

AERE - R 4440
Part 3

REF 29103

UNCLASSIFIED

AERE - R 4440
Part 3

MASTER



United Kingdom Atomic Energy Authority
RESEARCH GROUP
Report

REPROCESSING WITH AMINE ETHER SYSTEMS
Part 3 Counter-Current Trials With
ALAMINE 336 - DIBUTYL CELLOSOLVE

R. J. W. STREETON M. J. HOLDOWAY

Chemistry Division,

Atomic Energy Research Establishment,
Harwell, Berkshire.

1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Available from H. M. Stationery Office
PRICE FOUR SHILLINGS NET

(C) - UNITED KINGDOM ATOMIC ENERGY AUTHORITY - 1965
Enquiries about copyright and reproduction should be addressed to the
Scientific Administration Office, Atomic Energy Research Establishment,
Harwell, Didcot, Berkshire, England.

U.D.C.
621.039.59

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

REPROCESSING WITH AMINE ETHER SYSTEMS

PART 3 COUNTER-CURRENT TRIALS WITH ALAMINE 336 - DIBUTYL CELLOSOLVE

by

R. J. W. Streeton
M. J. Holdoway

ABSTRACT

15% (0.30M) Alamine 336/DBC has been tested in the reprocessing of fast reactor fuel (75% uranium; 25% plutonium), for the separation of plutonium from uranium and fission products. Miniature mixer-settler runs, using either uranium(IV) as a stand-in for plutonium, or plutonium(IV) have been carried out. Good separations of uranium(IV) and uranium (VI) can be achieved, without using excessive volumes of solvent and scrub, because concentrations up to 16-17 g uranium (IV)/l in the amine phase can be obtained. With plutonium(IV), however, owing to formation of a third phase, the limiting concentration in the amine phase is only 10.5 g plutonium(IV)/l, which is rather low for a satisfactory flowsheet. The behaviour of zirconium/niobium and ruthenium was investigated, and it has been found for ruthenium that only the tetraniitroso nitrosylruthenium cannot be scrubbed out of the solvent. Decontamination factors of 240 and 42 have been obtained for zirconium/niobium and ruthenium respectively.

Backwashing of uranium(IV) or plutonium(IV) from the amine phase was satisfactorily carried out with 1M acetic acid containing 0.05M HNO_3 . The solvent was reconditioned by contacting it with 1M HNO_3 .

Chemistry Division,
U.K.A.E.A. Research Group,
Atomic Energy Research Establishment,
HARWELL

August, 1965

/DB.

HL65/4365

(C.6)

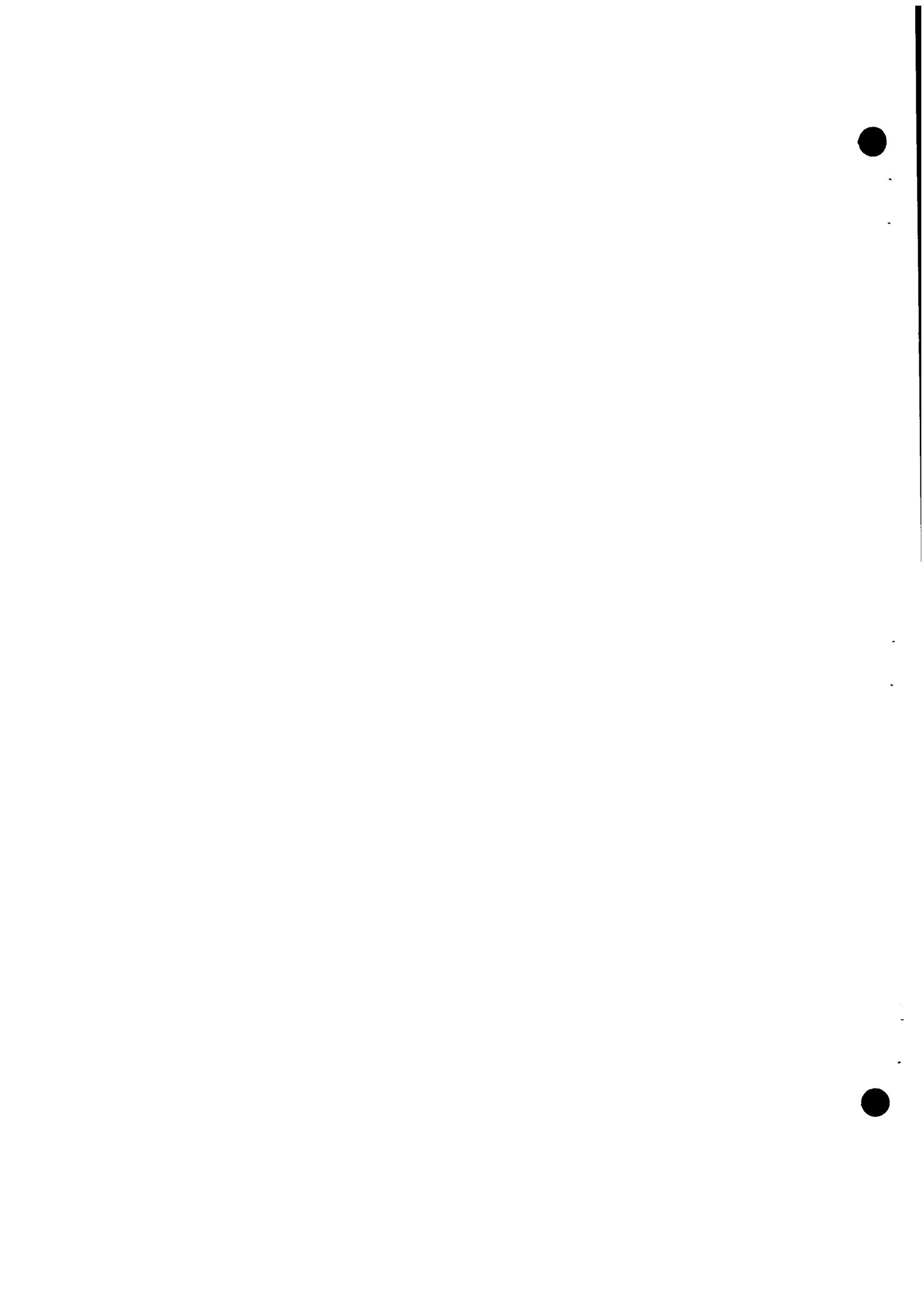
CONTENTS

	<u>Page</u>
1. Introduction	1
2. Experimental	1
2.1 Materials	1
2.2 Apparatus	2
2.3 Analysis	2
3. Results of Runs	2
3.1 Run AD1	3
3.2 Run AD2	3
3.3 Run AD3	3
3.4 Run AD4	3
3.5 Run AD5	4
3.6 Run AD6	4
3.7 Run AD7	4
4. Discussion	5
4.1 Behaviour of Uranium in Contactor I	5
4.2 Behaviour of Ruthenium in Contactor I	5
4.3 Behaviour of Zirconium/Niobium in Contactor I	6
4.4 Behaviour of Plutonium in Contactor I	6
4.5 Behaviour of Uranium(IV) and Plutonium(IV) in Contactor II	7
4.6 Behaviour of Acetic Acid in Contactor III	7
5. Conclusions	7
Acknowledgements	7
References	8
 <u>APPENDIX</u>	
Behaviour of Ruthenium in the Amine Phase	9

ILLUSTRATIONS

Fig.

1. Process Layout
2. The Partition of U(IV) and Pu(IV) between 1M HNO₃ and 15% Alamine 336/DBC
3. Run AD1 Concentration Profiles
4. Run AD2 Concentration Profiles of U(IV) in Contactor I
5. Run AD2 Concentration Profiles of U(VI) in Contactor I
6. Run AD2 Concentration Profiles of U(IV) in Contactor II
7. Run AD3 Concentration Profiles of U(IV) in Contactor I
8. Run AD3 Concentration Profiles of U(VI) in Contactor I
9. Run AD3 Concentration Profiles of U(IV) in Contactor II
10. Run AD4 Concentration Profiles of Acetic Acid and Nitric Acid in Contactor III
11. Run AD5 Concentration Profiles of U(IV) in Contactor I
12. Run AD5 Concentration Profiles of Ru in Contactor I
13. Run AD5 Concentration Profiles of Zr and Nb in Contactor I
14. The Distribution of Extractable Ruthenium Species vs Time of Stirring
- 15.



1. INTRODUCTION

The scheme described in Part 1¹ for processing irradiated fast reactor fuel elements with 15 vol. % Alamine 336 in dibutyl cellosolve (DBC) is shown diagrammatically in Fig. 1. No attempt has been made in this diagram to define volume ratios, concentrations or number of stages. These have been varied throughout the programme as experience has been gained; their optimum values are discussed below and in Parts 1 and 2.^{1,2}

In many of the runs in which uranyl and fission product concentration profiles were determined, uranium(IV) was used as a substitute for plutonium(IV). Such runs could be carried out without a glove box. Uranium(IV), although less strongly extracted than plutonium(IV) at low concentrations, loads the solvent to the same degree at high concentrations, and so gives essentially the same concentration profiles in the contactors.

2. EXPERIMENTAL

2.1 Materials

Dibutyl cellosolve was treated as described by Pilbeam³ to remove monobutyl cellosolve and peroxides. After Run AD3 this treatment was carried out within the 24 hours preceding the experiment. Alamine 336 was used as received and diluted to 15 vol % (0.3M) with DBC. Immediately before an experiment this solution was equilibrated three times with 1M HNO₃. Acetic acid, nitric acid, uranyl nitrate, hydrazine nitrate and water were all AnalaR reagents. All nitric acid used in experiments with uranium(IV) contained 10⁻² M hydrazine nitrate to destroy nitrous acid.

The uranium feed solutions for runs AD1, 2, 3 and 5 were prepared by the electrolytic reduction⁴ of a solution containing initially 200 g uranium(VI)/l in 1.4M HNO₃ such that the product had the following composition:-

$$U(IV) \sim 50 \text{ g/l}$$

$$U(VI) \sim 150 \text{ g/l}$$

$$HNO_3 \sim 1M$$

The uranium/plutonium feed solution for run AD6 was prepared by diluting a stock solution containing 300 g plutonium(IV)/l in 6M HNO₃ with uranyl nitrate solution to give a product of composition:-

$$Pu(IV) = 50 \text{ g/l}$$

$$U(VI) = 150 \text{ g/l}$$

$$HNO_3 \sim 1M$$

For run AD5, nitrato nitrosylruthenium (containing ¹⁰⁶Ru) complexes from R.C.C. Amersham were diluted with inactive ruthenium complexes in 1M

$\text{HNO}_3 + 1\text{M } \text{UO}_2(\text{NO}_3)_2$. This solution was refluxed with nitric oxide for 30 minutes and sparged with nitrogen while the refluxing continued for a further 15 minutes to remove nitrous acid; rapidly cooled; aged for 20 hours; and added to the feed. This treatment converts all the ruthenium to nitrato nitrosylruthenium complexes. Paper chromatographic tests⁵ carried out on this solution indicated that ~ 10% of the ruthenium was present as the tri- and tetranitrato (group D) complexes⁶.

For run AD5, ⁹⁵Zirconium oxalate from R.C.C. Amersham was fumed down six times with concentrated nitric acid and aged for one month. This material was found to contain 80% zirconium and 20% niobium (β counts) by paper chromatography⁷ and was made up to 1M HNO_3 and 1M $\text{UO}_2(\text{NO}_3)_2$ 20 hours before adding it to the feed.

2.2 Apparatus

The mixer settlers used were Mk I Wall⁸ machines with a stage volume of 12 ml (7 ml aqueous phase and 5 ml organic phase).

Feeds to the mixer settlers were metered by D.C.L. piston pumps, pumping from graduated vessels.

2.3 Analysis

The purity of the DBC was assessed by gas chromatography¹ and the molarity of the Alamine 336 was determined by non-aqueous titrimetry¹.

Quantitative analyses of uranium(IV) and total uranium were carried out spectrophotometrically as described by Streeton and Jenkins⁴. When uranium(VI) was present, the difference between the values for uranium(IV) and total uranium was taken as the value for uranium(VI).

Total plutonium was determined by α -counting and plutonium(III) by spectrophotometry.

Ruthenium and zirconium/niobium were determined by γ -spectrometry using a sodium iodide scintillator coupled through a photomultiplier to a LABEN 512 channel pulse analyser. The resolution of this detector is insufficient to distinguish between the energies of the γ -photons from ⁹⁵Zr and ⁹⁵Nb.

Analyses of acetic (HAc) and nitric acid mixtures were performed in the absence of uranium. The total acid concentration was obtained by direct aqueous titration. The nitric acid concentration was determined gravimetrically by precipitation as nitron nitrate and the acetic acid concentration obtained by difference.

3. RESULTS OF RUNS

Seven runs have been carried out, five using uranium(IV) and two using plutonium(IV). These were prefixed by AD (an abbreviation of Alamine 336/DBC). 15% Alamine/DBC and 1M HNO_3 (in both feed and scrub) were used

throughout. The runs are listed below.

<u>Run</u>	<u>Object</u>
AD1	Study of conditions in contactor I.
AD2	Study of conditions in contactors I and II.
AD3	Study of conditions in contactors I and II.
AD4	Study of conditions in contactor III.
AD5	Study of fission product behaviour in contactor I
AD6	Study of Pu behaviour in contactor I.
AD7	Study of Pu behaviour in contactor II.

3.1 Run AD1: This scouting run investigated the feasibility of using uranium(IV) as a substitute for plutonium(IV). A promising uranium(IV)/uranium(VI) separation was achieved (Fig. 3), in ten stages.

3.2 Run AD2: This run investigated the behaviour of uranium(IV) and uranium(VI) in contactors I and II. Feed concentrations and volumes are given in Figs. 4, 5 and 6. The apparatus was run for about 6 hours and then stopped. Each phase from alternate stages together with the feed stage of contactor I was sampled and analysed for uranium(IV) and total uranium. The results (Figs. 4, 5 and 6) show that whereas contactor I was operating satisfactorily, contactor II was not, and from the distribution of uranium(IV) at stage 10, could not be expected to do so at the flow ratio used.

