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PULSE COLUMN STUDIES USING STR AND SIR FEED SOLUTIONS

September 27, 1954

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PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
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PULSE COLUMN STUDIES
USING STR AND SIR FEED SOLUTIONS

PHILLIPS PETROLEUM COMPANY
ATOMIC ENERGY DIVISION

IDAHO FALLS, IDAHO

by

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TABLE OF CONTENTS

- I. Introduction
- II. Summary
- III. Development Studies
 - A. Extraction Process Flowsheets
 - 1. STR
 - 2. SIR
 - B. Column Test Program
 - 1. Test Equipment
 - 2. Experimental Procedure
 - a. Column Start-Up
 - b. Hold-Up Measurement
 - c. Feed Preparation
 - d. Solvent Treatment
 - e. Sampling and Analysis
 - f. Flooding Velocity
- IV. Results and Discussion
 - A. STR Extraction Column HTU Studies
 - 1. HTU Values Obtained
 - 2. Effect of Pulse Frequency and Amplitude on HTU
 - 3. Effect of Varying Aqueous-to-Organic Flow Ratio
 - 4. Effect of Operating with Organic Phase
 - B. SIR Extraction Column HTU Studies
 - C. STR-SIR Stripping Column HTU Studies
 - D. Flooding Characteristics of Extraction Systems
 - 1. STR "A" Column Flooding
 - 2. SIR "A" Column Flooding
 - 3. "B" Column Flooding Data
 - 4. "C" Column Flooding Data
- V. Conclusions
- VI. References
- Appendix A
- Appendix B

DECLASSIFIED

SECRET

IDO-14312
Page 6

I. INTRODUCTION

The recovery of unconsumed Uranium-235 from fuel elements utilized in the Submarine Thermal Reactor (STR) and the Submarine Intermediate Reactor (SIR) will be carried out in the Idaho Chemical Processing Plant. Because the chemical composition of the fuel elements used in these reactors differs markedly from that of the aluminum-uranium alloys for which the plant was designed, additional processing steps are required to convert these fuels to a form suitable for decontamination and recovery as uranyl nitrate in the existing plant. The added head-end processing steps, developed by other laboratories, involve dissolution of the fuel in acids other than nitric, and extraction of uranium from the resulting solution to separate uranium from the foreign metal ions present. The uranium solution is then suitable for decontamination by the same process as used for recovery of aluminum alloys and unalloyed uranium.

The Argonne National Laboratory developed a head-end process for STR fuel recovery involving hydrofluoric acid dissolution and tributylphosphate extraction. The Knolls Atomic Power Laboratory developed a similar process for SIR fuel recovery involving sulfuric and nitric acid dissolution and tributylphosphate extraction. Both processes were laboratory and pilot plant tested using miniature mixer-settler extractors and pulsed packed columns.

Pulsed, perforated-plate columns were selected for the SIR-STR extraction cycle at the ICPP. The design of these columns was based on the extrapolation of ANL, KAPL, ORNL, and Hanford data. Because such pulse columns had not been tested on the STR-SIR flowsheets, a development program was initiated by the American Cyanamid Company. Their test columns were constructed of two-inch stainless pipe, using the standard cartridge in the active length, and four-inch pipe for the disengaging sections at both ends. The first series of tests proved unsatisfactory because of poor column hydraulics. The second attempt, after redesigning, was stopped and the tests temporarily abandoned when it was discovered that methods used for the analysis of these solutions were unsatisfactory.

Following transfer of the contract for the operation of the ICPP to the Phillips Petroleum Company, these tests were resumed for the benefit of the engineer responsible for the design of the STR-SIR head-end process. (Blaw-Knox Company, Chemical Plants Division). The program initially required determination of stage heights and waste losses for flowsheet conditions. The Analytical Section meanwhile developed satisfactory methods for analyses of the solutions.⁽⁶⁾ This report summarizes the results of tests conducted by the Phillips Petroleum Company to develop column and flowsheet requirements. For these tests, the equipment was moved to a more suitable location and the stainless columns were replaced with ones constructed of glass pipe.

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II. SUMMARY

Pilot plant studies were made to determine operating characteristics of pulsed columns proposed as the solvent extraction contactors for the recovery of uranium from spent STR and SIR feed assemblies.

Twenty-five STR "A" Column runs, six SIR "A" Column runs, one "B" Column run and eight "C" column runs were made.

Variation of pulse conditions resulted in HTU values for the STR "A" Column ranging from 2.2 to 11.6 feet. Reduction of the aqueous-to-organic flow ratio from the original flowsheet value of 4.5/1 to 1.4/1 resulted in HTU values as low as 1.5 feet. The HTU values for the SIR "A" Column ranged from 1.0 to 1.6 feet. The HTU values for the "C" Column ranged from 1.5 to 1.9 feet.

The maximum flooding volume velocity was found to be 1300 gal./(hr.)(sq.ft.) for the "A" Column on both the STR and SIR flowsheets. The maximum "B" Column flooding point was found to be 800 gal./(hr.)(sq.ft.). The "C" Column flooding points were found to be dependent upon nitric acid concentration in the organic phase. The maximum flooding point varied from 800 gal./(hr.)(sq.ft.) for 0.002 molar acid feed to 1100 gal./(hr.)(sq.ft.) for 1.0 molar acid feed.

III. DEVELOPMENT STUDIES

A. Extraction Process Flowsheets

1. STR

The recovery and decontamination of irradiated fuel elements from the Submarine Thermal Reactor will be accomplished at the ICPP. Since the zirconium-clad zirconium-uranium alloy does not dissolve in nitric acid, the existing facilities for recovery are not adequate and a head-end process to convert it to a form compatible with the ICPP process has been developed by Argonne National Laboratory.⁽¹⁾

This process consists of the dissolution of the fuel elements with hydrofluoric acid, the complexing of the resulting solution with aluminum nitrate, the extraction of the uranium, and decontamination from the fission products with tributylphosphate (TBP) in a hydrocarbon diluent.

The STR extraction flowsheet is shown in Figure 1. An average coefficient of 14 was reported for the organic-to-aqueous distribution of uranium in the extraction column.

FIGURE 1

HEAD-END FLOWSHEET FOR STR FUEL RECOVERYPRE-EXTRACTION CYCLE

2. SIR

A similar head-end process was developed for SIR fuel by the Knolls Atomic Power Laboratory. The final proposals from KAPL (7) on the dissolution of SIR fuel elements includes the digestion of the stainless steel-magnesium oxide portion with sulfuric acid, and the uranium portion with nitric acid. The resulting dissolver solution is adjusted with nitric acid and water to prepare the feed for the first cycle extraction column. The nitric acid acts as the salting agent for the extraction.

