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AEC RESEARCH AND DEVELOPMENT REPORT

ORNL-1993 (Revised)
Chemistry-Separation
Processes for Plutonium and Uranium

CHEMICAL DEVELOPMENT OF

THE 25-TBP PROCESS

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CHEMICAL TECHNOLOGY DIVISION

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1.0 ABSTRACT

Laboratory development studies leading to a tributyl phosphate extraction process for recovering U^{235} 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 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 aluminum nitrate--containing waste are proposed.

2.0 INTRODUCTION

Although the hexone solvent-extraction process[1] for recovering U^{235} was proved successful by plant experience, tributyl phosphate extraction technology has advanced sufficiently that the development and design of a U^{235} 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 U^{235} 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 batch-countercurrently and in Mini mixer settler units to establish the chemical flowsheet conditions for quantitative recovery of uranium adequately

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decontaminated from fission products and nonradioactive impurities for reuse. Numerous test runs, with both nonradioactive and radioactive feeds, were conducted in 3/4-in.-dia pulsed columns to determine the mechanical operability of the flowsheet in plant-type equipment. Flowsheet performance was demonstrated at 10% of full process radioactivity.

Laboratory-scale investigations were also carried out 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. The small-scale turbine-mixer units of Savannah River design 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 scouted.

The process development work reported is applicable to any uranium-aluminum alloy fuel, but particular emphasis was placed on the processing of the Savannah River aluminum-clad uranium-aluminum alloy tubular fuel elements. These elements contain approximately 10 wt % uranium, the alloy itself being approximately 15 wt % uranium. A high burnup of the >90% enriched uranium fuel followed by 150 days' 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.

3.0 PROPOSED 25-TBP FLOWSHEET

In the 25-TBP process (Fig. 3.1) for recovering and decontaminating U^{235} from spent Savannah River 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, which is 1.8 M $Al(NO_3)_3$--1.0 M HNO_3--0.005 M $Hg(NO_3)_2$ and contains about 3.8 g of uranium per liter, is heated to the boiling point for 4-6 hr to dehydrate and coagulate silica and other emulsion-producing impurities. The impurities are removed by filtration, or other suitable means. From the clarified feed the uranium is extracted countercurrently with 6% tributyl phosphate (TBP) in oleum-pretreated hydrocarbon (Amsco). Any extracted plutonium and fission products are scrubbed from the solvent with 3 M HNO_3 containing 0.02 M ferrous sulfamate to reduce tetravalent plutonium to the trivalent state. The uranium is stripped from the solvent in a second column with 0.01 M HNO_3. The feed/scrub/extractant/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 organic solution 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/extractant/strip volume ratios are 3.06/2.0/9.6/9.6. In laboratory studies gross beta and gross gamma decontamination factors

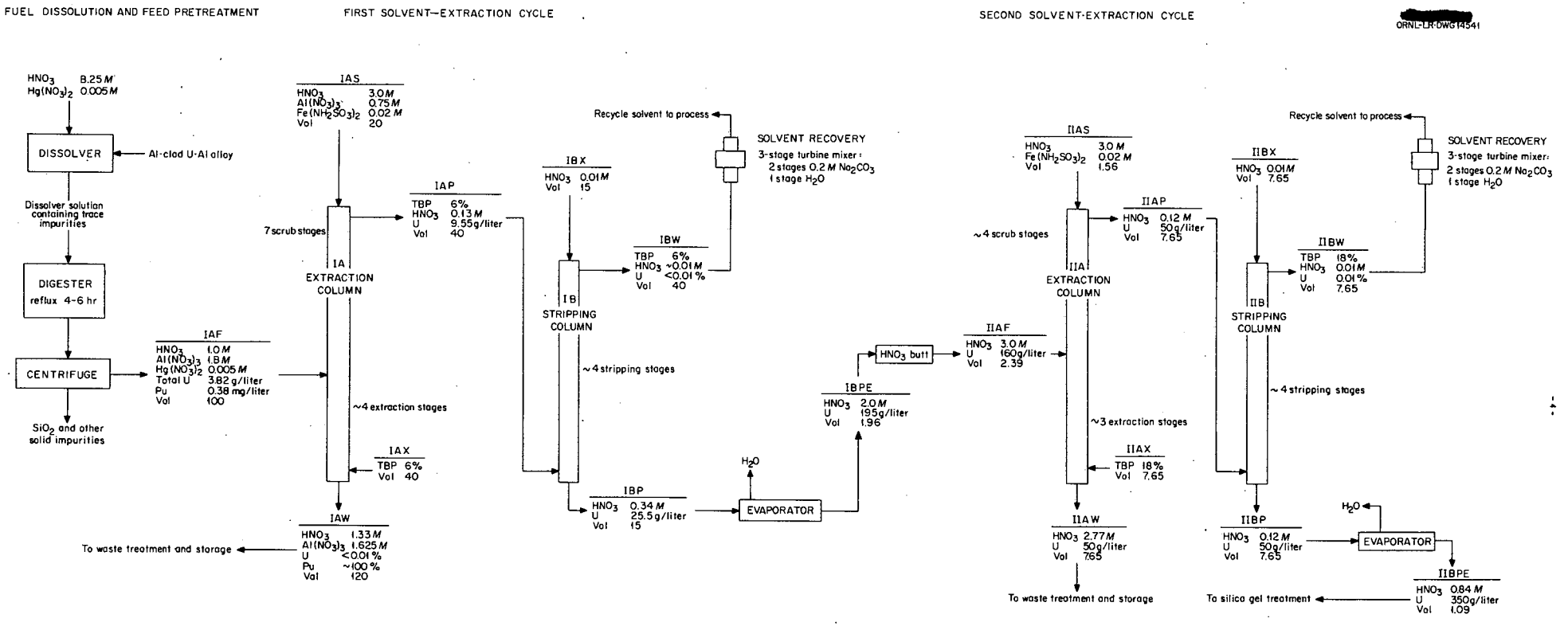

Fig. 3.1. Proposed 25-TBP Process Chemical Flowsheet

were 3.3×10^2 and 2.5×10^3, 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 sorbing them 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 4 extraction and 4 stripping stages are adequate to keep the uranium loss at 0.01%. The HETS values estimated from 0.75-in.-dia 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 3 extraction and 4 stripping stages were more than adequate to reduce the uranium concentrations in 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 increased proportionately in these cases.

4.0 DISSOLUTION STUDIES

Maximum batch dissolution rates of 185 and 140 mg/min/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 at least 15 wt % but was affected by the metallurgical history of the metal. 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 with regard to aluminum nitrate precipitation above 20°C. The studies were all 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 dissolver solutions.

4.1 Laboratory-Scale Batch Dissolution Studies

Effect of Nitric Acid Concentration. The dissolution rate of both extruded 15 wt % and of cast 5 wt % uranium alloy increased as the concentration of the nitric acid, which was catalyzed with 0.005 M $Hg(NO_3)_2$, increased from 0 to about 8 M and then decreased as the acid concentration was increased further to 12-16 M (Fig. 4.1). The optimum nitric acid concentration of about 8 M differs from Hanford's results,[7,8] in which the optimum dissolvent for cast 7.5 wt % uranium alloy was 4 M HNO_3—0.002 M $Hg(NO_3)_2$.

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 actual process application, the use of excess acid in the fuel dissolution step, which would lead to feed solutions containing 1 M HNO_3, is desirable from the standpoint of elimination of interfacial solids (Sec. 5.2) in the first-cycle extraction column.

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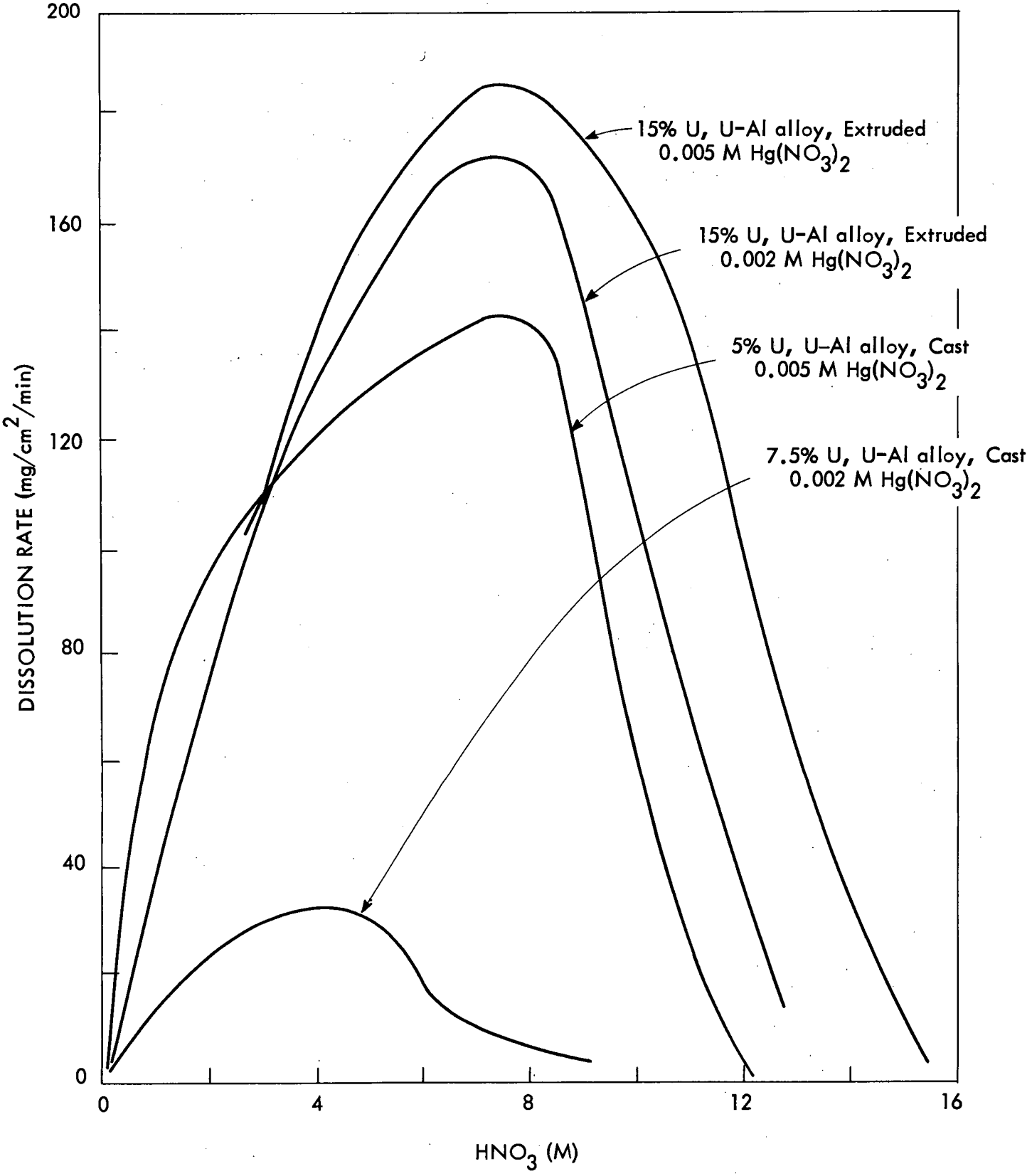

Fig. 4.1. Dissolution Rates of Uranium-Aluminum Alloy in Nitric Acid.

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Effect of Mercuric Nitrate Concentration. In batch studies with extruded 15 wt % uranium—85 wt % aluminum alloy, the dissolution rate in 8 M HNO_3 increased from nearly 0 to 185 mg/min/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 % uranium alloy was about 75% of this, i.e., 140 mg/min/cm^2 in 8 M HNO_3-0.002 M $Hg(NO_3)_2$. Extruded 15 wt % uranium alloy dissolved in 4 M HNO_3—0.002 M $Hg(NO_3)_2$ at a rate of 130 mg/min/cm^2, which was about four times the rate for cast 7.5 wt % uranium alloy in this reagent. The dissolution rates were calculated from the known average dimensions of the metal dissolved, the dissolution time, and the weight loss.

These results are to be contrasted with results of similar studies[7,8] at Hanford, where cast 7.5% uranium-aluminum alloys dissolved at a rate of 5 mg/min/cm^2 in 5 M HNO_3 with 0.0005 M $Hg(NO_3)_2$ present and at $\sim$0.5 mg/min/cm^2 with no catalyst, and at a maximum of 35 mg/min/cm^2 in 4 M HNO_3 with 0.002 M $Hg(NO_3)_2$.

The mercury catalyst action is explained as follows: Before the dissolution begins there is a brief induction period, during which it is postulated that the protective oxide film on the metal surface, which prevents attack of the alloy 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 tenacious oxide film. The area amalgamated in this way reacts vigorously with the nitric acid, leading to production of more metallic 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—

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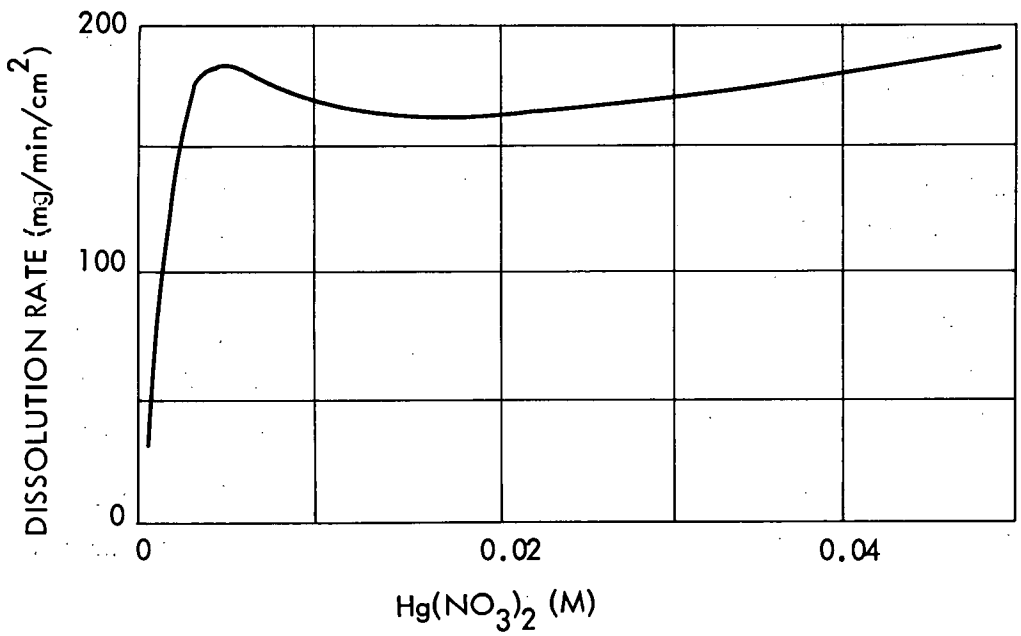

Fig. 4.2. Effect of Mercuric Nitrate Concentration on Dissolution Rate of Extruded 15 wt % Uranium—85 wt % Aluminum Alloy in 8 M HNO_3.

mercuric nitrate experimental solutions to preform the amalgamated surface. The amalgamated alloy thus formed 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.

