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Purification of Zirconyl Sulfate by Solvent Extraction

By D. J. MacDonald, H. G. Henry, and D. J. Bauer

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°Be′	degree Baumé′	mg/L	milligram per liter
°C	degree Celsius	min	minute
cfm	cubic foot per minute	mL	milliliter
cP	centipoise	mL/g	milliliter per gram
dyn/cm	dyne per centimeter	mL/min	milliliter per minute
°F	degree Fahrenheit	mm	millimeter
g	gram	μm	micrometer
gal/min	gallon per minute	mol	mole
gal·min^{-1}·ft^{-2}	gallon per minute, per square foot	mol/L	mole per liter
		pct	percent
g/L	gram per liter	ppm	part per million
g/mL	gram per milliliter		
		psi	pound per square inch
h	hour		
kcal/mol	kilocalorie per mole	rpm	revolution per minute
lb	pound	torr	millimeter of mercury
		tpd	ton per day
L/min	liter per minute		
M̲	gram mole per liter		

PURIFICATION OF ZIRCONYL SULFATE BY SOLVENT EXTRACTION

By D. J. MacDonald,[1] H. G. Henry,[1] and D. J. Bauer[2]

ABSTRACT

The Bureau of Mines has conducted bench-scale investigations leading to the design of an integrated process for producing reactor-grade zirconium oxide (ZrO_2) from zircon sand, which avoids the air pollution, water pollution, fire hazard, and odor problems associated with the hexone-thiocyanate process.

The integrated process consists of three steps: production of crude zirconyl sulfate solution, solvent extraction, and production of ZrO_2 from strip liquor. This report describes the solvent extraction step. Multistage, countercurrent liquid-liquid extraction with a tertiary amine in kerosine was used to separate zirconium from a dilute H_2SO_4 solution containing hafnium and other impurities. Process steps described include extraction from an aqueous feed solution to form a hafnium-contaminated, zirconium-bearing organic-phase solution, scrubbing to separate zirconium from coextracted hafnium, stripping to transfer hafnium-free zirconium into an aqueous strip liquor, chloride-loading to produce a chloride-bearing organic solution, scrubbing with the chloride-loaded organic solution to remove traces of uranium impurity from the zirconium-bearing strip liquor, and regeneration to prepare the organic solution for reuse. These steps were performed simultaneously in steady-state, bench-scale experiments. Zirconium recovery of up to 93 pct was achieved. Results of an economic evaluation are included.

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INTRODUCTION

The hexone-thiocyanate process for purifying zirconium used by Teledyne Wah Chang Albany at Albany, OR, and by Western Zirconium Corp. at Ogden, UT, relies on solvent extraction of hafnium with methylisobutyl ketone from $HCl-NH_4SCN$ solution, to separate hafnium from zirconium. The process was pioneered by the Bureau of Mines at Albany, OR, during 1951-58 (33)[3] and was based on solvent extraction research sponsored by the U.S. Atomic Energy Commission (now part of the U.S. Department of Energy) at Oak Ridge, TN (2, 10-11, 17-18, 27-28, 36), and on discoveries published by the Bureau (1) and by Fischer (7-9). The solvent extraction system produces air pollutants consisting of methylisobutyl ketone, SO_2, H_2SO_4 mist, and 4-mercapto-4-methyl-2-pentanone, which is responsible for the notorious "catty" odor. Leakages of HCl and NH_3 also contribute to water pollution. Because methylisobutyl ketone is volatile, flammable, and toxic (vapor pressure, 16 torr at 20° C; flashpoint, 73° F; threshold limit value, 100 ppm), its vapors pose fire and health hazards at the workplace (32).

The disadvantages of the hexone-thiocyanate process constitute part of the justification for the present research. An additional incentive is the expectation that an improved process for nuclear-grade zirconium could decrease the cost of Zircaloy[4] cladding used on fuel elements for nuclear reactors.

