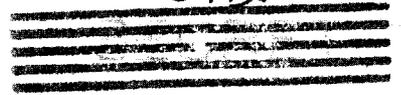


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Chemistry-Separation Processes
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THE CHELATE PROCESS, VI. PROCESS FLOW INVOLVING
o-DICHLOROBENZENE AS THE SOLVENT FOR TTA

M. W. Davis, Jr., T. E. Hicks, and T. Vermeulen

January, 1951

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THE CHELATE PROCESS, VI. PROCESS FLOWS INVOLVING *o*-DICHLOROBENZENE
AS THE SOLVENT FOR TTA

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ABSTRACT

Comparative studies of a series of halogenated solvents, as carriers for TTA in the chelate process for plutonium extraction, indicate that ortho-dichlorobenzene most nearly satisfies the requirements that are set forth. A complete process design is presented for use with this solvent, and flow data and equipment capacities are given for dissolver solution and for uranium-free fission product solution as alternate feeds to the process. Vertical mixer-settlers are recommended as the contactors, although pulsed columns or packed columns are also believed to be suitable. The size of such units is estimated from the best available rate and equilibrium data, and the effects of several operating variables are considered.

THE CHELATE PROCESS, VI. PROCESS FLOWS INVOLVING
o-DICHLOROBENZENE AS THE SOLVENT FOR TTA

The chelate process for plutonium extraction has been described in previous reports from this laboratory.¹⁻⁶ It provides efficient recovery of plutonium from solutions containing uranium, fission products, or both, such as are involved in the processing of neutron-irradiated uranium. As developed previously, the chelate process has used benzene as the solvent for the chelating agent (thenoyltrifluoroacetone, or TTA). Because of the volatility of benzene and the flammability of its vapor, a search for an alternate solvent has been undertaken.

CHOICE OF A SOLVENT

A solvent for use in this process must satisfy several requirements: The solubility of $\text{Pu}(\text{TTA})_4$ in the solvent must be of the order of 0.01M or greater. The solvent must be resistant to oxidation and nitration by strong HNO_3 , and its vapors should be relatively non-inflammable. It must also be available in large quantities at a reasonable price. Finally, to avoid excessive losses, it should be very insoluble in water.

The requirement of oxidation stability suggests the use of a halogenated solvent. Several available materials of this type have been considered, and their solvent properties investigated in comparison to those of benzene. Distribution data obtained by Doris Heisig of this laboratory, listed in Table I, show that all of the solvents considered give similar distribution ratios. However, considerable variation is observed in the solubility measurements of uranium chelate by K. L. Mattern, which are used to predict the solubility of plutonium chelate, $\text{Pu}(\text{TTA})_4$. Even when benzene is used, this solubility is a limiting factor in reducing the volume of the organic phase; thus it is desirable that any alternate solvent have a chelate solubility at least equal to that in benzene.

Of the solvents considered, only chlorobenzene and orthodichlorobenzene had chelate solubilities approaching the solubility in benzene. The higher density of dichlorobenzene relative to water, and its greater chemical stability, are two important factors in its favor.

TABLE I
EXTRACTION PROPERTIES OF HALOGENATED SOLVENTS

	<u>Solubility of U(TTA)₄* at 25° C</u>	<u>K** x 10⁻⁶ Distribution for Pu^{IV}</u>	<u>Solubility Parameter (7)</u>
CHBr ₃	0.0007	0.076	10.5
CHCl ₃	0.0019	0.045	9.3
C ₆ H ₅ Cl	0.0037	0.55	9.5
o-C ₆ H ₄ Cl ₂	0.004	0.43	--
C ₆ H ₆	0.005	1.39	9.15
C ₆ H ₃ Cl ₃	0.0006	0.29	--
C ₂ Cl ₄	0.0002	0.50	--
CCl ₄	0.0002	1.6	8.6
C ₄ Cl ₆	0.00004	1.4	--

*Solubilities of Pu(TTA)₄ are estimated to be twice those of U(TTA)₄.

$$K^{**} = \frac{(\text{Pu}(\text{TTA})_4)_o}{(\text{Pu}^{\text{IV}})_a} \frac{(\text{H}^+)_a^4}{(\text{TTA}_o)^4} \quad \text{Conditions: } 0.474 \text{ M HNO}_3$$

If ortho-dichlorobenzene is used for extracting plutonium from dissolver solution of high density, it will be necessary to have one mixer-settler or column for the extracting section and another separate unit for the washing section. This follows because the density of orthodichlorobenzene (1.30 at 20° C) lies between the densities of dissolver solution and of the acid scrub. However, since the total number of contacting stages required would not be increased by dividing the column, this requirement is considered incidental.

A qualitative explanation of the observed solvent behavior is afforded by the solubility parameter first defined by Hildebrand.⁷ The solubility of the chelate would be expected to decrease as the difference between its solubility parameter and that of the solvent increased. This suggests that the parameter for the chelate is probably in the range 9.2 to 9.6.

PROCESS ALTERNATIVES

There are two ways in which the chelate process may be operated. One is to remove the plutonium from the dissolver solution containing uranium; the other is to remove the uranium first and then to separate plutonium from the fission products. The detailed conditions for plutonium recovery are somewhat different in these two cases, and will be referred to as Process A and Process B, respectively. In either case, the removal of uranium is accomplished by some other process such as a solvent extraction process using pentaether or a solution of tributylphosphate, or in Process B, by non-aqueous fluorination. However, the calculations presented here for process B assume a preceding solvent extraction process using nitric acid as the salting agent.

The appended drawing of Process A shows all equipment and the composition of all streams connected with the purification of plutonium by extraction from dissolver solution, based upon one metric ton per day of irradiated uranium. If a solvent with the density of ortho-dichlorobenzene is used, the first column will have to be split at the center feed point, as discussed previously.

The drawing of Process B shows all equipment and the composition of all streams connected with the purification of plutonium by extraction from a solution from which uranium has already been extracted.

The feed to Process B is much higher in HNO_3 concentration than the feed to Process A, because of the acid requirements for the uranium-extraction step. As a result, the TTA concentration and the relative volume of organic phase are both much larger in Process B, and a proportionately larger column will also be required. Therefore, from the standpoint of plutonium extraction, Process A would be preferred. Should dry fluorination be used, Process B would be modified considerably.

