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TO: W. J. Larkin
FROM: J. B. Robinson, and H. T. Tupper
SUBJECT: The Operation of a Pulse Column for the Production of Hafnium-free Zirconium

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INTRODUCTION

In order to produce hafnium-free zirconium at Y-12, hafnium thiocyanate complexes are currently being extracted from an aqueous feed by an organic phase. The organic phase is i-butyl methyl ketone containing both hydrogen and thiocyanate ions, which are extracted from the aqueous phase along with the hafnium. The extraction is accomplished in an unpacked column, 60 feet high. To investigate the feasibility of decreasing the height of the column, while maintaining the same separation, a pilot-size pulse column has been constructed and subjected to preliminary tests by Jasny and group (1).

The purpose of this investigation was to continue the tests on the pulse column. The effect of pulse frequency and through-put on the operation of this column was investigated. Also, an attempt was made to determine flooding conditions.

Work for this investigation was performed from May 4 to May 26, 1950.

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RESULTS

The results of the ten runs made are tabulated in Table I. Fig. 1 indicates the effect of flow rate and frequency of pulse on column operation. Fig. 2 is a plot of flooding conditions.

For Run 15, when the separation factor was 154, and the organic flow rate 261 gal/(hr)(sq ft), an HETS was found to be approximately 2 feet, but may range from 0.55 to 3.1 feet.

DISCUSSION OF RESULTS

For this work, pulse displacement was kept constant at 1.25 inches, and the organic to aqueous feed ratio was maintained at 3.1. Through-put and frequency were the variables studied.

Column efficiencies may be measured with the separation factor, α , which is defined:

$$\alpha = \frac{\frac{[Hf]_{in}}{[Hf]_{out}}}{\frac{[Zr]_{in}}{[Zr]_{out}}}$$

where [] represents the concentrations of the element in question in the aqueous phase. Hafnium concentrations are reported as parts per million parts of zirconium.

Fig. 1 shows that as the through-put is decreased, the efficiency of this column increases. A reduction in through-put increases the contact time for the two phases so that equilibrium conditions may be more closely approached.

An increase in frequency should also tend to give better separation because, for a given flow rate, the phases would be broken up and dispersed a greater number of times in their passage through the column. Emulsion formation would be expected to determine the maximum frequency that could be applied. The data plotted in Fig. 1 indicate that increasing frequency does give better separation, although the trend that is indicated is neither marked nor consistent. The point representing the highest frequency and the lowest flow rate would be expected to give the highest separation factor. That it does not is considered to result from imprecision of the data.

Runs 12 through 16 gave an exit hafnium concentration of 150 parts per million parts of zirconium or less in the leaving aqueous phase, a concentration closely approximating that achieved by the present plant. The best run from the standpoint of separation efficiency, which is commonly measured by the separation factor, was Run 15. This run was made at 261

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Table I

Summary of Results

Run	Aqueous Flow gal/(hr)(sq ft)	Organic Flow gal/(hr)(sq ft)	Fre- quency cyc/min	Zr Entering in Aqueous Molar	Hf Entering in Aqueous ppm in Zr	% Zr Extracted from Aqueous	% Hf Extracted from Aqueous	Hf Leaving in Aqueous ppm in Zr	Separation Factor for Aqueous*
7	173	528	55	1.27	22,000	26.7	98.7	275	59
8	243	756	45	1.21	14,300	20.7	91.2	1250	9
9	282	631	25	1.24	18,600	24.7	85.4	2700	5
10	171	514	25	1.32	24,000	26.2	98.3	400	44
11	132	404	55	1.29	20,000	37.5	98.7	250	50
12	85	256	55	1.33	23,500	31.7	99.4	120	134
13	48	139	55	1.20	22,000	18.3	99.3	140	131
14	40	130	70	1.34	23,500	38.3	99.5	100	145
15	83	261	70	1.33	23,700	35.2	99.5	100	154
16	124	382	20	1.38	14,000	43.9	98.9	150	52

*The separation factor, α , is defined as

$$\alpha = \frac{\frac{[Hf]_{in}}{[Hf]_{out}}}{\frac{[Zr]_{in}}{[Zr]_{out}}}$$

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PULSE DISPLACEMENT = 1.25 IN.

RATIO OF ORGANIC TO AQUEOUS FEED: 3/1

$$\text{SEPARATION FACTOR} = \frac{(Hf_{in})(Zr_{out})}{(Hf_{out})(Zr_{in})}$$

FREQUENCIES: (PULSES PER MINUTE)

Δ 25
○ 55
x 70

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EFFECT OF FREQUENCY AND FLOW
UPON SEPARATION FACTOR

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○ CONSTANT SOLID CONTENT
 × POINTS TAKEN FOR VARYING SOLID CONTENT
 PULSE DISPLACEMENT 125 IN.
 HEXONE: AQUEOUS FEED: 3:1

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FLOODING DATA

DATE 5-30-50	DRAWN BY JBR	FILE NO. EPS-Y93	FIG. 2
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gal/(hr)(sq ft) and a frequency of 70 cycles per minute. The separation factor was 154.

