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Computer Simulation of Zirconium-Hafnium Separation by Countercurrent Extraction

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ABSTRACT

In carrying out research and development on an improved method for production of reactor-grade zirconium oxide, the Bureau of Mines has prepared a computer program capable of accurately predicting the stage-by-stage performance of a multistage countercurrent solvent extraction system for separation of zirconium from hafnium using a tertiary amine extractant. The results were used to plan laboratory experiments using a multistage countercurrent mixer-settler unit. The number of extractor stages, number of scrubber stages, feed solution concentrations, scrubber solution concentration, feed flow, scrubber flow, and organic-phase flow are the significant variables. The computer simulation indicates the effects of changes in the pertinent variables and makes it possible to locate the best combination of variables without a prohibitively large number of time-consuming experiments.

INTRODUCTION

This research was performed by the Bureau of Mines, U.S. Department of the Interior, in accordance with its mission to contribute toward the continued viability of the domestic minerals and materials economy and the maintenance of an adequate minerals base.

Zirconium alloys are commonly used in nuclear reactors because these alloys are highly resistant to corrosion, strong at high temperature, and nearly transparent to thermal neutrons. In nature, zirconium minerals contain 1 to 4 wt-pct of neutron-absorbing hafnium. The desirable properties of zirconium can be used in nuclear reactor construction only if the hafnium content is decreased to 60 ppm or less. However, the removal of hafnium is difficult because of its chemical similarity to zirconium.

The present industrial process for purifying zirconium (hexone-thiocyanate extraction) has problems of air and water pollution. Bureau of Mines research was undertaken to develop an alternative system for liquid-liquid separation of zirconium from hafnium. The system consists of an aqueous phase containing zirconyl-hafnyl sulfate in dilute H_2SO_4 and a water-immiscible organic phase containing 10 pct Alamine 336 (1) and 5 pct decanol in kerosene. The computer simulation is applicable only to this system. A typical flow chart for this separation, assuming the use of mixer-settlers, or other equipment providing an integral number of contacting stages, is shown in Fig. 1. The aqueous feed solution, consisting of zirconyl and hafnyl sulfates in dilute H_2SO_4, enters at the first extractor stage (EX1), while lean neutralized Alamine 336 solution enters at the last extractor stage (EX2). Scrubber acid (dilute H_2SO_4) enters at the first scrubber stage (SC1). In each scrubber and extractor stage, both zirconium and hafnium are distributed between the aqueous and organic phases. Zirconium prefers the organic phase. Distribution of H_2SO_4 between the two phases also occurs. In the last extraction stage, uptake of H_2SO_4 by the incoming neutral organic phase is substantial. In the stripper stages (ST1 and ST2), zirconium is removed from the loaded organic phase, producing an aqueous strip liquor low in hafnium. The

