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ORNL 1481
Chemistry-Separation Processes
for Plutonium and Uranium

INV. 52

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LABORATORY RECORDS

PROCESS LABORATORY DEVELOPMENT

PROGRESS REPORT

MAY THROUGH JULY 1952

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

PUREX PROCESS LABORATORY DEVELOPMENT PROGRESS REPORT, MAY THROUGH JULY, 1952

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0.0 ABSTRACT

The progress of continued Purex process laboratory development for May, June, and July, 1952 is presented. The results of further investigation of techniques for final purification of reactor-irradiated uranium, basic solvent extraction studies, and pilot-scale operation of the ORNL process for plutonium recovery from metallurgical wastes are reported.

1.0 INTRODUCTION

As during the previous quarter,[1] much of the Purex laboratory effort has been expended on continued study of process modifications intended to increase the decontamination of uranium from residual fission products such that all specifications placed upon uranium recovered from Hanford production metal may be routinely met with two-cycle solvent extraction and the uranium product tail-end treatment. Treatment of the second-uranium-cycle feed with nitrite to limit the carryover of ruthenium with the uranium product appears most promising in the laboratory and has been recommended for pilot plant demonstration. Continued study of the adsorption of zirconium and niobium on silica gel, designed to remove the last traces of these contaminants from the uranium product, has led to a better understanding of this complex adsorption system.

The development of the ORNL process for recovery of plutonium from metallurgical wastes was largely completed this quarter, and a terminal report covering this work is in preparation.[2]

Further study was devoted to the problems of chemical stability of Purex solvent and the laboratory mixer-settler operation. A scouting investigation was begun to determine the nature of uranium, plutonium, and fission product extraction by TBP at elevated temperatures and thus to estimate the effects of such operation upon the process.

2.0 SUMMARY

IA Column Extraction Studies at Elevated Temperatures. Uranium, Pu(IV), and specific fission product distribution between 30% TBP in Amsco and nitric acid solutions ranging from 0.5 to 6 M have been determined at 25, 50, and 75°C to establish the advantages, if any, of solvent extraction at elevated temperature. The data show that as the temperature rises, the uranium extraction coefficient is repressed, whereas Pu(IV), fission products, and nitric acid extraction increase. Therefore, operation of the IA contactor at 50 or 75°C would undoubtedly reduce the uranium and plutonium separation from fission products from that presently achieved at 25°C.

Chemical Stability of Purex Solvent. Freshly prepared 30% TBP in Amsco was contacted with inactive IIAF solution at room temperature, at 50°C, and at 67°C for 70 hr or longer to determine the percentage of nitrogen fixation in the solvent (after 0.1 M Na_2CO_3 wash). The results indicated that degradation was quite limited, as measured solely by the formation of nitrogen-containing compounds. (Oxidative degradation which may occur was not measured in these studies.) After 70 hr contact at 67°C, the washed solvent contained 0.5% nitrogen, whereas 408 hr contact at 25°C resulted in only 0.065% nitrogen pick-up.

Aliquots of ICW, IEW, and IIBW solution from pilot plant run HCP-7 were washed with 1% Na_2CO_3 and analyzed for residual nitrogen. Nitrogen fixation was quite low in all samples, with a maximum of 0.013% in the ICW.

It has been observed that, as solvent nitration continues, mechanical difficulties such as emulsification and crud formation increase. Thus the useful life of the solvent may be limited in this manner rather than by significant changes in solvent physical properties (i.e., viscosity, density, flash point).

Nitrite Feed Treatment for Ruthenium Decontamination. Further study of the nitrite feed treatment developed to enhance ruthenium decontamination across the second uranium cycle has served to verify earlier results. Addition of 0.05 M $NaNO_2$ to the IDF followed by 3 hr digestion at 85°C increases the uranium-ruthenium separation achieved in the ID extraction by a factor of 5 to 10. Residual nitrous acid in the feed is destroyed by a 20-min air sparge to avoid reaction of the nitrite with ferrous sulfamate in the ID scrub stream and resultant gassing (N_2) in the column.

The nitrite feed treatment has been tested using N_2O_4 in place of sodium nitrite, and has proved to be equally effective as regards ruthenium decontamination.

Uranium Product Tail-End Treatment. Laboratory study of the adsorption of zirconium and niobium on silica gel has been carried out which supports the following conclusions:

(a) Adsorption at 70°C is not appreciably better than at 30°C.

(b) The degree of zirconium and niobium adsorption varies considerably as successive batches of pilot plant uranium product are processed in the laboratory.

(c) Apparently, the uranium product carries more than one form of zirconium and niobium, and the different forms have different affinities for silica gel. In a recent pilot plant product, about 20% of the niobium was present in a form possessing only a moderate affinity for silica gel.

(d) Plutonium(IV) is not significantly adsorbed on silica gel from concentrated uranyl nitrate solution.

Total Phosphate Analysis. In cooperation with the Special Analysis Section of the Analytical Chemistry Division, a satisfactory procedure has been found for wet digestion of TBP and its hydrolysis products to orthophosphoric acid, for purposes of analysis. The sample is heated in the presence of nitric and perchloric acids and hydrogen peroxide to effect the digestion (see Appendix 1).

Plutonium Recovery from Metallurgical Wastes. During the quarter, seven pilot-scale slag and crucible dissolution runs were made with an average plutonium loss of 0.43% to the solid residue. These runs have served to fix the flowsheet conditions required to give 99.5% plutonium recovery: (a) controlled dissolution with 50 to 60% HNO_3 in the presence of free fluoride and (b) a dissolution time of 70 min or longer at temperatures above 100°C.

The use of dilute HNO_3 (6 to 9 M) in the initial dissolution has eliminated the need for $NaNO_2$, originally added to reduce iodate to iodine. The iodine is volatilized from the dissolver, leaving only 0.05 to 0.16 g/liter in solution. This concentration is not considered harmful to the process.

A revised procedure for plutonium assay of the dissolver residue has been developed which is rapid and simple. Approximately 99% of the residue is dissolved by treatment with 48% HF. Complete dissolution is accomplished by adding excess concentrated H_2SO_4, heating to fumes, and slowly adding a mixture of 36% $HClO_4$ and 35% HNO_3.

Spectroscopic analyses of the residue indicate its composition to be 34% Cr, 8.8% Al, and 8.8% Fe (as the oxides), with traces of Ni, Mn, Nb, Cr, Si, Mg, Mo, Sn, V, and Zn.

Corrosion studies of 309Cb stainless steel were continued. The results of ten (24 hr) exposure cycles in synthetic slag and crucible solution showed that the average penetration rates during the last five cycles (0.0265, 0.0089, and 0.0171 in./year in the vapor, liquid, and interface, respectively) were about 30% less than those determined for the first 120 hr exposure. One welded sample and the ring weld at the bottom of the dissolver failed because of faulty heliarc welding.

About 12 g of purified plutonium was recovered from 120 liters of slag and crucible solution by solvent extraction (TBP) and ion exchange (Dowex 50 resin) according to the tentative recovery flowsheet. This product has been shipped to Los Alamos for evaluation. Overall decontamination factors of the product from aluminum, calcium, and magnesium were 8.5×10^5, 1.7×10^4, and 4.5×10^4, respectively. The plutonium purity was comparable to that of the Purex product after two solvent extraction cycles and concentration by ion exchange. Further study of the proposed solvent extraction system has revealed that appreciable amounts of Pu(VI), as much as 18%, may exist in the dissolver solution owing to extended reflux (up to 9 hr) of the dissolver contents at 120°C. A feed treatment involving reduction to Pu(III) with 0.003 M $Fe(NH_2SO_3)_2$ followed by oxidation to Pu(IV) with 0.02 M $NaNO_2$ has been found satisfactory at the laboratory scale.

ORNL "Mini" Mixer-Settler. The results of comparative laboratory-scale mixer-settler and batch countercurrent extractor runs made with radioactive solutions under conditions specified for the IA column operation (ORNL Purex Flowsheet No. 1) indicated that the mixer-settler scrubbing efficiency is equal, and perhaps superior, to that experienced with batch countercurrent operation. No appreciable gain in decontamination was observed with either unit beyond eight scrub stages.

3.0 IA COLUMN EXTRACTION STUDIES AT ELEVATED TEMPERATURES

S. V. Castner

It has long been known that in the Redox system large amounts of thermal heat are liberated in diluting and extracting during the primary extraction. This heat is taken up in expanding volumes and thus causes changes to take place in the distribution coefficients and separation factors. While there is only a slight amount of heat liberated when uranium is extracted by TBP, it was nevertheless deemed advisable to investigate the effects of higher temperatures on the Purex process, since ambient temperatures at the Savannah River plant reach 40 to 45°C in the hottest season and there might be some definite advantages to be gained with operation at elevated temperature.

An apparatus for maintaining elevated temperatures during a batch equilibration (see Fig. 3.1) was devised. The mixing chamber is double walled, and a thermometer is mounted in the inner section. An organic liquid of suitable boiling point is boiled in the kettle, and the hot vapors are conducted through the silvered vacuum-jacketed tube to the outer section of the mixing chamber. From here they pass to the condenser, from which they return to the boiling kettle as liquid. There is a temperature drop across the mixing chamber wall of approximately 1.5°C. Hence tert-butyl chloride (b.p. 51°C) will give a temperature of 49.5°C and carbon tetrachloride (b.p. 76°C) will give a temperature of 74.5°C.

The particular volume ratio needed to produce 80 or 90% uranium saturation of the solvent phase at each acid concentration was determined by equilibrating aqueous uranyl nitrate solutions containing 200 g of uranium per liter and varying concentrations of nitric acid with 30% TBP-Amsco for 10 min at 25°C. The solvent-to-aqueous volume ratio was varied for each acid concentration and the separated phases were analyzed for uranium. The results of this preliminary experiment were plotted (see Fig. 3.2).

Uranyl nitrate solutions (200 g of uranium per liter) of varying acid strength were spiked with tracer Pu(IV) and fission products and then equilibrated with the correct volume of 30% TBP-Amsco to produce first 80% organic saturation and secondly 90% organic saturation by uranium. The volume ratio was held constant and the experiments were repeated at 50 and 75°C. The phases were separated while hot, and each phase was analyzed for uranium, plutonium, nitric acid, and the principal fission products. From these data, distribution coefficients for each component were computed (see Tables 3.1 through 3.7 and Figs. 3.3 through 3.9).

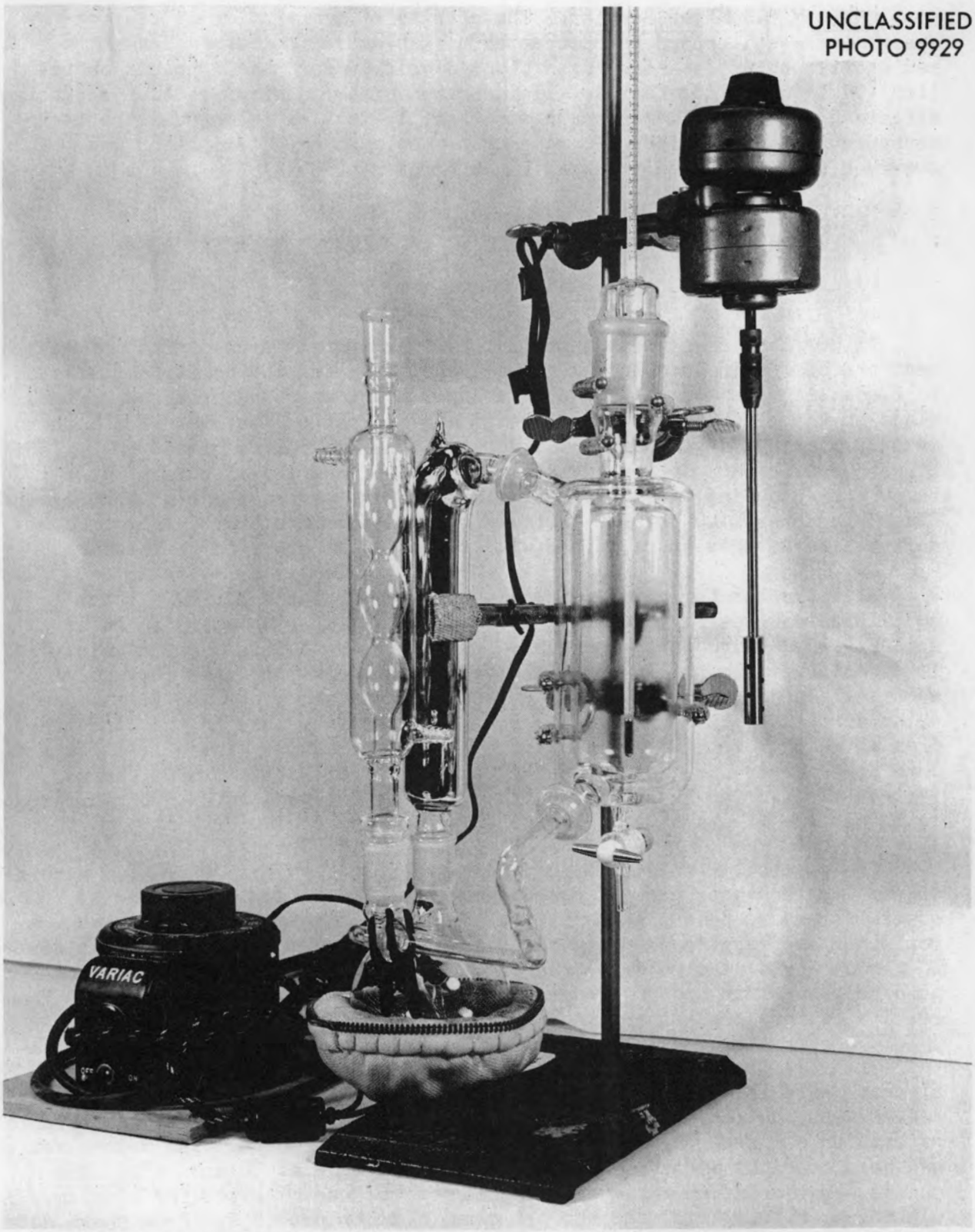

FIG. 3.1. APPARATUS FOR MAINTAINING ELEVATED TEMPERATURES DURING BATCH EQUILIBRATION STUDIES.