The flowsheet was developed using three miniature mixer-settler contactors. The flowsheet was so designed that only the first column would differ from that of the STR process. This flowsheet is shown on Figure 2.

B. Column Test Program

Pulsed perforated plate columns were selected as the contactors for the STR-SIR pre-extraction cycle. The initial column test program specified certain flow rates and pulse conditions based upon extrapolation of data obtained at other Sites. When the actual column runs were started, it became apparent that these procedures would not give satisfactory data. A series of runs were set up to find operable conditions for STR extraction.

The variables which affect pulse column performance include the following:

Column and cartridge geometry

Physical and chemical properties of the solutions

Choice of dispersed phase

Phase flow ratio

Throughput rates

Pulse frequency and amplitude

The cartridge geometry, chemical composition of solution and dispersed phase were specified by the design engineer. The aqueous-to-organic flow ratio of 4.5 : 1 and volume velocity of 800 gal./(hr.) (sq.ft.) were also specified. Pulse amplitudes from 0.25 inch to 1.0 inch and pulse frequencies from 50 to 100 were tried. When none of these combinations gave satisfactory HTU values, pulse frequency and

amplitude were set at 50 cycles and one inch, respectively, and the aqueous-to-organic flow ratio varied over the range 4.5 : 1 to 1 : 1. Satisfactory operation resulted.

A series of runs were made for both SIR and STR processes to determine flooding curves. For these operations it was necessary to establish all but one variable, usually the frequency, and vary only this one until the column reached an unstable operation. The flooding curves thereby obtained could be used to determine the throughputs and operating conditions for plant installations. Detailed discussion of these variables and of column instability is presented by Sege and Woodfield (4).

1. Test Equipment

Two standard columns made of Fischer and Porter precision-bore glass pipe were used in conducting the pulse column studies. The "A" Column was 2.00 inch I.D. and had a 14.3 foot cartridge length, with four-inch dia. Pyrex glass pipe disengaging sections. This column contained 86 Type 304 stainless steel perforated plates placed on two-inch spacing. Each plate was 1-15/16-inch in diameter, 3/64-inch thick, and was perforated with 1/8-inch diameter holes spaced on 1/4-inch pitch. The free area per plate was 23 percent. This packing configuration is commonly known as a "standard cartridge". The column installation and cartridge details are shown in Figures 3 and 4.

Both "B" and "C" Column studies were conducted on a two-inch I.D. column with 7.8 feet cartridge length and four-inch diameter Pyrex glass pipe disengaging sections. The column contained 47 Type 304 stainless steel perforated plates, placed on two-inch spacing. The plate dimensions were identical to those contained in the "A" Column.

The feed and receiver tanks used in conjunction with the column operations consisted of an organic feed tank (AX), an "A" Column aqueous feed tank (AF), an "A" Column aqueous waste receiver tank (AW), a solvent wash tank (SW), a "B" Column feed tank (BF), two "C" Column waste receiver tanks (CW-1 and CW-2), a "C" Column aqueous feed tank (CX), and several auxiliary polyethylene bottles. The AF and AX tanks were identical in size and construction. These tanks, constructed of stainless steel, measured approximately three feet I.D. and had a capacity of 805 liters (212 gallons). Both were equipped with a mechanical agitator. All other tanks listed above were stainless steel drums. Each tank had a capacity of approximately 54 gallons. All tanks were equipped with gage glasses.

FIGURE 3

Pulse Column and Auxiliary Equipment Installation

Figure 3 shows the pulse column and auxiliary equipment installation in the Chemical Engineering Laboratory. The right-hand column was used for the "A" Column studies, the left-hand column for the "C" Column studies. The tank in the right foreground is the "A" Column aqueous feed tank. The barrel tanks are waste receiver, product receiver, and auxiliary feed tanks. All feed and pulser pump units are located below the rotameters. The large, diagonally-mounted pipe is the batch dissolver condenser. The recording instrument shown was installed since the conclusion of the column studies.

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FIGURE 4

Pulse Column Cartridge Assemblies

Figure 4 shows the cartridge assemblies withdrawn from the pulse columns used in making the studies described in this report. The two assemblies are identical except for length. Each assembly is bound together by a stainless steel rod passing through each plate and spacer.

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All column and auxiliary piping consisted of 1/2-inch or 3/4-inch stainless steel tubing joined by Parker fittings.

The feed pumps used in the operation of the columns were standard laboratory-type pumps, products of the Eco Engineering Company and the Vanton Pump Company. These pumps, which had a maximum capacity of approximately 5 GPM, were driven by fractional horsepower A.C. Motors.

Column pulsations were provided by two Milton Roy Standard Simplex-type pump and motor gear units. These pumps were of the liquid-end step valve and double ball check design, from which the check balls had been removed. Each pump had a plunger diameter of 1-1/8 inch, a maximum stroke length of four inches, and was equipped with a Thymotrol current rectifying unit speed control. Variable column frequency rates were obtained by adjusting pump speed, and variable amplitudes were obtained by adjusting the pump stroke.

With the exception of the column organic overflow streams, all stream flow rates were controlled by adjustment of hand valves to obtain the desired flow as measured by Fischer and Porter rotameters.

All "A" Column feed stocks were prepared in a batch, pipe-type, dissolver. The hydrofluoric, nitric, and sulfuric acid solutions required in the preparation of these feeds were prepared in auxiliary stainless steel acid feed tanks. The acid solutions were fed into the dissolver by a Milton Roy air-powered, controlled-volume pump. Dissolver product solutions were transferred to the AF tank by means of a centrifugal pump.

2. Experimental Procedure

Early column runs were made at a volume velocity of 800 gal./(hr.)(sq.ft.) and at other column conditions as specified by the design engineer. However, several of these runs resulted in column floodings before the specified conditions could be reached and also in high uranium waste losses. It was apparent that additional data were necessary to determine the optimum column conditions for this portion of the program. Consequently, additional series of column runs were made to study the effect of individual variables. Higher frequency-amplitude products and the effect of reduced aqueous-to-organic flow ratio were investigated. All the SIR runs for stage determination were preceded by flooding runs. The conditions for the subsequent stage height runs were then determined from these flooding data.