[redacted]minum Nitrate Concentration. The dissolution rate decreased rapidly as the aluminum nitrate concentration of the solution increased (Fig. 4.3). This was true for initial nitric acid concentrations ranging from 2 to 10 M.

Effect of Composition and Metallurgical History of Metal. There was no difference in the dissolution rates of the 5, 7.5, and 15 wt % uranium alloy, but extruded metal dissolved much more rapidly than cast. Different regions of a single piece of metal dissolved at very different rates, especially in the case of cast alloy. The reproducibility of rate data for cast alloy was poorer than for extruded.

Small-scale batch dissolvings of aluminum-clad 15% 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 sections of full-sized aluminum-clad 15% natural uranium tubular fuel elements with 7.4* M HNO_3—0.005 M $Hg(NO_3)_2$, 10-12 hr was required for complete dissolution. In a fourth run, dissolution was essentially complete in less than 2 hr. The reduction in dissolution time is attributed to improved equipment-handling techniques developed through experience. The dissolution progress as a function

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

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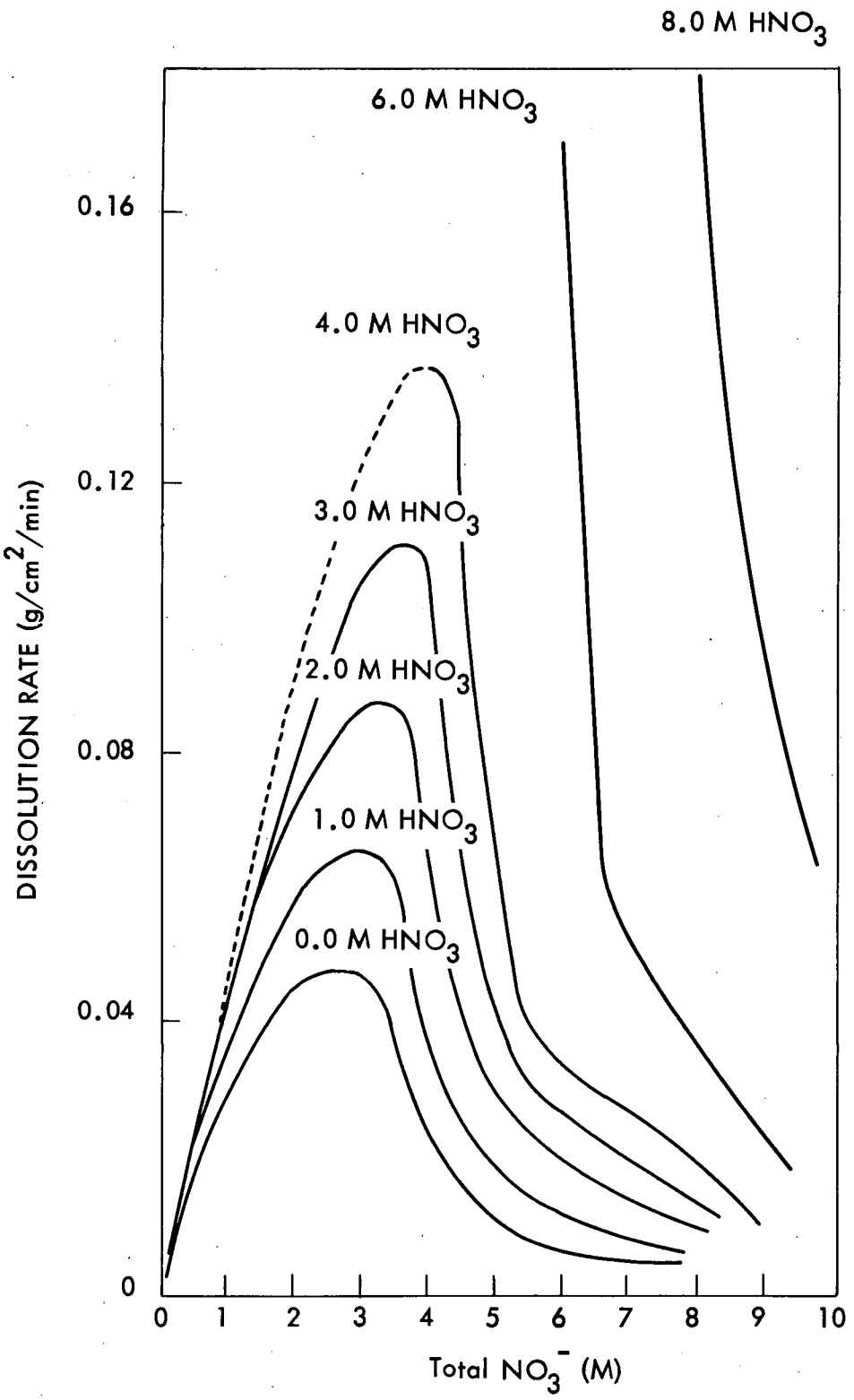

Fig. 4.3. Dissolution Rates of Extruded 15% Uranium–85% Aluminum Alloy in Aluminum Nitrate–Nitric Acid Containing 0.005 M Mercuric Nitrate.

of time was obtained in the final run by periodic analyses of the dissolver 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 to 90°C; the initial, almost violent, reaction was controlled by applying cooling water for about 1 hr. Steam was then reapplied to maintain the dissolver temperature at approximately 105°C.

4.3 Continuous Dissolution Studies

In continuous dissolution studies of miniature extruded 15 wt % uranium—85 wt % aluminum alloy slugs, the dissolution rate was 12% higher when the cold condensate was returned to the column in the middle of the slug bed 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 increase the dissolution rate further.

The experiments were made in a trickle-type glass column (Fig. 4.4) with a 1-in. diameter and a slug bed 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.-long by 0.2-in.-dia slugs of 15 wt % natural uranium alloy. In this case 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 to precipitation of aluminum nitrate above 20°C (Fig. 4.5). The stability should not be affected by up to 11% variations in feed acid concentrations or by

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*See footnote on p. 10.

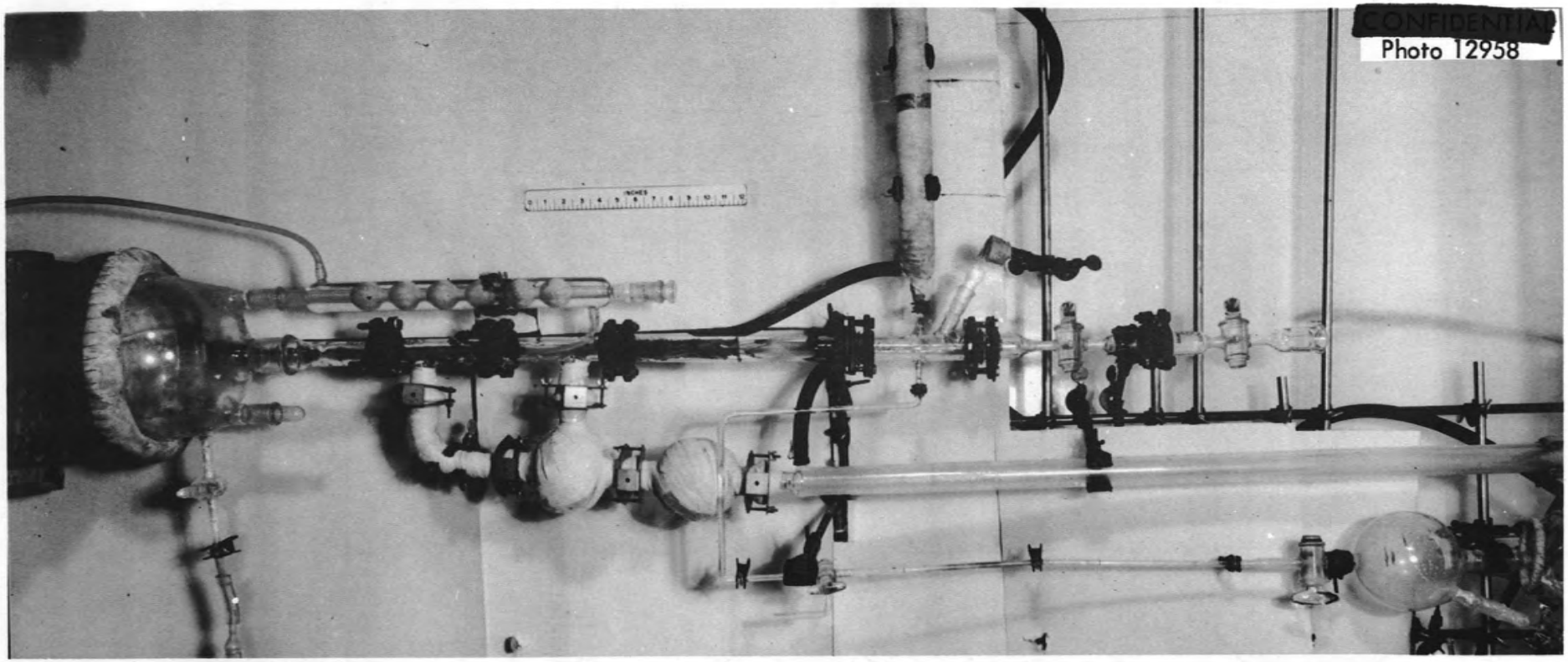

Fig. 4.4. Trickle-Type Glass Column.

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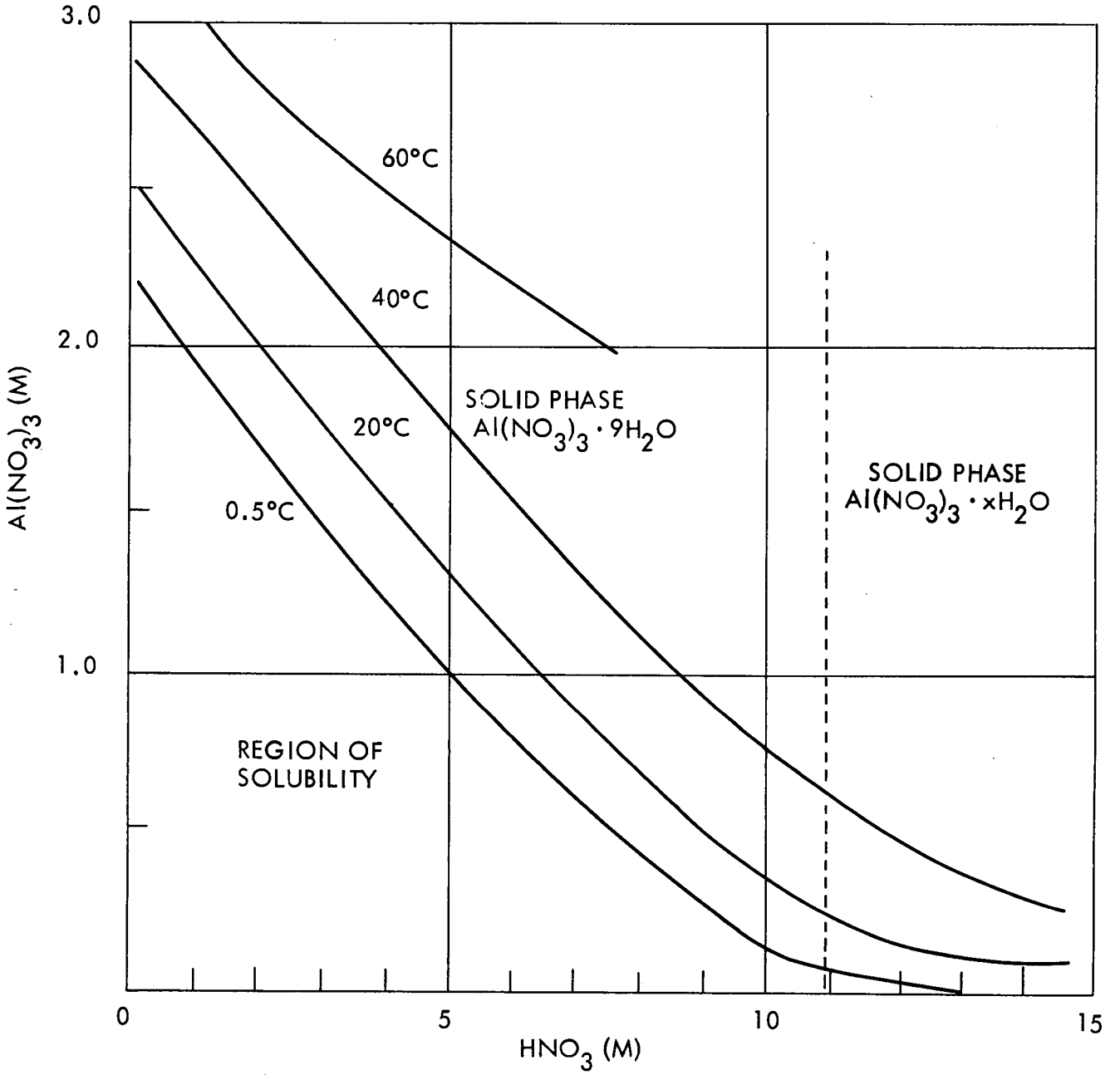

Fig. 4.5. Compositions at 20°C of Solutions Saturated at Various Temperatures in the $Al(NO_3)_3$-HNO_3-H_2O System. Taken from A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds."

