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UNITED STATES ATOMIC ENERGY COMMISSION

THE DESIGN, CONSTRUCTION, AND OPERATION
OF A PULSE COLUMN FOR THE PURIFICATION
OF ZIRCONIUM

By
P. M. Blair
H. C. Harrison
G. R. Jasny
G. R. Nelson

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ENGINEERING PRACTICE SCHOOL
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Union Carbide and Carbon Corporation

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INTRODUCTION

These two factors result in greater dispersion of both phases and increased mass transfer between phases, thus improving column efficiency.

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The purpose of this investigation was to design and construct a pilot size pulse column, and to determine its applicability to the Y-12 zirconium separation process. Preliminary experiments were designed to study the effect of throughput, pulse displacement and pulse frequency on product purity.

The work was performed during the period of April 10 to May 3, 1950.

RESULTS

The quantitative results of the investigation are summarized in Table I.

The following qualitative observations were made:

1. The column assembly did not leak.
2. No carryover of either phase was observed in the exit streams over the range of variables studied.
3. The solids present as a result of the condensation of some of the thiocyanic acid molecules tended to collect at the interface, and did not plug the plate perforations. No observations were made as to their effect on the efficiency of the column.
4. Good dispersion of the organic phase was obtained during the upstroke only. As a result, a certain amount of agglomeration of the organic phase was noticed between the plates during the downstroke.

DISCUSSION OF RESULTS

Operating Variables

Pulse Variations

Although the data presently available are not sufficient to be conclusive, they indicate that, within the conditions of the experiment, when other variables are held constant:

1. An increase of upulse frequency from 55 to 90 cycles/min. improves product purity (Runs 2 and 3).
2. Similarly, an increase of pulse amplitude to the point where the surge carries through two plates instead of only one plate also improves product purity (Runs 5 and 6).

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TABLE I
SUMMARY OF QUANTITATIVE RESULTS

Run	Total Flow Rate gal/(sq ft)(hr)	Pulse Frequency Cycles/min	Duration of run hrs	Pulse Displacement inches	ppm Hf in Feed	Molarity of Zr in Feed	Separation Factor	% Zr Extracted	% Hf Extracted	ppm Hf in Product	Appr. HETS ft
1	283	55	6.5	$\frac{1}{2}$	27000	1.23	20	38	97	800	-
2	1080	55	8	$\frac{1}{2}$	22000	1.28	8	28	90	2200	-
3	940	90	4	$\frac{1}{2}$	30000	1.20	24	26	97	900	-
4	655	90	6	$\frac{1}{2}$	14400	1.14	5	20	84	2300	-
5	655	55	4	$\frac{1}{2}$	31000	1.11	5	21	85	4600	-
6	660	55	4	$1\frac{1}{4}$	25000	1.15	30 ± 15	26	98	500	2.5 ± 1.8

CNS Concentrations

Organic Feed : 2.0 N
Organic Product: 2.6 N
Aqueous Feed : Not determined

- Note: 1. All runs were made at room temperature
2. All runs were made pulsing through one plate except Run 6 in which the pulse extended through two plates
3. In all runs, the ratio of flow rates, aqueous to organic, was $\frac{1}{3}$

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These results appear logical in view of the fact that a rise in either pulse frequency or displacement represents an increase in energy input to the column, the increase resulting in better dispersion and mass transfer. However, emulsification is undoubtedly a factor in setting an upper limit on the improvement in separation efficiency which can be achieved by raising pulse frequency and displacement. A very long pulse displacement may also decrease efficiency by causing a mixer-settler effect which would decrease the overall mass transfer obtainable.

Throughput Variations

An increase in total throughput seems to decrease column efficiency (Runs 1 and 5). In this respect, the pulse column differs from spray towers. The difference may be explained by considering the fact that in spray towers good dispersion is caused by high flow rates, while in the pulse column dispersion is largely independent of flow rates. In the pulse column, the decrease in contact time caused by higher flow rates is not counterbalanced by increased dispersion and mass transfer, resulting in a lower efficiency of separation.