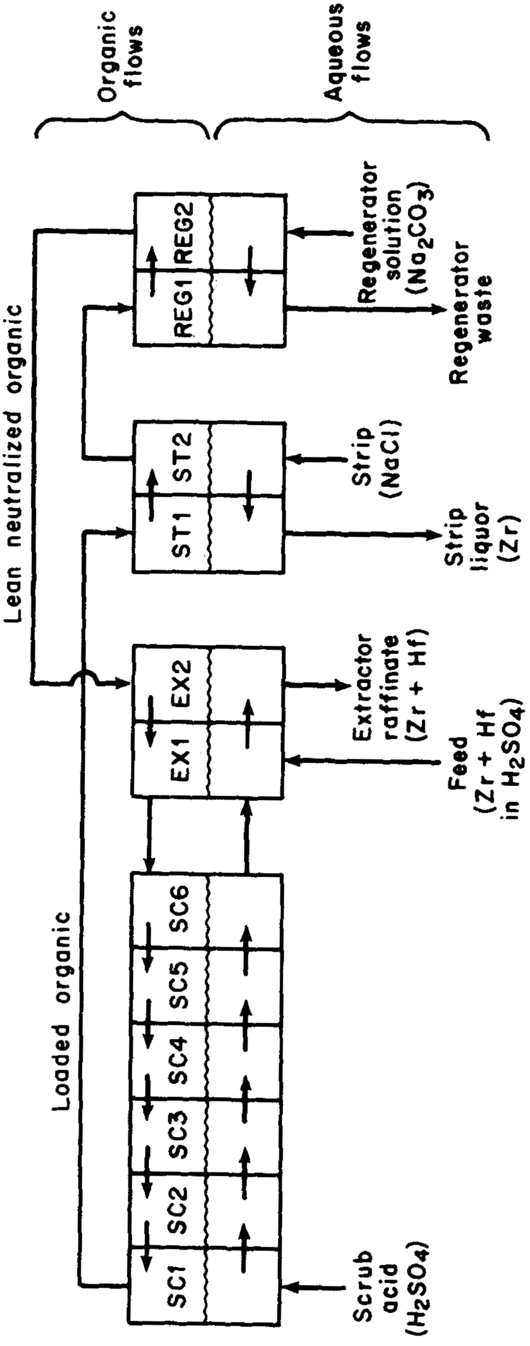

Fig. 1. Flow chart for multistage countercurrent solvent extraction.

organic solution is restored to a lean and neutralized condition in the regenerator stages (REG1 and REG2).

The computer program simulates only the scrubber and extractor stages--that part of the system responsible for Zr-Hf separation. Effective separation depends on maintaining appropriate aqueous and organic-phase concentrations of both zirconium and hafnium. Benedict and Pigford (2) indicate that the concentrations for most effective separation of a two-component mixture by liquid-liquid extraction depend on a phase ratio or flow-rate ratio given by

$$Q_{aq}/Q_{org} = \sqrt{D_1 D_2} \ . \qquad (1)$$

In the case of zirconium and hafnium, the distribution coefficients (D_1 and D_2) are not constants, but are nonlinear variables dependent on the aqueous-phase acid concentration and the total organic-phase loading. Therefore, the ideal situation described by Benedict and Pigford can be only approximated in each mixer-settler stage. Only the system as a whole can be optimized, because none of the scrubber or extractor stages can operate independently of the others. The complexity of these factors made it desirable to develop a predictive technique to guide the planning of bench-scale experiments and to indicate the effect of individual variables. Without the computer simulation it would have been difficult, if not impossible, to determine suitable operating conditions.

A literature search on liquid-liquid extraction did not indicate any prior mathematical analysis of a two-component separation that would be directly applicable to the problem of zirconium-hafnium separation in mixer-settler equipment.

ZIRCONIUM EXTRACTION

The extraction of zirconium and hafnium into Alamine 336-kerosene solution from aqueous sulfuric acid takes place according to the equation

$$2(R_3NH)_2SO_{4\,(org)} + ZrO(SO_4)^{2-}_{2(aq)} \rightleftharpoons$$

$$(R_3N)_4ZrOSO_{4\,(org)} + H_2SO_{4\,(aq)} + 2HSO^{-}_{4\,(aq)}, \qquad (2)$$

in which R_3N signifies the tertiary amine, Alamine 336.

The distribution of zirconium and hafnium can be represented by an empirical equation:

$$[Zr]_{org} = \frac{[Zr]_{aq}}{\dfrac{[Zr]_{aq}}{A} + B}, \text{ where} \qquad (3)$$

$A = 4.39 + 0.36\ (1.10 - [H_2SO_4])$, and (4)

$B = 0.039 - 0.056\ (1.10 - [H_2SO_4])$. (5)

The empirical relation was developed by linear regression analysis of Bureau data (to be published) on equilibrium distribution of zirconium between the aqueous and organic phases. The equation applys to an organic phase consisting initially of 10 wt-pct Alamine 336, 5 wt-pct decanol, and 85 wt-pct kerosene and to a range of H_2SO_4 concentrations from 0.65 to 1.3 molar and $[Zr]_{aq}$ of not less than 0.1 g/l. Equation (3) is plotted in Fig. 2. The graph shows the nonlinear relationship of $[Zr]_{org}$ to $[Zr]_{aq}$ and its dependence on H_2SO_4 concentration.

