5 is represented by the following equation:

$$Y = 0.527 X - 0.0012.$$

Based on the assumption that 80 per cent of the hexone is vaporized from the feed plate, the composition of the feed plate overflow is 0.12 mole fraction hexone. The feed plate effluent is mixed on Plate 6 with the cold (77°F.), hexone-saturated aqueous return ($X_r = 0.0032$ mole fraction hexone) from the condenser, and the mixture is heated to the boiling point. The straight portion of the operating line for the hexone stripping section is represented by the following equation:

$$Y_s = 1.06 X - 0.0003.$$

Based on the assumption that the remaining hexone phase (approximately 20 per cent of the hexone fed to the column) is vaporized from Plate 6, the overflow from Plate 6 is caustic solution saturated with hexone (0.0032 mole fraction hexone). If Plate 7 and the reboiler each have an overall efficiency of 20 per cent (i.e., 0.2 theoretical plate per actual plate), the composition of the waste caustic solution leaving the column (X_w) is 0.00048 mole fraction hexone.

For the caustic treatment section of the column (Plates 1, 2, 3, and 4), the operating line is represented by the following equation:

$$Y_c = 0.053 X + 0.352$$

Since the numerical value of X to be substituted in the equation is small (never exceeding 0.003), this operating line is nearly horizontal at a value of $Y = 0.352$. As the caustic flows down through Plates 1, 2, 3, 4, it becomes saturated with hexone, and the vapor actually decreases in hexone concentration slightly as it rises through the column. One theoretical plate is essentially adequate to achieve hexone saturation of the caustic, and since the plate efficiencies are expected to be high (approximately 100%) in this section of the column, one actual plate is adequate. However, three additional plates are provided so that the time of contact (approximately 5 seconds) of hexone with the caustic scrub solution is sufficient to achieve removal of the oxidation products. The hexone-water

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vapor leaving the column is condensed, cooled to approximately 77°F., and the resulting immiscible liquids are decanted continuously. As discussed in the previous section, the liquids are cooled to 77°F. so that water of saturation does not settle out of the hexone at a later point in the process. This cooling would not be important if the hexone were retreated following each distillation cycle because the hexone would be in contact with water again.

3. Retreatment

Recycled hexone, which was pretreated before introduction into the Redox process, should be free of impurities and oxidation products of hexone after it has been through the Solvent Recovery System. Therefore, the hexone is usually returned to the Organic Header Feed Tank, O-3 (Figure IX-1), without further treatment. However, a routine sample of the hexone is taken and analyzed specifically for MIBC. Although MIBC is not known to be formed in the Redox process, hexone does decompose slowly during prolonged storage to yield MIBC. The concentration of hexone oxidation products (methyl isopropyl diketone and 1,1-dinitroisobutane) are determined at less frequent intervals than MIBC. Empirical methods (e.g., distribution ratio test) for ascertaining the quality of the hexone are currently being developed and may replace the tests for individual impurities. Analytical methods are described in Chapter XX.

If these routine analyses of hexone indicate an accumulation of impurities the entire supply of hexone in the system, approximately 24,000 gallons, is retreated in batches of 10,000 gallons each before it is returned to the Organic Head Tank, 804. If a specific tank-full of hexone is found to be unsatisfactory, this one batch may be retreated without retreating the entire inventory. This retreatment procedure is identical with that described in Section D1 for pretreatment of raw hexone; however, the specific weights and volumes of chemicals indicated in Section D1 are for 4000-gallon batches and must be increased proportionally for 10,000-gallon batches.

D. PROCEDURE

1. Normal Procedure

1.1 Pretreatment

Raw hexone is added to the system when the normal hexone inventory of approximately 24,000 gallons drops to approximately 20,000 gallons. Based on the assumption that routine retreatment is not necessary, the hexone losses to process wastes are approximately 150 gallons per day which drops the inventory to 20,000 gallons in approximately 4 weeks. Figure IX-1 is a schematic diagram of the Organic Treatment facilities where raw hexone is added. A batch of 4000 gallons of raw hexone is pumped to the Organic Sampler and Treatment Tank, O-2 (working volume, 11,000 gallons), from one of two, 21,500-gallon Organic Storage Tanks, SO-141 and 142, buried north of the 276-S Building.

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The pretreatment procedures described below apply to typical raw hexone having an initial MIBC concentration of less than 0.4 per cent.

- (a) The hexone is agitated for two hours with a 400 gallon (ten per cent by volume) wash solution that is 1 M each in HNO_3 (5.3 weight per cent) (350 pounds 60 per cent HNO_3) and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (22.2 weight per cent) (1000 pounds solid).
- (b) Following the acid-dichromate wash, a stoichiometric quantity of caustic (270 pounds 50 per cent NaOH) is added to neutralize the acid. After twenty minutes of continued agitation, a twenty-minute settling period is allowed for disengagement of the two phases. The aqueous phase is decanted to the 276-S Building Crib, a single crib for disposal of hexone-saturated aqueous wastes of negligible activity.
- (c) The hexone is given two 200-gallon (five per cent by volume) water washes to remove salts (primarily NaNO_3) formed during the neutralization. Twenty minutes are allowed for each agitation and settling period. These washes are also cribbed.
- (d) Neutralization of residual acids is accomplished by a 400 gallon (ten per cent by volume) wash which is 0.13 M NaOH (0.5 weight per cent NaOH) (35 pounds 50 per cent NaOH). After twenty-minute agitation and settling periods, this wash is cribbed.
- (e) One 200-gallon (five per cent by volume) water wash is used for removal of residual caustic. This wash is performed at a temperature below 77°F. After a twenty-minute agitation, a sixty-minute settling period is allowed so that complete disengagement is accomplished. The wash is decanted to the 276-S Building Crib.
- (f) A sample of the hexone is taken and analyzed for MIBC. When the MIBC content is 0.05 volume per cent or less, the hexone is suitable for use in the Redox process.

Note: If the hexone is previously known to contain more than 0.4 per cent MIBC, two-stage acid-dichromate washing is performed with one-hour agitation periods.

1.2 Solvent recovery

Figure IX-2 is a schematic presentation of the Organic Recovery System. Hexone from the solvent-extraction columns (i.e., ICW, 2BW, 2EW, 3BW, and 3EW) flows at 16.5 gallons per minute into the base of the IO Column where it is contacted countercurrently with water or a two per cent (0.192 M) sodium carbonate wash. Water or dilute sodium carbonate is fed to the top of the column at 0.84 gallon per minute from the Organic Wash Addition Tank, 801-0 (holdup time, 12 hours) by gravity flow through a remotely controlled valve. The aqueous effluent, IOW, leaves the column through a valve remotely controlled by the interface recorder-controller (see Chapter

XIX) and flows to the Waste Header Receiver, Tank D-13. Provisions are made for sampling this stream.

The hexone effluent, I00, from the IO Column overflows to the Organic Distillation Column, G-3, where it is caustic washed and distilled. In addition, a hexone-water mixture (58 weight per cent hexone) from the Condensate Stripper, D-5 (described in Chapter X) is blended into the I00 and increases the average hexone feed rate to the column from 16.5 to 16.8 gallons per minute. The hexone feed enters the column at the fifth plate from the top. Steam vaporizes the hexone, and a hexone-water vapor passes up the column where it is scrubbed with dilute caustic, and leaves the column at a temperature of 193°F. or higher.

The temperature of the vapor leaving the top of the column regulates the steam supply to the reboiler by means of a temperature controller and automatically-operated steam valve. For positive control of the steam, the vapor temperature is maintained at least as high as 193°F., four degrees higher than the azeotropic boiling point of 189°F. at 740 mm. Hg, so that the vapor (25 weight per cent water) is richer in steam than the azeotropic vapor (24 weight per cent water). Thus, if the steam supply to the reboiler coils decreases slightly, the steam content and the temperature of the vapor leaving the top of the column decreases, and the controller responds. However, if the vapor temperature were maintained at 189°F., the azeotropic boiling point, any decrease in the steam supply to the reboiler would decrease the rate of vaporization, but the vapor would still have the azeotropic composition, and thus its temperature would be unaffected, and the controller would not respond. If the quantity of hexone distilled is less than the feed rate, hexone accumulates in the column and eventually is lost in large quantities by overflowing from the reboiler to the Organic Waste Receiver, G-4.

The vapor is condensed in a Condenser-Cooler-Separator, and the two immiscible liquids are continuously decanted at 77°F. The aqueous phase returns to the sixth plate of the column as reflux. The hexone, distilled and caustic washed, overflows from the separator to the Organic Surge Tank, G-1. The Organic Surge Tank has a normal operating volume of 1000 gallons; however, its capacity of 5000 gallons can be used in case additional holdup time (four hours maximum) is needed. A submerged pump continuously pumps the recovered hexone to the Organic Receiver, Tank O-1, in Building 276-S.

The 5 per cent (1.3 M) caustic scrub solution in the column is made by dilution of 25 per cent (8.0 M) caustic in Tank G-3-B (working capacity, 170 gallons). The caustic flows by gravity at a rate of 0.31 gallon per minute through a controlling rotameter and automatically operated valve to the distillation column. Normally Tank G-3-B is used as the feed tank; however, during make-up and adjustment in Tank G-3-B, an auxiliary feed tank, G-3-A, is used. The caustic flows downward through seven bubble-cap plates to a closed-steam reboiler (capacity, 1140 gallons), overflows to the Organic Waste Receiver, Tank G-4 (holdup time, eight hours), and is jettted periodically to the Waste Header Receiver, Tank D-13.

Recycled hexone is routed from the Organic Receiver, Tank O-1 (working volume, 11,000 gallons), to the Organic Sampler and Treatment Tank, O-2. This step is the transition from the continuous recovery process to a batchwise treatment process. Normally, a routine sample is taken of the hexone while it is in Tank O-2. Then the hexone is pumped to the Organic Header Feed Tank, O-3 (working volume, 11,000 gallons) from which it is continuously pumped to the Organic Head Tank, 804 (holdup time, 25 minutes).

1.3 Addition of nitric acid to hexone

Nitric acid may be added to each "cold" organic feed stream (i.e., IAX, ISX, 2AX, 3AX, 2DX, and 3DX) individually before it enters the column. A reciprocating, piston pump (automatically controlled) injects the acid into hexone as the solvent flows through an enlarged "blending" section of the feed line. The details of this pumping system are described in Chapter XVII. Resistance thermometers, located on both sides of the point of acid addition, are wired to a Brown instrument which records any temperature increase as the acid is added. During operation, an increase (2 to 3°C.) in this temperature difference indicates chemical reaction of the nitric acid and hexone. (The normal temperature rise due to the heat of mixing upon addition of 60% nitric acid to hexone until a concentration of 0.5 M HNO_3 is reached is 1 to 2°C.)

There are two reasons for prohibiting hexone and nitric acids from being in contact with each other longer than necessary: (a) slow oxidation occurs which results in products having deleterious effects on column performance, and (b) the remote hazard of a violent hexone-nitric acid reaction exists. This hazard is discussed in Chapter XXIV.

2. Remedy of Off-Standard Conditions

Two methods are provided for detection of off-standard solvent treatment conditions. A radiation recorder (described in Chapter XIX) is installed on the inlet line to the Organic Receiver, Tank O-1. Normally, the process radiation level cannot be detected above background (natural radiation level). However, if any radiation is detected, investigation of the entire process (particularly the IQ Column and the Organic Distillation Column) should be made to detect improper operation. The radiation-recorder instrument is located on the inlet line to Tank O-1 rather than on the tank proper. This location allows an early and accurate detection of off-standard conditions involving radiomaterials before a large volume of undesirable material is accumulated or the off-grade material is masked by accumulated liquid in the tank. If the hexone contains a significant amount of radioactive materials, i.e., greater than 200 co./min./ml., it is washed in the Organic Sampler and Treatment Tank, O-2, with water or dilute (0.1N) nitric acid solution until the radiomaterials are removed. The washes, after neutralization in the case of the nitric acid wash, are cribbed with an adequate amount of dilution water so that they do not exceed cribbing tolerances (see Section B2, Chapter X).

The second method for detection of off-standard conditions involves the routine sampling and analysis of the recovered hexone as it passes

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through the Organic Sampler and Treatment Tank, O-2. Normally, MIBC content is determined for each batch, and analyses for hexone oxidation products are made at less frequent intervals. When these analyses indicate an excessive amount (specifications tabulated in Section A) of impurities, the solvent is retreated. Although it is not anticipated, the hexone may become unsatisfactory for use even after repeated retreatment, a condition which would necessitate disposal of the used hexone and replacement with raw hexone. No facilities are provided in the Redox Plant for the disposal of large quantities of hexone. However, it could be stored in a tank car until facilities for disposal (e.g., burning) could be provided.