The proposed alternative process may be divided into three major sections. The first section, consisting of the preparation of crude zirconyl sulfate solution by treating zircon sand with NaOH at 600° C and leaching with H_2O and H_2SO_4, was described in RI 8718 (21). The second section is the subject of this report and comprises a liquid-liquid extraction system using crude zirconyl sulfate solution as feed. The third section, in which a purified zirconium-bearing strip liquor is converted into reactor-grade ZrO_2, will be the subject of a subsequent report. Zirconium oxide from which nuclear-grade zirconium is to be made must have a Hf/(Zr+Hf) weight ratio of less than 60 ppm.

ACKNOWLEDGMENT

Figures 14-19 showing flowsheets containing mass flow rates for each component in each process stream, were adapted from flowsheets originally prepared at the Bureau's Boulder City Engineering Laboratory, Boulder City, NV, by J. Younghans, electronics engineer (no longer with the Bureau), and D. T. Rogers, research chemist (now with Albany (OR) Research Center).

METHODS, MATERIALS, AND DISCUSSION

SELECTION OF EXTRACTANT

Selection of an extractant for separating zirconium from hafnium is influenced by four factors. First, zirconium in aqueous solution is extraordinarily prone to undergo hydrolysis. For zirconium ions, even pH 2 is basic (23). At moderate concentrations of zirconium, for example, at >5 g/L Zr, hydrous zirconium oxide slowly precipitates from solutions containing as much as 0.5 mol/L H_2SO_4. Complexing agents, such as fluoride, chloride, EDTA, or thiocyanate, can be used to prevent precipitation, but their presence may cause problems of corrosion and odor formation, as in the hexone-thiocyanate process.

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[3]Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

[4]Reference to specific brand names or trademarks is made for identification only and does not imply endorsement by the Bureau of Mines.

Second, to achieve the most effective zirconium-hafnium separation at each stage of countercurrent liquid-liquid contacting, appropriate organic- and aqueous-phase concentrations of zirconium and hafnium must be maintained. According to Benedict and Pigford (3), the flow rate ratio or phase ratio for effective separation of a two-component mixture by liquid-liquid extraction is given by

$$Q_{aq}/Q_{org} = (D_1 D_2)^{1/2}, \qquad (1)$$

where Q_{aq} = flow rate of aqueous phase,

Q_{org} = flow rate of organic phase,

D_1 = distribution coefficient for component 1,

and D_2 = distribution coefficient for component 2.

For example, for a flow rate ratio of Q_{aq}/Q_{org} equal to 1.0, the best separation of components 1 and 2 at a given stage would be achieved when the product $D_1 D_2$ equals 1.0. For a flow rate ratio of Q_{aq}/Q_{org} equal to 0.5, the best separation would be achieved when $D_1 D_2$ equals 0.25. For a flow rate ratio of Q_{aq}/Q_{org} equal to 2, the best separation would be achieved when $D_1 D_2$ equals 4. A suitable extractant must be capable of providing metal concentrations in both phases neither too high nor too low to satisfy the above relation over a range of practical flow rate ratios. The separation factor, α, given by

$$\alpha = D_1/D_2, \qquad (2)$$

should be as large as possible.

Third, to be environmentally clean and nonhazardous, an extractant should be nonvolatile, not soluble in water, non-toxic, and should have a high flashpoint.

Fourth, because of its low cost, H_2SO_4 was chosen to hold zirconium in solution and provide for the variation of acidity

needed to regulate the distribution of zirconium and hafnium between the organic and aqueous phases. Suitable extractants are limited to those capable of extracting zirconium from H_2SO_4 solution.