Evaluation of Optimum Column Performance

The most favorable run to date was conducted with a total flow rate of 660 gal/(hr)(sq ft), pulse frequency of 55 cycles per second, and a $1\frac{1}{4}$ inch pulse. The results of this run indicate that:

1. The purification resulted in a reduction of the hafnium concentration from 20,000 ppm to 500 ppm. This represents a 98% removal of hafnium but is not quite as good as present plant operation which reduces hafnium concentration to 100 ppm.
2. Twenty-six per cent of the zirconium was also extracted.
3. The separation factor was 30 ± 15 .
4. On the basis of hafnium removal, an approximate HETS of $2.5 \text{ ft} \pm 1.8 \text{ ft}$ was calculated.

A comparison of these results with mixer-settler data on the same system and approximately the same concentrations (2) indicate that the column was approximately equivalent to six mixer-settler stages. If this extrapolation and comparison is correct, the separation obtained would result in an estimated reduction of the required height by at least 80%, or from 60 feet to 13 feet, assuming a scale-up factor of unity.

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Separation Factor

A measure of the efficiency of column operation is the separation factor which is expressed by the following equation:

$$\alpha = \frac{\frac{[Hf]_{in}}{[Zr]_{in}}}{\frac{[Hf]_{out}}{[Zr]_{out}}} \quad (1)$$

where α = separation factor

$[Zr]$ = concentrations of zirconium in the inlet and outlet aqueous streams

$[Hf]$ = concentrations of hafnium in the inlet and outlet aqueous streams.

The best separation factor obtained in the current experiments has a value of 30 ± 15 as compared to a factor of approximately 100 for the pilot plant under optimum operating conditions. These separation factors correspond to hafnium removals of 98% and 99.5% in the pulse column and pilot plant respectively. Thus, the reader is cautioned against interpreting the wide variation in separation factors as an indication of poor hafnium removal in the pulse column.

H.E.T.S.

The calculation of the height equivalent to a theoretical stage was based on the following assumptions: Complete immiscibility of the two solvents, no change in the volume of either phase, and constant partition coefficient for the hafnium. In view of the relatively low mutual solubilities of methyl isobutyl ketone and water the first two assumptions appear quite justified. The assumption of constant partition coefficient was dictated by the absence of equilibrium data for the distribution of hafnium between methyl isobutyl ketone and water. The value which was used for the partition coefficient (Hf in organic/ Hf in aqueous) was 0.75. This value was determined by Barton (4) under conditions similar to those of Run 6. However, because small variations in acid and thiocyanate concentrations greatly affect the value of the partition coefficient, the calculated HETS of 2.5 ft for the best run was found to be precise within 70%.

This low precision precludes a comparison of this HETS with the 14 in. HETS which was estimated to be a safe guess at the time the column was designed.

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Effect of Solids

The solids in the column did not plug the plate perforations. In this respect, the pulse column appears more suitable to the zirconium process than packed towers which suffered markedly from solid accumulation on the packing (2). However, it must be remembered that solids seem to hamper mass transfer in the spray towers (5), and there is no evidence as yet to show that they do not decrease the efficiency of the pulse column in a similar manner.

Effect of Pulsation

Visual inspection of the column in operation showed organic dispersion only on the upstroke with some agglomeration and very little backflow of this phase occurring on the pulse downstroke.

Therefore the beneficial action of the pulse may be thought of as consisting of two phases:

1. A dispersing action with the corresponding increase in interfacial area available for mass transfer on the upstroke.
2. A sweeping action of the continuous aqueous phase past the essentially stationary organic bubbles on the downstroke which promotes a good concentration gradient or driving force.

CONCLUSIONS

1. The experimental pulse column constructed for this investigation appears satisfactory for zirconium purification.
2. Structurally, the column performed well, showing no plugging by solids and no leakage.
3. Increasing the frequency and displacement of the pulse appears to increase column efficiency in the range of variables studied. On the other hand, increasing the total flow rate appears to decrease column efficiency.
4. Under the conditions of Run 6, the most favorable run of this investigation, the height of the column is approximately equivalent to six mixer-settler stages.
5. For the same run, an HETS of 2.5 ft $\pm$ 1.8 ft was calculated on the basis of hafnium removal.
6. If conclusion 4 is correct, a pulse column would reduce the height necessary to obtain the present product purity of 100 ppm of hafnium by at least 80%, assuming a scale-up factor of unity.