The initial period of each run, designated as the pre-HETS portion, was that period in which stream flows were started, constant flow rates established, and column equilibrium conditions reached. Column equilibrium conditions were considered to have been reached when a minimum volume of four column aqueous throughputs had been passed through the column. These volumes were 60 liters for the "A" Column and 40 liters for the "C" Column.

The HETS portion of a run utilized for efficiency measurements was that period after equilibrium conditions had been reached, when a constant rate of stripping or extraction was assumed to take place. During this period, waste and product streams were sampled. The analytical results of these samples were used to calculate HETS, HTU, and uranium balances.

a. Column Start-Up

A general column start-up procedure consisted of the following steps. Solvent was fed to the empty column to a one-foot level. The pulser pump was then started and the desired amplitude set by adjusting the pump stroke length. The aqueous feed was then introduced. When the interface level had been raised to within the normal interface range in the top disengaging section, the aqueous feed was stopped. Organic feed was then resumed. When organic overflow appeared, the aqueous feed was resumed and the aqueous effluent flow begun. Constant flow rates and interface were then established. Interface level was maintained by holding a constant aqueous effluent rate and adjusting aqueous feed rates. After reasonably constant flow rates had been reached, as determined by rotameter settings, the rates were verified by tank level checks. Where discrepancies occurred the tank readings were used to correct the rotameter settings.

Columns were shut down by raising the interface to within one inch of the organic overflow point and then stopping the aqueous feed flow. The organic feed flow was continued for several minutes, then stopped and the column drained.

b. Hold-Up Measurement

Organic hold-ups were determined in the following manner. During constant column operating conditions, the interface level was marked on the top disengaging section.

All rotameter valves were then closed, and the feed pumps shut down. The pulser pump was permitted to operate until separation of the organic and aqueous phases was complete. When separation was complete the pulser was shut down and the new interface level was marked. The column was then drained until the organic level was dropped to the original interface level mark. The volume of aqueous effluent displaced in lowering the organic level from the original interface level to the lower interface level was then considered to be the organic hold-up. This volume was then converted to a volumetric percentage.

c. Feed Preparation

The SIR and STR feed stocks were prepared in a batch-type, pipe dissolver located immediately adjacent to the pulse columns. Acid solutions required for the preparation of these stocks were made in the auxiliary acid feed tanks, and were transferred to the dissolver via a Milton Roy air-powered, controlled-volume pump.

The virgin SIR feeds were prepared by dissolving stainless steel strips, steel wool, and magnesium oxide in sulfuric-nitric acid solutions. The dissolution procedure consisted of water flushing the dissolver, solute charging, nitrogen purging, sulfuric acid dissolution, and nitric acid dissolution. During the sulfuric acid refluxing period, which was of approximately twelve hours duration, the dissolver was maintained at a temperature (approximately 250°F.) such that the off-gas pressure would not exceed ten inches water. Dissolver temperature during the nitric acid feed and refluxing period was maintained at approximately 210°F. After a refluxing period of one hour, the dissolver product was allowed to cool to 80°F. to 90°F. and then transferred to the AF tank. After sampling and analysis of the feed stock, uranyl nitrate solution and nitric acid were added, as required for the final adjustment of the feed to run feed specifications. Subsequent SIR feeds were made by returning the AW solution back to the AF tank, and adjusting feed to desired specifications.

The virgin STR feeds were prepared by dissolving zirconium in a 7.43 molar hydrofluoric acid solution. Dissolution procedure was similar to that used in the preparation of SIR feeds. The hydrofluoric acid solution

was fed to the dissolver at a rate of approximately 500 cc/min. During the acid feed and the digestion period, the dissolver was maintained at a temperature (160-180°F.) such that the off-gas pressure would not exceed twenty inches of water. Dissolution was assumed to have been completed when 4-1/2 moles of hydrofluoric acid had been added for each mole of zirconium charged. The AF tank was then charged with about 80 percent of the calculated required amount of aluminum nitrate and the dissolver product transferred. The purpose in charging the aluminum nitrate prior to product transfer was to decrease the corrosive effects of the fluoride ion by complexing it with aluminum nitrate. A sample of the AF solution was then drawn, analyzed, and final feed adjustment made by adding the required amounts of hydrofluoric acid, chromic oxide, aluminum nitrate, and uranyl nitrate solution.

d. Solvent Treatment

After each cycle of column runs, reconditioning of the organic was necessary in order to remove the decomposition products of tributylphosphate and any uranium retained by the organic from the previous "C" Column run. At the conclusion of each "C" Column run, the organic was returned to the AX tank. Here it was washed for 1/2 hour with a 5 percent (by weight) solution of sodium carbonate, using a 10-to-1 ratio of organic to carbonate solution. The mixture was then permitted to separate for 3/4 hour, after which the aqueous phase was decanted. The washing procedure was repeated, using a 5-to-1 volumetric ratio of organic to demineralized water.

e. Sampling and Analysis

During each HETS run an adjusted feed sample, an organic feed sample, five column products, and five column waste stream samples were drawn. The column product and waste stream samples were drawn at scheduled intervals. All other samples were usually drawn at the beginning of the run. Generally, only three samples of the product and waste streams were submitted for immediate analysis. The remaining two samples were retained for later analysis, should poor duplication of analytical results occur on the original three. The methods used in the analysis of the column samples were as follows:(6)

Procedure	Applicable Sample	
	STR	SIR
1. Potentiometric Titration of Free Acid in the Presence of High Concentrations of Uranium	CP	CP
2. Volumetric Titration of Free Acid in Tributylphosphate-Kerosene Solutions	AP, CW	AP, CW
3. Potentiometric Titration of Free Acid in the Presence of Large Amounts of Zirconium and Aluminum	AF, AW	- - - -
4. Conductometric Titration of Free Acid in the Presence of Hydrolyzable Ions	- - - -	DP, AF, AW
5. Volumetric Titration of Chromium	- - - -	DP, AF
6. Colorimetric Determination of Nitrates	- - - -	DP, AF
7. Kjeldahl Determination of Nitrates	DP, AF	- - - -
8. Westphal Balance Determination of Specific Gravity	All Samples	All Samples
9. Amperometric Titration of Sulfate	- - - -	DP, AF, AW
10. Dielectric Constant Determination of Tributylphosphate	AX	AX
11. Amperometric Titration of Zirconium	DP, AF	- - - -
12. Colorimetric Determination of Uranium	DP, AF, AP, CP	DP, AF, AP, CP
13. Fluorophotometric Determination of Uranium by the Spike Method	AW, CW, AX	AW, CW, AX

(DP = Dissolver Product)

f. Flooding Velocity

During the course of this program, several series of flooding point determinations were made. The column flooding points were determined by one of two methods. With amplitude, volume velocity, and aqueous-to-organic

ratio held constant, the frequency was increased until flooding occurred. Using the second method, frequency, aqueous-to-organic ratio, and amplitude were held constant, and volume velocity was increased until flooding was reached. During the course of the second flooding method reasonable flow rate checks were required prior to each increase in volume velocity. A flooding point was established as that point when definite column instability occurred. This was usually evidenced by several distinct column actions. In each flooding determination, a rise in interface level was observed. In most determinations, a definite increase in coalescence of the organic globules was noted. Usually complete phase inversion occurred. In other instances tight emulsions formed, which progressed downward through the column, sometimes resulting in considerable organic being discharged with the aqueous effluent stream.