PROCESS DESCRIPTION

The main decision to be made in connection with this plant design concerns the type of contacting equipment to be used. The TTA process is considered workable with packed columns, pulse columns, or mixer-settlers. The choice of the contacting equipment is dependent upon expense, size necessary for a given separation, and ease of operation. It is believed that these advantages can be best attained by the use of vertical mixer-settlers of the McKittrick type shown in Part I of this dissertation UCRL-1013. This unit is relatively inexpensive, is easy to assemble, and should be free from operating difficulties.

Due to the use of HNO_3 and TTA, all equipment connected with the plant must be made of stainless steel and Teflon.

In column I of Process A, two extra mixing chambers are added to the extracting section in order to contact the leaving fission products and uranium with fresh solvent. This serves to lower the TTA concentration in the aqueous phase, in order to reduce TTA losses, and to prevent build-up

of TTA in the organic phase of the following process for extracting uranium.

In order to recover the organic solvent and TTA used in the plutonium purification steps, an extraction with 0.5M $\text{Na}_2\text{C}_2\text{O}_4$ in HNO_3 is necessary to remove the zirconium from the organic stream leaving column II. After the oxalate extraction, a water wash removes traces of oxalate remaining entrained in the organic solvent. The solvent then goes to storage tanks. Two distillation columns for the purification of the solvent and the TTA at the end of each cycle are included. It should prove possible to recycle the TTA solution without distillation, in which case the columns will be reserved for occasional use.

Calculations indicate about six feet of concrete would be necessary for shielding all concentrated fission product streams. The activity assumed for the solution was 6×10^5 curies of beta and 10^5 curies of gamma. It was further assumed that the average gamma energy was 1 Mev.

CALCULATIONS

Plutonium separation and recovery were calculated for various conditions of mixer-settler operation, assuming volumes per stage of 14.2 liters in process A and 21.2 liters in process B. The method of calculation may be found in a later section. The equations used indicate that the aqueous holdup per stage is an important variable in plutonium chelate extraction. Accordingly, calculations were made for Column I, process A, with aqueous holdup volumes of 25, 50, and 75 percent of the total stage volume.

The following tables give the calculations made to determine the number of mixer-settler stages required for plutonium separation, based on a recovery of at least 99.99% of the plutonium.

Shown in Fig. I is a plot of residence time of the aqueous phase versus the number of mixing stages required in the extraction section to remove greater than 99.99 percent of the plutonium from the aqueous phase. It can be seen that the aqueous/organic phase ratio in each mixing chamber should be set as high as possible, subject to requirements for good mixing.

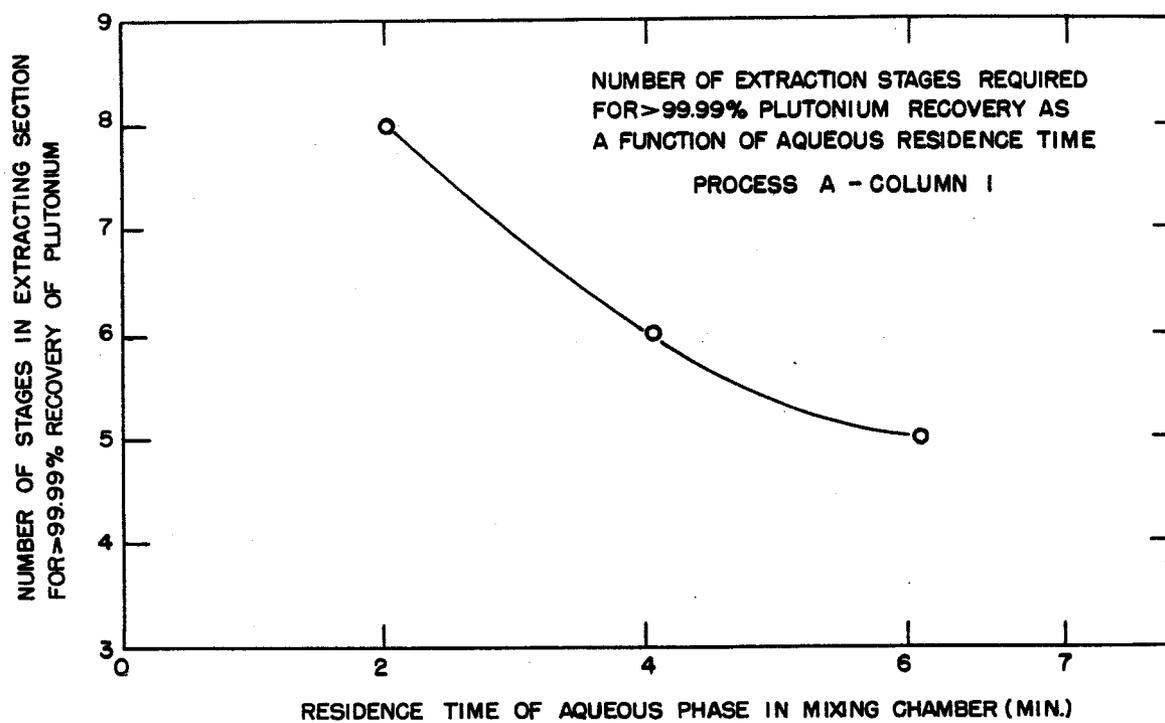


FIG. 1

MU 1317

TABLE IIA

Process A - Column I

Summary of Calculations, Based on Equation (18)

Aqueous Volume per Mixing Stage (V_a) = 10640 ml. = 75% of Mixing Stage Volume

Stage No.	Pu conc. in Organic Phase, M x 10 ⁵	Org./Aq. Equilib., e	C _{k-1} (b)	E _k (c)	Pu conc. in Aqueous Phase, M x 10 ⁵	Pu Leaving In Aqueous Moles/Min x 10 ⁵	Pu Entering in Organic Moles/min x 10 ⁵
1	275(a)	1.20	∞	1.39	198	52	197
2	374	1.20	1.89	1.27	295	77.5	222
3	421	1.20	1.43	1.24	341	89.7	234
4	444	1.20	1.30	1.22	363	95.2	240
5	455	1.20	1.26	1.22	374	98.1	243
6	461	1.30	1.23	12.9	35.7	62.3	62.3
7	118	1.30	3.31	30.0	3.93	6.85	6.85
8	130	1.30	3.31	30.0	0.433	0.755	0.755
9	1.43	1.30	3.31	30.0	0.048	0.0837	0.0837
10	0.16	1.30	3.31	30.0	0.005	0.00925	0.00925