Since zirconium is present in greater concentration than hafnium throughout the process, hafnium is not treated as a separate component but is lumped together with zirconium for computations using Eq. (3). The difference in extractability

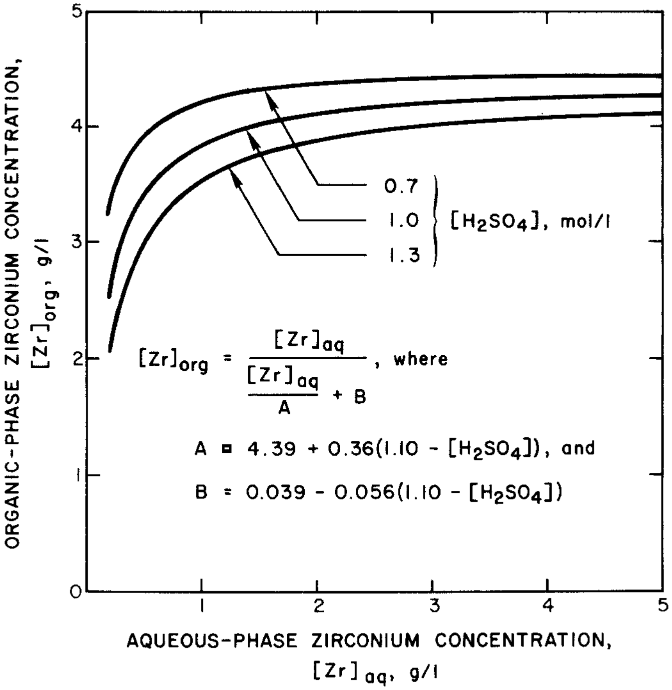

Fig. 2. $[Zr]_{org}$ versus $[Zr]_{aq}$, according to empirical Eq. (3).

between zirconium and hafnium is expressed in terms of the separation factor, α, defined by

$$\alpha = \frac{[Zr]_{org} \quad [Hf]_{aq}}{[Zr]_{aq} \quad [Hf]_{org}} \quad . \qquad (6)$$

The value of α is approximately 9, but varies slightly with H_2SO_4 concentration. In the computation, values of α are determined by interpolation between smoothed experimental values obtained at the Reno Research Center through chemical analysis of equilibrium mixtures over a range of H_2SO_4 concentrations. Zirconium concentrations were measured by X-ray fluorescence analysis employing separate aqueous-matrix and organic-phase-matrix standards. Hafnium concentrations were measured by a radioisotope tracer technique.

COMPUTER SIMULATION METHOD

The program is written in FORTRAN IV, and has been run on a CDC Cyber 171/96 computer in interactive mode under the KRONOS operating system. The program requires 46,000 words of octal memory. Copies of the program are available on request.

The general operation of the program is shown in the flow chart, Fig. 3. Subroutine STAGE is used to calculate the equilibrium distribution of combined Zr and Hf for each scrubber and extractor stage according to Eq. (3). Subroutine SEPFAC yields a value of α for each stage, which is returned to STAGE to control the adjustment of $[Zr]_{aq}$, $[Zr]_{org}$, $[Hf]_{aq}$, and $[Hf]_{org}$. Agreement is reached between phase distribution of total metals and the required value of α. Control then returns to the main program for assessment of an overall mass balance on both Zr and Hf. Results are printed when the desired mass balance is achieved, or when 40 cycles of iteration are completed.

The computational routine simulates the stage-by-stage adjustment of aqueous-phase and organic-phase concentrations that would occur in a typical multistage system such as that shown in Fig. 1. Any stage can be selected as the feed stage or first extractor stage, but in analogy to a distillation column, better separation is achieved if the feed is introduced at the stage whose steady-state aqueous-phase composition most closely approximates the composition of the feed solution.

The program accounts for transfer of H_2SO_4 from aqueous phase to organic phase to reacidify the organic extractant in the last extractor stage.