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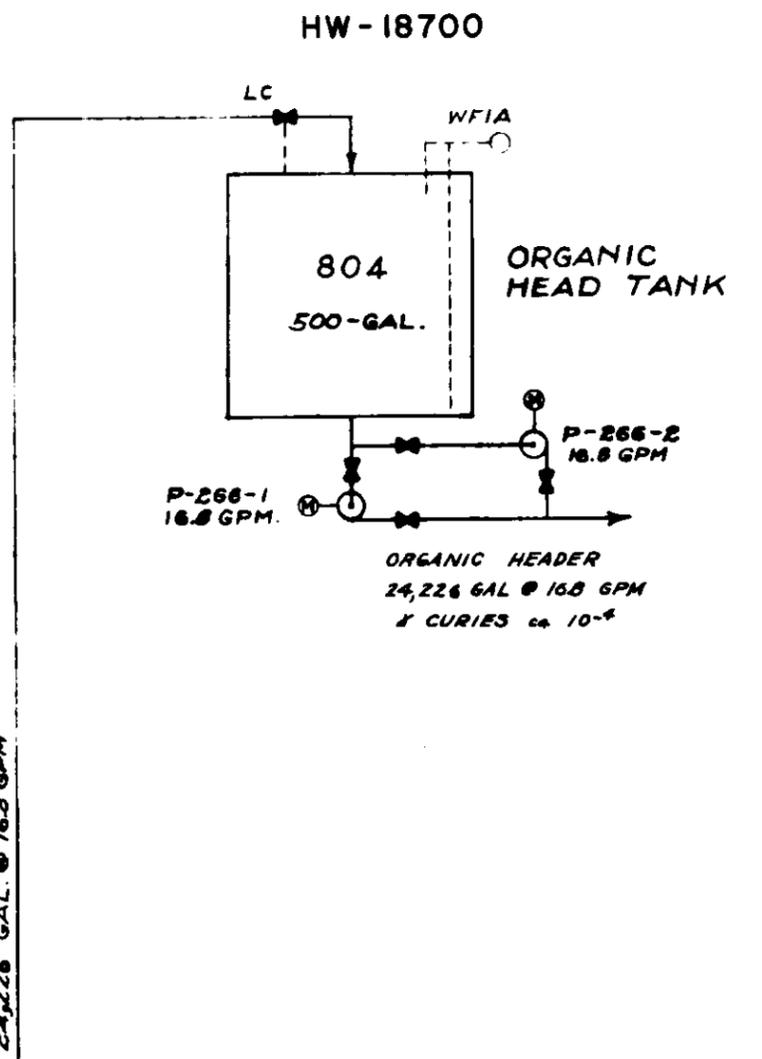
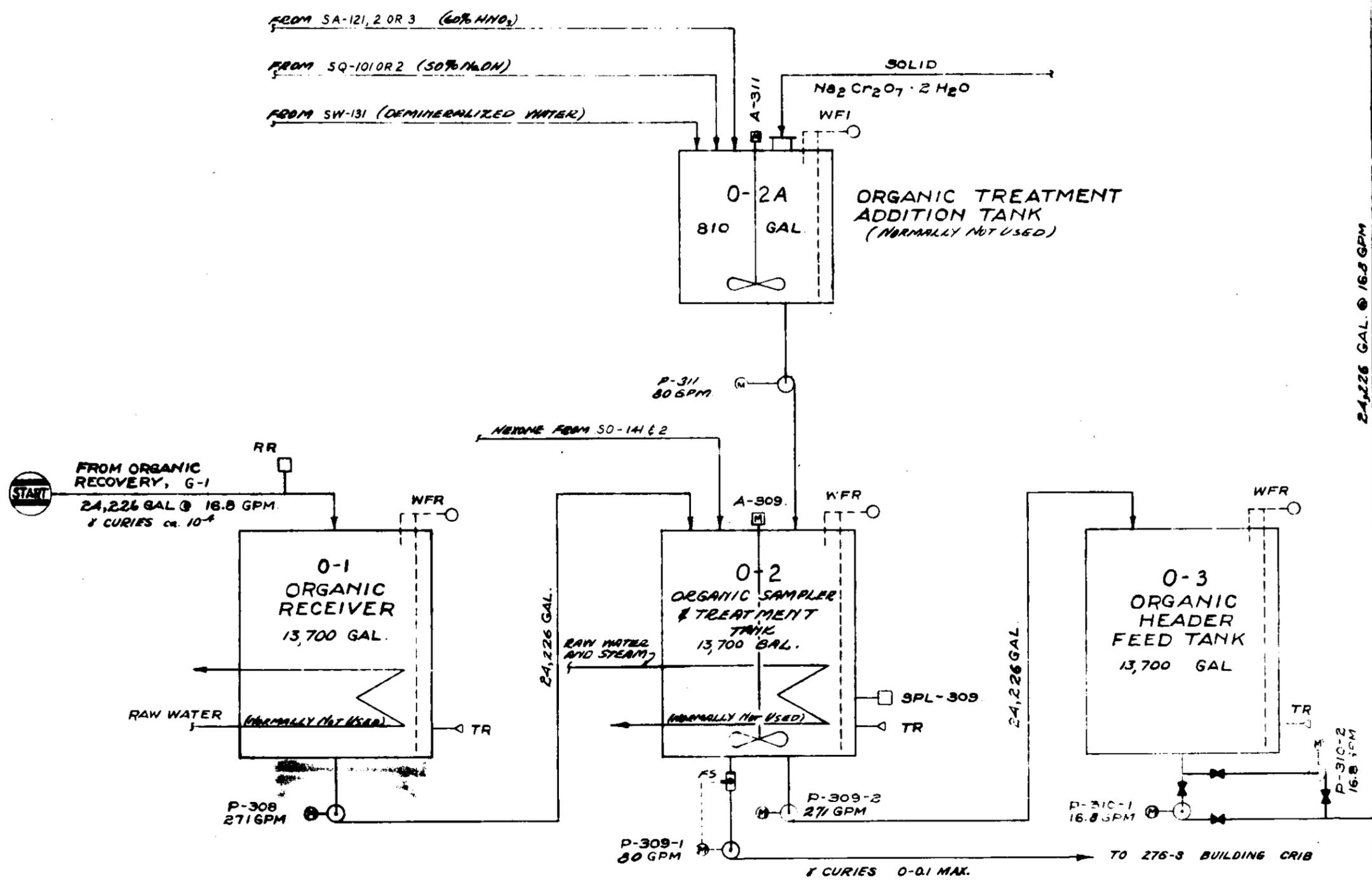


Figure IX-1
ORGANIC TREATMENT FLOW SKETCH
 (From Drawing No. SK-2-5317)
 Basis: 6250 lb. U/24 hr.

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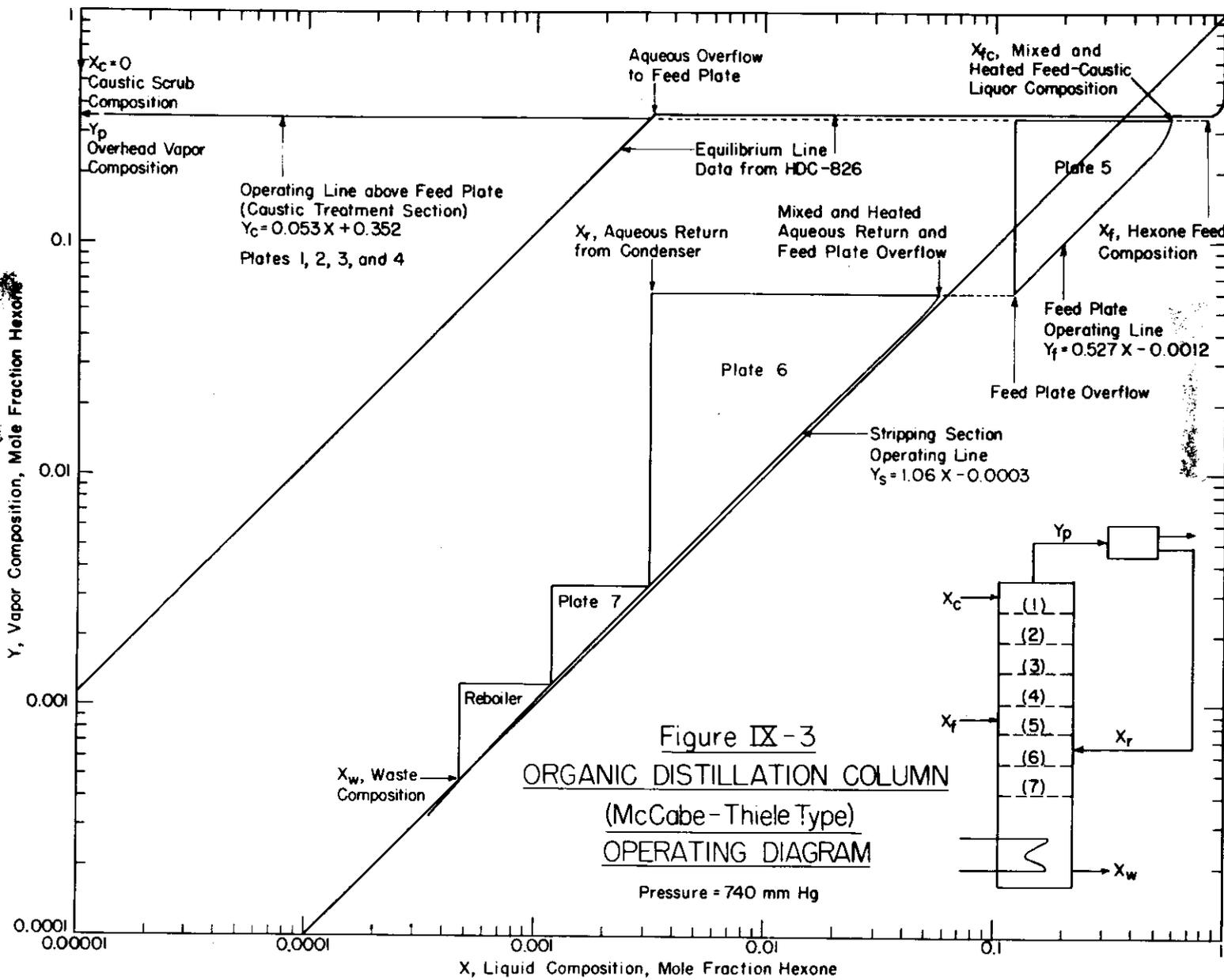
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Figure IX-3

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PART II: PROCESS, continued

CHAPTER X. WASTE TREATMENT AND DISPOSAL

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CHAPTER X. WASTE TREATMENT AND DISPOSALA. INTRODUCTION

The radioactive wastes from the Redox Plant are treated and disposed of so that they do not cause a hazardous pollution of the environs of the Hanford Works. Liquid wastes which contain appreciable quantities of radiomaterials are concentrated and stored in large underground tanks. On the other hand, liquid wastes which contain only trace quantities of radiomaterials are discarded into cribs from which the water percolates into the ground with the accompanying absorption of residual radiomaterials by the soil. Process cooling water, which should not be contaminated, is collected in a retention basin and monitored before being discharged to a pond from which it seeps into the ground or is evaporated. Gaseous wastes are treated to remove radioactive iodine and particulate matter. ~~The radioactive noble gases (xenon, krypton) are discharged to the atmosphere where they are diluted to a safe concentration.~~ Although these basic methods of waste disposal are not known to be causing a hazardous condition, the storage of large volumes of high-activity wastes is extremely expensive, and the disposal of any radioactive materials to the ground or atmosphere is not desirable as a long range practice. Therefore, a constant effort is being made to devise new methods which will decrease the costs of waste storage and the hazards of pollution of the atmosphere and potable water sources.⁽⁷⁾ In addition, routine monitoring is used to ascertain the extent of pollution and to follow the courses of the radiomaterials which are discharged to the environs, because it is necessary to know with accuracy that the wastes released are not adversely affecting the welfare of the region.

The following table based upon a probable maximum instantaneous capacity of 3-1/8 tons of uranium per day presents the sources of Redox Plant liquid wastes, their volumes, radioactivities (expressed in "countable" curies as defined in Chapter II), and intended disposal methods:

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LIQUID WASTES — PLANT

Instantaneous Capacity: 3-1/8 T.U./Day of 300 G.Pu/T. Material

Source of Waste	Volume, Gal./Day*			Activity Level (3-Cycle Basis) Curies/Gal.	Estimated Pu Content (3-Cycle Basis) μ g./Ml.	Disposal Method
	3U, 3Pu Cycles	2U, 2Pu Cycles	1U, 2Pu Cycles			
Zr and Nb Scavenging	90	90	90	150 β 630 γ 780 Total	3.0	Underground Storage
Ru Scrub.	80	80	80	90 β 68 γ 158 Total	trace	Underground Storage
Main Process (Extraction Columns, Organic Wash Column, Org. Dist. Column bottoms, Condensate Evap. bottoms.)	9000	5700	3500	18 β 9 γ 27 Total	0.3	Underground Storage
Coating Removal Slurry	590	590	590	5×10^{-2}	0.9	Underground Storage
Dissolver Flush	650	650	650	1×10^{-1}	1.2	Underground Storage
Condensate	16,000	10,400	5800	1×10^{-6}	trace	216-S Crib
Solvent Treat. Wastes	3600 gallon/10,000 gallons hexone treated			0 to 10^{-4}	trace	276-S Crib
Cooling Water	3×10^6	2.2×10^6	1.8×10^6	0 to 10^{-7}	0	Retention Basin

*) The Redox Plant is provided with 3 extraction-stripping cycles for uranium and 3 for plutonium. It is a distinct possibility that decontamination specifications may be met in fewer than 3 cycles thus resulting in reduced waste volumes due to the elimination of cycles.

Daily, on a three cycle basis, a total of 10,500 gallons of liquid wastes representing a total of 250,000 "countable" curies (explained in Chapter II) is sent to underground storage. At expected plant yields, approximately 17 grams of plutonium accompany this waste. For two cycle operation, about 7200 gallons per day of liquid wastes and 14 grams of plutonium are disposed of to underground tanks. This would be decreased to 5000 gallons and 12 grams of plutonium for operation of one uranium and two plutonium cycles.

Daily, on a three-cycle basis, approximately 16,000 gallons of liquid wastes are sent to the 216-S Crib, meeting established Hanford Works limits (see Subsection B2). Over a period of one year, an estimated 20 curies of activity and 10 milligrams of plutonium are expected to be sent to cribs.

In the following table, the sources of the Redox Plant gaseous wastes are itemized with their approximate volumes and activities (expressed as "countable" curies).

GASEOUS WASTES -- PLANT

Instantaneous Capacity: 3-1/8 T.U./Day of 360 G.Pu/T. Material

<u>Source of Waste</u>	<u>Approx. Peak Volume Rate, Cu.Ft./Min. (S.T.P.)</u>	<u>Estimated Total Activity/Day</u>		
		<u>β Curies</u>	<u>γ Curies</u>	<u>Total Curies</u>
Silver Reactor	150	200	1	201 *
Ru Scrubber	200	-	-	trace
Process Vent Header	250	-	-	1
Condenser Vent Header	200	-	-	1 x 10 ⁻⁵
Ventilation Air	35,000	-	-	<1 x 10 ⁻⁶

*) Practically all of this activity is attributable to the inert gas, krypton-85.

Prior to disposal to the atmosphere from a 200-foot stack, each of the gas streams is filtered, the process gaseous wastes through individual Fiberglas filters and the ventilation air through a sand filter to remove any radioactive particulate matter. Almost all of the activity in the stack gases is due to the beta-emitting krypton-85, an inert gas which is evolved during the pile-metal dissolution.

The disposal of radioactive wastes from the Laboratory Building (222-S) is governed by the same principles as the disposal of wastes from the Redox Plant. The disposal of liquid and gaseous radioactive wastes from the Laboratory Building is discussed in Sections E and F, below.