No equilibrium data for the distribution of hafnium between the aqueous and organic phases are available for the concentrations employed in this investigation. However, a partition coefficient under conditions of acid and thiocyanate concentrations closely approximating those of Run 15 was obtained (2). The HETS was calculated assuming complete immiscibility of the two phases, a constant partition coefficient, and no change in the volume of either phase in passing through the column (3).

Because the acid and thiocyanate concentrations have a marked effect upon the distribution of the hafnium, a precision of 30% was assumed for the value of the distribution coefficient. This, together with the 54% precision allowed for the fraction unextracted from the aqueous phase, resulted in a value of HETS of approximately 2 feet, though it may range from 0.55 to 3.1 feet. This is shown in the Precision Analysis of this report.

Flooding was defined for this work as the conditions under which appreciable loss of aqueous feed occurred in the organic effluent or of organic in the aqueous product. In most cases it was accompanied by a sudden change of interface position.

As shown in Fig. 2, the flooding point for the same conditions of flow, frequency and pulse displacement are not the same. The circled points of the plot were obtained on the same day in a period of about four hours. Each of the points represented by "X" was taken on a different day.

Solids in the system are believed to be the cause of this scattering. These solids are produced by the polymerization of thiocyanic acid, largely in the organic phase. They collected at the interface of the pulse column and had a marked effect upon flooding. As the result of differences in surface tension between the two phases, the solids may have encouraged emulsification, an effect that probably resulted in decreasing flooding rates with increasing solids content.

These points show, however, that the pulse column as built may not be expected to equal the spray columns presently used on the basis of throughput per square foot. The plant was operating at an approximate total flow of 2000 gal/(hr)(sq ft) during this investigation. The range of flooding points presented, 1000 to 500 total gal/(hr)(sq ft), is seen to be considerably below this value. No values are available in the literature for spray or packed columns using these phases, but the plant generally operates at about 80 percent of flooding.

Modification of the column at the top and bottom, through the use of either longer or larger diameter calming sections, would probably improve the flooding characteristics of the column.

Because of variation in the pressure at which the organic feed was available from the plant, the flow rate of this stream as it was delivered by

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the centrifugal pump varied correspondingly. In the worst instance this variation amounted to 36 gal/(hr)(sq ft). Detection of such changes was attempted through periodic checking of the flow rate as described in the procedure, but correction of such deviations was not rapid. The use of an indicating flow measuring device, such as a rotameter or an orifice would enable the reduction of such variations. The installation of a similar device in the aqueous feed line would also allow control of this stream to be more precise, though variations here were not as serious.

CONCLUSIONS

1. At a frequency of 55 cycles per minute and a pulse amplitude of 1.25 inches, the separation factor was observed to increase approximately two-fold as the aqueous flow rate decreased from 173 to 48 gal/(hr)(sq ft).
2. At the same amplitude and at an aqueous flow rate of about 84 gal/(hr)(sq ft), the separation factor increased from 134 to 154 when the frequency was changed from 55 to 70 cycles per minute.
3. The height of a theoretical stage at maximum efficiency, i.e., when the separation factor was 154, was approximately 2 feet, although precision calculations indicate that it may range from 0.55 to 3.1 feet.

RECOMMENDATIONS

1. Further investigations of the effect of variation in pulse displacement, plate spacing, plate hole size, through-put, and frequency should be carried out.
2. Flow measuring devices should be designed and installed for both incoming organic and aqueous streams, to facilitate adjustment and control.

PROCEDURE AND APPARATUS

The apparatus used in this investigation is described by Jasny and group (1). No changes were made in the equipment except that a mixer was installed on the feed tank.

To begin a run the pulse pump was started to insure that entering streams

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would not flood the column. The frequency was adjusted at this time. The flow of aqueous and organic streams was then started and the organic return pump started. After the flow of aqueous and organic streams was adjusted, the interface was moved to within the top ten plates of the column.

Flow of the two phases was measured by collecting the effluent streams in graduated cylinders for a known length of time.

Run 7 showed that a three-hour period was sufficient for the column to come to equilibrium, so all runs were five hours long, samples being taken for the last three.

For the experiments carried out in this investigation, column height, plate spacing, hole size, ratio of aqueous to hexone stream, and pulse displacement were kept constant. The variables were pulse frequency and flow rates. The data taken for each run were:

1. Flow rate of aqueous product and entering organic every half hour.
2. Spectrometer analysis of aqueous feed and product every hour.
3. Thiocyanate concentration in the organic entering and leaving the column and in the aqueous feed every hour.

Because Jasny and group completed six runs, similar to those carried out in this investigation, the first run was numbered 7 and subsequent runs were numbered in the order of completion.

