MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349876 6

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-1993 (Rev. 2)
UC-10 – Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (32nd ed.)

CHEMICAL DEVELOPMENT OF THE 25-TBP PROCESS

J. R. Flanary
J. H. Goode
A. H. Kibbey
J. T. Roberts
R. G. Wymer

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

Printed in USA. Price $1.50. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-1993 (Revision 2)

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

CHEMICAL DEVELOPMENT OF THE 25-TBP PROCESS

J. R. Flanary
J. H. Goode
A. H. Kibbey
J. T. Roberts
R. G. Wymer

OCTOBER 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0349876 6

CONTENTS

	Page
1. Abstract	1
2. Introduction	1
3. Proposed 25-TBP Flowsheet	3
4. Studies on the Dissolution of the Al-U Alloy	5
4.1 Laboratory-Scale Batch Dissolution	5
4.2 Large-Scale Batch Dissolutions	9
4.3 Continuous Dissolution Studies	11
4.4 Product Stability	11
4.5 Behavior of Fission-Product Iodine	14
5. First-Cycle Extraction-Column Emulsions and Interfacial Solids	16
5.1 Pretreatment of the Solvent	16
5.2 Dissolution Conditions	17
5.3 Pretreatment of the Feed Solution	17
5.4 Effect of Aqueous-Phase Acidity in the Extraction Column	19
5.5 Effect of Phase Mixing	22
5.6 Behavior of Mercury under Extraction Column Conditions	22
6. First-Cycle Uranium Losses and Decontamination in the First Cycle	23
6.1 Uranium Recovery	24
6.2 Uranium Decontamination	28
7. Second Solvent Extraction Cycle	35
7.1 Uranium Decontamination	35
7.2 Uranium Recovery	36
8. Solvent Treatment	36
8.1 Solvent Pretreatment	36
8.2 Solvent Recovery	39
9. Methods and Cost of Waste Storage	46
10. References	49
11. Appendix	50
11.1 Stripping of Uranium from TBP with Aqueous Citrate Solutions	50
11.2 Solvent Pretreatment	60

CHEMICAL DEVELOPMENT OF THE 25-TBP PROCESS

J. R. Flanary J. H. Goode A. H. Kibbey
J. T. Roberts R. G. Wymer

1. ABSTRACT

Laboratory development studies leading to a tributyl phosphate extraction process for recovering ^{235}U from irradiated, enriched, uranium-aluminum alloy reactor fuel elements are described. The fuel is dissolved in excess nitric acid, and the solution is digested to eliminate emulsion-forming substances and then extracted with tributyl phosphate, aluminum nitrate being the salting agent. The uranium is then stripped with dilute nitric acid, and, after evaporation, is re-extracted in a second cycle. Nitric acid is used as the salting agent in the second cycle.

The solvent diluent is pretreated to remove impurities. Procedures for recovering the solvent for process reuse and for reducing the volume of the radioactive waste, which contains aluminum nitrate, are proposed.

---

2. INTRODUCTION

Although the hexone solvent-extraction process[1] for recovering ^{235}U was proved successful by plant experience, knowledge of extractions based on tributyl phosphate (TBP) has advanced sufficiently that the development and design of a ^{235}U recovery process based on this solvent could be undertaken with confidence. Considerable experience with Purex,[2] Thorex,[3] and (ORNL) Metal Recovery[4] processes had shown that ^{235}U and other fertile and fissionable materials can be recovered more efficiently and with less cost by TBP extraction than by other methods in use.

Laboratory-scale development work was conducted by batch-countercurrent methods and in Mini-mixer settler units to establish the chemical flowsheet conditions for quantitative recovery of uranium adequately decontaminated from fission products and nonradioactive impurities for reuse. Numerous test runs, with both nonradioactive and radioactive feeds, were conducted in 3/4-in.-diam pulsed columns to determine the mechanical operability of the process in plant-type equipment. Process performance was demonstrated at 10% of full process radioactivity.

Laboratory-scale investigations were also conducted on batch and continuous dissolution of uranium-aluminum alloy fuel elements in nitric acid. A feed treatment designed to eliminate emulsions in the first-cycle extraction column, a solvent-diluent pretreatment, and a solvent recovery procedure were investigated. Small-scale turbine-mixer units were evaluated for solvent recovery. Radiation damage to the solvent was studied in relation to process performance, and a method of reducing the volume of the aluminum nitrate-containing waste was examined.

The process development work, applicable to any uranium-aluminum alloy fuel, was done with aluminum-clad uranium-aluminum alloy fuel elements containing about 10 wt % uranium, the alloy itself containing about 15 wt % uranium. A high burnup of the greater than 90% enriched uranium fuel followed by several months' decay was envisioned for the process. Under these conditions the required overall decontamination factors for gross beta, gross gamma, and plutonium (alpha) of 4.6×10^6, 1×10^7, and 1×10^4, respectively, were assumed. The permissible uranium loss was specified as no more than 0.01% to each waste stream.

Sufficient data were accumulated to permit design of a full-scale chemical processing facility.[5]

Appreciation is expressed to the ORNL Analytical Chemistry Division for their cooperation in this program. Special thanks are given to L. T. Corbin, W. R. Laing, and G. R. Wilson for routine chemical analyses, to E. I. Wyatt and C. E. Lamb for radiochemical analyses, to J. H. Edgerton and P. F. Thomason for nonroutine analytical problems, and to Cyrus Feldman for spectrographic analyses.

3. PROPOSED 25-TBP FLOWSHEET

In the 25-TBP process (Fig. 3.1) for recovering and decontaminating ^{235}U from spent, enriched, uranium fuel elements, the aluminum-clad uranium-aluminum alloy fuel is dissolved in 8.25 M HNO_3--0.005 M $Hg(NO_3)_2$. The resulting solution [1.8 M $Al(NO_3)_3$--1.0 M HNO_3--0.005 M $Hg(NO_3)_2$, containing about 3.8 g of uranium per liter] is heated to the boiling point for 4 to 6 hr to dehydrate and coagulate silica and other emulsion-producing impurities. The impurities are removed by filtration or other means. From the clarified feed the uranium is extracted countercurrently with 6% TBP in a hydrocarbon (Amsco) pretreated with oleum. Any extracted plutonium and fission products are scrubbed from the solvent with 3 M HNO_3 which is 0.02 M in ferrous sulfamate to reduce plutonium(IV) to the trivalent state. The uranium is stripped from the solvent in a second column with 0.01 M HNO_3. The feed/scrub/solvent/strip volume ratios are 100/20/40/15. In laboratory studies, plutonium alpha, gross beta, and gross gamma decontamination factors were 3×10^5, 5×10^4, and 1×10^4, respectively.

The first-cycle product is evaporated and adjusted to 3 M HNO_3 and 164 g of uranium per liter, and the uranium is extracted with 18% TBP in Amsco. The solvent is scrubbed with 3 M HNO_3--0.02 M ferrous sulfamate, and the uranium is stripped with 0.01 M HNO_3. The feed/scrub/solvent/strip volume ratios are 3.06/2.0/9.6/9.6. In laboratory studies, gross beta and gross gamma decontamination factors were 330 and 2500, respectively; zirconium and niobium were the chief product contaminants. These results indicate that further purification will not be needed; however, if it is, the zirconium and niobium may be removed by sorption on silica gel.

The various radioactive waste streams are neutralized, evaporated, and stored. Used solvent is washed with sodium carbonate solution and water and is recycled.

In the first cycle, four extraction and four stripping stages are adequate to reduce the uranium loss to 0.02%. The HETS values estimated from 0.75-in.-diam pulsed column demonstration runs are 4 and 2.4 ft, respectively, for the extraction and stripping stages. Batch countercurrent tests showed that in the second cycle three extraction and four stripping stages were more than adequate to reduce the uranium loss in

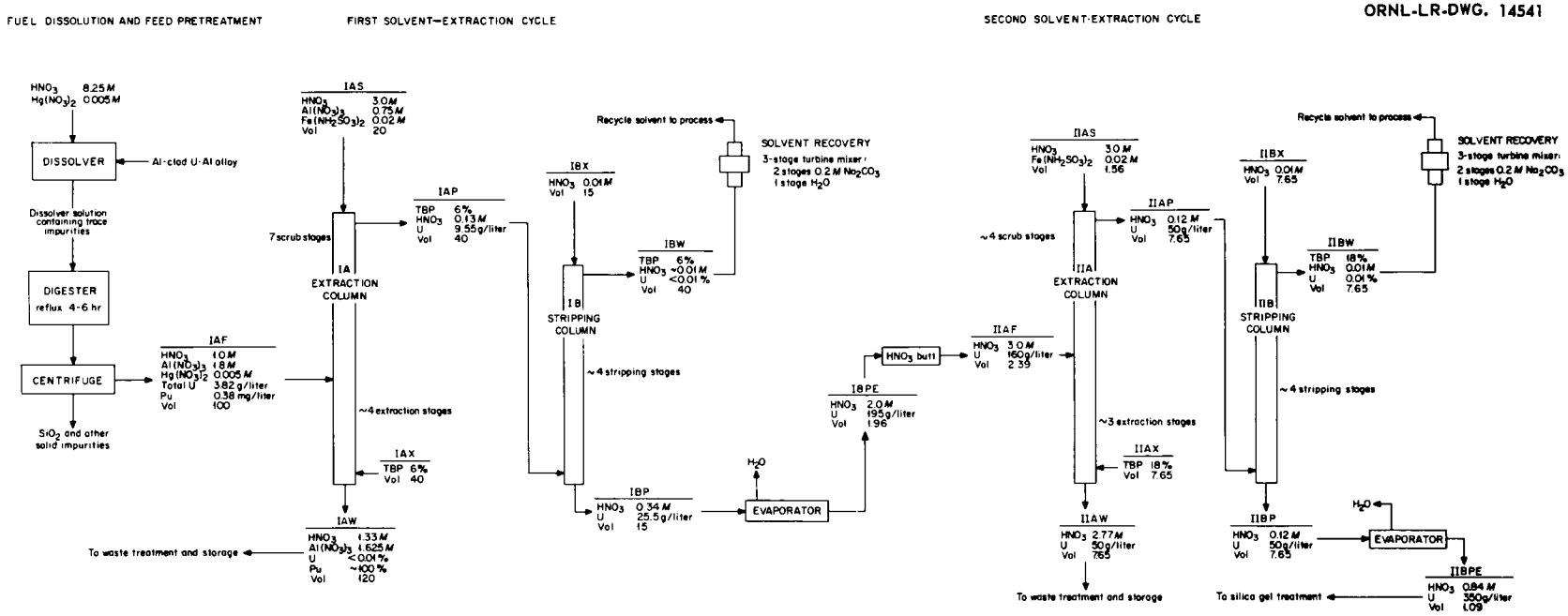

Fig. 3.1. Proposed 25-TBP Process Chemical Flowsheet.

each waste stream to less than the design value of 0.01%. The estimated HETS values, based on previous experience, were roughly 2.5 and 5 ft for the extraction and stripping stages, respectively. No excessive uranium losses are anticipated as a result of radiation damage to the solvent.

The volume of the first-cycle extractant may be adjusted when processing fuels having different irradiation histories in order to compensate for varying uranium concentrations in the feed and thus maintain the uranium concentration at 9.55 g/liter in the extraction-column product. Likewise, the stripping solution volume would have to be adjusted proportionately in these cases.

4. STUDIES ON THE DISSOLUTION OF THE Al-U ALLOY

Maximum batch dissolution rates of 185 and 140 mg min^{-1} cm^{-2} for extruded and cast uranium-aluminum alloy, respectively, were obtained with about 8 M HNO_3 catalyzed with 0.005 M $Hg(NO_3)_2$. The dissolution rate was independent of the uranium concentration of the alloy up to 15 wt % but was affected by the metallurgical history of the alloy. In continuous dissolution, return of the condensate to the midpoint of the column increased the dissolution rate 12% over that when the condensate was returned to the top. The column product was stable above 20°C with regard to aluminum nitrate precipitation. The studies were made with natural uranium-aluminum alloy.

Dissolutions in caustic and caustic-nitrate systems[6] were considered early in the 25-TBP process development program, but the work was discontinued, largely because of the many engineering and criticality problems encountered in separating the uranium solids from the caustic solutions of dissolved fuel.

4.1 Laboratory-Scale Batch Dissolution

4.1.1 Effect of Nitric Acid Concentration

The dissolution rates of both extruded 15 wt % and of cast 5 wt % uranium alloy increased as the nitric acid, catalyzed with 0.005 M $Hg(NO_3)_2$, was increased from

0 to about 8 M. The rate then decreased as the acid concentration was increased further to 12-16 M (Fig. 4.1).

A twofold increase in the ratio of dissolvent volume to alloy area had no perceptible effect on either the dissolution rate or the optimum acid concentration. In process application, excess acid in the fuel dissolution step to produce feed solutions containing 1 M HNO_3 is needed to help eliminate interfacial solids (Sec 5.2) in the first-cycle extraction column.

4.1.2 Effect of Mercuric Nitrate Concentration

In batch studies with extruded 15 wt % U--85 wt % Al alloy, the dissolution rate in 8 M HNO_3 increased from nearly 0 to 185 mg min^{-1} cm^{-2} as the mercuric nitrate concentration was increased from 0 to 0.005 M. Above 0.005 M $Hg(NO_3)_2$, the rate increased only slightly (Fig. 4.2). Under comparable conditions the dissolution rate of cast 5.37 wt % U alloy was about 140 mg min^{-1} cm^{-2} in 8 M HNO_3--0.02 M $Hg(NO_3)_2$. Extruded 15 wt % U alloy dissolved in 4 M HNO_3--0.002 M $Hg(NO_3)_2$ at a rate of 130 mg min^{-1} cm^{-2}, which was about four times the rate for cast 7.5 wt % U alloy in this reagent. The dissolution rates were calculated from the known average dimensions of the alloy dissolved, the dissolution time, and the weight loss.

In similar studies at another site, cast 7.5% U-Al alloys dissolved at a rate of 5 mg min^{-1} cm^{-2} in 5 M HNO_3 with 0.0005 M $Hg(NO_3)_2$ present, at about 0.5 mg min^{-1} cm^{-2} with no catalyst, and at a maximum of 35 mg min^{-1} cm^{-2} in 4 M HNO_3 with 0.002 M $Hg(NO_3)_2$.

The catalytic action of the mercury is postulated as follows: Before the dissolution begins there is a brief induction period during which the protective oxide film on the metal surface, which resists attack by the nitric acid, is destroyed. Small amounts of mercuric ion near the slowly reacting aluminum surface are reduced to metallic mercury, which, during its transient existence in nitric acid, amalgamates the metal surface and so prevents further formation of the protective oxide film. The amalgamated area reacts vigorously with the nitric acid producing more metallic

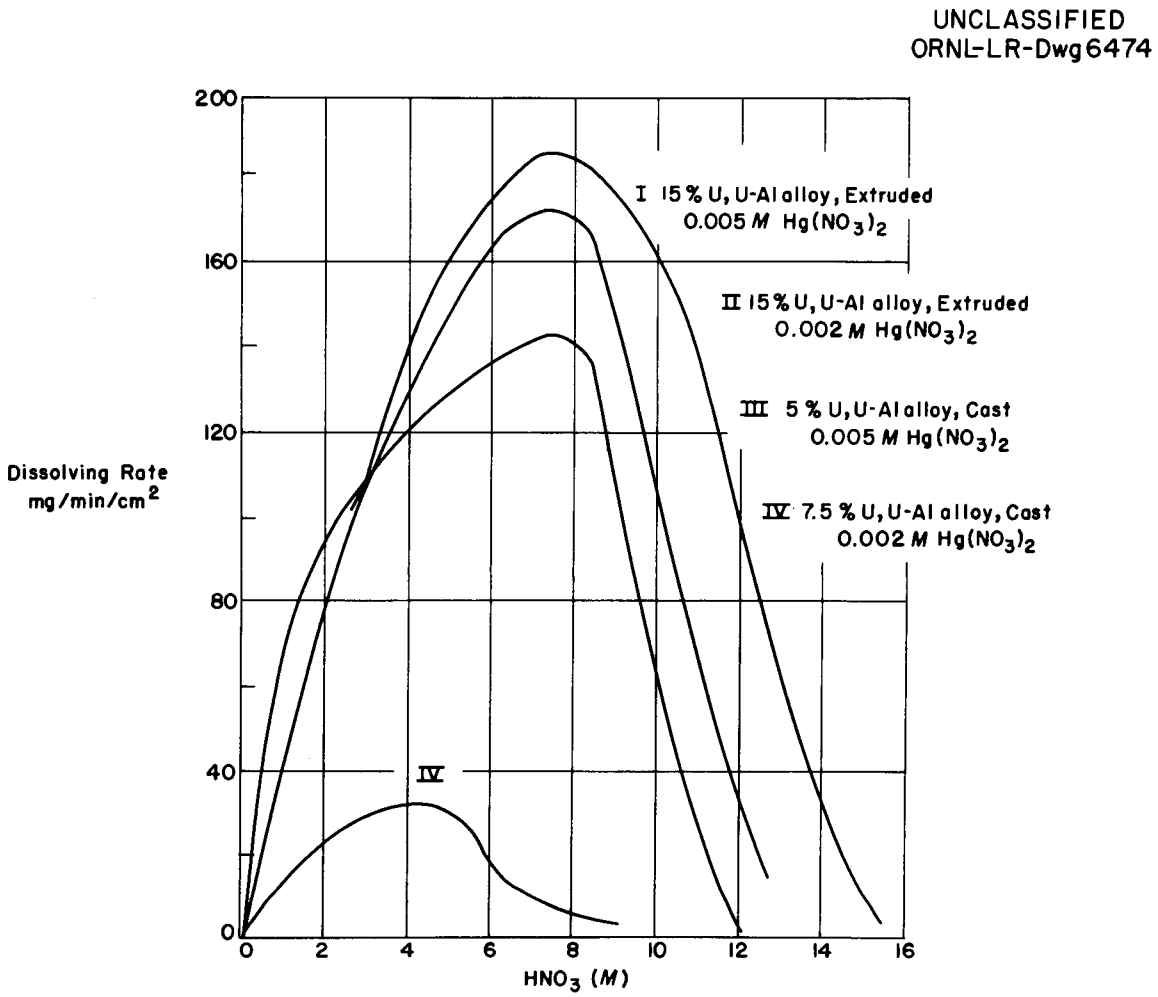

Fig. 4.1. Dissolution Rates of Uranium-Aluminum Alloy in Nitric Acid.