DECLASSIFIED**B. PLANT LIQUID WASTES****1. High-Activity Wastes****1.1 Definition of problem**

Pertinent data for all of the high-activity wastes from the Redox Plant to be stored in underground tanks are listed in Table X-1. The quantities of chemicals indicated are based on an instantaneous capacity of 3-1/8 tons U per day (400 megawatt-days integrated exposure for 360 days, followed by 90 days "cooling"). The wastes are divided into four sections (head-end wastes, extraction-column wastes, hexone-recovery wastes, and condensate-evaporator purges) which, in turn, are subdivided into the specific waste streams in the Redox Plant. Wastes listed as item A of Table X-1 are transferred directly from their sources through a holdup vessel to the underground storage tanks. Item E shows the composite of the wastes listed as items B, C, and D, which are all collected in the Waste Header Receiver, Tank D-13 (Figure X-3), prior to treatment. The waste solution represented by the data in item E is concentrated and transferred to the Waste Concentrate Sampler, Tank D-9, where it has the properties listed as item F. This solution is neutralized with 50 weight per cent caustic in the Neutralizer, Tank D-8, and then is represented by item G. The total wastes stored in underground tanks, item H, are a combination of wastes listed under items A and G. Data are presented in Table X-1 for operation of the Solvent Extraction Battery (Chemical Flow-sheet H W. No. 4) under three conditions: (a) 3 uranium and 3 plutonium decontamination cycles; (b) 2 uranium and 2 plutonium decontamination cycles; and (c) 1 uranium and 2 plutonium decontamination cycles.

The coating-removal solution and the Dissolver acid flush, listed under item A, are solutions having the same composition as those which have been used in the BiPO₄ precipitation plants. The other two wastes are produced during head-end treatments of the Dissolver solution for partial removal of ruthenium, zirconium, and niobium, as discussed in Chapter III. The Ruthenium Scrubber solution, 25 weight per cent caustic, is assumed to contain 7240 beta "countable" curies and 5400 gamma countable curies of ruthenium based upon an assumption of 90% removal (by distillation) of the ruthenium activity present in Dissolver solution (from uranium having 400 megawatt-days integrated exposure for 360 days, followed by 90 days "cooling"). The assumption that the entire 90% of ruthenium distilled passes into the Ruthenium Scrubber caustic gives a ruthenium concentration there which is probably a maximum. Tests have shown (see Chapter III) that some of the volatilized ruthenium may plate out on lines and equipment before reaching the Scrubber. Scrubber removal of the remaining ruthenium activity is, however, almost quantitative. The scavenger solution, formed by dissolution of the MnO₂ scavenger with HNO₃ and Fe(NH₂SO₃)₂ (or any other dissolution chemical), is assumed to contain 13,500 beta countable curies and 56,800 gamma countable curies of zirconium and niobium activity, representing 90 per cent of the total zirconium and niobium activity present in the Dissolver solution. These figures are based on an assumed D.F. of 10 for ruthenium, zirconium, and niobium in the head-end treatment which is a conservative estimate based

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on the limited amount of data available at the time of writing. Since other process considerations may make it desirable to eliminate these head-end treatments, the activities reported under the extraction column wastes, listed as item B of Figure X-3, include the total ruthenium, zirconium, and niobium activities present in the Dissolver solution as though there were no head-end decontamination. The following table shows the approximate activity levels of the IAW solution under the three conditions of head-end decontamination:

<u>Head-End Treatment</u>	<u>"Countable" Curies/Gallon in IAW</u>		
	<u>Beta</u>	<u>Gamma</u>	<u>Total</u>
No head-end decontamination	57	30	87
Ruthenium volatilization only	54	28	82
Ruthenium volatilization and zirconium, niobium scavenging	49	8	57

Since the IAW contains almost all of the radioactive fission products fed to the solvent-extraction columns, the activities of the other waste streams (2DW, 3DW, 2AW, and 3AW) are negligible in comparison to IAW whether or not head-end decontamination methods are used.

1.2 Technical and process background

All of the waste solutions which have been itemized in Table X-1 contain appreciable quantities of radiomaterials and, therefore, must be confined because they cannot be disposed of to the environs (see Subsection B2). For economic reasons, the total volume of wastes to be stored must be a minimum. Concentration of the waste solutions is the primary method employed. Reduction in the total volume of wastes to be stored would also result from: (a) operation of the Redox process on only 2U, 2Pu or 1U, 2Pu decontamination cycles, and (b) recovery of aluminum nitrate from the waste solutions for reuse in the process. The use of the first method is dependent upon the success of head-end decontamination methods. The possibility of aluminum nitrate recovery is discussed later in this chapter.

1.21 Hexone removal from wastes

Prior to concentration of the wastes, the hexone dissolved in the slightly acid, aqueous solution should be removed for several reasons:

- (a) It is desirable to eliminate the possibility of hexone decomposition during concentration. As mentioned in Chapter IX, hexone is oxidized by nitric and nitrous acids and forms decomposition products, primarily organic acids, which precipitate the ions of Pu or U present in the waste solution. (However, during concentration of acid-deficient hexone-saturated solutions, laboratory studies under the rigorous conditions of total reflux have shown that a period of from 8 to 10 hours is required before any detectable hexone decomposition is brought about.⁽¹⁾) If partial decomposition of

hexone with the formation of precipitates does occur in the Waste Concentrator, D-12 (Figure X-3), two difficulties might be incurred: first, the precipitate would scale the heating coils, thus decreasing their heat-transfer rate, a condition which could conceivably prevent the concentrator from having a high enough evaporation rate to maintain the continuous concentration; and, second, the precipitate might cause excessive foaming in the concentrator which would decrease the effectiveness of deentrainment.

- (b) Streams to be reworked might behave adversely during solvent-extraction under conditions (storage for extended periods before accomplishing the rework, for example) which might favor the decomposition of dissolved hexone. This possibility is discussed further in Chapter IX.
- (c) The recovered hexone has an important economic value. Approximately 500 gallons of hexone are recovered daily from the aqueous streams prior to concentration, 225 gallons from the Waste Concentrator, D-12, above.
- (d) A potential safety hazard (although considered extremely remote and of small magnitude) might exist if hexone remained in solutions sent to underground storage.

The hexone is stripped from the aqueous waste streams in the column on top of the Waste Concentrator, D-12, which is described in Chapter XV. Briefly, steam rising from the concentrator pot through six bubble-cap plates, 49-1/2 inches in diameter, spaced at 14-inch intervals, strips the hexone from the aqueous phase. This stripping job is similar to that done in the lower section (plates 6, 7, and Reboiler) of the Organic Distillation Column, G-3 (Chapter IX). Essentially all of the hexone is removed from the aqueous wastes when they enter the concentrator pot.

1.22 Concentration

As mentioned previously, concentration of the wastes is performed to minimize the volume which must be stored underground. The concentration is done continuously in the Waste Concentrator, D-12 (Figure X-3). As shown in Figure X-3, the nominal volume reduction is three-fold. The concentrated solution collected in the Waste Concentrate Receiver, Tank D-10, after overflowing from the concentrator is jetted at a temperature above 100°F. to the Waste Concentrate Sampler, Tank D-9, where it is cooled to room temperature (77°F.) for sampling. The solution in Tank D-9 consists of about 65 weight per cent ANN (after approximately 3 weight per cent jet dilution) and has a freezing point of about 41°F.; i.e., crystallization begins at 41°F. as the solution is cooled. (Freezing points of solutions of various concentrations are reported in Chapter IV.) The following table lists the freezing points of several typical waste solutions as a function of their ANN concentration:

<u>Weight Per Cent $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in Waste Solutions</u>	<u>Approximate Freezing Point, °F.</u>
64	30
66	50
68	70

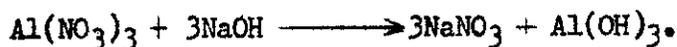
The freezing point of the salt solution in Tank D-9 is the limiting factor as to degree of concentration permissible. An increase of only about 2.3 weight per cent ANN, from 65.0 to 67.3 weight per cent, raises the freezing point to 65°F. Concentrating to this slightly higher figure would reduce the daily volume of extraction column wastes (on a 3-cycle basis -- item F1 in Table X-1) from 4795 to 4540 gallons, a tankage saving of approximately 250 gallons per day or 2.5 volume per cent of all wastes. The feasibility of concentrating to this degree must be determined during normal operation, however, because at these high concentrations over-concentration is easily achieved (i.e., the rate of ANN concentration increases more rapidly than the rate of water boil-off). In order to prevent over-concentration, and its accompanying crystallization, the designed basis for ANN concentration in Tank D-9 is 65 weight per cent ANN. Under this condition the concentration of the solution overflowing from the Waste Concentrator, D-12, is 67.7 per cent; this solution boils at approximately 240°F. and has a hot specific gravity of approximately 1.37. The distillate from the concentration operation passes through 3-1/2 feet of one-inch stainless steel Raschig rings; a distillate fission-product decontamination factor of 10^4 to 10^5 is anticipated. The method for disposal of this condensate is discussed in Subsection B2.

1.23 Neutralization

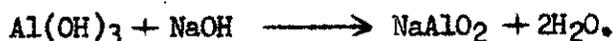
Prior to storage in the underground tanks, the waste solution (listed under item F, Table X-1) is neutralized and adjusted to a pH of 13. corrosion studies⁽¹⁸⁾ indicate that the pH must be greater than 9.5 to minimize the corrosion of the mild steel tank liners; a solution having a pH of 13 is slightly less corrosive than one having a pH of 9.5. However, the specification for a pH of 13 is not required on the basis of corrosion resistance. This specification is based on the desirability of having the large quantities of aluminum salts present in the neutralized wastes in a soluble form, i.e., as aluminates rather than oxides. A 50 weight per cent caustic solution is used for the neutralization. Based on a laboratory titration of a simulated waste (65 per cent ANN) with caustic to a pH of 13, 0.685 volumes of caustic are required per volume of waste; the volume of the neutralized waste is approximately 105 per cent of the combined volumes of the waste solution and caustic.⁽¹⁹⁾ The heat of neutralization of simulated wastes is approximately 1750 B.t.u. per gallon (65 per cent ANN)⁽²⁾. This heat evolution is adequate to cause a 120°F. temperature rise during neutralization if no cooling is achieved. For reasons discussed below, the temperature during neutralization should not exceed 120°F.

Although the neutralization procedure described in Subsection D1 requires that the waste solution be added to the caustic ("reverse strike"), consider for purposes of this discussion that caustic (50 weight per cent)

is added to the waste solution. At a pH of about 2, the aluminum begins to precipitate according to the equation(9):



As the caustic addition is continued, the pH rises slowly to 4 at which point it begins to rise more rapidly. At a pH of 4 or 5, the gelatinous precipitate, $\text{Al}(\text{OH})_3$ (or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), becomes so extremely heavy that agitation is very difficult. However, as more caustic is added, the mass becomes less viscous, and at a pH of 6 to 7, the precipitation is complete. Aluminum hydroxide, being amphoteric, acts as an acid in the presence of additional strong caustic and may be represented as behaving according to the following equation:

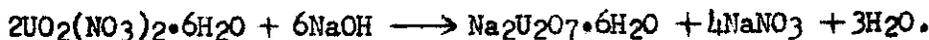


The freshly precipitated hydroxide is readily soluble in excess caustic, but this reactivity drops rapidly as the temperature of formation is raised. Dissolution is slower or incomplete if (a) the caustic is added too slowly with insufficient agitation, (b) the precipitate is allowed to age for any extended period (several hours) before being dissolved, or (c) if the temperature is allowed to go too high (greater than 120°F.) during neutralization. These contingencies all result in "ageing" the precipitate, thus causing a corresponding decrease in solubility. However, if these conditions are prevented, the soluble NaAlO_2 is formed as the pH is increased toward 13, at which point the dissolution is essentially complete. About 25 to 30 per cent excess caustic is required, above that stoichiometrically needed to form NaAlO_2 , in order to reach a pH of 13. (19) It is presumed that the excess NaOH reacts with the NaAlO_2 in the following manner:



The difficulties which may be encountered during dissolving of the $\text{Al}(\text{OH})_3$ precipitate can be largely avoided by reversing the procedure and adding the waste to the caustic. In such case, an excess of caustic is always present (pH greater than 13), and the precipitate of aluminum is peptized almost as rapidly as it is formed if adequate agitation is provided so that the temperature remains below 120°F. This prevents the formation of the large, gelatinous mass of $\text{Al}(\text{OH})_3$ which must be ultimately redissolved. Therefore, a "reverse strike" is used as the Redox Plant procedure for waste neutralization.

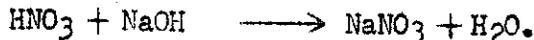
The minor components in the waste which are neutralized are UNH , HNO_3 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}(\text{NH}_4\text{SO}_4)_3$. The UNH forms highly insoluble uranates in the basic solution. One reaction may be represented by the following equation for the formation of sodium diuranate:



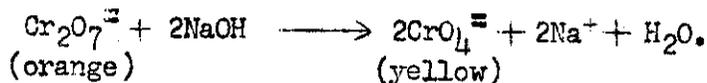
This equation cannot be considered as the complete explanation of what

takes place, but it may be interpreted as an indication of one of several possibilities. Polyuranates containing as many as six molecules of UO_3 in combination with the sodium are known and are more or less distinguishable by colors from light yellow (diuranate) to deep red-orange (polyuranates).

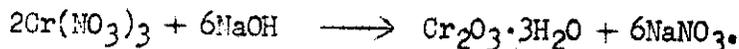
Nitric acid is neutralized according to the simple reaction:



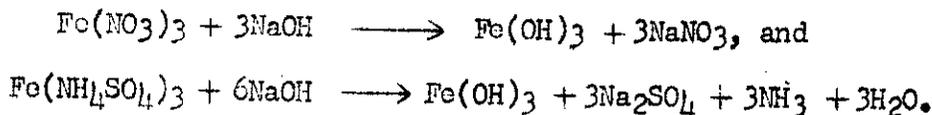
The neutralization of $Na_2Cr_2O_7$ is represented by the following equation:



The chromate ion (CrO_4^{2-}) is stable in basic solution. However, the dichromate ion ($Cr_2O_7^{2-}$) which has been reduced prior to neutralization to the chromic ion (Cr^{+3}) reacts as follows:



This oxide is a highly hydrous gel when the caustic is added slowly to the solution. However, when freshly precipitated, the oxide is readily peptizable in excess caustic and forms a green colloidal sol. The $Fe(NO_3)_3$ and $Fe(NH_4SO_4)_3$, oxidation products of $Fe(NH_2SO_3)_2$, react with the caustic as follows:



$Fe(OH)_3$ is another gelatinous precipitate.