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 thermodynamically stable to aluminum nitrate precipitation down to about 1°C.

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 I^{131} present in the dissolver off-gas from mercury-catalyzed nitric acid dissolution of spent short-decayed uranium-aluminum 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 for 90-day-decayed fuel. This

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 activity that could not be recovered, which accounts for the poor material balance.

decontamination was not achieved by mercuric iodide complex formation in the dissolver (Table 4.2).

In previous studies with simulated dissolver 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 95-100°C for 1 hr, provided the iodine concentration was no more than 10^{-5} M.[9] Similar results were obtained at Hanford.[10,11] However, these experiments do not completely represent process conditions since no oxides of nitrogen were present, and in the actual dissolution process aluminum competes with the iodine for the mercury.

Nine laboratory-scale dissolvings 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. The slugs were of 5.37% uranium-aluminum alloy and weighed approximately 3.5 g each. The dissolvent was 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 5% value is the normal process level. The iodine was added to the system in amounts varying from 0.5 to 4 times the normal process level, the I/U weight ratio being 36/20,000. A stock solution of 0.2 M NaOH--0.0036 M Na_2SO_3 containing dissolved molecular iodine and I^{131} tracer was used. The dissolvings were made in a glass pot equipped with a 30-in. glass reflux condenser followed by a series of gas traps. The first was a dead trap, containing nothing but air. The next two traps contained 8 M caustic, and were cooled in an ice bath during the dissolutions. 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 β counting. The calculated decontamination factors ranged from 78.2 to 376 for the conditions studied, with the exception of one case in which the condenser was not functioning and the decontamination factor was <3.

5.0 FIRST-CYCLE EXTRACTION-COLUMN EMULSIONS AND INTERFACIAL SOLIDS

When the raw feed was extracted, fine, stringy solid material collected in the column at the phase interface and/or organic emulsions formed. 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 Solvent Pretreatment

Oleum pretreatment of the Amsco diluent alleviated interfacial solids formation 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 in the presence of excess acid—to give 1 M HNO_3, 1.8 M $Al(NO_3)_3$, 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 Feed Pretreatment

Dissolution in the presence of excess acid eliminated the interfacial solids problem, the effect being attributed to the decreased solubility of silica in the stronger acid. However, feed prepared under these conditions 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 dissolver solution at the boiling point for 4-6 hr, then filtering through a coarse glass filter 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 was more than adequate to prevent 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 organic emulsion formation with similar feed prepared by dissolving 2S aluminum barstock and adding uranyl nitrate. The only obvious difference between the two solutions was the silica content, which was approximately 1% of the aluminum barstock weight and was negligible in the actual alloy samples dissolved. The effectiveness of this procedure was independent of both the acid and aluminum concentration (0.6-1.7 M) when the initial acid concentration was 2 M or higher. Since conditions are rather corrosive

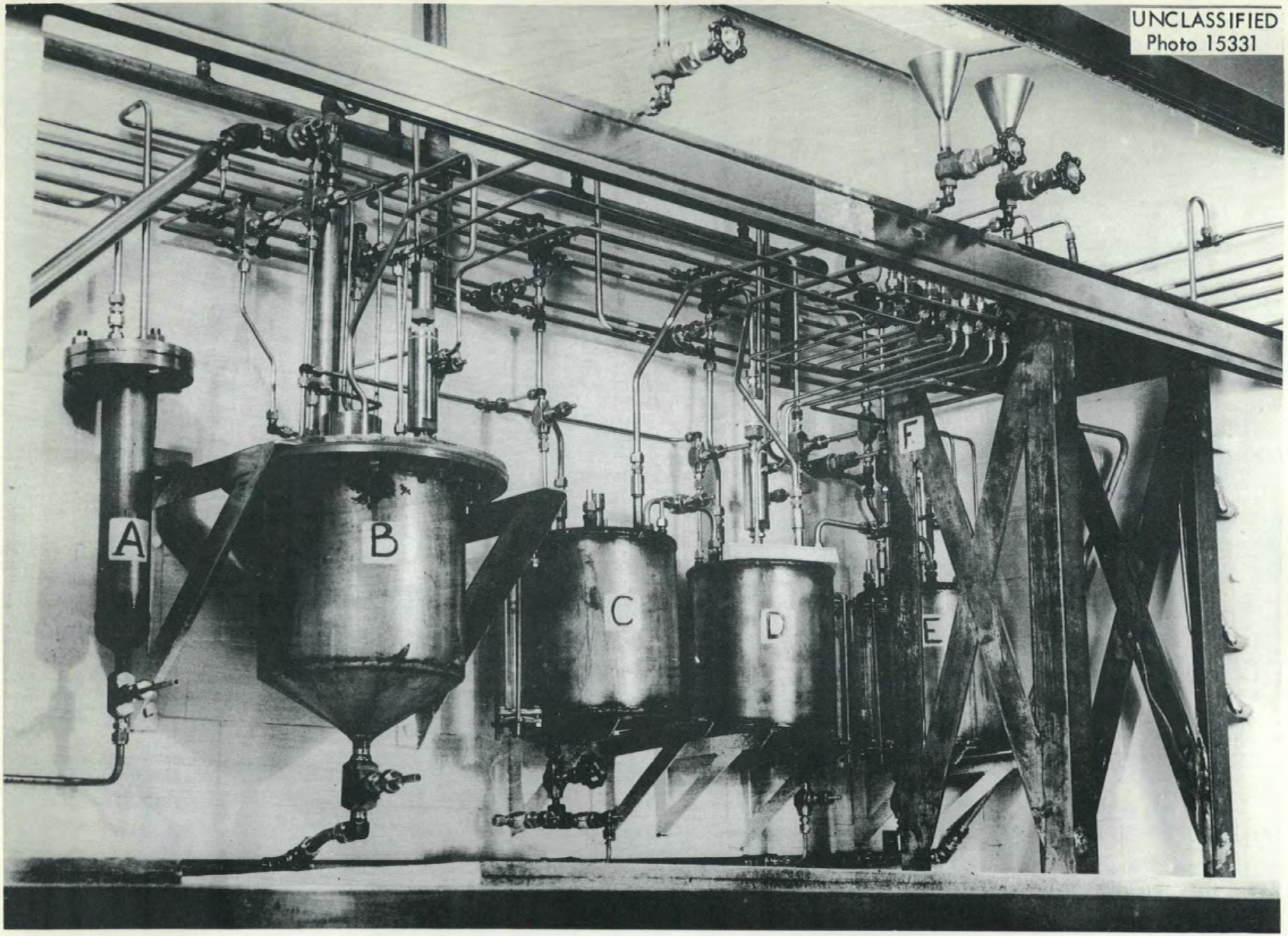

Fig. 5.1. Equipment Used in Feed-Adjustment Studies. (A) Vacuum trap. (B) Dissolver. (C) Hold tank. (D) Feed-adjustment tank. (E) Aqueous raffinate tank. (F) Sample blister support.

during the evaporation, this more drastic 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.

Batch equilibrations were used in the laboratory development work on adaptation of 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 concentrated 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. This corresponded to a reduction in volume to approximately half that of the original barstock solution. When this was diluted back to the original volume with water, the acidities ranged from 0.5 to 0.6 M for the 1.5 and 2.0 M H^+ 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 were used as a measure of the effectiveness of the treatment, the longest time being indicative of 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 N for 3 hr produced a stable organic emulsion in the batch-equilibration test. In all other cases, essentially clear organic phases were obtained in 50-90 sec and completely clean interfaces in 3-3.5 min. Digestion times ranging from 0.25 to 3 hr gave phase disengagement times of 30-240 sec, showing no apparent correlation with digestion time. Possibly, variations in acid loss during the

digestion periods because of condenser inefficiency and fluctuations in the agitator speed during the batch equilibrations are factors contributing to the erratic results.

Effect of Aging. Apparently, aging the 1 M HNO_3 dissolver solution at room temperature for a long period of time also gradually dehydrates and coagulates the emulsion-forming contaminants. This effect was shown by applying the emulsification test to an untreated portion of the barstock dissolver solution approximately 2.5 months after the initial test had been made on the freshly prepared untreated solution. The aged solution showed a significant improvement in emulsion-breaking tendencies with 1.5-2 hr being required as compared to overnight for the fresh solution in the earlier experiments.

5.4 Effect of Extraction Column Aqueous Phase Acidity

A scrub solution of 3 M HNO_3—0.75 M $Al(NO_3)_3$ containing 0.02 M ferrous sulfamate is recommended for eliminating organic emulsions and preventing excessive uranium reflux in the 25-TBP process extraction column. This provides an aqueous acidity at the feed plate of 1.33 M. No organic emulsification or excessive uranium reflux was noted in pulsed column runs with this scrub when digested and filtered natural uranium tubular element dissolver solution containing 1 M HNO_3 was used as the extraction column feed. It was necessary to maintain the acidity at the feed plate at a minimum of 1 M in nitric acid to prevent the yellow mercury precipitate observed in early experiments (Sec. 5.6).

In a series of 0.75-in.-dia pulsed column runs with the emulsion-producing 2S aluminum barstock dissolver solution (Sec. 5.3),

scrub solutions of 0.75 M $Al(NO_3)_3$ with acidities ranging from neutrality to 1 M HNO_3 and of 2.5-4.0 HNO_3 alone were investigated. The organic phase was 6% TBP in oleum-treated Amsco diluent. The proposed flowsheet flow ratios of AF/AS/AX = 100/20/40 were used in all runs. Stable organic emulsions were obtained with all 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 2.75-4.0 M HNO_3. Because of excessive uranium reflux, owing to insufficient salting strength (Sec. 6.1), when the scrub was nitric acid alone, the mixed scrub was recommended.

Laboratory batch-equilibration studies, in which simulated feed-plate solution was prepared from chemically pure reagents, corroborated the pulsed column data in that phase disengagement times varied inversely as the nitric acid concentration. Stable emulsions were not obtained 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 ferrous sulfamate, and 0.1 to 2.0 M HNO_3, were digested at the boiling point for 15 min prior to addition of the sulfamate (Sec. 6.1), and were subsequently batch-equilibrated for 1.5 min with 1/3 volume of 6% TBP in oleum-treated Amsco. The disengagement times, which varied from about 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). In an equilibration with 0.1 M HNO_3 done separately, about 24 hr after the rest of the series, the disengagement time dropped back to 90 sec.

When digested and filtered tubular element dissolver solution 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,

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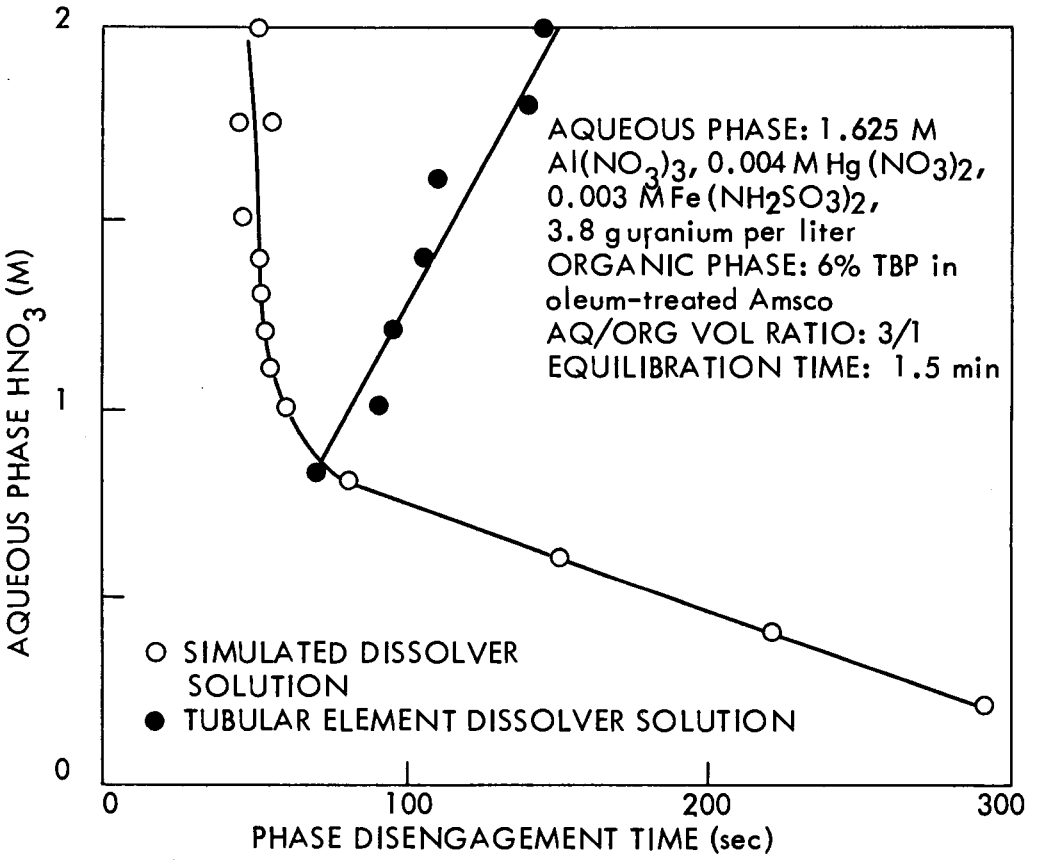

Fig. 5.2. Phase Disengagement Time as a Function of Feed Plate Acidity.

clear, bubbly organic emulsions, which were stable for more than 18 hr, were obtained in every case. The disengagement time was considered as the interval required for effervescence to cease in the organic phase. 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 dissolver 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 AF/AS ratio was 100/20, the aqueous phase acid concentration was adjusted to the desired molarity. The solvent phase was again 6% TBP in oleum-treated Amsco, and 1/3 the volume of the total aqueous phase. The batch-equilibration time used in the experiments was again 1.5 min.

5.5 Effect of Phase Mixing

The method of phase mixing very likely has a bearing on organic emulsification, as is evidenced by the anomalous behavior of natural uranium tubular element dissolver 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 laboratory batch equilibrations under identical conditions of volume and concentration at aqueous phase acidities of 1.25-1.5 M. In the former case, 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 study of the behavior of mercury under 25-TBP process IA column conditions was undertaken since little or nothing was known of its chemical properties in a TBP solvent extraction system utilizing scrub solution containing ferrous sulfamate—the Purex process aqueous feed contains no mercury catalyst.