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RECOMMENDATIONS

1. Further experimentation should be carried out to determine optimum operating conditions with regard to the following column variables: throughput, pulse height, pulse frequency, plate spacing, and plate hole size. Flooding characteristics should also be determined.
2. The applicability of the pulse column to the scrubbing of the organic extract with hydrochloric acid should also be investigated.

DESCRIPTION OF APPARATUS

The test column (Figs. 1, 2, 3, 4) has an effective height of 9 ft 6 in. It consists of 92 stacked $1\frac{1}{2}$ in. i.d. glass pipe sections, each 1 in. high. These are assembled in three 45 in. lengths, each of which is maintained in compression by means of Hastelloy end plates connected by steel tie rods. The plates are made of 2 in. platinum squares 0.005 in. thick, perforated with 130 holes per square inch, each hole 0.043 in. in diameter. Each plate has a free area of 19%. Triangular Koroseal gaskets are used throughout the column. An adjustable gravity leg, connected to the aqueous outlet, controls the level of the interface.

The pulse column is similar to a conventional liquid-liquid extraction column with regard to inlet and outlet streams, i.e., the aqueous solution enters at the top and the organic at the bottom. Both feeds are drawn from plant streams in Building 9211 at Y-12. The organic phase is fed to the column by means of a glass-lined centrifugal pump. Two $1/16$ in. Teflon orifices are located in the organic feed line to create a pressure drop which limits the pump capacity to the desired range; a bypass valve is used for final flow regulation. A "Squeegee" pump is used for the aqueous feed. In this pump the fluid passes through a flexible hose which is subjected to a milking action by a row of steel fingers connected to a variable speed camshaft.

The pulse is applied above the organic inlet at the bottom of the column. It is provided by a variable stroke, positive displacement Milton-Roy pump with all check valves removed. This pump is equipped with a thymatrol regulator which allows the pulse frequency to be varied.

Glass or Saran piping is used throughout the apparatus. All valves are glass lined and are equipped with Teflon-covered Tygon diaphragms.

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PROCEDURE

Experimental data were taken in order to determine the effect of total throughput, pulse displacement, and pulse frequency on product quality. No studies were made of column operation without pulse, nor were the flooding characteristics of the column investigated. The organic aqueous feed ratio was kept constant at approximately three to one and the interface was maintained near the top of the column between the first and fifth plates. Column height, hole size, plate spacing, and free area of the plates were also kept constant during this investigation.

The organic and aqueous feeds were drawn directly from existing plant lines. The organic overflow was piped back directly into the main system, but the aqueous product was collected in carboys and returned to the plant feed tanks.

The conditions for any run or set of runs were obtained as follows:

1. The desired vertical displacement was obtained by adjusting the length of the stroke of the pulse pump piston. The actual pulse amplitude was determined by measuring the movement of the fluid meniscus at the top of the column.
2. The pulse frequency was set by means of the thymatrol.
3. The organic flow rate was adjusted by the regulation of a valve on the bypass line of the centrifugal feed pump.
4. The aqueous flow was set by adjusting the speed of the "Squeegee" pump.

Both aqueous and organic flow rates were determined by volumetrically measuring the flow from the outlet streams for a given time interval.

All experimental runs were of sufficient duration to insure at least several hours of operation near steady state conditions. Approximately 4 hours were required to obtain steady state operation when the column had not been in operation before the run. However, runs which were merely continuations of other runs with a minor change of a variable required about 2 hours.

Samples of both aqueous streams and of the exit organic stream were taken for laboratory analysis once an hour. Thiocyanate concentrations were determined by titrations carried out by this group in Building 9211. Hafnium and zirconium concentrations were determined

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by the process control laboratory; gravimetric analysis was used for the zirconium determination and spectrographic analysis was used for the hafnium.