Under normal conditions of neutralization, the neutralized waste solution will consist of about 0.2 to 0.4 per cent by weight solids.

1.24 Conditions in underground storage tanks

After concentration and neutralization, the high-activity waste, listed under item G in Table X-1, is combined with the head-end wastes, listed under item A, in the underground storage tanks where the wastes have the properties listed under item H. Small quantities (approximately 200 gallons per day) of radioactive wastes from the Laboratory Building (222-S) are also added to these wastes, but they are not included in item H because they are insignificant in comparison with the Redox Plant quantities. The 222-S Building waste disposal system is described in Section E of this chapter.

The radiation intensity due to the decay of the radioactive wastes in the tank is very high. Calculations show that the intensity at the center of a waste tank and one foot above the surface is approximately

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3600 r./hr., based on an assumed 90-day "cooling" period of the upper two-foot layer of solution(12). The intensity at a ten-foot distance above the surface of the tank is estimated at 2700 r./hour. These figures are on the high side because they are based on the conservative assumption of no mixing in the tank which would expose material at the surface of the liquid that had "cooled" for a period longer than 90 days. The "cooling" curves in Chapter II may be used to calculate the radioactivity of the wastes at different "cooling" periods.

The radioactive decay of fission products causes considerable heat evolution. It is estimated that at the time the liquid level in the first tank in a 3-tank cascade first reaches the overflow point, 22.7 feet, (and at design production rates with 3U and 3Pu extraction cycles) the heat developed in the tank is approximately 7000 B.t.u./minute.(12) Since the heat losses from the tank to the ground are relatively small, the heat liberated during the radioactive "cooling" period raises the temperature of the solution in the tank and the tank itself. Shortly after the tank is full (i.e., approximately two or three weeks afterwards), the contents are expected to boil. The boiling point is in the neighborhood of 225±5°F., depending upon the degree of mixing and amount of precipitation in the tank. The solution is not expected to boil until the tank is full because the intermittent additions of current waste solutions have a significant thermal cooling effect on the tank contents when the liquid level is low. The boiling will continue for an extended period of several months until the heat developed by the radioactive decay is insufficient to maintain the thermal equilibrium. Similar conditions of radiation intensity and heat evolution are present in the second and third tanks in a given 3-tank cascade, but the radiation intensities are expected to be lower in the second tank than in the first and lower in the third tank than in the second. This decrease in intensity is caused by two factors: (a) the first tank contains the majority of solids (e.g., Cr(OH)₃ and Fe(OH)₃) and, thus, a larger portion of fission products (occluded by the precipitate) than the other tanks; and (b) the solutions entering the lower tanks (second and third in cascade) have "cooled" for a longer period than those entering the first tank. For example, solutions entering the first tank have "cooled" approximately 90 days. By the time any solution overflows into the second tank, it has "cooled" for a period between 90 and 165 days because approximately 75 days' accumulation of waste were required to fill the first 750,000-gallon tank. Because the solutions in the underground storage tanks are expected to boil (or at least they will be very hot), air-cooled condensers are provided on the tanks. A brief description of the underground tanks and auxiliaries is presented later in this chapter (under B1.3).

1.25 Aluminum nitrate recovery

No facilities for aluminum nitrate nonhydrate (ANN) recovery are installed in the Redox Plant. However, provisions have been made for the possible future installation of ANN recovery facilities if ANN recovery is deemed feasible. These provisions are discussed briefly later in this chapter (Subsection D1). The recovery process which has been contemplated but not fully developed utilizes the solubility characteristics of ANN in concentrated nitric acid (70 per cent).(20) The salt is

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only slightly soluble in cold (32°F.) acid, but it is very soluble in nitric acid above 170°F. The basic procedure which would be followed for ANN recovery is illustrated below in consecutive order⁽¹³⁾:

- (a) The aqueous waste streams (i.e., IAW, 2DW, 2AW) containing ANN are first stripped to remove hexone.
- (b) The hexone-free salt solution is then concentrated until the boiling temperature is 250°F. (freezing point is 165°F.).
- (c) The concentrated ANN solution is combined with hot 70 per cent nitric acid and hold at approximately 175°F. until solution is complete.
- (d) From this solution, the ANN is crystallized at 32°F.
- (e) After separation of the crystals from the mother liquor, a cold (32°F.) 70 per cent nitric acid wash is used to remove residual impurities.
- (f) This cycle is repeated by redissolving ANN in hot (175°F.) 70 per cent nitric acid and again crystallizing and washing at 32°F.
- (g) Following this, the free nitric acid is removed from the crystals which are then redissolved in water for reuse in the Redox process solutions.
- (h) The mother liquors from the crystallization steps are combined with washes and distilled; thus, the nitric acid is recovered as the partially-decontaminated constant boiling (70 per cent) acid and recycled to the ANN recovery process.
- (i) The bottoms from the nitric acid distillation, containing the bulk of the fission products, are neutralized and sent to waste storage.

The feasibility of ANN recovery from the Redox process wastes is dependent on an economic evaluation⁽¹⁴⁾. The cost of construction and operation of the additional facilities necessary for the recovery process must be overcome by the savings in costs of chemicals, primarily ANN (at \$5.00 per 100 pounds) and NaOH (at \$3.30 per 100 pounds), and waste storage tank capacity (at \$0.36 per gallon). If the Redox process is operated on 2U and 2Pu extraction cycles, a conservative estimate for the pay-off period is five to ten years.

1.3 Description of underground storage facilities

A plot plan of the 200-West Area, showing the layout of the waste disposal facilities, appears in Chapter XI. The Underground Storage Tank Farm, Building 241-S (described and illustrated in Chapter XI) is slightly

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less than one mile northwest of the Redox Production Plant, Building 202-S. This tank farm is the first of four which are planned, provisions being made in the present piping for future installation of three more farms. The total storage capacity of Building 241-S is 9,000,000 gallons. If the Redox Plant is operated on 3U and 3Pu extraction cycles (production rate of 6250 lb. U/day) this capacity will be reached in 2.9 years. However, it will last 4.3 years with operation of only 2U and 2Pu cycles or 6.2 years with only 1U and 2Pu cycles.

Building 241-S consists of twelve 750,000-gallon tanks made of reinforced concrete with mild steel liners on the bottoms and sides. These tanks are arranged in four cascades of three tanks each. The overflow line (22.7 feet from tank bottom) of the first tank in each cascade (Tanks 101, 104, 107, and 110, respectively) is the inlet line to the second tank (Tanks 102, 105, 108 and 111). Similarly, the second tank overflows to the third tank (Tanks 103, 106, 109, and 112). In order to provide the necessary gradient for gravity cascade, the second tank is one foot lower than the first, and the third tank is one foot lower than the second. As mentioned previously (under 1.24) the concentration of radioelements and the heat evolution in the first tank in series is highest, lower in the second than the first, and lowest in the third tank. This distribution is the basis for the presence of two air-cooled condensers on the first tank and only one on the second and third tanks in a cascade. The air-cooled condensers, provided to minimize the escape of radioactive droplets, are made of fin tube, hot dip galvanized pipe extending 20 feet into the air and have no filter or raincap. Shielding from the radioactivity in the tanks is provided by a one-foot-thick concrete dome on top of each tank plus the six to sixteen feet of backfill. Tank cover is designed so that the intensity of radiation at grade level above the tanks is less than 1 mr./hr. In addition, the hatchways for the air-cooled condensers are formed in two right-angled bends to retard the escape of radiation through these openings.

The neutralized waste line from the Neutralizer, D-8 (Figure X-3) is connected to only one of the cascades at one time. The necessary connections are made in two Diversion Boxes, 240-S-151 and 241-S-151, which are concrete boxes buried in the ground just below grade (Chapter XI). Remote operation (Chapter XVIII) is required when the connections are changed. In addition to the lines used for waste disposal to Building 241-S, lines to the 216-S Building Cribs are also tied in at the Diversion Boxes. Also, connectors are available so that three additional tank farms, similar to Building 241-S, can be connected at a future date. The waste disposal lines are encased in concrete throughout their entire length. Two concrete Catch Tanks, 302 and 302A (17,000-gallon capacities), are located near the 240-S-151 and 241-S-151 Diversion Boxes, respectively. A third Catch Tank, 302B, is located near the end of the encasement which contains the lines directly connected to the Underground Storage Tanks. These Catch Tanks are provided to collect any drainage (which indicates line leakage) from the encasements. The liquid which is collected is jetted through lines connected at one or both of the Diversion Boxes to the Underground Storage Tank Cascade in use. Each catch tank is provided with an air-cooled condenser, approximately 6 feet high and having a raincap. This condenser contains a 20 by 20-inch Fiberglas filter, 2 inches thick, which is easily interchangeable.

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A "conductivity reel" (described in Chapter XIX) is provided on each of the Underground Storage Tanks, 101 through 112, and Catch Tanks, 302, 302A, and 302B, for measurement of the liquid level in these tanks. Liquid level measurements are made daily.

Eight test wells are placed at selected locations among the waste storage tanks in Building 241-S. They are all 6-inch wells with cast iron casings, seven of the wells being 150 feet deep and one being 300 feet deep (to the water table). These wells receive no wastes but are used by the Health Instrument Division for monitoring to detect possible leaks in the twelve 75-foot diameter waste storage tanks. In addition to their use for monitoring, these test wells and many others throughout the Hanford Works vicinity are used in a comprehensive geologic study of the area⁽⁴⁾⁽¹⁶⁾. In the deep wells, a Side-Hole Sampler is used to drill through the side-wall of the black iron casing, collect a sample of the soil, and plug the hole. This soil sample is counted for alpha and beta activity with standard radiation detection instruments described in Chapter XXI. In addition to these deep wells, shallow wells, 20 to 30 feet deep, are drilled in the vicinity of lines, tanks, etc. for use by both the Health Instrument and S Divisions. Monitoring for gamma radiation in these shallow wells is done with a glass GM tube enclosed in a rugged waterproof brass case 5 inches in diameter and approximately 14 inches long⁽⁸⁾. A one-tube "cathode follower" circuit is also included in this case in order to convert the GM tube pulses to a form capable of being transmitted through the necessarily long cable to the grade level. The GM tube assembly is supported by a light chain and two cables, one for the high-voltage supply to the GM tube and the other for the filament and plate voltages and the signal lead. A reel for handling the cables, a scaler, timer, and recorder are mounted on a cart so that the monitoring equipment is portable.

2. Low-Activity Wastes

2.1 Definition of problem

Thousands of gallons of liquid wastes containing only trace quantities of radiomaterials are discharged from the Redox Plant daily. The following table lists the sources and the volumes (based on a production rate of 6250 lb. uranium/day) under three operating conditions of the Redox process:

Source	Approximate Volume, Gal./Day			Estimated Activity Level, "Countable" Curies/Gal.	Estimated Pu Content, Grams	Disposal Site
	3U, 3Pu Cycles	2U, 2Pu Cycles	1U, 2Pu Cycles			
Redistilled condensate	16,000	10,400	5800	$< 5 \times 10^{-6}$	5×10^{-5}	216-S Cribs
Hexone washes	3600 gallons/10,000 gallons hexone treated			0×10^{-4}	trace	276-S Crib
Building 202-S drainage	Normally not used			-	-	216-S Cribs
Building 203-S drainage	Normally not used			-	-	276-S Crib
Building 216-S drainage	Normally not used			-	-	276-S Crib

It is neither practical nor necessary to store these large volumes of wastes containing only trace quantities of radiomaterials. Therefore, these low-activity wastes are routed to underground cribs (approximately 20 feet beneath the earth's surface) from which they seep into the subsoils.

Figure X-5 indicates the amount and the disposal of the various liquid process wastes from the Redox Plant. It is believed that the amount of radioactivity shown on the flowsheet as delivered to the cribs is a conservatively high estimate because of the use of feed having a rather high level of activity (about twice the level for process solutions from 400-megawatt-day/ton, 40-day-"cooled" slugs) coupled with what may be conservative decontamination factors for the evaporators. The amounts of radioactivity as shown in Table X-1 more nearly represent average values for 400 Mw-day/ton material "cooled" for ninety days.

The decontamination factors for the evaporators as listed in the following table have been estimated based on information contained in Documents BNL 90 (T-20)^(9a) and HW-17986⁽¹⁰⁾. Under plant conditions D.F.'s higher than those estimated here may be obtained because of at least two reasons:

- (a) At higher levels of activity, better D.F.'s are generally observed because of the difficulty encountered in laboratory experiments (from which the above estimates were made) which attempt to count correctly the very low-activity product streams (i.e., radioactivities approaching the background level).
- (b) The use of "chevron baffles" in the Condensate Evaporator may raise the D.F. by "knocking back" a fraction of the entrained liquid in the vapor stream.

Estimated D.F. On Evaporation

3-1/8 Tons Uranium/Day
400 Mw.-Days/Ton, 90 Days "Cooling"

	<u>2U and 2Pu Cycles</u>	<u>3U and 3Pu Cycles</u>
Waste Concentrator, D-12		
D.F., feed to tower	450	275
D.F., tower	95	50
Condensate Evaporator, D-4		
D.F., feed to tower	70	25
D.F., tower	25	15
Overall D.F.	7.5×10^7	5×10^6
Final radioactivity, (absolute) beta curies/gal.	3×10^{-7}	5×10^{-6}
Cribbing limit, (absolute) beta curies/gal.	1.5×10^{-5}	

Although sufficient information is not available for an accurate estimate of obtainable D.F.'s at higher rates of production, it is expected that the overall D.F. may be lower by a factor of 10 to 100 at a uranium processing rate of 5.5 tons U/day.

2.2 Technical background

2.21 Basis for selection of disposal method

The crib method of disposal of low activity wastes is a necessary expedient for operation of the Redox Plant. This method of disposal is contingent on three factors: (a) absorption of a large fraction of the radiomaterials by the subsoils; (b) decay of the short-lived radiomaterials during the period (assumed as 10 to 20 years⁽¹⁵⁾) before they reach the river; and (c) dilution of waste by ground water. Quantitative assumptions for these factors have allowed the following specifications (cribbing tolerances) to be set on the wastes discarded to cribs:

Plutonium -- less than 0.5 micrograms/liter
Beta emitters -- less than 4 microcuries/liter
pH -- greater than 5.