UCRL-1032

a This value was given by the conditions assumed

b Concentration in organic phase divided by concentration in entering aqueous phase. C_{k-1} is used in equation (18) instead of C_k + 1, because of reverse numbering of the stages

c Ratio of actual conc in Organic phase to conc in Aqueous phase

TABLE IIB

Process A - Column I

Flow Diagram Showing Concentrations and Transfer Between Stages

Aqueous Volume per Mixing Stage (V_a) = 10640 ml. = 75% of Mixing Stage Volume

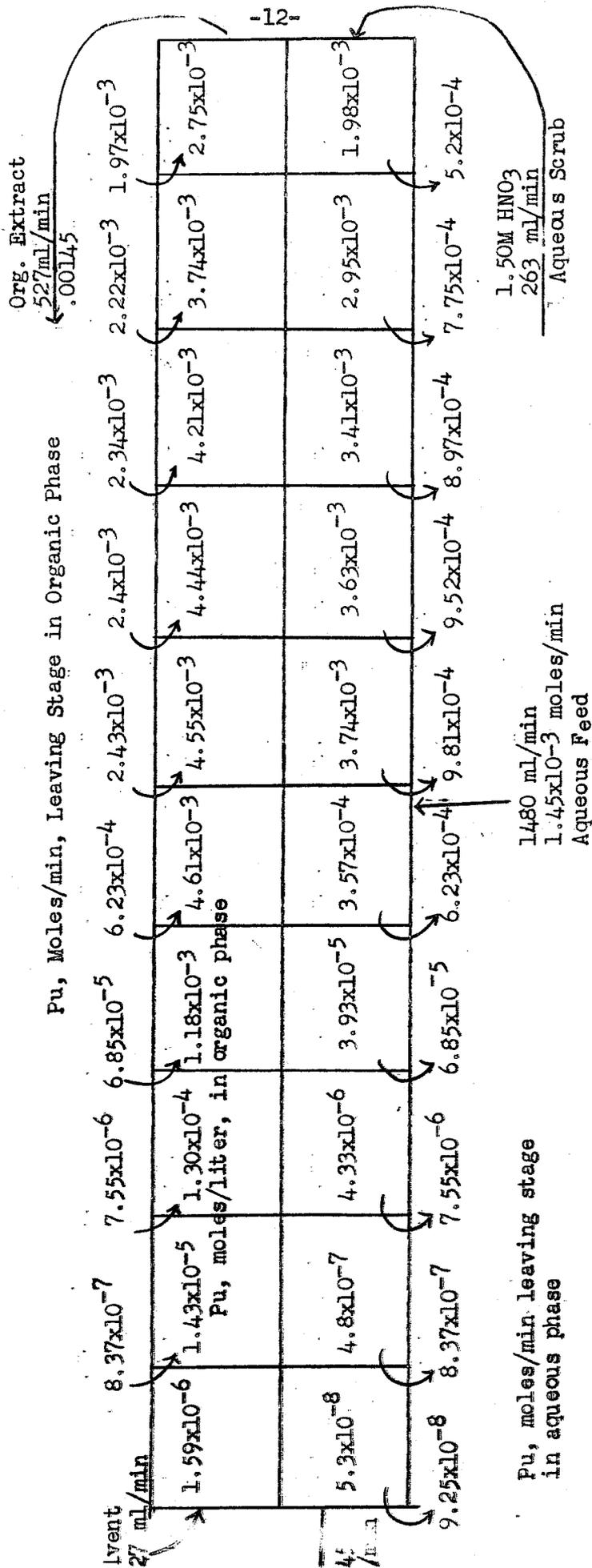
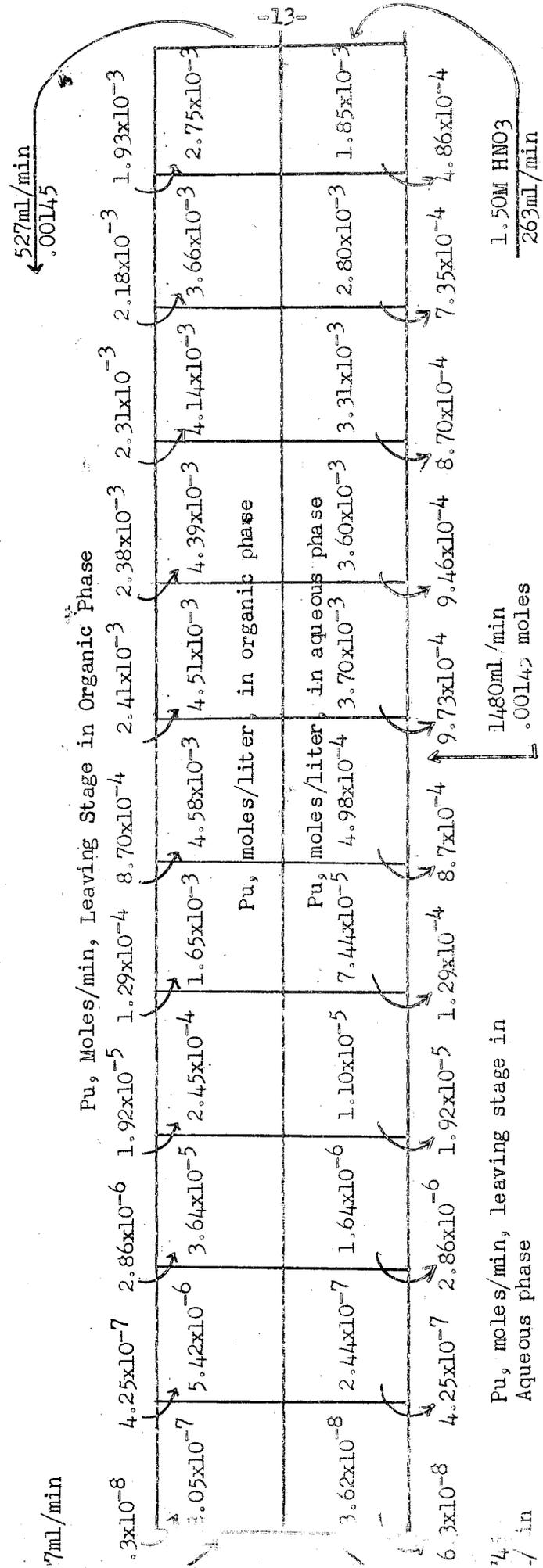


TABLE III

Process A - Column I

Flow Diagram and Summary of Calculations

Aqueous Volume per Mixing Stage (V_a) = 7090 ml = 50% of Mixing Stage Volume.