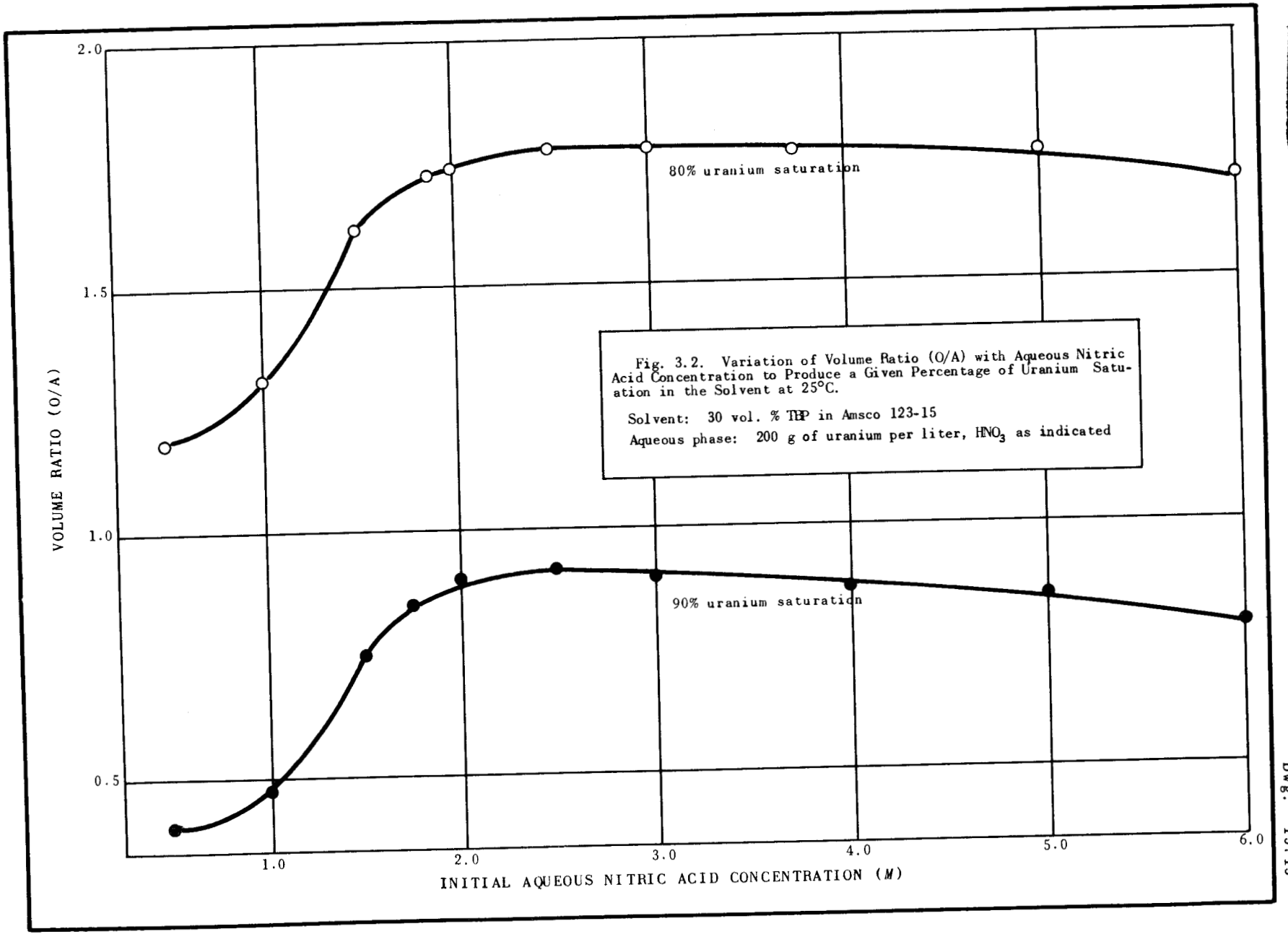

Fig. 3.2. Variation of Volume Ratio (O/A) with Aqueous Nitric Acid Concentration to Produce a Given Percentage of Uranium Saturation in the Solvent at 25°C.

Solvent: 30 vol. % TBP in Amsco 123-15

Aqueous phase: 200 g of uranium per liter, HNO_3 as indicated

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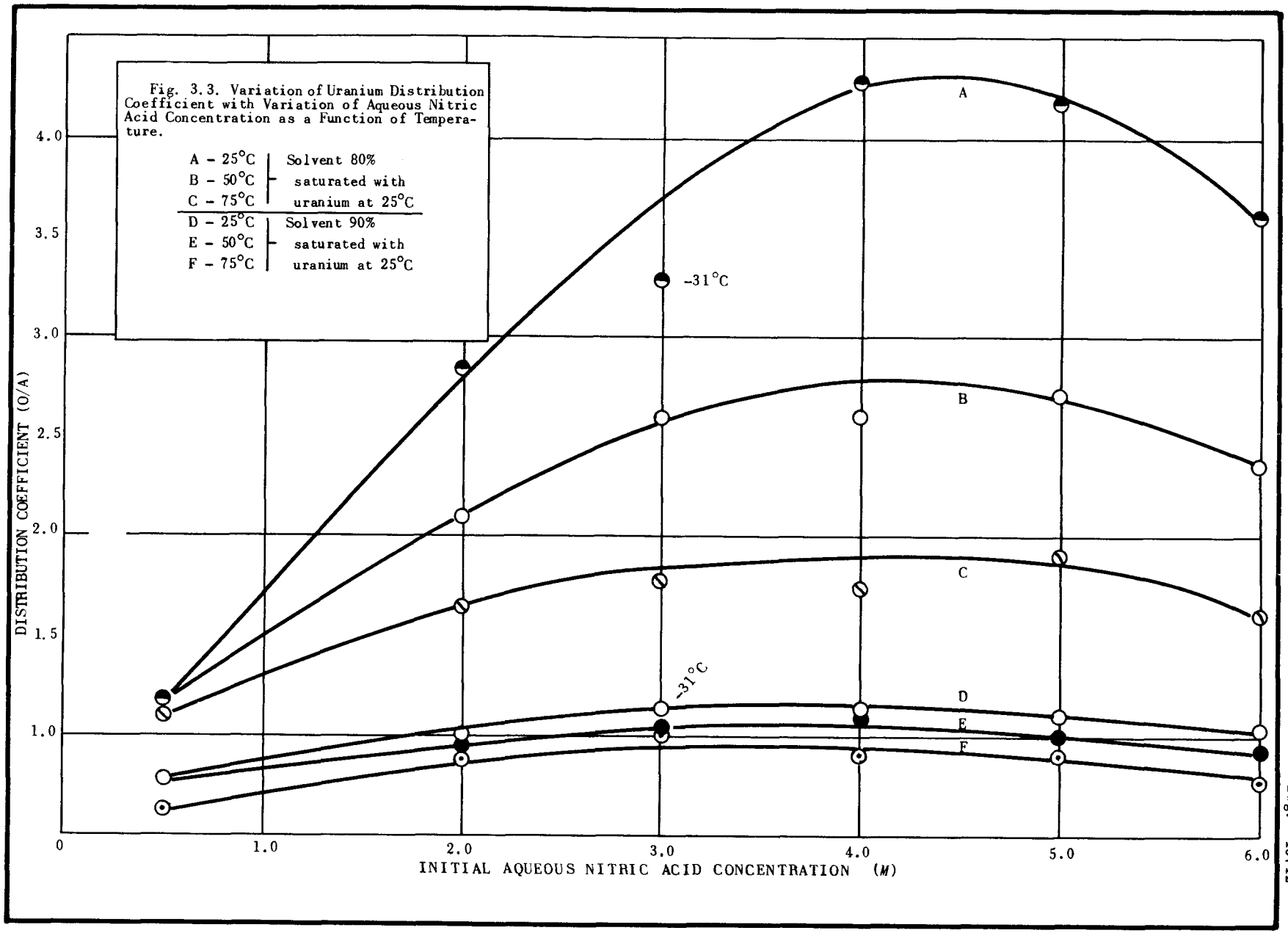

Fig. 3.3. Variation of Uranium Distribution Coefficient with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature.

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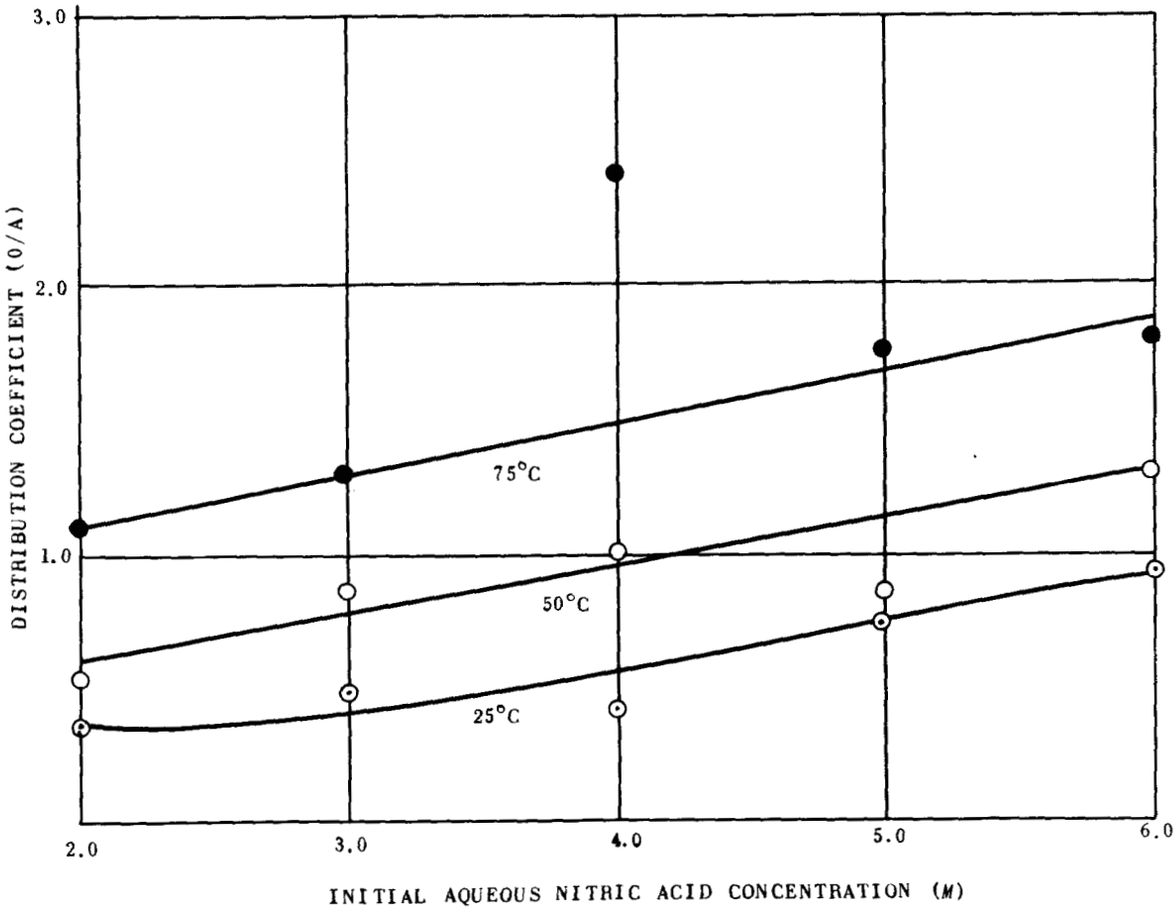
Fig. 3.4. Variation of Pu(IV) Distribution Coefficient with Aqueous Nitric Acid Concentration as a Function of Temperature. Solvent 90% saturated with uranium at 25°C.



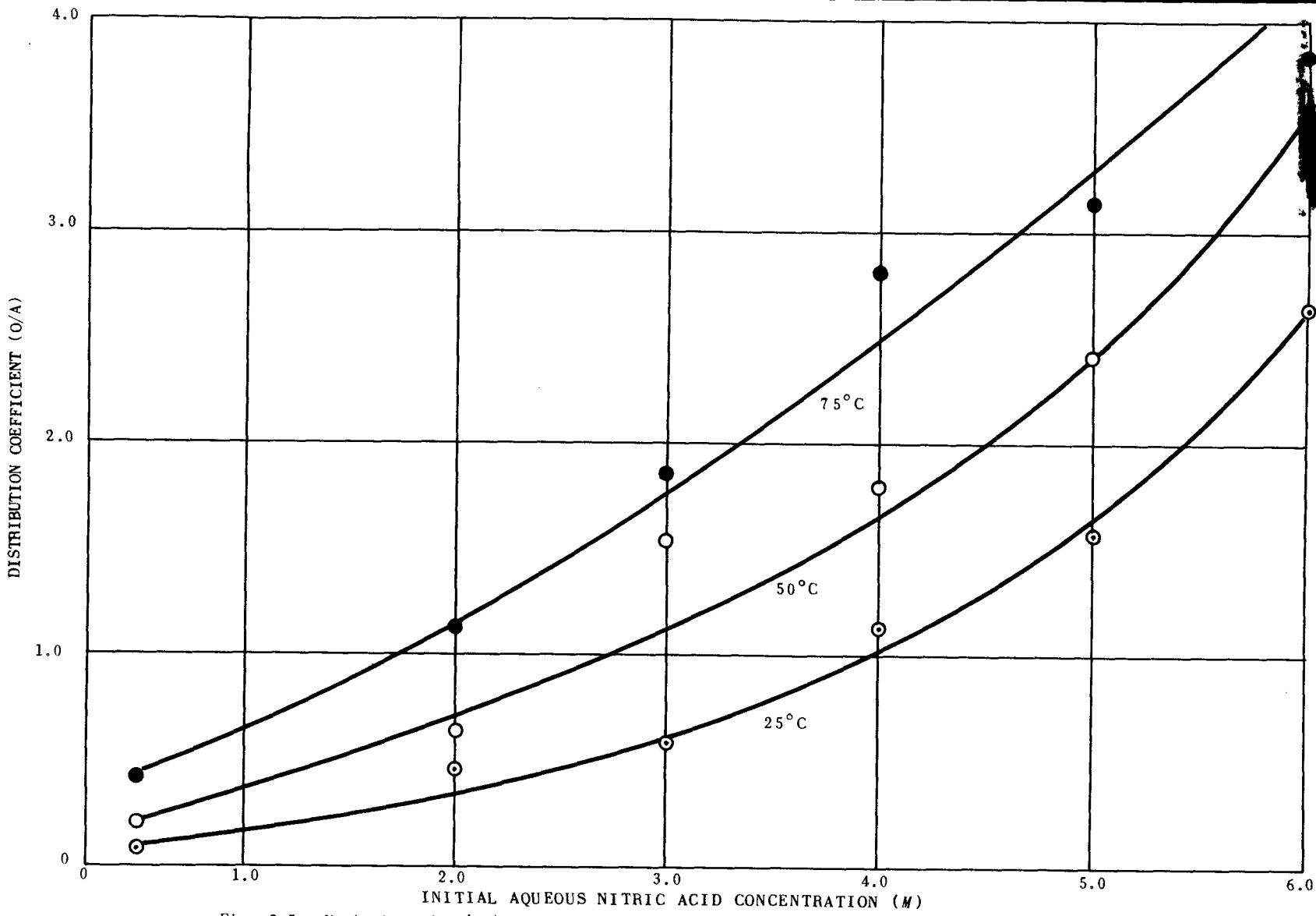


Fig. 3.5. Variation of Pu(IV) Distribution Coefficient with Aqueous Nitric Acid Concentration as a Function of Temperature. Solvent 80% saturated with uranium at 25°C.

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Fig. 3.6. Variation of Gross Beta Distribution Coefficient with Aqueous Nitric Acid Concentration as a Function of Temperature. Solvent 90% saturated with uranium at 25°C.