The printed results include a list of calculated concentrations of Zr and Hf for aqueous and organic phases of each scrubber and extractor stage and the calculated H_2SO_4 concentration for the aqueous phase of each scrubber and extractor stage. The aqueous-phase Hf/(Zr+Hf) ratio for each stage is also printed. This tabulation can be used to verify

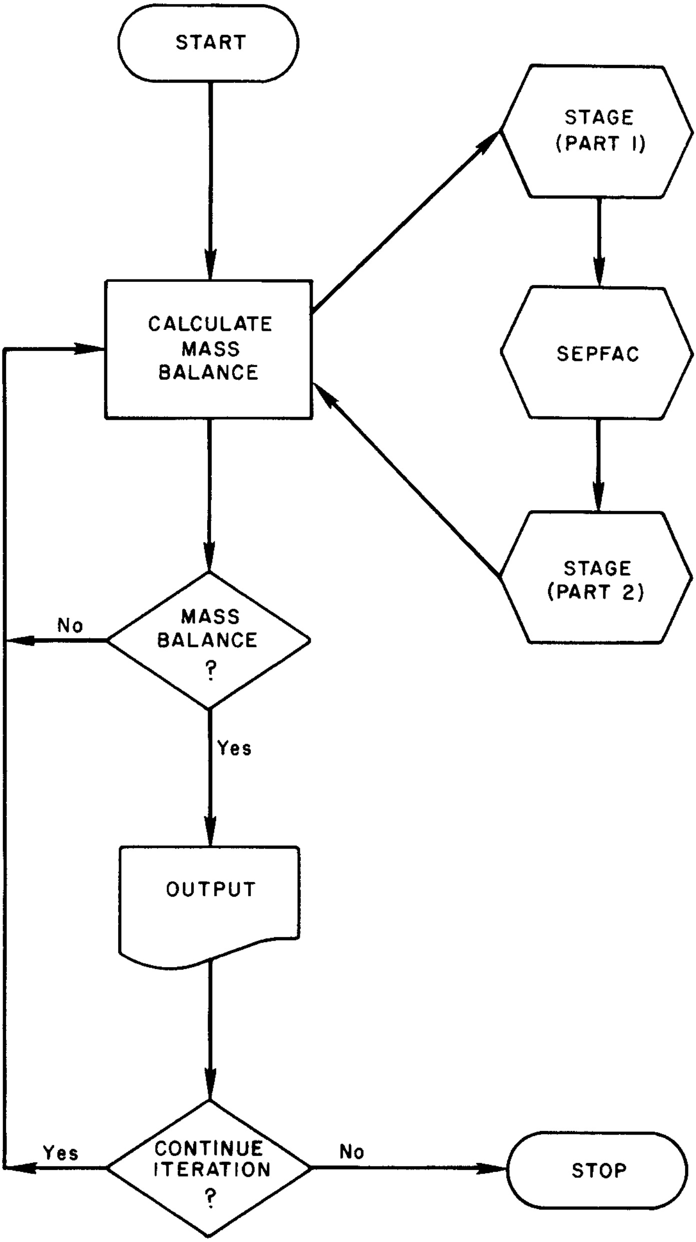

Fig. 3. Program flow chart.

that the Hf/(Zr+Hf) ratio at the feed stage is close to that of the feed solution. The most significant items of output are recovery of Zr, that is, the percentage of Zr mass in strip liquor relative to Zr mass in feed solution; and product purity, that is, the weight ratio Hf/(Zr+Hf) in strip liquor, given in parts per million.

RESULTS

Tables 1 and 2 show the numerical results of the program for input that describes the operating conditions used in two representative mixer-settler experiments. For comparison, the corresponding experimental values for concentrations at steady state in each stage are shown. The program predicts recovery within a few percentage points, but at the very low levels of Hf the prediction of product purity may be in error by ±20 ppm Hf. The error is not necessarily attributable to the computer program, because the experimental result contains substantial error caused by imperfect control of flow rates and reagent concentrations. The computer simulation affords higher precision than can be achieved experimentally in successive mixer-settler runs.

EFFECT OF VARIATIONS IN OPERATING CONDITIONS

Computer-predicted variations in recovery and purity of zirconium in the strip liquor are shown in Figs. 4 through 7 as functions of the operating variables. These variations result from parametric changes from the following basis conditions:

$N_{sc} = 9$, $N_{ex} = 3$

$[Zr]_{feed} = 15$ g/l $[Hf]_{feed} = 0.201$ g/l

$[H_2SO_4]_{feed} = 1.0$ mol/l $[H_2SO_4]_{scr} = 1.0$ mol/l

$Q_{feed} = 12$ ml/min $Q_{strip} = 12$ ml/min

$Q_{scr} = 25$ ml/min $Q_{org} = 45$ ml/min

Table 1. Comparison of Computer-Simulated Results with Experimental Results (Mixer-Settler Run A)