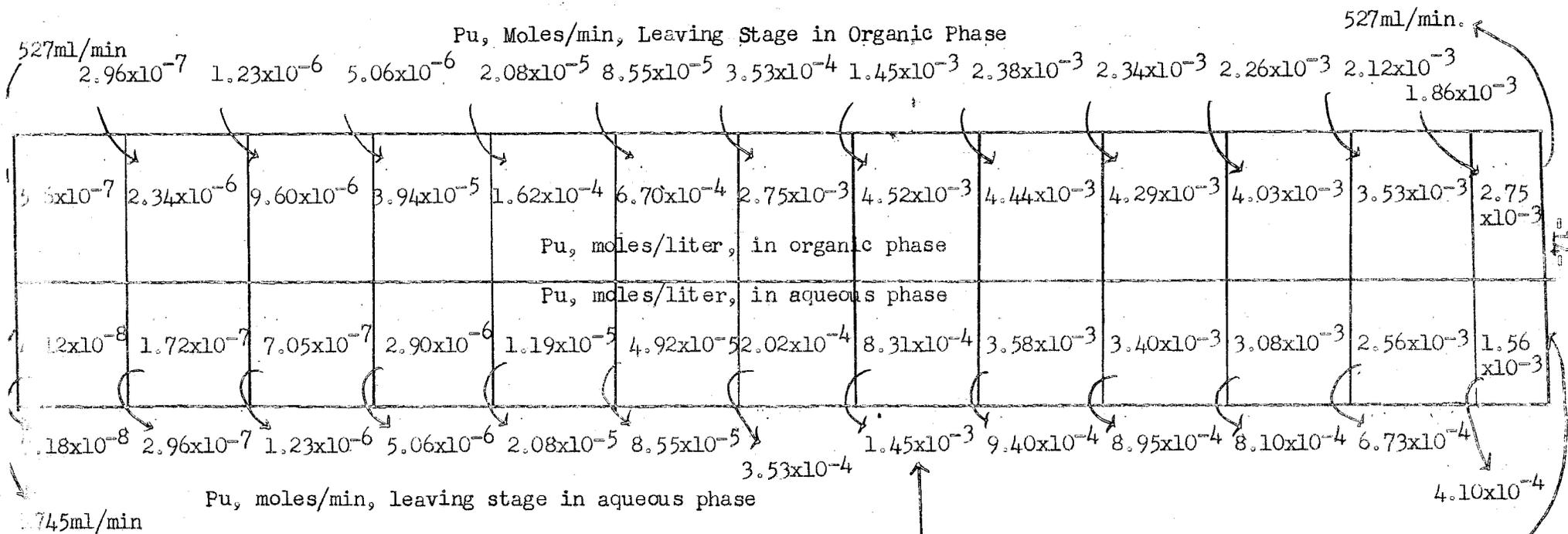
Stage	11	10	9	8	7	6	5	4	3	2	1
Pu, moles/min, leaving stage in Aqueous phase	22.2	22.2	22.2	22.2	1.30	1.30	1.20	1.20	1.20	1.20	1.20
Pu, moles/liter, leaving stage in Aqueous phase	4.25x10 ⁻⁸	5.42x10 ⁻⁷	3.64x10 ⁻⁶	2.45x10 ⁻⁵	1.65x10 ⁻³	4.58x10 ⁻³	4.51x10 ⁻³	4.39x10 ⁻³	4.14x10 ⁻³	3.66x10 ⁻³	2.75x10 ⁻³
Pu, moles/liter, in organic phase	3.62x10 ⁻⁸	2.44x10 ⁻⁷	1.64x10 ⁻⁶	1.10x10 ⁻⁵	7.44x10 ⁻⁵	4.98x10 ⁻⁴	3.70x10 ⁻³	3.60x10 ⁻³	3.31x10 ⁻³	2.80x10 ⁻³	1.85x10 ⁻³
Pu, moles/liter, in aqueous phase	6.3x10 ⁻⁸	4.25x10 ⁻⁷	2.86x10 ⁻⁶	1.92x10 ⁻⁵	1.29x10 ⁻⁴	8.7x10 ⁻⁴	9.73x10 ⁻⁴	9.46x10 ⁻⁴	8.70x10 ⁻⁴	7.35x10 ⁻⁴	4.86x10 ⁻⁴
Flow Rate (ml/min)	3x10 ⁻⁸	527	1480	263	527	1480	263	527	1480	263	527

TABLE IV

Process A - Column I

Flow Diagram and Summary of Calculations

Aqueous Volume per Stage (V_a) = 3540 ml = 25% of Mixing Stage Volume



Stage No.	13	12	11	10	9	8	7	6	5	4	3	2	1
ϵ	130	130	130	130	130	130	130	130	1.20	1.20	1.20	1.20	1.20
E_k	13.6	13.6	13.6	13.6	13.6	13.6	13.6	5.44	1.24	1.26	1.31	1.38	1.76

TABLE VA

Process A - Column II

Summary of Calculations, Based on Equation (17)^aAqueous Volume per Mixing Stage (V_a) = 7090 ml. = 50% of Mixing Stage Volume

Stage No.	Pu conc. in Aqueous Phase $\underline{M \times 10^4}$	$\underline{C_c^k}$ (c)	$\underline{E_c^k}$ (d) ^k	Pu conc. in Organic Phase $\underline{M \times 10^6}$	Pu Leaving in Organic, Moles/ min $\times 10^6$	Pu Entering in Aqueous, Moles/min $\times 10^6$
1	230 ^b	0	.00897	206	10.8	1460
2	232	.00888	.00897	208	10.9	1460
3	232	.00888	.00897	208	10.9	1460
4	232	.00888	.00897	208	10.9	1460
5	232	.00888	.00897	208	10.9	1460
	232	.00888	.00900	209	121	121
7	19.2	.109	.0140	26.8	15.0	15.0
8	2.38	.109	.0141	3.36	1.95	1.95
9	0.309	.109	.0140	0.433	0.25	0.250
10	0.0397	.109	.0140	0.0556	0.0322	0.0322

a Organic/aqueous equilibrium ratio $\epsilon = .009$

b Given by the conditions assumed for one calculation

c Concentration in organic phase, divided by concentration in entering aqueous phase

d Ratio of actual concentration in organic phase to concentration in aqueous phase