An extractant that satisfies most of these requirements is Alamine 336[5] in kerosine. Alamine 336 is a tertiary amine commonly used in extractive metallurgy, is insoluble in water, and is a symmetrical, straight-chain, saturated tertiary amine similar to tri-n-octylamine (TOA). The alkyl groups are C_8 and C_{10}, with C_8 predominating. Its average molecular weight is 392. Typical composition of Alamine 336 is

Tertiary amine..... 95 pct

Secondary amine.... 1 pct

Primary amine...... 0.2 pct

Decanol[6] is added to improve phase separation. A solution consisting of 10 pct Alamine 336, 5 pct decanol, and 85 pct kerosine had the following properties:[7]

Pensky-Marten closed cup flashpoint............. 155° F

Cleveland open cup flashpoint............. 169° F

Reid vapor pressure..... 0.2 psi

Alamine 336 is moderately irritating to human skin but is toxic to some species of trout at concentrations as low as 5 ppm in water (5, 29) and to Thiobacillus ferrooxidans bacteria (35). Toxicities of decanol and components of kerosine at the very low concentrations in aqueous waste streams are not known.

[5]Alamine 336 (CAS Registry No. 39421-47-1) is made by Henkel Corp.
[6]Decyl alcohol, Exxon Chemical Corp., Houston, TX.
[7]Determined by EAL Corp., Richmond, CA.

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Neutralized Alamine 336 in organic solution reacts in the presence of excess H_2SO_4 solution according to the equation:

$$R_3N_{(org)} + H_2SO_{4(aq)}$$

$$\rightarrow (R_3NH \cdot HSO_4)_{(org)}, \quad (3)$$
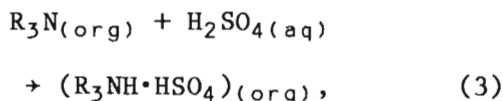
in which R_3N represents the tertiary amine.

Although the exact composition of the zirconium-bearing molecular species involved in extraction with Alamine 336 is not known, the predominant extractable species requires 4 mol of the amine per mole of zirconium (4). The extraction equilibrium probably corresponds to the equation (omitting possible water of hydration):

$$4(R_3NH \cdot HSO_4)_{(org)} + Zr(SO_4)_3^{2-}{}_{(aq)}$$

$$= (R_3NH)_4Zr(SO_4)_{4(org)}$$

$$+ 3HSO_4^-{}_{(aq)} + H^+{}_{(aq)}. \quad (4)$$

Although the tertiary amine acts as an anion exchanger extracting anionic sulfate complexes of zirconium, the overall effect is to exchange Zr^{4+} ions for the H^+ ions of H_2SO_4. The distribution coefficient is strongly dependent on H^+ concentration, but variation of SO_4^{2-} or HSO_4^- concentration has little effect.

Research by Malek (22) on the mechanism of zirconium extraction indicated that the zirconium-bearing species in the organic phase consisted of $(R_3NH)_4Zr(SO_4)_4$ $\cdot 4H_2O$. The degree of hydration may be variable, but it is not a significant factor in the process.

EQUILIBRIUM EXTRACTION ISOTHERMS

Preliminary measurements of extraction isotherms for zirconium spanned a wide range of Alamine 336 concentration, H_2SO_4 concentration, zirconium concentration, and temperature. Results were reported in 1976 (13). Subsequent measurements of zirconium extraction isotherms were made

under conditions providing more accurate control of aqueous-phase acidity, i.e., by analyzing aqueous- and organic-phase samples taken from mixer-settler cells in a multistage mixer-settler apparatus after periods of steady-state operation.

Zirconium concentrations were determined by X-ray fluorescence, using acidified aqueous standards for aqueous-phase samples and zirconium-loaded organic-phase standards for organic-phase samples. Concentration of H_2SO_4 in the aqueous-phase samples was determined by titration with standard NaOH solution in the presence of a fivefold excess of NaF over zirconium. Sodium fluoride was used to complex the zirconium and prevent it from hydrolyzing before the equivalence point for titration of H_2SO_4 was obtained.