3.3 AD3: This was a repeat of run AD2 but with the uranium(IV) feed concentration closer to the postulated plutonium(IV) value of 50 g/l and with the solvent/aqueous flow ratio (S/A) in contactor II = 1/1. The first hour's running showed that at the flow ratio solvent/aqueous feed $S/A_F = 2/1$ complete extraction of uranium(IV) was not being achieved. The solvent flow was therefore increased stepwise until good extraction was obtained at a flow ratio $S/A_F = 3/1$. Stage analyses were carried out as in run AD2 and the results are plotted in Figs. 7, 8 and 9.

Some retention of uranium(VI) was observed in the organic raffinate from contactor II, due to peroxides in DBC. (See section 2.1 above)

3.4 Run AD4: The purpose of this run was to test the backwash, in contactor III, of acetic acid from the organic raffinate, obtained as the mixed nitrate and acetate from contactor II. Preliminary work⁹ had shown that acetic acid had a partition coefficient of approximately 0.27 between 15% Alamine 336 nitrate/DBC and 1M HNO_3 . A McCabe-Thiele diagram indicated that at a flow ratio S/A = 1/1 the acetic acid concentration would be reduced to $2 \times 10^{-3} M$ in the solvent after four theoretical stages. This flow ratio was therefore adopted.

Contactor II uses 0.05M HNO₃, 1M HAc as the aqueous backwash solution, and in run AD3, yielded an organic raffinate which contained 0.34M HNO₃, 0.28M HAc. A solution of this composition was made up for run AD4 to avoid the presence of trace uranium and was contacted with 1.06M HNO₃ in nine stages. Fig. 10 shows that the concentration of acetic acid in the amine phase was easily reduced to the limits of detection.

3.5 Run AD5: This investigated the behaviour of fission product zirconium/niobium and ruthenium in contactor I. Runs AD2 and AD3 had shown that flow ratios solvent/aqueous feed/aqueous scrub ($S/A_F/A_S$) = 3/1/1, were satisfactory for the major components uranium(IV) and uranium(VI), so these values were adopted. Radioactive zirconium/niobium and ruthenium were added to the feed before the start of the run (see section 2.1). During the run, samples of solvent product were analysed by γ -spectrometry and at the termination of the run, samples of each phase from all stages were taken for γ analysis. Care was taken during sampling to avoid mixing of the phases, with attendant transfer of solute. Sufficient samples were taken and analysed for uranium(IV) and uranium(VI) to show that conditions were similar to those in run AD3. The results are plotted in Figs. 11, 12 and 13.

3.6 Run AD6: This run investigated the behaviour of plutonium(IV) in contactor I, and was intended to repeat run AD3 substituting plutonium(IV) for uranium(IV). The initial flow ratios were $S/A_F/A_S$ = 2.5/1/1, calculated to give a solvent product of 20 g plutonium(IV)/l. After 2 hours apparently satisfactory operation, a third phase was observed in the scrub section, although no third phase could be observed in the feed stage.

The run was stopped. The mixer settler was cleaned out and re-started using flow ratios $S/A_F/A_S$ = 3/1/1 (to give a solvent product of 16.6 g plutonium/l); this again formed a third phase. This procedure was repeated, with an increased solvent flow rate each time, until with flow ratios $S/A_F/A_S$ = 4.8/1/1 (giving a product containing 10.5 g plutonium/l), a satisfactory two phase system was obtained.

It was also observed that the aqueous raffinate was green, due to ~ 0.25 g plutonium(III)/l in this uranium stream.

3.7 Run AD7: Sufficient solvent product was obtained from run AD6 to study the backwash conditions in contactor II, using 1.0M HAc and 0.05M HNO₃. Eleven stages of the mixer settler were used for this experiment at a flow ratio S/A = 1/1. The plutonium concentration in the solvent was reduced from 10.5 g plutonium/l in the feed to 10⁻³ g plutonium/l in the raffinate.

4. DISCUSSION

4.1 Behaviour of Uranium in Contactor I

It is apparent both from the profiles and Fig. 2, that the organic phase will extract no more than 16-17 g uranium(IV)/l (i.e. 0.067M); this is true even at the feed stage in run AD3, where the aqueous concentration is 42 g uranium(IV)/l. Since the amine concentration is 0.3M, the maximum solvent loading with uranium(IV) appears to be 45% of the saturation value. However, reference to the concentration profiles for uranium(VI) shows that also at the feed stage, the solvent contains 39-47 g uranium(VI)/l (0.165-0.20M uranium(VI)), i.e. the additional solvent loading with uranium(VI) is 55%-65% of the saturation value. The apparent excess solvent loading over 100% is due to extraction of uranium(VI) by DBC. At 1M HNO₃, 11.5 g uranium(VI)/l is to be expected in DBC alone.¹

4.2 Behaviour of Ruthenium in Contactor I

The ruthenium concentration profiles for each phase are plotted in Fig. 12. It can be seen that there is no change in ruthenium concentration in the organic phase between stages 6 and 1, showing that 2.4% of the ruthenium is present as a species X with (from Stage 1) a distribution coefficient greater than 24. Subsequent measurements indicated a value of ~ 25 for this quantity (see Appendix). The presence of 2.4% of this species limited the possible overall DF_{Ru} to 42.

If the counts due to X are subtracted from the counts in the organic phase a straight line parallel to the aqueous profile between stages 6 and 10 is obtained (see Fig. 12). This line together with the aqueous profile over stages 1-10 indicates a species Y with a partition coefficient of 0.1-0.2 which is being effectively scrubbed from the amine phase. Extrapolation of the linear section of the aqueous profile to the feed stage indicates that the concentration of Y at the feed stage is 10% of that of ruthenium at this stage. A McCabe-Thiele diagram for a solute with distribution coefficient of 0.15 and the flow ratios used in this experiment indicates a 25% build up at the feed stage above the aqueous product. The percentage of species Y in the feed is therefore

$$10 \times \frac{100}{125} \times 2 = 16.$$

(The factor 2 corresponds to the dilution of the feed by the scrub.)

If the maximum overall distribution coefficient, which occurs at stages 19 and 20, is considered to be 0.11, then the remaining species Z, comprising ~ 81% of the total, has an average distribution coefficient of 0.04.

The species X and Y described above may be identified both by their partition coefficients and by the percentage composition as being the species D₄ and D₃ described by Scargill⁶.

4.3 Behaviour of Zirconium/Niobium in Contactor I

Zirconium and niobium cannot be treated separately for the reason discussed in section 2.3. However, the pattern is generally similar to that for ruthenium.

Reference to Fig. 13 shows that, as with ruthenium, there is a small amount (~ 0.4%) of a highly extractable species with a distribution coefficient > 6. A second species, ~ 4.5% of the feed, has a distribution coefficient of ~ 0.15, while the other 95% has a distribution coefficient of ~ 0.02. There appears to be a peak in the organic phase profile at stage 13, which may be an analytical error, as such a peak should have reflected a similar peak in the aqueous phase profile, at the same or adjacent stages. In any future run this section of the contactor should be examined for any sign of refluxing.

4.4 Behaviour of Plutonium in Contactor I

The unexpected formation of a third phase in the scrub section of contactor I during run AD6 is not completely understood. Pilbeam^{1,10} investigated third phase formation with solutions of thorium in 15% Alamine 336 in DBC, and showed that there exists a limiting concentration of free acid in the amine phase, above which no third phase formed. He also showed that below this limit there is a metastable region where the third phase is formed slowly or indistinctly. It is likely, therefore, that a similar situation exists in the plutonium(IV)/amine system, but to date, no further work to establish this has been carried out.

It seems probable that at concentrations of plutonium in amines above $\sim 10^{-2}$ M there is some aggregation of the plutonium(IV)/amine complex. In the limit this aggregation produces a third phase. The fact that no third phase was formed in the feed stage is in agreement with Allen's work¹¹. He has shown that, in a sulphate system, the presence of uranium(VI) causes deaggregation of the amine even at very low uranium concentrations.

Third phase formation in a mixer settler completely disrupts the normal flow pattern. The third phase, being denser than the remaining organic layer, sinks to the interface in the settlers and does not pass on to the next stage.

The later work on third phase formation in Part 1 indicates that an acidity of 2M would probably avoid this problem. The counter current trials were stopped before the third phase study was complete, but it is hoped to continue the investigation later.

The appearance of plutonium(III) in the contactor I aqueous raffinate can be ascribed to disproportionation of plutonium(IV). Rabideau¹² has shown that in 1M perchloric acid at 50 g plutonium(IV)/l, 1% of plutonium(III) will be formed in half an hour. Although the rate is slower in nitric acid, it is sufficiently fast to produce the observed 1% in the course of the

experiment. Rabideau also showed that the rate of disproportionation is inversely proportional to the cube of the perchloric acid concentration. Thus increasing the nitric acid concentration in contactor I, as suggested above, should reduce the disproportionation by a large factor.

4.5 Behaviour of Uranium(IV) and Plutonium(IV) in Contactor II

In part 2 of this paper,² it has been shown that the rate of backwash of plutonium(IV) or uranium(IV) by acetic acid is somewhat slow and it was suggested that the rate would only be increased if acetic acid entered the amine phase. Analysis of the solvent product from contactor II during run AD3 showed that acetic acid had entered the amine phase and it was also observed that uranium(IV) or plutonium(IV) was backwashed from the amine (run AD3 and run AD7) by a solution of 1M HAc and 0.05M HNO₃. It appears therefore, that the acetic acid enters the amine phase, complexes the uranium(IV) or plutonium(IV), and that this acetate complex is backwashed.

4.6 Behaviour of Acetic Acid in Contactor III

Although as stated above (para. 3.4) the partition coefficient for acetic acid (D_{HAc}) is ~ 0.27 the profile for run AD4 (Fig. 10) indicates, in stages 9-5, $D_{HAc} \sim 0.4$. The latter value is however, sufficiently low to ensure that the acetic acid in the solvent product is reduced to a level considerably lower than that which has been found to affect the solvent performance in subsequent cycles.²

5. CONCLUSIONS

A limited study has been made of one amine system and its performance in three contactors of a solvent extraction scheme. Conditions in the first contactor have shown three aspects which require more development work:-

1. A rather poor D.F. for ruthenium,
2. The formation of a third phase in the scrub section leading to low solvent loadings with plutonium,
3. A small amount (0.5%) of plutonium lost as plutonium(III) in the aqueous raffinate.

The backwash (contactor II) and solvent reconditioning (contactor III) operated well.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. I. L. Jenkins, Dr. E. S. Lane, Mr. B. O. Field and Mr. D. Leach for their assistance with the experimental work. Thanks are also due to Dr. J. M. Fletcher and Dr. H. A. C. McKay for their advice and encouragement.

REFERENCES

1. E. S. Lane, A. Pilbeam and J. M. Fletcher, AERE-R 4440 Part 1 (1965).
2. I. L. Jenkins, H. A. C. McKay, C. G. C. Shorthill and A. G. Wain, AERE-R 4440 Part 2 (1965).
3. A. Pilbeam, AERE-M 1387 (1965).
4. R. J. W. Streeton and E. N. Jenkins, AERE-R 3938 (1962).
5. A. G. Wain, P. G. M. Brown and J. M. Fletcher, J. Inorg. Nucl. Chem. 12, 346 (1960).
6. D. Scargill, C. E. Lyon, N. R. Large and J. M. Fletcher, J. Inorg. Nucl. Chem. 27, 161 (1965).
7. C. J. Hardy and D. Scargill, J. Inorg. Nucl. Chem. 9, 332 (1959).
8. G. F. Wall, AERE-R 1730 (1956).
9. M. J. Holdoway, unpublished work.
10. A. Pilbeam, private communication.
11. K. A. Allen, J. Phys. Chem. 62, 1119 (1958).
12. S. W. Rabideau, J. Amer. Chem. Soc. 75, 798 (1953).
13. D. Scargill, AERE-R 4922 (1965).

APPENDIX

Behaviour of Ruthenium in the Amine Phase

by

C. E. Lyon and R. J. W. Streeton

1. Tests were carried out on the ruthenium in the 15% (0.3M) Alamine 336/ DBC phase produced in run AD5 (Fig. 12) with the object

- (a) of examining its distribution with a nitric acid-acetic acid phase such as might be used for backwashing plutonium, and
- (b) to obtain information about the composition and kinetics of the nitrosylruthenium complexes in it.

2. Results with Acetic Acid-Nitric Acid

The results of stirring an equal volume of the amine phase with a mixture of 1M acetic acid and 0.05M nitric acid over a period of 30 minutes are shown in Fig. 14. They suggest that in a backwash contactor using this as the aqueous phase, there would be a split of the ruthenium in approximately equal amounts between the two phases.