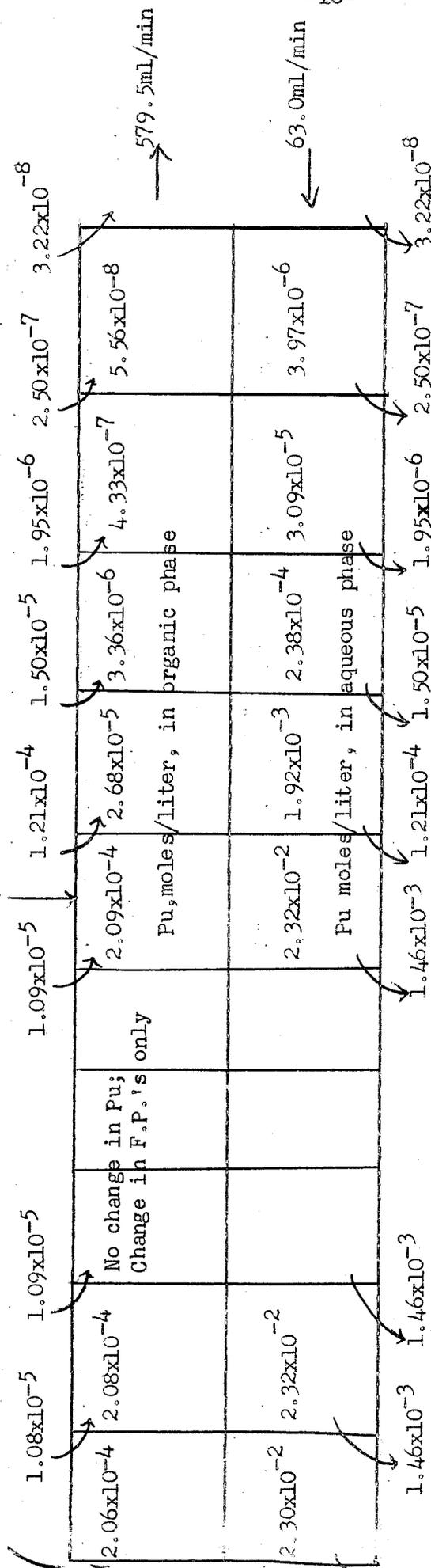
TABLE VB

Process A - Column II

Flow Diagram Showing Concentrations and Transfer Between Stages

Aqueous Volume per Stage (V_a) = 7090. ml = 50% of Mixing Stage Volume

org. 52.5ml/min
 1.45×10^{-3} Pu, Moles/min, Leaving Stage in Organic Phase
 527 ml/min



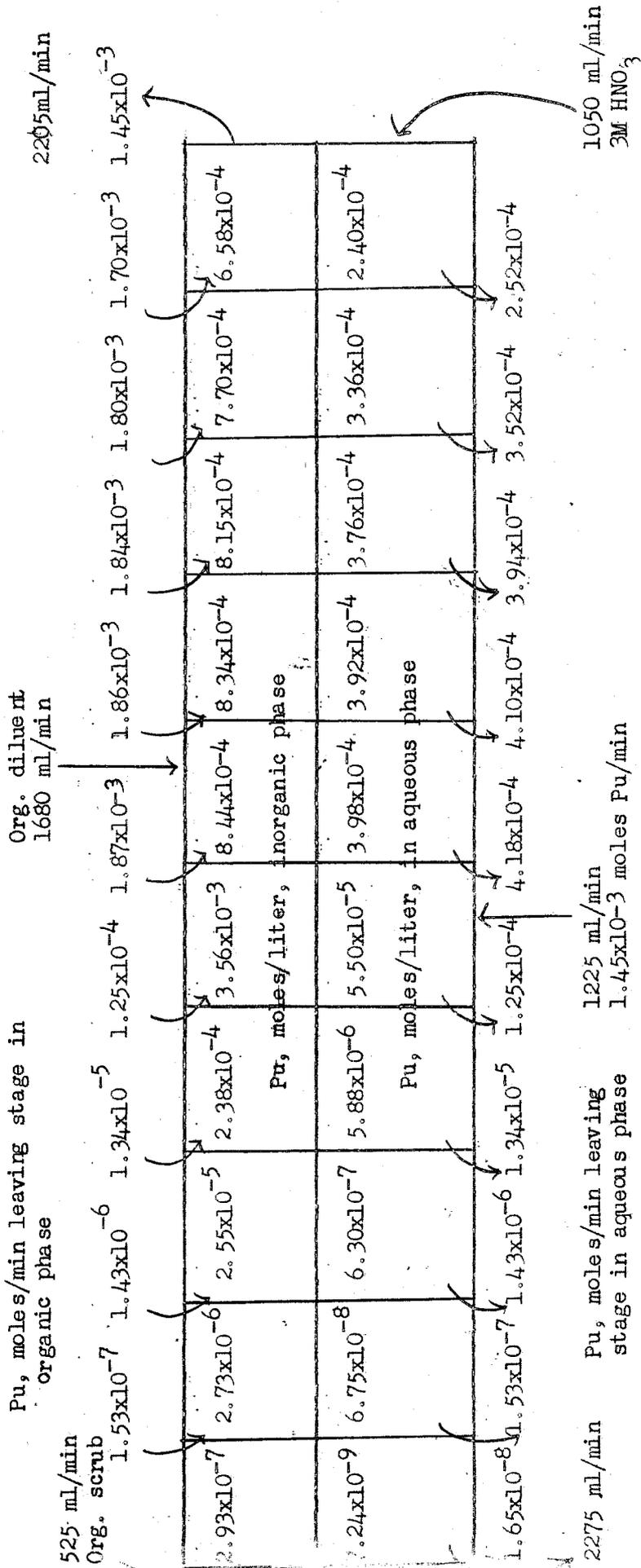
63.0 ml/min
 1.45×10^{-3} moles/min Pu, moles/min leaving stage in aqueous phase

TABLE VI

Process B - Column I

Flow Diagram Showing Concentrations and Transfer Between Stages

Aqueous Volume per Stage (V_a) = 15,900 cc = 75% of Mixing Stage Volume



Stage No.