In a preliminary experiment it was found that a nitric acid concentration of at least 1.5 M is required to prevent precipitation of mercuric ion in the presence of ferrous sulfamate at their feed-plate concentrations of 0.004 and 0.003 M, respectively. At lower acid concentrations, 0.08 to <1.5 M, a fine, white crystalline precipitate is formed. Mercurous ion, however, under identical conditions is soluble over the entire acid concentration range studied.

The addition of feed-plate concentrations of reagent aluminum and uranyl nitrates, i.e., 1.6 M aluminum and 3 to 6 g of uranium per liter, to 0.08 M HNO_3—0.004 M $Hg(NO_3)_2$ solution, followed by either boiling for 5 min or aging at room temperature for approximately one week, converted the mercuric ion to a form which did not precipitate upon addition of the ferrous sulfamate. 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 mercuric sulfamate precipitation. 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 made under IA column conditions showed that the free acid concentration of the aqueous phase must be at least 1 M or mercury precipitation of a second type occurs upon contact with the solvent. The chemical composition of this precipitate, which is flocculent and pale yellow in color, was not determined, but it was established that it did not occur in the absence of mercury and that the presence or absence of ferrous sulfamate had no effect. It was therefore concluded 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 uranium-aluminum alloy. The scrub solution was neutral 0.75 M $Al(NO_3)_3$-0.02 M ferrous sulfamate, and 6% TBP in oleum-treated Amsco diluent was used as the organic phase. A feed/scrub/solvent volume ratio of 100/20/40 was used in all equilibrations.

6.0 FIRST-CYCLE URANIUM LOSSES AND DECONTAMINATION

It is expected that in process the uranium first-cycle extraction and stripping losses can be limited to the design values of 0.01% each with 4 extraction and 4 stripping stages. Uranium loss resulting from radiation decomposition of the solvent will be negligible after 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, 10 ppb, with about 4 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 specification, i.e., a maximum of 0.01% in the extraction column aqueous waste and the same in the stripping column organic waste, can be met with 4 extraction and 4 stripping stages (see McCabe-Thiele diagrams in Figs. 6.1 and 6.2). HETS values estimated for a 0.75-in.-dia pulsed column were 4 and 2.4 ft for the extraction and stripping sections, respectively.

Effect of Total Nitrate Concentration. The efficiency of uranium extraction depends on the salting strength, i.e., the total nitrate concentration, and the hydrogen ion concentration. In the presence of 1.0-1.8 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 homogeneous reactor chemical processing studies have shown that uranium extraction by 30% TBP passes through a maximum at approximately 8 M HNO_3.

While such behavior is not well understood, it had to be 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

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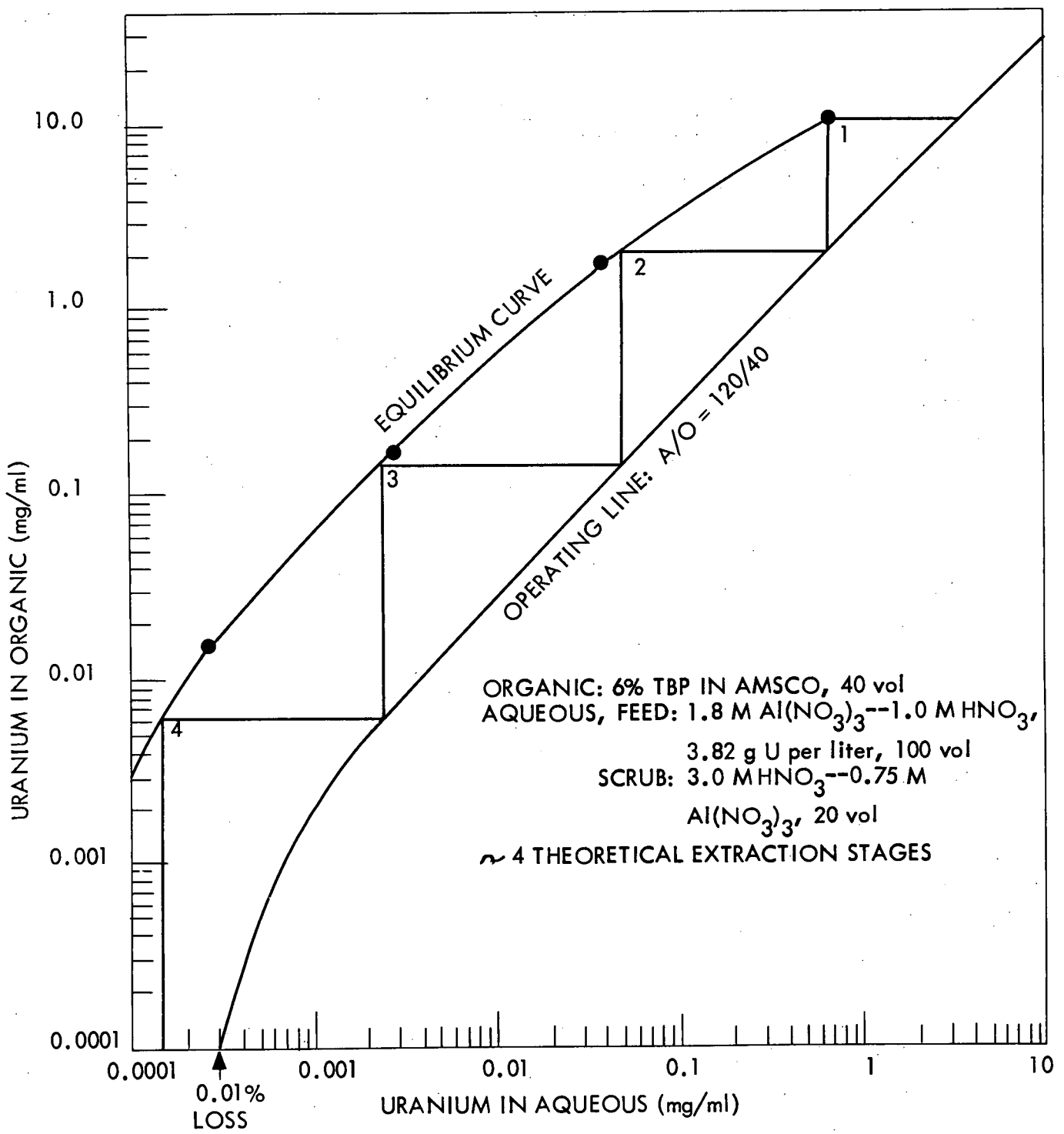

Fig. 6.1. Uranium Concentrations in Organic and Aqueous Phases under 25-TBP Process First-cycle Extraction Column Conditions.

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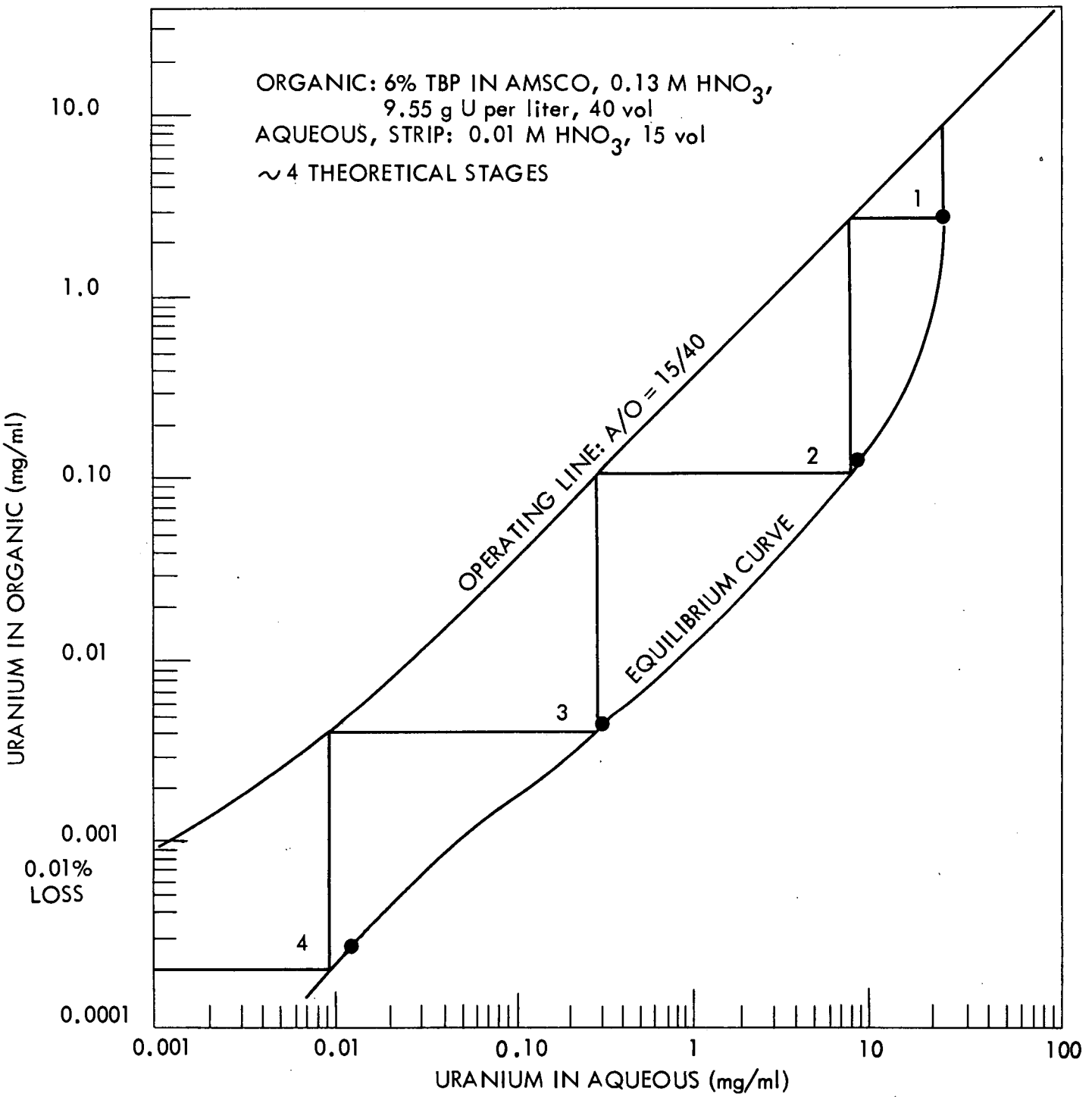

Fig. 6.2. Uranium Concentrations in Organic and Aqueous Phases under 25-TBP Process First-cycle Stripping Column Conditions.

phase feed-plate aluminum nitrate concentration was 1.5-1.6 M showed that neither 3-4 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).

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

$Al(NO_3)_3$ (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.

Effects of Radiation Damage to Solvent. Uranium retention in solvent samples that had received up to 14 times the radiation dosage expected in a single pass through the extraction-scrub column indicated that uranium losses to the organic waste 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 IA 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. A more detailed discussion of the radiation damage studies is given in Sec. 8.2.

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 product solution made this method unattractive. The potassium citrate was more soluble than sodium and the product was more stable, but the permissible operating range was still too narrow for practical application on a large scale. 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.)

HETS Calculations. In the HETS studies in the 0.75-in.-dia 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*

To attain the plutonium specification of not more than 10 ppb in the recovered uranium product, a decontamination factor of 10^4 is

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

required in the process. In batch countercurrent runs under recommended flowsheet conditions, with 6 scrub stages the plutonium decontamination factor was 3.3×10^5, indicating that very likely plutonium will be eliminated in the first cycle with approximately 4 scrub stages. The 0.02 M ferrous sulfamate used in the scrub was satisfactory for reducing tetravalent plutonium to the nonextractable trivalent state. In two Mini mixer-settler runs (Fig. 6.3), gross beta and gamma decontamination factors averaged 7×10^4 and 1×10^4, respectively. In four 0.75-in.-dia pulsed column runs (Fig. 6.4), gross beta and gamma decontamination factors averaged 5×10^4 and 3×10^3, respectively.

Decontamination from Plutonium. The plutonium decontamination experiments were made with synthetic feed containing 3.9 g of uranium per liter. It was prepared from natural uranium fuel elements, and was spiked with Pu(IV) to 9.2×10^6 c/m/ml.

In earlier work 0.02 M sulfate ion had been ineffective for forming a nonextractable plutonium complex in the presence of 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.