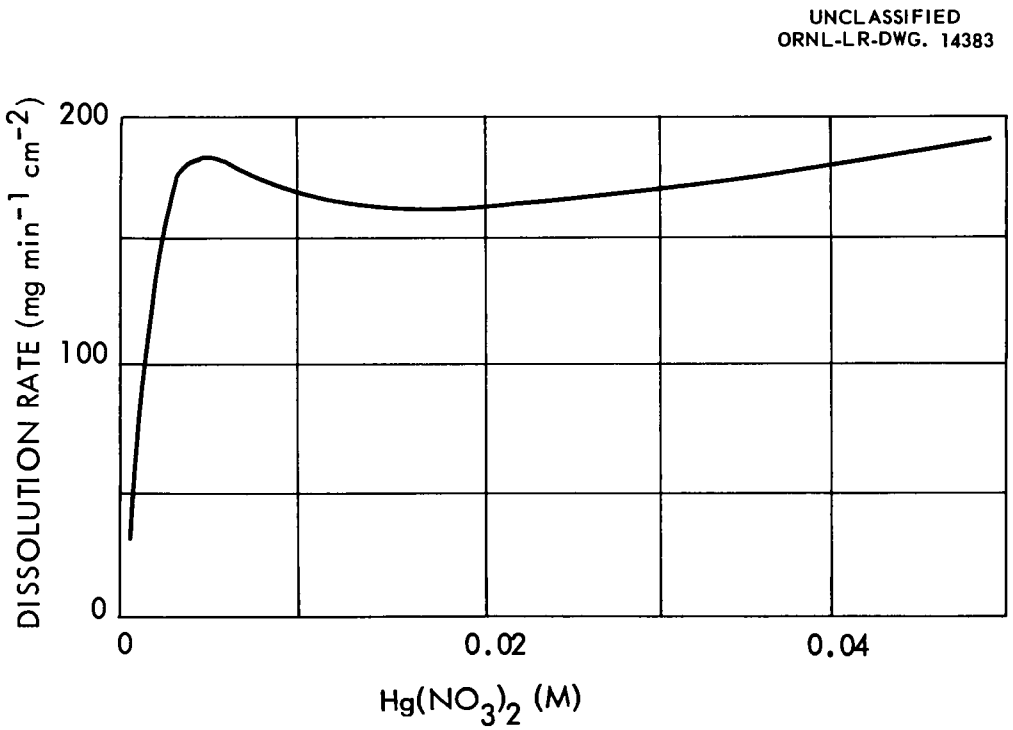

Fig. 4.2. Effect of Mercuric Nitrate Concentration on Dissolution Rate of Extruded 15 wt % Uranium --85 wt % Aluminum Alloy in 8 M HNO_3.

mercury, which perpetuates the cyclic reaction until a balance is reached between the mercury reduction by the dissolving alloy and dissolution of the mercury in nitric acid.

To avoid the induction period in the batch dissolution studies, the metal was pretreated in a separate portion of the nitric acid-mercuric nitrate experimental solutions to preform the amalgamated surface. The amalgamated alloy was quite reactive and rapidly formed a bulky oxide coating in air. To avoid handling difficulties caused by this coating, the specimens were weighed in tared bottles of 2-propanol to exclude air.

4.1.3 Effect of Aluminum Nitrate Concentration

The dissolution rate decreased rapidly as the aluminum nitrate concentration of the solution increased, using initial nitric acid concentrations from 2 to 10 M (Fig. 4.3).

4.1.4 Effect of Composition and Metallurgical History of the Alloy

There was no difference in the dissolution rates of the 5, 7.5, and 15 wt % U alloy, but extruded metal dissolved much faster than cast. Different regions of a single piece of alloy dissolved at very different rates, especially the cast alloy. The reproducibility of rate data for cast alloy was poorer than for extruded.

Small-scale batch dissolution of aluminum-clad 15 wt % U alloy in mercury-catalyzed nitric acid solutions showed that there is no marked preferential dissolution of the alloy or the cladding.

4.2 Large-Scale Batch Dissolutions

In three dissolutions of aluminum-clad 15 wt % U alloy fuel elements with 7.4* M HNO_3--0.005 M $Hg(NO_3)_2$, 10 to 12 hr was required for complete dissolution. In a fourth run, dissolution was complete in 2 hr. The reduction in dissolution time

---

*To produce 1.8 M $Al(NO_3)_3$ product, 8.25 M HNO_3 is required, assuming no reflux.

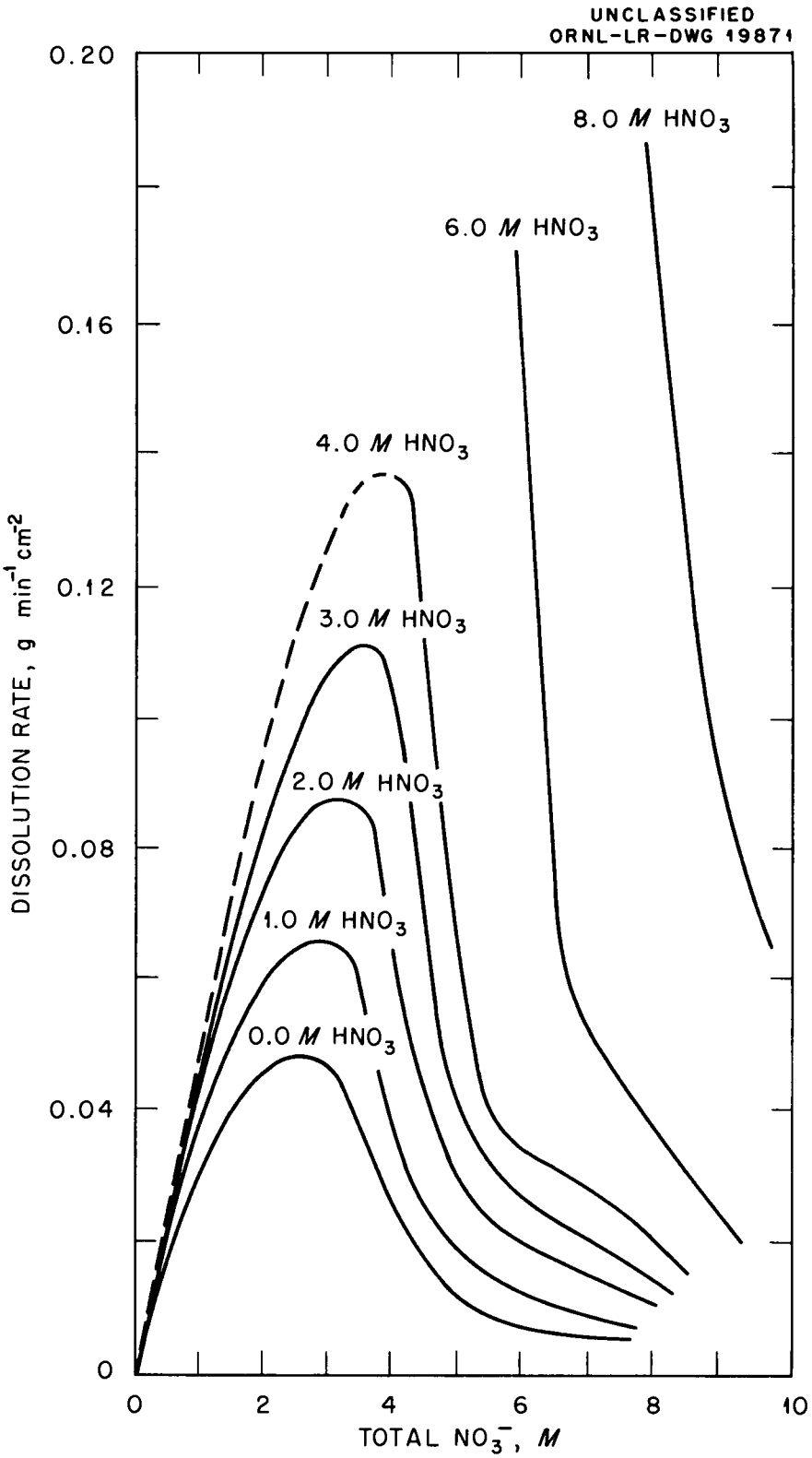

Fig. 4.3. Dissolution Rates of Extruded 15% Uranium -- 85% Aluminum Alloy in Aluminum Nitrate-Nitric Acid Containing 0.005 M Mercuric Nitrate.

is attributed to improved equipment-handling techniques. The dissolution progress as a function of time was obtained in the final run by periodic analyses of the dissolved fuel solution for uranium, aluminum, and nitric acid (Table 4.1). In each run, 2500 g of fuel and 50 liters of dissolvent were used. The reaction was started by heating the dissolvent to 90°C; the initial violent reaction was controlled by cooling water for about 1 hr. Steam was then reapplied to hold the dissolver temperature at about 105°C.

4.3 Continuous Dissolution Studies

In continuous dissolution studies of miniature extruded 15 wt % U alloy rods, the dissolution rate was 12% higher when the cold condensate was returned to the middle of the column of fuel rods than when it was returned at the top. Heating of the condensate prior to returning it to the column, to eliminate the quenching action of the cold solution, did not further increase the dissolution rate.

The experiments were made in a 1-in.-diam trickle-type glass column (Fig. 4.4) packed with rods to a height of 6 in. The dissolvent was 6 M* HNO_3--0.005 M $Hg(NO_3)_2$, and the fuel was extruded 2.4-in. by 0.2-in. diam slugs of 15 wt % natural uranium alloy. Here, an acid deficient 1.8 M $Al(NO_3)_3$ product was obtained.

4.4 Product Stability

Any product containing excess acid obtained from acid feeds of 10 M HNO_3 or less should be completely stable (no precipitation of aluminum nitrate) above 20°C (Fig. 4.5). The stability should not be affected by up to an 11% variation in feed acid concentrations or by unusually low dissolution rates in the dissolver. All realizable product $Al(NO_3)_3/HNO_3$ ratios in the mole ratio ranges 0/9 to 2.25/0 are stable down to about 1°C.

---

* See footnote on p 9.

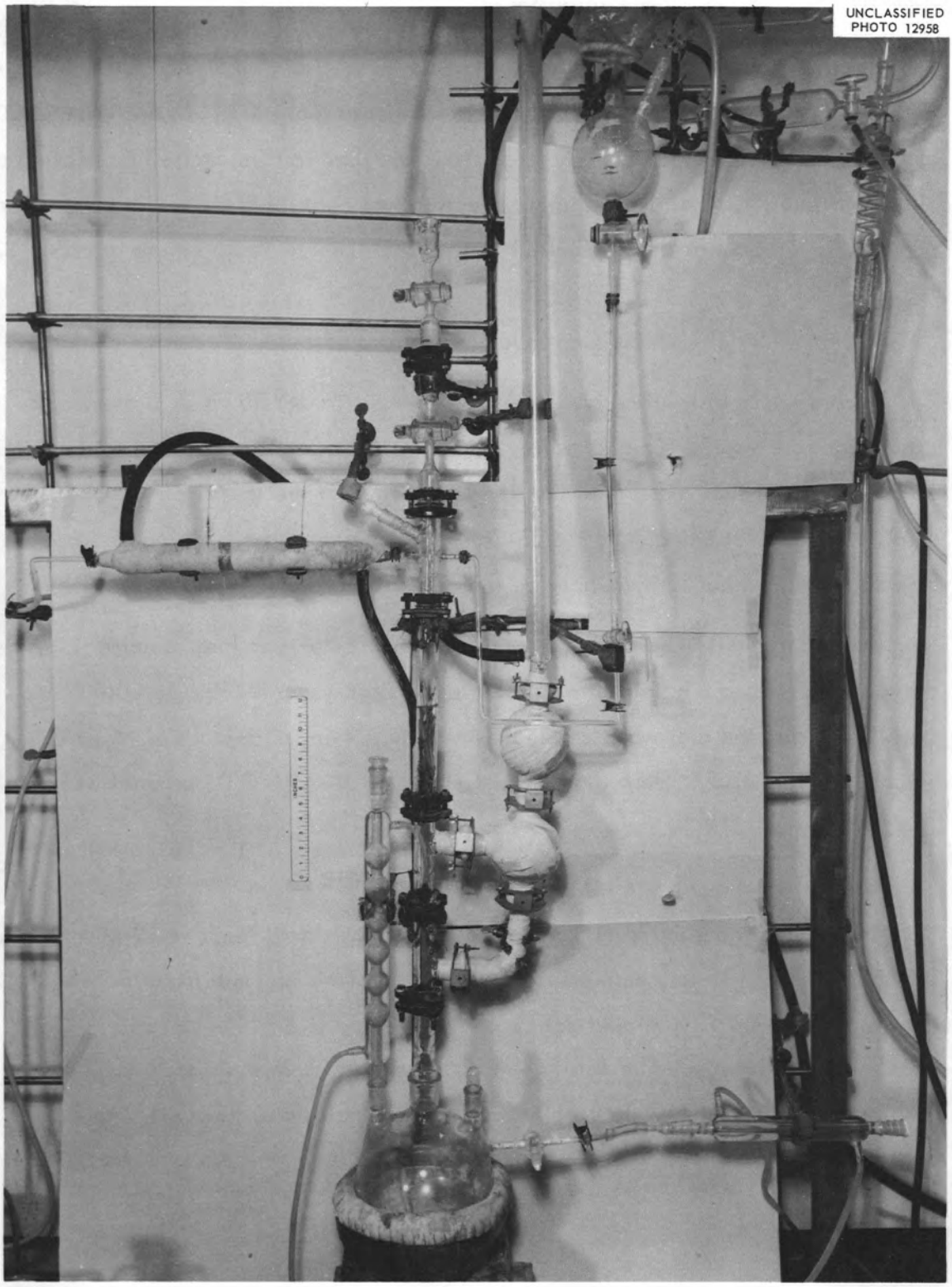

Fig. 4.4 Trickle-Type Glass Column.

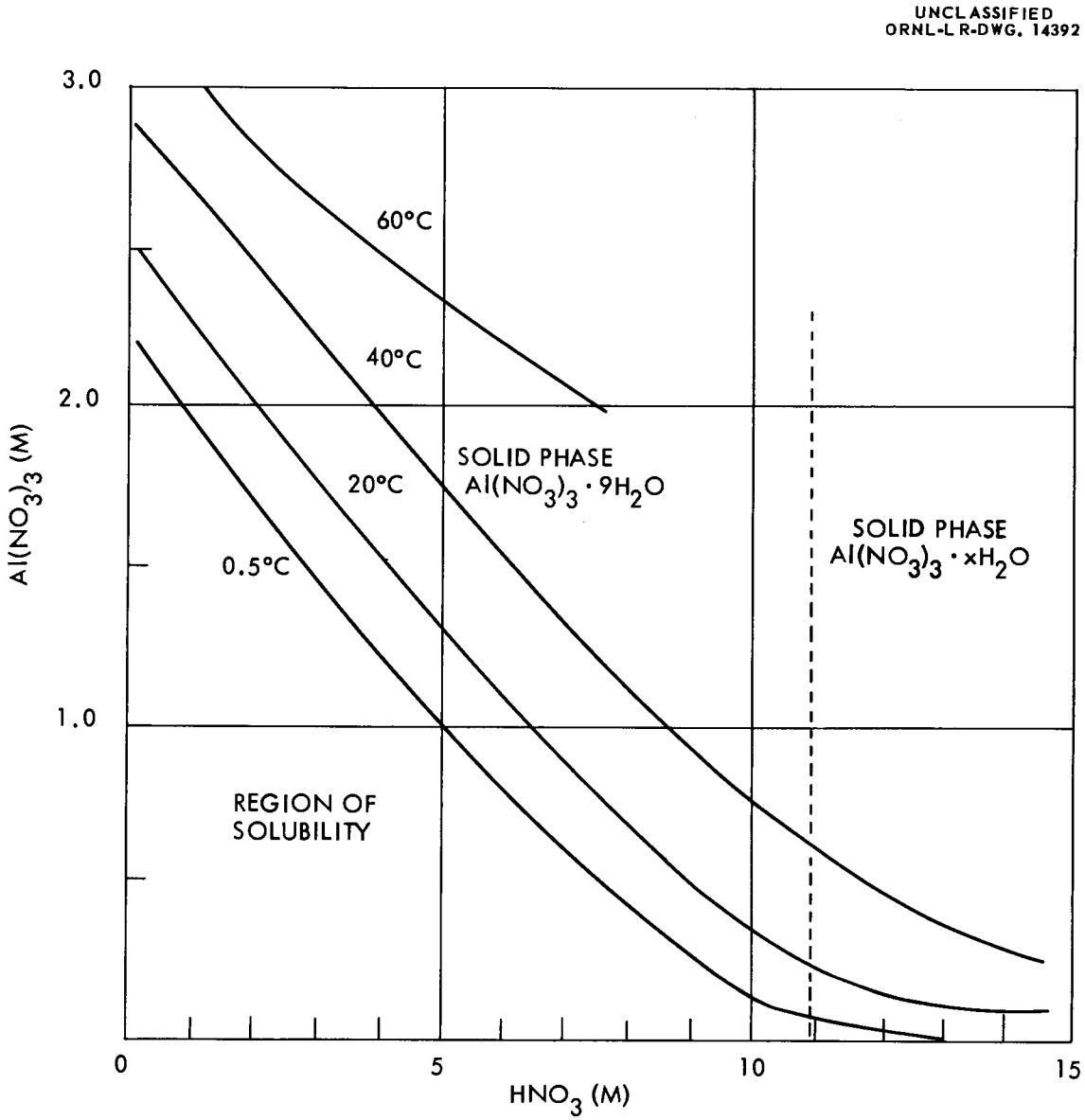

Fig. 4.5. Compositions at 20°C of Solutions Saturated at Various Temperatures in the $Al(NO_3)_3$-HNO_3-H_2O System. Taken from A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds."

Table 4.1 Dissolution of Aluminum-Clad 15% Natural Uranium Alloy in Boiling 7.4 M HNO_3--0.005 M $Hg(NO_3)_2$

Dissolution Time (hr)	H^+ Conc. (M)	U Conc. (mg/ml)	Al Conc. (mg/ml)	Volume (liters)	Amount Dissolved (wt %)
0.5	1.76	2.89	36.7	50	84.5
1.0		3.80	40.9		
2.0	0.74	4.12	42.7		
2.5		3.97	43.7		
3.0	0.79	4.01	44.1		
3.5		4.05	47.2		
4.0	0.83	4.01	44.3	48	99

4.5 Behavior of Fission-Product Iodine

Fission-product ^{131}I in the dissolver off-gas from mercury-catalyzed nitric acid dissolution of spent, short-decayed, U-Al alloy fuels must be removed before the off-gas is released to the atmosphere. A minimum iodine-removal factor of 10^4 is required under the proposed process conditions. This decontamination was not achieved by forming the mercuric iodide complex in the dissolver (Table 4.2).

In previous studies with simulated dissolved fuel solutions, 2.2 M $Al(NO_3)_3$--0.5 M HNO_3, the presence of 0.01 M $Hg(NO_3)_2$ prevented significant iodine evolution when the solutions were heated at 95 to 100°C for 1 hr, provided that the iodine concentration was no more than 10^{-5} M.[7] However, these experiments do not completely represent process dissolution conditions where oxides of nitrogen are present, and aluminum competes with the iodine for the mercury.