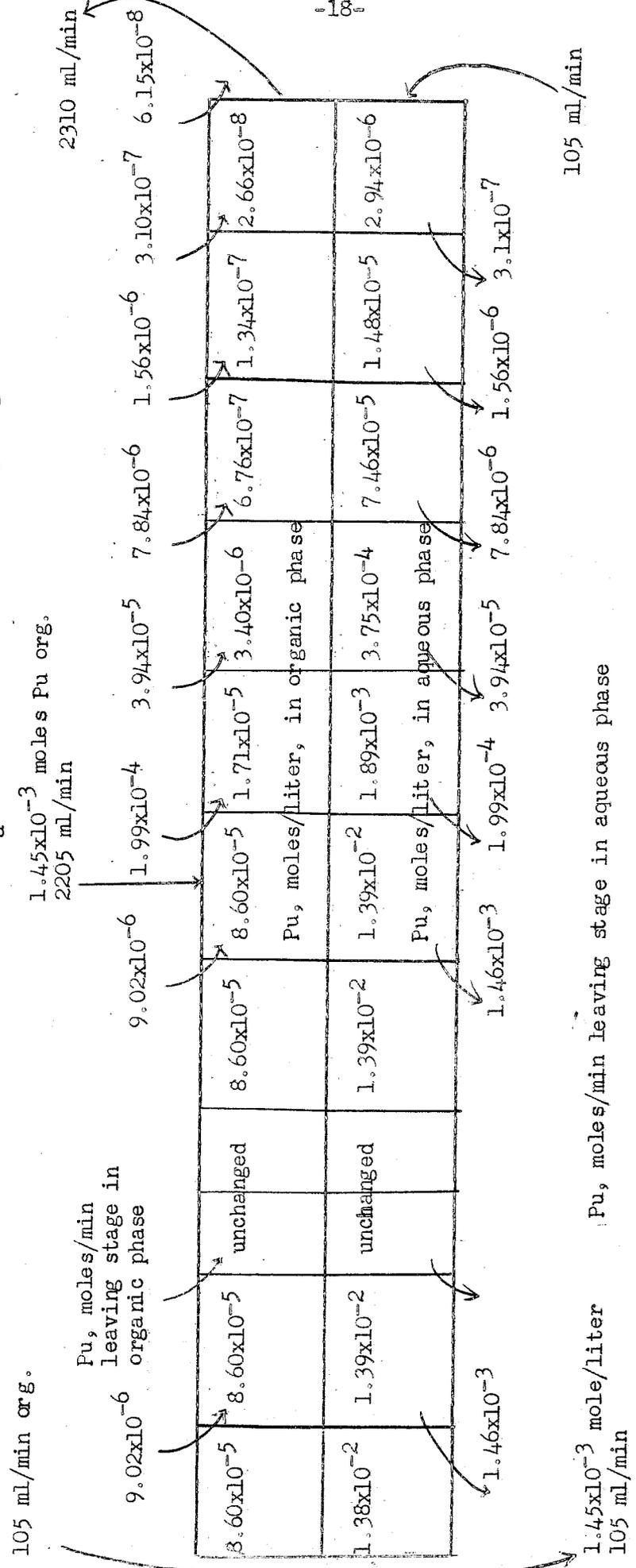
10	133.5	40.5	40.5	2.12	2.13	2.17	2.29	2.74
9	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
8	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
7	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
6	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
5	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
4	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
3	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
2	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10
1	133.5	40.5	40.5	2.10	2.10	2.10	2.10	2.10

TABLE VII

Process B - Column II

Flow Diagram Showing Concentrations and Transfer Between Stages

Aqueous Volume per Mixing Stage (V_a) = 15,900 cc = 75% of Mixing Stage Volume



Stage No.	1	2	3	4	5	6	7	8	9	10	11
E_k	.00624	.00624	.00624	.00624	.00624	.00624	.00905	.00905	.00905	.00905	.00905

$\epsilon = .00620$ throughout

CALCULATION METHOD

The equations for calculating the number of stages required for 99.9 percent recovery of plutonium in mixer-settlers are reproduced here from UCRL-400.

At steady state in any mixing chamber

$$dE/dt = (\partial E/\partial t)_{\text{flow rate}} = 0 + (\partial E/\partial t)_{\text{mass transfer}} = 0 = 0 \quad (1)$$

where $E = Y/X$ ($X =$ moles of plutonium per liter of aqueous phase and $Y =$ moles of plutonium per liter of organic phase) and $t =$ time in min.

$$\text{Therefore } (\partial E/\partial t)_{\text{f.r.}} = 0 = (1/X)(\partial Y/\partial t)_{\text{f.r.}} = 0 - (E/X)(\partial X/\partial t)_{\text{f.r.}} = 0 \quad (2)$$

and since

$$X + \rho Y = \text{const.} \quad (3)$$

where $\rho =$ the volume of organic phase divided by the volume of aqueous phase

$$(\partial X/\partial t)_{\text{f.r.}} = 0 + \rho (\partial Y/\partial t)_{\text{f.r.}} = 0 \quad (4)$$

Therefore

$$(\partial E/\partial t)_{\text{f.r.}} = 0 = \frac{1 + \rho E}{X} (\partial Y/\partial t)_{\text{f.r.}} = 0 \quad (5)$$

Next consider A ml/min. of an aqueous solution of plutonium entering and leaving a mixer containing V_a ml. of aqueous phase, and at the same time B ml/min of an organic solution of plutonium entering and leaving the same mixer containing V_b ml of the organic phase. Let this be the k th mixer with X_k moles/liter of plutonium in the aqueous phase of the mixer; since this phase is homogeneous, substantially perfect mixing is obtained, and the average composition of this entire phase will be the same as that of the portion leaving the mixer.

Let the entering aqueous phase containing $X_k + 1$ moles/liter of plutonium, and the entering organic phase contain $Y_k - 1$ moles/liter of plutonium; while the organic phase in the stage and in the exiting organic stream contain Y_k moles/liter of plutonium. This mixer is one stage of a mixer-settler.