IV. RESULTS AND DISCUSSION

A total of twenty-five STR "A" Column runs, six SIR "A" Column runs, one "B" Column run and eight "C" column runs were made. This test program and a discussion of their significance are separately reported for STR and SIR "A" Column stage height tests, for stripping column stage height tests, and for flooding velocity studies in the following paragraphs. Methods used in calculation of stage height, transfer unit heights, and flooding data are outlined in Appendix B.

A. STR Extraction Column HTU Studies

A summary of the results of 23 STR "A" Column tests are presented in Table 1. The effects of operating variables on extraction efficiency are discussed below.

1. HTU Values Obtained

The minimum height of a transfer unit (HTU) obtained using STR solutions was 1.5 feet. To obtain this value, it was necessary to reduce the aqueous-to-organic flow ratio to 1.4 : 1 from the 4.5 : 1 specified by ANL. Values for HTU ran as high as four feet for aqueous-to-organic flow ratios of 4.0 at favorable pulse conditions. Using aqueous-to-organic flow ratios of 4.5 and low pulse energies, the HTU values ranged as high as 11.6 feet.

20

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TABLE 1
STR EXTRACTION COLUMN STUDIES

Flowsheet: See Figure 1 (organic-to-aqueous flow ratio varied from values shown)
 Solvent: 10 percent (Vol) TBP in Amsco 123-15
 Column: 2" x 14.3' standard cartridge
 Run Duration: Pre-HETS Period 1 to 3.5 hrs. (3.5 - 9.9 aqueous thruputs)
 HETS Period 0.9 - 2.3 hrs. (0.8 - 8.1 aqueous thruputs)

STR Run No.	Feed Composition				Specific Gravity	Extract Composition U ₂ g/l	Superficial Vol. Vel. gal/(hr.) (sq.ft.)	Pulse Conditions		Average Feed Rate During HETS Period				Flow Ratio Aqueous-to-Organic	Volume Bal. %	Stream Uranium Analyses				Exper. Percent U		Waste Loss Percent of Feed	HTU, Ft.	HETS, Ft.	Percent Organic Hold-up
	U ₂ g/l	H ² (M)	NO ₃ (M)	Zr(M)				Frequency Cycles/min	Amp. In.	AF	AX	AW	AP			Waste(AW)		Product(AP)		Dist. Coeff.	Mat. Bal.				
4A	0.466	0.73	2.11	0.567	1.2023	4 x 10 ⁻⁴	820	50	0.25	900	203	910	228	4.48	103.1	0.166	17.5	1.46	3.3	10.85	115.6	36.0	11.6	17.5	----
5A	0.466	0.73	2.11	0.567	1.2023	4 x 10 ⁻⁴	842	75	0.25	910	230	912	210	3.97	98.5	0.133	1.5	1.35	0.7	10.85	95.6	28.5	9.2	14.5	----
6A	0.466	0.73	2.11	0.567	1.2023	4 x 10 ⁻⁴	791	100	0.25	890	216	858	219	3.92	97.3	0.103	14.7	1.46	5.5	10.85	98.4	21.2	6.9	11.1	----
7A	0.65	0.65	1.91	0.528	1.1864	3 x 10 ⁻⁵	806	50	0.50	923	204	890	215	4.36	98.2	0.21	28.5	2.01	3.5	13.0	103.8	31.4	10.9	17.9	----
8A	0.65	0.65	1.91	0.528	1.1864	3 x 10 ⁻⁵	837	75	0.50	923	226	913	271	4.04	103.1	0.178	12.4	2.05	1.0	13.0	120.2	27.2	9.5	16.3	----
9A	0.65	0.65	1.91	0.528	1.1864	4 x 10 ⁻⁴	915	50	0.75	1060	192	1050	212	5.5	100.8	0.205	14.6	1.88	6.9	13.0	89.6	31.7	10.4	15.2	----
10A	0.339	0.67	2.14	0.487	1.1884	4 x 10 ⁻⁵	854	110	0.50	965	244	916	153	3.75	89.9	0.044	----	1.38	----	12.3	115.2	12.3	4.3	6.9	----
11A(1)	0.339	0.67	2.14	0.487	1.1884	4 x 10 ⁻⁵	824	60	1.4	867	212	907	95	4.27	----	0.015	16.1	1.50	8.0	10.3	----	4.4	3.2	4.8	----
12A(2)	0.339	9.67	2.14	0.487	1.1884	4 x 10 ⁻⁵	877	80	0.75	948	211	980	208	4.64	102.3	0.027	15.0	None	----	10.3	----	3.9	3.9	5.6	32
13A(3)	0.360	0.72	2.20	0.491		1 x 10 ⁻³	830	75	0.75	934	226	902	221	4.0	96.8	0.055	10.2	1.35	5.9	11.1	103.2	14.8	5.4	8.6	4.6
14A(4)	0.360	0.72	2.20	0.491		1 x 10 ⁻³	909	85	0.75	1033	199	---	237	5.2	----	0.0063	16.1	1.55	37.2	11.1	100.5	1.75	2.2	3.1	20
15A	0.360	0.72	2.20	0.491		1 x 10 ⁻³	862	65	0.75	588	606	564	578	0.93	95.6	0.0017	50.6	0.363	6.3	11.1	100.5	0.45	2.5	6.7	16
16A	0.310	0.74	2.21	0.478	1.1884	3 x 10 ⁻⁵	756	50	1.0	866	197	831	195	4.22	96.5	0.032	18.8	1.185	1.3	10.5	96.5	10.1	4.6	7.1	----
17A	0.363	0.76	2.17	0.478	1.1844	5 x 10 ⁻³	810	50	1.0	897	200	900	213	4.5	101.4	0.014	92.5	1.59	6.3	14.15	110.7	3.5	3.3	5.7	13
18A	0.365	0.75	2.16	0.460	1.1803	5 x 10 ⁻⁴	806	50	1.0	534	560	534	554	0.95	99.5	0.0015	87.0	0.353	2.6	8.69	97.3	0.43	2.4	5.2	----
19A	0.371	0.79	2.02	0.452	1.1786	6 x 10 ⁻⁵	830	50	1.0	746	400	728	399	1.82	97.9	0.0022	13.8	0.743	11.9	8.69	108.5	0.6	2.0	4.0	----
20A	0.371	0.79	2.02	0.452	1.1786	6 x 10 ⁻⁶	820	50	1.0	835	289	825	226	2.85	92.6	0.0166	31.4	0.965	5.2	16.1	94.6	4.5	4.1	7.7	7
21A	0.313	0.54	2.37	0.570	1.2165	2 x 10 ⁻⁵	835	50	1.0	656	474	660	458	1.39	99.1	0.00044	40.8	0.525	1.0	16.1	101.7	0.12	2.0	5.3	14
22A	0.313	0.54	2.37	0.570	1.2165	2 x 10 ⁻⁵	820	50	1.0	645	459	654	436	1.43	98.5	0.00004	0.0	0.574	2.4	23.6	123.8	0.006	1.5	4.4	11.5
23A	0.313	0.54	2.37	0.570	1.2165	9 x 10 ⁻⁵	800	50	1.0	900	290	796	311	2.74	93.0	0.00088	17.1	1.08	5.3	34.6	115.0	0.24	2.2	5.4	5.5
24A	0.48	0.658	2.21	0.569		1 x 10 ⁻²	852	50	0.5	933	222	934	251	4.2	102.7	0.0489	46.8	1.86	9.7	(14)	111.6	10.3	5.1	8.7	----
26A(5)	0.43	0.78	2.11			0	758	50	1.0	---	370	659	346	1.78		0.00027	32.4	1.04	4.8	(14)		0.06	1.7	4.1	----
28A	0.38	0.73	2.205			0	786	50	1.0	865	213	855	214	4.0	99.2	0.0183	34.4	1.72	19.8	(14)	115.0	4.8	3.8	6.6	----