Dissolution experiments were made to determine whether sufficient iodine would be complexed by the mercury under process conditions to eliminate the necessity for additional iodine-removal equipment. Rods of 5.37 wt % U alloy (3.5 g) were

Table 4.2 Iodine Evolution During Acidic Dissolution of Uranium-Aluminum Alloy as a Function of Iodine and Mercury Concentrations

Run No.	Conditions [I][a]	Conditions [Hg][a]	Iodine Distribution (%) Pot	Condenser	Dead Trap	1st NaOH	2nd NaOH	$AgNO_3$	Total I_2 Evolved (%)	D.F.	Material Balance (%)
1	0.5	1	102.79	0.093	0.051	0.037	0.067	0.018	0.27	376	103.06
2	1	1	98.79	0.123	0.070	0.106	0.051	0.061	0.41	243	99.18
3	2	1	99.38	0.177	0.042	0.460	0.461	0.139	1.28	78.2	100.63
4	4	1	100.75	0.196	0.081	0.104	0.026	0.087	0.49	202	101.23
5	1	0.5	97.35	0.245	0.124	0.149	0.058	0.104	0.68	146.9	98.02
6[b]	2	1	51.23	0.736	3.505	32.923	0.258	0.040	37.5-48.9	< 2.7	88.69
7	2	1	100.63	0.216	0.090	~0.040	0.246	0.064	0.61	164.5	101.24
8	4	1	95.27	0.120	0.175	0.158	<0.021	~0.044	0.51	193.4	95.77
9	4	1	98.43	0.135	0.045	0.065	0.018	<0.009	0.27	368.6	98.71

[a]Unity = normal process concentration; i.e., I/U weight ratio = 36/20,000, $Hg(NO_3)_2$ = 5% of total alloy weight.

[b]Condenser not functioning; Tygon tubing lines were contaminated with radioactivity that could not be recovered, which accounts for the poor material balance.

dissolved in 5 M HNO_3, containing mercuric nitrate catalyst equivalent to either 2.5 or 5% of the total alloy weight. The HNO_3/Al mole ratio was 4.25/1. The iodine was added to the system in amounts varying from 0.5 to 4 times the expected level. A stock solution of 0.2 M NaOH--0.0036 M Na_2SO_3 containing dissolved molecular iodine and ^{131}I tracer was used. The dissolutions were made in a glass pot equipped with a 30-in.-high glass reflux condenser followed by a series of gas traps. The first was a "dead" trap, containing air, and the next two traps contained cooled 8 M caustic. The final trap contained a 1 M $AgNO_3$ solution. Air was used as a sweep gas to oxidize NO to NO_2. After each run, the pot, traps, lines, and condenser were washed with caustic, water, and acetone, and the wash solutions, pot solutions, and trap solutions were analyzed by gross beta counting. The decontamination factors ranged from 78.2 to 376, with one run producing a decontamination factor of 3 when the condenser failed.

5. FIRST-CYCLE EXTRACTION-COLUMN EMULSIONS AND INTERFACIAL SOLIDS

When the dissolved fuel solution (feed) was extracted, fine, stringy, solids collected in the column at the phase interface, or organic emulsions formed. Sometimes both happened. As the solids built up, smooth column operation was impossible, and decontamination factors were poor as a result of radioactive fission products being carried over into the stripping column with the solids. When the aqueous phase acid concentration was less than 1 M during the extraction, a yellow mercury precipitate formed. The emulsions and interfacial solids were reduced in amount or eliminated by pretreatment of the solvent diluent, dissolution in excess acid followed by feed digestion, and control of the acidity of the solution at the feed plate. With the higher acid concentration in the aqueous phase, the yellow mercury precipitate was also eliminated.

5.1 Pretreatment of the Diluent

Pretreatment of the Amsco diluent with oleum helped prevent the formation of interfacial solids but did not eliminate the problem altogether. The recommended procedure is given in the Appendix (Sec 11.2).

5.2 Dissolution Conditions

Dissolution of aluminum-clad 15 wt % uranium--85 wt % aluminum alloy with excess acid to produce a feed 1 M in HNO_3, 1.8 M in $Al(NO_3)_3$, and 3.82 g of uranium per liter followed by feed digestion (Sec 5.3) eliminated or greatly reduced the amount of interfacial solids.

5.3 Pretreatment of the Feed Solution

Dissolution with excess acid eliminated the interfacial solids problem, the effect being attributed to the decreased solubility of silica in the stronger acid. However, feed thus prepared formed organic emulsions, although these had never been encountered with feed prepared under acid-deficient dissolution conditions. The emulsions were eliminated by digesting the 1 M HNO_3 dissolved fuel solution at the boiling point for 4 to 6 hr, filtering through a coarse glass frit, and finally adjusting to the solvent extraction flowsheet feed conditions. The laboratory-scale equipment required for this head-end treatment is shown in Fig. 5.1. This treatment also prevented the precipitation of white mercury sulfamate in the extraction column (Sec 5.6).

A more drastic treatment, digestion with 2 M acid followed by evaporation to a relatively high boiling point to drive off the water, was necessary to eliminate emulsion formation with similar feed prepared by dissolving 2S aluminum barstock and adding uranyl nitrate. The silica content was about 1% of the aluminum barstock weight and was negligible in the actual alloy samples dissolved. This procedure was effective when the initial acid concentration was 2 M or higher. Since the solutions are rather corrosive during the evaporation, this treatment should be used only if organic emulsions or prohibitive amounts of interfacial solids persist after the milder 4- to 6-hr digestion with 1 M HNO_3.

Laboratory studies were made in order to adapt the Thorex procedure[3] for dehydrating silica to 25-TBP process conditions. The feed was prepared by adjusting aliquots of the barstock solution to acidities ranging from 1.5 to 11 M by adding

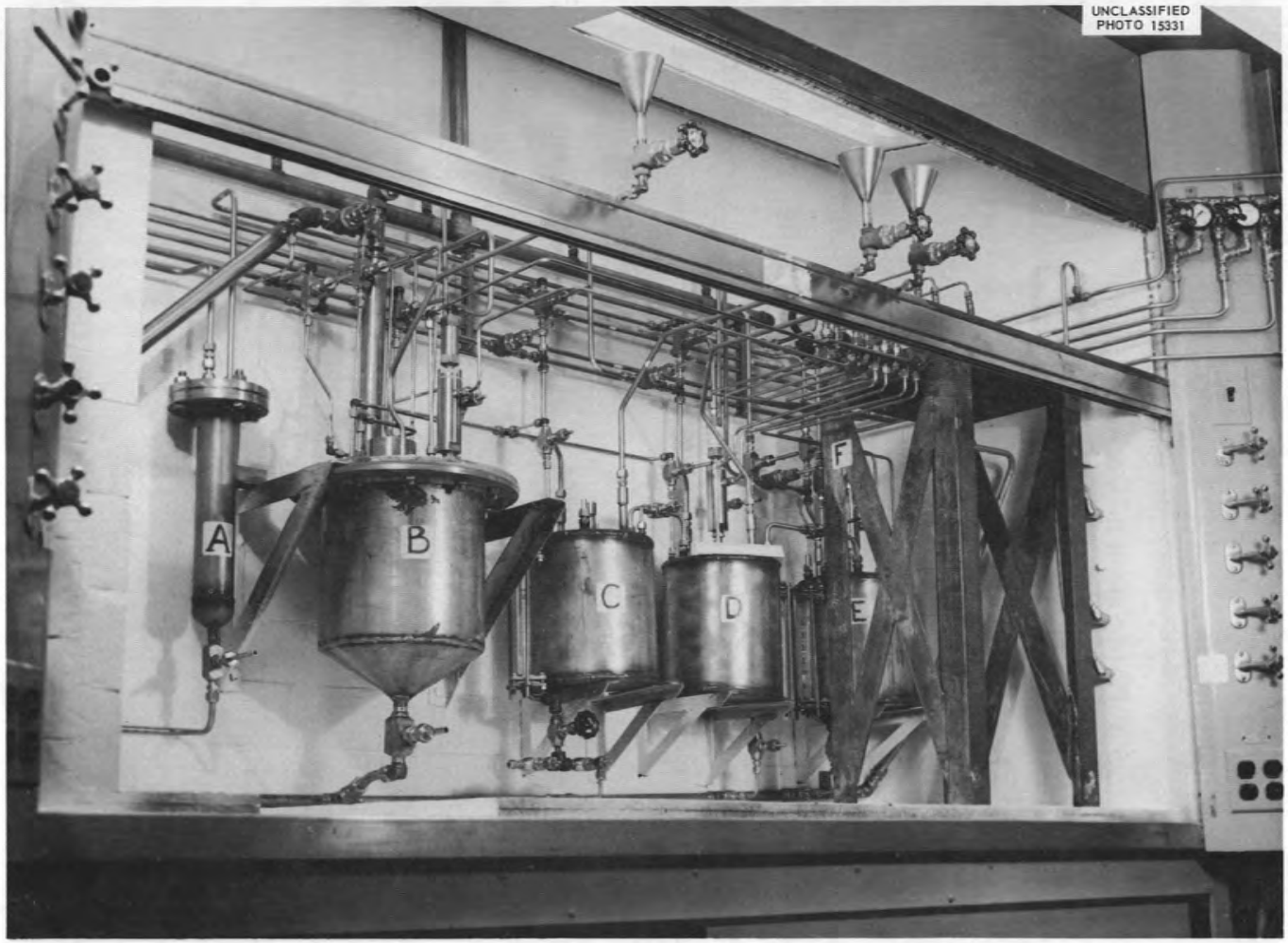

Fig. 5.1. Equipment Used in Feed-Adjustment Studies. (A) Vacuum trap. (B) Dissolver. (C) Hold tank. (D) Feed-adjustment tank. (E) Aqueous raffinate tank. (F) Sample blister support.

nitric acid. The aluminum concentrations varied from 1.74 to 0.6 M. The solutions were refluxed at the boiling points (110 to 120°C) for 0.25 to 3 hr and then evaporated until a boiling point of 130°C was reached, with a final volume approximately half that of the original barstock solution. After dilution to the original volume with water, the acidities ranged from 0.5 to 0.6 M for the 1.5 and 2.0 M acid digestions, and from 0.86 to 1.0 M for the digestions at 4 M acid and greater. The acid initially present came off in the distillate and was reclaimable.

Solutions were tested for emulsion formation by vigorously stirring, for 1.5 min, 100 volumes of the unfiltered solution and 20 volumes of neutral 0.75 M $Al(NO_3)_3$--0.02 M ferrous sulfamate with 40 volumes of 6% TBP in oleum-treated Amsco diluent. The phase disengagement times indicated the effectiveness of the treatment, the longest time indicating the least dehydration. Disengagement times of up to 90 sec were considered satisfactory for smooth column operation. The barstock solution digested at an acidity of 1.5 M for 3 hr produced a stable organic emulsion in the batch-equilibration test. In other tests, nearly clear organic phases were obtained in 50 to 90 sec, and completely clean interfaces in 3 to 3.5 min. Digestion times of 0.25 to 3 hr gave phase disengagement times of 30 to 240 sec, showing no apparent correlation with digestion time.

5.4 Effect of Aqueous-Phase Acidity in the Extraction Column

A scrub solution of 3 M HNO_3--0.75 M $Al(NO_3)_3$--0.02 M $Fe(NH_2SO_3)_2$ is recommended for eliminating organic emulsions and preventing excessive uranium reflux in the extraction column. This provides an aqueous acidity of 1.33 M at the feed stage. No organic emulsification or excessive uranium reflux was seen in pulsed-column runs with this scrub when digested and filtered uranium-aluminum fuel solution containing 1 M HNO_3 was used as the extraction column feed. The acidity at the feed plate was held to a minimum 1 M to prevent the yellow mercury precipitate observed in early experiments (Sec 5.6).

In a series of 0.75-in.-diam pulsed-column runs with the emulsion-producing solution from 2S aluminum barstock (Sec 5.3), scrub solutions of 0.75 M $Al(NO_3)_3$--0

to 1 M HNO_3 and of 2.5 to 4.0 M HNO_3 alone were investigated. The solvent was 6% TBP in oleum-treated Amsco diluent. The proposed flowsheet flow ratios of feed (AF)/scrub (AS)/solvent (AX) = 100/20/40 were used in all runs. Stable organic emulsions were obtained with acidities up to 1.0 M when the scrub stream was 0.75 M $Al(NO_3)_3$. With 2.5 M HNO_3 alone as scrub, there was a faint, hazy, emulsion layer, but there was none with 2.75 to 4.0 M HNO_3. Because of excessive uranium reflux from insufficient salting strength (Sec 6.1) when the scrub was nitric acid alone, the mixed scrub was recommended.

Batch-equilibration studies with simulated feed-stage solution prepared from chemically pure reagents corroborated the pulsed-column data; phase disengagement times varied inversely as the nitric acid concentration. Stable emulsions were not generated in any case. The simulated aqueous phases, containing 1.6 M $Al(NO_3)_3$, 2.7 g of uranium per liter, 0.004 M $Hg(NO_3)_2$, 0.003 M $Fe(NH_2SO_3)_2$ and 0.1 to 2.0 M HNO_3, were refluxed 15 min prior to addition of the sulfamate (Sec 6.1) and then batch-equilibrated for 1.5 min with 1/3 volume of 6% TBP in oleum-treated Amsco. The disengagement times, from 50 sec with 2 M acid to 290 sec with 0.2 M, showed a trend (Fig. 5.1) which may indicate inverse correlation with the solubility of mercury, as a function of acid concentration, under simulated extraction column conditions (Sec 5.6).

When digested and filtered solution from fuel element dissolution was substituted for the simulated feed in a similar batch-equilibration experiment, the phase disengagement times increased from 70 sec to 145 sec as the aqueous phase acidity increased from 0.8 to 2.0 M. Also, clear, bubbly organic emulsions, which were stable for more than 18 hr, were obtained in every case. The discrepancy between these data and those obtained with the simulated fuel solution (see Fig. 5.2) suggests that either the actual fuel solution contains different emulsion-producing impurities, or the emulsion formers exist in different forms in the two solutions. The fuel solution used in this experiment contained 1.4 M $Al(NO_3)_3$, 0.94 M HNO_3, 0.004 M $Hg(NO_3)_2$, 15 ppm of SiO_2, and 3.97 g of uranium per liter. The scrub solutions were all 0.75 M $Al(NO_3)_3$--0.02 M ferrous sulfamate and contained nitric acid in amounts such that when the

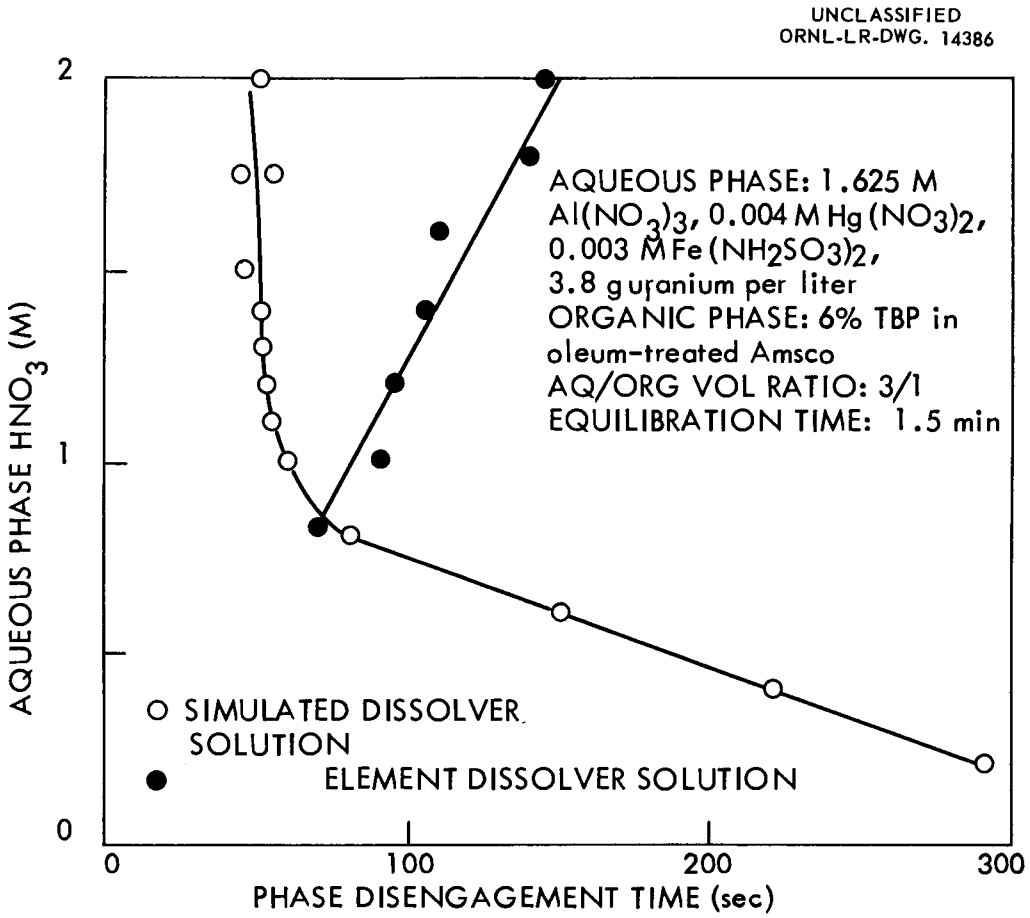

Fig. 5.2. Phase Disengagement Time as a Function of Feed Plate Acidity.

AF/AS ratio was 100/20, the aqueous phase acid concentration was adjusted to the desired molarity. The solvent was 6% TBP in oleum-treated Amsco, 1/3 the volume of the total aqueous phase. The batch-equilibration time was 1.5 min.

5.5 Effect of Phase Mixing

The method of phase mixing may influence organic emulsification, as evidenced by the anomalous behavior of uranium-aluminum fuel solution in the pulsed column and laboratory batch studies (Sec 5.4), but more quantitative data are required. In the pulsed-column runs, no emulsification was noted with a feed-plate acidity of 1.33 M. However, stable emulsions were obtained in batch equilibrations under identical conditions of volume and concentration at aqueous-phase acidities of 1.25 to 1.5 M. The column was filled with aqueous phase and the solvent was gently dispersed by means of sieve plates and the applied pulse, but in batch equilibration very intimate and intense phase mixing was accomplished in a wide-mouth separatory funnel equipped with a high-speed impeller, which pumped the aqueous phase upward and dispersed it into the organic phase.

5.6 Behavior of Mercury under Extraction Column Conditions

The behavior of mercury under extraction column conditions was studied since little was known of its chemical properties in a TBP solvent extraction system with scrub solution containing ferrous sulfamate. The Purex process aqueous feed contains no mercury catalyst.

At least 1.5 M HNO_3 is required to prevent precipitation of mercuric ion in the presence of ferrous sulfamate at their feed-stage concentrations of 0.004 and 0.003 M, respectively. At less than 1.5 M HNO_3, a fine, white, crystalline precipitate is formed. Mercurous ion under identical conditions is soluble over the range of acidity studied.

When simulated feed-stage solution, 1.6 M $Al(NO_3)_3$, 0.08 M HNO_3, 0.004 M $Hg(NO_3)_2$ and 3 to 6 g of uranium per liter was boiled 5 min or aged at room temperature for one week, the mercuric ion was converted to a form that did not precipitate

when ferrous sulfamate was added. A negative test obtained on the boiled or aged solutions upon addition of chloride ion indicated that the mercuric ion had not been reduced to the soluble mercurous state. When either the aluminum and uranyl nitrates or the nitric acid was omitted from the simulated process solution, boiling or aging failed to prevent the precipitation of mercuric sulfamate. Hence, it is apparent that both high nitrate concentration and the presence of free hydrogen ion are required to effect the conversion.