3. Composition

Distribution coefficients (D_{Ru}) after stirring for 30 sec with 1M nitric acid at room temperature and using the amine phase diluted with DBC to give different molarities of amine, showed that the dependence on the Alamine 336 concentration was approximately first power. The results were:-

Amine (M)	0.3	0.15	0.075	0.038
D_{Ru}	25	12.5	7.4	4.2

The profiles (Fig. 12) for the run which produced this amine phase indicate that ruthenium emerging in the solvent phase was fractionated and consisted essentially of one species, probably the 2:3:4:5-tetrannitro complex referred to in other work as D_4 .⁶ This was confirmed by measuring D_{Ru} at room temperature after stirring for 30 sec with aqueous phases consisting initially of 1M and 6M HNO_3 respectively:-

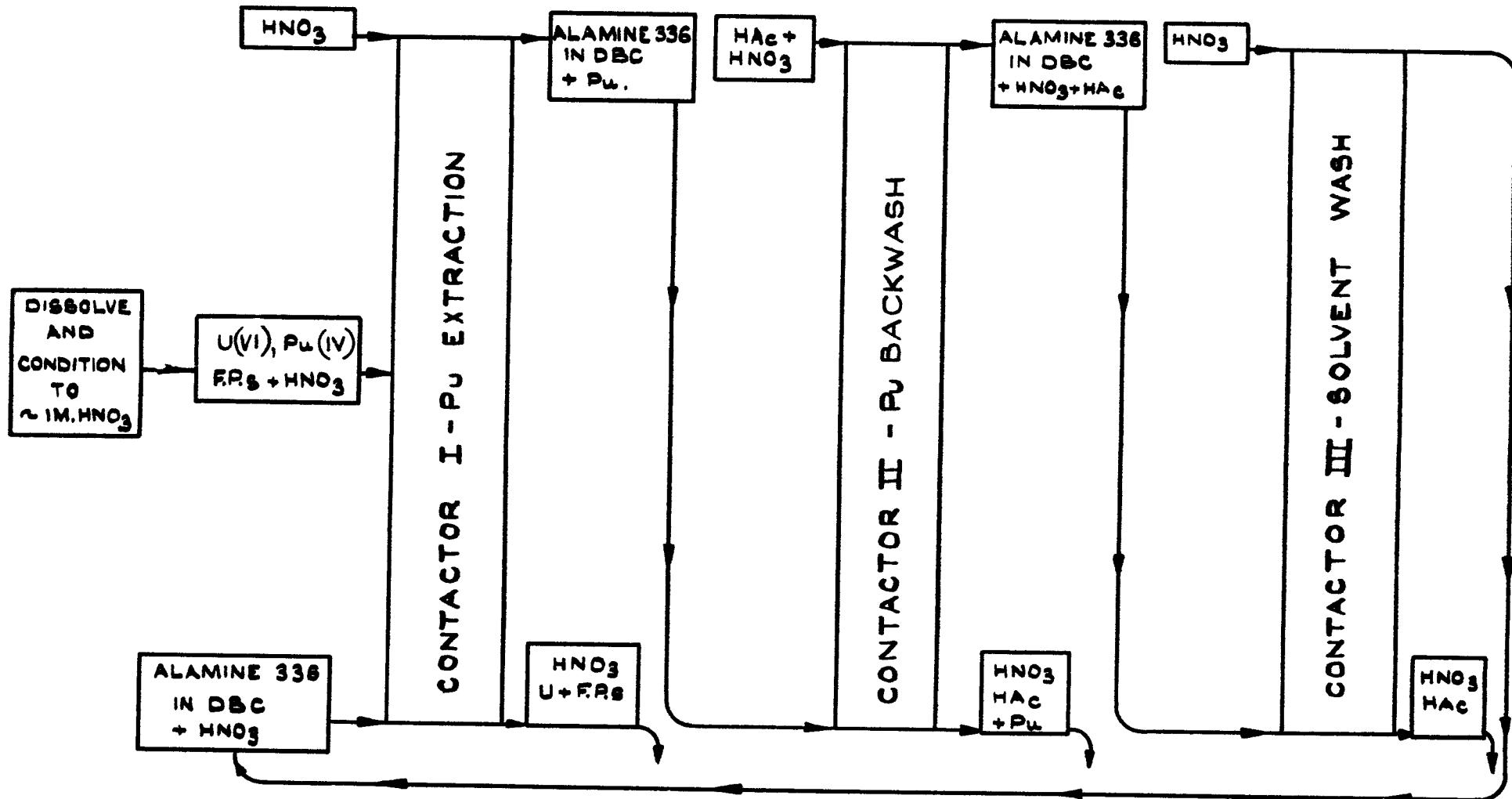
	<u>Aqueous phase at equilibrium</u>		<u>Partition Coefficients for</u> <u>0.3M Alamine 336/toluene</u>	
	HNO_3	<u>U IV</u>	D_{Ru}	P_4
(a)	1M	< 0.1M	25	80
(b)	5	< 0.1	2	1.1
				P_3
				0.5
				< 0.005

The results are compared in the last two columns with the partition coefficients (P_4 and P_3) for the tetra- and trinitrato complexes (D_4 and D_3) found for similar aqueous conditions by Scargill¹³; his results for 0.25M TLA in toluene have been multiplied by 1.2 so as to refer to 0.3M amine.

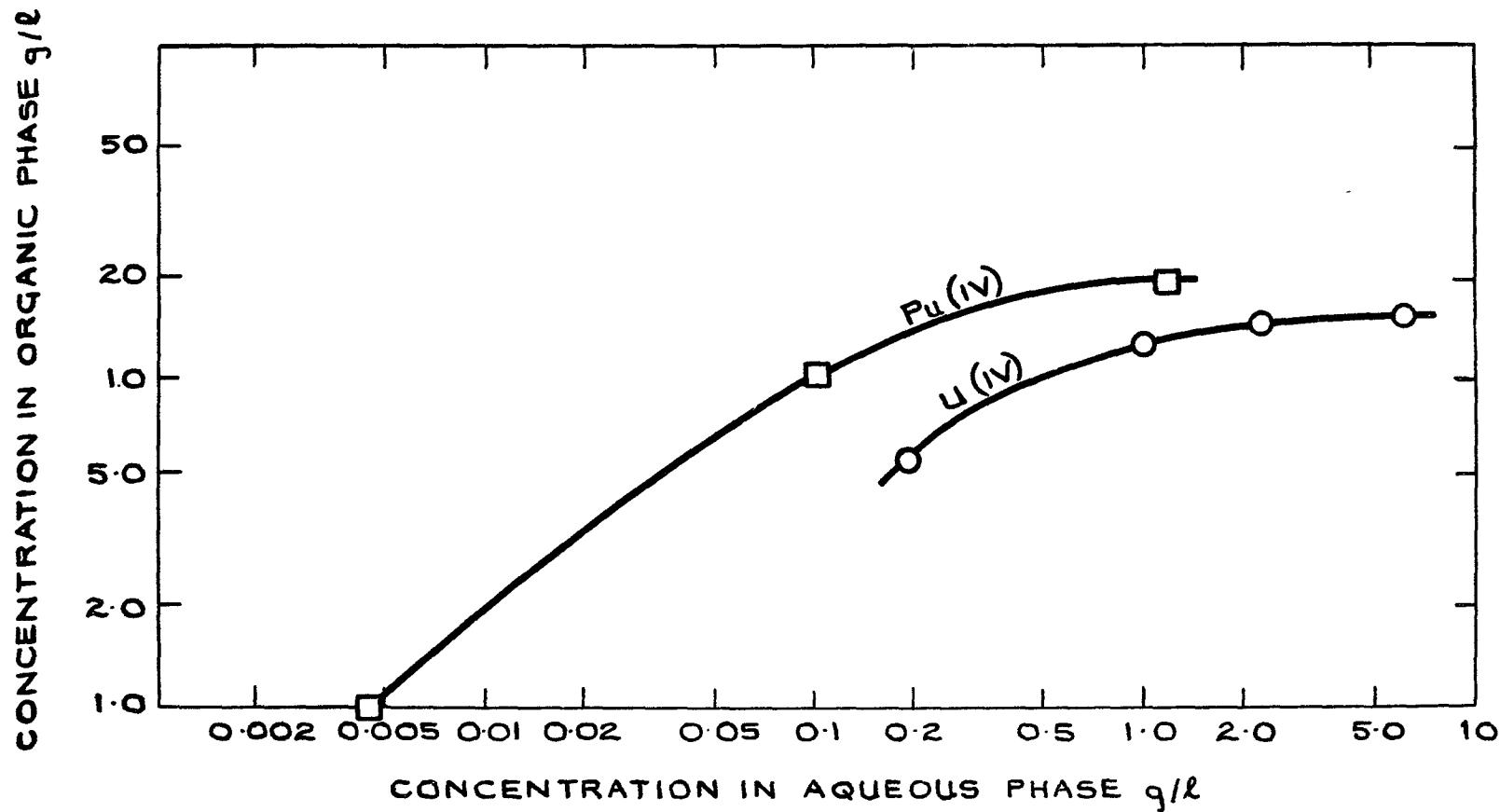
The results at a final acidity of 1M HNO_3 imply that there is ca. 96% of the complex D_4 and 4% of D_3 in the amine phase (which had been aged for 1-2 hours before the experiment). The fact that D_{Ru} with a final acidity of 5M HNO_3 is greater than P_4 is due to the influence of the diluent; other results (Part 2, page 6) show that the use of DBC instead of toluene as a diluent gives substantially higher distribution coefficients.

4. Kinetics

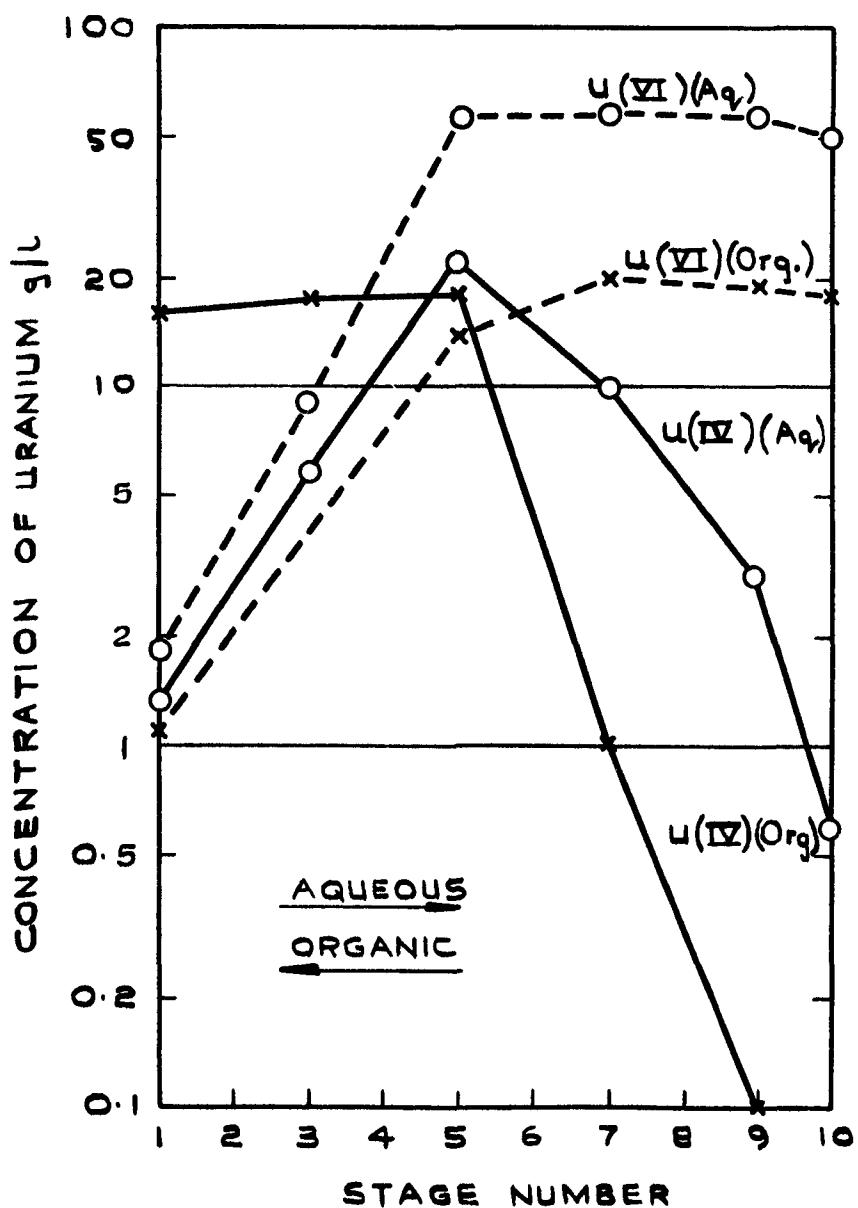
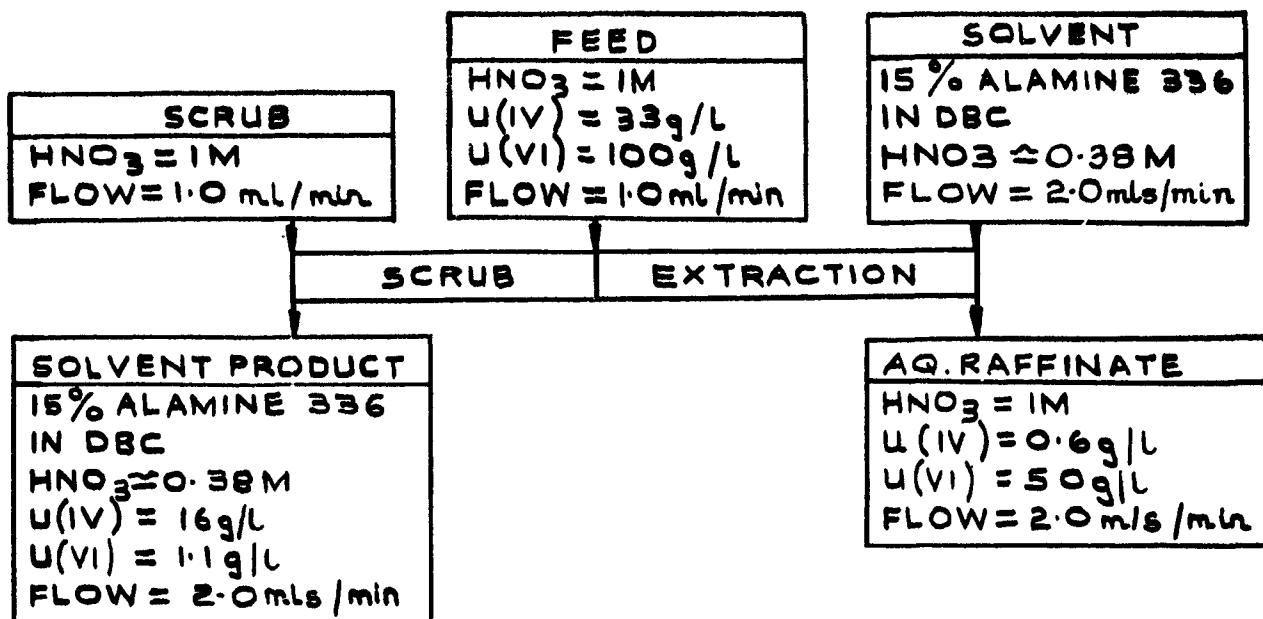
Fig. 14 shows the effect of stirring the amine phase over a period of time at room temperature with equal volumes of 1M and 6M nitric acid respectively. With 6M nitric acid (final acidity 5M) the results are consistent with equilibrium being reached after 1-2 hours with 25% of the ruthenium in the organic phase, since with this value a semi-log plot (Fig. 15) of fraction of ruthenium in organic phase minus fraction at equilibrium against the time gives a straight line. The first order reactions which control the rate are the aquation reactions $D_4 \rightarrow D_3 \rightarrow B + C \rightarrow A$ in the aqueous phase. The results and similar ones in ref. 6 applicable to 3M nitric acid imply that the rate of the first step, $D_4 \rightarrow D_3$, is $0.4-0.1 \text{ min}^{-1}$ ($t_{\frac{1}{2}}$, 1 to $1\frac{1}{2}$ min) in 3-5M nitric acid.