- NOTES: 1. Incorrect reading of product volume; no uranium or volume balance. Column appeared to be approaching a flood at time of shutdown.
 2. No product stream analyses. Column appeared to be approaching a flood at time of shutdown.
 3. Waste volume not recorded; run terminated by column flooding.
 4. Organic phase continuous; inverted and run stopped.
 5. Error in feed volume.

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2. Effect of Pulse Frequency and Amplitude on HTU

The effect of pulse conditions on extraction column HTU values is shown in Figure 5. Upon increasing the frequency and amplitude, a marked decrease in HTU values is observed.

The frequency-amplitude product represents the mixing energy to the column. Higher frequency-amplitude products resulted in greater organic hold-up in the column, finer dispersion of the organic phase with greater interfacial area for mass transfer, and lower HTU values. However, the effect of variation of pulse amplitude was not fully accounted for by the frequency-amplitude product. At higher amplitudes, higher frequency-amplitude products were required to realize the same values of HTU. This effect is shown in Figure 6.

Column flooding establishes the upper limit on frequency-amplitude product. Several runs were flooding or were approaching a flood at the shutdown time, and flooding might have developed upon prolonged operation. Although increasing the frequency-amplitude product did result in HTU values as low as two feet, this was still too high for satisfactory operation of plant columns, and other means of reducing HTU values were investigated. One run, STR-23A, did not correlate with the others in the series as the calculated HTU of 5.1 feet was only about half that indicated by the correlation.

3. Effect of Varying Aqueous-to-Organic Flow Ratio

The effect of varying the aqueous-to-organic flow ratio is shown in Figure 7. The curve indicates a two-fold increase in the HTU values when the aqueous-to-organic flow ratio is changed from 1.5 : 1 to 3.5 : 1. This effect is attributed to the decrease in organic hold-up and interfacial area as the dispersed phase flow (organic) is decreased. The effect of flow ratio on interfacial area is illustrated by the photographs in Figure 8, showing solvent hold-up in the column at aqueous-to-organic ratios of four and two at constant pulse conditions and volume velocity.

The points plotted in Figure 7 are for Runs STR-21A, 22A, 26A, and 28A. These runs were made using fresh feed and solvent. A similar series of runs (STR-16A through 20A) were made using recycled feed and solvent. These runs show the same trend as Figure 7, although the points are not as consistent and the HTU values are somewhat higher. It is believed that the recycled solutions had been contaminated, since phase disengaging times were two to four times as long as those obtained using fresh solvent. Two of the runs flooded prematurely and had to be rerun after rewashing the solvent.

FIG. 5

HEIGHT OF A TRANSFER UNIT
VS
FREQUENCY

SECRET

STR FLOWSHEET
VOLUME VELOCITY = 800 GAL./HR - SQ. FT
AQUEOUS TO ORGANIC = 45:1
COLUMN 2" x 14.3'
STD. CARTRIDGE

DECLASSIFIED

FIG 6

HEIGHT OF A TRANSFER UNIT
VS
FREQUENCY-AMPLITUDE PRODUCT

SECRET

STR FLOWSHEET

VOLUME VELOCITY=800 GAL/HR - SQ FT

AQUEOUS TO ORGANIC = 45:1

COLUMN 2" x 14.3'

STD. CARTRIDGE

DECLASSIFIED

FIG. 7

HEIGHT OF TRANSFER UNIT
VS
AQUEOUS TO ORGANIC FLOW RATIO

SECRET

STR FLOWSHEET
VOLUME VELOCITY = 800 GAL/HQ - SQ. FT.
FREQUENCY = 50 CYCLES/MIN
AMPLITUDE = 1.0 INCHES
COLUMN = 2" x 14'3"
STD. CARTRIDGE

SECRET

DECLASSIFIED

$A/O = 2$

$A/O = 4$

Figure 8

Effect of Varying Aqueous-to-Organic Flow Ratio (A/O)

Conditions: Volume Velocity = 800 gal./ (hr.) (sq.ft.)
Pulse Amplitude = 1.0 inch
Pulse Frequency = 40 cycles/min.