Decontamination from Fission Products. The gross beta and gamma decontamination factors in the Mini mixer-settler runs, 7×10^4 and 1×10^4, respectively, are averages of values obtained in runs 2 and 3 (Table 6.2). 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 accounted for by adsorption of radioactive fission products on equipment surfaces. Analysis of organic samples from each scrub stage showed that maximum decontamination requires 7 mixer-settler scrub stages. Preliminary runs with feed containing no fission products showed that one Mini mixer-settler stage was

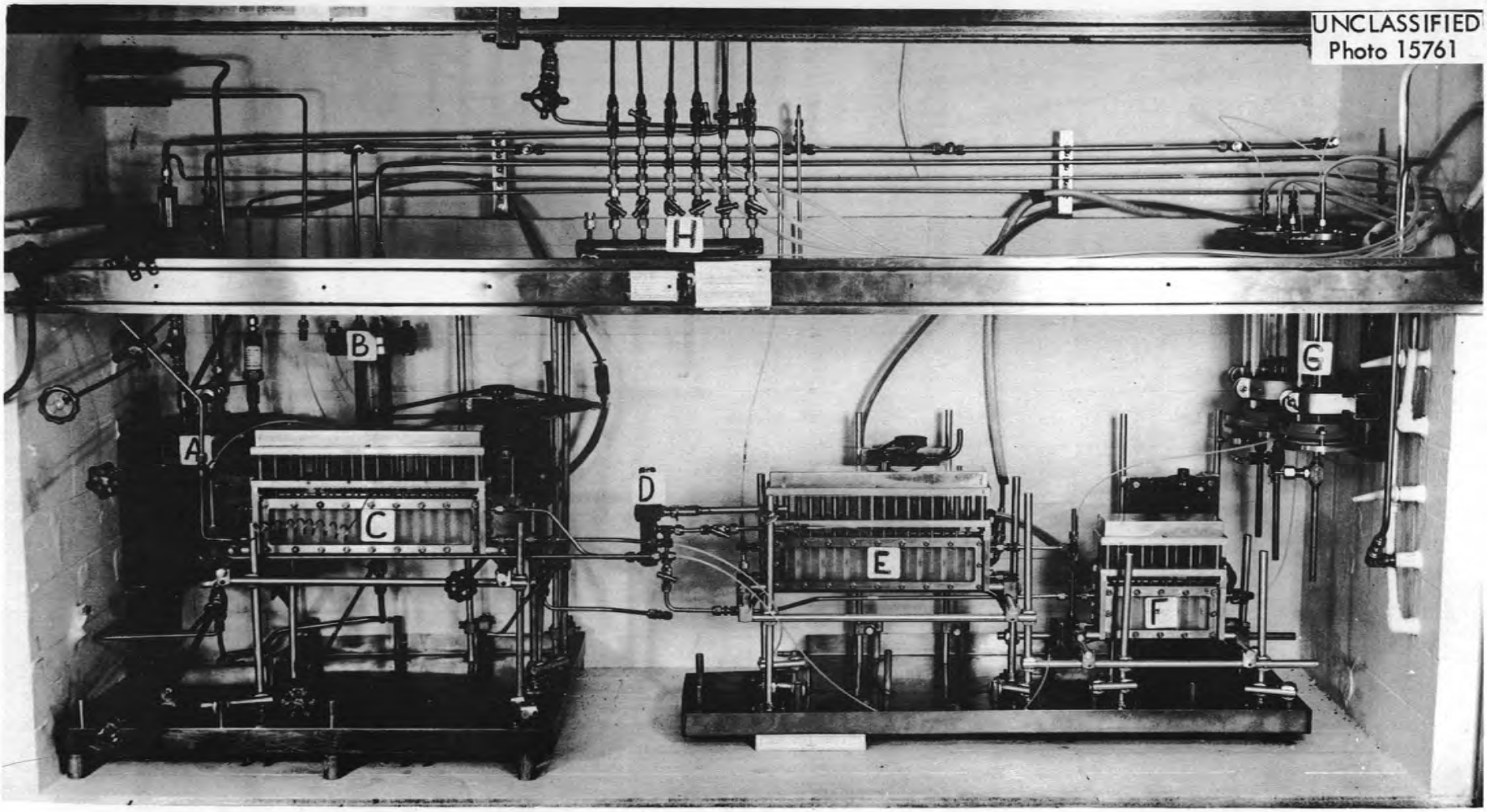

Fig. 6.3. Mini Mixer-Settler Equipment. (A) Feed displacement tank. (B) Vacuum trap. (C) Extraction-scrub bank. (D) A-column product (sample holdup pot). (E) Partitioning bank (not used). (F) Strip bank. (G) Product collection vessels. (H) Vacuum manifold.

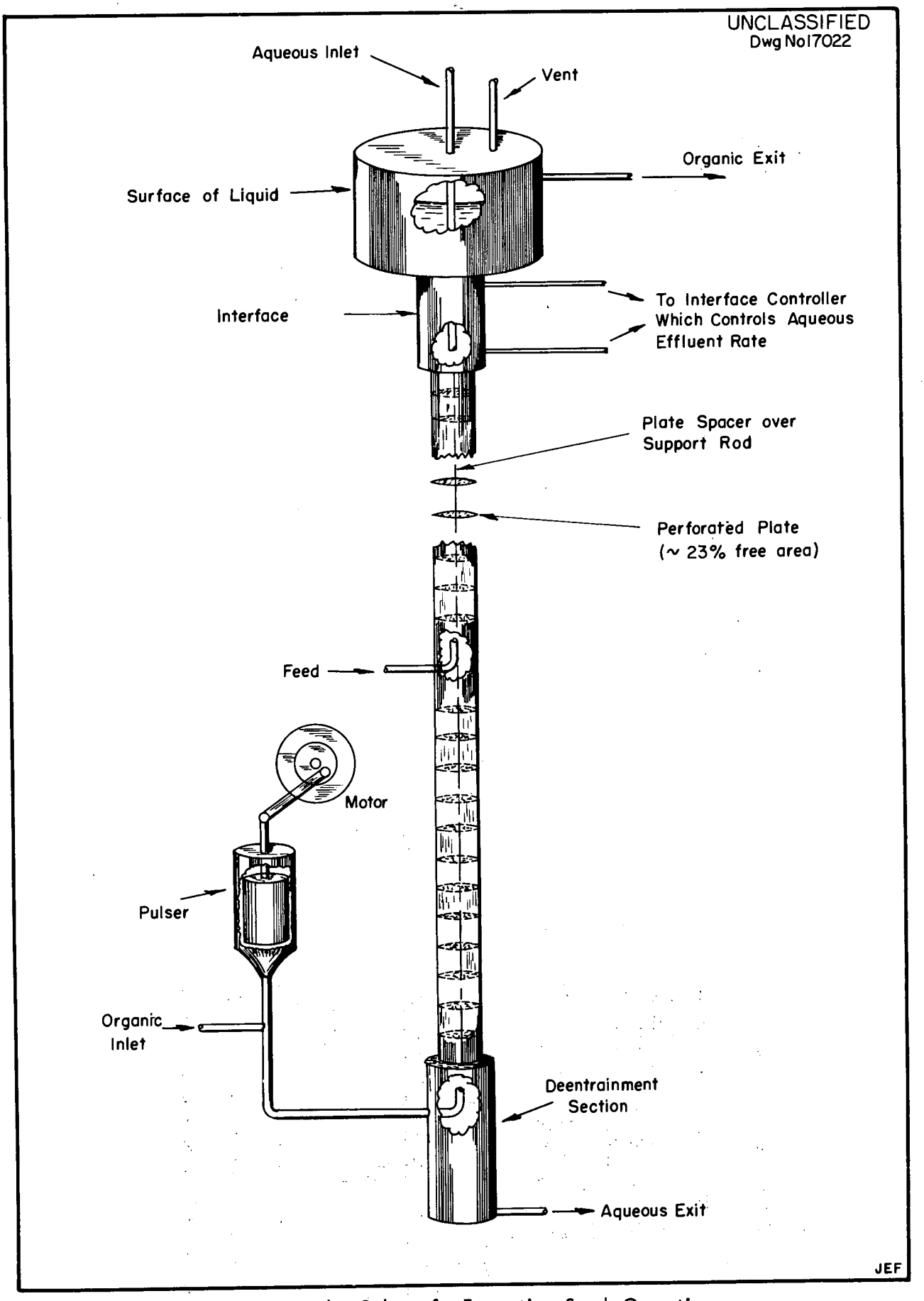

Fig. 6.4. Pulse Column for Extraction-Scrub Operation.

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

Feed: Irradiated J-slug or LITR element dissolver solution adjusted to contain: 0.5-1.5 g U/l, 1.8 M $Al(NO_3)_3$, 1 M HNO_3, and 0.005 M $Hg(NO_3)_2$; gross $\beta = 2.2\text{-}4.3 \times 10^9$ c/m/ml; gross $\gamma = 0.55\text{-}2.26 \times 10^9$ c/m/ml
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 diluent
Strip: 0.01 M HNO_3
AF/AS/AX/BX = 100/20/40/15
8 extraction stages; 8 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 IAW stream analysis.

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 8-ft scrub sections were used, gross beta decontamination factors were generally in good agreement with those in the Mini mixer-settler runs, but gross gamma were 2- to 3-fold lower (Table 6.3). In the fourth column run (run 7), in which the scrub section was cut in half, the gross beta decontamination factor was decreased 20-fold while the gross gamma was decreased only 4-fold. 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 IA column scrub section. In the first column run (run 4), as in the Mini 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 product contaminants.

The mixer-settler runs 1 and 2 were made with Hanford J-slug wafers which had been irradiated 1 year and had decayed 1 year after shutdown. For the third run, portions of a LITR element which had been irradiated 377 days, and had decayed approximately 225 days after shutdown were used. In each case the fuels were dissolved, and the solution was digested and adjusted to approximate flowsheet 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 U^{235} with natural uranium. However, it is felt that this condition had very little influence on decontamination. The gross beta and gross gamma activities

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

Feed: tubular fuel element dissolver solution spiked with fission products from irradiated U-Al alloy: 3.8 g U/l, 1.8 M $Al(NO_3)_3$, and 0.005 M $Hg(NO_3)_2$; gross β = 1.47-5.09 x 10^7 c/m/ml; gross γ = 0.94-3.75 x 10^7 c/m/ml
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 diluent
Strip: 0.01 M HNO_3
AF/AS/AX/BX = 100/20/40/15
Length of extraction section = 6 ft
Length of stripping section = 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
4	8	~9	7	7.87×10^4	1.04×10^4	---	---	---
5	8	~9	7	2.52×10^4	5.33×10^3	4.93×10^3	$>10^5$	3.91×10^4
6	8	~14	11	5.08×10^4	2.70×10^3	1.79×10^3	$>10^5$[a]	8.25×10^4
7	4	~16	6	2.7×10^3	6.2×10^2	---[b]	---	---

[a]Estimated.

[b]97% of gross γ in product was accounted for by Zr-Nb; decontamination factor not calculated because these elements were not determined in feed solution.

were 2.2×10^9 and 5.5×10^8, respectively, in the J-slug solutions and 4.3×10^9 and 2.26×10^9 c/m/ml, respectively, in the LITR element solution.

Feeds for the column runs were prepared by dissolving sections of natural uranium-aluminum tubular fuel elements, digesting, filtering, and spiking with fission products obtained from irradiated uranium-aluminum 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 c/m/ml for gross β, and from 9.42×10^6 to 2.28×10^7 for gross γ.

Miscellaneous Studies. Mention should be made of some of the preliminary decontamination studies which had direct bearing on the development of the recommended first solvent-extraction cycle flowsheet. In a series of 0.75-in.-dia pulsed column tests, fission product decontamination factors were determined as functions of the aluminum nitrate concentration in neutral scrub and of feed and scrub acidities. The feeds used in these experiments were prepared by dissolving portions of irradiated Hanford J slugs and subsequently adjusting the feed solutions to contain 1.8 M $Al(NO_3)_3$, 0.005 M $Hg(NO_3)_2$, and 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. These runs were made under conditions simulating the conditions eventually used in the column runs.

In the first set of runs, with a 0.1 M HNO_3 feed and neutral scrub solutions containing 0.5 to 1.0 M $Al(NO_3)_3$ vs a 6% TBP-Amsco organic phase, the gross β, ruthenium β, and rare earth β 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 0.75 M $Al(NO_3)_3$ scrub was chosen as a compromise between maximum decontamination and most efficient uranium recovery. Substitution of 3 M HNO_3 for 1 M $Al(NO_3)_3$ as the scrub solution significantly increased the ruthenium β decontamination factor, but lowered the zirconium-niobium γ decontamination factor. This latter observation is not consistent with Purex experience.

The second set of experiments consisted of two pulsed column runs in which neutral 0.75 M $Al(NO_3)_3$ and 6% TBP--Amsco were used as the scrub and organic streams, respectively. The first run of the set used a feed which was 0.15 M acid deficient, whereas an 0.86 M acid feed was used in the second run. In both cases, the ruthenium β decontamination factors were significantly higher than the value of 10^3 obtained under the same conditions with a 0.1 M HNO_3 feed. In the acid-deficient system the ruthenium β decontamination factor was 1.3×10^4, and in the high-acid system it was 3×10^3. The behavior of ruthenium in these pulse column runs is in agreement with observations made in earlier laboratory batch equilibration studies.[12] The anomalous behavior of zirconium and niobium in these solvent extraction studies is attributed to their colloidal nature and their tendency to adsorb and concentrate on particles of interfacial solids.

7.0 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 subsequently butted to 3 M HNO_3 by addition of concentrated nitric acid 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. The single radioactive laboratory batch countercurrent run which was done under conditions approximating the recommended second cycle flowsheet conditions, using 6 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 solvent extraction cycle product obtained in pulse column run No. 7 (Sec. 6.2), in which only 4 ft of scrub section was used. The first cycle product was evaporated and adjusted to contain 157.2 g of uranium per liter in 3.17 M HNO_3. Radiochemical analyses of the adjusted feed showed gross β, 2.50×10^5 c/m/ml; gross γ, 1.11×10^6 c/m/ml; Zr-Nb γ, 1.04×10^6 c/m/ml; total rare earth β, 2.81×10^3 c/m/ml; Ru β, 780 c/m/ml. Results of the experiment indicated that the radioactive fission products were not extracted to any great extent; maximum decontamination was attained in approximately 4 scrub stages.

Decontamination factors were difficult to calculate because of the low residual activity and the U^{235} 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 β, 210 c/m/ml; gross γ, 124 c/m/ml; Zr-Nb γ, 115 c/m/ml; total rare earth β, <50 c/m/ml; and Ru β, <25 c/m/ml—show that in the second cycle, as in the first,

zirconium and niobium are the limiting product contaminants.

Plutonium decontamination in the second solvent extraction cycle is not expected to be a problem, since first cycle studies (Sec. 6.0) indicated that plutonium is approximately 100% removed in 4 scrub stages in the IA column. The use of ferrous sulfamate in the second cycle scrub is merely a precautionary measure.

7.2 Uranium Recovery

As in the first solvent extraction cycle, the permissible uranium loss specification for the second cycle is 0.01% to each waste stream. A laboratory batch countercurrent run, made under the proposed second cycle flowsheet conditions, using 5 extraction, 6 scrub, and 6 strip stages, showed that the uranium loss specification can be met with 3 extraction and 4 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. However, previous hydraulic studies of a similar system, where aqueous feed containing approximately 140 g of uranium per liter and 3 M HNO_3 was extracted with 15% TBP in Amsco diluent, yielded average HETS values of 2.5 and 5 ft in a 2-in.-diameter pulsed column for the extraction and stripping stages, respectively.