Batch-equilibration studies under extraction-column conditions showed that the aqueous-phase acidity must be at least 1 M or mercury precipitation of a second type will occur upon contact with the solvent. The chemical composition of this precipitate, which is flocculent and pale yellow, was not determined. Tests showed that the precipitate was a mercury compound, other than a sulfamate, which required excess free acid to remain in solution. The occurrence of such a precipitate was considered to be a possible cause of organic emulsion formation (Sec 5.4). In these experiments, digested feeds, containing 3 to 6 g of uranium per liter, 0.005 M $Hg(NO_3)_2$, 1.8 M $Al(NO_3)_3$, and varying amounts of nitric acid, were prepared either from chemically pure reagents or by actual dissolution of U-Al alloy. The scrub solution was neutral 0.75 M $Al(NO_3)_3$-0.02 M $Fe(NH_2SO_3)_2$; 6% TBP in oleum-treated Amsco was used as the solvent. A feed/scrub/solvent volume ratio of 100/20/40 was used in all equilibrations.

6. URANIUM LOSSES AND DECONTAMINATION IN THE FIRST CYCLE

In process the uranium first-cycle extraction and stripping losses can be limited to the design values of 0.01% each with four extraction and four stripping stages. Uranium loss resulting from radiation decomposition of the solvent will be negligible with exposures up to 14 times the radiation dosage expected in a single pass through the first extraction column. Plutonium in the uranium product can be reduced to specifications with about four scrub stages. Gross beta and gamma decontamination factors of 5×10^4 and 1×10^4, respectively, may be expected in the first solvent

extraction cycle, the principal fission product contaminants in the product being zirconium and niobium.

6.1 Uranium Recovery

Batch-countercurrent runs made under the proposed first solvent extraction cycle flowsheet conditions (Fig. 3.1) showed that the uranium loss can be held to 0.01% each in the extraction column aqueous waste and in the solvent from the stripping column with four extraction and four stripping stages (see McCabe-Thiele diagrams in Figs. 6.1 and 6.2). HETS values estimated for a 0.75-in.-diam pulsed column were 4 and 2.4 ft for the extraction and stripping sections, respectively.

6.1.1 Effect of Total Nitrate Concentration

For a specific solvent (TBP) concentration, the efficiency of uranium extraction depends on the salting strength (total nitrate concentration) and the hydrogen ion concentration. In the presence of 1.0 to 1.8 M $Al(NO_3)_3$, the extraction of uranium by 6% TBP decreased with increasing nitric acid concentration (Table 6.1). This effect is the reverse of that observed in Purex-type systems over a limited range of nitric acid salting strength; however, results of similar chemical processing studies have shown that uranium extraction by 30% TBP passes through a maximum at approximately 8 M HNO_3.

This effect was considered in the design of the first solvent extraction cycle flowsheet, where a high nitric acid concentration is needed to minimize the collection of interfacial solids and to prevent organic emulsion formation and mercury precipitation. Column runs in which the aqueous phase at the feed stage was 1.5 to 1.6 M $Al(NO_3)_3$ showed that neither 3 to 4 M HNO_3 nor 0.5 M $Al(NO_3)_3$ scrub solutions alone provided sufficient salting strength to prevent excessive uranium reflux in the scrub section. A mixed scrub, 3 M HNO_3--0.75 M $Al(NO_3)_3$, was therefore recommended (see p 39).

6.1.2 Effects of Radiation Damage to Solvent

Uranium retention in solvent samples that had received up to 14 times the

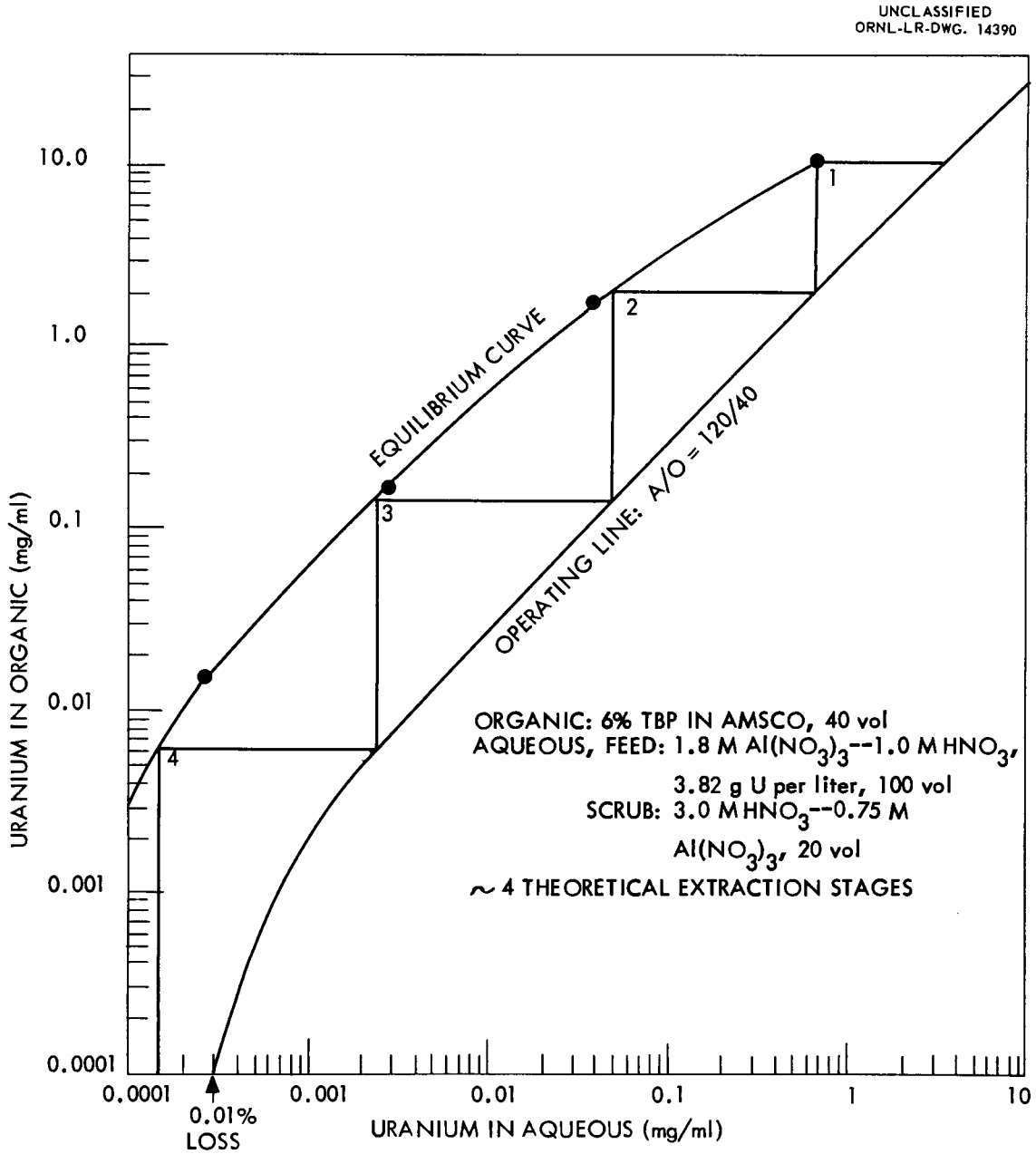

Fig. 6.1. Uranium Concentrations in Organic and Aqueous Phases under 25-TBP Process First-cycle Extraction Column Conditions.

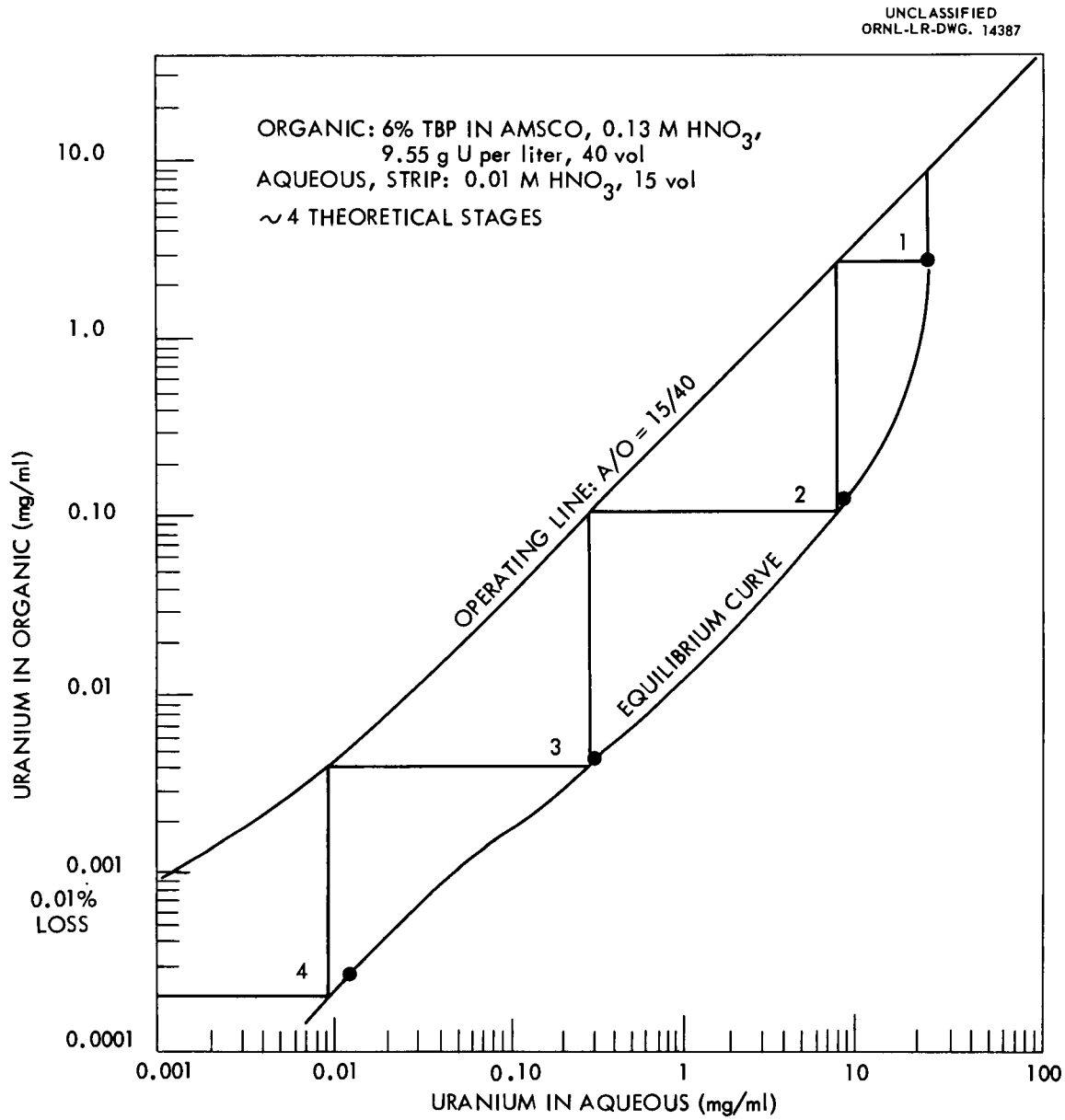

Fig. 6.2. Uranium Concentrations in Organic and Aqueous Phases under 25-TBP Process First-cycle Stripping Column Conditions.

Table 6.1 Uranium Extraction Coefficient at Various Concentrations of Aluminum Nitrate and Nitric Acid

Aqueous phase: 2 g uranium per liter + $Al(NO_3)_3$ and HNO_3 as shown

Equal-volume batch equilibrations; 1.5 min at 25°C

$Al(NO_3)_3$ (M)	Uranium Extraction Coefficient, org/aq[a]			
	0.0 M HNO_3	0.3 M HNO_3	0.6 M HNO_3	1.0 M HNO_3
0.5	2.15	3.12	4.12	4.72
1.0	34	25	26	19.6
1.4	330	83	85	64
1.6	1150	432	138	83.5
1.8	2320	534	276	98.6

[a]Uranium concentration in organic phase/uranium concentration in aqueous phase under equilibrium conditions.

radiation dosage expected in a single pass through the extraction-scrub column indicated that uranium losses to the solvent stream from the stripping column attributable to radiation-induced decomposition of the solvent will be negligible. The uranium-retaining decomposition products present in solvent irradiated to 14 times the extraction column process level were adequately removed by intercycle washings with sodium carbonate, nitric acid, and water. Therefore no gradual increase in uranium loss is expected as the number of solvent recycles increases (Sec 8.2).

6.1.3 Effect of Citrate in Stripping Solution

Stripping with aqueous citrate solutions under proper pH conditions gave higher product concentrations because of the uranyl citrate complex formed. However, the low solubility of sodium citrate, and the instability of the uranyl citrate solution, made this method unattractive. Potassium citrate was more soluble than the sodium salt, and the product was more stable, but the permissible operating range was still too narrow for process application. Ammonium citrate was considered undesirable because of the

hazard of evaporating ammonium nitrate solutions for final waste storage. A cost analysis on the sodium citrate system indicated that the process would be uneconomical because of reagent and waste-disposal costs. (See Sec 11.1 for details.)

6.1.4 HETS Calculations

In the HETS studies in the 0.75-in.-diam pulsed column, the heights of the extraction and stripping sections were 6 ft each and the scrub was 8 ft. Uranium loss specifications were approached but not met owing to insufficient column heights.

6.2 Uranium Decontamination*

In batch countercurrent runs under recommended flowsheet conditions, with six scrub stages the plutonium decontamination factor was 3.3×10^5, indicating that plutonium will be eliminated in the first cycle with four scrub stages. The 0.02 M ferrous sulfamate used in the scrub effectively reduced tetravalent plutonium to the nonextractable trivalent state. In two mixer-settler runs (Fig. 6.3) uranium was decontaminated from gross beta and gamma activities by average factors of 7×10^4 and 1×10^4, respectively. In four 0.75-in.-diam pulsed column runs (Fig. 6.4), gross beta and gamma decontamination factors averaged 5×10^4 and 3×10^3, respectively.

6.2.1 Decontamination from Plutonium

The plutonium decontamination experiments were made with synthetic feed containing Pu(IV) tracer (9.2×10^6 counts min^{-1} ml^{-1}).

In earlier work 0.02 M sulfate ion had been ineffective for forming a nonextractable plutonium complex at the high nitrate concentrations required in the process solutions for adequate uranium recovery. The highest plutonium decontamination factor with the sulfate system in pulsed column runs was 200.

6.2.2 Decontamination from Fission Products

The gross beta and gamma decontamination factors in the mixer-settler runs, 7×10^4 and 1×10^4, respectively, are averages of values obtained in runs 2 and 3 (Table 6.2).

* The decontamination factor is defined as $\frac{A_f U_p}{A_p U_f}$, where A is the activity in counts min^{-1} ml^{-1}, U is the uranium concentration in g/liter, and the subscripts f and p designate the feed and product streams, respectively.

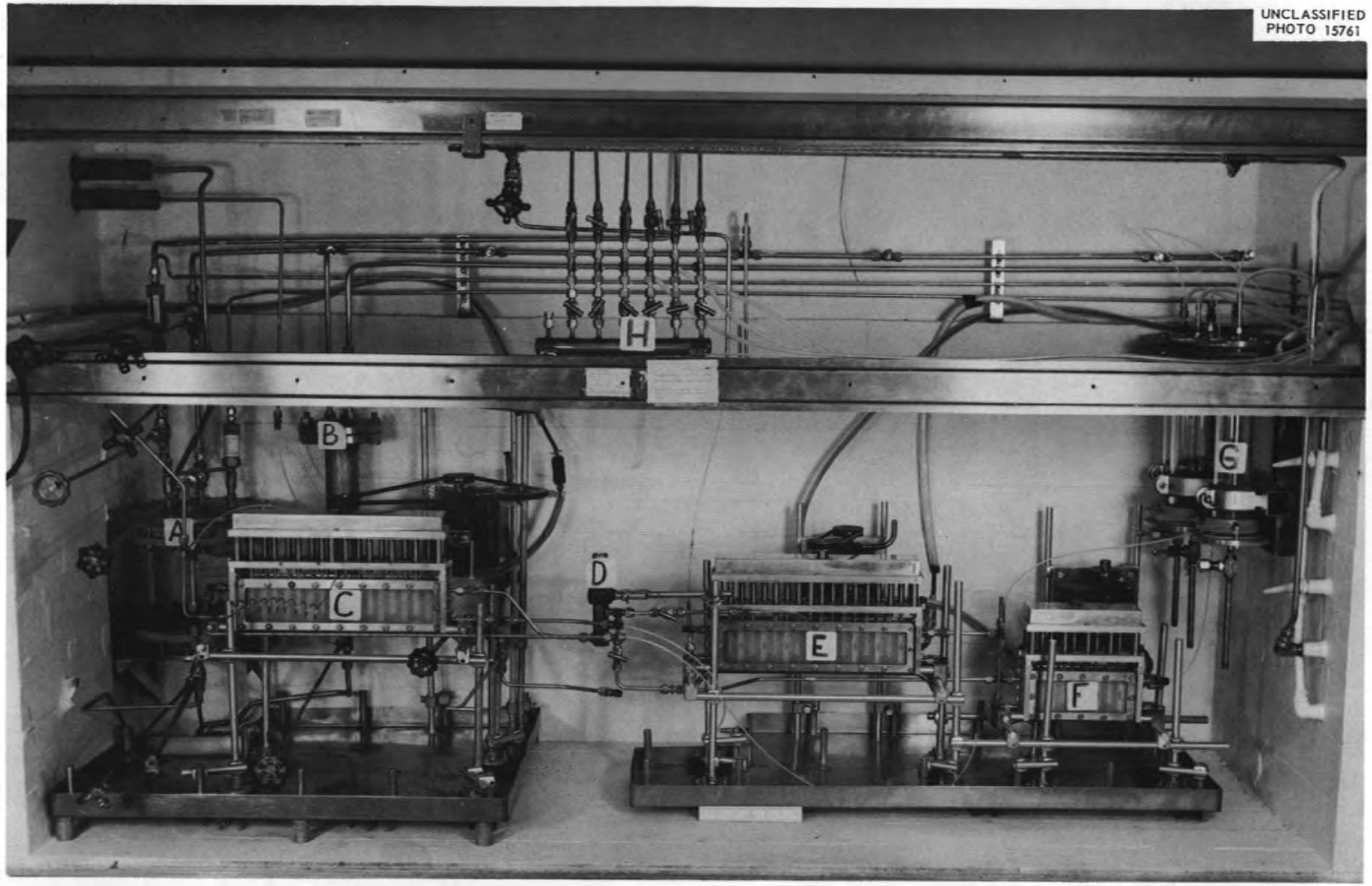

Fig. 6.3. Mini Mixer-Settler Equipment. (A) Feed displacement tank. (B) Vacuum trap. (C) Extraction-scrub bank. (D) A-column product (sample holdup pot). (E) Partitioning bank (not used). (F) Strip bank. (G) Product collection vessels. (H) Vacuum manifold.