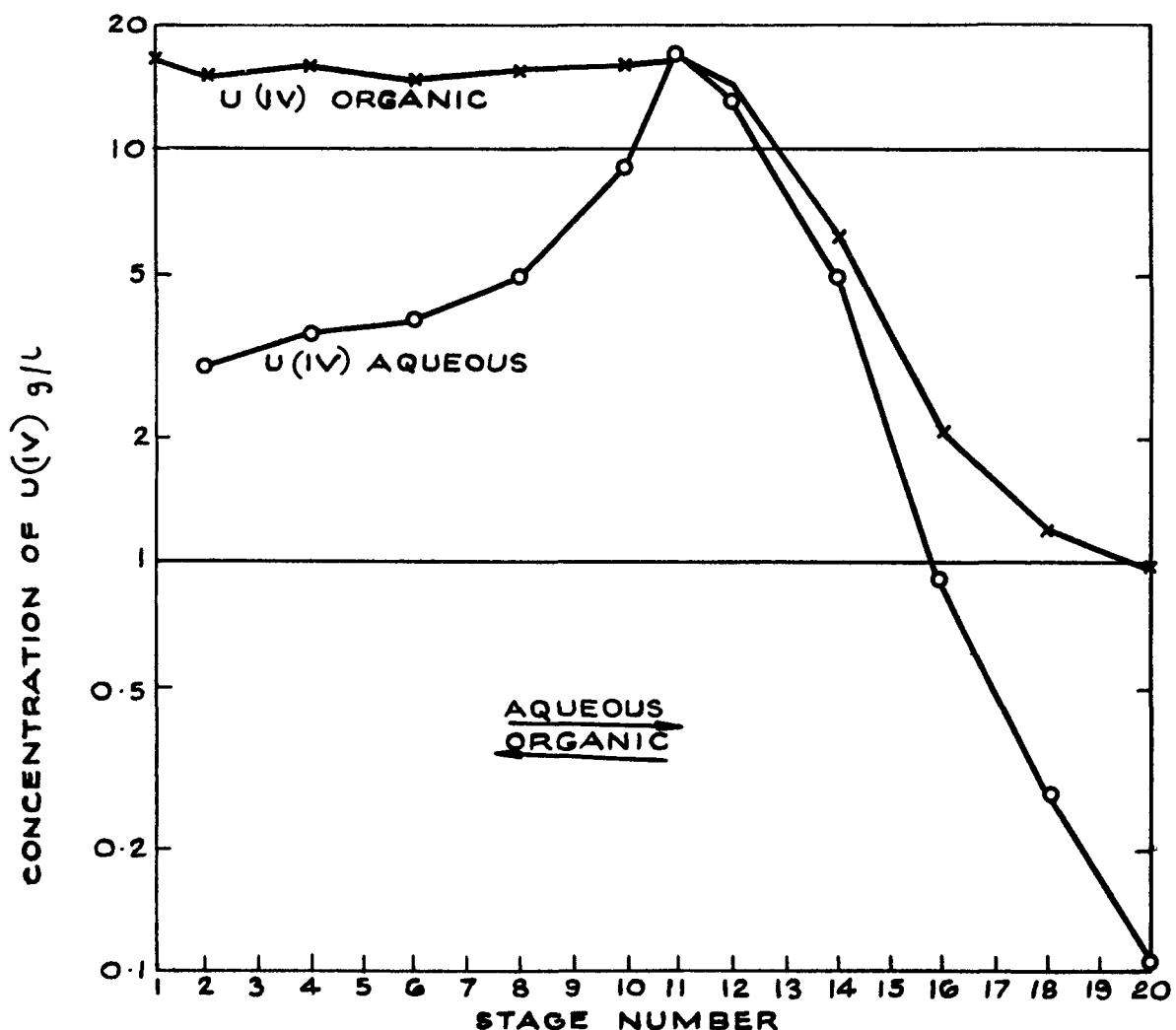
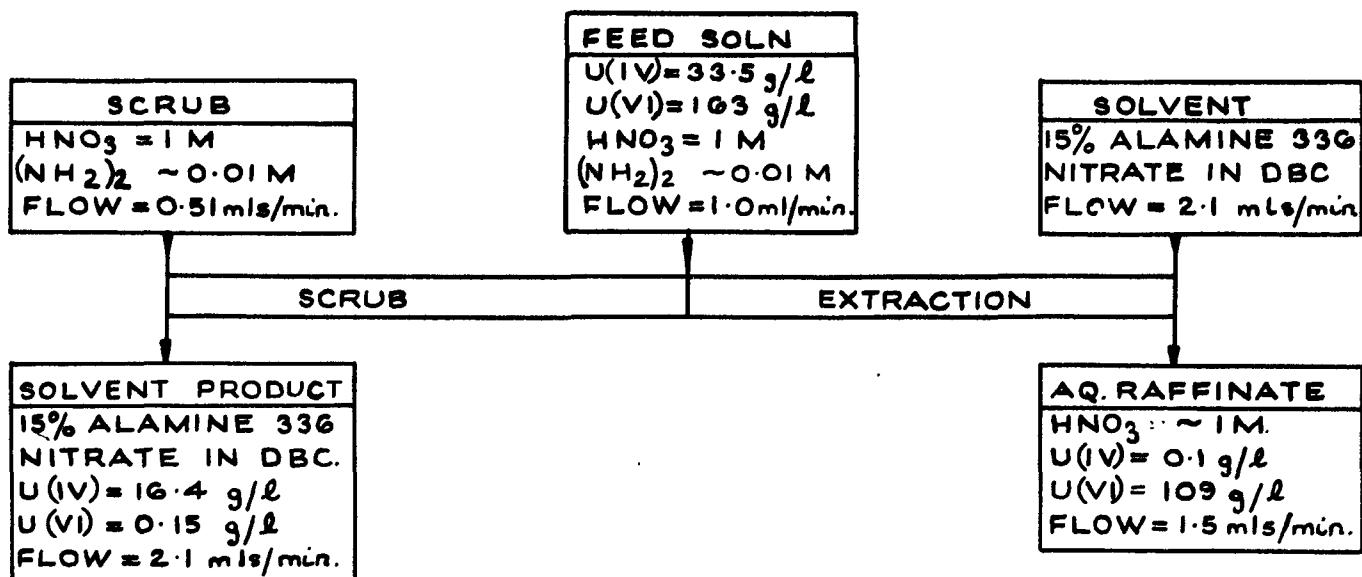
A.E.R.E. R4440 (PART 3) FIG. 1. PROCESS LAYOUT



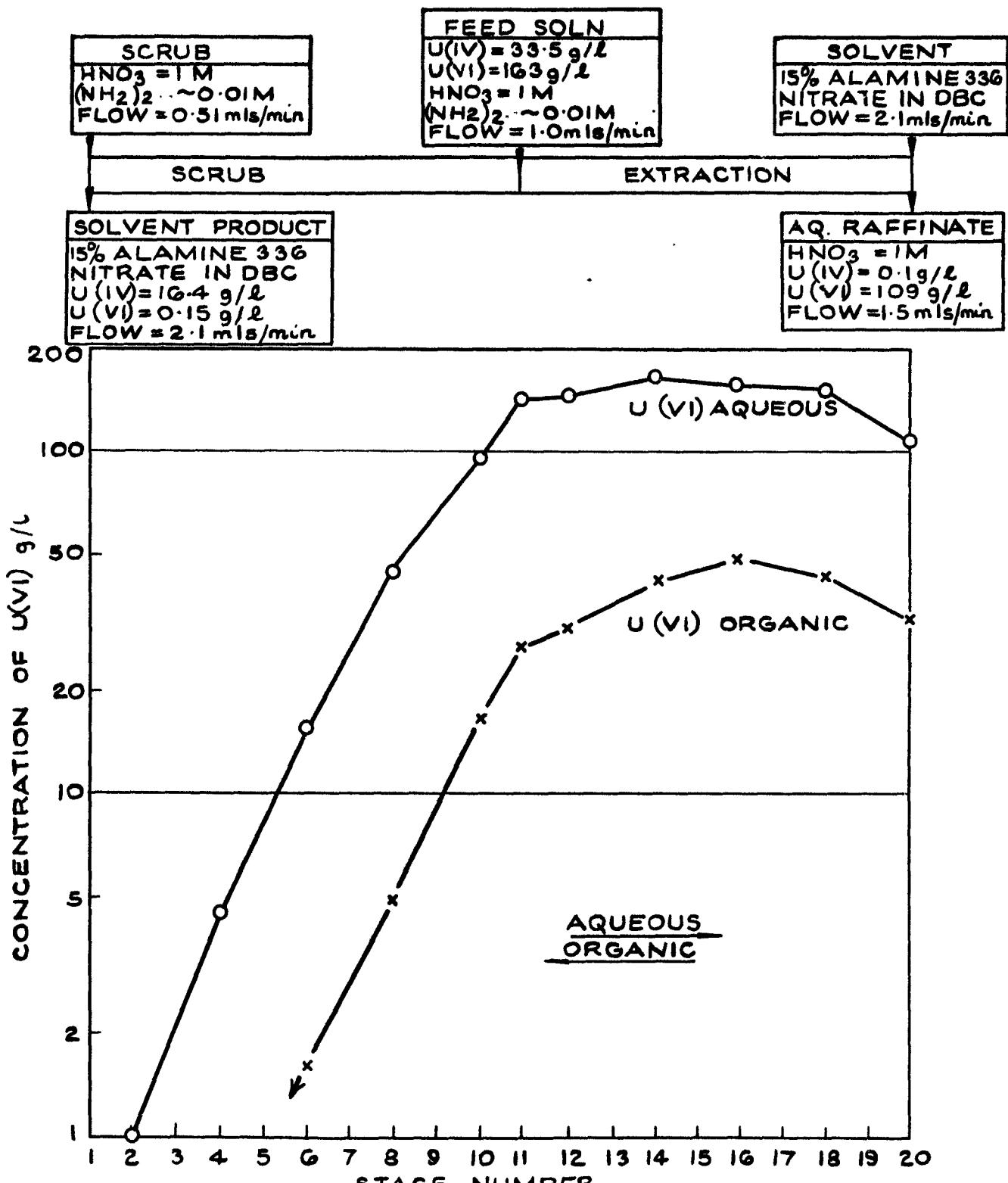
A.E.R.E. R4440 (PART 3) FIG. 2. THE PARTITION OF U(IV) AND Pu(IV)
BETWEEN 1M HNO₃ AND 15% ALAMINE 336/DBC



A.E.R.E. R.4440 (PART 3) FIG. 3. RUN ADI
CONCENTRATION PROFILES.