$N_{sc} = 9$, $N_{ex} = 3$

$[Zr]_{feed} = 14.31$ g/l

$[Hf]_{feed} = 0.256$ g/l

$[H_2SO_4]_{feed} = 1.0$ mol/l

$[H_2SO_4]_{scr} = 1.0$ mol/l

$Q_{feed} = 12$ ml/min

$Q_{strip} = 12$ ml/min

$Q_{scr} = 25$ ml/min

$Q_{org} = 46$ ml/min

	$[Zr]_{aq}$ (g/l)		$[Hf]_{aq}$ (g/l)		$[Zr]_{org}$ (g/l)		$[Hf]_{org}$ (g/l)		$[H_2SO_4]$ (mol/l)	
Stage	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
SC1	.45	.46	.00017	.00010	3.36	3.2	.00013	.00006	1.00	1.12
SC2	.65	.66	.00037	.00017	3.61	3.4	.00022	.00014	1.00	1.11
SC3	.77	.79	.00063	.00036	3.71	3.5	.00033	.00024	1.00	1.11
SC4	.86	.88	.00098	.00072	3.78	3.6	.00045	.00041	1.00	1.09
SC5	.94	1.0	.00150	.00105	3.83	3.7	.00065	.00059	1.00	1.09
SC6	1.03	1.1	.00231	.00166	3.87	3.7	.00093	.00081	1.00	1.09
SC7	1.15	1.2	.00274	.00251	3.92	3.7	.00137	.00121	1.00	1.08
SC8	1.33	1.3	.00665	.00600	3.98	3.7	.00214	.00199	1.00	1.10
SC9	1.75	1.7	.01487	.01414	4.08	4.1	.00372	.00326	1.00	1.09
EX1	5.80	6.0	.10272	.1083	4.31	4.7	.00819	.00816	1.00	1.05
EX2	4.92	4.6	.16996	.1658	4.29	4.3	.01592	.01699	1.00	1.08
EX3	.46	.51	.08302	.0859	3.58	3.6	.06993	.06969	.88	.94

Hf in extractor raffinate (Hf as wt-pct of (Zr+Hf))		Hf in strip liquor (Hf/(Zr+Hf), ppm)		Zr recovery (pct)	
Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
15.18	12.6	39	18	90	88

Table 2. Comparison of Computer-Simulated Results with Experimental Results (Mixer-Settler Run B)

$N_{sc} = 9$, $N_{ex} = 3$

$[Zr]_{feed} = 14.0$ g/l $[Hf]_{feed} = 0.188$ g/l

$[H_2SO_4]_{feed} = 1.36$ mol/l $[H_2SO_4]_{scr} = 1.0$ mol/l

$Q_{feed} = 12$ ml/min $Q_{strip} = 12$ ml/min

$Q_{scr} = 27.6$ ml/min $Q_{org} = 46.25$ ml/min

	$[Zr]_{aq}$ (g/l)		$[Hf]_{aq}$ (g/l)		$[Zr]_{org}$ (g/l)		$[Hf]_{org}$ (g/l)		$[H_2SO_4]$ (mol/l)	
Stage	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
SC1	.44	.42	.00010	.00013	3.31	3.3	.00008	.00012	1.00	1.08
SC2	.62	.61	.00022	.00035	3.57	3.5	.00014	.00026	1.00	1.09
SC3	.73	.76	.00038	.00064	3.68	3.7	.00021	.00028	1.00	1.09
SC4	.81	.79	.00061	.00102	3.74	3.8	.00030	.00052	1.00	1.09
SC5	.89	.88	.00097	.00154	3.79	3.8	.00044	.00069	1.00	1.07
SC6	.97	.96	.00153	.00262	3.84	3.9	.00065	.00144	1.00	1.09
SC7	1.07	1.2	.00254	.00435	3.89	3.9	.00099	.00176	1.00	1.08
SC8	1.23	1.3	.00462	.00777	3.95	4.0	.00159	.00276	1.00	1.08
SC9	1.56	1.6	.01020	.01628	4.04	4.3	.00282	.00461	1.00	1.07
EX1	5.28	4.8	.07172	.100	4.24	4.2	.00616	.00936	1.12	1.17
EX2	4.15	2.7	.11741	.182	4.20	4.1	.01272	.0326	1.12	1.23
EX3	.38	.12	.05678	.0505	3.23	2.0	.05191	.100	1.00	1.02

Hf in extractor raffinate (Hf as wt-pct of (Zr+Hf))		Hf in strip liquor (Hf/(Zr+Hf), ppm)		Zr recovery (pct)	
Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
13.02	24.4	24	34	91	93

Variables other than these can affect process economics, but only these influence purity and recovery.