It should be emphasized that these limits are the maximum concentrations allowable. More conservative limits, which should be the ultimate aim, are the maximum permissible concentrations in drinking water:

Plutonium -- 0.024 micrograms/liter
Beta emitters -- 0.1 microcuries/liter.

The cribbing and drinking water tolerances listed above are in a state of review at the present time. Consequently, the values quoted are subject to revision. Efforts should be made to reduce the quantities of radiomaterials discharged into cribs since the advisability of this method of disposal is still questionable. (7)(11)

2.22 Deentrainment

Deentrainment involves the separation of droplets which tend to be carried over with the vapor from a concentrator, due to the fact that the vapor velocity is greater than the rate of settling of the droplets. In the Redox Plant, six concentrators (i.e., ICU, 2EU, and 3EU Concentrators and Plutonium Pre-Concentrator, Plutonium Concentrator, and the Waste Concentrator; also the Cross-Over Oxidizer when operated) discharge condensed vapors to the Condensate Stripper, D-5 (Figure X-3). All of these condensates are partially decontaminated (see Chapter XV) by deentrainment columns which remove the entrained droplets. The two types of deentrainment columns used in the Redox Plant are columns packed with Raschig rings and bubble-cap plate columns. More detailed description of the equipment and its function is presented in Chapter XV. The overall decontamination factors (based on dissolver solution) required for cribbing of condensates are as follows:

Plutonium 4×10^4
Beta emitters 2×10^6

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The anticipated D.F. across the deentrainment column on the Waste Concentrator, D-12, is 10^4 to 10^5 based on the fission-product activity in the feed to the Concentrator. Further decontamination is achieved by redistillation of the condensate in the Condensate Evaporator, D-4, where an additional D.F. of about 400 (based on fission-product activity in the feed to the Evaporator) is expected.

2.23 Course of cribbed wastes

Since the start-up of operations, extensive work has been done to determine the geologic and hydrologic features of the Hanford Works area and to correlate these features with the underground disposal of liquid wastes. (4)(16) As determined from test-well drilling and geologic reconnaissance, the chief geologic formations underlying the area are of three types:

- (a) Yakima basalt, a dense rock of volcanic origin, is the deepest formation investigated, at or near the water table, approximately 250 feet below grade. The Yakima basalt has folded and faulted since its deposition, and, as a whole, is slightly or even moderately permeable.
- (b) Ringold formation is a sediment which is inferred to form the main part of the core of the high terrace on which both the 200-East and 200-West Areas are built. This formation has a relatively low permeability, due largely to the high proportion of fines. The formation is about 2.4 per cent carbonate.
- (c) Undifferentiated terrace deposits range from boulders and coarse gravel to clay, which have resulted from erosion.

It is inferred that, under natural conditions, the water table of the area slopes gently down from the flanks of the Yakima Range and the Rattlesnake Hills to the Columbia and Yakima Rivers. Water is alternately stored and drained by seasonal changes in the stages of the river in a strip adjacent to the Columbia River and averaging perhaps 3 miles wide. Beneath the 200 Areas this ground water occurs chiefly in the Ringold formation, but in some places it also occurs in the Yakima basalt and in the terrace deposits. Waste water discharged into ponds (Subsection B3) in the 200 Areas has built upon the water table two distinct mounds and a low bridging spur between the two areas. These mounds are expected to grow as long as disposal ponds are used, but growth can be largely controlled as desired by changing the locations of the ponds. In effect, for a considerable period, the mounds will act as ground-water dams behind which contamination can be confined. Eventually, when the areas behind the "dams" fill up, they will no longer confine any contaminated water. Deep artesian water is not a factor in waste disposal practices at Hanford, because it is effectively separated from the non-artesian water body above.

Liquid wastes discharged from the Redox cribs, approximately 20 feet below grade, enter a Ringold formation which has a higher proportion of silts and fine sands than that under the older cribs. These

silts are ideal for the removal of the activity from the waste solutions, but they are considerably less permeable than coarser materials and are capable of receiving smaller daily volumes of liquid than the coarser sediments. The cribs accordingly were built on beds of crushed stone (retained on 1/2-in. screen) to assure adequate throughput, 100 gallons per minute. Only meager data are available on the absorption and retention of plutonium and fission products by the soil. However, indications are that more than 90 per cent of the plutonium and fission products are absorbed and retained by the soil, either by ion exchange or adsorption. It is the opinion of Health Instrument Division personnel (although conclusive experimental evidence is lacking) that retention of the plutonium is favored when the pH of the cribbed solution is between 5 and 7, and retention of fission products is favored at a pH of 8. The pH of cribbed wastes should be greater than 5 so that the alkaline soil is not leached, a condition which could cause channeling with a resultant decrease in absorption of radiomaterials. Those radiomaterials which are not removed from the wastes are diluted by the natural and artificial ground water. Apparently, a relatively impermeable layer of sediment minimizes the flow of waste water into the water table, because no contamination has been discovered in the ground water due to this cribbing practice. However, the water table has been contaminated in the past by wastes discharged into "reverse-flow" wells; this method of disposal has been discontinued. It has been estimated⁽¹⁵⁾ that cribbed wastes do not reach the Columbia River in less than 20 years with the present hydraulic gradient. An available decay time of 10 years has been conservatively assumed for calculation of cribbing tolerances of short-lived radioisotopes.

2.3 Description of disposal facilities

As indicated previously, two separate crib disposal areas, Building 216-S and Building 276-S Crib, are provided for the Redox Plant. (See plot plan in Chapter XI.) Condensates (and any cell drainage which meets cribbing limits) are jetted from the Condensate Receiver, D-2, or Cell Drainage Collection Tank, D-1 (Figure X-3), through two Diversion Boxes, 240-S-151 and 241-S-151 (described under 1.3 above) to the Building 216-S Cribs. These consist of two cribs in series. If the first has insufficient capacity, the second in series takes the overflow. A "conductivity reel" described in Chapter XIX is provided on each crib for measurement of the liquid level.

The Building 276-S Crib, located 400 feet west of Building 276-S, Solvent Facilities Building, is a single crib identical in construction to each of the Building 216-S Cribs. This separate crib is provided to handle the hexone-saturated washes from Building 276-S.

Three test wells, 150 feet deep, are located in a triangle around the Building 216-S Cribs. In addition, a 150-foot well is sunk in the center of each of the three cribs.

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 3. Negligible-Activity Wastes.

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3.1 Definition of problem

Waste sewers from the Redox Plant are segregated into two types, chemical sewers and process sewers. The chemical sewers drain all non-regulated portions (e.g., operating galleries, service areas, aqueous make-up areas, etc.), and the process sewers drain water (and steam condensate) from process equipment jackets and coils. Wastes from the chemical sewers flow directly to a pond (approximately 3500 feet southwest of Building 202-S) where they percolate into the soil or evaporate. The process sewer wastes, however, flow into a Retention Basin, Building 207-S, before they are discharged to the pond. This segregation is required so that the process vessel wastes can be monitored for radiomaterials which may be present due to leakage. The quantities of radiomaterials which can be disposed of to the pond are those amounts that do not appreciably exceed background monitoring levels for plutonium and beta emitters. With this as a basis, an approximate tolerance limit for disposal of radiomaterials to the pond is:

Plutonium -- 1×10^{-4} micrograms/liter
 Beta emitters -- 0.5 microcuries/liter.

The volumes of waste water passing through the basin daily are listed below for three operating conditions of the Redox Plant:

3U, 3Pu Extraction Cycles -- 2,900,000 gallons/day
 2U, 2Pu Extraction Cycles -- 2,250,000 gallons/day
 1U, 2Pu Extraction Cycles -- 1,770,000 gallons/day.

3.2 Description of disposal facilities

The Retention Basin (see Chapter XI) is located due west of Building 202-S. It consists of a 130-foot square concrete pool having a capacity of 853,000 gallons (6.75 feet deep). The inlet and outlet lines, 24-inch vitreous clay pipe, are equipped with gate valves and located so that flow is from north to south. A continuous monitoring instrument (limits to be compatible with safe disposal of the waste), located at the inlet to the basin and tied in to an annunciator in the Dispatcher's office (in Building 202-S), is used as an alarm for indicating beta-gamma radioactivity in the basin. An assay of a 500-ml. sample is made daily to determine the presence of plutonium. The holdup time of the basin (with the outlet valve closed) is indicated below for three operating conditions of the Redox process:

3U, 3Pu Extraction Cycles -- 7 hours
 2U, 2Pu Extraction Cycles -- 9 hours
 1U, 2Pu Extraction Cycles -- 11 hours.

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C. PLANT GASEOUS WASTES

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1. Definition of Problem

Gaseous wastes discharged from the Redox Plant consist of canyon, silo, and cell ventilation air; air or nitrogen from the various equipment vent headers; and gaseous products formed as a result of a process operation. The latter group is the most important because it contains the majority of the radiomaterials in the gaseous wastes.

Ventilation air is filtered by a graduated gravel and sand filter bed where radioactive particulate matter in the air is removed by the filter media. Likewise, the gases discharged from the vent headers pass through capsule-type Fiberglas filter units where radioactive particles are removed.

The gaseous products formed during process operations (i.e., uranium dissolution and ruthenium volatilization) are treated to remove the absorbable gases (I-131, RuO₄) in addition to being filtered to remove particulate matter. Under current operating practices, the radioactive noble gases (Kr-85, Xe-133) are diluted and discharged to the atmosphere from a 200-foot stack.

The gaseous wastes discharged to the atmosphere are itemized in Table X-2. This table is based on an instantaneous plant production rate of 3-1/8 tons U per day (400 megawatt-days integrated exposure for 360 days, followed by 90 days "cooling"). The Silver Reactor off-gas represents the gaseous waste from the Dissolvers after essentially all (assumed D.F. of 10³) of the I-131 is removed. Similarly, the Ruthenium Scrubber off-gas represents the gaseous waste from the Ruthenium volatilization after essentially all (assumed D.F. of 10⁵) of the RuO₄ is removed. It should be emphasized that almost all of the radioactivity in the gases discharged to the atmosphere is due to Kr-85.

Silver Reactor operation and off-gas scrubbing methods for treating Dissolver off-gas and ruthenium scrubbing methods for treating Oxidizer off-gas are discussed in detail in Chapter III, but these operations are summarized briefly below.

2. Technical Background

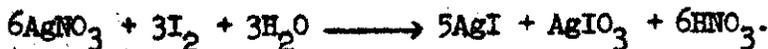
2.1 Iodine removal by Silver Reactor

Although radioiodine-131 has a relatively short half life (approximately 8 days), it is the most hazardous gas evolved during pile-metal dissolution because of its tendency to concentrate in plant and animal tissues if allowed to pass into the atmosphere. The Redox Plant will be provided with Silver Reactors (to replace Dissolver Off-Gas Scrubbers discussed under 2.6) for removal of iodine from the Dissolver off-gases. At the time of writing, Redox Plant Silver Reactors are under design; however, they will be the operation equivalents of the reactor installed in Building 221-B canyon.

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The Silver Reactor is 2 feet in diameter and packed to a depth of 8 feet with 1/2-inch ceramic Berl saddles coated with silver nitrate. The exact iodine removal mechanism is not known with surety but may be represented by the usual iodine reaction in the presence of an excess of silver nitrate:



There may be some AgNO_3 dissolution under operating conditions so that the following series of reactions can occur to a limited degree:



At an average off-gas temperature of 475°F., the iodine removal efficiency from the off-gas is greater than 99.9 per cent. The temperature of the off-gas should be maintained less than 500°F, because the silver nitrate starts to soften at this gas temperature and is quite fluid at an off-gas temperature of 600°F. As discussed in Chapter III, the potential life of the 221-B Silver Reactor (based upon available silver) may be on the order of 10 to 15 years.

It should be mentioned that not all (only about 50%) of the iodine is liberated during dissolving. The exact distribution of iodine not evolved during dissolution is obscured by difficulty of detection due to high radioactivity levels in the ruthenium off-gas and solvent-extraction column waste streams.

2.2 Ruthenium scrubbing with NaOH

The hot (195 to 200°F.) gases passing into the Ruthenium Scrubber from the Oxidizer contain an estimated maximum of 90 per cent (approximately 7200 beta and 5400 gamma "countable" curies) of the radioactive ruthenium in the form of a volatile compound, RuO_4 .

Large amounts (approximately 200 cu.ft./min.) of an air carrier gas serve as the sweeping agent for RuO_4 removal from the Oxidizer. Only trace amounts of fission products other than ruthenium are present in the carrier gas. A 25 per cent NaOH solution, recirculated through the Ruthenium Scrubber, absorbs the RuO_4 so that the gases leaving the scrubber contain less than 0.001 per cent of the ruthenium. Although the mechanism by which caustic absorbs RuO_4 is unknown, it is generally assumed that Ru(VIII) is reduced to Ru(VI) and absorbed as the soluble salt, Na_2RuO_4 . It is necessary to operate the Ruthenium Scrubber at approximately 200°F. so that large amounts of water vapor in the carrier gas do not condense in the scrubber and dilute the recirculating caustic. The recirculating caustic is replaced about every 3 to 4 days with fresh caustic, and is transferred to underground storage via the Neutralizer, Tank D-8 (Figure X-3).

2.3 Filtration of process equipment vent discharges

Process gaseous wastes are removed from the Redox Plant by six individual headers which are maintained under vacuum (varying from -5 to -30 inches water) by steam/air jets. This header system is necessary to maintain all cells as free of process gases and radioactive particulate matter as possible. As mentioned previously, gases in four of the headers (Ruthenium Scrubber and three Dissolver Off-Gas Headers) are treated for removal of radioactive iodine and ruthenium. In addition, the gases in all headers are filtered through capsule-type Fiberglas units for removal of radioactive particulate matter before they are discharged into the atmosphere. The following table lists the six sources of gaseous wastes and their respective filters:

- (a) Dissolver A-2-A, through Filter A-4;
- (b) Dissolver A-2-B, through Filter B-4;
- (c) Dissolver A-2-C, through Filter C-4;
- (d) Ruthenium Off-Gas Scrubber H-5, through Filter J-1;
- (e) Process Vent Header through Filter J-3;
- (f) Condenser Vent Header through Filter J-4.