8.0 SOLVENT TREATMENT

Impurities present in the Amsco diluent, as shipped, were responsible for some of the interfacial solids. Radiation decomposition

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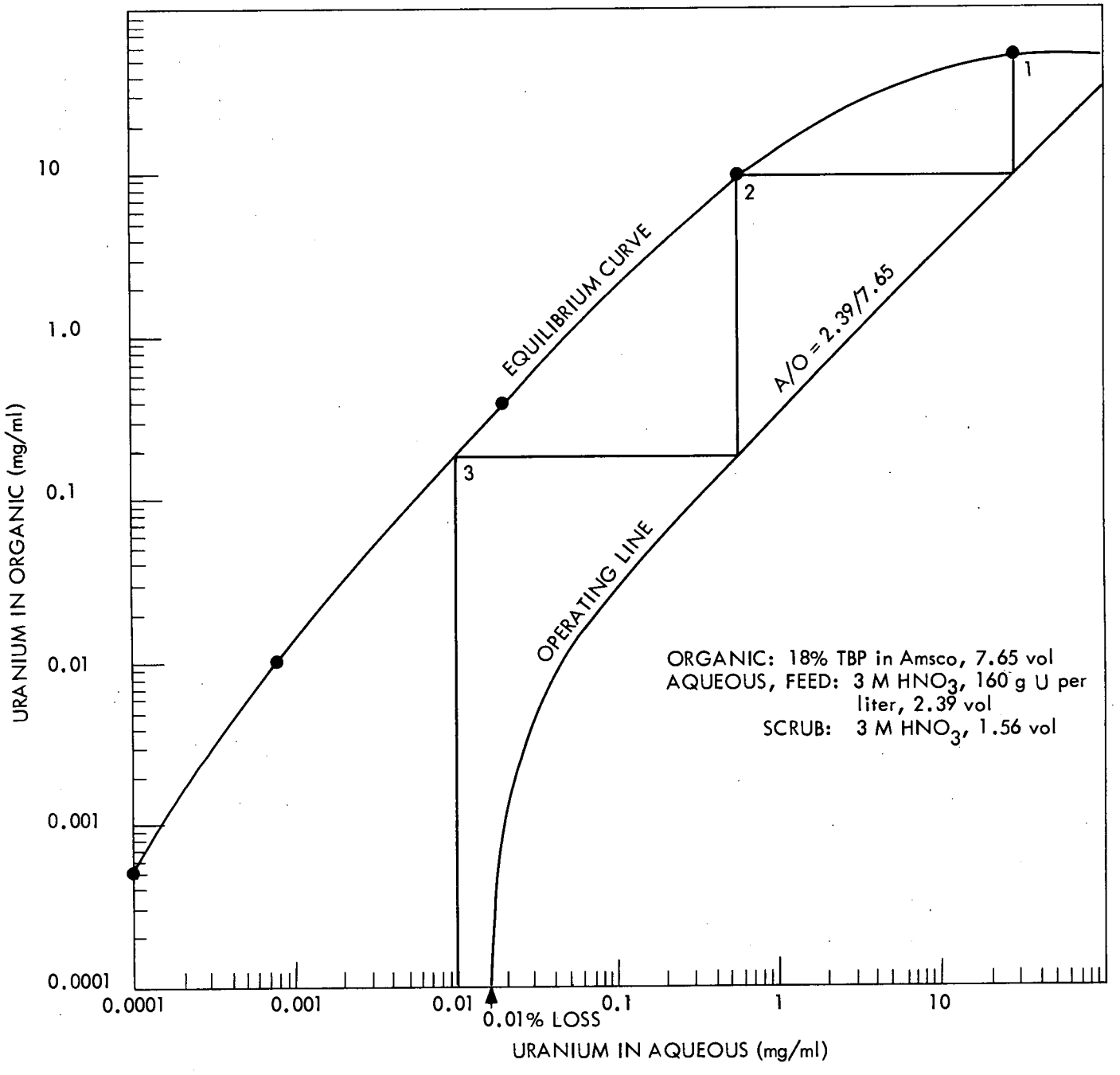

Fig. 7.1. Uranium Concentration in Organic and Aqueous Phases under Second-cycle Extraction Column Conditions.

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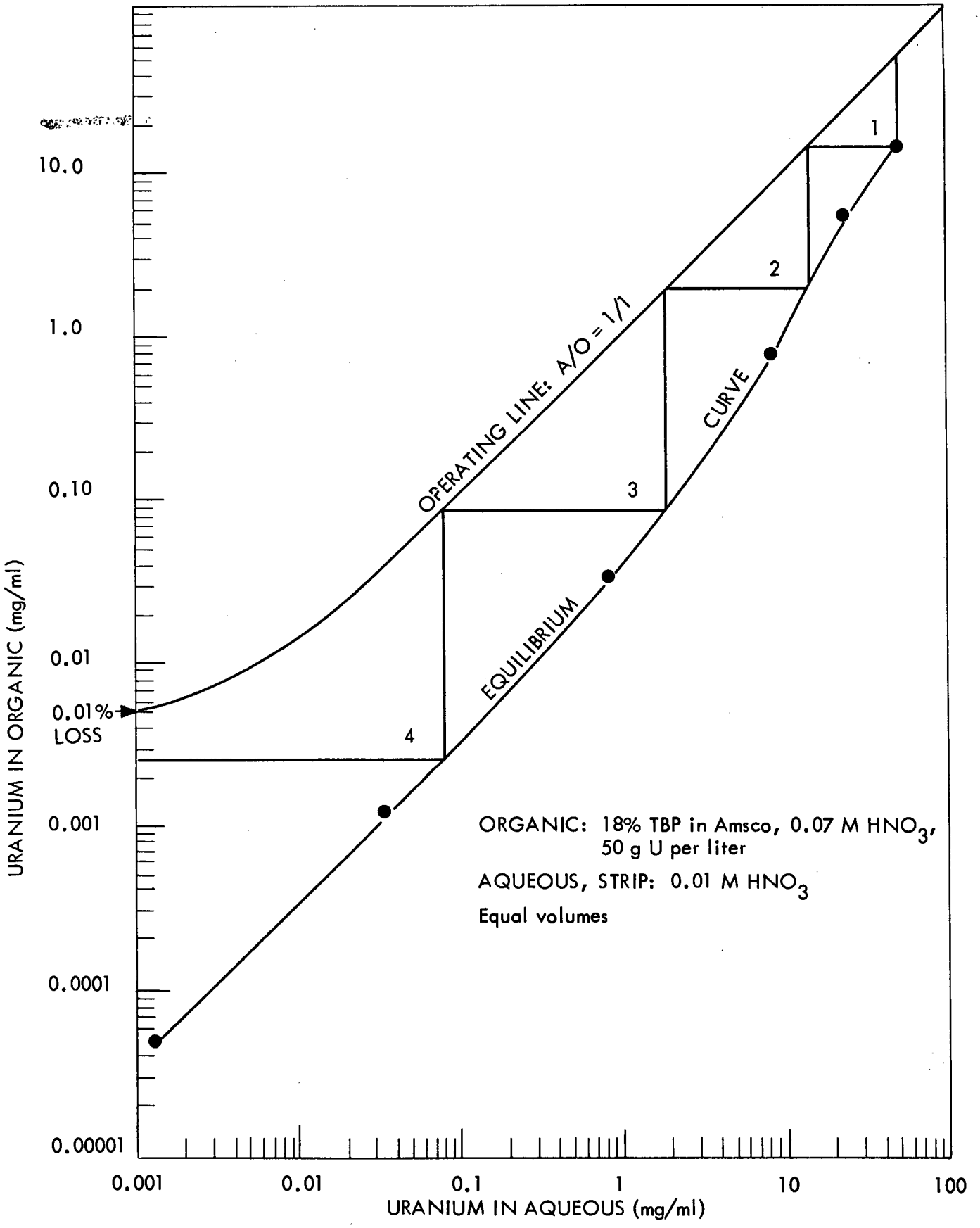

Fig. 7.2. Uranium Concentration in Organic and Aqueous Phases under Second-cycle Stripping Column Conditions.

products could cause high uranium losses, and residual radioactive substances 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 solvent discoloration from water-white to orange-yellow and the buildup of gray to black interfacial solids were noted when untreated Amsco diluent was used in early 25-TBP process pulsed column test runs with material containing radioactive fission products. The solids built up in the column and interfered with operation and resulted in poor uranium decontamination.

A significant decrease in interfacial solids buildup and 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 the TBP. Uranium decontamination was also improved, presumably because entrainment of the highly radioactive solids in the IA column product stream was substantially decreased when less solids accumulated. No I^{131} was present in the test runs because only long-decayed irradiated fuel was used in feed preparation. It is expected, however, 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 decomposition products and residual radioactive substances must be removed from the strip column waste streams prior to recycling of these as extractant. A buildup of radiation decomposition products in the solvent phase 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 eventually present health hazards which would necessitate installation of additional shielding and remote-handling equipment in the solvent makeup area, increasing the plant capital and operating costs. The procedure recommended for removing both radiation decomposition products and residual fission products from solvent that is to be recycled is washing, successively, with two 1/3 volumes of 0.2 M Na_2CO_3, and finally one 1/3 volume of demineralized water in a turbine mixer.

Removal of Radiation Decomposition Products. Previous work[13,14] 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 the uranyl nitrate forms with it an organic-soluble complex which is even stronger than the one formed with TBP, its presence could result in retention of large amounts of uranium in the organic phase. Experiments on Co^{60} 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 the set of experiments where only the organic phase was irradiated, samples of 18% TBP in oleum-pretreated Amsco diluent were

exposed to 0.175, 0.7, 3.5, 17.5, and 35 β watt-hr/liter radiation. These values correspond, respectively, to approximately 0.7, 3, 14, 70, and 140 times the 0.238 watt-hr/liter expected in the separation process for a single pass through the IA column. Aliquots of 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 β watt-hr/liter or less, three strip passes were sufficient to reduce the uranium concentrations in the equilibrated organic phase to 0.001 g/liter (0.01% uranium loss) or less. With solvent that had been exposed to 17.5 and 35 β watt-hr/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 β watt-hr/liter radiation was washed with two 1/5 volumes of 0.1 M Na_2CO_3, then 0.1 M HNO_3, and finally 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 β watt-hr/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 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 just prior to each

irradiation. The organic phase was 6% TBP in oleum-pretreated Amsco. The aqueous phase was made from a natural uranium--aluminum alloy tubular fuel element and contained 1.8 M $Al(NO_3)_3$, 1 M HNO_3, 0.005 M $Hg(NO_3)_2$, and 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 mixed by means of an electric stirrer during the irradiation. After each irradiation, the phases were separated and the organic phases were exhaustively stripped with five consecutive double volumes of water. Nonirradiated control samples were given the same treatment.

The continuously exposed solvent required four strip passes to reduce the uranium loss to 0.01%. These results are in good agreement with those obtained when only the solvent phase was irradiated. In the intermittent experiments, without intercycle solvent cleanup, three strip passes were adequate for a 0.01% uranium loss after the first, second, and third 10-min exposures, but four strip passes 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 strip passes were required after every exposure period, and there was no uranium buildup in the organic phase, even after the last irradiation. Generally, all the uranium retention values from the intermittent run without intercycle cleanup were a factor of 2 to 10 higher than those 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.

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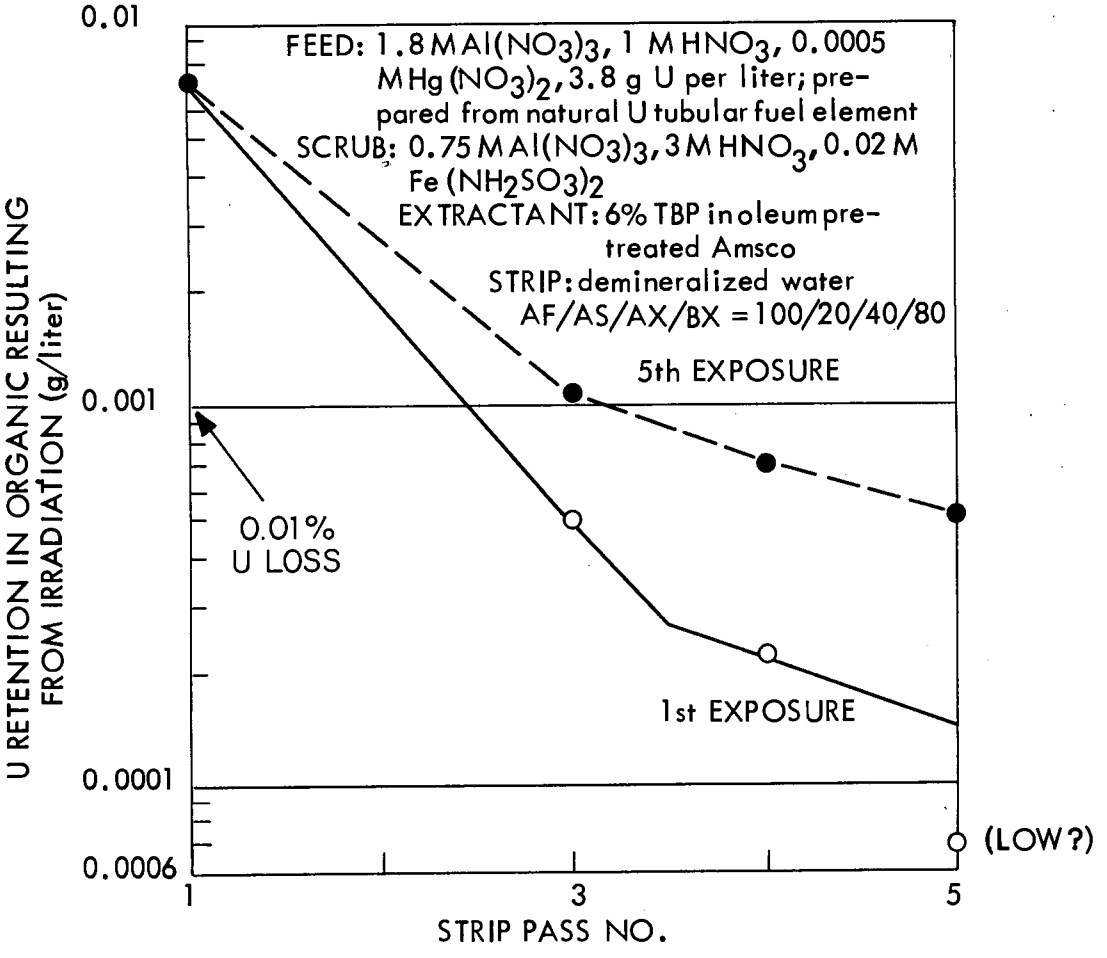

Fig. 8.1. Cumulative Effect of Irradiation on Uranium Retention in Solvent. No washing between exposures. Irradiation dosage to solvent = 3.3 ± 0.2 β watt-hr/liter, given in five 10-min exposures. Phases mixed and irradiated in Co^{60} source.

