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Union Carbide and Carbon Corporation

MEMORANDUM

EPS Y-108

KT-84

September 13, 1950

TO: T. F. Furlong
FROM: H. A. Larsen (leader), D. L. James, G. T. Parish, and
J. D. Roarty
SUBJECT: Pulse-Column Operating Conditions for Uranium Recovery
from Waste Solutions.

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INTRODUCTION

A pulse column is a vertical column for liquid-liquid extraction. The column is equipped with many perforated plates through which the liquid is pulsed by a reciprocating pump without check valves. This pulsing action, superimposed upon the normal throughput flow, results in a high degree of extraction with short columns due to the intimate mixing produced.

The use of such a pulse column for the removal of small quantities of uranium from solutions containing relatively large amounts of impurities is being studied on a pilot-plant scale. The work reported herein is a continuation of this study (6) and has as its primary objective the determination of ranges of flow rate and pulse frequency at which the column will operate without flooding.

This investigation was carried on from August 25, 1950, to September 13, 1950.

RESULTS

The possible range of operating frequencies for the extractor column is presented in Figure 1. Also presented in Figure 1 is a theoretical correlation of the minimum pulse frequency, for satisfactory operation, as a function of aqueous feed rate. This correlation assumes that only the aqueous phase flows through the plates during the downward pulse and that there is downward flow only during the downward pulse. Analyses, other operating data, and calculated HETS values are presented in Table IA.

The following distribution coefficients were determined and used to calculate HETS for the extractor:

<u>Batch No.</u>	<u>D.</u>
91-0341	27.8
91-0345	24.8
91-0346	24.8
91-0347	24.8

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FLOODING FREQUENCY
VS
AQUEOUS FEED RATE

DATE 9-11-50	DRAWN BY G.T.P.	FILE NO. EPS Y-108	FIG. 1

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Measured values of surface tension, interfacial tension, and viscosity of the component liquids are presented in Table IIA.

DISCUSSION OF RESULTS

Extractor Operating Range

Satisfactory operation of the pulse column is possible only over a limited range of pulse frequencies and feed rates. As shown in Fig. 1 the extraction column will flood at extreme frequencies and at high flow rates, while satisfactory operation can be realized at the conditions represented by the area to the left of the curve. Under flooding conditions the carbitol flows out the bottom of the column with the raffinate while the aqueous feed overflows at the top with the carbitol.

Two distinct types of flooding may be observed in the column. At high frequencies the liquids are pulsed through the plates so rapidly that the droplets formed do not have time to coalesce, i.e. emulsification occurs. No distinct separation of the phases takes place, and flooding results at both ends of the column. Minimum frequency flooding, as distinct from high frequency flooding, is not due to emulsification. Instead, the column floods at the top as the result of failure of the aqueous feed to descend through the top plate.

During satisfactory operation of the column, net throughput is achieved primarily by the pulsing action. Without the pulse the difference in liquid densities is insufficient to cause appreciable flow of the viscous feed solution through the small plate holes. If the assumptions are made that there is perfect settling between pulses so that only the aqueous phase flows through the plates during the downward pulse and that there is downward flow only during the downward pulse, it becomes possible to calculate a minimum flooding frequency for any given feed rate. This frequency, equal to the aqueous feed rate divided by the volume displaced during one stroke of the pulse pump, is a theoretical minimum independent of the solution treated. A line through the minimum frequency values of Fig. 1 would be slightly above the theoretical value and would have an equivalent slope. The vertical displacement shows that settling is imperfect and that carbitol as well as aqueous feed passes through the plates during the downward pulse.

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The type of solution treated as well as its previous history has a pronounced effect upon the conditions under which the column will operate. The two feed batches treated in this investigation were both "slag" solutions with calcium fluoride and aluminum nitrate as the principle impurities. The main difference between the two batches was that batch No. 91-0341 had been boiled about five times as long as No. 91-0345,6, and 7. The resulting difference in the maximum feed rates of 276 ml/min and 409 ml/min points out the importance of careful preparation of the feed batches. The fact that the two batches treated did not have the same ratios of feed to carbitol rates is relatively unimportant as previous work has shown that this parameter has little effect on the range of pulse column operability, (2).