Flow rates were checked every half hour. The interface level was checked and adjusted by raising or lowering the gravity leg as often as was necessary to maintain it at the proper height.

The original data are located in Data Book No. 1556 on pages 12-17.

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APPENDIX

A. Design Considerations

The design of the experimental pulse column was governed by the following overall considerations:

1. Availability of corrosion-resistant materials.
2. Adaptability of the column for experimental modifications.
3. Results from previous investigation of pulse columns at Hanford (1).
4. Desire to duplicate the present pilot-plant product purity so that the pulse column might be integrated into the present system.

Detailed considerations were as follows:

1. Column size

The choice of the column height was influenced by the following:

- a. Plant estimates indicate that the present plant column operation represents eight mixer-settler stages.
- b. The Hanford report cites a maximum height of 7 in. for an HETS at a flow rate of 1500 gal/(sq ft)(hr) for uranium extraction in a 2" column (1).

It was decided that an estimated HETS of 14 in. would allow a sufficient margin of safety. Therefore, an effective height of 9½ ft was chosen, this being equal to eight 14 in. stages.

A column diameter of 1½ in. i.d. was chosen because of the immediate availability of gasket and plate materials of this size. By comparison with the Hanford column, a pulse column of this size was expected to allow a maximum throughput of more than 1500 gal/(sq ft)(hr).

2. Column assembly

Two types of column construction which did not require extensive glass work were feasible. One of these was the system used at Hanford where a single glass section was used, inside of which plates were supported and spaced on a center rod. The other alternative was a column composed of stacked glass sections, with gaskets and plates inserted between each section. The Hanford column design

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has more flexibility with regard to plate spacing and less with regard to column height than the stacked column. It offers fewer structural problems from the point of view of rigidity, but requires uniform glass tubing and accurate machining of the plates.

The stacked column was chosen because in this type of column the thin perforated platinum sheet available could be utilized as plates. This type of construction would eliminate any chance of side leakage around the plates.

The column was assembled in three separate units which were bolted together end to end. This was done to prevent any tendency on the part of the column to bow or buckle, and also to facilitate future changes in column height. Added rigidity was obtained by using three-cornered gaskets throughout the column, and by passing the tie rods through the holes in the corners of the gaskets.

A plate spacing of $1\frac{1}{4}$ in. (1 in. glass section with two $1/8$ in. gaskets) was chosen because.

- a. Good results were obtained at Hanford with 1 in. spacing.
- b. With a small original plate spacing a large number of different spacings could be obtained by the removal of appropriate plates.

A Hastelloy Milton-Roy proportioning pump equipped with a thymatrol and with all check valves removed was chosen as the pulse pump because of the wide range of pulse frequency and displacement that it affords. A "Squeegee" pump was used in the aqueous feed line, because it offers a suitable range of flow rates and accurate control at the low flow rates used. A glass-lined centrifugal pump was selected for the organic feed since it was feared that in view of the relatively high organic aqueous volume ratio, a positive displacement pump might set up a pulse which would interfere with the desired effect. Each of these pumps had the necessary corrosion resistance.

Rotameters were not used to measure flow rates because of the corrosiveness and turbidity of the fluid streams. Instead, it was decided to determine flow rates by weighing samples of the outlet streams.

3. Column Materials

The major consideration in choosing the column materials was corrosion. The column itself was constructed of standard $1\frac{1}{2}$ in. i.d. glass pipe because glass pipe is now in satisfactory use in pilot plant operations, showing no corrosion damage.

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—KEY—

- PULSE COLUMN

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FLOW SHEET
FOR
EXTRACTION PROCESS

DATE 4-24-50	DRAWN BY HH	FILE NO EPS-Y88	FIG 2
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PULSE COLUMN

DATE	DRAWN BY	FILE NO.	FIG.
30 JUNE '50	-	EPS - Y88	3

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EXPLODED VIEW
OF
COLUMN

DATE	DRAWN BY	FILE NO.	FIG.
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The plates were cut out of perforated platinum sheets. These were not expected to suffer from corrosion, and had the added advantage of being perforated in a manner similar to the plates used in the Hanford experiment. Porcelain filter plates were considered, and subsequently discarded because of their friability under pressure. Various plastics such as Saran and Fluorothene, were also found to be satisfactory from the corrosion standpoint, but the ready availability of the platinum sheets determined the choice of the latter.