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 β activity, which was essentially all ruthenium, was accomplished by washing with one 1/5 volume of 0.1 M Na_2CO_3 which yielded a gross beta decontamination factor of 4×10^2. Three additional carbonate washes, i.e., four total, 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 only one acid wash instead of two, the overall decontamination factor was 1.7×10^4. It is therefore seen that little is accomplished by using more than two carbonate washes, and that the nitric acid washes have little effect on the gross beta decontamination. However, in batch washings, interfacial solids formed, 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, yielded 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 addition of Yorkmesh packing in the solvent effluent lines between stages.

The initial turbine-mixer shakedown tests were made with 6% TBP in oleum-treated Amsco diluent, containing 1.24×10^7 gross γ c/m/ml. 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

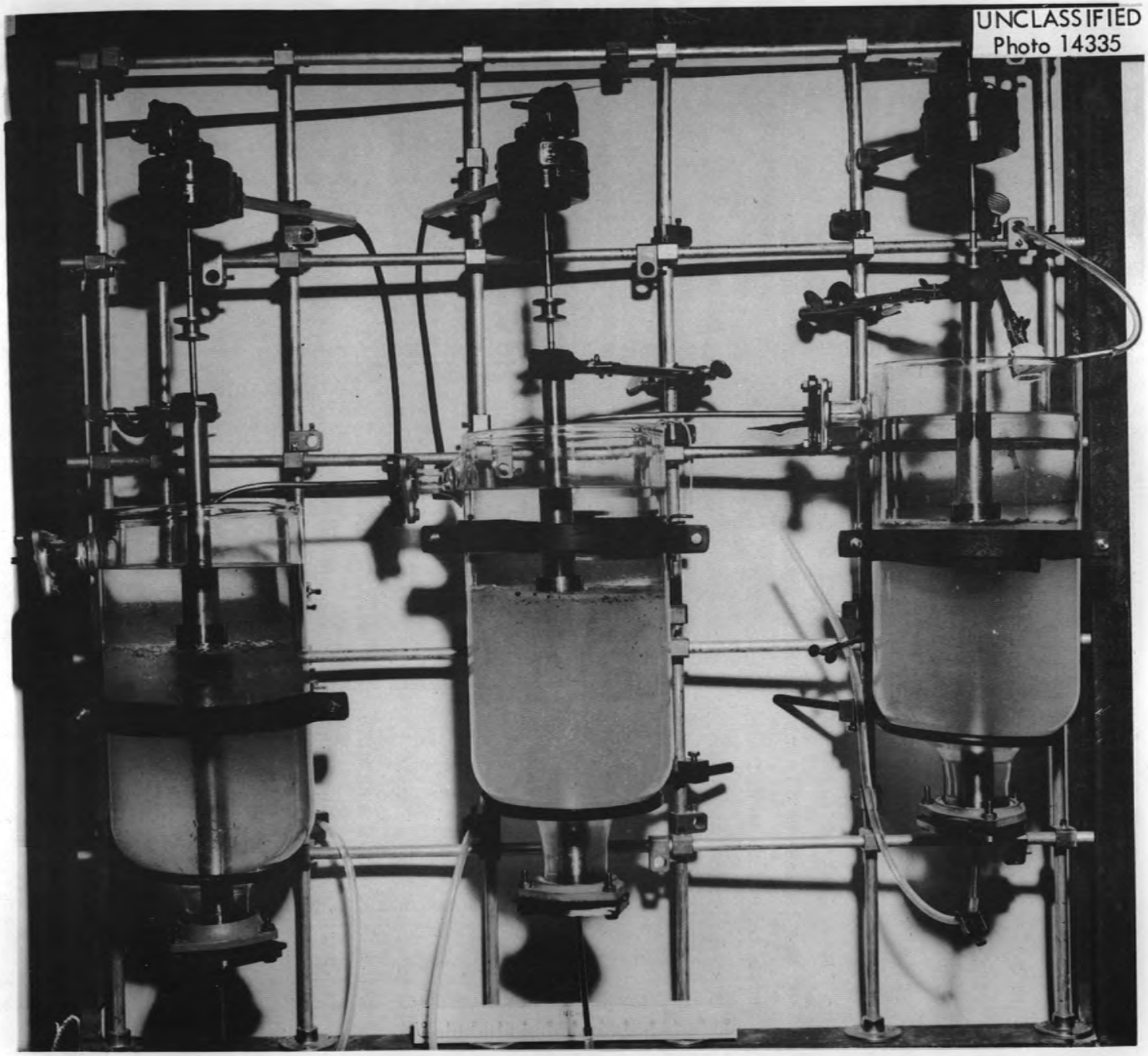

Fig. 8.2 Turbine Mixer.

40 ml/min, which corresponds to 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. Modification of the equipment to provide increased recirculation of the organic phase and also de-entrainment of contaminated aqueous droplets from the solvent effluent streams increased the turbine-mixer decontamination efficiency to 50% of the laboratory batch control result in the third shakedown run with material containing radioactive fission products.

Table 8.1. Effect of Washing on Decontamination of Used Solvent

Solvent Sample	Initial Gross β Activity (c/m/ml)	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 (high?)	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 a still greater solvent recycle rate and increased mixing speed. A series of runs without fission products made under these conditions indicated that it was possible to operate the turbine-mixer 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 material containing radioactive fission products was made in the revamped equipment. For this run, the concentration of the sodium carbonate wash solution was increased to 0.2 M. Furthermore, the turbine-mixer equipment was 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 again demineralized water. The feed was contaminated 6% TBP in oleum-treated Amsco, obtained from a pulsed column run with radioactive fission products which was made under the proposed first cycle flowsheet conditions. Radiochemical analyses of the feed for gross β and γ activities were 8.02×10^4 and 7.16×10^5 c/m/ml, respectively. Decontamination factors for the run averaged 1.4×10^3 for gross β and 3.6×10^3 for gross γ. The solvent effluent streams were sampled at each stage after having passed through the Yorkmesh packing de-entrainment section. Centrifugation of these samples failed to separate out any detectable solids or aqueous phase. These results indicated that the modified turbine-mixer was capable of reconditioning solvent with efficiency equal to that attained in a laboratory batch-washing control experiment made under the same conditions.

9.0 WASTE STUDIES

The cost of waste storage is one of the major items considered in the evaluation of a process from the economic standpoint. Both the volume and the chemical and physical properties of the waste affect the storage costs. For example, nitric acid waste must be stored in stainless steel tanks because of corrosion, 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)[15] followed by addition of caustic is a promising method of reducing storage costs.

In laboratory studies on distillation of simulated IA column waste, diban was formed when the pot temperature reached approximately 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 waste volume as compared to the original volume of the acidic waste. It is expected that the radioactivity of the distillate will 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 approximately 12 hr. The solutions so formed were very 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 because of a small amount of suspended solids, which are apparently highly charged since they settle very slowly. The solutions are nonviscous and boil at about 100°C, even when concentrated to 6 M diban. Apparently as a result of the characteristics of these solutions, bumping during evaporation will not be as serious a problem as it is 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. It should be mentioned, however, that, in

any neutralized waste, iron, mercury, and many of the fission products will exist as hydroxide solids which will represent between 1 and 5% of the total neutralized waste volume.

Evaporation of the acidic 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 which initially contained 1.67 M $Al(NO_3)_3$ and 1.5 M HNO_3. No extraneous materials such as ferric nitrate or mercuric nitrate were 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 gradually rose to 144°C, at which point it was assumed 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 sharply, to 0.5 and 1.1 mils/year, respectively.

These results indicate that although the stainless steel corrosion encountered in evaporation of acidic waste solutions to diban may be prohibitive if conventional, simple distillation methods are used, the problem may possibly be eliminated by the use of flash evaporators. Otherwise, it may be necessary to construct the evaporator of a more resistant metal, or to neutralize the wastes prior to boildown.

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*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.

In view of the corrosion test results, further laboratory experiments were conducted to determine the maximum waste 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% sodium hydroxide yielded 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

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

The specific gravity of the resultant neutralized solution was 1.256 at 25°C. No precipitation occurred when this solution was tumbled end-over-end for 20 hr at room temperature or upon reflux at the boiling point for 8 hr. Upon distillation, a volume reduction of more than 1.41 but less than 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 neutralized conditions, the solution was found to be 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, solid aluminum oxide, which only partially dissolved upon heating, lay on the bottom of the vessel. The specific gravity of the slurry was 1.296 at 25°C.

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11.0 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 uranyl nitrate self-salting effects. 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 pulse 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[16-18] 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:

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 2-3, 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 3-6, 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 6-8, 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, $\sim 2.5 \times 10^{-5}$ 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,

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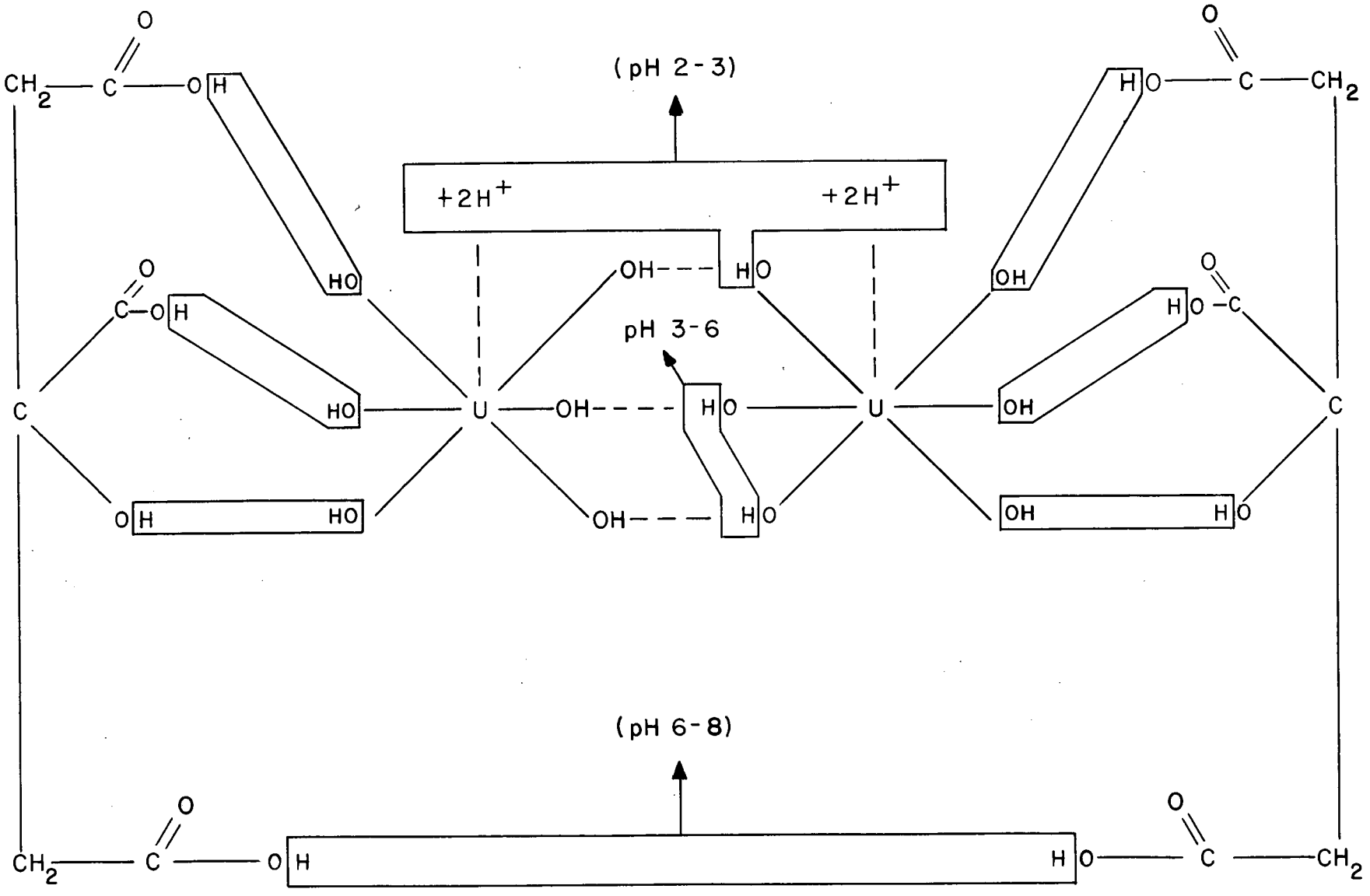

Fig.11.1. Complexing of Uranium with Citrate.

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 ~50 g of uranium per liter and ~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 scouting runs 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 <0.12 to 3.9; the initial uranium concentrations in the organic 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 M 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 3-4, distribution coefficients of 10^{-5}-10^{-7} were obtained as compared to 10^{-1}-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 also found to be relatively independent of the citrate concentration as long as the citrate/uranium mole ratio was ≥1/1. It should be noted that 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. Further development work with the ammonium system was abandoned because of the explosion hazard involved in evaporating ammonium nitrate waste solutions prior to storage.

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

O/A Vol. Ratio	Initial Conditions						Equilibrium Conditions				Uranium Distribution Coefficient (O/A)
	Aqueous			Organic			Aqueous		Organic		
	Citrate (M)	NO_3^- [a] (N)	Uranium (g/liter)	TBP (%)	Uranium (g/liter)	HNO_3 (N)	Uranium (g/liter)	pH	Uranium (g/liter)	H^+ (N)	
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.