Individual pairs of aqueous- and organic-phase zirconium concentrations at equilibrium, and in the range most useful for practical operation of the process, are given in table 1. Linear regression analysis of these data yielded an empirical relation for equilibrium distribution of zirconium:

$$[Zr]_{org} = [Zr]_{aq}/(([Zr]_{aq}/A)+B), \quad (5)$$
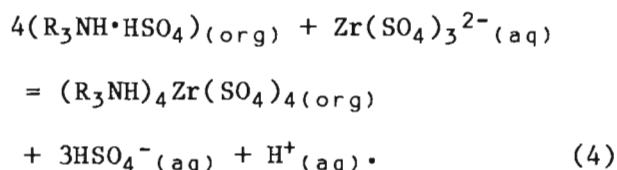
where $\quad A = 4.39 + 0.36(1.10$

$$- [H_2SO_4]), \quad (6)$$

and $\quad B = 0.039 - 0.056(1.10$

$$- [H_2SO_4]), \quad (7)$$

with the concentration of zirconium in the organic phase ($[Zr]_{org}$) and in the aqueous phase ($[Zr]_{aq}$) in grams per liter and $[H_2SO_4]$ in moles per liter. Equation 5 applies to an organic phase based on 10 pct Alamine 336 and 5 pct decanol in kerosine, and is accurate within 10 pct for $[H_2SO_4]$ between 0.65 and 1.3 mol/L and for $[Zr]_{aq}$ not less than 0.1 g/L.

Equation 5 is graphed in figure 1. The graph shows the nonlinear relationship of

TABLE 1. - Equilibrium distribution of zirconium
between a solvent organic phase consisting of
10 pct Alamine 336, 5 pct decanol, and 85 pct
kerosine, and an aqueous phase containing dilute
H_2SO_4 at 25° C

$[H_2SO_4]$ at equilibrium: 0.85±0.01 mol/L		$[H_2SO_4]$ at equilibrium: 1.10±0.02 mol/L	
$[Zr]_{org}$, g/L	$[Zr]_{aq}$, g/L	$[Zr]_{org}$, g/L	$[Zr]_{aq}$, g/L
3.4	0.34	3.2	0.46
3.7	.51	3.4	.66
3.7	.56	3.5	.79
3.7	.62	3.6	.88
3.8	.63	3.7	1.00
3.9	.81	3.7	1.10
4.0	.83	3.7	1.20
4.1	1.11	3.7	1.30
4.1	1.51	4.1	1.70
4.4	5.57	4.3	4.68

$[Zr]_{org}$ to $[Zr]_{aq}$ and its dependence on H_2SO_4 concentration. By a procedure of successive approximations, equation 5 can be used to estimate aqueous- and organic-phase concentrations resulting from equilibration of given volumes of aqueous and organic solutions whose initial zirconium concentrations are known.
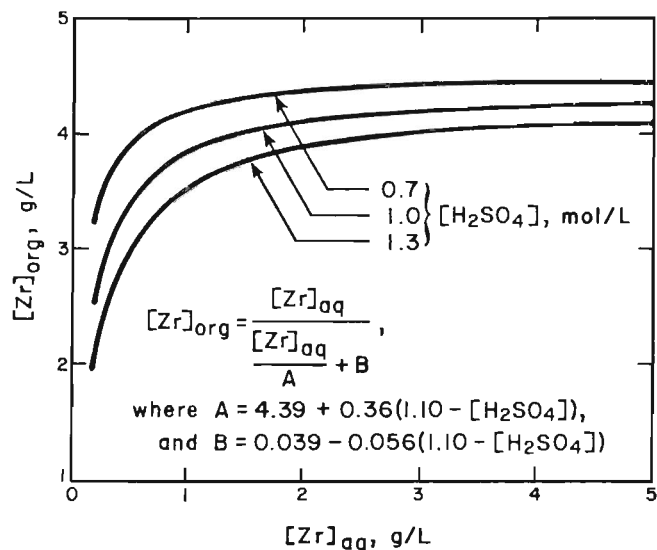
FIGURE 1. - Equilibrium distribution of zirconium between a dilute H_2SO_4 aqueous phase and a 10 pct Alamine 336, 5 pct decanol in kerosine organic phase, according to equation 5.