A.E.R.E. R.4440(PART3)
FIG. 4. RUN AD2 CONCENTRATION PROFILES OF
U(IV) IN CONTACTOR I



STAGE NUMBER
A.E.R.E. R.4440 (PART 3)
FIG. 5. RUN AD2 CONCENTRATION PROFILES OF
U(VI) IN CONTACTOR I

U(IV) BACKWASH SOLN
 $\text{HAC} = 1.0\text{M}$
 $\text{HNO}_3 = 0.05\text{M}$
 $\text{FLOW} = 1\text{ml/min.}$

SOLVENT PRODUCT FROM AD2 CONTACTOR I
15% ALAMINE 330 NITRATE IN DBC
 $\text{U(IV)} = 16.4\text{ g/l}$
 $\text{U(VI)} = 0.15\text{ g/l}$
 $\text{FLOW} = 2.1\text{ ml/s/min.}$

SOLVENT RAFFINATE
15% ALAMINE 330 NITRATE AND ACETATE IN DBC.
 $\text{U(IV)} = 0.62\text{ g/l}$
 $\text{FLOW} = 2.1\text{ ml/s/min.}$

U(IV) EXTRACT
 $\text{U(IV)} = 22.5\text{ g/l}$
 $\text{HNO}_3 \sim 0.05\text{M}$
 $\text{HAC} \sim 0.5\text{M}$
 $\text{FLOW} = 1\text{ml/min.}$

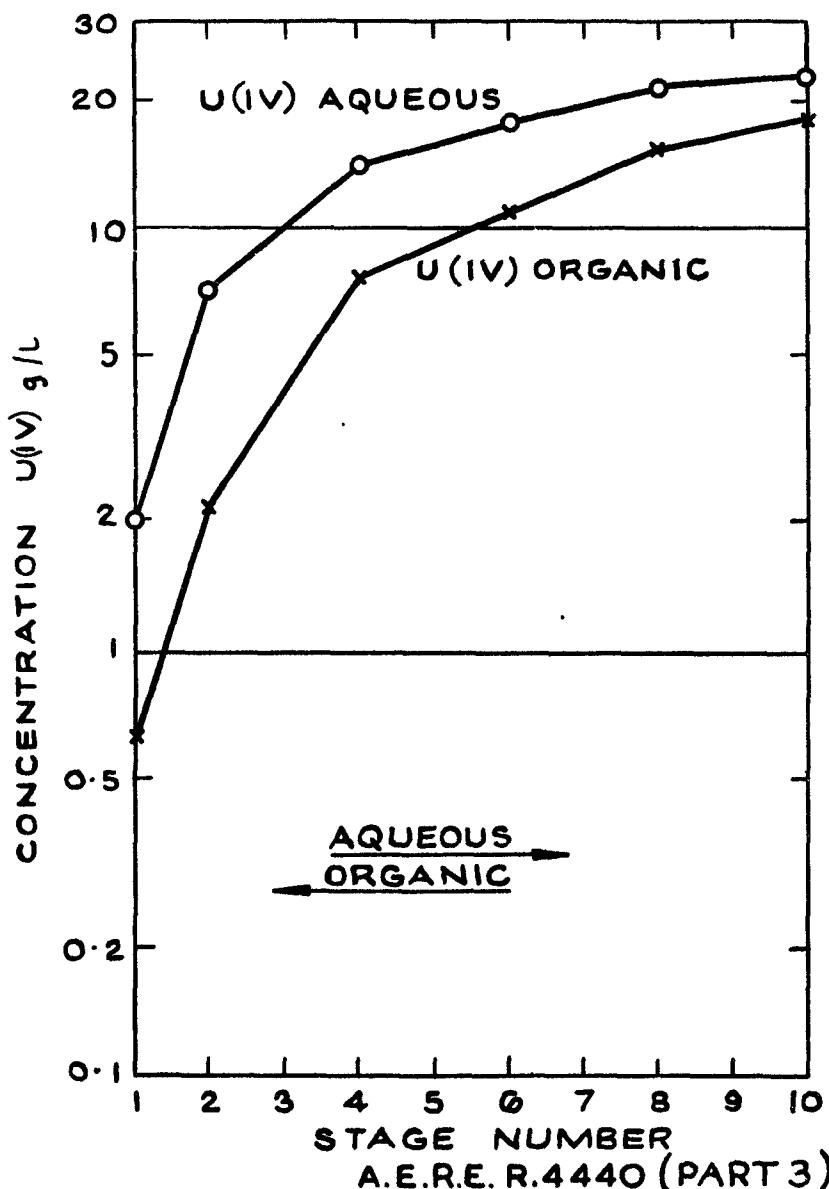
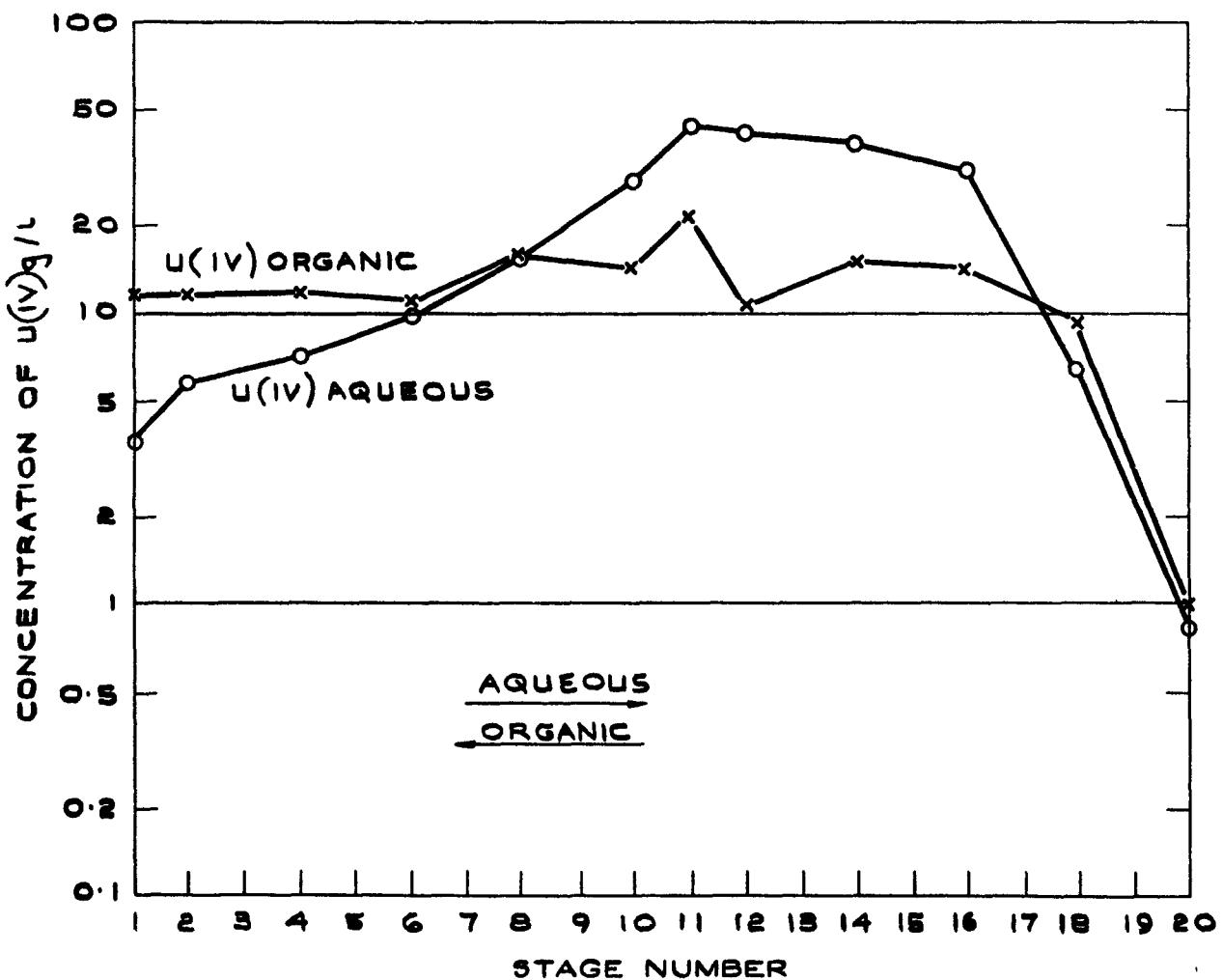
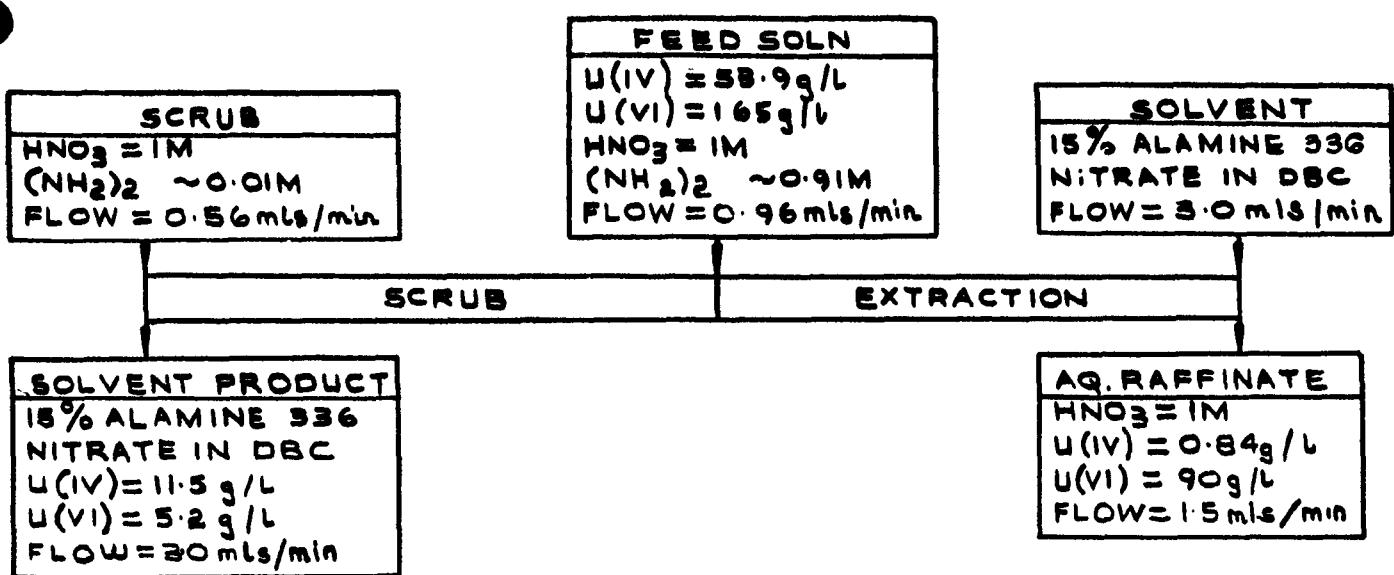
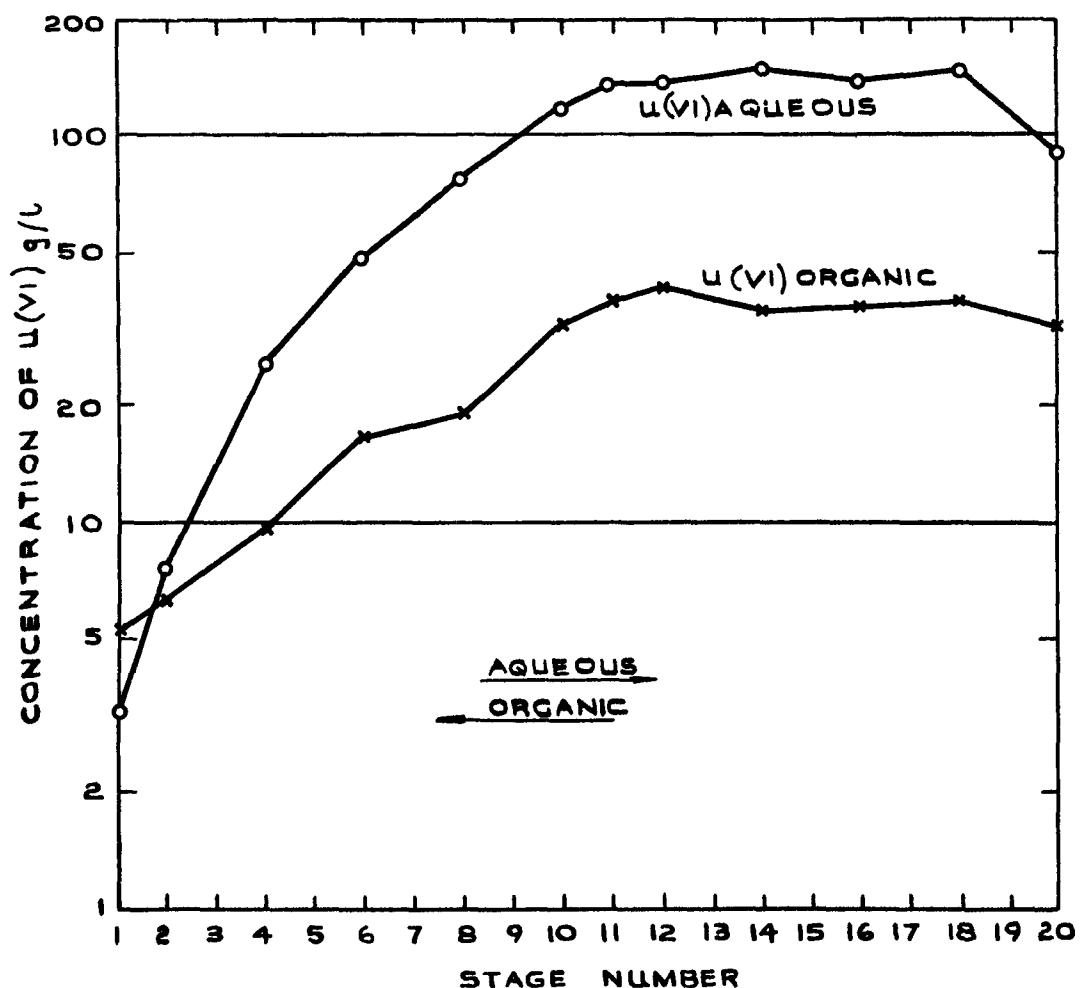
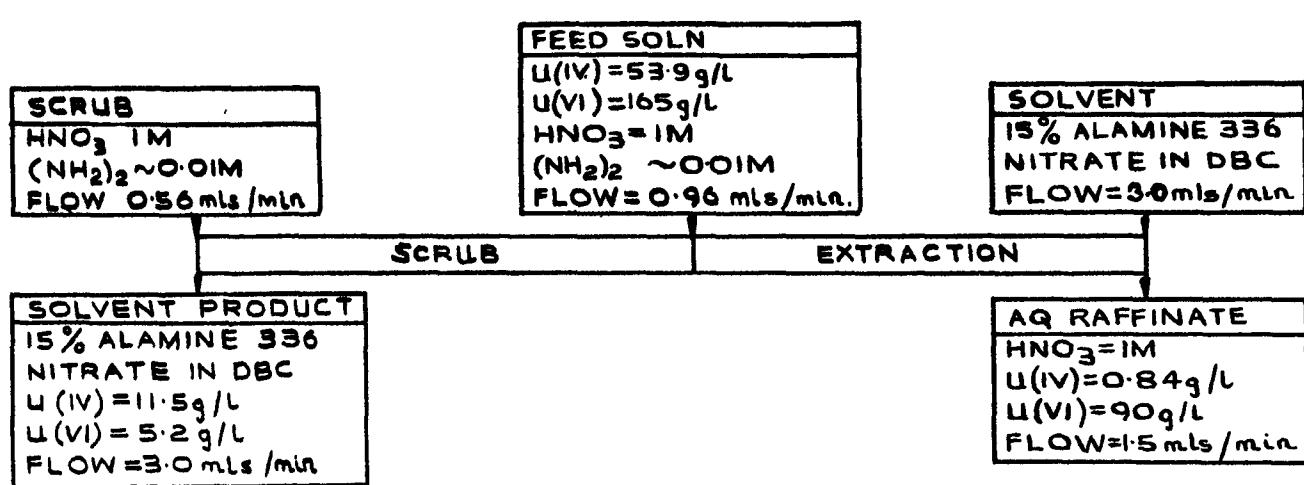