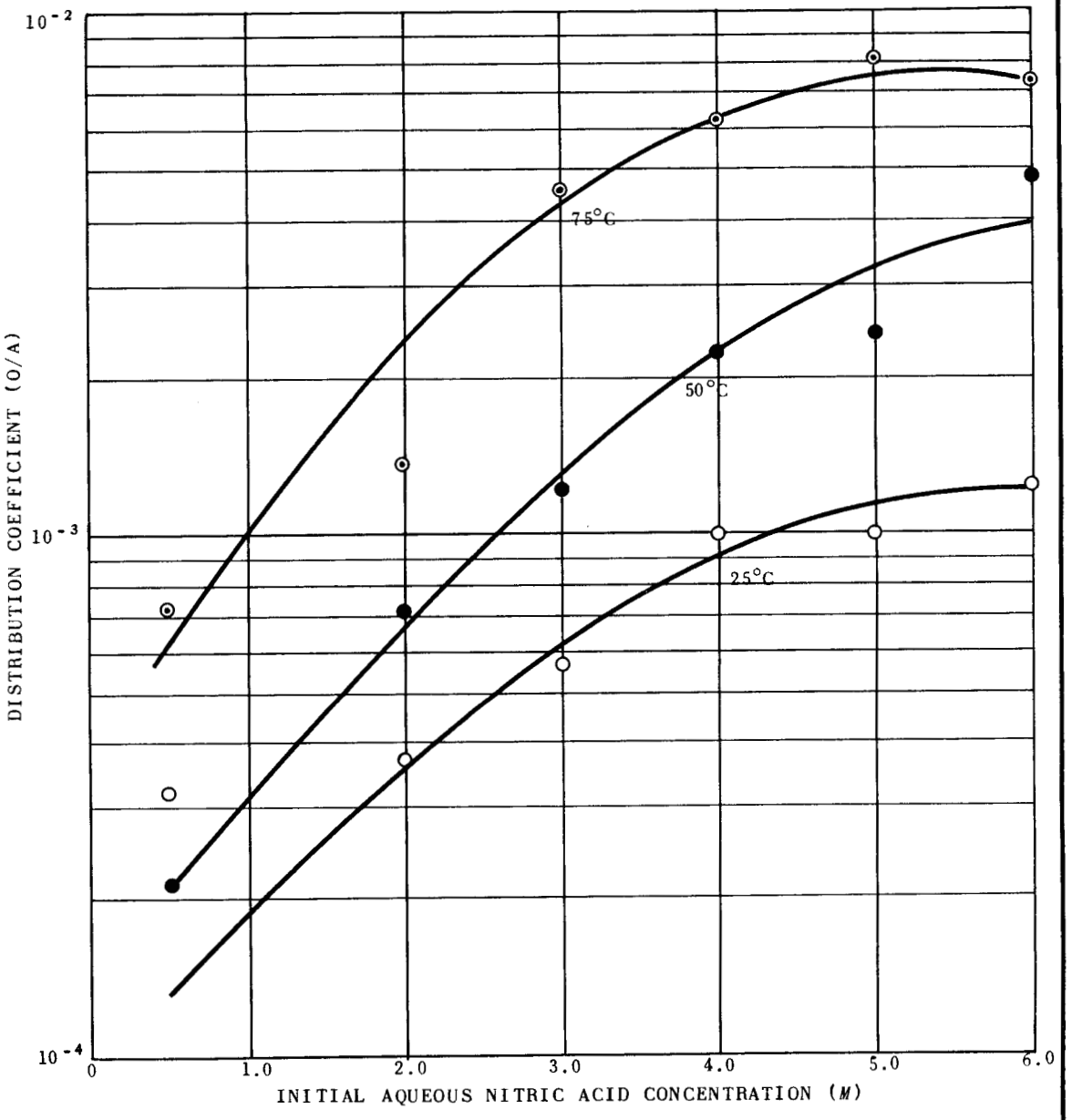

Fig. 3.7. Variation of Gross Beta Distribution Coefficient with Aqueous Acid Concentration as a Function of Temperature. Solvent 80% saturated with uranium at 25°C.

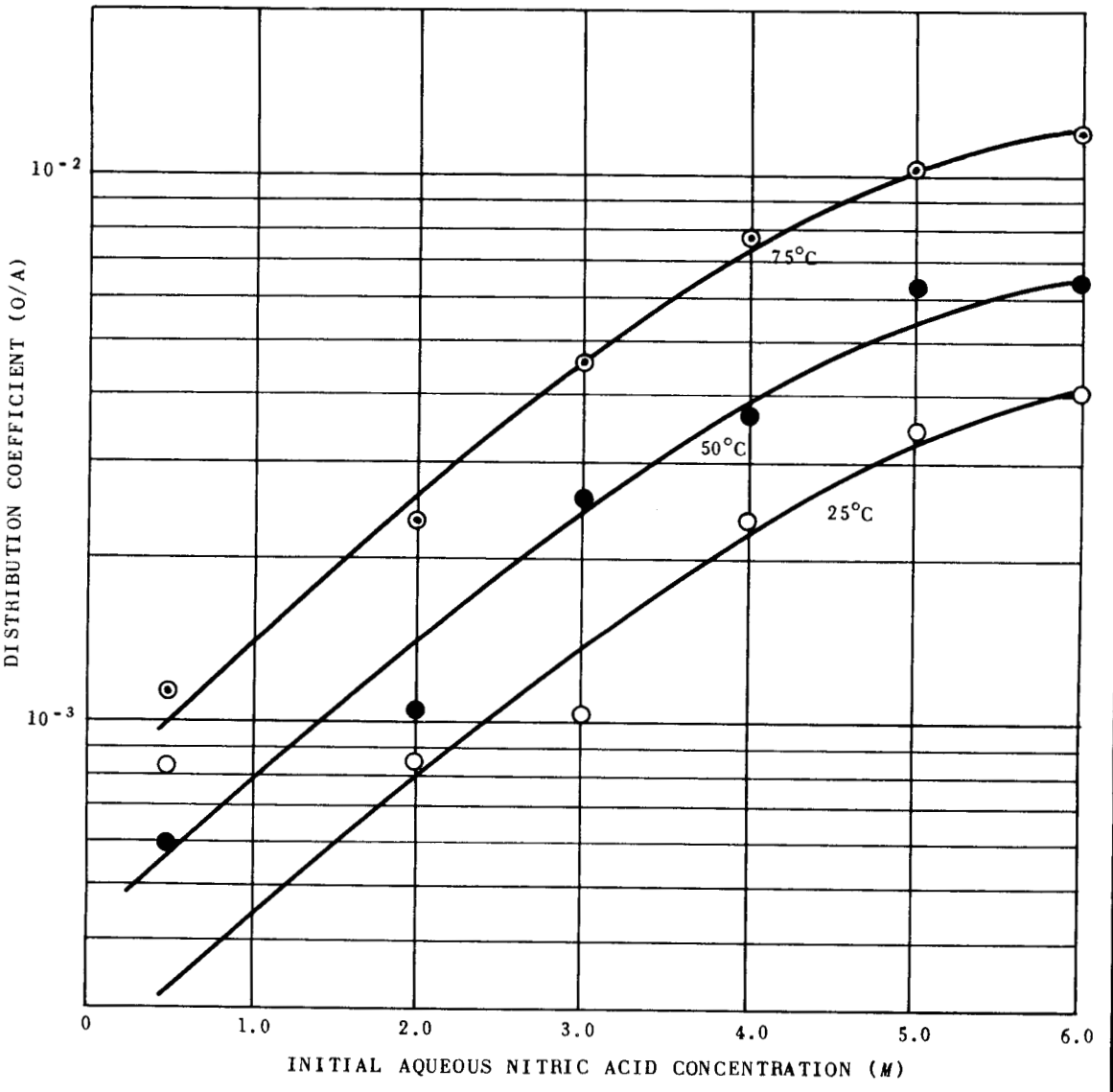

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Fig. 3.8. Variation of Ruthenium Distribution Coefficient with Aqueous Nitric Acid Concentration as a Function of Temperature.

A - 50°C, B - 75°C: Solvent 90% saturated with uranium at 25°C

C - 50°C, D - 75°C: Solvent 80% saturated with uranium at 25°C

Data for 25°C not plotted since they give scattered points only.

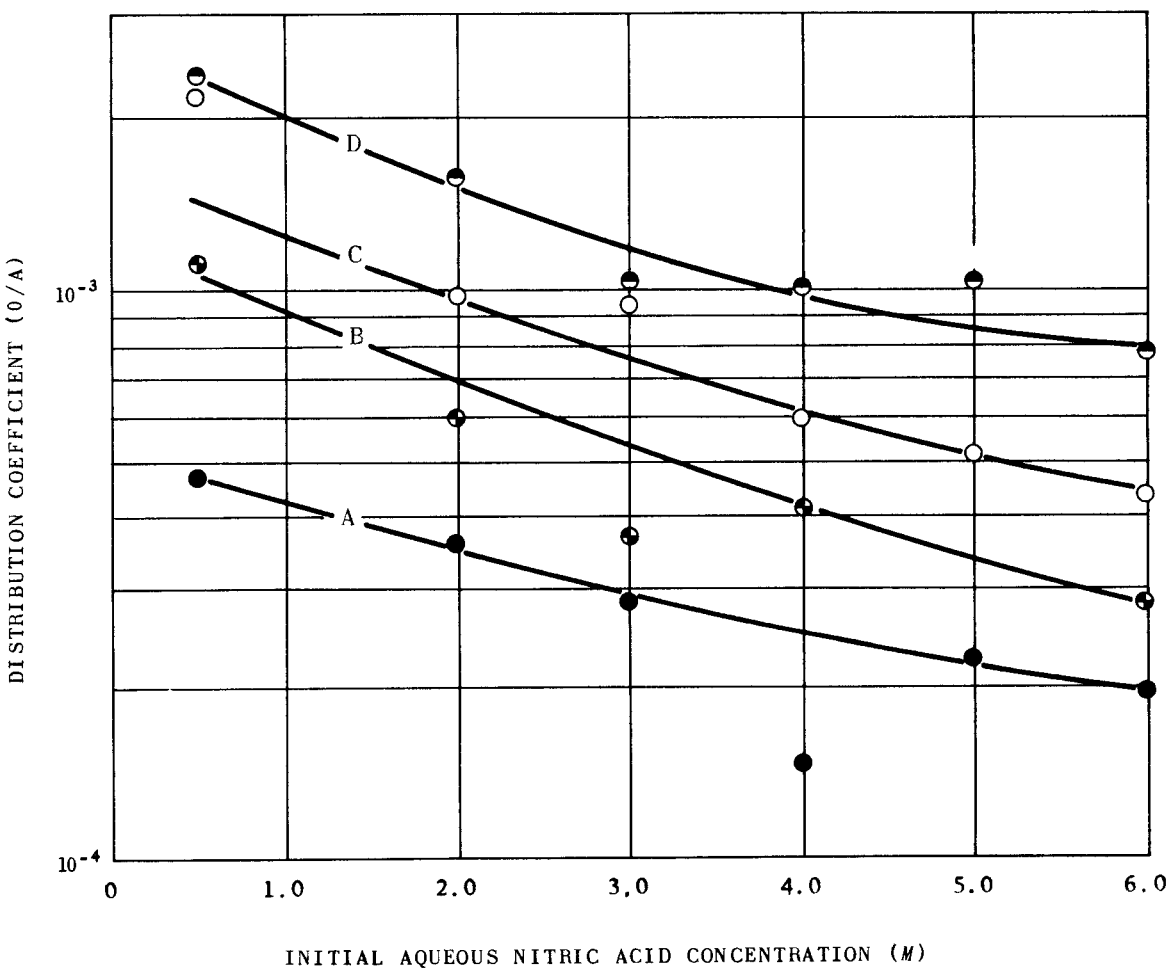

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Fig. 3.9. Variation of Zirconium Distribution Coefficient with Aqueous Nitric Acid Concentration as a Function of Temperature.

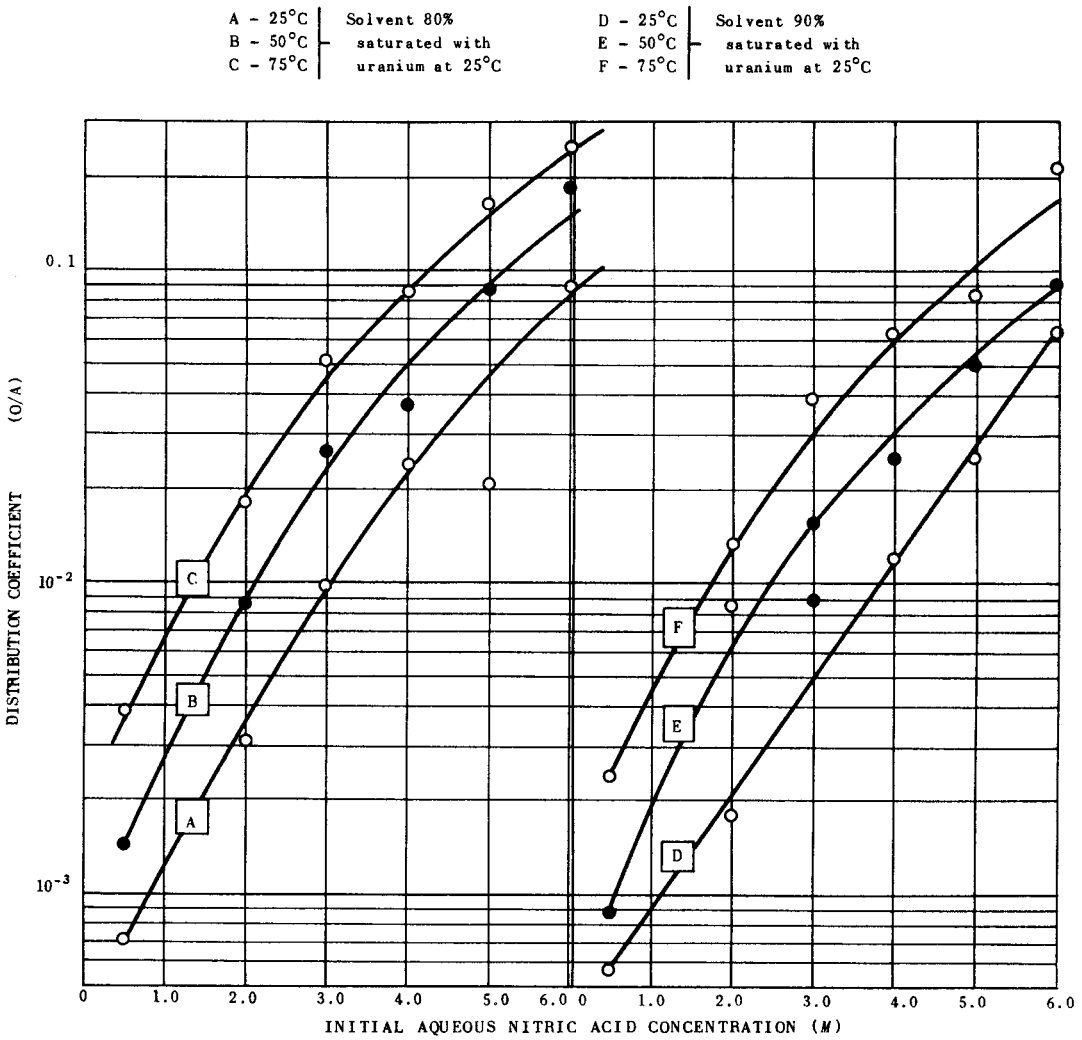

Table 3.1

Variation of Uranium Distribution Coefficient with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

(See Fig. 3.3)

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient (O/A)					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	1.18	2.83	3.28	4.28	4.16	3.61
	50	1.18	2.10	2.61	2.60	2.71	2.35
	75	1.10	1.65	1.78	1.74	1.89	1.60
90	25	0.78	1.00	1.13	1.12	1.09	1.03
	50	0.76	0.95	1.04	1.09	0.99	0.92
	75	0.62	0.87	1.01	0.89	0.89	0.76

Table 3.2

Variation of Pu(IV) Distribution Coefficient (O/A) with Variation in Aqueous Nitric Acid Concentration as a Function of Temperature

(See Figs. 3.4 and 3.5)

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	0.10	0.46	0.59	1.11	1.55	2.62
	50	0.20	0.63	1.53	1.79	2.40	3.53
	75	0.41	1.13	1.86	2.80	3.11	3.81
90	25	1.09[a]	0.36	0.49	0.41	0.74	0.92
	50	2.18[a]	0.53	0.86	1.02	0.85	1.20
	75	5.00[a]	1.11	1.31	2.41	1.75	2.04

(a) These points are approximately a factor of 10 too high. They are lowered by this factor in computing the separation factors (see Figs. 3.4 and 3.5).