LOCATION OF THE ORIGINAL DATA

The original data for this investigation are in Data Book 1556, pages 17 through 34.

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APPENDIX

A. Supplementary Detail

To facilitate comparison of the results obtained in this investigation with those of past and future work, the thiocyanate concentrations have been recorded in Table II.

B. Sample Calculations

1. Calculation of number of equilibrium stages for Run 15:

$$Z_N = \frac{E - 1}{E^{N+1} - 1}, \text{ or}$$

$$N + 1 = \frac{\log \left(\frac{E-1}{Z_N} + 1 \right)}{\log E}$$

where: Z_N = X_N/X_O , the fraction unextracted after the Nth stage.

X_N = concentration of hafnium leaving Nth stage

X_O = entering hafnium concentration

N = number of stages

E = extraction factor, $\frac{SD}{H}$

S = hexone rate (volumetric)

H = aqueous rate (volumetric)

D = partition coefficient

$$Z_N = \frac{\frac{100}{0.653}}{\frac{23,700}{1.008}}$$

$$= 0.00652$$

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$$\begin{aligned} E &= \frac{(3)(0.92)}{1} \\ &= 2.76 \end{aligned}$$

$$\begin{aligned} \frac{E-1}{Z_N} + 1 &= \frac{1.76}{0.00652} + 1 \\ &= 270 + 1 \end{aligned}$$

$$\begin{aligned} N + 1 &= \frac{\log 271}{\log 2.76} \\ &= 5.51 \end{aligned}$$

$$N = 4.51 \text{ stages}$$

$$\begin{aligned} \text{HETS} &= \frac{9.5}{4.51} = \\ &= 2 \text{ feet.} \end{aligned}$$

2. Calculation of separation factor, α :

$$\alpha = \frac{[Hf]_{in} [Zr]_{out}}{[Hf]_{out} [Zr]_{in}}$$

Where $[]$ are concentrations of the elements and Hf concentrations are given as ppm Hf in Zr.

For Run 15

$$\begin{aligned} \alpha &= \frac{(23,700)(0.653)}{(100)(1.008)} \\ \alpha &= 154 \end{aligned}$$

C. Precision Analysis

1. The spectrographic analysis of hafnium in zirconium was reported as being precise within 25%. The analysis of zirconium, done gravimetrically, was within 2%. Thus the separation factor was precise with-

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Table II

Thiocyanate Concentrations

<u>Run</u>	<u>Molarity</u>		<u>Aqueous Feed</u>
	<u>Organic Entering</u>	<u>Organic Leaving</u>	
7	2.22	2.55	2.27
8	2.35	2.63	2.11
9	2.20	2.74	2.23
10	2.25	2.71	2.38
11	2.34	2.75	2.31
12	2.21	2.79	2.45
13	2.29	2.66	2.37
14	2.22	2.72	2.51
15	2.17	2.75	2.34
16	2.16	2.66	2.47

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in 54%.

2. The thiocyanate concentrations, done volumetrically, are precise within 3%.
3. Because the HETS is calculated by a logarithmic function of E, the extraction factor, and Z_N , the fraction of hafnium unextracted from the feed, the following method of determining the precision of HETS was used:

From Sample Calculations:

$$N + 1 = \frac{\log \left(\frac{E-1}{Z_N} + 1 \right)}{\log E}$$

where $E = \frac{SD}{H}$

$$\frac{S}{H} = \frac{3}{1} \pm 20\%$$

$$D = 0.92 \pm 30\%$$

$$E = 2.76 \pm 50\%$$

$$Z_N = \left[\frac{H_f}{Z_r} \right]_{in} \left[\frac{Z_r}{H_f} \right]_{out} \pm 54\%, \text{ as pointed out above.}$$
$$= 0.00652 \pm 54\%.$$

From this, 4 cases of extreme imprecision seem possible:

1. $E = 1.38$
 $Z_N = 0.00300$

2. $E = 4.14$
 $Z_N = 0.01004$

3. $E = 1.38$
 $Z_N = 0.01004$

4. $E = 4.14$
 $Z_N = 0.00300$

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Using the same method of calculation shown in the sample calculations, the following values were obtained:

<u>Case</u>	<u>E</u>	<u>Z_N</u>	<u>N + 1</u>	<u>HETS</u>
1	1.38	0.0030	15.0	0.68
2	4.14	0.01004	4.05	3.1
3	1.38	0.01004	14.4	0.55 .92
4	4.14	0.0030	4.9	2.4

D. Literature Citations

1. Jasny, G. R., et al, "The Design, Construction, and Operation of a Pulse Column for the Purification of Zirconium", M.I.T. Practice School Report EPS-Y88, KT-69, Oak Ridge (1950).
2. Barton, C. J., Private Communication, Y-12, Oak Ridge, May 26, 1950.
3. Perry, J. H., "Chemical Engineers' Handbook", 2nd Edition, p 1247, New York, McGraw-Hill Book Co., Inc. (1941).

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