HETS

For each set of conditions presented in Fig. 1 sufficient operating data were taken to determine the height equivalent to a theoretical stage (HETS). The data taken during several hours of operation were averaged to obtain the most representative flow rates and analyses for a given set of operating conditions. These values were then used to calculate HETS. In a few cases a reading was of the order of 100% from the mean of the other values taken for the same operating conditions. It was felt better to discard such readings as obvious errors than to average them in with the other values.

No trend was observed for the relationship among pulse frequency, flow rate, and HETS. Previous workers have shown the HETS to be decreased by an increase in frequency or a decrease in flow rate. (1), (2), (4), (5), (6). However, there were no deviations from these predictions which could not be adequately explained by analytical errors alone.

Stripper Operation

No calculations of HETS were made for the stripper column because the equilibrium data obtained were inadequate. Four equilibrium batches, made up from mixtures of extractor carbitol and water, gave distribution coefficients of 2.96, 1.70, 1.25, and 0.91 as the ratio of carbitol to water was increased from batch to batch. Since the carbitol from the extractor is more acidic than the water, the total amount of acid in the equilibrium batch and, hence, the acid concentration in each phase increases with an increase in the ratio of carbitol to water. The data show that the stripper distribution coefficient (ppm uranium in water/ppm

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uranium in carbitol) decreases with increasing acid concentration in the system. Actual pH measurements of the separate phases in the equilibrium batches showed a non-uniform variation in total acid content and, hence, did not substantiate the expected trend. Whether the pH measurements were in error or the experimental procedure in making up equilibrium batches was faulty is problematical. New equilibrium batches should be mixed, and care should be exercised in obtaining accurate measurements of both uranium and acid concentration in each phase. The acid content could be obtained more accurately by titration to a phenolphthalein end-point than by using a pH meter. If acid content is definitely shown to have a pronounced effect on the distribution coefficient in the stripper, a new procedure for mixing equilibrium batches will have to be developed which duplicates the actual conditions of uranium and acid concentrations at various points along the column.

Mixing And Emulsification

Mixing between two countercurrent streams is more thorough for turbulent than for laminar flow. The maximum Reynold's number attained in this investigation was of the order of 100, well within the region of laminar flow. The required Reynold's number to insure a turbulent flow regime is impractical in the present pulse column because other opposing factors develop. Increased flow rates and higher pulse frequencies to attain better mass transfer can be realized only by preventing the emulsification which causes flooding. Another possibility would be to use fewer holes or smaller holes, but again emulsification would provide a limit. Lowering the feed viscosity or adding an agent to break up the emulsion formed might permit operation of the column with a higher degree of turbulence.

The greatest difficulty with emulsification was experienced in the stripper column. Low interfacial tension usually accompanies emulsification, and as can be seen by Table IIA, the lowest interfacial tensions were encountered in the stripper column.

Accuracy

Flow rates could be determined to within 1% but were reproducible only to within 10%. Errors, inherent in the analytical method used, caused uncertainties in the reported uranium concentrations as high as 70%. As shown in Appendix D, the calculated values of HETS are accurate to within $\pm 68\%$.

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The frequencies at which flooding occurred could be determined and reproduced to within ± 2 cycle/sec.

CONCLUSIONS

1. For any given flow rate, satisfactory operation of a pulse column is possible only within a specific range of pulse frequencies. At frequencies above and below this range, flooding occurs. Increasing the feed rate decreases the range of operating frequencies until a flow rate is reached at which flooding occurs at all frequencies.
2. Two distinct types of flooding may be observed in the column. Minimum-frequency flooding occurs when the amount of liquid pulsed through the plates is exceeded by the feed rate, and maximum-frequency flooding is the result of emulsification.
3. The type of solution treated as well as its previous history has a pronounced effect upon the conditions under which the column will operate.
4. The required flow rates and pulse frequencies to insure a turbulent flow regime are impractical in the present pulse column due to the development of opposing effects such as emulsification and phase inversion.
5. HETS values as low as 4.46 ft were achieved in the extractor.