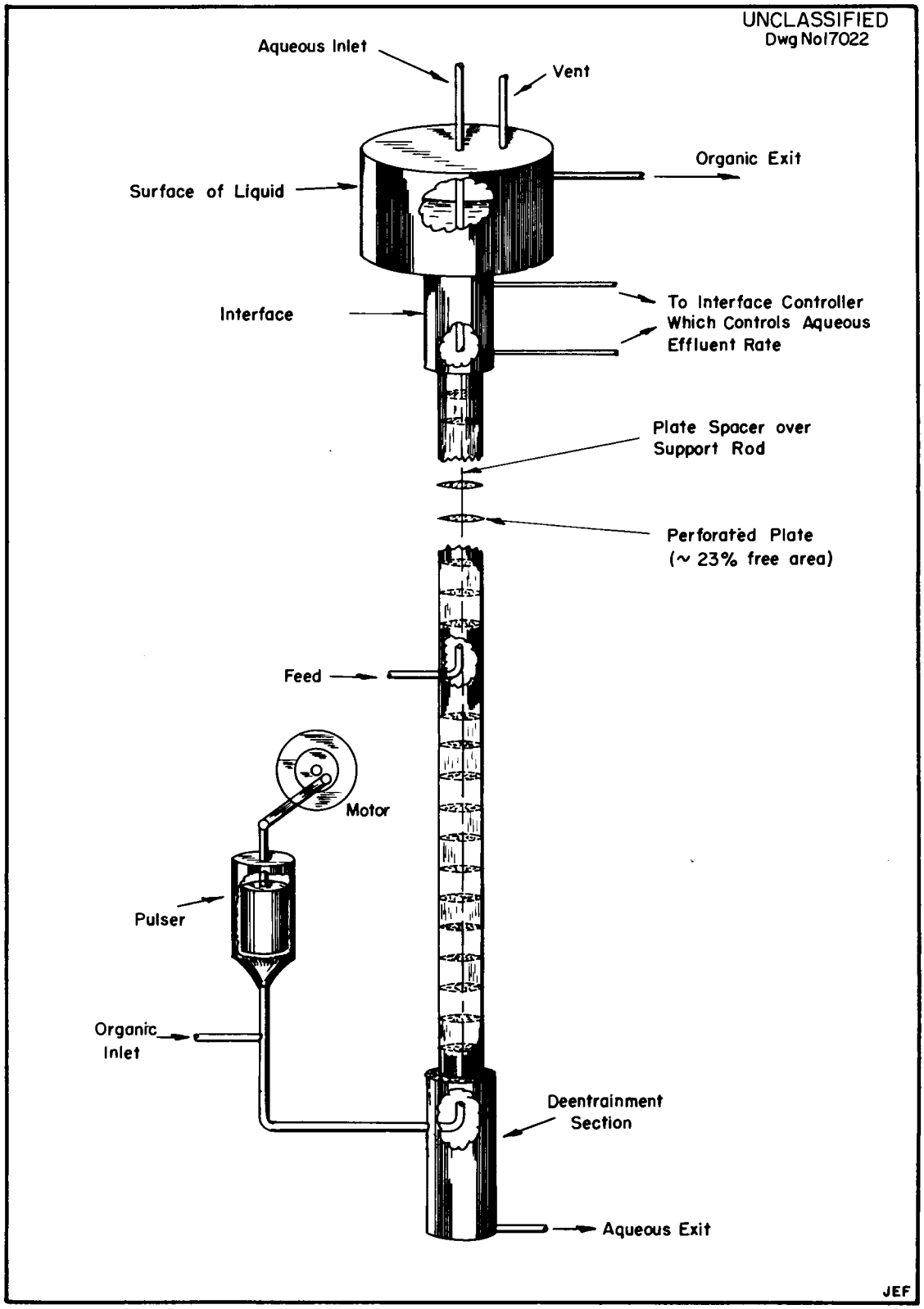

Fig. 6.4. Pulse Column for Extraction-Scrub Operation.

Table 6.2 Mixer-Settler Flowsheet Test Runs -- First Solvent Extraction Cycle Decontamination

Feed: Dissolved fuel solution containing 0.5-1.5 g U/liter, 1.8 M $Al(NO_3)_3$, 1 M HNO_3, and 0.005 M $Hg(NO_3)_2$; gross $\beta = 2.2\text{-}4.3 \times 10^9$ counts min^{-1} ml^{-1}; gross $\gamma = 0.55\text{-}2.26 \times 10^9$ counts min^{-1} ml^{-1}

Scrub: 0.75 M $Al(NO_3)_3$, 3 M HNO_3, 0.02 M $Fe(NH_2SO_3)_2$

Extractant: 6% TBP in oleum-treated Amsco

Strip: 0.01 M HNO_3

AF/AS/AX/BX = 100/20/40/15

Eight extraction stages; eight stripping stages

Run No.	No. of Scrub Stages	No. of Scrub Volume Changes	Duration of Run (hr)	Decontamination Factors				
				Gross β	Gross γ	Zr-Nb γ	TRE β	Ru β
1	6[a]	7	6	3.0×10^5	1.7×10^4	1.1×10^4	1.1×10^7	No sample
2	8	~12	10	8.4×10^4[b]	1.5×10^4	8.0×10^3	1.0×10^5	1.9×10^5
3	8	8	~7	5.8×10^4	6.2×10^3	4.9×10^3	No sample	1.6×10^6

[a]Fission products were still being removed in last stage.

[b]Estimated on the basis of analysis of IAW stream.

In the first run the values were high, 3×10^5 and 1.7×10^4, and were not reproducible. The discrepancy between these and later values may be due to adsorption of radioactive fission products on the equipment. Analysis of organic samples from each scrub stage showed that maximum decontamination requires seven mixer-settler scrub stages. Mixer-settler evaluation showed that one mixer-settler stage was approximately equivalent to 50% of a theoretical stage. This value is lower than the normally expected 75 to 80% stage efficiency and was probably caused by insufficient mixing, or diffusion, during sampling operations. Steady-state conditions with respect to fission product scrubbing were reached after the seventh volume change, or 6 hr of operation.

In the column runs, when an 8-ft scrub section was used, gross beta decontamination factors agreed closely with those in the mixer-settler runs, but gross gamma decontamination was from two- to threefold lower (Table 6.3). In the fourth column run in which the scrub section was 4 ft, the gross beta decontamination factor was decreased twentyfold, while the gross gamma was decreased only fourfold. This indicates that the gamma emitters (zirconium and niobium) are not removed from the organic phase as readily as the beta (rare earths) in the scrub section. In the first column run, as in the mixer-settler runs, decontamination factors were very high and were not reproducible. In both mixer-settler and column runs, zirconium and niobium were the chief contaminants in the product.

The mixer-settler runs 1 and 2 were made with solutions of fuel samples that had been irradiated 1 year and had decayed from 8 to 12 months. The fuels were dissolved, and the solution was digested and adjusted to approximate flowsheet-recommended feed acid and aluminum nitrate concentrations. Uranium concentrations were low, 0.5-1.5 g/liter, and could not be adjusted without dilution of the ^{235}U with natural uranium. However, it is felt that this condition had very little influence on decontamination.

Feeds for the column runs were prepared by dissolving sections of unirradiated U-Al alloy fuel elements, digesting, filtering, and adding fission product solution obtained from irradiated U-Al alloy. The uranium concentrations in the feed solutions varied from 3.72 to 4.11 g/liter. Fission product activities ranged from 1.47×10^7 to 5.09×10^7 counts min^{-1} ml^{-1} for gross beta, and from 9.42×10^6 to 2.28×10^7 for gross gamma.

Table 6.3 Pulsed Column Flowsheet Test Runs--First Solvent Extraction Cycle Decontamination

Feed: Dissolved fuel solution with tracer fission products from irradiated U-Al alloy: 3.8 g U/liter 1.8 M $Al(NO_3)_3$, and 0.005 M $Hg(NO_3)_2$; gross $\beta = 1.47\text{-}5.09 \times 10^7$ counts min^{-1} ml^{-1}; gross $\gamma = 0.94\text{-}3.75 \times 10^7$ counts min^{-1} ml^{-1}

Scrub: 0.75 M $Al(NO_3)_3$, 3 M HNO_3, 0.02 M $Fe(NH_2SO_3)_2$

Extractant: 6% TBP in oleum-treated Amsco

Strip: 0.01 M HNO_3

AF/AS/AX/BX = 100/20/40/15

Extraction and stripping sections each 6 ft

Run No.	Length of Scrub Section (ft)	No. of Scrub Volume Changes	Duration of Run (hr)	Decontamination Factors				
				Gross β	Gross γ	Zr-Nb γ	TRE β	Ru β
1	8	~9	7	7.87×10^4	1.04×10^4	---	---	---
2	8	~9	7	2.52×10^4	5.33×10^3	4.93×10^3	$>10^5$	3.91×10^4
3	8	~ 14	11	5.08×10^4	2.70×10^3	1.79×10^3	$>10^5$	8.25×10^4
4	4	~ 16	6	2.7×10^3	6.2×10^2	---	---	---

6.2.3 Miscellaneous Studies

In preliminary studies with 0.75-in.-diam pulsed columns, fission product decontamination factors were determined as functions of the aluminum nitrate concentration in neutral scrub and of feed and scrub acidities. Feed solutions were prepared by dissolving portions of irradiated uranium rods and adjusting to be 1.8 M in $Al(NO_3)_3$, 0.005 M in $Hg(NO_3)_2$, and to contain 0.1 to 2 g of uranium per liter, with acidities ranging from 0.15 M acid deficiency to 0.86 M HNO_3. The feasibility of each of these systems with respect to uranium recovery was first determined in laboratory batch countercurrent runs with nonirradiated material. All runs were conducted with 6% TBP-Amsco.

With a 0.1 M HNO_3 feed and neutral scrub solution 0.5 to 1.0 M in $Al(NO_3)_3$ the gross beta, ruthenium beta, and rare earth beta decontamination factors varied inversely with the salting strength. However, with a 0.5 M $Al(NO_3)_3$ scrub, uranium reflux was prohibitive, and therefore a 0.75 M $Al(NO_3)_3$ scrub was chosen as a compromise between maximum decontamination and controlled reflux of uranium. Substitution of 3 M HNO_3 for 1 M $Al(NO_3)_3$ as the scrub solution significantly increased the ruthenium decontamination factor, but lowered the zirconium-niobium decontamination factor. This latter observation is not consistent with Purex experience.

Two pulsed column runs were performed with neutral 0.75 M $Al(NO_3)_3$ as the scrub. The first run used a feed which was 0.15 M acid deficient, whereas an 0.86 M acid feed was used in the second run. In the acid-deficient system the ruthenium decontamination factor was 1.3×10^4, and in the high-acid system it was 3×10^3 as compared to 10^3 obtained under the same conditions with a 0.1 M HNO_3 feed. The behavior of ruthenium in these pulse column runs is in agreement with observations made in earlier laboratory batch-equilibration studies.[8] The anomalous behavior of zirconium and niobium in these studies is attributed to their colloidal nature and their tendency to adsorb and concentrate on particles of interfacial solids.

7. SECOND SOLVENT EXTRACTION CYCLE

The proposed second-cycle flowsheet conditions (Fig. 3.1) were demonstrated in laboratory batch countercurrent runs to give the desired uranium recovery and decontamination. The first-cycle product is evaporated to a uranium concentration of approximately 195 g/liter, and adjusted to 3 M HNO_3 before being fed to the second cycle.

7.1 Uranium Decontamination

Overall gross beta and gamma decontamination factors of 4.6×10^6 and 1×10^7, respectively, are specified for the 25-TBP process. Since decontamination factors of 5×10^4 and 1×10^4 for gross beta and gamma, respectively, are expected in the first solvent extraction cycle, corresponding second-cycle decontamination factors of 92 and 10^3 are required. A laboratory batch countercurrent run under proposed second-cycle flowsheet conditions, using six scrub stages, indicated that these decontamination requirements probably will be met. A silica-gel treatment of the second-cycle product stream which is expected to yield a minimum Zr-Nb gamma decontamination factor of 10, may be necessary. The feed for this run was prepared from the slightly radioactive first-cycle product obtained in pulsed-column run 4 (Sec 6.2), in which only 4 ft of scrub section was used. The first-cycle product was evaporated and adjusted to contain 157 g of uranium per liter in 3.17 M HNO_3. Radiochemical analyses of the adjusted feed showed gross beta, 2.50×10^5 counts min^{-1} ml^{-1}; gross gamma, 1.11×10^6 counts min^{-1} ml^{-1}; Zr-Nb gamma, 1.04×10^6 counts min^{-1} ml^{-1}; total rare earth beta, 2.81×10^3 counts min^{-1} ml^{-1}; Ru beta, 780 counts min^{-1} ml^{-1}. Results of the experiment indicated that the fission products were not appreciably extracted; maximum decontamination was attained in approximately four scrub stages.

Decontamination factors were difficult to calculate because of the low residual activity and the ^{235}U background. However, assuming that all the activity in the second-cycle product stream was attributable to fission products, decontamination factors of 3.30×10^2 and 2.50×10^3 were obtained for gross beta and gamma, respectively. The product stream analyses - gross beta, 210 counts min^{-1} ml^{-1}; gross gamma,

124 counts min^{-1} ml^{-1}; Zr-Nb gamma, 115 counts min^{-1} ml^{-1}; total rare earth beta, <50 counts min^{-1} ml^{-1}; and Ru beta, <25 counts min^{-1} ml^{-1} - show that in the second cycle, as in the first, zirconium and niobium are the limiting product contaminants.

Plutonium decontamination in the second cycle is not expected to be a problem, since first-cycle studies (Sec 6.) indicated that plutonium is approximately 100% removed in four scrub stages in the extraction column. The use of ferrous sulfamate in the second-cycle scrub is merely a precautionary measure.

7.2 Uranium Recovery

The uranium loss specified for the second cycle is 0.01% to each waste stream. A batch countercurrent run simulating the proposed second-cycle flowsheet conditions, using five extraction, six scrub, and six strip stages, showed that the uranium loss can be met with three extraction and four stripping stages (see McCabe-Thiele diagrams, Figs. 7.1 and 7.2).

No column runs were made under the recommended second-cycle flowsheet conditions and therefore no estimates of HETS values for the extraction or stripping sections were obtained. Previous studies of a similar system, where aqueous feed containing about 140 g of uranium per liter and 3 M HNO_3 was extracted with 15% TBP in Amsco, yielded average HETS values of 2.5 and 5 ft in a 2-in.-diam pulsed column for the extraction and stripping stages, respectively.

8. SOLVENT TREATMENT

Impurities in the Amsco diluent, as shipped, were responsible for some of the interfacial solids. Radiation decomposition products could cause high uranium losses; also, residual radioactivity in recycled solvent would present health hazards. Methods for pretreatment of the solvent and diluent and for intercycle cleanup were therefore developed.

8.1 Solvent Pretreatment

Intense discoloration of the solvent, from water-white to orange-yellow, and the buildup of gray-black interfacial solids were noted when untreated Amsco was used in

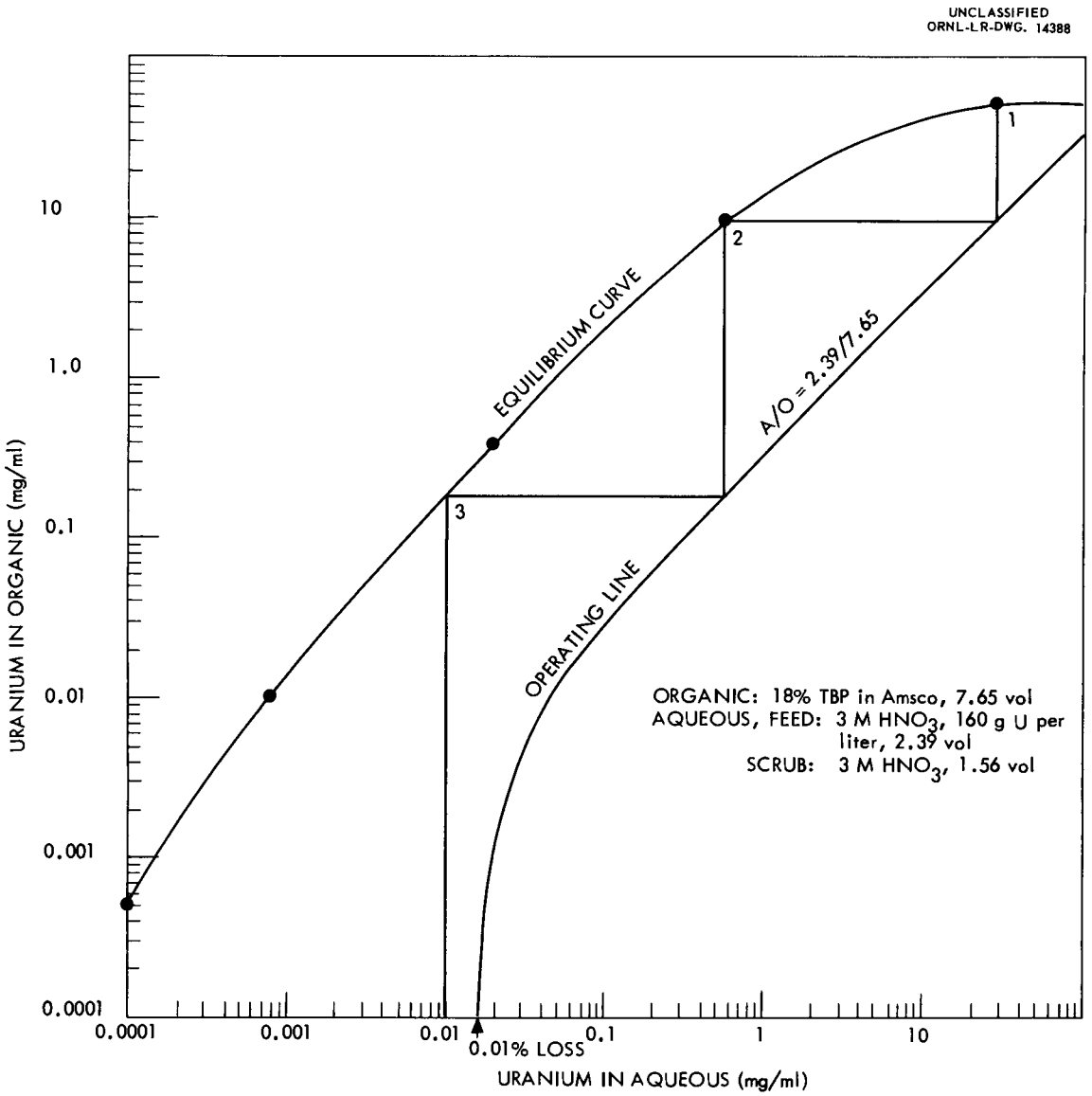

Fig. 7.1. Uranium Concentration in Organic and Aqueous Phases under Second-cycle Extraction Column Conditions.