4. Effect of Operating with Organic Phase Continuous

A single run was made with organic as the continuous phase (interface at the bottom). The HTU value observed was 4.6 feet, as compared to 3.3 feet obtained on a similar run with aqueous phase continuous. A generalization often quoted is that by dispersing the phase having the larger volumetric flow rate, the interfacial area is increased and lower HTU values result. However, to realize this reduction in HTU, the plates should be preferentially wetted by the continuous phase. Since this was not the case, operating with organic phase continuous actually resulted in higher HTU values. The aqueous phase left the plates in large globules and streams rather than uniform drops. The column exhibited a tendency to revert to a continuous aqueous phase.

B. SIR Extraction Column HTU Studies

Four SIR runs were made to determine HTU values under extraction column conditions. The run conditions and results are summarized in Table 2. HTU values of 1.0-1.6 feet were observed for volume velocities of 330-1410 gal./(hr.)(sq.ft.). The maximum waste loss was 0.04 percent.

Some concern had been expressed earlier that columbium carbide particles which might be present in the feed solutions would interfere with the column operation. However, there was no evidence of particulate material in the column feeds.

Due to an error in the analysis of dissolver solution, both the stainless steel and sulfate ion concentrations in the feed were low. Since complete feed analyses were not received until after the runs were completed, there was no chance to rectify the error. It was believed that this composition difference would not effect HTU values significantly.

C. STR-SIR Stripping Column HTU Studies

The stripping column flowsheet is the same for both STR and SIR processing and, since compositions are similar at this stage, tests with a single feed are sufficient. The results of three stripping column runs indicated HTU values of 1.5 - 1.9 feet, as summarized in Table 3.

27

SECRETTABLE 2SIR EXTRACTION COLUMN STUDIES

Flowsheet: See Figure 2

Solvent: 10 percent (Vol) TBP in Amoco 125-15
 Column: 2" x 14.3' standard cartridge
 Run Duration: Pre-HETS period 1.5 - 4.8 hrs. (5 - 6 aqueous thruputs)
 HETS period 1.5 - 4.5 hrs. (4.5 - 5 aqueous thruputs)

SIR Run No.	Feed Composition					Superficial Vol. Vel. gal/(hr.) (sq.ft.)	Pulse Conditions		Average Feed Rate During HETS Period				Flow Ratio Aqueous-to- Organic	Volume Bal. %	Stream Uranium Analyses -				Percent U Mat. Bal.	Waste Loss Percent of Feed	HTU,Ft.	HETS,Ft.
	U,g/l	H ⁺ (M)	NO ₃ (M)	SO ₄ (M)	Stainless Steel g/l		Frequency Cycles/min	Amp. In.	cc/min						Waste(AW)		Product(AP)					
									AP	AX	AW	AP			Av.	Var'n	Av.	Var'n				
2A	2.50	2.83	2.54	0.275	2.43	330	70	1.0	228	240	212	243	0.88	97.5	<0.00001	----	2.48	9.3	105.8	0.004	1.02	2.4
3A	2.50	2.83	2.54	0.275	2.43	1110	35	1.0	745	734	775	707	1.05	100.0	0.00052	30.8	2.80	8.6	106.5	0.02	1.5	3.6
4A	2.53	3.06	3.1	0.31	2.02	365	103	0.5	263	244	251	243	1.03	97.4	0.0011	31.6	3.07	14.0	112.0	0.04	1.6	3.7
5A	2.53	3.06	3.1	0.31	2.02	1410	50	0.5	1000	919	993	875	0.925	97.5	0.00028	64.8	2.63	11.4	93.0	0.012	1.4	3.3

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TABLE 3

STRIPPING COLUMN EFFICIENCY TESTS
STR-SIR Flowsheets

<u>Run No.</u>	<u>Volume Velocity</u> <u>gal./ (hr.) (sq.ft.)</u>	<u>Frequency</u> <u>Cycles/min.</u>	<u>Amplitude</u> <u>Inches</u>	<u>HTU</u> <u>Ft.</u>
7C	828	72	0.75	1.5
8C	794	50	1.0	1.9
9C	1025	70	1.0	1.9

Cyclic flooding occurred during Run 9C, but the HTU value was not significantly higher than in its absence. Flooding curves were not obtained until these runs were completed. Detailed data for these tests are given in Table 4.

TABLE 4

STR-SIR STRIPPING COLUMN STUDIES

<u>Run No.</u>	<u>7C</u>	<u>8C</u>	<u>9C</u>
Feed Composition			
Uranium, g/l	1.50 ⁽¹⁾	1.77 ⁽²⁾	1.43
Nitric Acid, M	0.017	----	----
Volume Velocity, gal./ (hr.) (sq.ft.)	830	790	1025 ⁽³⁾
Pulse Conditions			
Frequency, cycles/min	75	50	70
Amplitude, in.	0.75	1.0	1.0
Run Duration			
Pre-HETS period, hrs.	3.8	4.0	3.0
HETS period, hrs.	2.3	3.3	2.8
Flow Ratio, Aqueous/Organic	0.23	0.33	0.28
Stream Uranium Analyses			
Waste (CW), g.U/l Av.	0.0105	0.0355	0.0279
Waste (CW), percent variation in anal.	48	8	33
Product (CP), g.U/l av.	6.07	6.04	5.15
Product (CP), percent variation in anal.	2	7	4
Uranium waste loss, percent of feed	0.72	1.86	1.92
Height of a Transfer Unit (HTU), ft.	1.5	1.9	1.9
Height Equivalent Theoretical Stage (HETS), ft.	4.2	5.6	6.0
Uranium Material Balance, percent	98.9	----	102.0
Volume Balance, percent	----	93.8	100.4

- NOTES: 1. Synthetic feed.
2. Feed not sampled; calculated from CW and CP compositions.
3. Column in cyclic flood during test.

D. Flooding Characteristics of Extraction Systems1. STR "A" Column Flooding

The flooding volume velocities for the STR "A" Column System are shown in Figure 9 as a function of frequency for one-inch pulse amplitude. Flooding runs were made at aqueous-to-organic volume ratios of 2 and 3. At low frequencies, the effect of aqueous-to-organic flow ratio is not significant. However at high frequencies, the column flooding volume velocity was as much as 75 percent greater when operating at an aqueous-to-organic ratio of 3 as compared to values obtained at a flow ratio of 2. With a smaller proportion of organic phase in the column, there may be less tendency to form emulsions which would result in flooding. The details of the tests are given in Table 5.