Table 3.3

Variation of Gross Beta Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

(See Figs. 3.6 and 3.7)

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	0.83×10^{-3}	0.85×10^{-3}	1.06×10^{-3}	2.32×10^{-3}	3.44×10^{-3}	4.07×10^{-3}
	50	0.59×10^{-3}	1.05×10^{-3}	2.62×10^{-3}	3.67×10^{-3}	6.34×10^{-3}	6.48×10^{-3}
	75	1.14×10^{-3}	2.35×10^{-3}	4.48×10^{-3}	7.80×10^{-3}	10.58×10^{-3}	12.04×10^{-3}
90	25	0.73×10^{-3}	0.37×10^{-3}	0.57×10^{-3}	1.00×10^{-3}	1.01×10^{-3}	1.27×10^{-3}
	50	0.21×10^{-3}	0.73×10^{-3}	1.21×10^{-3}	2.27×10^{-3}	2.52×10^{-3}	4.83×10^{-3}
	75	0.32×10^{-3}	1.36×10^{-3}	4.45×10^{-3}	6.44×10^{-3}	8.25×10^{-3}	7.45×10^{-3}

Table 3.4

Variation of Ruthenium Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

(See Fig. 3.8)

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	7.33×10^{-3}	3.08×10^{-3}	0.96×10^{-3}	0.55×10^{-3}	0.22×10^{-3}	0.19×10^{-3}
	50	2.56×10^{-3}	1.39×10^{-3}	0.98×10^{-3}	0.58×10^{-3}	0.50×10^{-3}	0.44×10^{-3}
	75	2.35×10^{-3}	1.56×10^{-3}	1.10×10^{-3}	1.02×10^{-3}	1.07×10^{-3}	0.79×10^{-3}
90	25	1.28×10^{-3}	0.20×10^{-3}	0.11×10^{-3}	0.20×10^{-3}	0.07×10^{-3}	0.16×10^{-3}
	50	0.48×10^{-3}	0.35×10^{-3}	0.29×10^{-3}	0.14×10^{-3}	0.24×10^{-3}	0.19×10^{-3}
	75	1.10×10^{-3}	0.60×10^{-3}	0.36×10^{-3}	0.45×10^{-3}	1.10×10^{-3}	0.29×10^{-3}

From these results it is seen that, when the extraction temperature is increased from 25 to 75°C, the distribution coefficient of uranium decreases, but the distributions of Pu(IV), gross beta, ruthenium, zirconium, and niobium are somewhat increased in favor of the solvent. Rare earth distribution shows no trend with temperature variation. The nitric acid distribution coefficient increases as temperature increases. No conclusion can be drawn concerning the variation of the nitric acid distribution with variations in nitric acid concentration since the data were erratic.

The separation factors [ratio of distribution coefficient of uranium or Pu(IV) to that of gross beta] for both plutonium and uranium are plotted in Fig. 3.10, utilizing the equilibrium data obtained at 25 and 75°C, with the solvent 90% saturated with uranium. It is apparent that the separation factor for each product decreases rather uniformly as the aqueous nitric acid concentration is raised. It is noted that when the temperature is increased to 75°C, the plutonium separation factor is consistently less than that realized at 25°C, within the range of acid concentrations investigated. Likewise, the separation of uranium from gross beta is generally poorer at 75 than at 25°C. However, the uranium separation factor drops more sharply at 75°C as the aqueous nitric acid strength is increased.

From these studies, it is concluded that less efficient decontamination of plutonium and uranium from fission products would result from operation of Purex extraction contactors at elevated temperatures. However, since the distribution of uranium shifts toward the aqueous phase and gross beta activity favors the solvent as the temperature is increased, additional decontamination (perhaps a factor of 2 or 3) might be gained by stripping uranium at 50 to 75°C. Further study is planned to determine if this effect presents a significant process advantage.

4.0 CHEMICAL STABILITY OF PUREX SOLVENT

L. E. Line, Jr.

Because of concern about the chemical stability of the Purex solvent mixture (30% TBP in Amsco 123-15) and the fear that degradation products might affect process efficiency, a program of investigation of this matter was started. The general objective is that of gathering any information that might give clues as to the prospective life of the recycled solvent.

In the last quarterly report[1] some observations concerning solvent discoloration and measurements of the distribution of nitrous acid between the organic and aqueous phases were given. It was reported that some of the nitrous acid was absorbed by the organic phase and that the yellow discoloration was more evident, and that the extent of "nitration" might therefore be greater, in the presence of nitrous acid. Previous work[3] had shown

[redacted]

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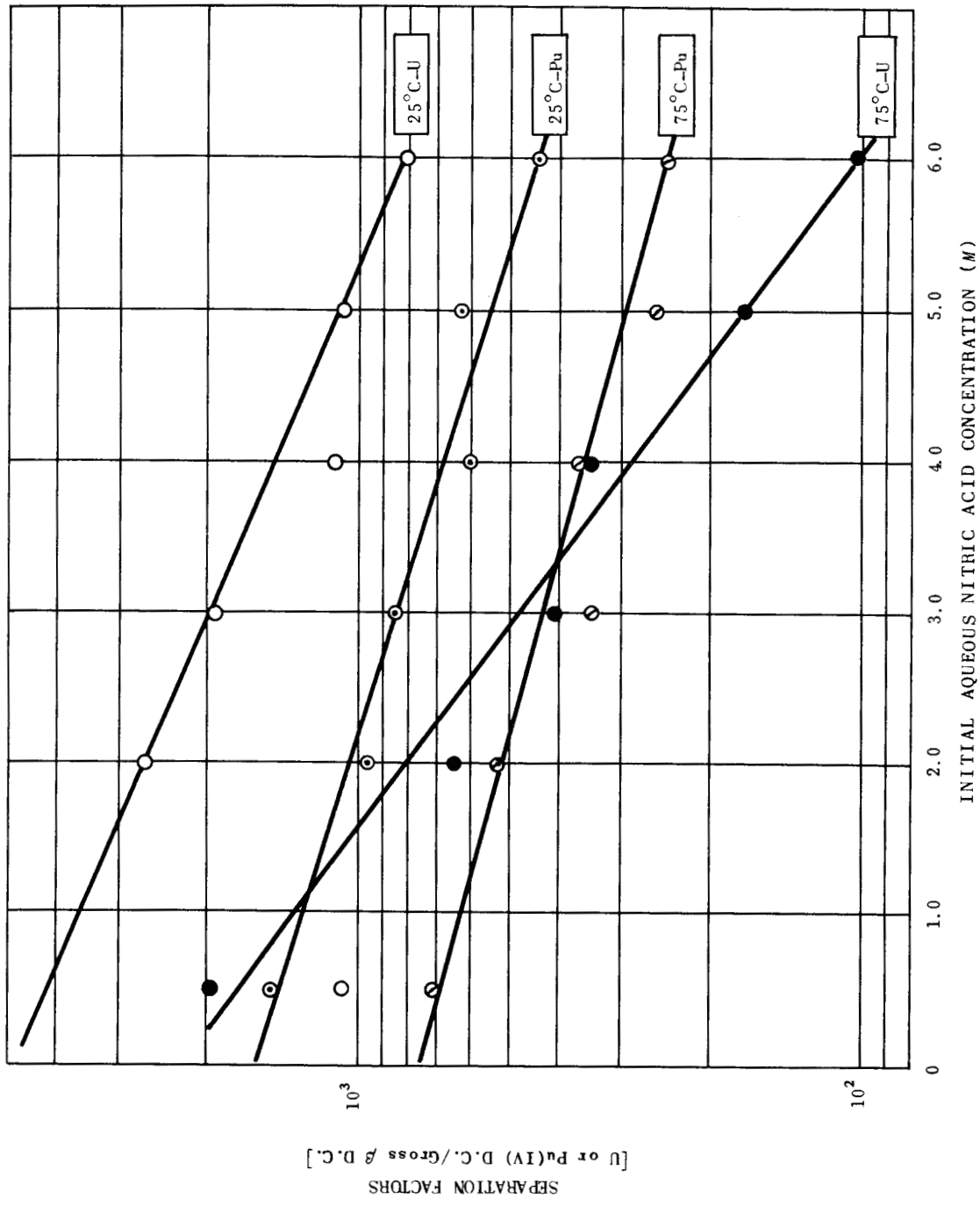
Fig. 3.10. Uranium-Gross Beta and Pu(IV)-Gross Beta Separation Factors as a Function of Aqueous Nitric Acid Concentration and Temperature. Solvent 90% saturated with uranium at 25°C.



[redacted]

Table 3.5

Variation of Zirconium Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

(See Fig. 3.9)

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	0.71×10^{-3}	3.09×10^{-3}	9.80×10^{-3}	24.2×10^{-3}	20.7×10^{-3}	89.6×10^{-3}
	50	1.44×10^{-3}	8.48×10^{-3}	26.8×10^{-3}	36.5×10^{-3}	88.9×10^{-3}	186×10^{-3}
	75	3.87×10^{-3}	18.11×10^{-3}	52.3×10^{-3}	86.5×10^{-3}	166×10^{-3}	251×10^{-3}
90	25	0.56×10^{-3}	1.79×10^{-3}	8.91×10^{-3}	---	25.4×10^{-3}	64×10^{-3}
	50	0.86×10^{-3}	8.51×10^{-3}	15.6×10^{-3}	---	50.0×10^{-3}	91.9×10^{-3}
	75	2.34×10^{-3}	13.42×10^{-3}	38.4×10^{-3}	---	83.3×10^{-3}	216×10^{-3}

Table 3.6

Variation of Niobium Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	0.12×10^{-3}	0.38×10^{-3}	0.39×10^{-3}	1.15×10^{-3}	1.82×10^{-3}	3.17×10^{-3}
	50	0.22×10^{-3}	0.98×10^{-3}	1.44×10^{-3}	2.44×10^{-3}	4.17×10^{-3}	3.17×10^{-3}
	75	0.22×10^{-3}	0.81×10^{-3}	4.57×10^{-3}	1.34×10^{-3}	2.22×10^{-3}	6.19×10^{-3}
90	25	0.11×10^{-3}	0.13×10^{-3}	0.32×10^{-3}	0.24×10^{-3}	0.86×10^{-3}	1.40×10^{-3}
	50	0.17×10^{-3}	0.27×10^{-3}	0.70×10^{-3}	1.62×10^{-3}	1.70×10^{-3}	4.00×10^{-3}
	75	1.00×10^{-3}	0.56×10^{-3}	2.66×10^{-3}	1.14×10^{-3}	0.57×10^{-3}	7.84×10^{-3}

Table 3.7

Variation of Total Rare Earth Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	3.66×10^{-4}	5.18×10^{-4}	4.57×10^{-4}	4.04×10^{-4}	2.72×10^{-4}	1.69×10^{-4}
	50	3.06×10^{-4}	4.82×10^{-4}	5.61×10^{-4}	6.56×10^{-4}	2.94×10^{-4}	1.05×10^{-4}
	75	3.90×10^{-4}	5.61×10^{-4}	4.23×10^{-4}	3.87×10^{-4}	3.48×10^{-4}	1.53×10^{-4}
90	25	1.20×10^{-4}	1.52×10^{-4}	0.62×10^{-4}	1.27×10^{-4}	0.26×10^{-4}	0.17×10^{-4}
	50	1.41×10^{-4}	1.46×10^{-4}	1.34×10^{-4}	4.03×10^{-4}	0.22×10^{-4}	0.21×10^{-4}
	75	2.57×10^{-4}	1.95×10^{-4}	2.00×10^{-4}	1.75×10^{-4}	0.23×10^{-4}	0.71×10^{-4}

Table 3.8

Variation of Nitric Acid Distribution Coefficient (O/A) with Variation of Aqueous Nitric Acid Concentration as a Function of Temperature

Solvent: 30% TBP in Amsco 123-15

Percentage Saturation of Solvent with Uranium	Temp. (°C)	Distribution Coefficient					
		0.5 M HNO_3	2.0 M HNO_3	3.0 M HNO_3	4.0 M HNO_3	5.0 M HNO_3	6.0 M HNO_3
80	25	0.078	0.054	0.057	0.060	0.048	0.045
	50	0.080	0.066	0.073	0.064	0.062	0.055
	75	0.088	0.083	0.085	0.078	0.088	0.073
90	25	0.078	0.030	0.031	0.036	0.027	0.040
	50	0.056	0.041	0.053	0.048	0.041	0.041
	75	0.074	0.058	0.059	0.073	0.062	0.057

that when a solution of 30% TBP in Amsco 123-15 was shaken with 6 M HNO_3 for 17 days at room temperature, the nitrogen pick-up was only 0.02%. It was therefore considered worthwhile to measure the extent of nitrogen fixation by the organic phase at room temperatures when the solvent mixture is brought into prolonged contact with an acid feed corresponding to the IIAF solution, which is the Purex stream containing the highest concentration of nitrous acid (0.1 M).

4.1 Runs at Room Temperature

Results of experiments in which TBP-Amsco was contacted for 17 days with nitric and nitrous acids at room temperature showed a steady decrease in the nitrous acid concentration in both the aqueous and organic phases (see Table 4.1 and Fig. 4.1). This would be expected if the nitrous acid was involved in the "nitration." The amount of nitrogen fixed in the organic in the presence of nitrous acid was a little more than twice as much as had been found[1] in its absence.

The experiments were carried out with 50 ml of 30% TBP in Amsco 123-15 and 200 ml of 0.1 M HNO_2, which were placed in a 250-ml graduate. This was stoppered and shaken end over end for 17 days (408 hr) at room temperature (25 to 30°C). At intervals samples were removed for nitrite and nitrogen determinations. The nitrite was determined colorimetrically, after appropriate dilution of a small sample, in the aqueous phase directly and in the organic phase after washing with dilute sodium carbonate solution.[4] Fixed nitrogen in the organic phase was determined according to the method given by Pregl[5] on a 5-ml sample that had been washed twice with 20-ml portions of 1% Na_2CO_3 and three times with water or dilute nitric acid. In the analyses, 200-μl portions of the 5-ml samples were digested, and the ammonia was distilled into 2% boric acid and titrated with 0.01 N HCl, using methyl red--bromcresol green mixed indicator.*

It will be observed (Table 4.1) that the percentage pick-up of nitrogen is quite small under the conditions of the experiment, being only 0.065% after 408 hr (17 days). It should be remembered, however, that these and similar data to follow represent analyses after the sodium carbonate wash and, therefore, do not represent the total extent of nitrogen fixation, as the washing probably removes some of the nitro compounds. It was noticed that when the acid solution was brought in contact with the solvent mixture, the latter attained its maximum yellow discoloration within 3 to 5 min, showing scarcely any change over the remainder of the entire 17-day period.