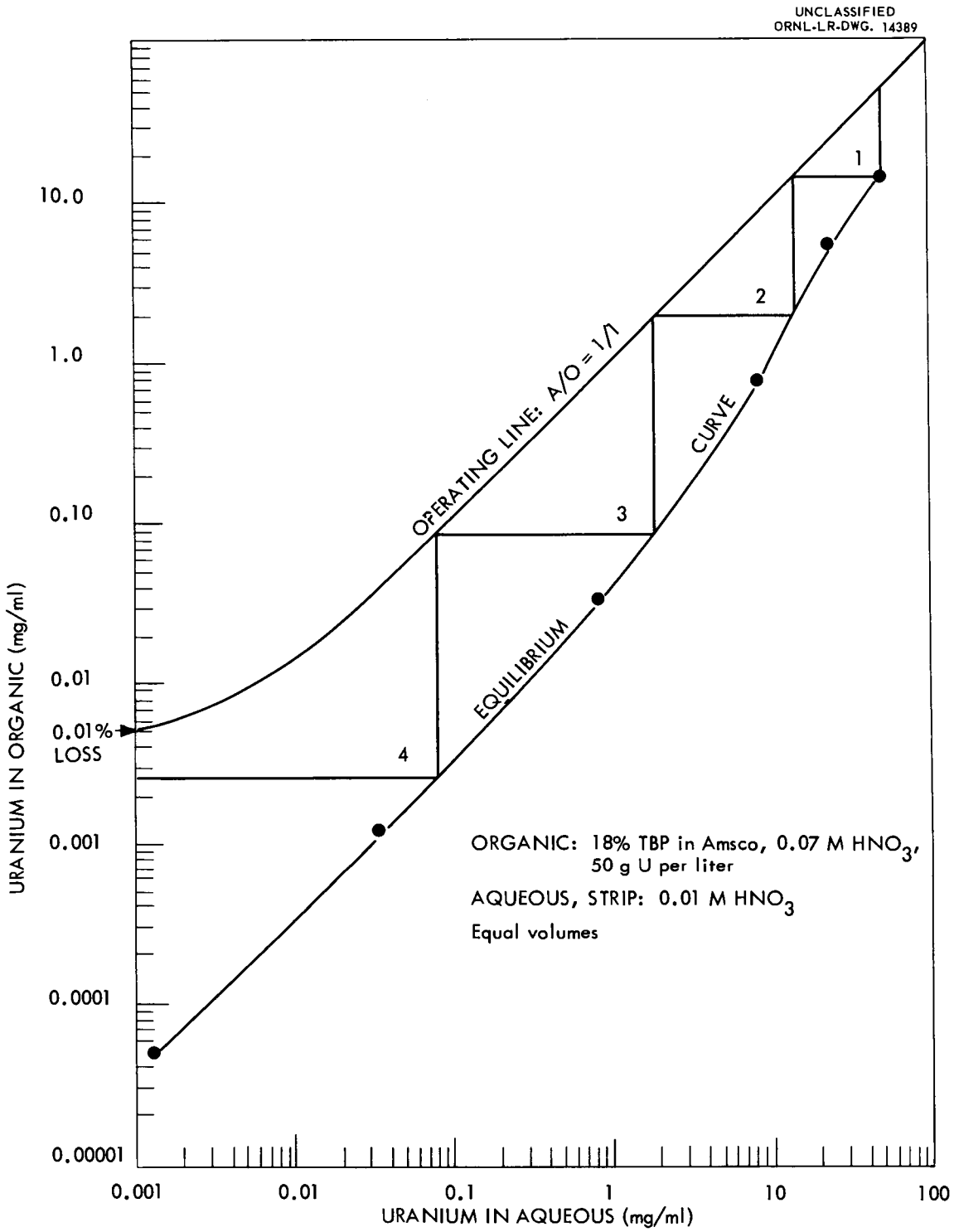

Fig. 7.2. Uranium Concentration in Organic and Aqueous Phases under Second-cycle Stripping Column Conditions.

early 25-TBP process pulsed-column runs with radioactive feed solutions. The solids built up in the column, interfered with operation and caused poor uranium decontamination.

A significant decrease in the amount of interfacial solids and the elimination of solvent discoloration were noted when the diluent was pretreated with oleum[3] and the solvent with calcium hydroxide before they were combined. The oleum treatment (Sec 11.2) sulfonated the aromatic and unsaturated components in the diluent, making them water-soluble so that they were removed by washing with water and caustic. The calcium hydroxide removed acidic constituents from tributyl phosphate. Uranium decontamination was also improved, presumably because entrainment of the highly radioactive solids in the extraction column product stream was substantially decreased when less solids accumulated. No ^{131}I was present in the test runs because only long-decayed irradiated fuel was used in feed preparation. It is expected that oleum pretreatment will improve iodine decontamination when iodine is present since the unsaturated compounds with which iodine combines are removed by this method. Better decontamination from residual activity in the used solvent was also realized in the solvent reconditioning step when the Amsco had been pretreated with oleum than when untreated diluent was used.

8.2 Solvent Recovery

Radiation-induced decomposition products and residual radioelements must be removed from the stripped solvent prior to recycling it as extractant. A build-up of radiation-induced decomposition products in the solvent could result in excessive uranium retention in the waste streams, and hence intolerable uranium losses. The accumulation of residual activity to a high background level would necessitate installation of additional shielding and remote-handling equipment in the solvent makeup area, increasing the capital and operating costs of the plant. The procedure recommended for removing both radiation decomposition products and residual fission products from solvent before recycle is successive washing with two 1/3 volumes of 0.2 M Na_2CO_3 and one 1/3 volume of demineralized water in a turbine-mixer.

8.2.1 Removal of Radiation Decomposition Products

Previous work[9,10] had shown that radiation induces the hydrolysis of TBP to dibutyl phosphate (DBP), monobutyl phosphate (MBP), and phosphoric acid. The amounts of MBP and phosphoric acid formed under reasonable irradiation conditions are very small, but the amount of DBP formed is significant. Since DBP and uranyl nitrate form an organic-soluble complex much stronger than the one formed with TBP, its presence could result in the retention of excessive amounts of uranium in the solvent. Experiments on ^{60}Co irradiation of diluted solvent alone and of intimately mixed solvent and aqueous phase indicated that radiation damage to the solvent in process will not be a major source of uranium loss, and that buildup of decomposition products can be prevented by intercycle washing.

In experiments where only the organic phase was irradiated, samples of 18% TBP in oleum-pretreated Amsco were exposed to radiation dosages of 0.175, 0.7, 3.5, 17.5, and 35 beta whr/liter. These values correspond, respectively, to approximately 0.7, 3, 14, 70, and 140 times the 0.238 whr/liter expected in the separation process for a single pass of solvent through the extraction column. The irradiated solvents were batch-equilibrated with equal volumes of 3 M HNO_3 solution containing 40 g of uranium per liter added as uranyl nitrate. The phases were separated, and the organic layers were stripped several times with double volumes of demineralized water or 1/4 volumes of 1.5 M triammonium citrate. Control samples of nonirradiated solvent were treated identically.

When the solvent had been exposed to radiation of 3.5 beta whr/liter or less, three strips reduced the uranium concentrations in the solvent to 0.001 g/liter (0.01% uranium loss) or less. With solvent that had been exposed to 17.5 and 35 beta whr/liter radiation, uranium retention was 0.08 and 0.4 g/liter (0.2 and 1% loss), respectively, after four passes of either water or citrate strip solution. The background uranium retention in the nonirradiated control was 0.0002 g/liter.

The solvent that had been exposed to 35 beta whr/liter radiation was washed with two 1/5 volumes of 0.1 M Na_2CO_3, then 0.1 M HNO_3, and finally with water. When this washed solvent was equilibrated with an equal volume of the uranyl nitrate-nitric

acid solution and then stripped four times with double volumes of demineralized water, the uranium retention in the organic phase was only 0.001 g/liter.

In the mixed-phase studies, the liquid received 3.3 beta whr/liter of solvent, in one case as a continuous 50-min irradiation, and in two cases as five 10-min irradiations. In one of the intermittent-irradiation experiments the solvent was washed with two successive 1/5 volumes each of 0.1 M Na_2CO_3, 0.1 M HNO_3, and water before each irradiation. The organic phase was 6% TBP in oleum-pretreated Amsco. The aqueous feed from a U-Al alloy fuel element was 1.8 M in $Al(NO_3)_3$, 1 M in HNO_3, 0.005 M in $Hg(NO_3)_2$, and contained 3.8 g of uranium per liter. A 0.75 M $Al(NO_3)_3$--3 M HNO_3--0.02 M ferrous sulfamate scrub was used. To simulate IA-column feed-plate conditions as nearly as possible, the AF/AS/AX ratio was 100/20/40. The phases were intimately mixed during the irradiation. After each irradiation, the phases were separated, and the organic phases were stripped with five consecutive double volumes of water. Nonirradiated control samples were given the same treatment.

The continuously exposed solvent required four strips to reduce the uranium loss to 0.01%, results comparable to those obtained when only the solvent phase was irradiated. In the intermittent-irradiation experiments, without intercycle solvent cleanup, three strips were adequate for a 0.01% uranium loss after the first, second, and third 10-min exposures, but four strips were needed after the fourth and fifth exposures to achieve this. There was a gradual buildup of uranium in the organic phase, amounting to a factor of 3 from the first to the fifth irradiation (Fig. 8.1). With intercycle solvent cleanup, only three strips were required after every exposure period, and there was no uranium buildup in the solvent, even after the last irradiation. Generally, uranium retention in the intermittent-irradiation run without intercycle cleanup was a factor of 2 to 10 higher than that obtained on corresponding samples from the run which included intercycle solvent cleanup. The uranium-retention values were determined by subtracting the uranium retained by nonirradiated controls from that retained by the irradiated sample.

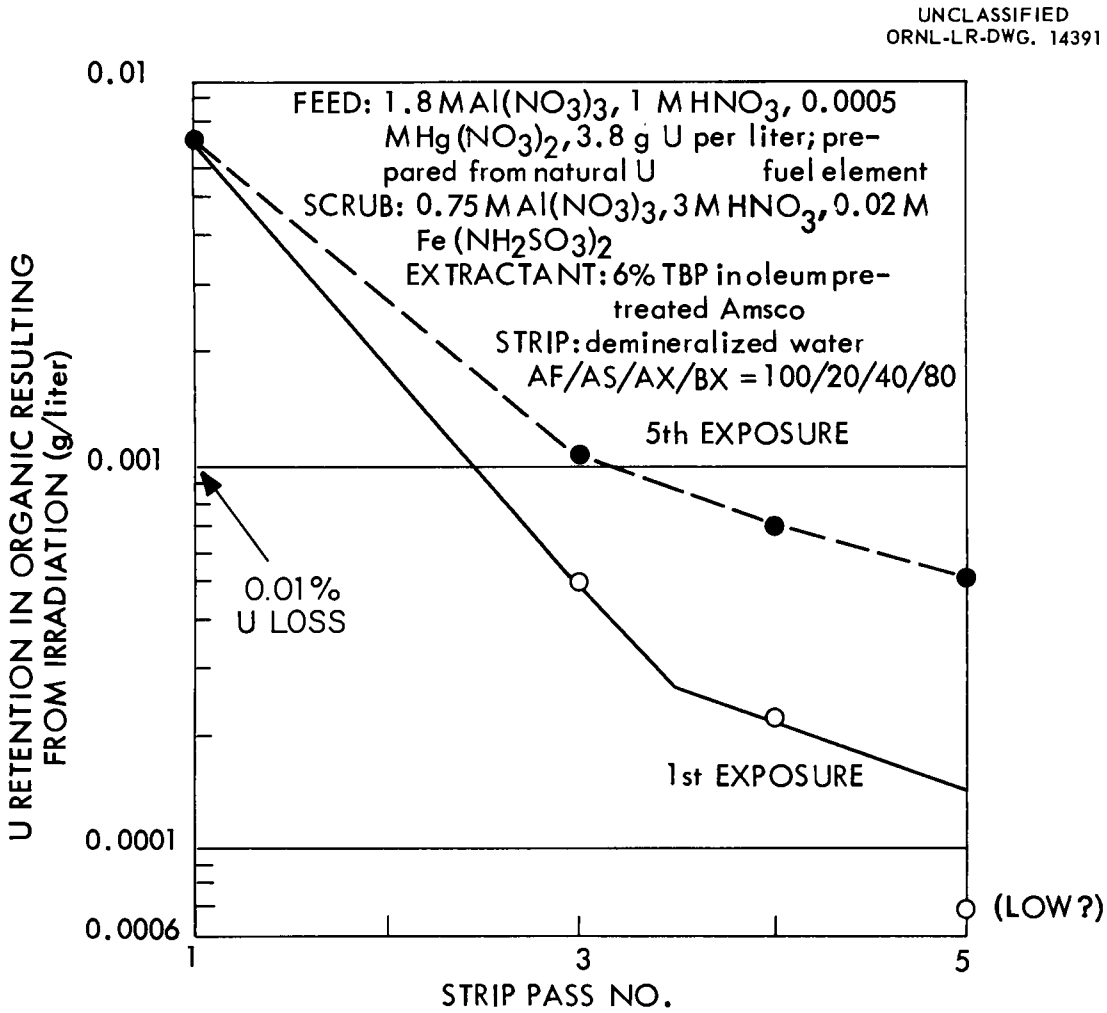

Fig. 8.1. Cumulative Effect of Irradiation on Uranium Retention in Solvent. No washing between exposures. Irradiation dosage to solvent = 3.3 ± 0.2 Beta whr/liter, given in five 10-min exposures. Phases mixed and irradiated in ^{60}Co source.

8.2.2 Removal of Residual Fission Products

The treatment that was successful in the removal of radiation decomposition products, namely, two successive 1/5 volume washes each of 0.1 M Na_2CO_3, 0.1 M HNO_3, and demineralized water, was investigated for removing residual fission products. Results of batch-washing experiments (Table 8.1) showed that most of the solvent decontamination from gross beta activity, which was largely ruthenium, was accomplished by washing with one 1/5 volume of 0.1 M Na_2CO_3 which produced a gross beta decontamination factor of 4×10^2. Three additional carbonate washes plus two nitric acid washes resulted in an additional decontamination factor of 37.5, giving an overall value of 1.5×10^4. With four carbonate washes and one acid wash, the overall decontamination factor was 1.7×10^4. Apparently, little is accomplished by using more than two carbonate washes, and the nitric acid washes have little effect on the gross beta decontamination. However, interfacial solids formed during batch washings and the nitric acid helped eliminate them.

Continuous operation of a turbine-mixer (Fig. 8.2) with contaminated first-cycle solvent, using two 0.2 M Na_2CO_3 stages and a third demineralized water stage, gave gross beta and gross gamma decontamination factors of 1.4×10^3 and 3.6×10^3, respectively. Contacting phases in the first two stages were emulsified by high-speed mixing. The emulsions were broken by Yorkmesh packing in the solvent effluent lines between stages.

The turbine-mixer shakedown tests were made with 6% TBP in oleum-treated Amsco diluent, containing 1.24×10^7 gross gamma counts min^{-1} ml^{-1}. The solvent was cascaded through three stages containing successively 0.1 M Na_2CO_3, 0.1 M HNO_3, and demineralized water at a flow rate of 40 ml/min, the flow rate used in the 0.75-in. pulsed-column first-cycle solvent extraction runs. A gross gamma decontamination factor of 6 was attained in the initial turbine-mixer run, whereas a gamma decontamination factor of 88 was obtained in the comparable laboratory batch-washing control run in which the organic/aqueous volume ratio was 1/3. With the equipment modified to provide increased recirculation of the organic phase and de-entrainment of contaminated aqueous droplets from the solvent effluent streams the turbine-mixer decontamination efficiency increased to 50% of the laboratory batch control.

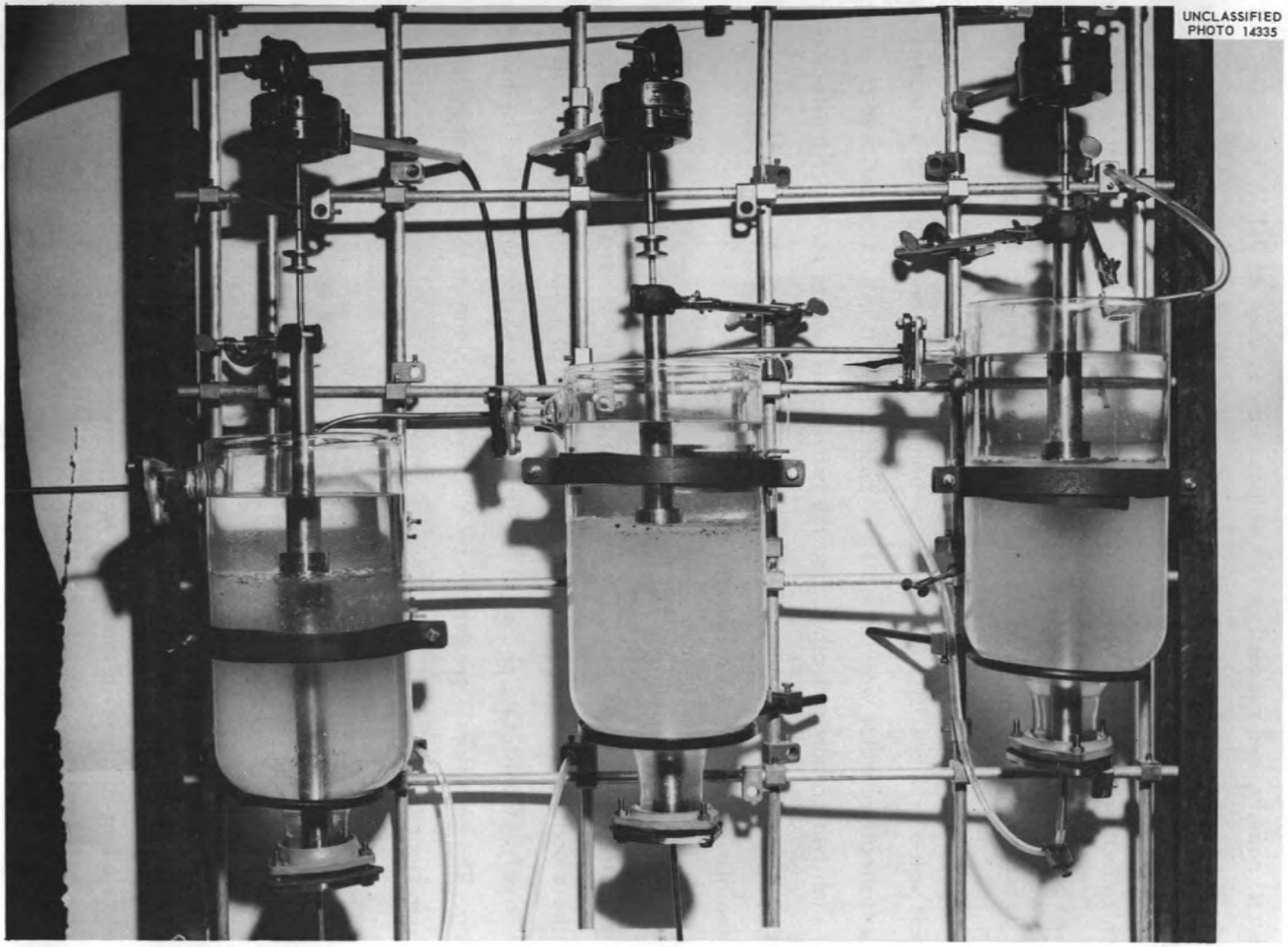

Fig. 8.2. Turbine Mixer.