TABLE 5STR "A" COLUMN FLOODING DATA

Column: 2" x 14.3' standard cartridge
 Solvent: 10% TBP (by vol) in Amsco 123-15
 Pulse Amplitude: 1.0 inch

<u>STR Run No.</u>	<u>Uranium grams/l</u>	<u>Acidity H⁺, M</u>	<u>Nitrate Conc., M</u>	<u>Aqueous/ Organic Flow Ratio</u>	<u>Flooding Points Frequency Cycles/minute</u>	<u>Volume Velocity gal./ (hr.) (sq.ft.)</u>
24A	0.45	0.89	2.26	3	104	400
				3	85	800
				3	65	1100
25A	0.36	0.782	2.28	3	55	1200
				2	90	400
				2	70	1000
26A	0.43	0.78	2.11	2	50	1200
				2	35	1300
27A	0.38	0.73	2.21	3	45	1300

2. SIR "A" Column Flooding

The flooding volume velocities for the SIR "A" Column System are shown in Figure 10 as a function of frequency for a one-inch amplitude. All of the flooding points lie below those observed for STR "A" Column conditions; probably due to a smaller density difference for the SIR Column System. For the same pulse frequency

30

FIG. 9

"A" COLUMN FLOODING VELOCITY vs FREQUENCY
STR FLOWSHEET
IN PULSED PLATE COLUMNS

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FLOODING VELOCITY (GAL/HR PER SQ. FT.)

SECRET

FIG. 9

PAGE 30
100 143/2

FIG. 10

the flooding velocities observed for the SIR System were half to two-thirds the values noted for the SIR-System, the difference being more marked at higher pulse frequency. Test results are summarized in Table 6.

TABLE 6

SIR "A" COLUMN FLOODING DATA

Column: 2" x 14.3' standard cartridge
 Solvent: 10% TBP (by vol) in Amsco 123-15
 Aqueous-to-Organic: 1.0 (nominal)

<u>SIR Run No.</u>	<u>Uranium grams/l</u>	<u>Acidity H⁺, N</u>	<u>Nitrate Conc., M</u>	<u>Sulfate Conc., M</u>	<u>Stainless Steel, g/l</u>	<u>Frequency Cyc/min</u>	<u>Amplitude Inches</u>	<u>Volume Velocity gal./ (hr.) (sq.ft.)</u>
1A	1.89	2.98	2.89	0.28	3.0	85	1.0	350
						60	1.0	600
						40	1.0	900
						35	1.0	1200
						32	1.0	1300
4A	2.99	3.12	3.10	0.29	2.31	35	0.5	1300
						95	0.5	1200
						70	0.75	1275

3. "B" Column Flooding Data

One series of runs was made to determine "B" Column scrub section flooding data. The resulting curve is shown in Figure 11 and test data are given in Table 7. No "B" Column extraction data were obtained. Flooding velocities were somewhat below those noted for extraction conditions.

TABLE 7

"B" COLUMN SCRUB SECTION FLOODING DATA

Column: 2" x 7.8' standard cartridge
 BF Composition: (estimated from CF composition)
 U = 1.55 g/l, HNO₃ = 0.1M
 10% TBP (by vol) in Amsco 123-15
 BS Composition: 0.7M aluminum nitrate
 Aqueous-to-organic flow ratio: 1 : 2.5

<u>Amplitude Inches</u>	<u>Frequency Cycles/min</u>	<u>Flooding Volume Velocity gal./ (hr.) (sq.ft.)</u>
1.0	70	300
1.0	55	500
1.0	22	800

STR-SIR "B" COLUMN FLOODING

SECRET

FLOODING VELOCITY (GAL. PER SQ. FT.)

PULSED VOLUME
VELOCITY

$$\frac{\text{AQUEOUS}}{\text{ORGANIC}} = \frac{1}{2.5}$$

AMPLITUDE = 1.0 INCH

COLUMN = 2" x 7.8'

STD. CARTRIDGE

SECRET

PULSE FREQUENCY (CYCLES PER MINUTE)

FIG. 11

PAGE 33
100 H312

4. "C" Column Flooding Data

The flooding volume velocities for the "C" Column System are shown in Figure 12. It was found that small quantities of nitric acid had a marked effect on the flooding point. Run STR 26C, made with feed containing no uranium showed a significant increase in flooding volume velocity when the nitric acid in the organic was increased from 0.002M to 0.01M. Increasing the acid to 0.1M did not have a significant effect at high frequencies, but at low frequencies the flooding volume velocity was increased by forty percent. Runs STR 25C, 28C and SIR 3C confirmed these results. Data are summarized in Table 8.

TABLE 8"C" COLUMN FLOODING DATA

Column: 2" x 7.8'
Strip solution: Demineralized water
Aqueous-to-organic flow ratio: 1 : 4
Pulse Amplitude: 1.0 inch

<u>STR</u> <u>Run No.</u>	<u>Uranium</u> <u>grams/l</u>	<u>Acidity</u> <u>H⁺ N</u>	<u>Frequency</u> <u>Cycles/min</u>	<u>Volume Velocity</u> <u>gal./ (hr.) (sq.ft.)</u>
25C	1.0 ⁽¹⁾	0.09 ⁽¹⁾	75	400
			70	500
			45	700
			35	1000
26C(a)	0.0	0.002	70	300
			60	400
			40	600
			25	800
26C(b)	0.0	0.01	65	400
			45	600
			35	700
26C(d)	0.0	0.096	80	300
			65	450
			50	600
			45	800
			35	1100
28C	1.53	0.0	72	300
			25	800
<u>SIR</u> <u>3C</u>	3.25	0.093	85	400
			50	700
			35	1100

STR-51R "C" COLUMN FLOODING
AQUEOUS TO ORGANIC RATIO = 1:4
COLUMN = 2" x 7.8'
STD. CARTRIDGE

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V. CONCLUSIONS

As a result of the STR-SIR pulse column studies, the following conclusions were reached:

- A. Pulse columns are operable when processing STR and SIR solutions.
- B. The HTU values obtained for the SIR "A" Column and the "C" Column indicate the uranium waste loss from the columns designed for installation in the plant should meet flowsheet specifications.
- C. The HTU values obtained for the STR "A" Column when operating at aqueous-to-organic ratios of 4.5 : 1 indicate that the uranium waste loss would exceed 0.1 percent in the 21-foot column designed for the plant. Reducing the aqueous-to-organic flow ratio to 3.0 : 1 or less should result in waste losses less than 0.1 percent.
- D. The upper limits on column flow rates are given by the flooding curves. Operation at 40 to 80 percent of these values is recommended. Lower rates may result in high waste losses, while higher rates may cause column instability.