The first four sources are handled separately through individual filters because the off-gas volumes during processing periods are comparatively high (up to 200 cu.ft./min.) and cannot be combined without undue increases in equipment size. The Process Vent Header provides venting for all other "hot" process equipment with the exception of condensers which are vented through the Condenser Vent Header. Vessels containing organic or organic-saturated solutions are vented to the Inert Gas Vent Header which joins the Process Vent Header before Filter J-5.

The Fiberglas filter units are designed to give a pressure drop of less than 3 inches of water and a particle removal efficiency of 99.99 per cent at a maximum gas flow of 260 cu.ft./min. (5)

2.4 Filtration of ventilation air

Prior to disposal to the atmosphere, ventilation air from the canyon, silo, and process cells is passed through a sand filter for removal of radioactive particulate matter. Three mechanisms of particle removal are predominant in the operation of sand filters. (5) These are gravity settling, Brownian diffusion, and, to a very small degree, interception. Since these controlling mechanisms depend on eventual deposition of suspended particles on a collecting surface (sand particles), the particle size is a critical factor in performance. Collection efficiency increases with increasing bed depth and decreasing superficial gas velocity. The Redox Sand Filter is designed for a superficial gas velocity of approximately 5 feet per minute. The filtration bed is composed of successive strata of coarse (2 to 3-1/2 inch) to fine

(No. 30 sieve size) aggregate. The coarse bottom layers provide uniform air distribution. The settling of the larger particles in this section reduces the filtration duty of the fine upper layers, thus prolonging the life of the filter. The pressure drop across the filter at a superficial velocity of 5 feet per minute is approximately 7 inches of water. The pressure drop across the sand filters installed in 221-B and 221-T Plants has not increased appreciably after more than a year's use. The contamination removal efficiency is approximately 99.5 per cent. (?)

2.5 Disposal of gaseous wastes through Stack

The gaseous wastes discarded to the atmosphere contain essentially no radioactive particulate matter or ruthenium and little radioiodine. The exact amount of iodine going to the Stack, however, is not know. Practically the entire amount liberated in dissolving is expected to be removed. (See Subsection C2.1, above.) If any residual iodine is liberated (by volatilizing) elsewhere in the process, it may be expected to pass out the vent system and eventually to the Stack. However, it would be expected that iodine not volatilized in dissolving or ruthenium distillation would not distill at subsequent points in the process although, because of the less severe oxidizing conditions in the Waste Concentrator than in the Dissolvers or Oxidizer, it is possible that some iodine might be liberated during waste concentration. As shown in Table X-2, radiokrypton and small amounts of xenon discharged represent approximately 200 "countable" curies (670 theoretical curies) per day. This radioactivity must be diluted to a permissible concentration (1.4×10^{-5} microcuries (theoretical)/cu.cm.) by discharge from a stack at a 200-foot elevation and linear velocity of 3000 feet per minute. Partial dilution is achieved when the 200 cu.ft./min. of Dissolver off-gases are mixed with approximately 35,000 cu.ft./min. of ventilation air and 600 cu.ft./min. of other process gaseous wastes. However, an additional 500-fold dilution is required before the gases are safe for breathing by the operating personnel in the plant. Under unfavorable weather conditions (e.g., no wind, downdraft, or fog) when the dilution ratio is less than 500, dissolving cannot be carried out, because the dilution of the radiokrypton evolved would be insufficient. The dilution ratio is determined from meteorological data.

2.6 Scrubbing of Dissolver off-gases

Although Silver Reactors are to be installed for removal of radioiodine from Dissolver off-gases, stub connections have been provided in the off-gas lines for later installation of caustic scrubbers, if desired. These scrubbers may be required for removal of oxides of nitrogen from the off-gases. (See Chapter III.)

3. Description of Disposal Facilities

3.1 Fiberglas filters

The six Fiberglas filters are identical in internal design. Each filter is designed so that an entire unit is disposable when replacement is required. Each is 6-1/2 feet in diameter and 5 feet high and packed with Owens-Corning Fiberglas according to the following specifications:

<u>Filter Bed Layer</u>	<u>Type Fiberglass</u>	<u>Bed Depth</u>	<u>Packing Density, Lb./Cu.Ft.</u>
Cleanup layer	"AA"	1 inch	1.2
Third Layer	115-K	12 inches	6.0
Second layer	115-K	6 inches	3.0
Bottom or first layer	115-K	12 inches	1.5

Gases entering the filter pass through an entrainment separator before entering the filter medium. Mist separation is necessary to prevent the collection of moisture in the filter which would increase the pressure drop and probably cause channeling with resultant decrease in efficiency and decreased filter life due to fiber deterioration. An electrical connector is provided for powering a Calrod gas preheater for heating gases passing to the Ruthenium Off-Gas Scrubber Filter in order to reduce condensation in this filter. Spare electrical connectors are provided for possible future installation of Calrod preheaters for other filters if heating of the gases is necessary to reduce condensation. Air bleed-in to the inlet headers near the base of the Condenser Vent Filter and Process Vent Filter (controlled by header pressure so that the negative pressure is maintained) tends to reduce the dew point of the vapor passing through these filters.

3.2 Sand Filter and Stack

Reference is made to Chapter XI for a detailed description of the Sand Filter and Stack. However, a brief description will be given here. The Sand Filter consists of layers of gravel and sand placed horizontally in a concrete shell having a cross-sectional area of approximately 5000 square feet (108 by 46 feet inside dimensions). There are seven layers of material of successively smaller particle size from the bottom gravel layer (2 to 3-1/2 inches in size) to the top sand layer (particles approximately No. 30 sieve size). A by-pass damper system at the filter outlet allows the inlet plenum to serve as a by-pass duct after the filter has been removed in favor of future installations. Differential pressure taps are provided for measurement of the pressure drop across the filter.

The air is pulled through the filter by two, motor-driven, stainless steel fans installed in parallel. Each fan has a capacity of 20,000 cu.ft./min. with a pressure drop of 7 inches of water. Another identical fan, on emergency standby, is direct driven by a steam turbine which operates off the 225 lb./sq.in. steam supply. This fan has a capacity of 40,000 cu.ft./min. (at a higher speed) and automatically starts when the static pressure in the air duct to the Sand Filter rises to a pre-determined level. The blowers discharge into the Stack (Building 291-S) which also receives the discharges from the process equipment vent jets.

The Building 291-S Stack is 200 feet high above grade. It is concrete and contains a free-standing stainless steel liner of 3.75-foot inside diameter. Stack gas samplers (see Chapter XXI) are provided at

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points 4 feet from the top and 10 feet from the bottom of the Stack. In addition, spray rings are provided at three levels for washing down the liner of the Stack should it be necessary.

D. PROCEDURES

1. Normal Procedure

1.1 General

The Waste Treatment System, shown schematically in Figure X-3, comprises three sections; (a) the waste concentration system in which those wastes too highly radioactive to be cribbed are concentrated and neutralized; (b) the condensate evaporation system in which condensates from all portions of the Redox Plant are distilled to achieve decontamination necessary to permit cribbing; and (c) the rework preparation system in which off-grade solutions (those containing an excessive amount of plutonium or uranium) are adjusted to permit reworking in the IS Column. In the following discussion of these three systems, the basis for all quantitative data is an instantaneous production rate of 3-1/8 tons of irradiated uranium per day and a Redox process operating on 3U and 3Pu Extraction Cycles as indicated in Figure X-3. Reference is made to Table X-1 for quantitative data for operation of 2U and 2Pu or 1U and 2Pu Extraction Cycles.

1.2 Waste concentration

The waste concentration system receives the high-activity waste streams which require hexone stripping, concentration and neutralization prior to being stored in underground storage tanks. Waste streams are sampled between concentration and neutralization to determine whether the plutonium and uranium contents are excessive.

The solvent-extraction column wastes, IAW, 2AW, 3AW, 2DW, 3DW, IOW, (and ISW), are received continuously in the Waste Header-Receiver, D-13 (4700-gallon working capacity; 6-hour holdup), via the First Salt Waste Header. A second header, the Salt Waste Header, is provided for possible future use in diverting part or all of the salt wastes to an ANN Diversion Tank (not installed) if an ANN recovery process is installed. (Four spare connectors are provided in D Cell for connection with an ANN recovery plant which would probably be housed in an annex to Building 202-S.) In addition to these salt wastes, wastes from the Organic Distillation Column, G-3 (Chapter IX), Condensate Evaporator, D-4, and Cell Drainage Collection Tank, D-1, are routed batchwise to the Waste Header-Receiver. The wastes received in Tank D-13 (14,200 gallons daily) are pumped continuously to the Waste Concentrator (885-gallon capacity; 4.5-hour holdup), where the hexone is stripped from the hexone-saturated aqueous phase as it flows down through six 49-1/2 inch bubble-cap plates as described previously (under B1.21). Approximately a three-fold concentration is achieved in the concentrator, so that 4620 gallons of concentrate (67.7 per cent ANN) overflow daily to the Waste Concentrate Receiver, D-10 (1200-gallon working volume; 6.2-hours holdup).

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As indicated in Figure X-3, the steam supply to the Waste Concentrator, D-12, is controlled automatically by a specific gravity recorder-controller. This instrument is set to maintain a specific gravity of 1.37 in the concentration pot. Thus, the amount of steam (4,100,000 B.t.u./hour) to the concentrator coils is regulated so that the boil-up rate is high enough to maintain the 1.37 specific gravity in the pot. The water vapor boiled off from the concentrator pot passes up through the six bubble-cap plates, where it strips the hexone from the incoming concentrator feed and continues up the deentrainment column with the hexone vapor. The deentrainment section comprising the upper portion of the Waste Concentrator, D-12, is 49-1/2 inches in diameter and contains 3-1/2 feet of one-inch stainless steel Raschig rings. A decontamination factor of 10^4 to 10^5 based on the fission-product radioactivity in the feed to the Waste Concentrator is anticipated across this tower. A water spray is provided at the top of the deentrainment section instead of a reflux coil in order to reduce the required height of the unit. The water spray is used intermittently (twice per shift) to wash down the packing so that satisfactory deentrainment is not prevented by an accumulation of salts on the packing.

After being cooled to less than 120°F. in the Waste Concentrate Receiver, D-10, the concentrate is jettted to the Waste Concentrate Sampler, D-9 (2000-gallon working volume; 10-hour holdup). It is sampled and retained in Tank D-9 until analyses of the sample determine the plutonium and uranium content. (See under 2.1 below for a discussion of the treatment of high uranium or plutonium content wastes.) Normally the wastes are neutralized by a "reverse strike" procedure with 3290 gallons of 50 per cent caustic in the Neutralizer, D-8 (4700-gallon working volume; 12-hour holdup). As discussed under B1.23, the neutralization is performed by jetting the wastes into the caustic in Tank D-8 intermittently so that the temperature does not exceed 120°F.; agitation and cooling by coil water are also necessary to prevent overheating. The pH of the neutralized wastes, determined on a sample taken from Tank D-8, should be about 13 before the wastes are jettted to the underground storage tanks.

1.3 Condensate evaporation

The condensate evaporation system receives condensate from the ICU, 2EU, 3EU, Plutonium Transfer Trap Jet and Waste Concentrator Condensers; the Cross-Over Oxidizer Condenser; the Ruthenium Scrubber Condenser; and the Plutonium Pre-Concentrator and Plutonium Concentrator Condensate Receivers. All condensates (17,400 gallons per day) with the exception of those from the Ruthenium Scrubber Condenser join in a Condensate Header, the contents of which flow continuously into the Condensate Stripper, D-5, where the hexone is removed by steam stripping. The condensate from the Ruthenium Scrubber, containing no hexone, is sent directly to the Condensate Evaporator, D-4.

The Condensate Stripper, D-5 (described in detail in Chapter XV), is a 20-inch diameter column packed with one-inch Raschig rings and supported on a reboiler (144-gallon capacity). The hexone-saturated condensates (17,400 gallons) flow by gravity to the feed point where

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they are distributed across the packing. As they flow down through the packing, steam rising at a constant rate (heat input to the boiler is controlled at approximately 962,000 B.t.u./hour) from the reboiler vaporizes the hexone and carries it up through the deentrainment section. A reflux coil at the top of the column condenses approximately 25 per cent of the vapors rising out of the deentrainment section. The temperature of the outlet vapors is maintained at 203°F. automatically by a controller on the reflux coil water supply valve which regulates the flow of cooling water to coil. The hexone-water vapors (containing approximately 10⁻⁶ per cent of the radiomaterials processed daily) pass out of the Condensate Stripper, are condensed, and flow to the Organic Distillation Column, G-3, for further treatment, as described in Chapter IX. Reference is made to the discussion of the Organic Distillation Column (Chapter IX) for further explanation and data on hexone-water distillations. Approximately 500 gallons of hexone are recovered daily from the waste condensates.

The bottoms (16,700 gallons) from the Condensate Stripper, D-5, containing a negligible quantity of hexone, overflow continuously to the Condensate Evaporator, D-4 (described in detail in Chapter XV). Essentially, the Condensate Evaporator consists of a 53-1/2 inch diameter column, containing six bubble-cap plates (spaced at 18-inch intervals) and a reflux coil, and supported on a reboiler (1200-gallon capacity). In the Condensate Evaporator, approximately 94 per cent (15,700 gallons) of the feed is redistilled to achieve further decontamination (reduction by about 400-fold of the fission-product radioactivity in the feed to the Evaporator); the remaining 6 per cent (1000 gallons) is recycled to the Waste Header Receiver, D-13, to prevent an accumulation of radiomaterials in the reboiler. The redistilled condensate is received in the Condensate Receiver, D-2 (4700-gallon working volume; 7-hour holdup), where it is sampled. Normally, this water is jettied to cribs (see Section B), but if the water does not meet cribbing tolerances, it is jettied to underground storage tanks.

2. Remedy of Off-Standard Conditions

2.1 Excessive amounts of uranium or plutonium in the waste stream

As mentioned previously (Subsection D1), salt wastes which contain excessive quantities of either uranium or plutonium as detected by routine sampling of Waste Concentrate Sampler, D-9, are routed to the Rework Adjustment Tank, D-7. Rework of wastes may be required if Plant yield specifications (95 to 98% uranium and 98 to 99% plutonium)⁽⁶⁾ are not met or if higher-than-normal losses occur. Tank D-7, having the same capacity (2000 gallons) as the Waste Concentrate Sampler, D-9, is capable of receiving only one batch of off-grade wastes at a time. However, approximately 10 hours' holdup time is available in D-7; this fact allows adequate time to process the batch. In Tank D-7 the wastes, highly acid, are partially neutralized with 50 per cent NaOH and diluted with demineralized water from the Rework Chemical Addition Tank, D-7-A. Then they are pumped to the IS Feed Tank, F-8, from which they flow to the IS Column (or the Oxidizer, if oxidation is required) for reprocessing according to the procedure described in Chapter VI.