RECOMMENDATIONS

1. The effect of acid content upon distribution coefficients for the stripper operation should be more completely studied.
2. Surface and interfacial tension and viscosity data should be taken so that a future attempt can be made to discover what correlations, if any, exist between these properties and column operating characteristics.

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3. Provision should be made so that the extractor and stripper columns may be pulsed at independently controlled frequencies because the extractor will operate at frequencies which are not satisfactory for the stripper.

4. An attempt should be made to check the assumptions inherent in the proposed frequency correlation.

PROCEDURE

Pulse Column Data

Two pulse columns were operated to remove uranium from concentrated solutions of aluminum nitrate containing various secondary impurities. An extractor column selectively removed uranium from the aqueous feed solution, and a stripper column transferred the uranium back to an aqueous product solution. A detailed description of the apparatus is presented in the Appendix.

A feed rate was selected at which the extractor column could be expected to operate satisfactorily over a range of frequencies. The system was started up at this feed rate at a frequency which should be in the operating range and then the frequency was increased until flooding occurred. The maximum operating frequency is the highest frequency at which the extractor will operate without flooding. Similarly, a minimum operating frequency was determined. Feed rates were selected so as to adequately cover the range of maximum and minimum flooding frequencies. At low feed rates, the extractor would operate at the highest frequency which the pulse pump would produce. Therefore, one maximum frequency point was determined by setting the highest pulse frequency available and increasing the feed rate until flooding conditions were noted. The pulse height of the stripper was adjusted to assure its satisfactory operation at whatever frequency the two pulse columns were set. The ratio of aqueous feed to carbitol feed was kept constant throughout the operations on a given batch as was the pulse height in the extractor. After an operating point was chosen, the necessary data were taken for a period of four hours in order to assure that steady state had been attained.

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Hourly measurements were taken of aqueous feed rate, raffinate rate, and aqueous product rate. Samples were taken hourly of the aqueous product, carbitol from the extractor, carbitol feed to the extractor, and raffinate for fluorimetric analysis. Samples of the feed solutions were taken for analysis each hour during steady-state operation. The pH of the carbitol feed was also taken approximately every four hours.

Equilibrium Data

Samples taken for equilibrium data were contacted in separatory funnels, shaken for two to five minutes, and allowed to separate. For the extractor, samples of aqueous feed were contacted with low carbitol. Water and high carbitol were contacted to determine strip-per distribution coefficients. The uranium concentrations in each phase of the sample were obtained by fluorometric analysis. From these data distribution coefficients were obtained.

Surface Tension and Viscosity Data

Surface tension and interfacial tension measurements for the column liquids were obtained with a Cenco du Noüy Tensionmeter. Viscosity data for these same solutions were obtained with an Ostwald viscosity pipette calibrated with distilled water.

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APPENDIX

A. SUMMARY OF DATA AND RESULTS

TABLE IA

Batch No.	Avg ppm Aqueous Feed	Avg ppm Aqueous Product	Avg ppm Raff- inate	Avg ppm High Carbitol	Avg ppm Low Carbitol	Average Aqueous Feed Rate cc/min	Average Aqueous Product cc/min	Average Raff- inate cc/min	Average Carbitol Recycle (cycles/min) cc/min	Pulse Frequency (cycles/min)	Extractor Water Balance %	Extractor U Balance %	Stripper U Balance %	HETS for Extractor ft.
91-0341	32	104	0.26	133	1.25	188	63	179	55	38	5.05	21.0	10.6	6.67
91-0341	32	44	0.50	62	0.20	95	65	87	50	14	9.2	3.0	8.0	9.55
91-0341	32	49	1.30	66	0.08	97	59	95	50	90	2.1	9.7	14.2	12.70
91-0341	32	48	0.07	60	0.60	268	186	255	125	42	5.1	15.0	5.7	6.28
91-0345	49	136	0.06	123	0.95	179	77	170	60	90	5.3	19.5	42.7	4.78
91-0345	49	102	0.13	166	1.70	163	124	157	60	90	3.8	24.6	27.2	6.10
91-0345	49	97	0.06	129	0.51	191	81	188	55	16	1.6	32.0	11.2	4.46
91-0346	42	140	0.05	116	0.10	393	107	375	133	67	4.8	6.9	2.8	4.77
91-0347	48	141	0.07	101	0.03	398	150	389	133	42	2.6	42.0	36.8	4.95
91-0347	48	121	0.04	95	0.06	288	203	279	100	90	3.2	45.3	159	4.65
91-0347	48	60	0.53	81	0.33	298	126	218	100	35	26.0	74.4	37.3	6.75

NOTES:

Pulse height in the extractor was held constant at 0.62 in. throughout the entire investigation.