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APPENDIX ASymbols

- A/O = Aqueous-to-organic volume flow ratio.
- E_A^O = Equilibrium distribution coefficient, volumetric basis (ratio of uranium concentration in organic phase to uranium concentration in aqueous phase).
- HETS = Height equivalent to a theoretical stage.
- HTU = Height of a transfer unit, overall raffinate-film basis.
- M = Separation factor (i.e., ratio of solute concentration in feed stream to solute concentration in raffinate stream).
- N_s = Number of theoretical stages.
- N_t = Number of theoretical transfer units.
- p = Extraction factor; the ratio of A/O to E_A^O
- X = Concentration of solute in aqueous phase.
- Y = Concentration of solute in organic phase.
- Y* = Concentration of solute in organic phase which would be in equilibrium with a concentration X of the solute in the main body of the aqueous phase.

Abbreviations

- amp = amplitude
- c/m = cycles per minute
- freq = frequency
- TBP = tributylphosphate

APPENDIX BCalculation Methods

Flow rates and stream compositions were obtained directly from the run data sheets and analytical report forms. Pulse conditions were obtained from measurements at the start of the runs. Other values tabulated in the data summaries were calculated as follows:

1. Superficial Volume Velocity

The combined aqueous and organic flow rates at the dilute end of the column (AX and AW or CX and CW) were divided by the column cross sectional area to obtain the volume velocity.

2. Aqueous-to-Organic Flow Ratio

The dilute streams (AX and AW or CX and CW) were used to compute the aqueous-to-organic flow ratio.

3. Volume Balance

The influent and effluent flow rates were used to compute a volume balance for the HETS portion of the run, since essentially no volume change occurs within the column.

4. Number of Aqueous Throughputs

The number of aqueous throughputs was calculated by dividing total volume of aqueous feed entering the column during the pre-HETS or HETS period by that volume of the column which is normally filled with aqueous. These volumes were calculated to be 15 liters and 10 liters for the "A" and "C" Columns, respectively. These values do not include any allowance for organic hold-up or cartridge volume.

5. Percentage Variation of Uranium Stream Analyses from Average

The maximum variation of the uranium analyses of the effluent streams was calculated to give an indication of the uniformity of the product and waste streams. This variation is expressed as the percent difference between the maximum or minimum and the average uranium analysis.

6. Uranium Distribution Coefficient (E_A^O)

The uranium distribution coefficient was determined experimentally on the majority of the STR extraction column runs. Equal volumes of AF and AX were contacted in a separatory funnel, and both phases analyzed for uranium. The distribution coefficient is expressed as the ratio of uranium concentration in the organic phase to uranium concentration in the aqueous phase.

7. Uranium Material Balance

A percent uranium material balance for the HETS portion of the run was calculated by dividing the output uranium rate by the input uranium rate. The uranium rates were computed by multiplying the stream flow rates by the uranium concentrations in the stream for feed, product, and raffinate streams.

8. Percentage Waste Loss of Uranium

The percentage waste loss was computed by dividing product of raffinate flow rate and raffinate uranium concentration by the product of feed flow rate and feed uranium concentration. On several runs, feed samples were not taken. For these runs the waste loss was obtained by dividing the uranium content of the raffinate stream by the sum of the uranium contents of the product and raffinate streams.

9(a) Height of a Transfer Unit (HTU) for Extraction

The heights of a transfer unit were calculated by dividing the column height by the number of transfer units calculated from Colburn's equation. This equation is given in HW-18700 as follows:

$$N_t = \frac{\ln \left[\frac{(1-p)M+p}{(1-p)} \right]}{(1-p)}$$

where:

N_t = number of "overall water-film" transfer units,
for transfer from aqueous phase to organic phase

P = extraction factor = $A/O \times \frac{1}{E_A^O}$

M = separation factor = $\frac{X_f}{X_w}$ (assuming the uranium in the solvent may be neglected)

The equation above applies only to the condition where both the uranium distribution coefficient and aqueous-to-organic flow ratios are constant. On the STR runs where E_A^O was determined experimentally, the experimental value was used. On the remainder of the STR runs, a value of 14 was used. A value of 8 was used for the SIR runs.

9(b) Height of a Transfer Unit (HTU) for Stripping

Since the uranium distribution coefficient is not a constant for the stripping column, a graphical method was used to calculate the "C" Column HTU values. The number of transfer units was calculated from the following formula:

$$N_t = \int_{Y_w}^{Y_f} \frac{dY}{Y - Y^*}$$

where:

N_t = number of overall organic film transfer units for transfer from the organic to the aqueous phase.

Y = concentration of the uranium in the organic phase.

X = concentration of the uranium in the aqueous phase.

Y^* = concentration of the uranium in the organic phase in equilibrium with an aqueous phase composition X .

The value of the integral was determined graphically. The height of a transfer unit was calculated by dividing the column height by the number of transfer units. Hanford equilibrium data were used⁽²⁾.

10(a) Height Equivalent to a Theoretical Stage (HETS) for Extraction

The number of theoretical stages was calculated using Colburn's equation. The height equivalent to a theoretical stage was obtained by dividing the column height by the number of theoretical stages. Colburn's equation for theoretical stages is given in HW-18700 as follows:

$$N_s = \frac{\ln \left[\frac{(1-p) M+p}{1/p} \right]}{\ln 1/p}$$

where:

N_s = number of theoretical stages.

Again the equation is limited to constant aqueous-to-organic flow ratios and constant uranium distribution coefficients.

10(b) Height Equivalent to a Theoretical Stage (HETS) for Stripping

Since the stripping column uranium distribution coefficients are not constant, a graphical method was used to calculate the number of theoretical stages. The method is analogous to the McCabe-Thiele method for distillation. The equation for the operating line, as derived from a material balance around the top of the column, is as follows:

$$Y = X \left(\frac{A}{O} \right) + Y_w$$

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Page 42

The operating and equilibrium lines were plotted and the number of stages stepped off graphically. Fractional stages were computed arithmetically.

Additional information and background on the calculation methods for HTU and HETS can be found in the Redox Technical Manual⁽³⁾ since the calculation methods used were patterned after the methods outlined therein.

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REF ID: A54710