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2.2 Excessive radioactivity of Retention Basin contents

This condition may be detected by the alarm given by a continuous monitoring instrument in the case of beta-gamma radioactivity or from the results of a daily sample assay in the case of plutonium. Approximate tolerance limits are: plutonium, 1×10^{-4} micrograms/liter and beta emitters, 0.5 microcuries/liter.

If radiomaterials are detected, the outlet valve from the basin is closed allowing the liquid level to rise, and an investigation is made to determine the cause and extent of the contamination. If the cause is not remedied, operation of the Plant must be suspended. Since this condition is considered a very remote possibility, no equipment is installed for emptying the basin contents to cribs. However, suitable arrangements (e.g., pumping by portable pump) could be made.

2.3 Excessive radioactivity of wastes normally cribbed

If condensate in the Condensate Receiver, D-2, or cell drainage water in the Cell Drainage Collection Tank, D-1, is too "hot" to crib as indicated by samples of the materials in the tanks, the streams may be routed to underground storage tanks (by a separate jet-out line in the case of the Condensate Receiver and through the waste concentration and neutralization system by a jet-out line to the Waste Header Receiver in the case of the Cell Drainage Collection Tank) instead of being cribbed. Tolerance concentrations of cribbable wastes are:

uranium -- less than 100 micrograms/liter,
plutonium -- less than 0.5 micrograms/liter,
beta emitters -- less than 4 microcuries/liter.

2.4 Undissolved $\text{Al}(\text{OH})_3$ in neutralized waste

Undissolved $\text{Al}(\text{OH})_3$ in the neutralized waste may be detected by sampling or pH measurements of the contents of the Neutralizer, D-8. It may indicate insufficient caustic used in neutralization or insufficient agitation during the "reverse" strike procedure (as described under B1.23). Either cause may indicate addition of more caustic to redissolve the $\text{Al}(\text{OH})_3$. If the "ageing" phenomenon (discussed under B1.23) occurs, however, $\text{Al}(\text{OH})_3$ may be difficult to redissolve. If the pH of the solution is brought to 13, the entire contents of the Neutralizer may be jetted to underground storage whether or not $\text{Al}(\text{OH})_3$ is in solution.

E. LABORATORY LIQUID WASTES

1. Introduction

The process wastes from the Analytical and Plant Assistance Laboratory (Building 222-S) are handled in a three-part system comprising (a) "hot" wastes to storage, (b) cribbable wastes, and (c) retention basin wastes. Included in this system is the Retention and Neutralization Building (219-S) which is used for holdup, sampling, and routing of

liquid wastes to their destination. The separate parts of the system are described below and are shown in Figure X-4, "Laboratory Building (222-S) Aqueous Waste Disposal Flow Diagram". Estimated compositions, volumes, and degrees of contamination are shown in a table in Figure X-4. Sanitary wastes are sent via sewer mains to septic tanks and thence to a tile field.

The waste volumes, compositions, and radioactivity levels which are given in this section are estimates based on the use of the 222-S Building as a service and plant assistance laboratory for the Redox Plant, the Tributyl Phosphate Plant, and the Hot Semiworks. Because of the non-routine nature of much of the work conducted in the Laboratory Building, these estimates are subject to considerable uncertainty.

2. Underground Storage Wastes

Aqueous wastes containing more than one-half microgram of plutonium per liter or more than four microcuries of gross beta and/or gamma radioactivity per liter are placed in transfer vessels and emptied in the Slurping Hoods in Decontamination Rooms 1-A and 2-B, which drain by gravity to the 1365-gallon Waste Storage Receiving Tank (TK-103) in Building 219-S, equipped with agitator and temperature recorder. The wastes in this tank are analyzed and then jettted to the Waste Neutralizer Tank, D-8, in the Redox Production Plant (Building 202-S) where they are processed and jettted to the Redox Plant underground storage tanks. The design capacity of this system is 150 gallons per day of "hot" wastes. A spare cell is provided for the installation of another tank, TK-105, for the neutralization of "hot" wastes from Building 222-S if future conditions necessitate making the laboratory waste system of Building 222-S independent of Building 202-S facilities.

3. Crib Wastes

Aqueous wastes containing plutonium and/or gross beta and gamma radioactivity in concentrations exceeding the tolerance level for the Retention Basin (see Subsection 4, below), but which contain less than one-half microgram of plutonium per liter or less than four microcuries of gross beta and gamma radioactivity per liter are sent to the 4185-gallon Crib Waste Receiving Tank (TK-101) in Building 219-S. This tank is interconnected with the Crib Waste Treatment Tank (TK-102), a sampler tank of the same capacity, also provided with an agitator and temperature recorder. The waste batches accumulated in Tank 101 are jettted to Tank 102, analyzed for radioactivity, and the acidity is adjusted to a pH of 5 to 9 by addition of caustic solution from the 700-gallon Caustic Storage Tank (TK-201). Normal batches are then jettted from this tank to Building 216-SL, an underground crib as shown on the plot plan, Chapter XI. A connecting line is provided from Tank 102 to Tank 103 so that wastes intended to be cribbed, but which accidentally exceed the cribbing limits, may instead be jettted to Tank 103 whence they are jettted to Tank D-8 in Building 202-S and subsequently to storage underground. For a discussion of aqueous waste disposal by cribbing, see Subsection B2, this chapter.

The crib has a design capacity of 18,500 gallons per day, made up as follows: 3500 gallons per day from Building 222-S, and 15,000 gallons per day from the 300 Area Works Laboratory. Laboratory wastes from the 300

Area are transported to the 200 Area crib by tank trailer, and normally do not exceed 15,000 gallons per day. These are the only sources of wastes planned for this crib.

A list of key drawings under REFERENCES at the end of this chapter provides additional details.

4. Retention Basin Wastes

The Retention Basin waste disposal method permits conservation of underground storage capacity of both cribs and tanks, by directing aqueous streams containing not more than 1×10^{-4} micrograms of Pu per liter nor more than 0.5 microcuries of gross beta and/or gamma radioactivity per liter, to open ponds or ditches once it has been ascertained that these limits have not been exceeded. The Retention Basin is required for temporary storage of the waste solution while awaiting assay information indicating whether the tolerance limits have been satisfied.

The laboratory basin waste system is fed by gravity through a collection line from Buildings 222-S and 219-S discharging directly into a 50,000-gallon concrete basin built in two 25,000-gallon sections (Building 207-SL). No other sources contribute wastes to this system. This basin has a flow capacity of 45,000 gallons per day with an average holdup of twelve hours in each section. The retention basin is drained through a sluice gate into a pond. A connection is provided so that wastes exceeding the Pu or beta and gamma tolerances may be transferred by gravity flow to the crib.

5. Sanitary Wastes

Sanitary wastes are collected through a soil-pipe drainage system and conveyed to the area sanitary sewer main outside the building.

6. Organic Wastes

Organic wastes are decontaminated by scrubbing with aqueous solutions in the laboratories in which they are produced. The organic liquids are then transported to a designated site and burned. The aqueous scrub solutions are disposed of in the regular waste system, depending upon their degree of contamination.

7. Tunnel and Basement Drainage

The floor drains and underground piping from the "regulated" tunnel system lead to a sump from which any "regulated" drainage water is discharged through automatically operated steam jet siphons to the Retention Basin system.

The floor drains and underground piping from the "hot" tunnel system discharge into a "hot" sump. In the event of collection of drainage in the lines or sump, an alarm sound in the Senior Supervisor's Office and the contents of the sump are then automatically discharged.

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by a steam jet to Tank 103 for inclusion in the "hot" waste. There is also a three-way manual valve on this sump by which tunnel drainage may be sent to the crib if it is not "hot" enough to warrant underground tank storage.

8. Halogen Wastes

No special provisions are made for the disposal of halogen wastes. These are neutralized, if necessary, and sent to one of the above-mentioned waste systems. Solid fluoride pellets from the Fluorimeter Room may be disposed of as dry waste, as described in Section G, below.

F. LABORATORY GASEOUS WASTES

1. Introduction

All ventilation exhaust air, gaseous wastes, and chemical fumes from the Analytical and Plant Assistance Wing of the building are removed through hoods and ceiling ports, and leave the building via the stack. Those wastes from the Multicurie Wing are routed through the basement tunnels and to the main stack via an outside duct. See Chapter XI for a discussion of the ventilation of Building 222-S.

2. Millicurie Wing

Ventilation air for, and gaseous waste from the glove boxes, as well as exhaust air from open hoods, is removed via overhead canopies equipped with either Fiberglas or Chemical Warfare Service filters. The canopies for the Junior Caves are similar to those for the glove boxes and open hoods except that they exhaust only the air which passes through the cave. In addition to those in the throats of the canopies, small Fiberglas filters are mounted directly on the glove boxes to filter the box ventilation exhaust. These filtered gaseous wastes then pass through the Exhaust Air System to the main building stack and thence to the atmosphere.

3. Multicurie Wing (222-S)

Exhaust wastes from the cubicles, hoods, and canopies in the Multicurie Wing are handled in the same fashion as in 2, above, except that they are routed through filters in the basement and thence to the main building stack via an outside duct. Air in the tunnels flows from the "regulated" tunnel to the "hot" tunnel, through a Chemical Warfare Service filter and into the Exhaust Air System to the 222-S Building stack.

4. Vacuum System

Gases entering the two Vacuum Systems (see Chapter XI) pass through two sets of traps before reaching the pumps, and are then exhausted through Chemical Warfare Service filters to the building stack.

5. Counting Room

Methane from the sample counters in the basement is exhausted through a vent pipe (equipped with a flame arrester) located on the roof of the building.

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6. Liquid Waste Disposal Building (219-S)

Exhaust ventilation air from the Liquid Waste Disposal Building (219-S) and off-gases from the tanks are filtered through the 150-gallon Condensate Vent Tank (TK-104) filled with glass wool. They are then exhausted to the atmosphere by means of a Buffalo exhaust pump, through a 4-inch vent line extending 10 feet above the 219-S Building roof level.

G. DRY WASTES

Laboratory dry wastes, such as absorbent tissues, wood, metal parts, etc., of low radioactivity are placed (if possible) in quart cardboard containers which are in turn placed in larger cardboard cartons. When the radioactivity level of the contents of this carton reaches tolerance, the carton is sealed and removed to the 200-W Area Burial Ground.

On an emergency basis, highly contaminated dry wastes are placed in containers and disposed of in the Dry Waste Disposal Vault (232-S) adjacent to Building 222-S.

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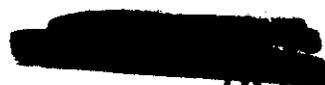
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TABLE X-1

HIGH-ACTIVITY WASTES FOR UNDERGROUND STORAGE

Chemical Flow Sheet HW No. 4

(Instantaneous Capacity Basis: 3-1/8 t.u./Day of 360 g. Pu/t.u. Material)

Item	Volume, Gallons/Day			Approx. Activity Level ^(e) ("Countable" Curies/Gallon)			Estimated Pu Content, g.	Estimated U Content, lb.	Major Components (d)(f)				Properties			
	3U, 3Pu Cycles	2U, 2Pu Cycles	1U, 2Pu Cycles	Beta	Gamma	Total			AMW Ht. %	NaAlO ₂ Ht. %	HNO ₃ Ht. %	NaOH Ht. %	NaNO ₂ Ht. %	Hexone Ht. %	Approx. Density at 75°F.	Freezing Point, °F.
A. Head-End Wastes																
1. Scavenger Solution ^(a)	90	90	90	150	630	780	1	6.0	(18 lb. Mn ⁺⁺ - 1.9 wt.%)				1.24			
2. Ru Scrubber Solution ^(b)	80	80	80	70	68	158	trace	trace	26.0 220				1.27			
3. Coating Removal Solution	590	590	590	—	—	5 x 10 ⁻²	2.0	1.0	(414 lb. NaNO ₂ , 11.8 560 7.4 wt.%)				1.14			
4. Dissolver Flush	650	650	650	—	—	1 x 10 ⁻¹	3.0	2.0	4.0 220				1.02			
B. Extraction Col. Wastes^(c)																
1. IAW	2869	2869	2869	57	30	87	2.5	12.5	31.1	8855	1.0	271	2.3	650	1.2	331
2. 3DW	2868	2868	—	5.3x10 ⁻³	4.9x10 ⁻³	1.0x10 ⁻²	2.5	12.5	31.4	8863	1.0	271	2.6	721	1.2	331
3. 3DW	2864	—	—	6.0x10 ⁻⁵	5. x10 ⁻⁵	1.2x10 ⁻⁴	—	12.5	31.5	8863	1.0	271	2.2	617	1.2	331
4. 2AW	1329	1329	1329	1.1x10 ⁻²	1.7x10 ⁻²	2.8x10 ⁻²	2.5	—	37.9	5120	2.3	314	0.1	8	1.2	163
5. 3AW	1304	—	—	5.0x10 ⁻⁵	5. x10 ⁻⁵	1. x10 ⁻⁴	2.5	—	38.9	5120	2.3	304	—	—	1.2	156
C. Hexone Recovery Wastes																
1. IOW	—	820	517	2 x 10 ⁻³	2 x 10 ⁻³	4 x 10 ⁻³	0.6-1.25	3.3-10	—				1.8	188		
2. Dist. Col. Scrub	—	496	313	—	—	1 x 10 ⁻⁴	trace	trace	5 320				—	—		
D. Cond. Evap. Purges																
—	—	700	430	—	—	—	—	—	—				—	—		
E. Unconc. Wastes (D-13) (Combination of E,C, and G)																
1. 3U, 3Pu Cycles	207	—	—	11.5	6	17.5	11.25	47.5	26.6	36821	1.0	1431	1.4	1992	1.1	1500
2. 2U, 2Pu Cycles	—	9082	—	18	9.5	27.5	8.	31.5	25.8	22838	1.0	856	1.5	1379	1.1	952
3. 1U, 2Pu Cycles	—	—	5428	30	16	46	5.5	15.8	26.4	13975	1.1	585	1.2	658	1.0	494
F. Concentrated Wastes (D-9)																
1. 3U, 3Pu Cycles	4795	—	—	34.1	17.9	52.0	11.25	47.5	65.4	36821	1.2	701	4.9	2780	1.41	41
2. 2U, 2Pu Cycles	—	2985	—	54.8	28.8	83.6	8	31.5	65.2	22838	1.2	420	5.3	1850	1.41	41
3. 1U, 2Pu Cycles	—	—	1830	89.4	47.0	136.4	5.5	15.8	65.1	13975	1.3	287	4.6	980	1.41	41
G. Heat. Wastes (From D-8)																
1. 3U, 3Pu Cycles	9000	—	—	17.8	9.4	27.2	11.25	47.5	7.6 8051				4.6	4787	27.6	29030
2. 2U, 2Pu Cycles	—	5700	—	28.6	15.1	43.7	8	31.5	7.6 4094				4.6	3010	27.6	18150
3. 1U, 2Pu Cycles	—	—	3500	46.9	24.7	71.6	5.5	15.8	7.6 3056				4.6	1850	27.6	11030
H. Undergr. Stor. Wastes (Combination of A and G Laboratory Wastes Excluded)																
1. 3U, 3Pu Cycles	10500	—	—	15.4	8.2	23.6	17.	57	7.4 8711				4.4	5145	25.7	30230
2. 2U, 2Pu Cycles	—	7200	—	22.3	12.1	34.9	14	41	7.3 5654				4.3	3375	24.8	19350
3. 1U, 2Pu Cycles	—	—	5000	33.0	17.5	50.5	11.5	25	7.1 3716				4.2	2215	23.1	12230