FIG.6. RUN AD2 CONCENTRATION PROFILES OF U(IV) IN CONTACTOR II



A.F.R.E. R.4440 (PART 3)

FIG. 7. RUN AD3 CONCENTRATION PROFILES OF U(IV) IN CONTACTOR I



A.E.R.E. R.4440 (PART 3) FIG. 8. RUN AD3 CONCENTRATION PROFILES OF U(VI)
IN CONTACTOR I

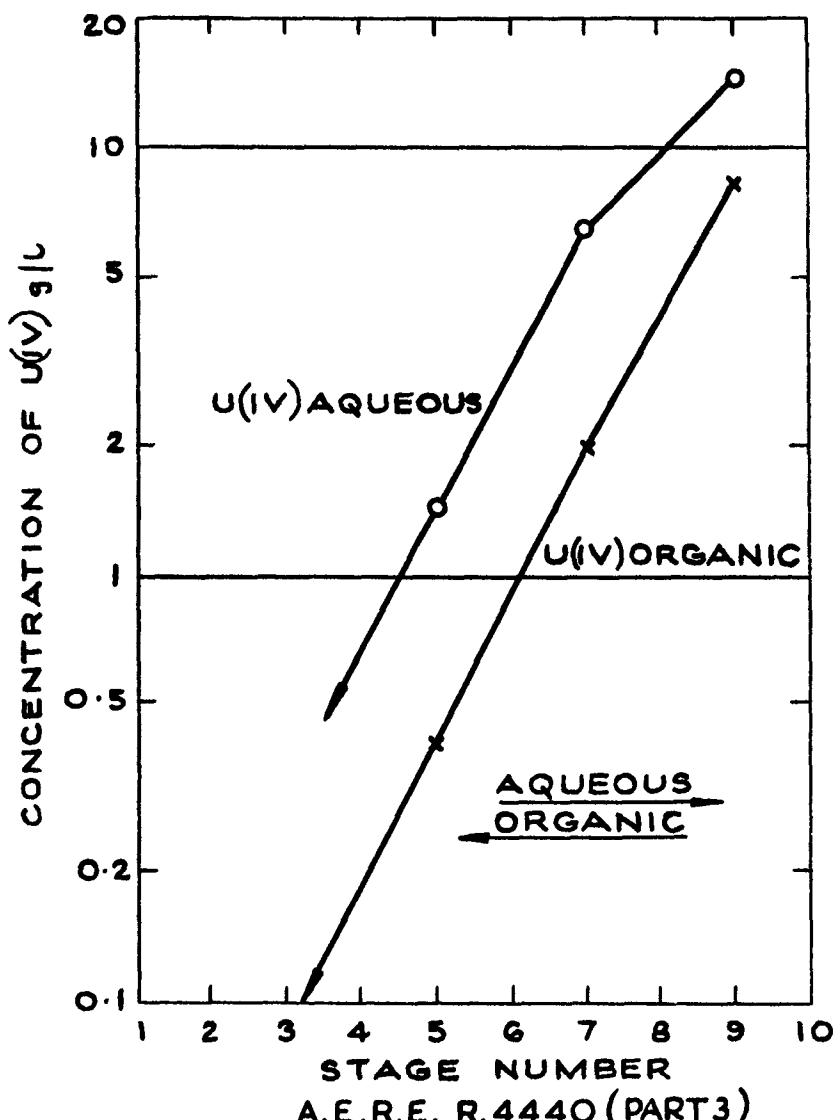
U(IV) BACKWASH SOLN
 $\text{HAc} = 1.0\text{M}$
 $\text{HNO}_3 = 0.05\text{M}$
 FLOW = 1.0 ml/min.

SOLVENT PRODUCT
 FROM AD3 CONTACTOR I
 15% ALAMINE 33G IN DBC
 $\text{U(IV)} = 11.5\text{ g/l}$
 $\text{U(VI)} = 5.2\text{ g/l}$
 FLOW = 0.96 mls/min

U(IV) BACKWASH

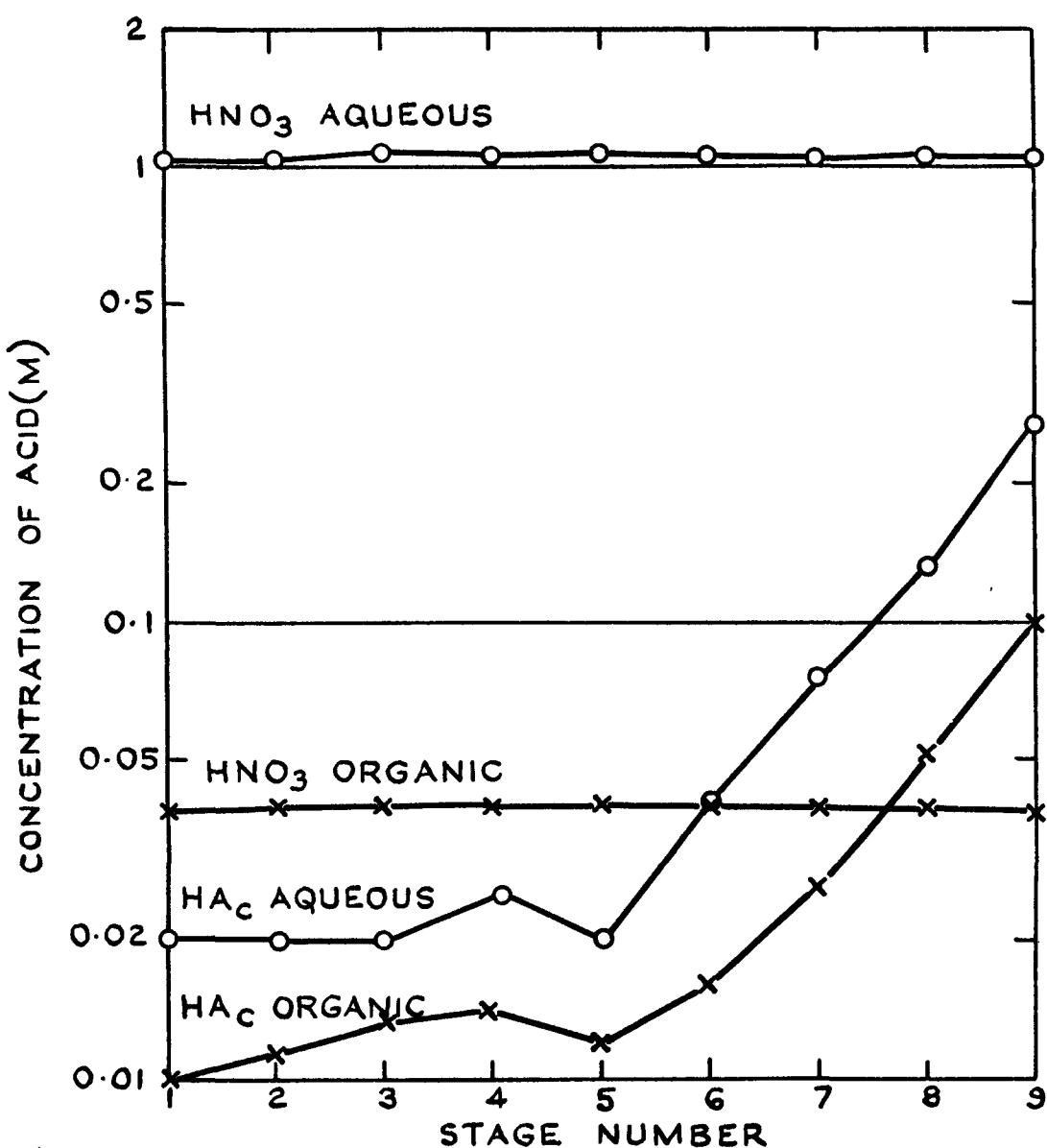
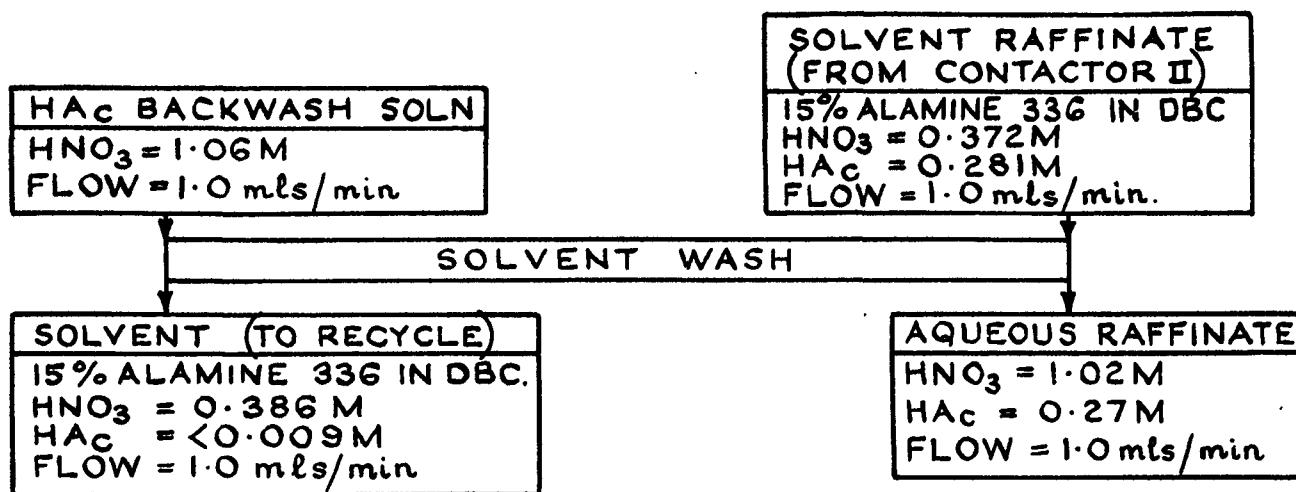
SOLVENT RAFFINATE
 15% ALAMINE 33G NITRATE
 AND ACETATE IN DBC.
 $\text{U(IV)} \sim 0\text{ g/l}$
 FLOW = 0.96 mls/min.

U(IV) EXTRACT
 $\text{U(IV)} = 14.8\text{ g/l}$
 $\text{HNO}_3 \sim 0.05\text{M}$
 $\text{HAc} \sim 0.7\text{M}$
 FLOW = 1 ml/min.

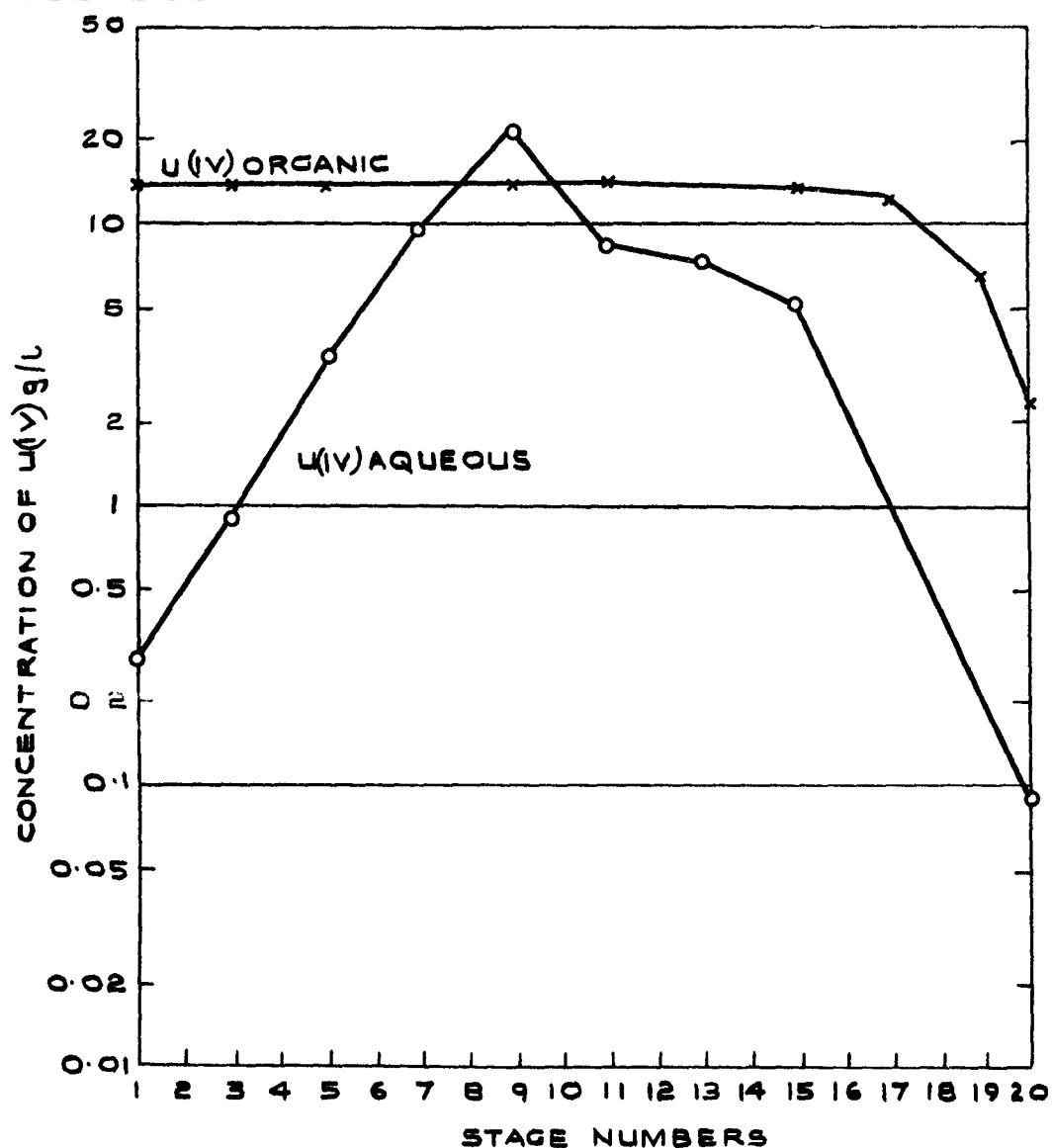
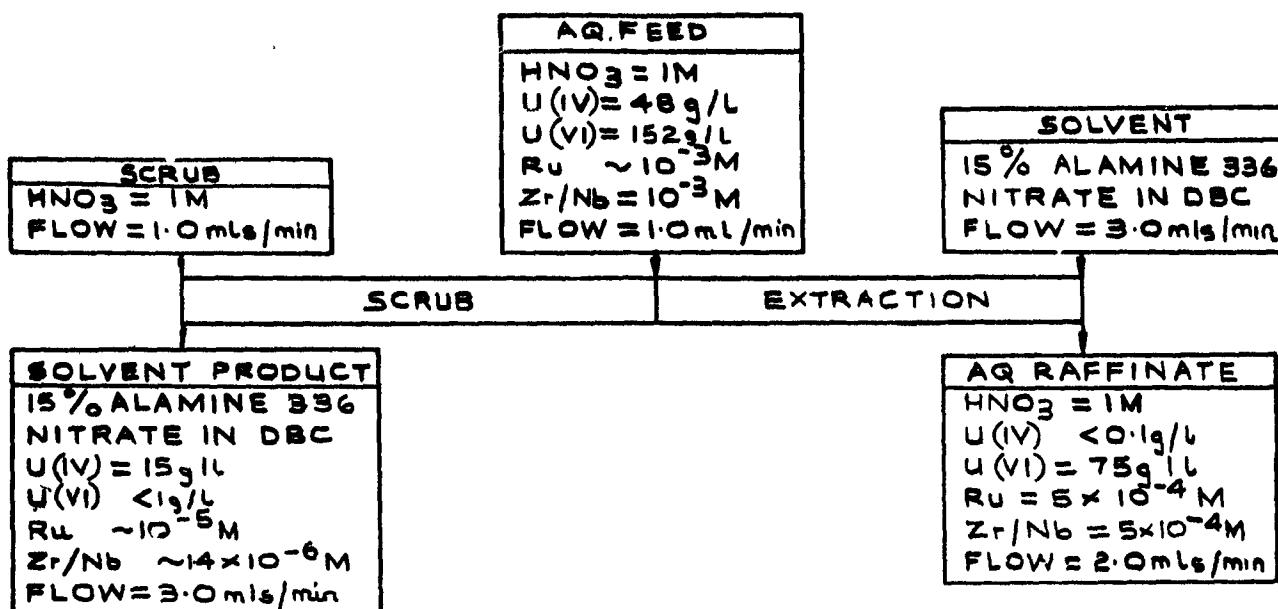