Recovery of zirconium is strongly affected by $[Zr]_{feed}$ and by organic-phase flow rate, and relatively unaffected by $[H_2SO_4]$ and by scrub acid flow rate, as shown in Figs. 4, 7, 5, and 6, respectively. Higher recovery of zirconium correlates with lower values of $[Zr]_{feed}$, lower values of $[H_2SO_4]$, lower scrub acid flow rate, and higher organic-phase flow rate.

Product purity is relatively unaffected by $[Zr]_{feed}$, moderately affected by scrub acid flow rate and by organic-phase flow rate, and strongly affected by $[H_2SO_4]$, as shown in Figs. 4, 6, 7, and 5, respectively. Improved purity correlates with higher values of $[H_2SO_4]$, higher scrub acid flow rate, and lower organic-phase flow rate.

There is a trade-off between recovery and purity. For a fixed number of stages, enhanced recovery can be achieved only by sacrificing strip liquor purity, and vice versa.

To meet a specification of 60 ppm Hf in zirconium sponge, operating conditions sufficient to achieve a purity of 40 ppm should be used so that transient departures from the desired steady state can be accommodated. This means that the purity, with regard to Hf in the strip liquor, is not a variable but is a fixed constraint to which the other operating variables must conform.

Since Zr recovery is strongly affected by the concentration of scrub acid, one might expect to minimize cost by using a lower scrub acid concentration, thereby decreasing consumption of H_2SO_4 while maintaining the required levels of purity and recovery by using a larger number of separative stages. However, the computation indicates that this approach would probably fail if scrub concentration were significantly less than 1.0 molar. At H_2SO_4 concentrations less than 1.0 molar, the organic-phase concentrations of zirconium and hafnium are too high relative to

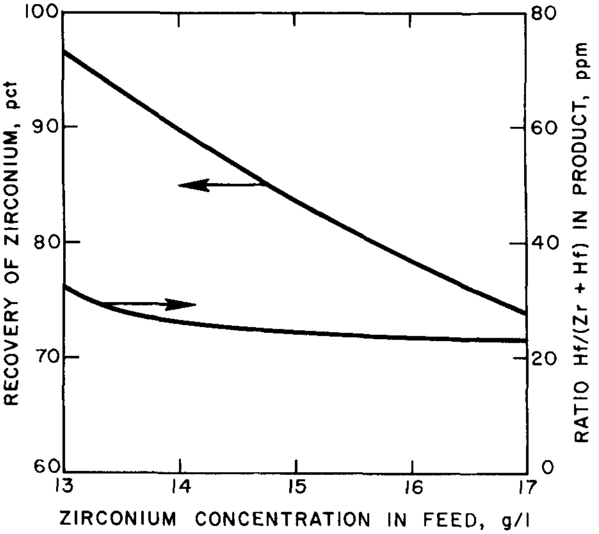

Fig. 4. Recovery and product purity versus $[Zr]_{feed}$ for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Hf]_{feed}$ at 1.34 pct of $[Zr]_{feed}$, $[H_2SO_4]_{feed} = 1.0$ mol/l, $[H_2SO_4]_{scr} = 1.0$ mol/l, $Q_{feed} = 12$ l/min, $Q_{scr} = 25$ l/min, and $Q_{org} = 45$ l/min.

their aqueous-phase concentrations, seriously impairing separative efficiency and making the use of additional stages ineffective.