Under steady-state conditions the amount of plutonium in the stage does not change, therefore the amount entering the stage must equal the amount leaving the stage. That is

$$AX_k + 1 + BY_k - 1 = AX_k + BY_k \quad (6)$$

$$\text{Since } E_k = Y_k/X_k$$

$$(\partial E_k / \partial t)_{m.t.} = 0 = (1/X_k)(\partial Y_k / \partial t)_{m.t.} = 0 - (E_k/X_k)(\partial X_k / \partial t)_{m.t.} = 0 \quad (7)$$

but

$$(\partial Y_k / \partial t)_{m.t.} = 0 = (B/V_b)(Y_{k-1} - Y_k) \quad (8)$$

$$\text{and } (\partial X_k / \partial t)_{m.t.} = 0 = (A/V_a)(X_k + 1 - X_k) \quad (9)$$

$$\begin{aligned} &= (B/V_a)(Y_k - Y_{k-1}) \\ &= -(\rho)(B/V_b)(Y_{k-1} - Y_k) \end{aligned} \quad (10)$$

Therefore substituting eq. (8) and eq. (10) in eq. (7) gives

$$(\partial E_k / \partial t)_{m.t.} = 0 = (B/V_b)(1 + \rho E_k)(Y_{k-1} - Y_k/X_k) \quad (11)$$

$$= (B/V_b)(1 + \rho E_k)(C_k - E_k) \quad (12)$$

$$\text{where } C_k = Y_{k-1}/X_k \quad (13)$$

Substituting eq. (12) and eq. (5) in eq. (1) gives

$$(1 + \rho E_k/X_k)(\partial Y_k / \partial t)_{f.r.} = 0 + (B/V_b)(1 + \rho E_k)(C_k - E_k) = 0 \quad (14)$$

$$\text{or } (1/X_k)(\partial E_k / \partial t)_{f.r.} = 0 = (B/V_b)(E_k - C_k) \quad (15)$$

This expression is applicable for the distribution of any component between immiscible solvents in any one extracting stage, and it is not necessary that the exact mechanism for extraction be known. In order to apply it, it is only necessary that a single mixer, similar to the one

to be used in the continuous apparatus, be built, and batch extractions performed to follow the transfer between the two phases of the element under consideration as a function of time and total concentration level.

The application of these equations to a particular system requires experimental data concerning the rate of transfer between phases. For the plutonium system Crandall and Thomas developed the following equation for the rate of extraction between 0.5M HNO₃ and benzene.

$$dY/dt = k_1 \frac{X}{\rho} (TTA/H^+)^2 = k_2 \frac{Y}{\rho} (H^+/TTA)^2 \quad (16)$$

$$k_1 = 185 \text{ min}^{-1}$$

$$k_2 = 1.24 \times 10^{-4} \text{ min}^{-1}$$

Y = plutonium conc in benzene phase

X = plutonium conc in aqueous phase

ρ = volume of organic phase divided by volume of aqueous phase

t = time

TTA = conc. of TTA in benzene

H⁺ = conc. of H⁺ ion in aqueous

By combining equations (16) and (15) Hicks developed an equation for the calculation of the dynamic equilibrium coefficient E_k.

$$E_k = \frac{.15V_a \sqrt{\epsilon} + B_k C_k}{.15V_a + B_k} \quad (17)$$

$$\text{or } E_k = \frac{.15 V_a \sqrt{\epsilon} + A_k}{.15 V_a + A_k/C_k + 1} \quad (18)$$

V_a = volume of aqueous phase in mixing chamber, ml

A_k = aqueous flow rate ml/min

B_k = organic flow rate, ml/min

$\epsilon = \left[\frac{4.6 \times 10^6}{(1 + 5(\text{NO}_3^-) + 10(\text{NO}_3^-)^2)} \right] \left(\frac{\text{HK}}{\text{H}^+} \right)^4$ = equilibrium constant for plutonium TTA system in benzene or CCl_4 and aqueous nitrates

$$C_k = \frac{Y_{k-1}}{X_k}$$

$$C_{k+1} = Y_k / X_{k+1}$$

These equations seem to give fair accuracy for high stirring speeds so they were used to make the calculations necessary to size the vertical mixer settlers.

Recent work on plutonium extraction by Doris Heisig has shown that the rate of extraction is diffusion controlled and therefore a function of stirring speed. This indicates that the values of k_1 and k_2 obtained by Crandall and Thomas are not strictly valid at different stirring speeds and in mixing chambers of different sizes and shapes. In order to make accurate calculations, a value for k_1 and k_2 must be determined for each case experimentally. If k_1 and k_2 were determined in this way the calculation to determine the number of mixing stages for a given separation would be quite accurate. Since the values of k_1 and k_2 used to size the large mixer settlers were determined in a small stirring chamber with high speed stirring the number of mixing stages arrived at for the large units must be regarded as a rough approximation to the truth.

OPERATING VARIABLES

The conditions chosen in Process A and B for the separation of plutonium are merely one possible combination among many that will work. In column I the flow rate of organic phase has been set at a value near that given by the solubility of $\text{Pu}(\text{TTA})_4$. The ER product in the washing or scrub section was chosen in order to prevent a large buildup of plutonium in the center of the column, and thus to prevent precipitation of $\text{Pu}(\text{TTA})_4$. Likewise, the ER product in the extracting section is given by the conditions that avoid buildup of fission products. As the ER product depends upon both the HNO_3 and the TTA concentrations, these are taken as low as possible in order to give minimum material and processing costs.

The following discussion will be connected with Column I of Process A, but applies also to Process B.

FLOW RATES (Column I)

A decrease in the flow rate of dissolver solution to the center of the column would have the following effect:

The H^+ concentration in the extracting section will be raised, lowering the E and raising the plutonium concentration in the waste stream of fission products.

An increase in the flow rate of dissolver solution would have the opposite effect.

An increase in the feed rate of 1.5M HNO_3 scrub would have the following effects:

(a) The only effect in the washing section is a decrease in the R which lowers the ER and therefore increases the reflux of plutonium in the column. If the concentration of $\text{Pu}(\text{TTA})_4$ is close to the saturation

limit, this could cause precipitation of the plutonium chelate.

(b) In the extraction section the H^+ concentration will be increased thus decreasing the E and increasing the plutonium lost in the waste stream with the fission products.

A decrease in the feed rate of 1.5M HNO_3 would have the opposite effect.

An increase in the organic-TTA feed would have the following effects:

(a) It would increase the R in the extracting section which would decrease the amount of plutonium lost with the fission products.