Later studies were devoted to the sodium and potassium citrate systems, with respect to aqueous product solution stability and attainable uranium distribution coefficients, as functions of pH and citrate concentration both in the presence and absence of corresponding acetate salt buffers.

The results of initial batch equilibrations with 4 volumes of 18% TBP in Amsco vs. 1 volume of aqueous ~0.7 M uranyl nitrate solution 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 $>8.5 \times 10^{-1}$ at pH <0 to $\sim 1.5 \times 10^{-7}$ at pH slightly over 5. In all cases where the equilibrium pH was >3, distribution coefficients of $<10^{-5}$ were obtained. Furthermore, it was observed in these experiments that the stability of the uranyl citrate solutions was also largely pH dependent. At equilibrium pH's less than 3, i.e., the reagent pH's of the solutions with citrate concentrations of 1 M or less, yellow crystalline precipitates formed. However, addition of sodium hydroxide pellets to the slurries, in an NaOH/citrate mole ratio of 4/1, readily redissolved the precipitates with resulting equilibrium pH's in the range 4.5-5.5. From these results, it was evident that 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 that would lead to stable uranyl citrate solutions at process uranium concentrations were determined by titration with standardized base 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 (see Fig 11.2). The range of stability was found to lie between pH 4.2 and 5.6. On the basis of these results, 1.0, 1.25, and 1.5 M

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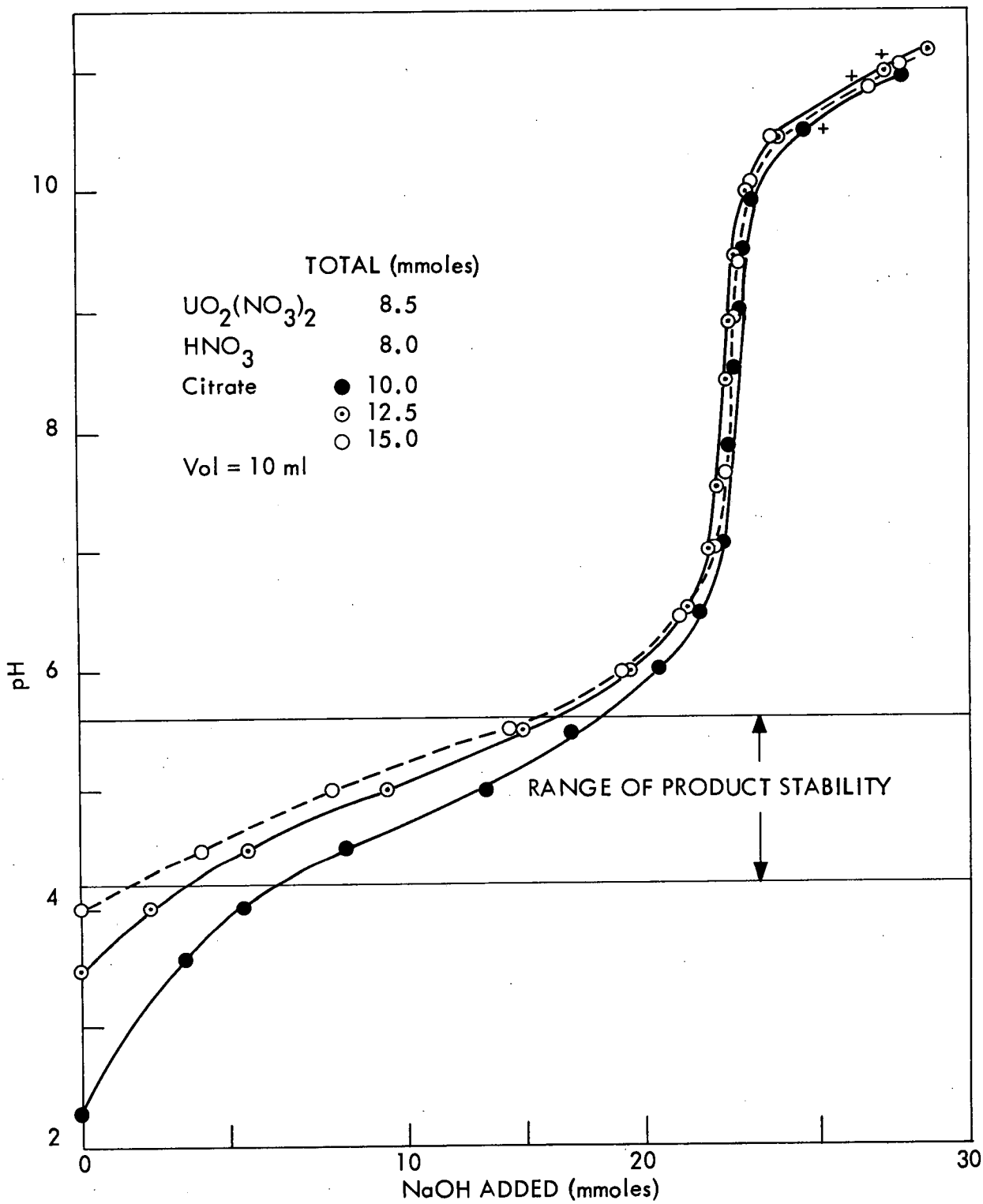

Fig. 11.2. Titration of Simulated IIBP Solution with 1.0 M Sodium Hydroxide.
* Precipitation noted.

sodium citrate strip solutions containing the proper amounts of caustic to produce stability were prepared. However, since the pH's of all these strip solutions were >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, $<10^{-2}$, were generally a factor of 10^2 to 10^3 higher than those obtained by the reverse procedure under identical conditions, i.e., aqueous uranyl citrate solutions containing the caustic vs. pure 18% TBP-Amsco, in which cases no precipitation occurred. Apparently the precipitate formation and redissolution required more than the 2-min equilibration time, and steady-state conditions were never reached. Although in actual countercurrent pulse column operation diuranate precipitation may never occur, because the aqueous phase pH gradient from ~4 to >11 would take place gradually in the stripping section from the bottom plate, where the uranium concentration in the organic is greatest, to the top plate where the organic uranium concentration is very low, the condition is recognized as undesirable. The optimum caustic-sodium citrate conditions for uranium stripping from the standpoint of strip solution solubility, aqueous product stability, and distribution coefficient were found to be 1.25 M sodium citrate-1.3 M sodium hydroxide, which gave reproducible distribution coefficients of $<10^{-5}$. The use of 1.25 M sodium citrate alone gave aqueous stability without diuranate precipitation, 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 equilibrated with pure solvent. Also, the addition of sodium hydroxide to the strip solutions lowered the solubility of the sodium citrate.

The hope of achieving maximum product stability and minimum uranium distribution coefficients without the risk of sodium diuranate precipitation, prompted the substitution of sodium acetate for sodium hydroxide in the high-pH sodium citrate system. In the buffered system, the reagent sodium citrate strip solution pH's were <8, making diuranate precipitation less likely, and the attainment of product solutions with pH's falling within the stability range more probable. The optimum stripping conditions in this system were determined to be 1.25 M sodium citrate-1.0 M sodium acetate which gave a uranium distribution coefficient of $\sim 4 \times 10^{-5}$ with no evidence of diuranate precipitation. 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 gave insoluble 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, thus eliminating one of the factors which limited the sodium system. The strip solution compositions investigated were 1.0, 1.25, 1.5, and 2.0 M potassium citrate containing 0-3.0, 1.0-2.0, 0.5, and 0-0.5 M potassium acetate, respectively. These strip solutions were batch-equilibrated with 4 volumes of 18% TBP in Amsco containing $\sim$ 50 g of uranium per liter and $\sim$ 0.1 M HNO_3. Evidences of potassium diuranate precipitation and aqueous product instability were recorded.

In the 1.0 M potassium citrate system, unstable aqueous products were obtained in the presence of 0-0.5 and 2.5-3 M potassium acetate. At acetate concentrations of 1.0-2.0 M, product stability was achieved.

At 1.25 M potassium citrate, a stable aqueous product was obtained in the presence of 1.0 M potassium acetate, but instability occurred at acetate concentrations of 1.25-2.0 M.

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

In the 2 M potassium citrate system, temporary, local potassium diuranate precipitation was observed in the absence of acetate. The addition of 0.5 M potassium acetate eliminated the diuranate precipitation but yielded an unstable aqueous product.

All the uranium distribution coefficients obtained in the potassium system were in the range 10^{-6}-10^{-4}. The solubility data for the potassium citrate-acetate system are summarized in the plot presented in Fig. 11.3, which 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 1-2 M acetate, 1.25 M citrate and 1 M acetate, and 1.5 M citrate in the presence of 0.5 M acetate.

When the 18% TBP organic phase contained ~50 g of U per liter and ~0.1 M HNO_3, as in previous experiments, but the organic/aqueous volume ratio was increased from 4/1 to 5/1, precipitation occurred in the aqueous product in all cases. Increasing the uranium concentration of the organic phase to 60 g/liter, and hence lowering the nitric acid

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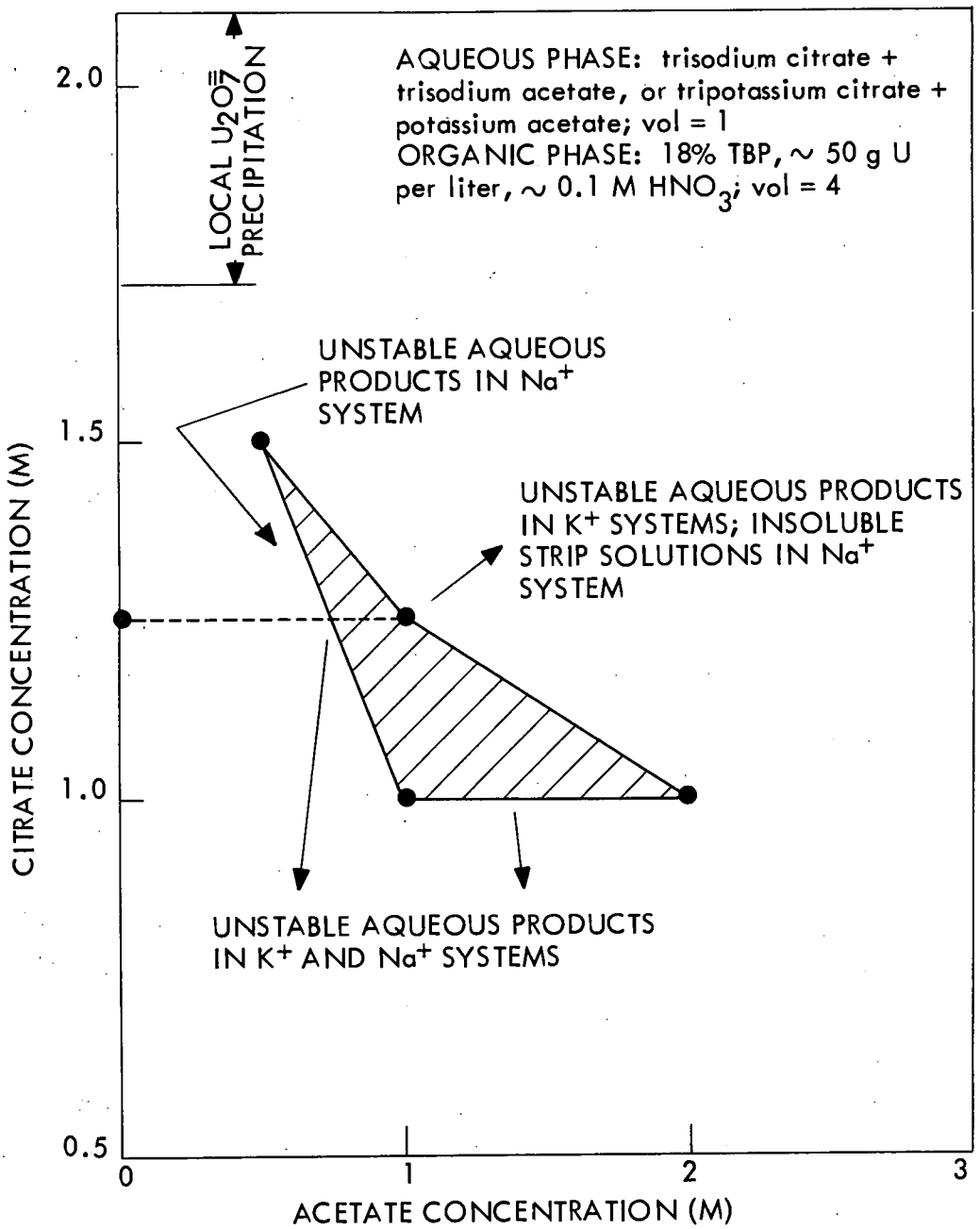

Fig. 11.3. Solubility Limits for the Citrate-Acetate Stripping of Uranium from TBP, Using the Sodium or Potassium Salts. ---Safe operating range of sodium system; ▨ safe operating range of potassium system.

concentration to 0.003 M, and again using an organic/aqueous volume ratio of 4/1, gave stable aqueous products in all cases except the 1 M citrate-2 M acetate system, in which a slight precipitate formed upon 24 hr standing. The uranium concentrations in the aqueous product solutions ranged from 222 to 227 g/liter, while the distribution coefficients ranged from 2×10^{-5} to 3×10^{-4}.

From the results of these experiments, in which the volume ratio and the organic uranium concentration were varied, it is evident that an increase of the solvent flow rate in the strip column could be critical in process, presumably owing to the resultant lowering of the pH in the aqueous product stream by the combined effects of increased uranium and nitric acid concentrations under this condition. However, an increase in the uranium concentration in the solvent phase would have no deleterious effect in process.

A cost analysis, comparing 1.25 M sodium citrate-1.0 M sodium acetate and 0.01 M nitric acid as 25-TBP process stripping agents, showed that the citrate could not compete with acid stripping, which requires intercycle and final product evaporation. In addition to 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 a factor of 2.5-3 less soluble than sodium nitrate on a molar basis. Further work on citrate stripping systems was abandoned at this point.

11.2 Solvent Pretreatment

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.

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.