Low carbitol is carbitol feed into the extractor and low in uranium concentration.

High carbitol is carbitol feed out of the extractor and high in uranium concentration.

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B. APPARATUS

Equipment

a. General Discussion. The principle elements of the pulse column apparatus are two 20-ft glass columns, two Milton-Roy pulse pumps, three Milton-Roy feed pumps, two Wilson Pulsafeeder diaphragm pumps, and a gear pump. Additional equipment includes a stainless steel storage tank for carbitol recycle, and a 55-gal stainless steel drum for water supplied to the stripper.

b. Glass Extraction Columns. The physical dimensions of the precision glass tubing were a column height of 20-ft and an inside diameter of 1.243 ± 0.001 in. Twenty-six gauge stainless steel plates perforated with 0.045 in. holes (21% free area) were assembled on a vertical rod through the entire height of the extraction section of the column. Plates were spaced 1-in. apart by stainless steel tubing. The columns were equipped with gravity legs for maintaining proper locations of phase interfaces.

c. Pumps. The Milton-Roy pulse pumps were positive displacement pumps with check valves removed. These pumps were located in the carbitol feed lines at the bottom of each column. There were two low-capacity Milton-Roy pumps admitting nitric acid to the system and a single Milton-Roy pump supplying carbitol to the bottom of the extractor column. The Wilson feed pumps were equipped with stainless steel diaphragms for pumping aqueous feed to the extraction column and carbitol to the stripper.

Regulation

a. General Discussion. Column control included a pulse frequency regulator on the pulse pumps, and a variable stroke for changing the pulse height. Gravity legs permitted a control on interface location in the columns. Variable strokes on the feed pumps permitted change of feed rates.

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PULSE COLUMN

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DATE 9-11-50 DRAWN BY G.T.P. FILE NO. EPS Y-108 FIG. A-1

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TABLE IV

PHYSICAL PROPERTIES OF LIQUID PHASES

Sample	Sp. Gravity	Viscosity (lb/(hr)(ft)	Surface Tension (dyne/cm)	Interfacial Tension (dyne/cm)
Water	1.000	2.165	70.06	-
Aqueous Product	1.06	2.572	40.00	-
Aqueous Feed	1.402	21.02	40.17	-
Affinate	1.30	12.27	40.96	-
Low Carbitol	0.925	7.57	31.72	-
High Carbitol	0.953	10.22	32.71	-
L. C. and affinate	-	-	-	14.90
H. C. and Aq. Feed	-	-	-	15.90
H. C. and Aq. Product	-	-	-	0.99
L. C. and Feed Water	-	-	-	11.01

NOTES:

Low carbitol refers to carbitol low in uranium content, that which enters the bottom of the extractor - and high carbitol refers to that which leaves the top of the extractor.

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C. TABLE OF NOMENCLATURE

D	partition coefficient, uranium concentration in the organic phase divided by that in the aqueous phase
E	extraction factor
H	aqueous feed rate, ml/min
HETS	height of an equivalent theoretical stage
N	number of stages
P	uranium analysis, ppm
R	raffinate rate, ml/min
S	organic rate, ml/min
Z_N	fraction of uranium unextracted after N stages

Subscripts

h	refers to aqueous feed
r	refers to raffinate

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D. SAMPLE CALCULATIONS

Batch No. 91-0341

Data taken from Data Book No. 1560 for August 29, 1950; 10:00 A.M.
to 7:00 P.M.