Two types of corrosion-resistant gaskets, Koroseal and Teflon-covered Chemiseal, were available. The Koroseal was not expected to have as long a life as the Teflon, but it was chosen because it offered the advantages of greater pliability, better fit, and much lower cost.

End plates were constructed of Hastelloy because this was the only metal available that was sufficiently resistant to the corrosive nature of the process fluids.

B. Sample Calculations

1. Separation Factor

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

where α = separation factor

$[\text{Zr}]$ = concentration of zirconium in aqueous stream,
lbs/gal

$[\text{Hf}]$ = concentration of hafnium in aqueous stream
parts of Hf per million parts of zirconium

For Run 6,

$$\alpha = \frac{20,000 \times 0.656}{0.889 \times 500} = 29.6 \cong 30$$

= 30 $\pm$ 15 (see precision analysis)

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2. H.E.T.S.

$$Z_N = \frac{E - 1}{E^{N+1} - 1} \quad (\text{Perry, 2nd ed. p. 1247})$$

where $Z_N = \frac{X_N}{X_0}$ = fraction unextracted after N stages

X = Hf concentration, parts/million parts Z_r

N = number of stages

E = extraction factor, $SD/H = 3D$

S = organic rate

H = aqueous rate

D = partition coefficient, organic/aqueous

$$Z_N = \frac{(500)(1.15)}{(25,000)(0.85)} = 2.7 \times 10^{-2} = 0.027$$

$$E = (0.75)(3) = 2.25 \quad (\text{see Ref. 2})$$

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

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

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

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

$$= \frac{\log\left(\frac{2.25 - 1}{0.027} + 1\right)}{\log 2.25}$$

$$= \frac{\log(46 + 1)}{\log 2.25}$$

$$= \frac{1.67}{0.352} = 4.74$$

$$N = 4.74 - 1 = 3.74$$

$$\text{H.E.T.S.} = \frac{2.5}{3.7} = 2.5 \text{ ft} \quad (\text{see precision analysis})$$

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C. Precision Analysis

1. Separation Factor, α

$$\alpha = \frac{[Hf]_{in} [Zr]_{out}}{[Zr]_{in} [Hf]_{out}} \quad (1)$$

The precision of α is the sum of the precisions of the entering and leaving metal concentrations in the aqueous stream.

<u>Concentration</u>	<u>Precision, %</u>	<u>Type of Analysis</u>
Hf in	25	spectrographic
Hf out	25	spectrographic
Zr in	2	gravimetric
Zr out	2	gravimetric

Precision of α = 54

2. H.E.T.S.

$$N+1 = \frac{\log(\frac{E-1}{Z_N} + 1)}{\log E} \quad (2) \quad (\text{see sample calculations})$$

where $E = \frac{\text{Organic rate}}{\text{Aqueous rate}}$ (Distribution coefficient)

$Z_N = \frac{[Hf]_{out}}{[Hf]_{in}}$ in aqueous stream.

Precision of flow rates = 10%

Precision of Distr. Coeff. = 30%

Precision of E = 10 + 10 + 30 = 50%

Precision of Hf = 25%

Precision of Z_N = 25 + 25 = 50%

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$$E = 2.5 \pm 1.25 = 3.75 \quad \text{or} \quad 1.25$$

$$Z_N = 0.027 \pm 0.014 = 0.041 \quad \text{or} \quad 0.014.$$

Possible combinations of E and Z_N, and resulting H.E.T.S.

	E	Z _N	HETS, ft
1	3.75	0.041	4.3
2	3.75	0.014	3.2
3	1.25	0.041	1.3
4	1.25	0.014	0.8

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