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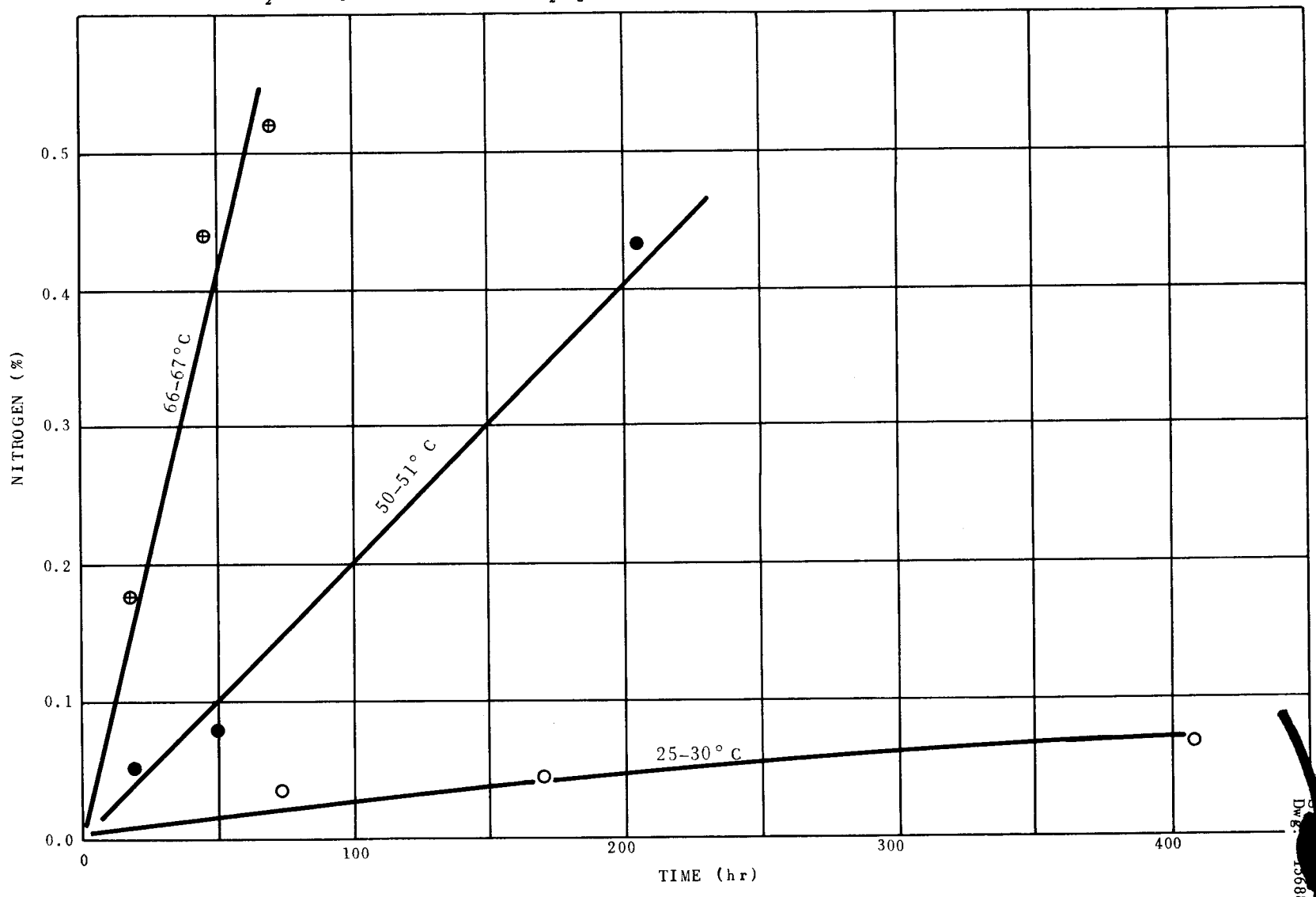
*The writer wishes to thank Houston Hemphill of the Analytical Chemistry Division for the use of his distillation apparatus in the micro-Kjeldahl analyses.

Fig. 4.1. Nitrogen Pickup by Organic (30% TBP in AMSCO) on Prolonged Contact with Aqueous Phase (6 *M* HNO_3, 0.1 *M* HNO_2). Samples washed with 1% Na_2CO_3 prior to analysis.



Dwg. 13688

Table 4.1

Nitrogen Fixation by TBP-Amsco in Contact with Nitric Acid in Presence of Nitrous Acid at Room Temperature

Aqueous phase: 6 M HNO_3 containing 0.1 M HNO_2

Organic phase: 30% TBP in Amsco 123-15

Conditions: 50 ml of organic plus 200 ml of aqueous in 250-ml container shaken end over end for 17 days at 25 to 30°C

Shaking Time (hr)	Nitrite Conc. (M)		Nitrogen in Organic (%)	
	Aqueous	Organic	Found	Increase
(blank)	0.096		0.027, 0.023, avg. 0.025	
1	0.063			
3	0.057			
72	0.057	0.075	0.062, 0.052, avg. 0.057	0.032
96	0.052			
120	0.050			
144	0.046			
168		0.071	0.061, 0.074, avg. 0.067	0.042
408	0.037	0.060	0.088, 0.092, avg. 0.090	0.065

Nitrogen determinations on the ICW, IIBW, and IEW streams from Purex pilot plant run HCP-7 after a washing with 0.1 M Na_2CO_3 showed that the solvent had picked up very little nitrogen while being recycled through the process (Table 4.2).

Table 4.2

Nitrogen Fixation by Various Purex Streams

Organic Stream	Nitrogen (%)	
	Found	Increase
(blank)	avg. 0.025	
ICW	0.033, 0.042, avg. 0.038	0.013
IIBW	0.029, 0.033, avg. 0.031	0.006
IEW	0.024, 0.037, avg. 0.031	0.006

4.2 Runs at Elevated Temperatures

Since the solvent temperature at the Savannah River plant may reach 40 to 50°C at times, the run with IAF solution, described in Sec. 4.1, was repeated at 51 and 67°C with only occasional shaking. No great error should have been introduced by eliminating the constant shaking since the reaction probably goes on within the organic phase and is not limited by the frequency of interfacial contact. As was expected, the nitrogen pick-up was greatly increased at the elevated temperatures (see Table 4.3 and Fig. 4.1). However, the maximum increase in nitrogen-containing compounds was only 5 parts per hundred. In one case nitrogen was determined on a sample that had been washed with 1% NaOH. The nitrogen found was less than that in a sample of the same solution washed with 1% Na_2CO_3. This is probably to be expected since nitro compounds containing alpha hydrogens would be more soluble in the stronger base.

4.3 Discussion

Chemical degradation of the type producing nitrogen compounds is seen to be small, even under drastic conditions, and it is probably safe to assume that the nitrogen compounds represented by the percentage reported here will not greatly affect the density, viscosity, or flash point of the organic phase. However, it has been observed that phase separation after

Table 4.3

Nitrogen Fixation at Elevated Temperature by TBP-Amsco in Contact with Nitric Acid in Presence of Nitrous Acid

Aqueous phase: 6 M HNO_3 containing 0.1 M HNO_2

Organic phase: 30% TBP in Amsco 123-15

Conditions: 50 ml of organic plus 200 ml of aqueous in 250-ml containers, shaken end over end for 17 days at 25 to 30°C

Temp. (°C)	Time (hr)	Nitrogen in Organic (%)	
		Found	Increase
(blank)	0	avg. 0.025	
51	20	0.077, 0.073, avg. 0.075	0.050
	51	0.103	0.078
	213	0.457	0.432
67	18	0.197, 0.205, avg. 0.200	0.175
	47	0.47	0.44
	70	0.49, 0.52, 0.63, avg. 0.55	0.52
	70[a]	0.39, 0.40, avg. 0.40	0.37

(a) Washed with 1% NaOH solution.

alkaline and aqueous washing becomes more difficult with increasing degradation. It is possible that this could become a limiting factor in solvent recycling, although in practice the solvent would be washed after each cycle and not at the end of many cycles. It was found that when the aqueous phase was made slightly acid with nitric acid, the phases disengaged easily.

Since nitric acid is a good oxidizing agent in the presence of nitrous acid, products of oxidation might be expected. The extent of this type of degradation has not been studied here. The carboxylic acids should be removable by alkaline washing, but any intermediate oxidation products might remain in the solvent.

Assuming that this type of degradation as well as formation of nitrogen-containing compounds is very small, there still remains the question of what effect these will have on plutonium stripping losses and the affinity of the organic phase for fission products. It is hoped that studies of this nature can be made.

5.0 NITRITE FEED TREATMENT FOR RUTHENIUM DECONTAMINATION

V. J. Reilly

Experimental work on the second-uranium-cycle feed pretreatment with nitrite to increase ruthenium decontamination has been extended to (a) explore the flexibility of the procedure and (b) substantiate the initial results.

The use of a short NO_2 sparge followed by simmering of the feed at 85°C for 3 hr was compared to the similar use of sodium nitrite, using the first-cycle uranium product (ICU concentrate) from Purex pilot plant run HCP-7. Nitrogen dioxide was sparged to the extent of 0.1 mole per liter of solution; nitrite was added to the extent of 0.05 mole per liter. A third run was also made with this feed without pretreatment. The treatments were evaluated by processing the feeds through batch countercurrent extraction, scrub, and strip runs simulating ID and IE column operation. Purex No. 1 flowsheet, modified to provide 90% uranium saturation at the feed plate, was used. Without feed pretreatment, the ruthenium decontamination factor was 25; with NO_2 sparging treatment, it was 220, and with $NaNO_2$, 250. Excess nitrite was removed at the end of the simmering by air sparging in both cases. These results indicate that NO_2 and $NaNO_2$ are essentially equivalent in improving the second-cycle ruthenium decontamination factor. It probably is not necessary to continue the NO_2 sparge during the simmering.

6.0 URANIUM PRODUCT TAIL-END TREATMENT

V. J. Reilly

Laboratory study of the use of a silica gel column to adsorb residual niobium and zirconium from the second-uranium-cycle product (supplied by the Purex pilot plant) has been continued. Increasing the temperature was shown not to increase the adsorption significantly. Determination of plutonium in the feed and effluent showed no removal of this contaminant from the uranium product at any volume of effluent. Investigations were made on the variation of zirconium and niobium decontamination from batch to batch.

Two runs were made in the temperature effect studies, one at 30°C (room temperature) and one at 70°C (see Table 6.1). The feed was filtered IEU boildown from run HCP-7, which contained 460 g of uranium per liter, 4.15 mv of gamma activity per milliliter (Bldg. 3550 ion chamber), and was 0.84 N in HNO_3. Plutonium was present to the extent of 1.5×10^3 c/m/ml prior to spiking with Pu(IV) to 1.1×10^4 c/m/ml. Care was taken in preparation of the spiking solution to use conditions that would prevent formation of Pu(IV) polymer. Both runs were made at a flow rate of approximately 1 ml/min, but, owing to difficulties in flow control, the rate in run SG-18 varied from 0.75 to 1.0 ml/min, while run SG-19 was made largely at a flow rate of 1.3 ml/min. In each run the adsorption bed was 1 cm^2 in cross-sectional area and was packed to a depth of 20 cm with Davison refrigeration grade silica gel of mesh -20, +40.

Plutonium determinations on feed and effluent showed no removal of this contaminant in either run at any volume of effluent. The values for gamma activity removal (see Table 6.1), as shown by both ion-chamber and radiochemical analyses of feed and effluent, agreed well with the values for gamma activity removed from the bed on elution with oxalic acid.

Adsorption of zirconium and niobium in a two-section silica gel column was studied in order to explore the limit of decontamination possible and to gain further insight into the mechanism of fission product adsorption. Results indicated that at least two species of each contaminant is present in the product concentrate, and that the relative amounts of the species vary from one solvent-extraction product to the next. Since the species vary in their affinities for silica gel, the decontamination obtained with a given column would depend somewhat on the proportions of the different species present in the feed.

The two sections of the column were each 1 cm^2 in cross section and 20 cm deep. Provision was made for sampling the solution after its passage through 20 cm and again after 40 cm. The feed to the column was IEU concentrate from Purex run HCP-9B, and the flow rate was 1.2 ml/min for the first 3 liters and 1.0 ml/min thereafter.

Table 6.1

Silica Gel Adsorption of Zirconium and Niobium from Uranyl Nitrate Solution at Room Temperature (30°C) and at 70°C

Feed: IEU boildown (1.93 M uranium, 0.84 N HNO_3) from Purex run HCP-7
Adsorption bed: 1 cm^2 cross-sectional area, filled to 20 cm depth with Davison refrigeration grade silica gel of mesh -20, +40
Flow rate: ~1 ml/min

Bed No.	Temp. (°C)	ml effluent / ml of bed	Flowing Stream Decontamination Factor	
			Zr	Nb
SG-19	30	70	2.9	7.0
		160	1.55	4.3
			1.35	2.3
		480	1.0	2.1
SG-18	70	75	2.9	4.3
		140	2.8	5.2
		250	3.7	4.0
		370	2.1	2.7
		435	2.2	2.2
		450	1.65	2.1

During the first part of the run, the decontamination across the second section was quite low, but it increased as the run progressed, and, toward the end of the run, exceeded that across the first section (see Table 6.2). In earlier runs with HCP-5 concentrate, the decontamination across a 40-cm bed was roughly the same as that across a 20-cm bed. These results indicate the existence of at least two species of zirconium and niobium, since if only one species was present, the same decontamination would be obtained with the second section as with the first, at least near the beginning of the run when the beds were essentially clean. An estimate of the relative proportions of the different forms of niobium, assuming two kinds, one with a high affinity and one with a low (see Appendix 2), indicates that about 80% of the niobium is of the high-affinity type. A similar calculation made on the basis of the zirconium data indicates approximately 50% of each kind, although neither form appears to have a very high affinity for silica gel.

A comparison of the results obtained with product concentrate from runs HCP-7 and 9B (see Tables 6.1 and 6.2) with those obtained in earlier runs with HCP-5 concentrate indicates that the niobium and zirconium decontamination factors were better by a factor of 2 or 3 with the HCP-5 product. This is

undoubtedly ascribable to a higher proportion of the more readily adsorbed forms of niobium and zirconium in the run HCP-5 product. No explanation is offered at present for the different distribution of chemical forms of the fission products in these several runs.