Table 8.1 Effect of Washing on Decontamination of Used Solvent

Solvent Sample	Initial Gross β Activity (counts min^{-1} ml^{-1})	No. of 1/5 Volume Wash Passes			Overall Gross β D.F.
		0.1 M Na_2CO_3	0.1 M HNO_3	H_2O	
1	2.2×10^5	1	0	2	4×10^2
2	5×10^6	2	1	1	5×10^2 (low?)
Recycle	1×10^4	2	0	1	1.7×10^4
3	1.5×10^6	4	2	4	1.5×10^4

The equipment was further modified to provide still greater solvent recycle and increased mixing speed. Test runs indicated that the turbine-mixer could be operated with the aqueous and organic phases in an emulsified condition, thus ensuring maximum phase contact. A de-entrainment section filled with Yorkmesh packing (stainless-steel wire interwoven with Fiberglas) was used to break the emulsion.

A final demonstration run with contaminated solvent (gross beta, 8.04×10^4; gross gamma, 7.16×10^5 counts min^{-1} ml^{-1}) was made in the improved equipment. The sodium carbonate wash solution was increased to 0.2 M, and the turbine-mixers were set up to provide two carbonate wash stages, rather than one carbonate and one nitric acid stage, since under the new operating conditions the presence of interfacial solids or emulsions was not a problem. The third wash stage was demineralized water. Decontamination factors for the run averaged 1.4×10^3 for gross beta and 3.6×10^3 for gross gamma. The solvent effluent streams were sampled at each stage after having passed through the Yorkmesh de-entrainment section. Centrifugation of these samples failed to separate out any detectable solids or aqueous phase. The modified turbine-mixer appears capable of reconditioning solvent with efficiency equal to that attained in a laboratory batch-washing control experiment under comparable conditions.

9. METHODS AND COST OF WASTE STORAGE

The cost of waste storage is one of the major items in the economic evaluation of a process. Both the volume and the chemical and physical properties of the waste affect the storage costs. Nitric acid waste must be stored in stainless steel tanks, whereas basic or neutralized wastes may be safely stored in less expensive vessels. Since sodium nitrate resulting from neutralization is not very soluble, it is desirable to remove the nitrate ion before the waste is neutralized to prevent storage of a slurry of precipitated sodium nitrate which may pose engineering problems and require special transfer equipment. Studies on evaporation and neutralization of aqueous aluminum nitrate-nitric acid solutions indicated that evaporation of the 25-TBP extraction column waste to dibasic aluminum nitrate (diban)[11] followed by addition of caustic is a promising method of reducing storage costs.

In laboratory studies on the distillation of simulated IA column waste, diban was formed when the pot temperature reached 160°C. The semisolid diban residue was readily soluble in excess 50% caustic solution, and clear, stable solutions were obtained which contained up to 3 M diban. This represents a 1.7-fold reduction in the original waste volume. The radioactivity of the distillate should be low enough to allow recovery of the acid for reuse in the process.

The diban residue was also readily dissolved in water by refluxing at the boiling point for 12 hr, forming solutions stable toward precipitation. Solutions 3 M in diban appeared to be stable indefinitely, and 6 M solutions were stable for several weeks, showing that a volume reduction factor of 3 or 4 may be possible. These solutions are milky white with suspended solids which settle very slowly. The solutions are nonviscous and boil at about 100°C, even when concentrated to 6 M diban. Bumping during evaporation is less than that experienced in equally concentrated caustic-aluminate systems formed by the usual method of waste neutralization. No engineering problems associated with transfer of the solutions are anticipated. However, in any neutralized waste, iron, mercury, and many of the fission products will exist as insoluble hydroxides (1 to 5% of the neutralized waste volume).

Evaporation of the acid waste solutions to diban leads to extremely corrosive conditions. In laboratory corrosion tests, specimens of type 304L stainless steel were corroded at rates of 4.1, 13, and 440 mils/year at 107, 130, and 144°C, respectively. Similar specimens welded with type 347 stainless steel were corroded at a rate of 6.9 mils/year at 107°C. For the tests, the specimens were immersed in a simulated IAW solution that was initially 1.67 M in $Al(NO_3)_3$ and 1.5 M in HNO_3. No ferric nitrate or mercuric nitrate was present. The specific gravity was 1.290 at 25°C. The boiling point of the simulated waste solution was 107°C, and, as the destructive distillation proceeded, the boiling point rose to 144°C, indicating that the pot residue was approaching molten diban.*

When the simulated IAW was neutralized with caustic, the boiling point remained at 107°C, but the corrosion rates for both the welded and unwelded specimens dropped to 0.5 and 1.1 mils/year, respectively.

Although the corrosion of stainless steel during the evaporation of acid waste solutions to diban may be prohibitive if conventional, simple distillation methods are used, the problem may be relieved by using flash evaporators. Otherwise, it may be necessary to construct the evaporator of a more resistant metal, or to neutralize the wastes prior to boildown.

Laboratory experiments were conducted to determine the maximum volume reduction attained when simulated IA-column waste solution was neutralized prior to evaporation. A 1.33 M $Al(NO_3)_3$--1.08 M HNO_3 solution, added to excess 50% NaOH produced a clear solution when the neutralization temperature was held below 28°C. The excess of sodium hydroxide was 7%, based on the total caustic equivalents required to satisfy the reactions:

$$Al(NO_3)_3 + 4NaOH \longrightarrow NaAlO_2 + 3NaNO_3 + 2H_2O\ ,$$

and

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O\ .$$

---

*Temperature measurements on the molten semisolid were erratic, and analysis of the distillate for the total amount of nitric acid removed was found to be a more reliable indication of the completeness of conversion of the aluminum nitrate to diban.

The specific gravity of the neutralized solution was 1.256 at 25°C. No precipitation occurred when this solution was agitated for 20 hr at room temperature or upon reflux for 8 hr. Upon distillation, a volume reduction of nearly 1.79 was attained without precipitation upon subsequent cooling to room temperature. Addition of the portion of distillate whose removal caused room temperature precipitation back to the pot did not result in redissolution of the solids upon further reflux. This behavior indicates the metastability of sodium aluminate solutions which have so little excess caustic.

In another similar experiment made under neutral conditions, the solution was saturated with aluminum at room temperature when the composition of the clear solution was 0.86 M $NaAlO_2$--4.33 M $NaNO_3$--0.72 M NaOH. At these concentrations, aluminum oxide, which only partially dissolved upon heating, was precipitated. The specific gravity of the slurry was 1.296 at 25°C.

10. REFERENCES

1. F. R. Bruce, The Laboratory Development of a Continuous Solvent Extraction Process for the Recovery of U^{235}, ORNL-343 (March 21, 1950).

2. J. R. Flanary, "The Purex Process at Oak Ridge National Laboratory," Reactor Sci. Tech., 3 (2): 105 (1953).

3. A. T. Gresky, et al., Laboratory Development of the Thorex Process: Progress Report, Aug. 1, 1953-June 30, 1954, ORNL-1757; ibid. for previous dates: ORNL-1610, 1431, 1518, 1367.

4. T. C. Runion, C. V. Ellison, TBP Process for Uranium Recovery from Metal Waste--Laboratory Summary, ORNL-557 (Jan. 18, 1950).

5. E. L. Nicholson, ORNL-1999 (Jan. 16, 1956).

6. R. G. Wymer, D. M. Helton, A. H. Kibbey, J. F. Land, Caustic Dissolution: Preliminary Studies, ORNL-1782 (Jan. 14, 1955).

7. R. A. Charpie et al., Project Hope: A Chemical Reprocessing Plant for a Nuclear Power Economy, ORNL-1638, pp 129-130 (Jan. 21, 1954).

8. J. R. Flanary, L. D. Frashier, The Effect of Acidity and Reducing Agents on Ruthenium Solvent Extraction by Tributyl Phosphate in the 25 Process, ORNL-1801 (Dec. 15, 1954).

9. G. I. Cathers, in Homogeneous Reactor Project Quarterly Progress Report for Period Ending October 1, 1952, ORNL-1424, pp 132-137.

10. Ibid. for January 1, 1953, ORNL-1478, pp 114-115.

11. I. R. Higgins, R. G. Wymer, Diban--Ion Exchange Waste Disposal Scheme I, ORNL-1984 (Nov. 10, 1955).

12. J. Rodgers, W. F. Neuman (U. Rochester), Titration Studies of Complex Ions of Uranium and Organic Anions, AECD-2216 (decl. Aug. 11, 1948).

13. I. Feldman, W. F. Neuman, J. R. Havill, Spectrophotometric Studies of the Uranyl Citrate Complex, UR-85 (Aug. 25, 1949).

14. I. Feldman, J. R. Havill, W. F. Neuman, "Polymerization of Uranyl Citrate, Malate, Tartrate, and Lactate Complexes," J. Am. Chem. Soc., 76: 4726-4732 (1954).

11. APPENDIX

11.1 Stripping of Uranium from TBP with Aqueous Citrate Solutions

When an aqueous solution of uranyl nitrate is equilibrated with the organic TBP in inert Amsco, the uranyl ion is distributed between the phases according to the reaction:

$$(UO_2^{++})_{aq} + 2(NO_3^-)_{aq} + 2(TBP)_{org} \rightleftharpoons (UO_2)(NO_3)_2(TBP)_{2\ org}\ .$$

In extraction, a high aqueous nitrate concentration is used to shift the equilibrium in the direction of the organic phase. Then, in subsequent stripping with water or very dilute nitric acid, the equilibrium shift is reversed. The uranium shift to the aqueous phase is not as favorable as is desired, however, even with water stripping, because of the self-salting of the uranyl nitrate. It is therefore advantageous to add an agent to the strip solution to complex the uranyl ion and thus further shift the equilibrium to favor the aqueous phase. By this means, a more highly concentrated uranium product is obtained, making possible in process an approach to the maximum concentration factor of 4 or 5 which is imposed by engineering limitations on pulsed column operability. Organic-to-aqueous flow ratios of more than 4 or 5 to 1 are generally not suitable. For this reason, the use of a complexing agent in 25-TBP process strip streams was considered advantageous only for cases where the uranium concentration in the organic phase was at least 40 g/liter. A uranium concentration of 160 to 200 g/liter in the aqueous strip column products would eliminate the need for intercycle and final product evaporation.

Investigators at the University of Rochester[12,13,14] found that uranyl ion combines with citrate in a mole ratio of 1-to-1 to form stable, water-soluble dimer complexes involving the α-hydroxy and two carboxyl groups of the citrate molecule. The complex form is pH dependent and has one, two, or three hydrogen bridges. At the reagent pH of uranyl nitrate solution, the uranyl ion exists as $(UO_2)(4H_2O)^{2+}$. The sequence of steps in uranium citrate complex formation (Fig. 11.1) with increasing pH is:

UNCLASSIFIED
ORNL-LR-DWG 14542

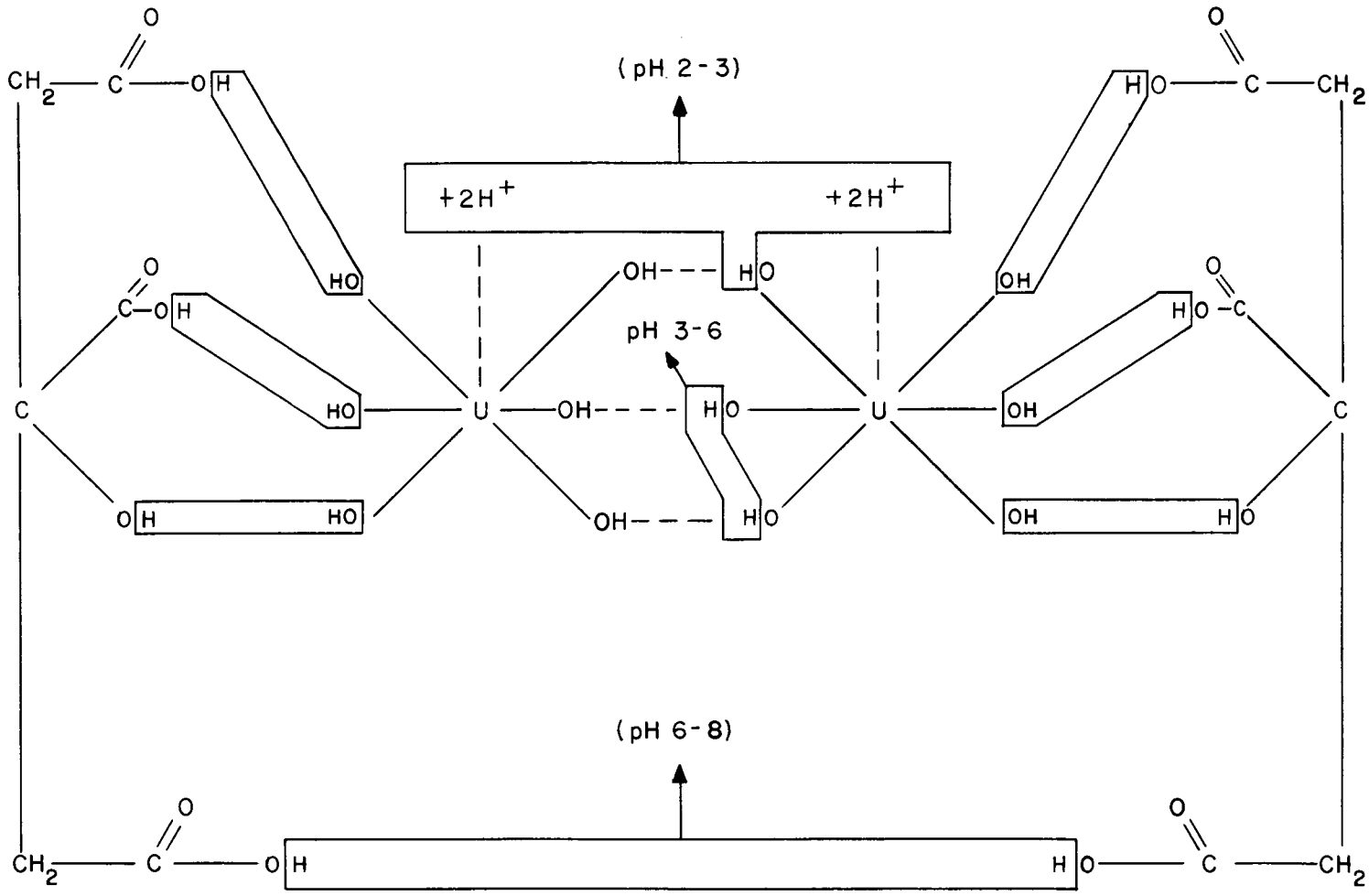

Fig. 11.1. Complexing of Uranium with Citrate.

Step 1. Complex bonds are formed by the splitting out of three water molecules for each uranyl ion combining with a citrate molecule. At pH 2 to 3, the first hydrogen bridge of the dimer forms with the loss of one H^+ for each two uranyl citrate molecules combining; in addition, $2H^+$ ions are also lost by each uranyl group (total H^+ ions furnished = 5).

Step 2. At pH 3 to 6, the second and third hydrogen bridges of the dimer are formed by the splitting out of two more H^+ from one of the uranyl groups (total H^+ ions furnished = 2).

Step 3. At pH 6 to 8, the hydrogens on the two remaining citrate carboxyl groups of the dimer are ionized off (total H^+ ions furnished = 2).

On the basis of these studies, citrate was investigated as uranium complexing agent in the 25-TBP process chemical development program. Furthermore, since the complex formation as a function of pH is a reversible reaction, simple neutralization to pH <2 was the only required intercycle adjustment.

The criteria for defining a suitable system for the process strip columns were: (1) a uranium distribution coefficient,

$$\frac{\text{uranium concentration}_{org}}{\text{uranium concentration}_{aq}},$$

of 10^{-2} or less, about 2.5×10^{-5} being the calculated maximum value which would permit single-stage stripping with a uranium loss of not more than 0.01%; (2) a stable uranium product solution containing at least 160 g of uranium per liter; and (3) a citrate stripping agent solubility greater than 1 M at room temperature to ensure that a reasonable excess of citrate over uranium would always be present. These conditions were met by using 1.25 M sodium citrate--1.0 M sodium acetate, 1.0 M potassium citrate--1 to 2 M potassium acetate, 1.25 M potassium citrate--1 M potassium acetate, or 1.5 M potassium citrate--0.5 M potassium acetate strip solutions when the organic phase was 18% TBP in Amsco containing about 50 g of uranium per liter and about 0.1 M nitric acid. Under conditions where metastable aqueous uranyl citrate products were obtained, immediate acidification with excess nitric acid would probably prevent precipitation.

Preliminary batch-equilibration tests were made with 0 to 2 M ammonium citrate aqueous phases vs 15 to 30% TBP-Amsco organic phases. The aqueous phase equilibrium pH's ranged from less than 0.12 to 3.9; the initial uranium concentrations in the solvent varied from approximately 55 to 125 g/liter. Organic to aqueous volume ratios of 0.33--9.5 to 1 were used. The salting strengths of the systems, here defined as the nitrate concentration other than that contributed by the uranyl nitrate itself, were varied from 0 to 4 by the addition of nitric acid or ammonium nitrate. The initial and equilibrium conditions and the distribution coefficients obtained in each run are summarized in Table 11.1. The great dependence of the citrate complexing upon pH is evident, the lowest distribution coefficient being obtained at the highest pH in any given system. With 2 M ammonium citrate at pH 3 to 4, distribution coefficients of 10^{-5}-10^{-7} were obtained as compared to 0.1 to 1 for similar systems when the pH was less than 2. The latter results are comparable to those obtained with pure water or 0.02 M HNO_3 stripping with no citrate present. The distribution coefficient was relatively independent of the citrate concentration as long as the citrate/uranium mole ratio was $\geq$ 1/1. Unstable aqueous phases were obtained when the citrate concentration was less than 2 M and/or the uranium concentration exceeded 190 g/liter over the pH range investigated. Development work with the ammonium system was abandoned because of the explosion hazard of evaporating ammonium nitrate waste solutions. The sodium and potassium citrate systems were studied with regard to aqueous product solution stability and attainable uranium distribution coefficients, as functions of pH and citrate concentration with and without corresponding acetate salt buffers.