A.E.R.E. R.4440 (PART 3)

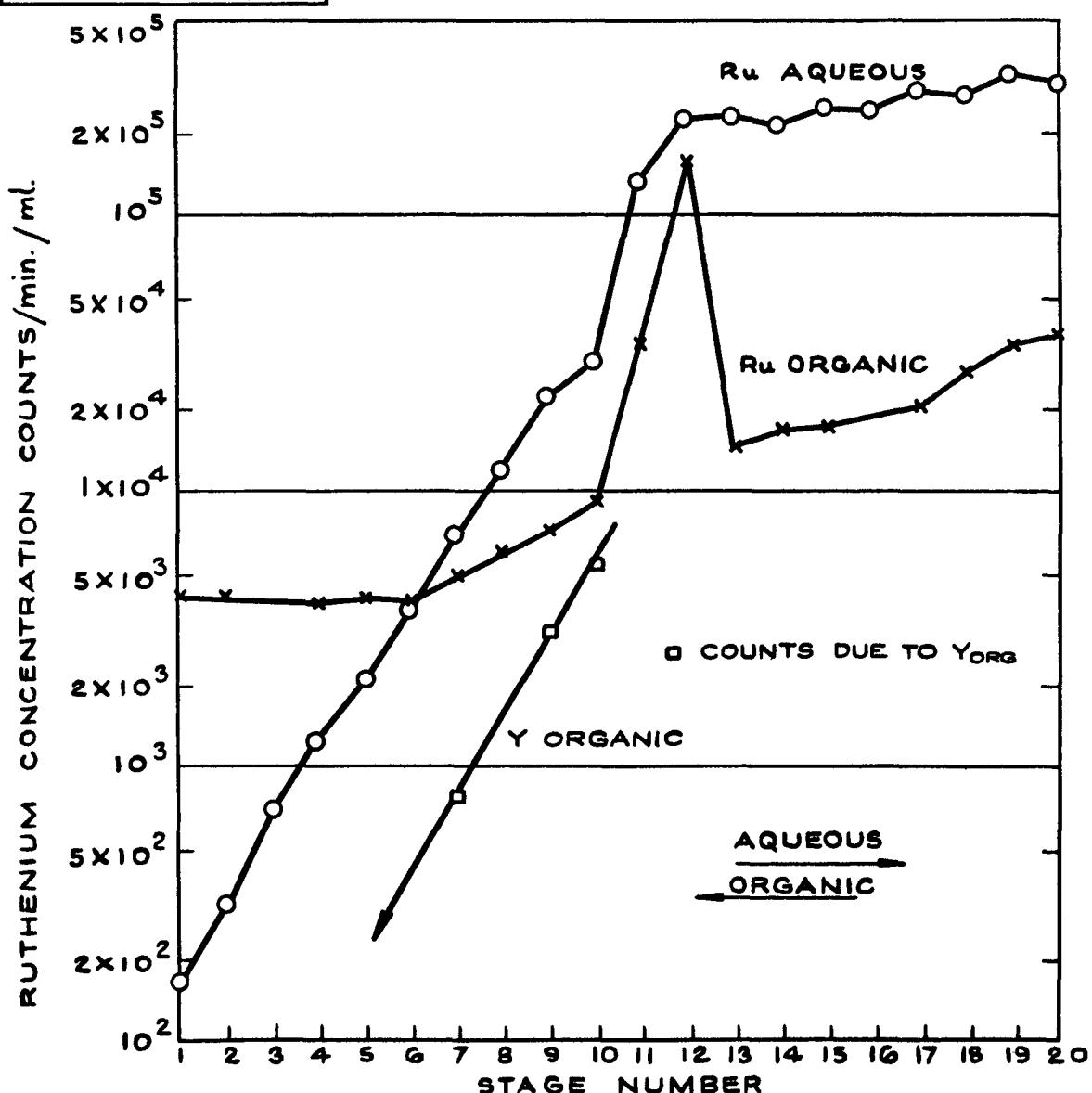
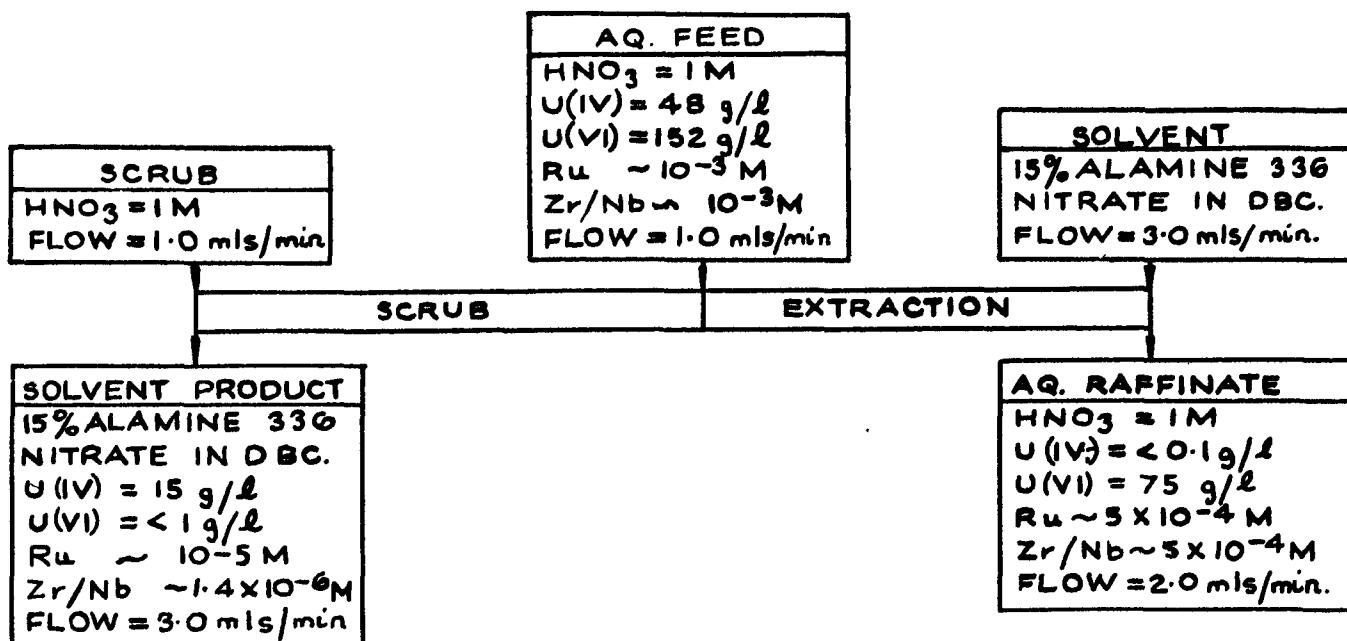
FIG. 9. RUN AD 3 CONCENTRATION
 PROFILES OF U(IV) IN CONTACTOR II



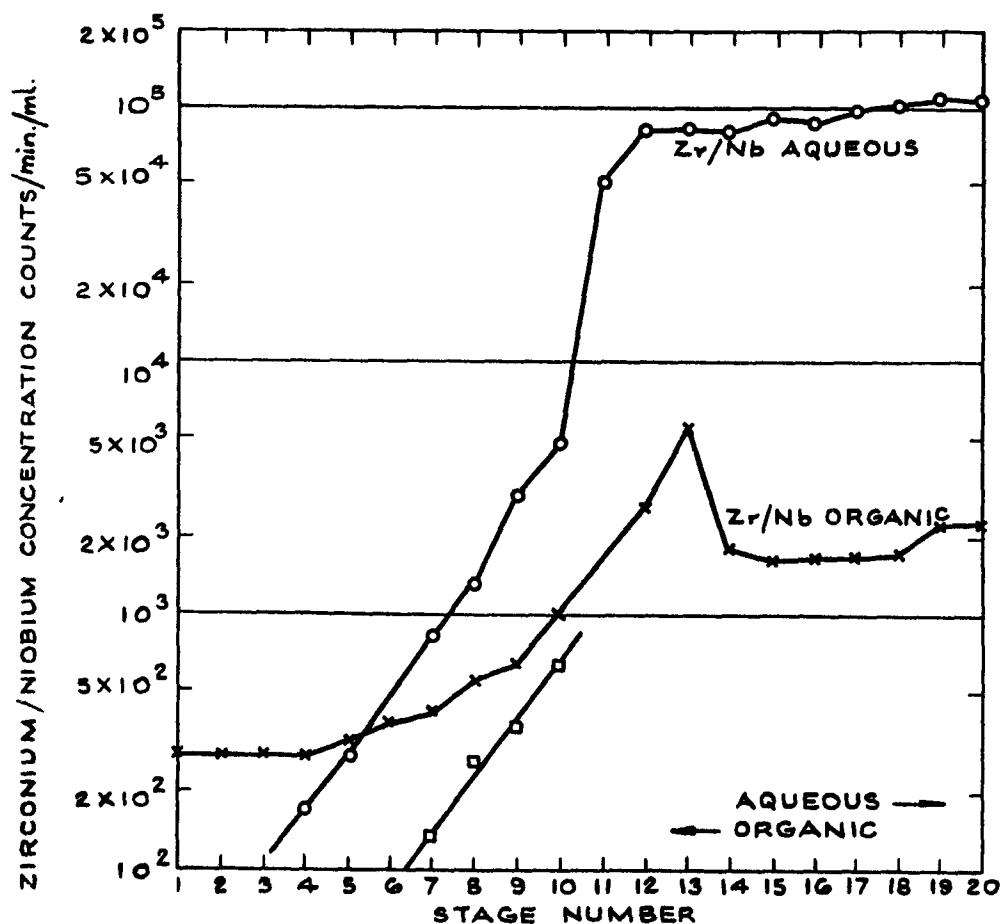
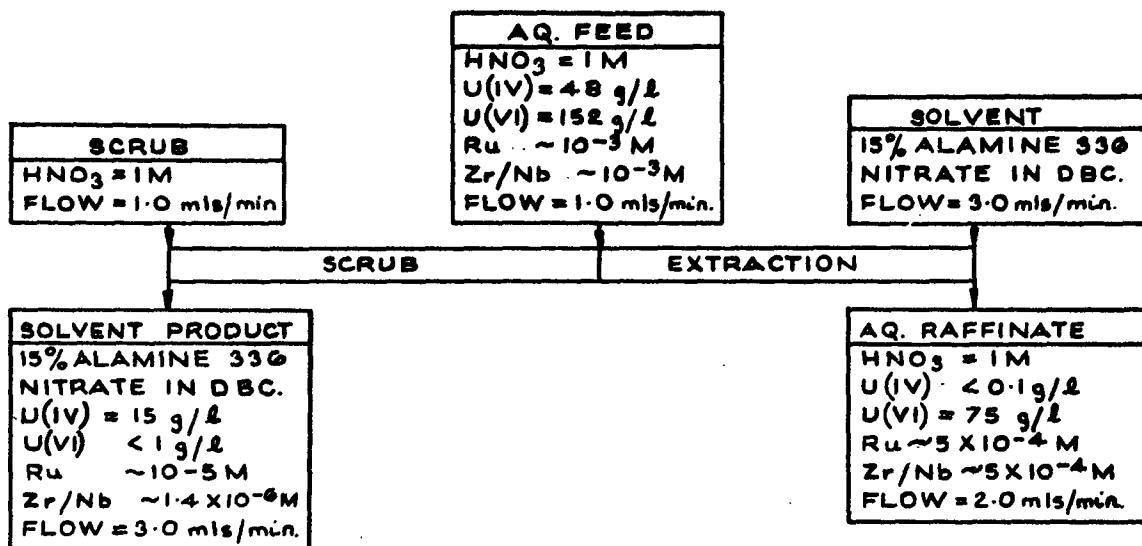
A.E.R.E. R.4440. (PART 3) FIG. 10. RUN AD4 CONCENTRATION PROFILES OF ACETIC ACID AND NITRIC ACID IN CONTACTOR III



A.E.R.E. R.4440 (PART 3) FIG. 11. RUN ADS CONCENTRATION PROFILES OF U(IV) IN
CONTACTOR I



A.E.R.E. R4440 (PART 3) FIG. 12. RUN AD5 CONCENTRATION PROFILES OF Ru IN CONTACTOR I.