Predicted practical operating conditions are $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/l, $[Hf]_{feed} = 0.201$ g/l, $[H_2SO_4]_{feed} = 1.0$ mol/l, $[H_2SO_4]_{scr} = 1.0$ mol/l, $Q_{feed} = 12$ l/min, $Q_{scr} = 25$ l/min and $Q_{org} = 50$ l/min. These conditions yield the calculated results shown in Table 3. Also shown for contrast, are calculated results for the same conditions of concentration and flow rate, but with different numbers of scrubber (N_{sc}) and extractor (N_{ex}) stages. The ratio Hf/(Zr+Hf) in feed solution assumed for this calculation was 0.0134. Data in the table demonstrate the principle that superior separative efficency is

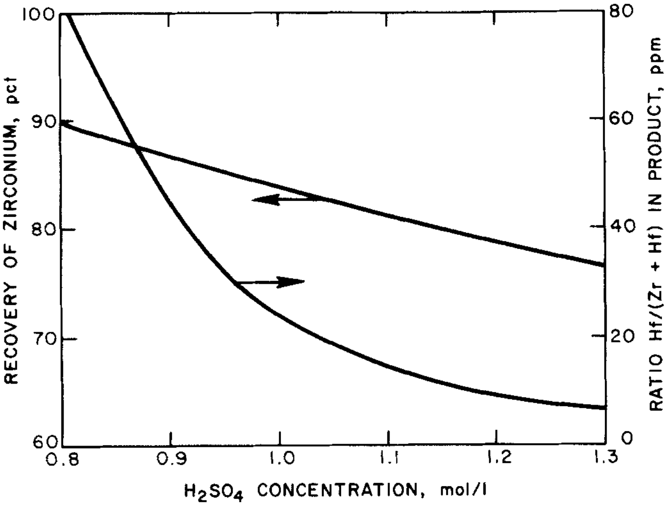

Fig. 5. Recovery and product purity versus H_2SO_4 concentration in feed solution and scrub acid for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/l, $[Hf]_{feed} = 0.201$ g/l, $Q_{feed} = 12$ l/min, $Q_{scr} = 25$ l/min, and $Q_{org} = 45$ l/min.

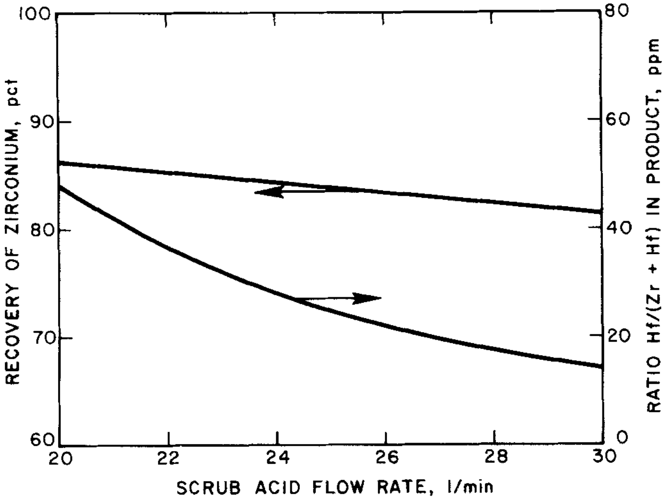

Fig. 6. Recovery and product purity versus scrub acid flow rate for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/l, $[Hf]_{feed} = 0.201$ g/l, $[H_2SO_4]_{feed} = 1.0$ mol/l $[H_2SO_4]_{scr} = 1.0$ mol/l, $Q_{feed} = 12$ l/min, and $Q_{org} =$ 45 l/min.