The effect of temperature on extraction of zirconium from H_2SO_4 solution by a tertiary amine, trioctylamine in chloroform, described by Sato and Watanabe (31), was small. The distribution coefficient was only 7.3 pct smaller at 50° C than at 10° C and indicated that the enthalpy of extraction was -0.31 kcal/mol Zr. Bureau experiments gave a similar result. At a 1:1 phase ratio, extraction of zirconium into a solution containing 10 pct Alamine 336 and 5 pct decanol in kerosine from an aqueous phase initially containing 1.00 g/L Zr and 2.0 mol/L H_2SO_4 gave a distribution coefficient, D_{Zr}, of 1.37 at 2° C and 1.23 at 46° C. The data indicate that the enthalpy of extraction is -0.43 kcal/mol Zr, or slightly exothermic. It is convenient that temperature has a negligible effect on operation of the process.

SEPARATION FACTOR

The distribution of hafnium was measured by using a mixture of Hf-175 and Hf-181 radioisotope tracers. In combination with X-ray fluorescence measurement of zirconium concentrations, this allowed determination of the zirconium-hafnium separation factor, α, defined by

$$\alpha = D_{Zr}/D_{Hf} = ([Zr]_{org}[Hf]_{aq})/([Zr]_{aq}[Hf]_{org}). \tag{8}$$

Values of α greater than unity correspond to cases in which zirconium is extracted into the organic phase in preference to hafnium. A large value for α is desirable. The magnitude of α is affected by the concentration of H_2SO_4, as shown in figure 2. Sulfuric acid concentrations less than $0.8\underline{M}$ would be undesirable because of the decrease in α.

ZIRCONIUM-HAFNIUM SEPARATION

The ability of the organic phase containing Alamine 336 to extract zirconium more strongly than hafnium is exploited by multistage countercurrent contacting of aqueous and organic streams. The hafnium content of the zirconium-bearing organic stream can be decreased to any desired level, while the ratio of hafnium to zirconium in the aqueous raffinate is increased. An applicable multistage countercurrent flow scheme is represented schematically in figure 3, which illustrates the graphic symbolism and part of the nomenclature used in this report. (Symbols are listed and identified in appendix A.) Contacting was done with mixer-settler units because they are easy to start and stop, attain equilibrium

distribution of metals in solution at each successive contacting stage, provide a fixed integral number of stages, and yield results that can be scaled up reliably.

At the contacting stage in each mixer-settler cell, incoming aqueous and organic streams were mixed with an intensity of shear sufficient to disperse one phase throughout the other as droplets ranging from 1 mm to 10 µm in diameter. Mass transfer of components in solution was facilitated by the large interfacial surface developed between the two immiscible liquids, and the small size of the droplets ensured that intraparticle diffusion of dissolved components would not be rate-limiting. In the case of zirconium, the approach to equilibrium distribution was too fast to measure relative to the time required for gravitational separation of the two phases. In mixer-settler equipment, the achievement of equilibrium distribution of zirconium and hafnium can be considered instantaneous for the Alamine 336-decanol-kerosine system.

Since the incoming scrubbing agent solution (dilute H_2SO_4) and lean organic solvent are devoid of zirconium and