To provide a clarified feed for the silica gel column, the concentrate from the pilot plant (16 liters, run HCP-9B) was decanted through a plug of glass wool. In order to isolate and identify the associated "crud," the dregs were diluted with water and centrifuged. The water dilution caused a rapid separation of a heavy oil, along with a small amount of particulate matter. The oil was separated and water-washed four times to remove uranium. Traces of oil on the glass wool filter were washed off with acetone and combined with the oil recovered by centrifuging. After evaporation of the acetone, the organic phase was shaken with potassium carbonate solution. The carbonate solution was scrubbed several times with kerosene to remove dissolved and entrained TBP, and was then analyzed for U and PO_4. A second carbonate wash of the oil was essentially colorless, indicating nearly comple removal of uranium by the first wash.

The carbonate solution contained 0.45 mg of phosphate per milliliter and 7.3 mg of uranium per milliliter, a U/PO_4 mole ratio of 6.5. (The PO_4 found here may be either MBP or DBP.) The washed oil analyzed 258 mg of phosphate per milliliter and 0.11 mg of uranium per milliliter. This phosphate value corresponds roughly to 75% TBP. The high U/PO_4 ratio in the carbonate solution is indicative of incomplete stripping of uncomplexed uranium. The volume of oil after carbonate washing was 2.5 ml; with an estimated maximum loss of 0.5 ml during the operations, about 3 ml of 75% TBP (0.8 g as PO_4) was present as undissolved TBP in 16 liters of concentrate (containing about 400 g of uranium per liter). This amounts to 50 parts of PO_4 per million parts of uranium.

The insoluble solid was also recovered from the concentrate. The weight recovered was 0.35 g, with an estimated maximum weight of 0.5 g, or 30 parts per million of uranium. Spectrographic analysis indicated: Fe, very strong; Mn, Cr, Ti, Al strong; Ca and Ni moderate; and Si weak.

Incidental to this work, but arising out of the isolation of free TBP as well as traces of MBP and/or DBP in the product, a sample of the filtered concentrate was checked for foaming tendency during denitration. There was found no tendency to foam whatsoever.

Table 6.2

Adsorption of Zirconium and Niobium from Uranyl Nitrate Solution on a Two-Section Bed of Silica Gel

Feed: Filtered IEU boildown (1.82 M uranium, 0.78 M HNO_3) from Purex run HCP-9B

Adsorption bed: 1 cm^2 cross-sectional area, filled with Davison refrigeration grade silica gel of mesh -20, +40; first section (SG-20), 20 cm deep; second section (SG-21), 20 cm deep

Flow rate: 1.0 to 1.2 ml/min

Vol. of Effluent (ml)	Flowing Stream Decontamination Factors					
	Zr			Nb		
	Across Section SG-20	Across Section SG-21	Across Both Sections	Across Section SG-20	Across Section SG-21	Across Both Sections
1600	3	1.5	4.5	6.7	1.6	10.7
3200	2.5	1.4	3.5	3.9	2.0	7.8
4700	1.95	1.8	3.5	3.0	2.7	8.1
7400	1.75	1.9	3.3	2.35	3.2	7.5

7.0 PLUTONIUM RECOVERY FROM METALLURGICAL WASTES

R. L. Folger, E. B. Sheldon, S. V. Castner, E. R. Johns

7.1 Slag and Crucible Dissolution

The Controlled Fluoride process for dissolution of slag and crucible material was described in detail in the progress report[1] for the previous quarter. Since that time dissolution studies have proceeded in an effort to evaluate the effect of process variables.

Seven crucible and slag batches have been processed with an average loss of only 0.43 percent to the solid residue (see Appendix 3). A total of 10 dissolution runs, having dissolving times in the presence of free fluoride in excess of 70 min at temperatures above 100°C, shows average plutonium recovery of 99.5 percent. The overall nitric acid concentration was varied between 50 and 60 percent with the nitric acid excess (nitric acid input divided by stoichiometric nitric acid requirement for dissolution) varying from 2.50 to 3.25. Although the solvent-extraction feed acidity varied from 4.5 to 6.0 M, there was no apparent effect on the plutonium recovery. Use of dilute HNO_3 (6 to 9 M) in the initial stage of the dissolution has eliminated the need for sodium nitrite to reduce iodate. The iodine is volatilized from the dissolver, leaving a residual concentration of 0.05 to 0.16 g of iodine per liter of solution.

In the filtration procedure, the use of filter aid has greatly improved the flow rate through the filter. A 4.3-in.-diameter filter was precoated with 10 g of Celite 545 followed by 5 g of Hy-Flo Supercel filter aid; 2.5 g of Hy-Flo Supercel was used per liter of solution to be filtered. Use of porosity F sintered stainless steel as a filter medium for solution which had been refluxed for 6 hr gave an average flow rate of 77 gal/ft^2/hr. Use of Filtros "H" as the filter medium for a solution which had been refluxed for 6 hr gave an average flow rate of 64 gal/ft^2/hr. In a run using solution which had been refluxed only 4 hr, a flow rate of 95 gal/ft^2/hr was obtained with the Filtros "H" medium. The above data were obtained using 17 to 18 liters of dissolver solution per run.

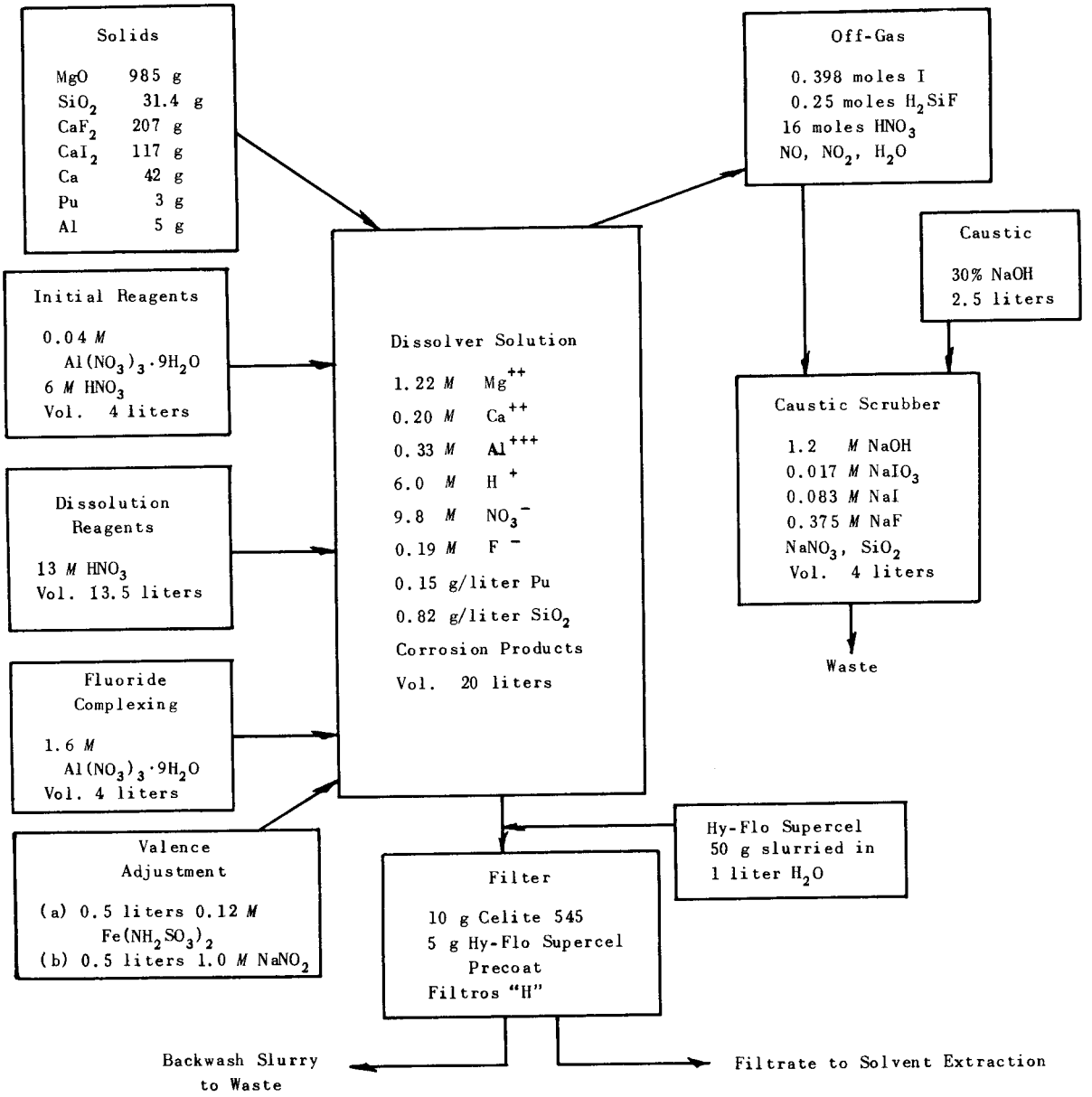
The revised dissolution procedure, based on one complete reduction crucible batch, is shown in Fig. 7.1.

7.2 Corrosion Studies

Based on the results of survey corrosion tests[1] of various materials considered for fabrication of the metallurgical waste dissolution equipment, type 309Cb stainless steel appeared most attractive. Further evaluation of this material, i.e., durability tests, that were carried out this quarter indicate that it should be satisfactory for this use if properly welded and heat-treated.

Dwg. 18066

Fig. 7.1. Revised Dissolution Procedure--Plutonium Recovery from Metallurgical Waste



Samples of unwelded, welded-unpickled, and welded-pickled type 309Cb stainless steel were subjected to the final five of ten 24-hr exposure cycles under the conditions previously described.[1] The results (see Table 7.1) showed that there was little difference in the rate of corrosive attack between welded and unwelded samples. The penetration was less severe for the second five cycles than for the first five, and the attack was greatest in the vapor phase and least in the liquid.

A crack that appeared in one of the welded specimens was apparently caused by tungsten inclusions that resulted from poor technique in heliarc welding. Pitting of the samples was very light, the maximum being 0.001 to 0.002 in. No intergranular attack was noticed on the welded or unwelded samples.

The dissolver itself showed signs of failure; continued use led to the exposure of a crack in the ring weld at the bottom of the dissolver. After completion of the tenth exposure cycle, the dissolver was cut apart and sent to the Metallurgy Division for examination. Their conclusion was that this weld had also failed because of poor fabrication technique. The cavity in the interior weld at the corner of the pot is shown in Fig. 7.2. It is evident that the metal of the side of the pot was not thoroughly fused to the bottom.

In spite of the failure of the ring weld, the pilot-scale dissolver currently in use for Los Alamos slag and crucibles has successfully withstood 18 dissolvings with no visible cracks or leaks.

Table 7.1

Corrosion of Type 309Cb Stainless Steel

Samples	Penetration[a] (in./year)					
	Vapor		Interface		Liquid	
	1st 5	2nd 5	1st 5	2nd 5	1st 5	2nd 5
Unwelded	0.0284	0.0256	0.0218	0.0169	0.0153	0.0111
Welded and unpickled	0.0313	0.0291	0.0236	0.0192	0.0164	0.0087
	Mild pitting					
Welded and pickled	0.0271	0.0249	0.0179	0.0153	0.0137	0.0080
	Cracked sample					
Average	0.0289	0.0265	0.0211	0.0171	0.0151	0.0093

(a) The penetration was calculated from the results of (1) the first five 24-hr exposure cycles and (2) the succeeding five 24-hr exposure cycles.

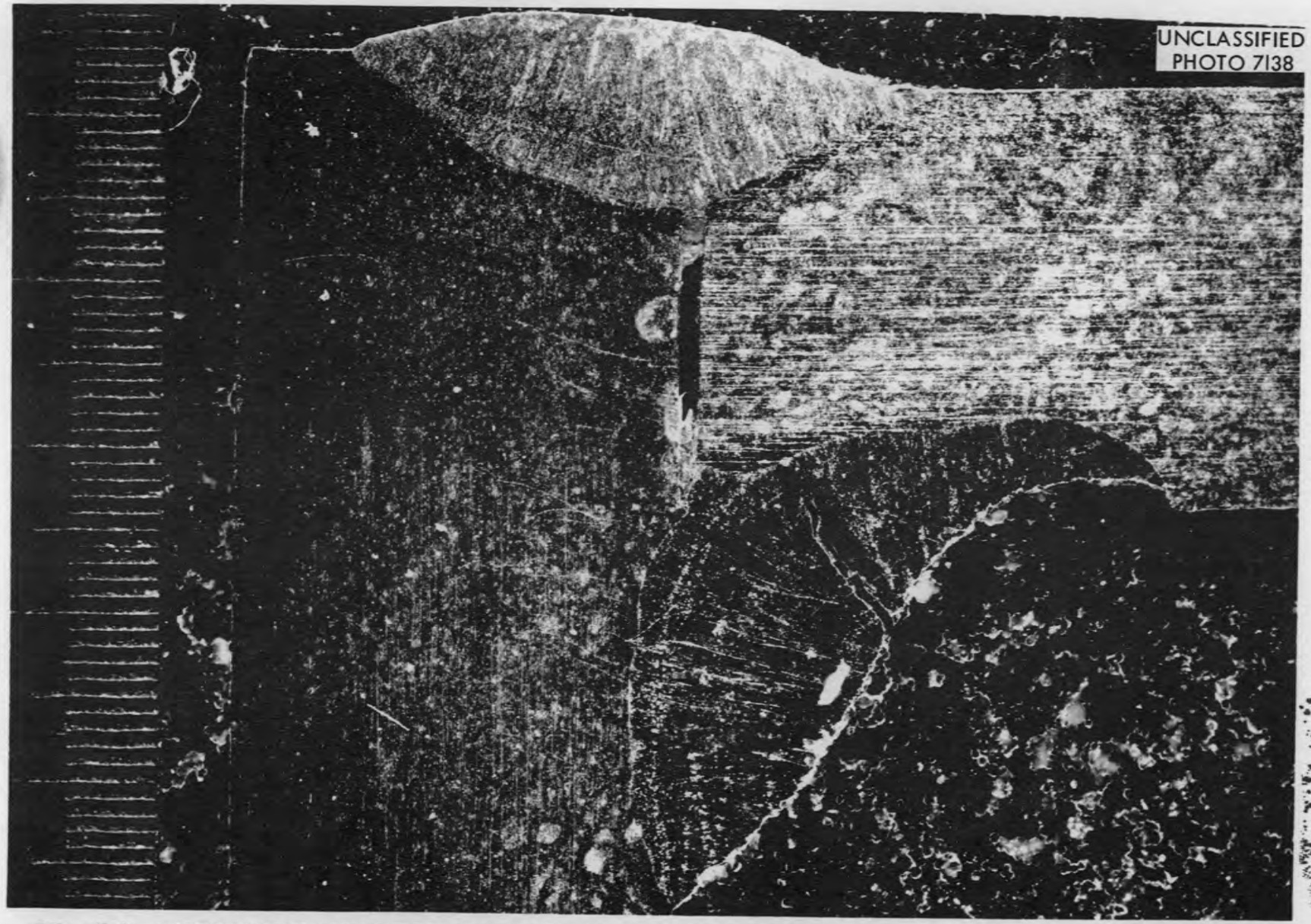


FIG. 7.2. MICROPHOTOGRAPH OF CAVITY IN INTERIOR WELD AT CORNER OF 309Cb STAINLESS STEEL DISSOLVER POT.