The results of initial batch equilibrations with 4 volumes of 18% TBP in Amsco vs 1 volume of aqueous uranyl nitrate solution (about 0.7 M) containing sodium citrate indicated again that the distribution coefficient was almost entirely pH dependent and relatively independent of citrate concentration over the range 0.75 to 2.0 M. The distribution coefficient varied inversely from 8.5×10^{-1} at pH less than 0 to about 1.5×10^{-7} at pH higher than 5. Where the equilibrium pH was higher than 3, distribution coefficients less than 10^{-5} were obtained. The stability of the uranyl citrate solutions was also largely pH dependent. At equilibrium pH's less than 3, i.e., the

Table 11.1 Stripping of Uranium from TBP in Amsco with Aqueous Ammonium Citrate

O/A Vol. Ratio	Initial Conditions: Aqueous: Citrate (M)	Aqueous: NO_3^-[a] (N)	Aqueous: Uranium (g/liter)	Organic: TBP (%)	Organic: Uranium (g/liter)	Organic: HNO_3 (N)	Equilibrium Conditions: Aqueous: Uranium (g/liter)	Aqueous: pH	Organic: Uranium (g/liter)	Organic: H^+ (N)	Uranium Distribution Coefficient (O/A)
9.5/1	0.96	0.76	---	15	62.3	0.05	157	1.3	42.0	---	0.268
9.5/1	1.4	0.76	---	15	62.3	0.05	201[b]	1.7	37.4	---	0.186
9.5/1	1.9	0.76	---	15	62.3	0.05	138	1.1	41.5	---	0.301
9.5/1	1.9	0.76	---	15	62.3	0.05	191[b]	1.5	35.5	---	0.186
9.5/1	1.9	0.76	---	15	62.3	0.05	194[b]	1.7	30.2	---	0.156
9.5/1	1.9	0.76	---	20	83.1	0.07	317[b]	1.8	41.5	---	0.131
9.5/1	1.9	0.76	---	25	103.8	0.08	270[b]	1.5	68.5	---	0.254
9.5/1	1.9	0.76	---	30	124.6	0.11	275[b]	1.5	80.8	---	0.294
4/1	~1.2	0.27	224	30	---	---	188	0.58	102.0	0.02	0.543
4/1	0	0.41	336	30	---	---	297.5	0.28 N H^+	113.0	0.02	0.380
3/1	0	0[c]	---	30	120.4	---	105.8	1.82	88.4	0.01	0.835
3/1	0	4.0[d]	---	30	102	0.11	28.2	2.3	102(?)	0.17	3.62
3/1	2	4.0	---	30	102	0.11	33.1	0.7	51.5	0.12	1.56
3/1	2	---	---	30	120.4	---	177.0	1.12	58.3	0.05	0.329
3/1	2	---	---	30	102	0.11	278[b]	2.3	19.0	0.06	0.068
1/1	2	---	---	30	120.4	---	52.9	0.12	67.5	0.07	1.28
1/1	~1.7	0.02	118.3	30	---	---	112.0	1.72	3.99	0.12	0.036
1/1	2	---	---	30	120.4	---	111.3	2.03	0.21	0.10	1.88×10^{-3}
1/1	2	---	---	30	120.4	---	111.3	3.9	3.6×10^{-5}	0	3.23×10^{-7}
1/1	0	0.02	118.3	30	---	---	56.8	0.04 N H^+	55	0.02	0.970
0.33/1	2	---	---	30	120.4	---	35.6	2.9	4.3×10^{-4}	0.05	1.21×10^{-5}

[a] $UO_2(NO_3)_2$ excluded.

[b] Precipitated on standing.

[c] H_2O only.

[d] NH_4NO_3 instead of HNO_3.

reagent pH's of the solutions with citrate concentrations of 1 M or less, yellow crystalline precipitates formed. However, addition of sodium hydroxide to a NaOH/citrate mole ratio of 4/1 readily redissolved the precipitates with resulting equilibrium pH's of 4.5 to 5.5. The high-pH citrate strip solutions not only gave the best uranium distribution coefficients but also showed greater stability toward precipitation.

The minimum amounts of citrate and caustic to produce stable uranyl citrate solutions at process uranium concentrations were determined by titration of 0.85 M $UO_2(NO_3)_2$–0.8 M HNO_3 containing 1.0, 1.25, and 1.5 M sodium citrate with standardized base (see Fig. 11.2). The range of stability was found to lie between pH 4.2 and 5.6. Based on these results, 1.0, 1.25, and 1.5 M sodium citrate strip solutions containing sufficient caustic to produce stability were prepared. Since the pH's of these strip solutions were higher than 11, temporary local precipitation of sodium diuranate was noted upon batch equilibration with 4 volumes of 18% TBP-Amsco containing 50 g of uranium per liter and 0.1 M HNO_3. The distribution coefficients obtained, less than 10^{-2}, were a factor of 100 to 1000 higher than those obtained by the reverse procedure i.e., aqueous uranyl citrate--caustic solutions vs pure 18% TBP-Amsco where no precipitation occurred. Apparently the precipitate formation and redissolution required more than the 2-min equilibration time, and steady-state conditions were never reached. In the strip-column operation diuranate precipitation may never occur since the aqueous phase pH would vary from greater than 4 in the uranium-rich bottom to greater than 11 at the top of the column, where the organic uranium concentration is very low. With regard to strip solution solubility and aqueous product stability, 1.25 M sodium citrate–1.3 M NaOH appeared optimum and gave reproducible distribution coefficients of less than 10^{-5}. Aqueous stability was obtained with 1.25 M sodium citrate alone, but the distribution coefficient was somewhat higher, 4.7×10^{-4}, because of the lower pH. When saturated 1.72 M sodium citrate was used, temporary sodium diuranate precipitation was noted. Apparently the presence of uranium increases the sodium citrate solubility, since a 2 M sodium citrate concentration was possible in the earlier experiments in which simulated aqueous product solutions were

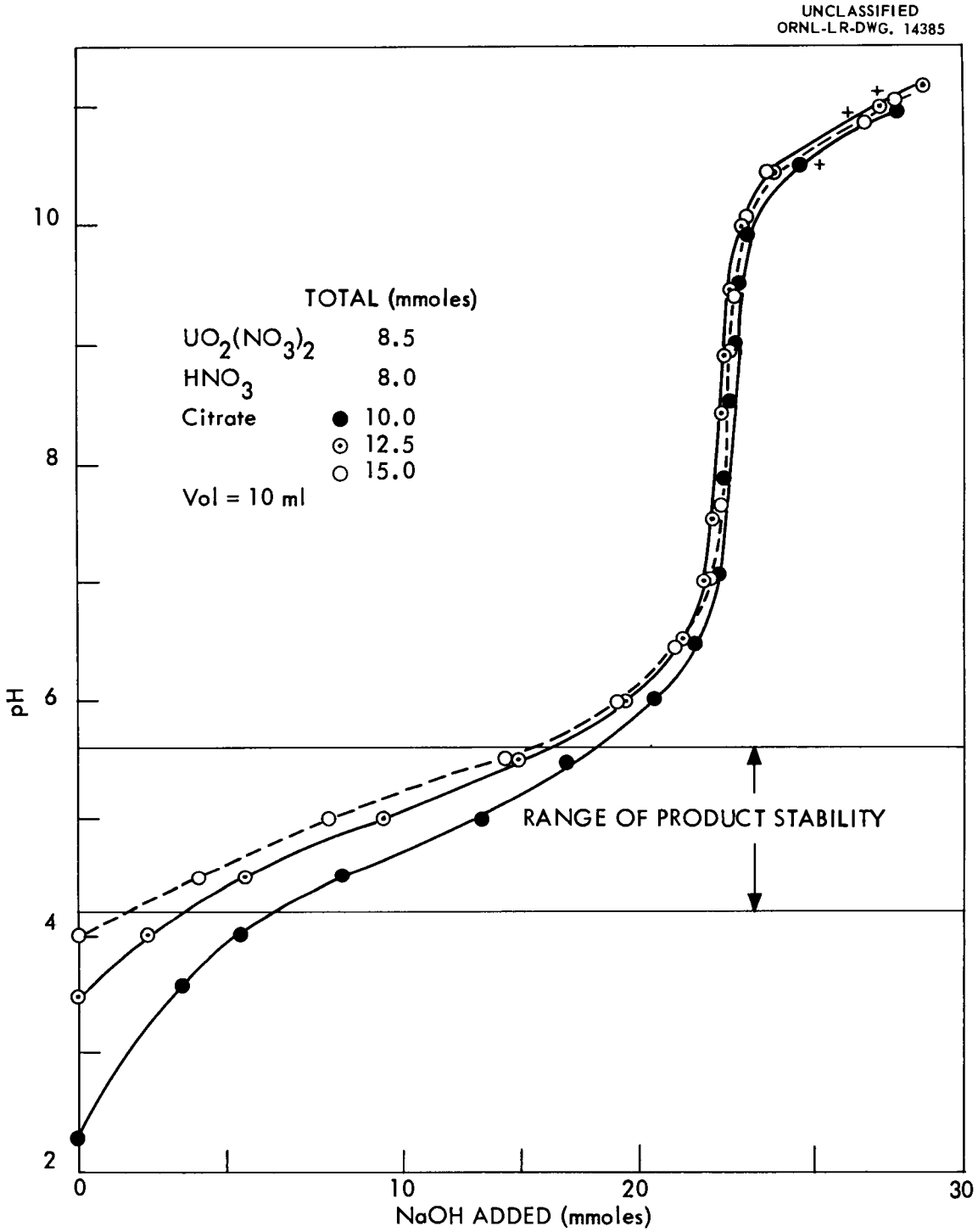

Fig. 11.2. Titration of Simulated IIBP Solution with 1.0 M Sodium Hydroxide. Precipitation noted.

equilibrated with pure solvent. Sodium hydroxide added to the strip solutions lowered the solubility of the sodium citrate.

To avoid sodium diuranate precipitation, sodium hydroxide was replaced by sodium acetate in the high-pH sodium citrate system. In the buffered system, the strip solution pH's were less than 8. The optimum stripping solution was 1.25 M sodium citrate-1.0 M sodium acetate, which gave a uranium distribution coefficient of about 4×10^{-5}. The stable aqueous product had a pH of 4.39 and contained 184 g of uranium per liter. However, when the acetate concentration was increased to 1.25 M at 1.25 M citrate, precipitates formed eventually in both the strip and product solutions. When the citrate concentration was reduced to 1.0 M at acetate concentrations of 1.0 to 2.0 M, unstable product solutions were obtained. Increasing the citrate concentration to 1.5 M produced unstable strip solutions at acetate concentrations as low as 0.75 M.

The very narrow safe-operating range for the sodium citrate systems, as defined by the limited solubilities of the strip and product solutions, led to the study of the potassium citrate system. The potassium salts of weak acids are known to be more soluble than the corresponding sodium salts.

The potassium citrate strip solutions were soluble over the entire range studied: 1.0, 1.25, 1.5, and 2.0 M potassium citrate containing 0 to 3.0, 1.0 to 2.0, 0.5, and 0 to 0.5 M potassium acetate, respectively. These solutions were batch equilibrated with 4 volumes of 18% TBP in Amsco containing about 50 g of uranium per liter and about 0.1 M HNO_3. Evidences of potassium diuranate precipitation and aqueous product instability were recorded.

With 1.0 M potassium citrate, unstable aqueous products were obtained with 0 to 0.5 and 2.5 to 3 M potassium acetate. At acetate concentrations of 1.0 to 2.0 M, product stability was achieved.

At 1.25 M potassium citrate, a stable aqueous product was obtained with 1.0 M potassium acetate, but instability occurred at acetate concentrations of 1.25 to 2.0 M.

When the potassium citrate concentration was 1.5 M, the aqueous product stability region was limited to maximum 0.5 M potassium acetate.

With 2 M potassium citrate, temporary potassium diuranate precipitation was observed. The addition of 0.5 M potassium acetate eliminated the diuranate precipitation but produced an unstable aqueous product.

In the potassium system uranium distribution coefficients varied from 10^{-6} to 10^{-4}. The plot of solubility data for the potassium citrate-acetate system (Fig. 11.3) also shows the safe operating range for the sodium citrate-acetate system.

The versatility of the potassium system with respect to possible variation in process conditions was investigated by batch-equilibration methods using strip solutions containing 1 M citrate and 1 to 2 M acetate, 1.25 M citrate and 1 M acetate, and 1.5 M citrate in the presence of 0.5 M acetate.

With 18% TBP-Amsco containing about 50 g of uranium per liter and about 0.1 M HNO_3 and the organic/aqueous volume ratio increased from 4/1 to 5/1, precipitation occurred in the aqueous product. Increasing the uranium concentration of the solvent to 60 g/liter, and hence lowering the nitric acid concentration to 0.003 M with an organic/aqueous volume ratio of 4/1 gave stable aqueous products except with 1 M citrate -- 2 M acetate, in which a slight precipitate formed after 24 hr. The uranium concentration in the aqueous product solutions was 225 g/liter, while the distribution coefficients ranged from 2×10^{-5} to 3×10^{-4}.

It is evident that increased solvent flow rate in the strip column could be critical in process, presumably owing to the decreased pH in the aqueous product stream from the increased uranium and nitric acid concentrations.

A cost analysis, comparing 1.25 M sodium citrate--1.0 M sodium acetate and 0.01 M nitric acid as stripping agents, showed that the citrate could not compete with acid stripping, which requires intercycle and final product evaporation. Aside from higher reagent costs, the cost of citrate-acetate waste storage was prohibitive since the volume reduction of neutralized waste is limited particularly by the solubility of sodium nitrate. Waste storage costs for the potassium system would be even higher, since potassium nitrate is about one third less soluble than sodium nitrate on a molar basis. Further work on citrate stripping systems was abandoned at this point.

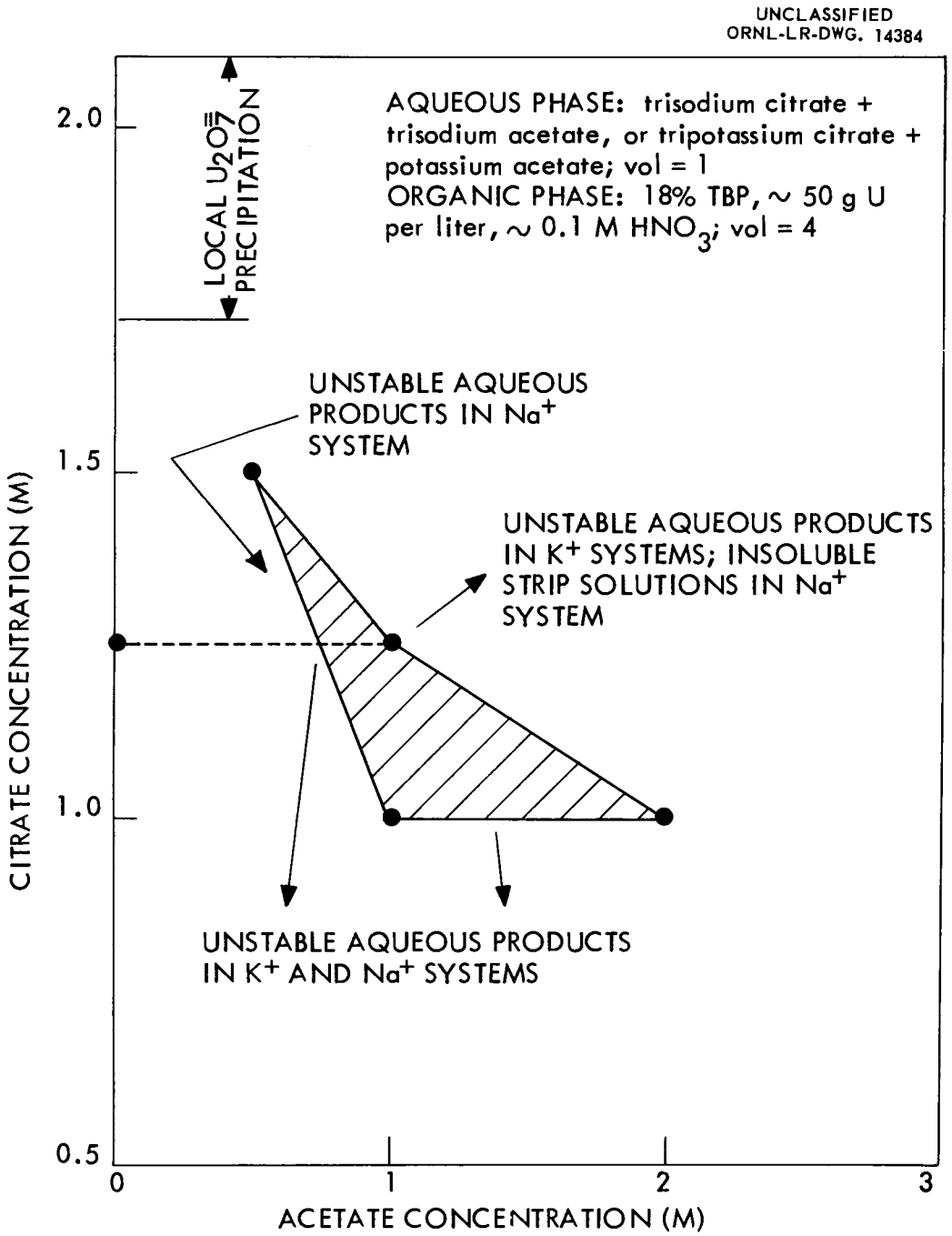

Fig. 11.3. Solubility Limits for the Citrate-Acetate Stripping of Uranium from TBP, Using the Sodium or Potassium Salts. Dotted line shows safe operating range of sodium system; ▨ safe operating range of potassium system.

11.2 Solvent Pretreatment

11.2.1 Treatment of Diluent

1. Set up vessel and agitator capable of holding 22 liters of diluent and reagent. Must be able to separate phases.

2. Put 20 liters of Amsco, as shipped, into vessel. Take 2 ml of Amsco, add 2 ml of chromyl chloride reagent, and mix. Note reaction (clear, precipitate, or color change). If precipitate forms and color changes, the following steps should be performed.

3. Add 2 liters of oleum to Amsco, and contact for 1 hr. Separate.

4. Contact with 2 liters of water for 45 min. Separate.

5. Contact with 2 liters of 1 M NaOH for 45 min. Separate.

6. Contact with 2 liters of water for 45 min. Separate.

7. Contact with 2 liters of water for 45 min. Separate.

8. Take 2 ml of Amsco, add 2 ml of chromyl chloride reagent, and mix. Note reaction (clear, precipitate, or color change).

9. If precipitate forms and color changes, repeat steps 3-7 and test again with chromyl chloride.

11.2.2 Treatment of TBP

1. Contact 1500 ml of TBP with 500 ml of water to saturation. Separate phases; discard water.

2. Add 45 g of $Ca(OH)_2$ and agitate for 1 hr. Settle.

3. Filter through filter paper to remove solid material.

4. Make up 20 liters of 6% TBP in the oleum-treated Amsco (1200 ml of purified TBP in Amsco). Allow dissolved water to settle out and separate.

5. Take 10 ml of saturated $Ca(OH)_2$ solution, put into 50 ml cylinder, add 40 ml of solvent, and shake for 30 sec. Allow to settle. Good solvent has rapid phase separation and no interfacial solids or films. Poor solvent has very slow disengagement of phases, interfacial solids or skin between phases, hazy appearance in one or both phases, or a stabilized emulsion layer.

ORNL-1993 (Rev. 2)
UC-10 – Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (32nd ed.)

INTERNAL DISTRIBUTION

1. Biology Library
2-4. Central Research Library
5. Reactor Division Library
6-7. ORNL – Y-12 Technical Library
Document Reference Section
8-27. Laboratory Records Department
28. Laboratory Records, ORNL R.C.
29. R. E. Blanco
30. G. E. Boyd
31. W. L. Carter
32. F. L. Culler
33. F. M. Empson
34. J. R. Flanary
35. H. E. Goeller
36. J. H. Goode
37. A. H. Kibbey
38. C. E. Larson
39. J. T. Long
40. J. T. Roberts
41. J. M. Schmitt
42. M. J. Skinner
43. J. A. Swartout
44. C. D. Watson
45. A. M. Weinberg
46. R. G. Wymer
47. P. H. Emmett (consultant)
48. J. J. Katz (consultant)
49. C. W. J. Wende (consultant)
50. C. E. Winters (consultant)

EXTERNAL DISTRIBUTION

51. Research and Development Division, AEC, ORO
52-558. Given distribution as shown in TID-4500 (32nd ed.) under Chemical Separations Processes for Plutonium and Uranium category (75 copies – OTS)