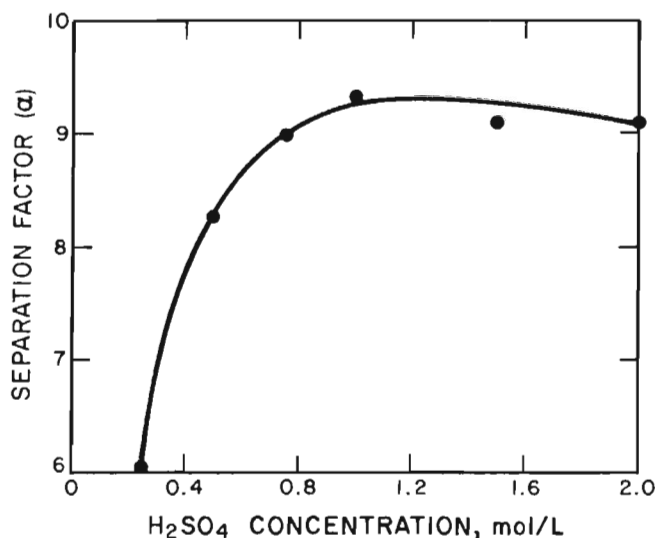FIGURE 2. - Zirconium-hafnium separation factor as a function of H_2SO_4 concentration, for 10 pct Alamine 336, 5 pct decanol in kerosine.
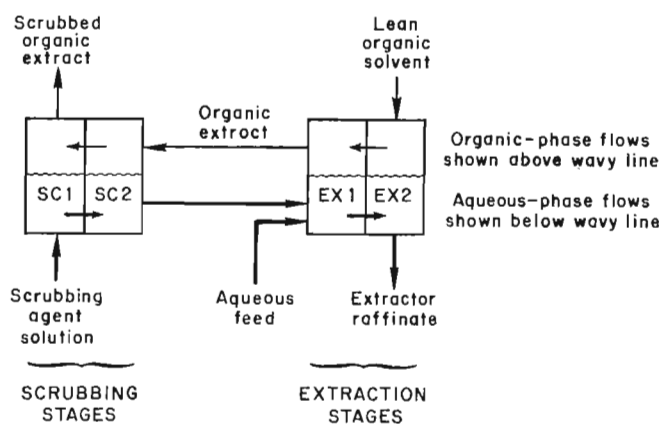

FIGURE 3. - Schematic diagram of a multistage countercurrent extraction system comprising four mixer-settler stages. Each rectangle bisected by a horizontal wavy line represents a mixer-settler stage. Heavier lines denote aqueous-phase flows, as distinguished from organic-phase flows.

hafnium, and since zirconium has a preference for the organic phase while hafnium prefers the aqueous phase, there is a net migration of zirconium toward the end of the system from which the organic extract emerges and a net migration of hafnium toward the end of the system from which the aqueous raffinate emerges. Mixer-settler stages whose aqueous flow is upstream from the feed inlet are called scrubbing stages. Their function is to remove hafnium from the organic stream. Mixer-settler stages whose aqueous flow is downstream from the feed inlet are called extraction stages. Their function is to transfer zirconium (and unavoidably some hafnium) into the organic stream. Separation of zirconium from hafnium is accomplished in both scrubbing and extraction stages. Aqueous-phase flow through the extraction stages consists of the sum of scrubbing solution and aqueous feed flow.

To predict and optimize the performance of the solvent extraction process, a computer program was developed that simulates the stage-by-stage adjustment of aqueous- and organic-phase concentrations that occur when a feed solution of known composition is introduced into a given stage of a multistage system ($\underline{19}$). The computer simulation was based on concentration data obtained in actual multistage, countercurrent mixer-settler experiments.

Any stage may be selected as the feed stage or first extraction stage, but a better separation is achieved if the feed is introduced at the stage whose steady-state aqueous-phase Hf/Zr ratio approximates that of the feed solution.

Table 2 shows actual values of parameters used in two representative mixer-settler runs. Tables 3 and 4 compare the experimental results obtained in those runs with corresponding values predicted by the computer simulation. The simulation can predict recovery within a few percentage points; but at very low levels of hafnium, the predicted product purity may deviate from experimental results by

±20 ppm Hf. The deviation is not necessarily attributable to the computer program, because experimental results contained substantial errors 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, which makes it useful in examining the effect of incremental changes in operating parameters.