8.0 ORNL "MINI" MIXER-SETTLER

V. A. Ryan, L. A. Byrd, E. R. Johns

In order to demonstrate the usefulness of the ORNL mixer-settler as a laboratory tool, a direct stage-by-stage comparison of the mixer-settler with the laboratory batch countercurrent extractor (BCE) was needed. Since the uranium extraction efficiency of the mixer-settler has been previously investigated, it was decided to study the stagewise removal of fission products in the scrub section. The decontamination achieved at each stage varied with the two extractors, but the overall decontamination (approximately 3000 for gross beta) was nearly equivalent for the two units.

Identical feeds were prepared for comparison runs, with the two extractors arranged with the same number of scrub stages. The conditions used are given in Table 8.1.

When steady state was reached, stage and end-stream samples were drawn for analysis (see Tables 8.2 and 8.3). These data were used to compute uranium and plutonium extraction losses and overall decontamination factors (through nine scrub stages) for gross beta, ruthenium, zirconium, and rare earths, based on uranium (see Table 8.4). Seven extraction stages were needed to reduce the uranium loss to 0.005% in the mixer-settler; with the BCE extractor, the uranium loss was negligible after five stages. The total plutonium loss in each extractor was 0.21 to 0.23%, representing 700 to 800 c/m/ml in the raffinate.

Stagewise decontamination factors based on uranium, for gross beta, ruthenium, and zirconium were plotted against stage numbers (see Figs. 8.1 through 8.3), starting at the feed plate and ending at the ninth scrub stage (product takeoff). Rare earth decontamination data were not plotted since these contaminants are sharply separated from the products at the feed plate. The profiles indicate that, for Purex Flowsheet No. 1 conditions, no appreciable decontamination is realized beyond eight scrub stages by either BCE or laboratory mixer-settler operation. The scrubbing efficiency of the mixer-settler appears to be slightly superior to that of the BCE in the first few stages. However, this deficiency is made up by the BCE in the last three or four stages, and the overall decontamination (about 3000 for gross beta) is nearly equivalent for both units. The apparently erratic behavior of ruthenium in the mixer-settler run is not understood and another run is planned.

During the quarter, valves capable of throttling the aqueous interstage flow in the mixer-settler block were fabricated and installed (Fig. 8.4). These make it possible to obtain stable operation with all stirrers rotating at the same speed.

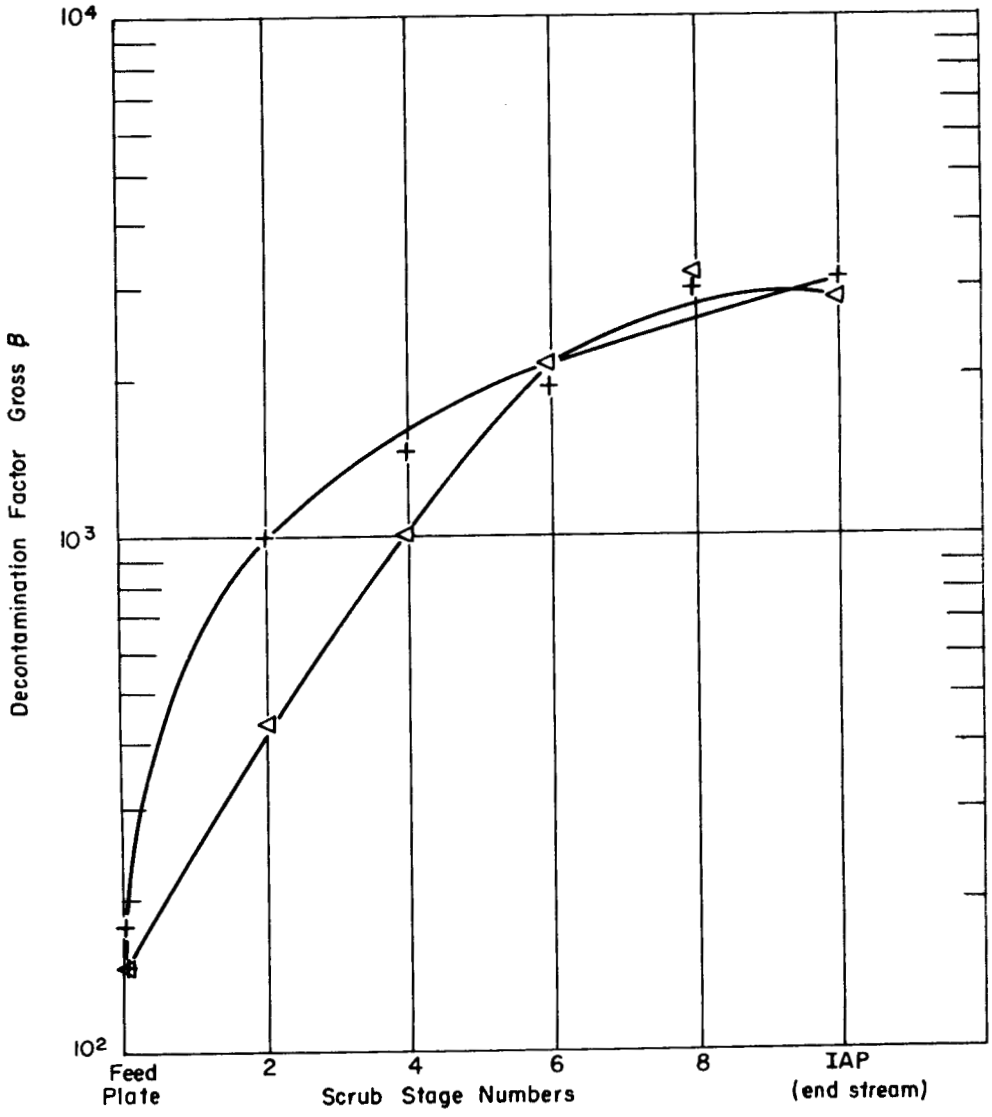
Table 8.1

Mixer-Settler and Batch Countercurrent Extractor Conditions Simulating Purex IA (Flowsheet No. 1) Operation

Feed (IAF)	U	328 g/liter
	HNO_3	2.13 M
	$NaNO_2$	0.05 M
	Pu(IV)	5.87×10^5 c/m/ml
	Gross β	3.15×10^7 c/m/ml
	Ru β	2.68×10^6 c/m/ml
	Zr β	9.45×10^5 c/m/ml (3.3×10^6 scin.ct./m/ml)
	TRE β	2.37×10^7 c/m/ml
Solvent (IAX)	30 Vol. % TBP in Amsco 123-15	
Scrub (IAS)	HNO_3, 3.0 M	
Flow ratio, AF/AS/AX	3/2/10	
Number of stages	5 extraction in BCE run, 7 extraction in mixer-settler run; 9 scrub	
Number of aqueous throughputs	5	

[redacted] [redacted]

Dwg 17298



◁ Countercurrent Extractor

\+ Mixer - Settler

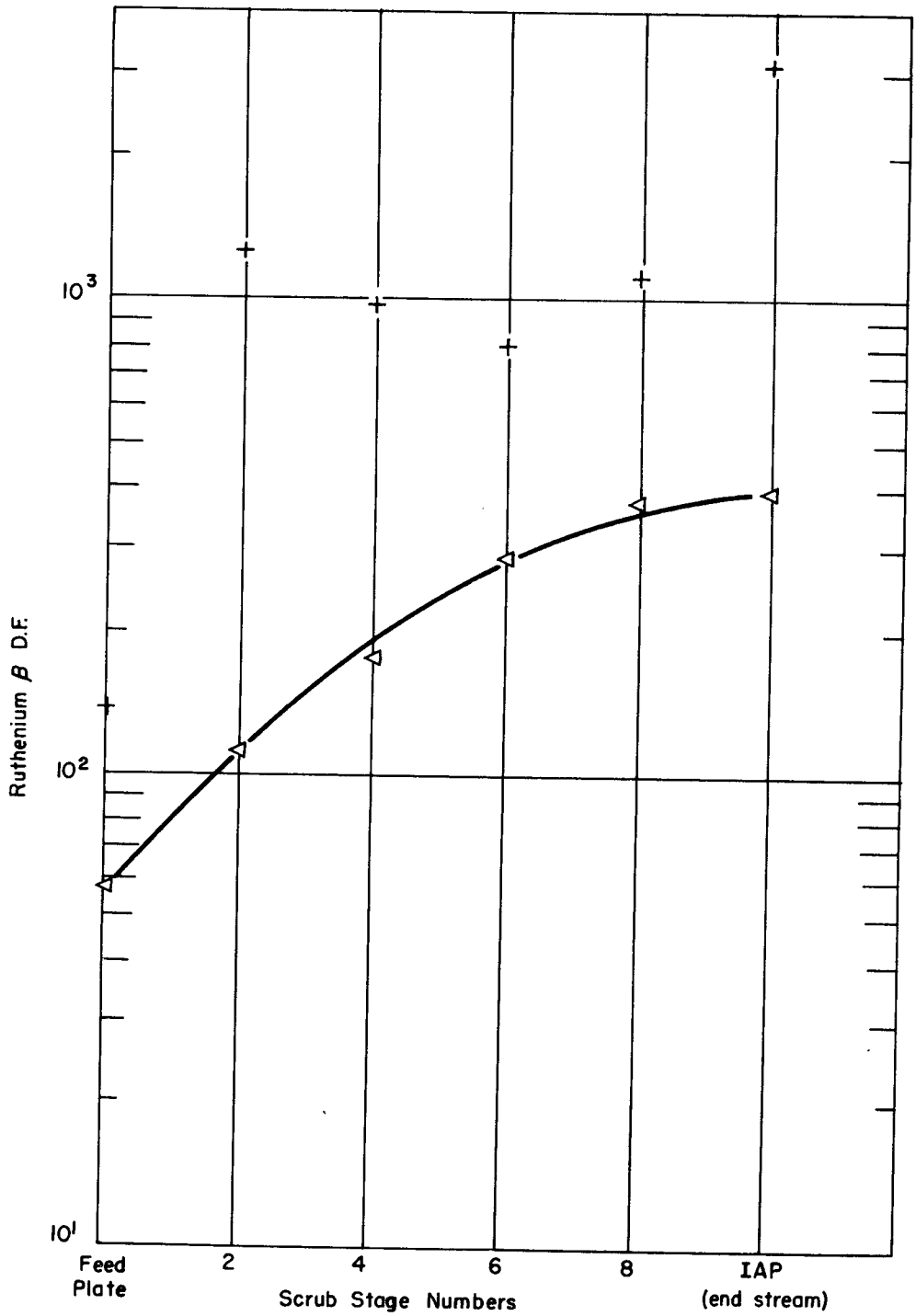
FIGURE 8.1: Comparison of Mixer-Settler and Countercurrent Extractor. Gross β D.F.'s

JEF

[redacted]

[redacted]

Dwg 17299



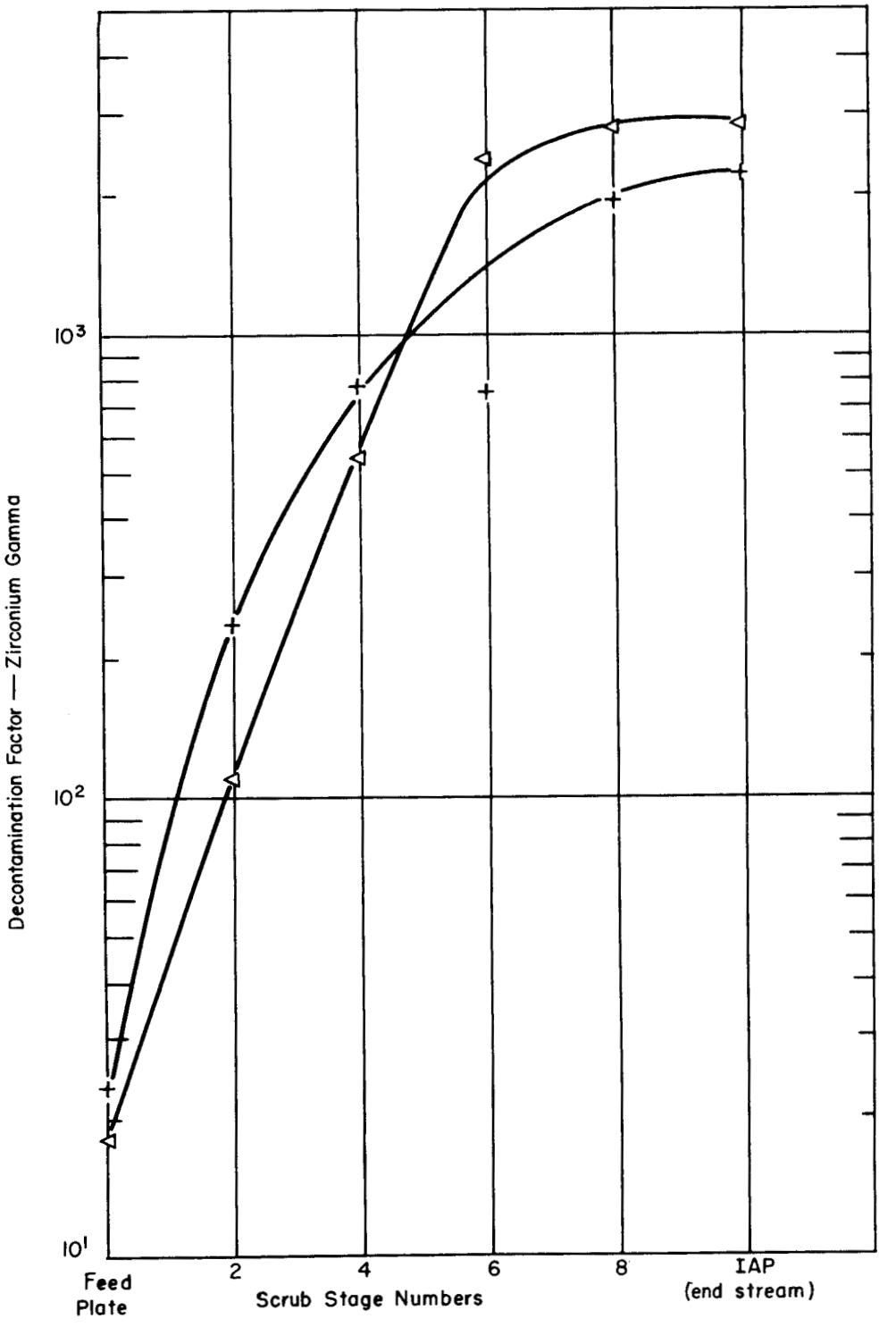
◁ Countercurrent Extractor

\+ Mixer-Settler

FIGURE 8.2 Comparison of Mixer-Settler and Countercurrent Extractor Ru β D.F.

JEF

[redacted] Dwg 17300 [redacted]



◁ Countercurrent Extractor

+ Mixer-Settler

FIGURE 8.3: Comparison of Mixer-Settler and Countercurrent Extractor — Zirconium Gamma D.F.