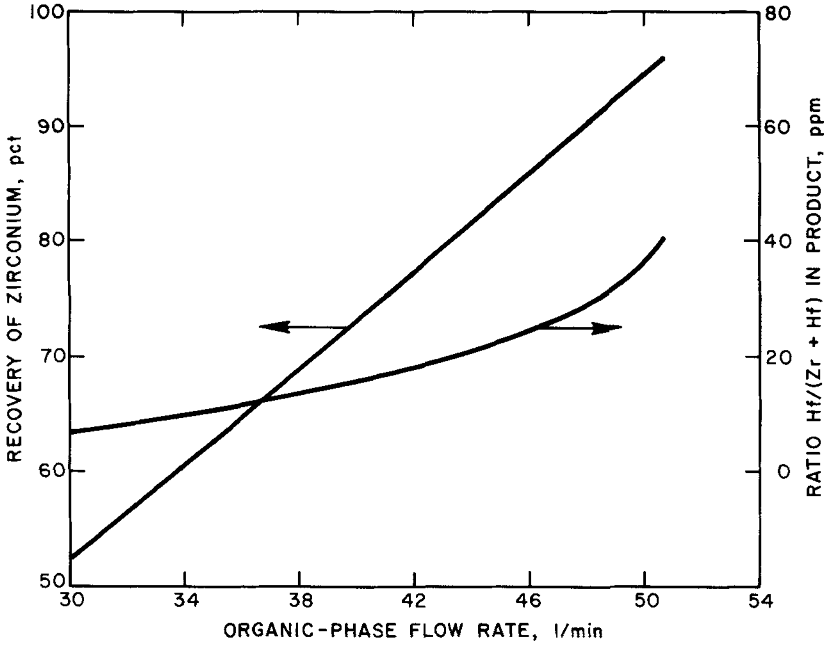

Fig. 7. Recovery and product purity versus organic-phase flow rate for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/l, $[Hf]_{feed} = 0.201$ g/l, $[H_2SO_4]_{feed} = 1.0$ mol/l $[H_2SO_4]_{scr} = 1.0$ mol/l, $Q_{feed} = 12$ l/min, and $Q_{scr} =$ 25 l/min.

achieved when the ratio Hf/(Zr+Hf) of the aqueous phase in the first extractor stage (EX1) is as close as possible to the ratio Hf/(Zr+Hf) in the feed solution. The data also show that using a greater number of stages produces better purity, other conditions being fixed.

SUMMARY AND CONCLUSIONS

Computer simulation was developed to predict the performance of a multistage countercurrent extraction system for zirconium-hafnium separation using Alamine 336. Results of the simulation indicate the effect of variations in operating

TABLE 3. Calculated Effect on Zr Recovery and Product Purity of Differing Numbers of Separative Stages

N_{sc}	N_{ex}	Zr recovery, pct	Product Hf, ppm	Ratio Hf/(Zr+Hf) in aqueous phase of EX1
8	4	95	41	.0120
9[a]	3	94	36	.0145
10	2	94	70	.0366
9	4	94	30	.0119
10[b]	3	94	28	.0144
11	2	94	55	.0357

[a] Best 12-stage combination.
[b] Best 13-stage combination.

parameters and indicate that a configuration comprising nine scrubber and three extractor stages would be satisfactory.

SYMBOLS

D_1	distribution coef., component 1 (dimensionless)
D_2	distribution coef., component 2 (dimensionless)
Q_{aq}	volume rate of flow of aqueous phase (l/min)
Q_{org}	volume rate of flow of organic phase (l/min)
$[Zr]_{aq}$	concentration of Zr in the aqueous phase (g/l)
$[Zr]_{org}$	concentration of Zr in the organic phase (g/l)
$[H_2SO_4]$	concentration of H_2SO_4 in the aqueous phase (mol/l)
α	separation factor (dimensionless)
$[Hf]_{aq}$	concentration of Hf in the aqueous phase (mol/l)
$[Hf]_{org}$	concentration of Hf in the organic phase (g/l)
N_{sc}	number of scrubber stages (dimensionless, integer)
N_{ex}	number of extractor stages (dimensionless,integer)
$[Zr]_{feed}$	concentration of Zr in feed solution (g/l)

$[Hf]_{feed}$	concentration of Hf in feed solution (g/l)
$[H_2SO_4]_{feed}$	concentration of H_2SO_4 in feed solution (mol/l)
Q_{feed}	flow rate of feed solution (l/min)
Q_{scr}	flow rate of scrub solution (l/min)
Q_{strip}	flow rate of strip solution (l/min)
Q_{org}	flow rate of organic phase (l/min)
$[H_2SO_4]_{scr}$	concentration of H_2SO_4 in scrub acid (mol/l)

REFERENCES

1. Alamine 336 is a trade name used by Henkel Corp. for a high-molecular-weight mixture of tertiary amines. Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

2. M. Benedict and T. H. Pigford. Nuclear Chemical Engineering, McGraw-Hill Book Co., Inc., New York, 1957, p. 211.