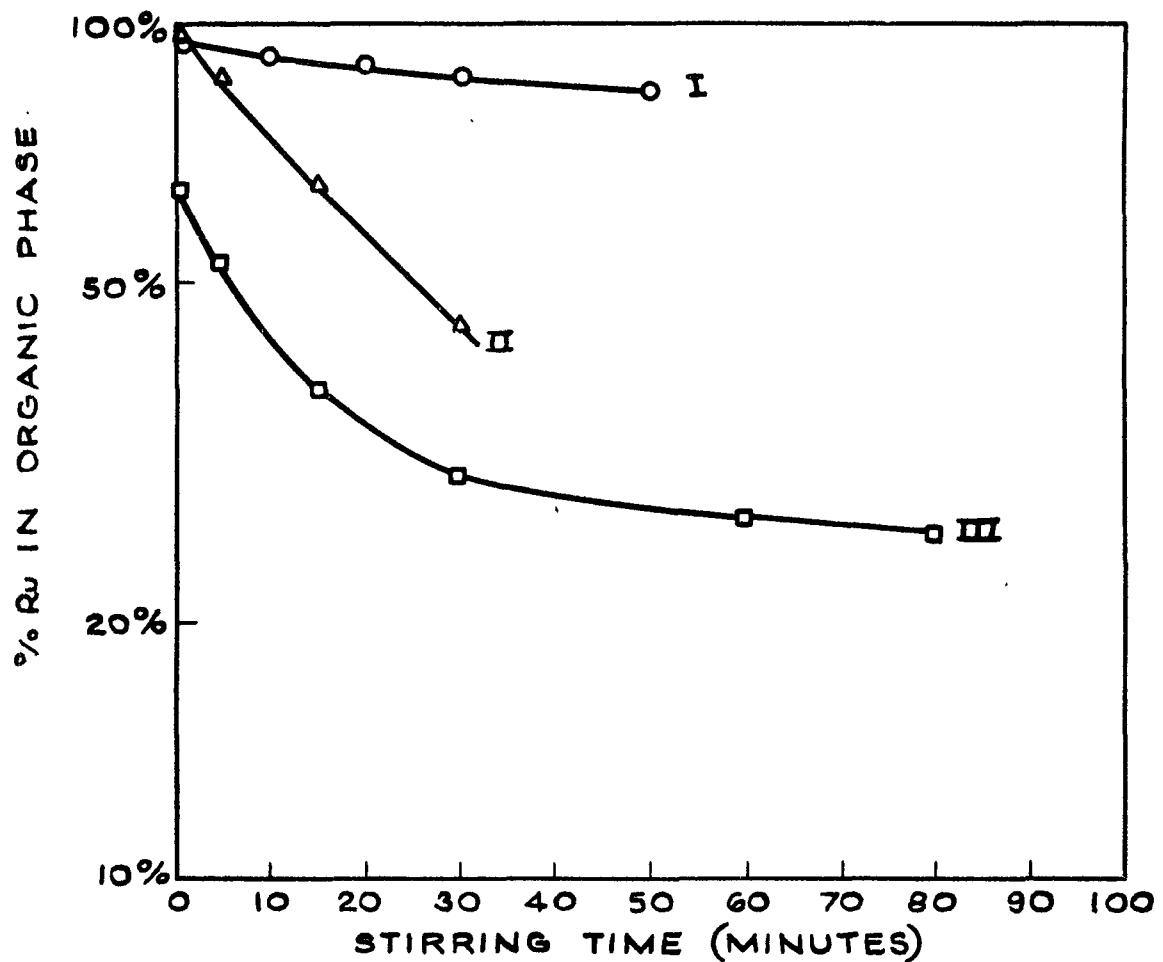


A.E.R.E.R4440 (PART 3) FIG.13. RUN AD5 CONCENTRATION PROFILES OF Zr AND Nb IN CONTACTOR I.

I SOLVENT PRODUCT FROM AD5 STIRRED WITH 1M HNO₃

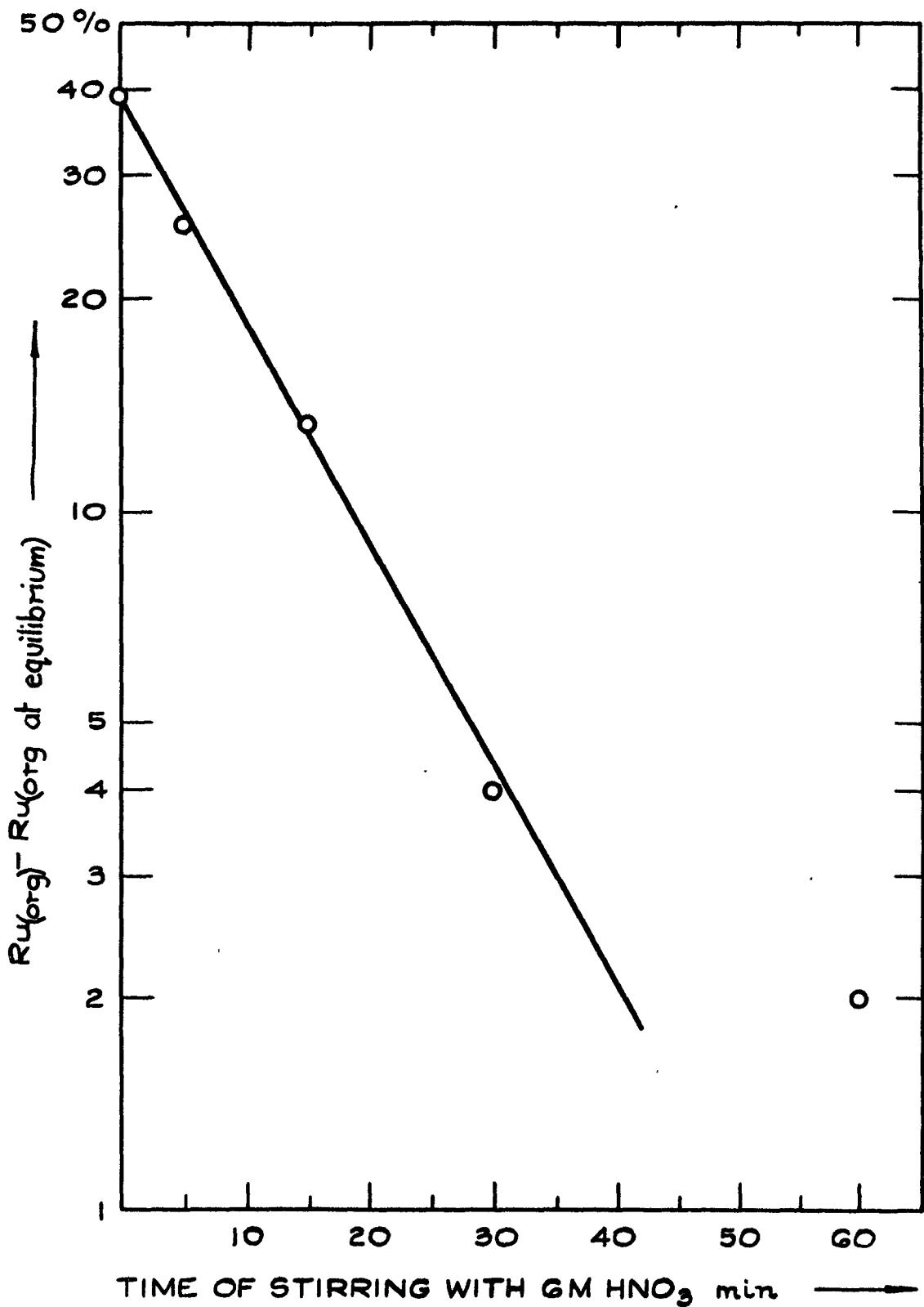
II SOLVENT PRODUCT FROM AD5 STIRRED WITH 1M HAc + 0.05M HNO₃

III SOLVENT PRODUCT FROM AD5 STIRRED WITH 6M HNO₃

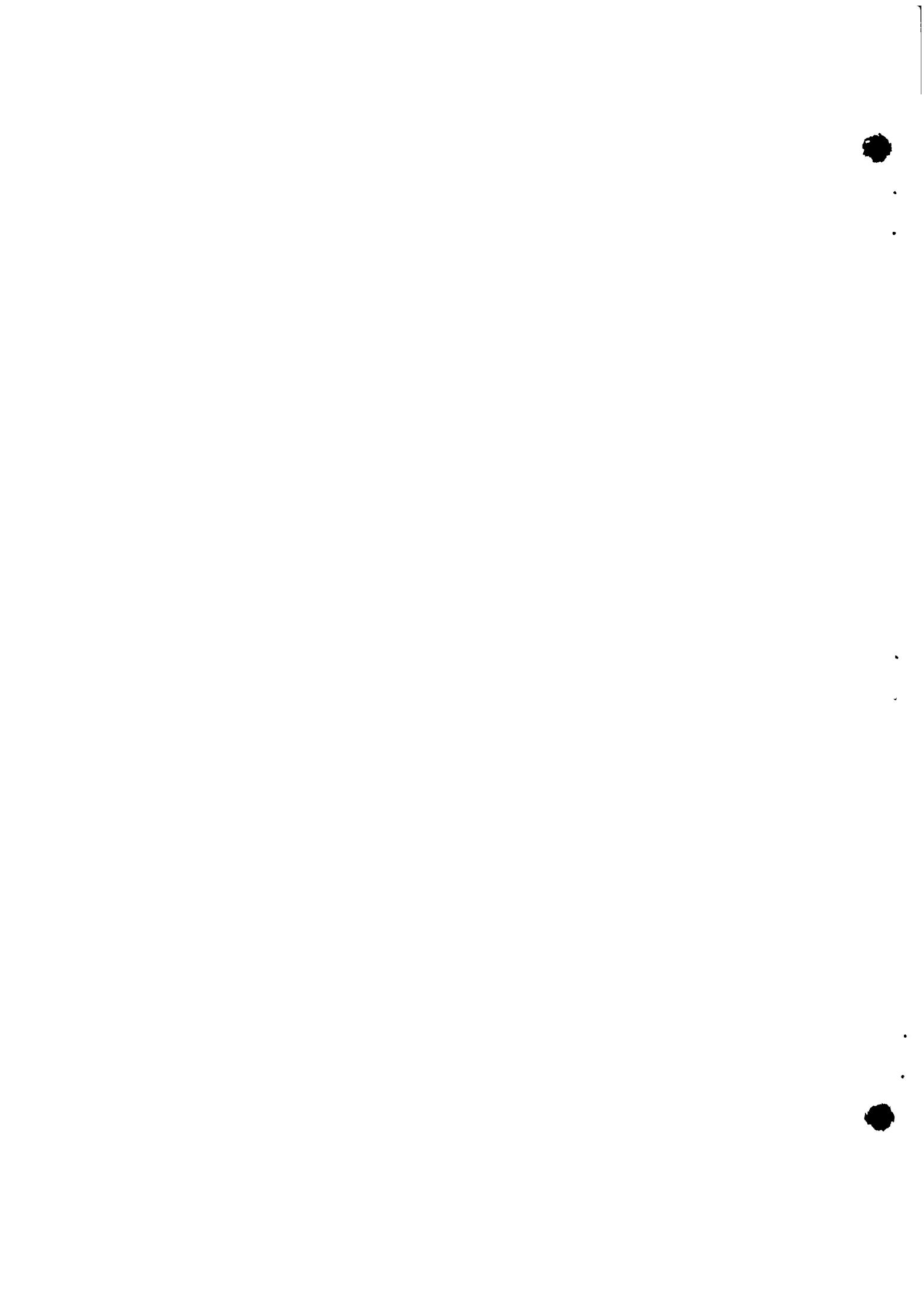


A.E.R.E. R.4440 (PART 3)

FIG. 14. THE DISTRIBUTION OF EXTRACTABLE
Ru SPECIES vs. TIME OF STIRRING.



A.E.R.E. R.4440. (PART 3) FIG. 15. THE DISTRIBUTION OF EXTRACTABLE RUTHENIUM SPECIES vs TIME OF STIRRING.
(For details see text.)



Available from
HER MAJESTY'S STATIONERY OFFICE
York House, Kingsway, London W.C. 2
423 Oxford Street, London W. 1
13a Castle Street, Edinburgh 2
109 St. Mary Street, Cardiff
39 King Street, Manchester 2
50 Fairfax Street, Bristol 1
35 Smallbrook, Ringway, Birmingham 5
80 Chichester Street, Belfast
or through any Bookseller.

Printed in England.