(b) It would increase the R in the washing section decreasing the reflux of plutonium but at the same time decreasing the separation from elements below plutonium.

A decrease in the organic TTA feed would have the opposite effect.

CONCENTRATIONS (COLUMN I)

An increase in the acid concentration entering in the dissolver solution will have the following effect:

It will increase the acid concentration in the extracting section lowering the E, allowing more plutonium to leave with the fission products.

A decrease in the acid concentration will have the opposite effect.

An increase in the acid scrub concentration will have the following effects:

(a) It will lower the E in the washing section increasing the reflux of plutonium and thus increasing the plutonium concentration in the center of the column.

(b) It will lower the E in the extraction section increasing the amount of plutonium leaving with the fission products.

A decrease in the acid scrub concentration will have the opposite effect.

An increase in the TTA concentration in the organic extractant will have the following effects.

(a) It will increase the E in the extracting section lowering the amount of plutonium lost with the fission products.

(b) It will raise the E in the washing section decreasing the plutonium reflux.

A decrease in the TTA concentration will have the opposite effect.

The following discussion will be connected with column II of Plant I.

FLOW RATES (COLUMN II)

A decrease in the flow rate of organic-TTA solution containing $\text{Pu}(\text{TTA})_4$ and $\text{Zr}(\text{TTA})_4$ to the center of column II will have the following effect:

The R in the extracting section will be lowered causing a decrease in the amount of plutonium lost with the zirconium in the organic stream but an increase in the zirconium reflux.

An increase in the flow rate of organic-TTA to the center of column II will have the following effect:

The R in the extracting section will be increased causing an increase in the amount of plutonium lost in the organic stream.

An increase in the flow rate of organic-TTA scrub will have the following results:

(a) In the washing section the R will be increased causing an increase in the plutonium reflux but a decrease in the zirconium leaving in the aqueous stream with the plutonium.

(c) In the extracting section the change in R will be almost negligible because of the large center feed rate.

A decrease in the organic-TTA scrub will have the following effect:

(a) The R will be decreased in the washing section which will reduce plutonium reflux and increase the zirconium impurity in the aqueous discharge although this will still be very small.

(b) There will be essentially no effect on the extracting section.

An increase in the HNO₃ flow rate will have the following effects:

(a) The R will be decreased in the extracting section decreasing the plutonium lost in the organic stream at the bottom and increasing the zirconium reflux.

(b) The R will be decreased in the washing section thus decreasing the reflux of plutonium.

A decrease in the HNO₃ flow rate will have the following effects:

(a) The R will be increased in the extracting section thus increasing the amount of plutonium lost in the organic stream and decreasing the zirconium reflux.

(b) The R will be increased in the washing section thus increasing the reflux of plutonium.

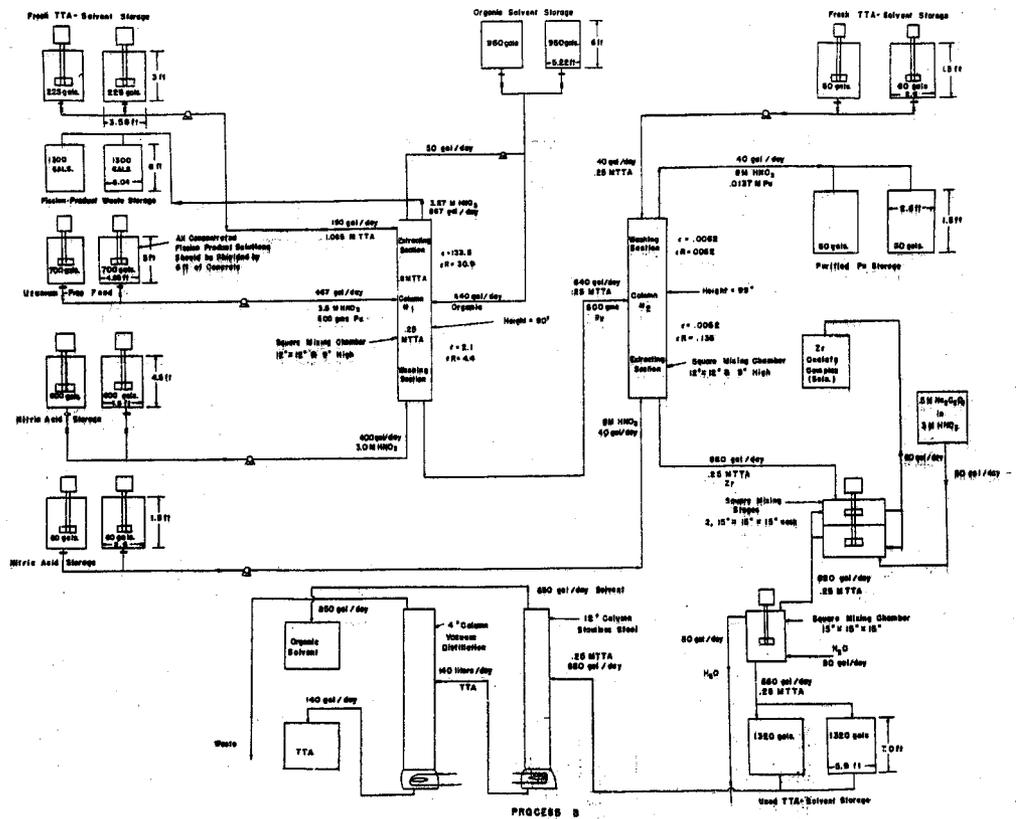
CONCENTRATIONS (COLUMN II)

An increase in the TTA concentration of the scrub would have the same effect in the washing section as increasing the flow rate except the magnitude of change would be greater. This is also true of the extraction section where the E will be increased, tending to increase the amount of plutonium lost in the organic discharge.

A decrease in the TTA concentration of the scrub will decrease the E in the washing section, decreasing the plutonium reflux.

SUMMARY

Comparative studies of a series of halogenated solvents, as carriers for TTA in the chelate process for plutonium extraction, indicate that ortho-dichlorobenzene most nearly satisfies the requirements that are set forth. A complete process design is presented for use with this solvent, and flow data and equipment capacities are given for dissolver solution and for uranium-free fission product solution as alternate feeds to the process. Vertical mixer-settlers are recommended as the contractors, although pulsed columns or packed columns are also believed to be suitable. The size of such units is estimated from the best available rate and equilibrium data, and the effects of several operating variables are considered.



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