- NOTES: (a) Based on the assumption that 90 per cent of Zr and Nb is removed by the MnO₂ scavenging, if used. These activities are included in the IAW (B1) activities also.
 (b) Based on the assumption that 90 per cent of Ru is removed from the oxidizer. These activities are included in the IAW (B1) activities also.
 (c) Activity levels for the Extraction Column Wastes assume no head-end decontamination by MnO₂ scavenging or Ru volatilization.
 (d) Weights are reported on the basis of 3U, 3Pu cycles unless otherwise noted.
 (e) Radiation is 400 megarad-days integrated exposure for 360 days, followed by 30 days "cooling."
 (f) Components present in neutralized wastes in low concentrations (less than 0.5 wt.%) are products from the neutralization of Na₂Cr₂O₇·2H₂O, Fe(NH₂SO₃)₂, and Mn(NO₃)₂ (e.g., insoluble compounds - Cr₂O₃·3H₂O, Fe(OH)₃, and Mn(OH)₂).

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TABLE X-2

PLANT GASEOUS WASTES

(Instantaneous Capacity Basis: 3-1/8 t.U/Day)
(400 Megawatt-Days Integrated Exposure for 350 Days
Followed by 90 Days "Cooling.")

Item	Approximate Volume. Rate Cu.Ft./Min.(STP)	Approximate Total Activity/Day, "Countable" Series									
		Kr-85		I-131		Xe-133		RuO4		Total	
		Beta	Gamma	Beta	Gamma	Beta	Gamma	Beta	Gamma	Beta	Gamma
A. Saver Reactor Off-Gas	150	200	0	trace	trace	1	1	--	--	201	1
B. Ru Scrubber Off-Gas	200	--	--	--	--	--	--	trace	trace	trace	trace
C. Process Vent Header	250	--	--	--	--	--	--	--	--	1	
D. Condenser Vent Header	200	--	--	--	--	--	--	--	--	10 ⁻⁵	
E. Ventilation Air	35,000	--	--	--	--	--	--	--	--	less than	10 ⁻⁶
F. Composite (A to E)	35,800	--	--	--	--	--	--	--	--	202	1

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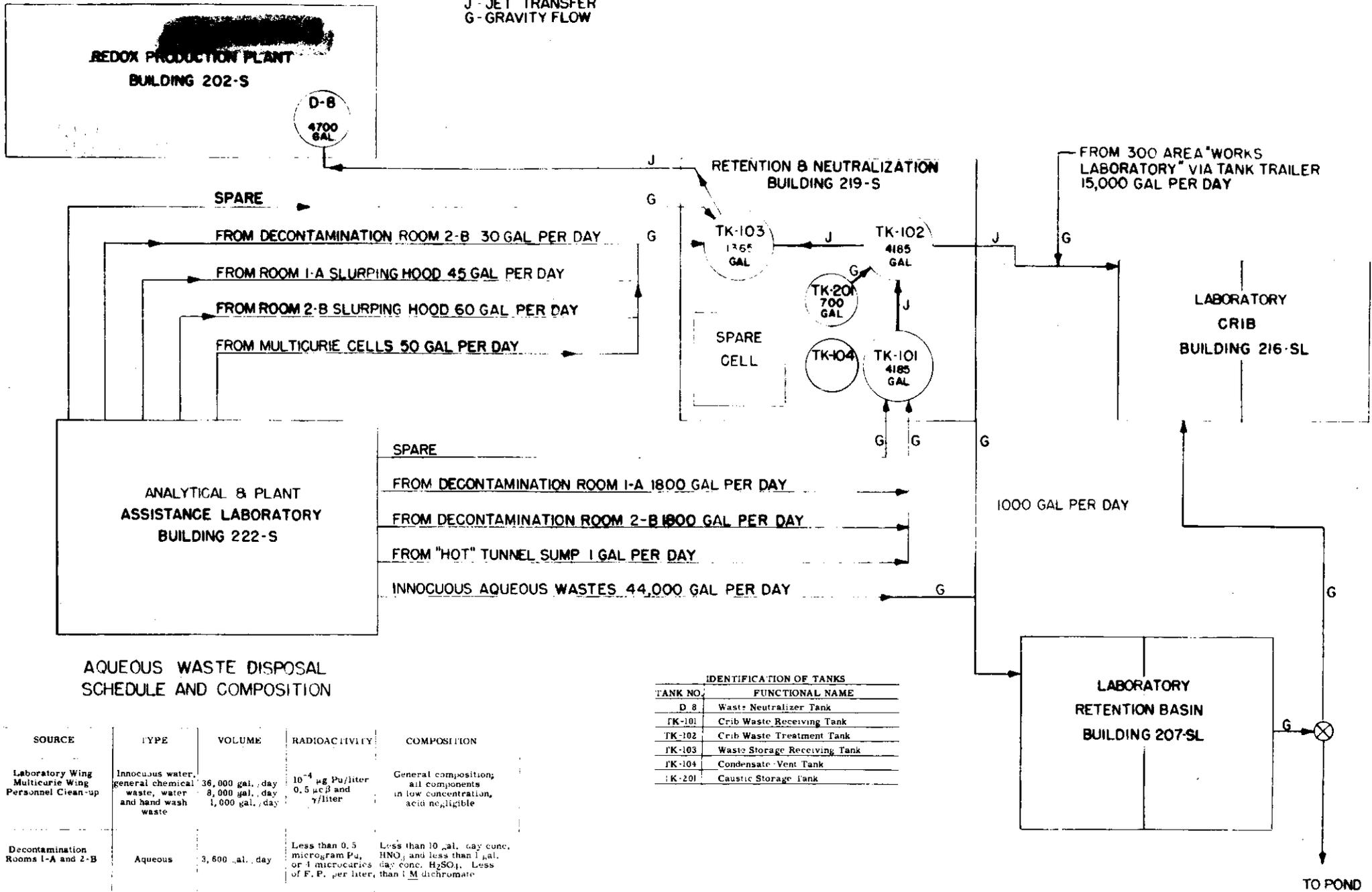
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FIG. X-4

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AQUEOUS WASTE DISPOSAL SCHEDULE AND COMPOSITION

DESTINATION	SOURCE	TYPE	VOLUME	RADIOACTIVITY	COMPOSITION
RETENTION BASIN	Laboratory Wing Multicurie Wing Personnel Clean-up	Innocuous water,	36,000 gal./day	10^{-4} μ g Pu/liter	General composition; all components in low concentration, acid negligible
		general chemical waste, water and hand wash waste	8,000 gal./day 1,000 gal./day	0.5 μ c β and γ /liter	
CRIB	Decontamination Rooms 1-A and 2-B	Aqueous	3,600 gal./day	Less than 0.5 microgram Pu, or 1 microcuries of F. P. per liter,	Less than 10 gal./day conc. HNO ₃ and less than 1 gal./day conc. H ₂ SO ₄ . Less than 1 M dichromate
		Gloved-Box Decontamination	Aqueous	50 gal./day	The same as Crib wastes, given above
UNDERGROUND STORAGE	Slurping Hood Room 1-A	Miscellaneous Aqueous (includes dissolved organic and halogens)	40 gal./day	Everything in excess of Crib tolerances, given above.	General chemical composition to 0.3 M, less than 10 gal./day conc. HNO ₃ , and 1 gal./day as HF.
				Averages 160 mg. Pu/da 100 mc. α /day 200 mc. β /day	Nitrate .01 M Dichromate .01 M Sulfate .01 M Chloride .01 M Oxalate .001 M Phosphate .001 M Iodide .001 M Borate .001 M Sulfamate .001 M
	Slurping Hood Room 2-B		60 gal./day	This may total as much as 20 c./day, alpha, beta and gamma	General chemical composition to 0.3 M. Less than 26 gal./day as conc. HNO ₃
	Multicurie Cells Rooms 1-E and 1-F	Aqueous and Organic Saturated Aqueous	50 gal./day		

IDENTIFICATION OF TANKS

TANK NO.	FUNCTIONAL NAME
D-8	Waste Neutralizer Tank
TK-101	Crib Waste Receiving Tank
TK-102	Crib Waste Treatment Tank
TK-103	Waste Storage Receiving Tank
TK-104	Condensate Vent Tank
TK-201	Caustic Storage Tank

Figure X-4
**LABORATORY BUILDING (222-S)
AQUEOUS WASTE DISPOSAL
FLOW DIAGRAM**

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PART III: PLANT AND EQUIPMENT

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CHAPTER XI. GENERAL DESCRIPTION OF PLANT

A. GENERAL LAYOUT OF PLANT

1. Layout of Hanford Works Production Areas

The production areas of Hanford Works, shown in Figure XI-1, were originally set up as independent, self-contained, parallel units located in widely separated districts. The wide separation of the individual units was intended to prevent any accidents in one unit from causing spread of radioactive contamination to others. The entire plant would not have to be shut down if any single unit were damaged, since other identical units could be operated. While for some recent additions to the plant no identical parallel facilities have been provided, continued operation of the plant despite damage to any one unit is still feasible, because of the availability of other facilities with the same function. Thus the Bismuth Phosphate and Uranium Recovery (TBP) Plants together parallel the function of the Redox Plant (recovery of plutonium and uranium).

Production units of the plant are located in three operating areas known as the 100, 200, and 300 Areas.

The piles for the production of plutonium are located in the 100 Areas. There are four of these areas, designated 100-B, 100-D, 100-F, and 100-H. One pile is located in each area with the exception of the 100-D Area which contains both the "D" and "DR" piles. The product of the 100 Areas is the raw material for the 200 Areas.

The 300 Area is located 5 miles north of Richland. The uranium metal charged to the 100 Area Piles is prepared in the 300 Area.

2. 200 Areas

The 200 Areas are located approximately 6 to 10 miles from the 100 Areas, and comprise the 200 North, 200 East, and 200 West Areas.

The 200 North Area contains facilities for the underwater storage of uranium after its discharge from the piles. In storage, irradiated slugs undergo "cooling" (decay of radioactive fission products) prior to processing in the separation plants. Three separate Metal Storage Basins, 212-N, P, and R, are provided in the 200 North Area.

During the "cooling" period the irradiated slugs are stored in the 212 Buildings. The slugs are kept in concrete pools under 16-1/2 to 20 feet of water. The water serves a dual purpose: it dissipates the heat generated in the radioactive metal, and it shields personnel from the radiation. Slugs are brought into and removed from the building in shielded tanks on a railroad car. The tank carries two casks, each holding a bucket of slugs. Details of the Metal Storage Basin (212 Building) are given in HW-10475, Hanford Works Technical Manual, Section C.

The 200 East and West Areas are approximately 2 to 3 miles from the 200 North Area, and are about 4 miles from each other (see Figure XI-1).

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Each of these areas is provided with power and service facilities.

Facilities for the separation and concentration of plutonium by the BiPO_4 precipitation process are located in both 200 East (Buildings 221 and 224-B) and 200 West Areas (Buildings 221 and 224-T). In addition, the 200 West Area contains facilities for plutonium isolation and metal fabrication (Buildings 231 and 234-5), a uranium recovery plant (Buildings 221 and 224-U) utilizing the TBP process for recovery of uranium in the stored metal wastes from the BiPO_4 process, and the new separations plant employing the Redox process, for the separation of uranium and plutonium from each other and decontamination of both from radioactive fission products.

3. Redox Plant Area

The Redox Plant is located in the south portion of the 200 West Area (see Figure XI-2), and consists of the following buildings, arranged as shown in Plot Plans, Figures XI-2 and XI-3.

3.01 Processing Building, 202-S

This building contains all of the equipment for the dissolution, separation, and decontamination of uranium and plutonium as well as equipment for waste concentration, waste neutralization, and solvent recovery. Facilities are provided for the make-up of aqueous process chemicals. Offices for the operating and servicing personnel are located in the service portion of the building. The 202-S Building is shown in Figure XI-4.

3.02 Chemical Tank Farm, 211-S

Bulk storage for the aqueous chemicals used in the Redox process is provided in the 211-S Building.

3.03 Solvent Treatment and Storage Building, 276-S

This building houses the equipment for chemical treatment of the solvent, and tanks for the bulk storage of the raw solvent.

3.04 Propane Storage Building, 2726-S

Bulk storage tanks and vaporization equipment for propane are located in the 2726-S Building.

3.05 Decontaminated UNH Storage Building, 203-S

Storage tanks for decontaminated UNH are provided in this facility.

3.06 Redox Mock-Up Shop, 277-S

The Redox Mock-Up Shop is located near the entrance to the 200 West Area, adjacent to the Bismuth-Phosphate Mock-Up Shop (see Figure XI-2). Two mock-up cells are provided, one to duplicate the canyon cells and one to duplicate the silo. It is possible to duplicate any section of the cells in 202-S Building in the canyon mock-up cell. The silo mock-up cell