JEF

Dwg 17301

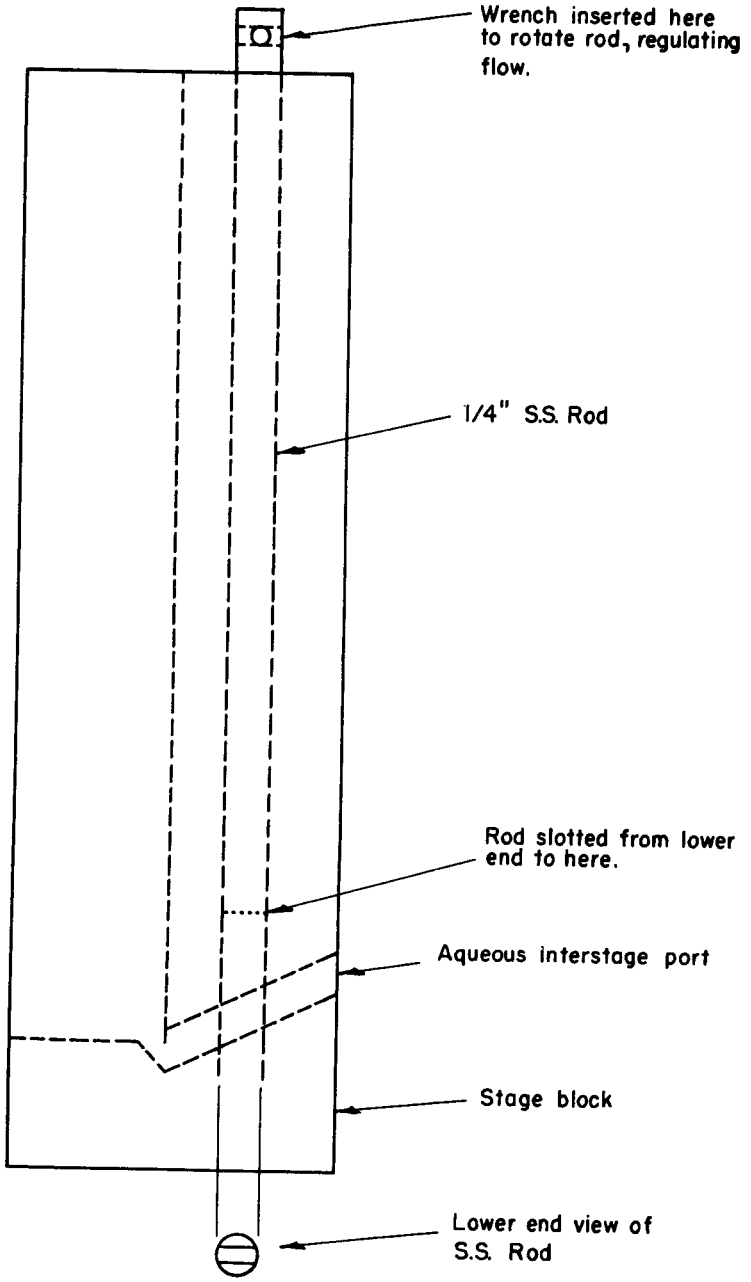


FIGURE 8.4: Aqueous Interstage Port Throttling Valve For ORNL "Mini" Mixer-Settler

JEF

[redacted]

Table 8.2

Analytical Results: Batch Countercurrent Extraction of Synthetic Feed Using Purex IA, Flowsheet No. 1; Stage and End-Stream

Description	Pu (c/m/ml)	U (g/liter)	HNO_3 (M)	Gross β (c/m/ml)	Zrγ [a] (c/m/ml)	TRE β (c/m/ml)	Ru β (c/m/ml)
Feed stage, organic	2.95×10^5	96.0	0.22	6.36×10^4	5.35×10^4	5.5×10^3	1.36×10^4
Feed stage, aqueous	1.20×10^5	19.8	3.70	2.16×10^7	4.7×10^6	1.34×10^7	1.80×10^6
Second scrub stage, organic	3.14×10^5	96.0	0.21	2.0×10^4	8.75×10^3	208	7×10^3
Fourth scrub stage, organic	3.19×10^5	96.0	0.21	9.04×10^3	1.75×10^3	~50	4.5×10^3
Sixth scrub stage, organic	2.98×10^5	99.2	0.19	4.5×10^3	415	~200	2.8×10^3
Eighth scrub stage, organic	2.63×10^5	97.8	0.19	3.0×10^3	350	~130	2.1×10^3
Organic end-stream	2.29×10^5	96.0	0.20	3.25×10^3	340	~5	2.0×10^3
Aqueous end-stream	795	8×10^{-5}	2.30	---	---	---	---

(a) Determined by scintillation counting.

[redacted]

Table 8.3

Analytical Results: Mixer-Settler Extraction of Synthetic Feed Using Purex IA, Flowsheet No. 1; Stage and End-Stream

Description	Pu (c/m/ml)	U (g/liter)	HNO_3 (M)	Gross β (c/m/ml)	Zrγ [a] (c/m/ml)	TRE β (c/m/ml)	Ru β (c/m/ml)
Feed stage, organic	2.80×10^5	96.0	0.21	5.23×10^4	4.1×10^4	1.65×10^4	5.63×10^3
Second scrub stage, organic	2.73×10^5	96.2	0.19	9.08×10^3	3.97×10^3	---	596
Fourth scrub stage, organic	2.76×10^5	96.0	0.20	6.4×10^3	1.24×10^3	---	804
Sixth scrub stage, organic	2.73×10^5	96.0	0.20	4.77×10^3	1.27×10^3	---	962
Eighth scrub stage, organic	2.43×10^5	84.0	0.20	2.7×10^3	436	---	618
Organic end-stream	2.11×10^5	86.0	0.20	3.02×10^3	1160(?) [b]	---	225
Aqueous end-stream	750	0.0092	2.10	---	---	---	---

(a) Determined by scintillation counting.

(b) Possibly a counting error.

Table 8.4

Uranium and Plutonium Losses and Fission Product Decontamination Factors from Comparative Mixer-Settler and Batch Countercurrent Extractor Runs Simulating Purex IA (Flowsheet No. 1) Operation

	Countercurrent Extraction	Mixer-Settler
Extraction loss (%)		
Uranium	0.00005	0.005
Plutonium	0.225	0.212
Decontamination factors[a]		
Gross β	2.84×10^3	3.05×10^3
Ru β	3.92×10^2	3.12×10^3
Zr γ	2.84×10^3	2.22×10^3
TRE β	1.39×10^6	---

(a) Based on uranium; through the scrub section.

9.0 REFERENCES

(1) J. R. Flanary, "Progress Report Purex Process Laboratory Development," ORNL-1343 (Aug. 14, 1952).

(2) R. L. Folger, E. B. Sheldon, and S. V. Castner, "Recovery of Plutonium from Metallurgical Wastes," ORNL-1442 (in preparation).

(3) V. J. Reilly, "Miscellaneous Studies," ORNL memo CF-52-2-53 (Feb. 11, 1952).

(4) L. E. Line, Jr., "A Method for the Analysis of Nitrogen Tetroxide in Dissolver Off-Gases," ORNL memo CF-52-2-72 (Feb. 12, 1952).

(5) F. Pregl, "Quantitative Organic Microanalysis," 5 ed, rev, p. 100, J. & A. Churchill, London, 1951.

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Appendix 1. TOTAL PHOSPHATE ANALYSIS OF URANIUM PRODUCT SOLUTIONS

The wet digestion procedure for analyzing uranium solutions for total phosphate (including TBP, DBP, and MBP) was evaluated by spiking small amounts of TBP in acetone into 5-ml aliquots of a uranium solution obtained by dissolving a sample of metal in nitric acid (to obtain a minimum value for the blank). Each solution was made up directly for digestion because of the inhomogeneity of the solutions. Digestion and analysis were performed by the Special Analysis Group of the Analytical Chemistry Division. Digestion consisted in mixing the sample with 5 ml of concentrated nitric acid + 5 ml 72% perchloric acid + 5 ml of 35% hydrogen peroxide, refluxing for 30 min, then heating to $HClO_4$ fumes, the heating being continued, while the residue is still moist, for 20 min.

The results, given in Table A1.1, indicate consistency at 85 to 90% of the calculated value. Since one experiment using orthophosphate gave only 90% of the calculated amount of PO_4, it is likely that the digestion of TBP to orthophosphate is complete under these conditions. Since DBP and MBP are formed in turn by hydrolysis of TBP, this procedure will also be sufficient for hydrolysis of these species.

An abbreviated digestion procedure employed by the Analytical Control Laboratory was also checked. This procedure requires up to 1 ml of sample, 5 ml of concentrated sulfuric acid, 1 ml of concentrated perchloric acid, and heating on a hot plate in an open beaker until most of the sulfuric acid has been fumed off. The three samples had 20 to 30 μg of PO_4 as TBP in 0.5 to 1 ml of uranyl nitrate solution. The analyses were 74, 86, and 112% of theory, indicating probably complete digestion to orthophosphate under these conditions, but with variable results due to nonsystematic errors.

Appendix 2. ESTIMATION OF RELATIVE AMOUNTS OF THE CHEMICALLY DIFFERENT SPECIES OF NIOBIUM AND ZIRCONIUM

If two chemical species of niobium and zirconium are present, each with a different affinity for silica gel, we can denote by A the more strongly adsorbed species and by B the species less strongly adsorbed by silica gel, and by subscripts 0, 1, and 2 the concentration in the feed before passage through silica gel, and after passage through 20 cm and through 40 cm of silica gel. Let $F = B_0/A_0$, the ratio of the less to the more strongly adsorbed species in the feed. We will assume that, near the beginning of the adsorption, the adsorption-desorption equilibria will not be important, and that the same fraction of either A or B will remain unadsorbed after passage through each equal increment of bad depth. Thus,

$$A_2/A_1 = A_1/A_0 = K_1$$

$$B_2/B_1 = B_1/B_0 = K_2$$

Table A1.1

Analysis of Uranyl Nitrate Solutions Containing Known Amounts of Phosphate

Sample: 5 ml of 400 g of uranium per liter + TBP in acetone

Sample No.	PO_4 Added as TBP (μg)	PO_4 Found (μg)	Less Blank (μg)	% of Theory
1	0	50	---	---
2	270	273	223	82
3	540	500	450	84
4	1350	1280	1230	91
5	0	49	---	---
6	179	182	133	75
7	357	354	305	85
8	893	888	839	94
9[a]	0	408	359	90

(a) 400 μg PO_4 added as Na_2HPO_4 instead of TBP.

Using these equations and the relation between B_0 and A_0, the following can be derived:

$$\frac{A_1 + B_1}{A_0 + B_0} = \frac{K_1 + K_2F}{1 + F}$$

$$\frac{A_2 + B_2}{A_1 + B_1} = \frac{K_1^2 + K_2^2 F}{K_1 + K_2F}$$

The left side of the equations are given directly by the experimentally obtained decontamination factors.

These equations cannot be solved without further information or assumptions. We see that the K values must be less than 1, and K_1 will be smaller than K_2, since A represents the more strongly adsorbed species. If it is assumed that A is much more strongly adsorbed than B, then $K_1 \ll K_2$, and, for the data obtained in runs SG-20 and 21, it can be shown that F = 0.31. It is obvious that K_2 can approach unity, but cannot exceed it. If K_2 is assumed equal to 1, F is found to be equal to 0.105, and K_1 = 0.071. This value for K_1 represents its maximum; if K_1 is taken as 0.05, F = 0.17, and if K_1 = 0.01, F = 0.29. Thus, with the mechanism assumed, F must lie in the range between 0.105 and 0.31, corresponding to the presence of 10 to 25% of the less strongly adsorbed form. Since earlier experience with run HCP-5 concentrate gave an initial decontamination factor of about 25, it is likely that K_1 is 0.04 or lower, giving more weight in this case to a higher value for F.

This method is probably not justified for application to the zirconium data because of the poorer adsorption by both species. However, if the same assumption is made, that is, that one form is much more readily adsorbed than the other, the total zirconium activity in the feed for run SG-20 is nearly evenly split between the two chemical species.

Appendix 3. DISSOLVER RESIDUE ANALYSIS

At the termination of the dissolution procedure 20 to 40 g of solid substance remains. This material is removed by filtering the solution through 65 g of diatomaceous earth as filter aid. This gives a total weight of residue (after air drying on the filter) of 85 to 150 g, part of which is absorbed moisture. To get an accurate analysis of the total plutonium charged to the dissolver, this residue must be dissolved completely and the resulting solution analyzed for plutonium.

A procedure which combines the virtues of rapidity and simplicity has been evolved, whereby the residue described above is dissolved in two treatments. The first of these dissolves approximately 99% of the material. The remaining 1% is totally dissolved in the second step. The dissolver

residue and filter aid are reverse-flow washed and removed from the filter with 2 to 3 liters of water. The residue is transferred to a sintered glass filter and vacuum filtered until dry. The gray solid material is weighed and transferred to a platinum crucible. Concentrated (48%) hydrofluoric acid is added slowly until all siliceous matter has dissolved. (The dissolution is accompanied by vigorous evolution of heat.) The solution is allowed to settle, and the supernatant is withdrawn through a polythene transfer pipet. The black residuum is evaporated to dryness and is then covered with concentrated sulfuric acid. The mixture is heated to fuming, and several drops of a 50-50 mixture of 72% $HClO_4$ and 70% HNO_3 are added cautiously. The mixture foams vigorously and turns green in color as the residuum dissolves. The filtrate from the initial residue slurry, the supernatant hydrofluoric acid solution, and the final sulfuric acid solution are all analyzed for plutonium. Only the plutonium in the hydrofluoric and sulfuric acid solutions is charged to waste.

The results for several dissolutions are presented in Table A3.1. From the first run (DG-8) some black solid was removed and analyzed spectroscopically. Quantitatively, it contained 34% Cr, 8.8% Al, 8.8% Fe, 3.7% Ti, 0.6% Ni, 0.5% Mn, 0.5% Nb, 0.14% Cu, and traces of Si, Na, Ca, Mg, Mo, Sn, V, and Zn. There was no Pb, Be, or U present. The elements present are presumed to be oxides although there is a possibility of carbides.

The black residuum was mixed with 10 times its weight of Na_2CO_3 and fused at 1000°C for 30 min. The fused mixture when cool was readily dissolved in 6 M HCl.

Attempts to dissolve the residuum in concentrated or 6 M HCl, concentrated or 6 M HNO_3, aqua regia, fuming $HClO_4$ plus HNO_3, or HCl did not succeed, at either room or boiling temperature.

[redacted] [redacted]

Table A3.1

Plutonium Content of Dissolver Residues

Run No.	Wt. of Residue (g)	HF Solution			H_2SO_4 Solution			Total Pu (mg)
		Vol. (ml)	Pu (c/m/ml)	Pu (mg)	Vol. (ml)	Pu (c/m/ml)	Pu (mg)	
DG-8[a]	101.0	300	1.03×10^6	4.37	500	2.32×10^5	1.64	6.01
DG-9	160	495	2.90×10^6	20.3	260	3.85	14.2	34.5
DG-10	160	300	8.62×10^5	3.68	400	1.59×10^5	.90	4.58
DG-11	150	300	4.43×10^5	1.88	485	2.64×10^5	1.81	3.69
DG-12	140.0	425	9.25×10^5	5.85	275	1.44×10^5	.56	6.41
DG-13	88.5	330	8.07×10^5	3.77	315	4.06×10^5	1.81	5.58

(a) Approximately 1 ml of DG-8 HF solution containing black solid material in slurry was removed before the treatment with sulfuric acid and other reagents was started.