<u>Average Values</u>	<u>Rate ml/min</u>	<u>Analysis ppm</u>
Aqueous feed	95	32
Low Carbitol	50	0.2
High carbitol	50	62
Aqueous product	65	44
Raffinate	87	0.5

Overall Water Balance on Extractor

$$\left(\frac{95-87}{87} \right) 100 = 9.2\%$$

Uranium Balance on Extractor

In = Feed + Low Carb.

$$= (95)(32) + (50)(0.2) = 3040 + 10 = 3050 \text{ micrograms/min}$$

Out = Raff. + High Carb.

$$= (87)(0.5) + (50)(62) = 44 + 3100 = 3140 \text{ micrograms/min}$$

$$\% \text{ Diff.} = \left(\frac{3140-3050}{3050} \right) 100 = 3.0\%$$

Uranium Balance on Stripper†

In = High Carb.

$$= (50)(62) = 3100$$

Out = Aqu. Prod. + Low Carb.

$$= (65)(44) + (50)(0.2) = 2860 + 10 = 2870$$

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$$\% \text{ Diff.} = \left(\frac{3100-2870}{2870} \right) 100 = 8.0\%$$

Calculation of HETS for Extractor

Calculation of HETS is based on Eqn. 30 page 1247, Chemical Engineers Handbook

$$Z_N = \frac{E-1}{(E)^{N+1} - 1} \quad (1)$$

$$Z_N = \frac{R P_R}{H P_H} = \frac{(87)(0.5)}{(95)(32)} = 0.0143 \quad (2)$$

$$E = \frac{S D}{H} = \frac{(50)(27.8)}{95} = 14.61 \quad (3)$$

$$N+1 = \frac{\log \left(\frac{E-1}{Z_N} + 1 \right)}{\log E} = \frac{\log 953}{\log 14.61} = \frac{2.98}{1.16} = 2.57$$

$$N = 1.57$$

Although the total length of six 32-in. sections is 16 ft, the flanged joints reduce the column height to 15 ft.

$$\text{HETS} = \frac{15}{1.57} = 9.55 \text{ feet}$$

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Calculation of Theoretical Minimum Frequency

Column Pulse Height = 0.62 in

$$\begin{aligned}\text{Cross-Sectional Area of Column} &= \pi/4 \left(\overline{1.243}^2 - \overline{0.375}^2 \right) \\ &= 1.108 \text{ in.}^2\end{aligned}$$

$$\text{Volume in one Pulse} = 1.108 \times 0.62 = 0.686 \text{ in.}^3$$

$$\text{Volume in one Pulse} = 11.25 \text{ cc.}$$

Assume pulse to pull all of the organic down through plates

<u>cycle/min</u>	<u>cc/min</u>
10	112.5
30	337.5

E. SAMPLE PRECISION ANALYSIS

The analytical results were reported as being reliable to within the following percentages (2):

<u>ppm of sample</u>	<u>% error</u>
0.1	70
1.0	40
10.0	20
500	10

The estimated errors in the distribution coefficient and in the flow rates are as follows:

dD/D	=	± 0.60
dH/H	=	± 0.10
dR/R	=	± 0.10
dS/S	=	± 0.10

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$$E = \frac{SD}{H} \quad (3)$$

Then,

$$dE/E = dS/S + dD/D - dH/H = 0.80, \text{ and} \quad (4)$$

$$Z_N = \frac{R P_R}{H P_H} \quad (2)$$

$$dZ_N/Z_N = dR/R + dP_R/P_R - dH/H - dP_H/P_H \quad (5)$$

$$\begin{aligned} \left(\frac{dZ_N}{Z_N} \right)_{\max} &= 0.10 + 0.40 + 0.10 + 0.20 \\ &= 0.80 \end{aligned}$$

$$\text{Maximum } Z_N = (1.80)(0.0143) = 0.0258$$

$$\text{Minimum } Z_N = (0.20)(0.0143) = 0.00286$$

$$\text{Maximum } E = (1.80)(14.61) = 26.3$$

$$\text{Minimum } E = (0.20)(14.61) = 2.92$$

When Z_N is a minimum ($N+1$) will be a maximum. The calculation of ($N+1$) using both the high and the low value of E shows that the maximum value of ($N+1$) occurs when E is a minimum value. Similarly, the minimum value of ($N+1$) occurs at the maximum value of Z_N and the maximum value of E . The resulting maximum and minimum values of HETS are 13.5 ft and 3.0 ft as compared with a reported average of 9.55 ft.

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