TABLE 2. - Parameters for mixer-settler runs A and B

Parameter	Run A	Run B
N_{sc}	9	9
N_{ex}	3	3
$[Zr]_{feed}$ g/L	14.31	14.0
$[Hf]_{feed}$ g/L	0.256	0.188
$[H_2SO_4]_{feed}$ mol/L	1.0	1.36
$[H_2SO_4]_{scr}$ mol/L	1.0	1.0
Q_{feed} mL/min	12.0	12.0
Q_{scr} mL/min	25.0	27.6
Q_{st} mL/min	12.0	12.0
Q_{org} mL/min	46.0	46.25

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

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

N_{sc} 9

N_{ex} 3

$[Zr]_{feed}$ ....g/L.. 15

$[Hf]_{feed}$ ....g/L.. 0.201

$[H_2SO_4]_{feed}$...mol/L.. 1.0 Q_{st}..........mL/min.. 12

$[H_2SO_4]_{scr}$....mol/L.. 1.0 Q_{org}.........mL/min.. 45

Q_{feed}........mL/min.. 12   The variables considered were zirconium concentration in the feed ($[Zr]_{feed}$),

Q_{scr}.........mL/min.. 25 H_2SO_4 concentration in the feed

TABLE 3. – Stage-by-stage comparison of computer-simulated concentrations with experimental concentrations for mixer-settler runs A and B

Stage[1]	$[Zr]_{aq}$, g/L		$[Hf]_{aq}$, g/L		$[Zr]_{org}$, g/L		$[Hf]_{org}$, g/L		$[H_2SO_4]$, mol/L	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
RUN A										
SC1...	0.45	0.46	0.00017	0.00010	3.36	3.2	0.00013	0.00006	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
RUN B										
SC1...	0.44	0.42	0.00010	0.00013	3.31	3.3	0.00008	0.00012	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

Calc. Calculated.   Exp. Experimental.   [1]SC—scrubbing; EX—extraction.

TABLE 4. – Comparison of computer-simulated results with experimental results for mixer-settler runs A and B

	Run A		Run B	
	Calc.	Exp.	Calc.	Exp.
Hf in extractor raffinate...pct of (Zr+Hf)..	15.18	12.6	13.02	24.4
Hf in strip liquor, Hf/(Zr+Hf)........ppm..	39	18	24	34
Zr recovery...............................pct..	90	88	91	93

Calc. Calculated.   Exp. Experimental.
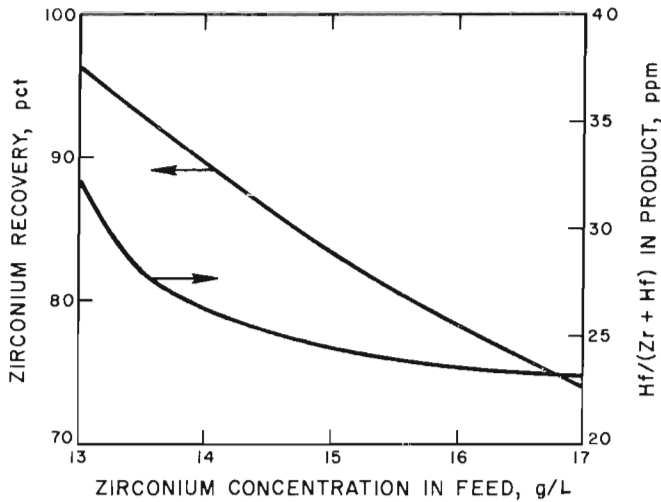
FIGURE 4. - Recovery and product purity versus $[Zr]_{feed}$, for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Hf]_{feed}$ at 1.34 pct of $[Zr]_{feed}$, $[H_2SO_4]_{feed} = 1.0$ mol/L, $[H_2SO_4]_{scr} = 1.0$ mol/L, $Q_{feed} = 12$ mL/min, $Q_{scr} = 25$ mL/min, and $Q_{org} = 45$ mL/min.
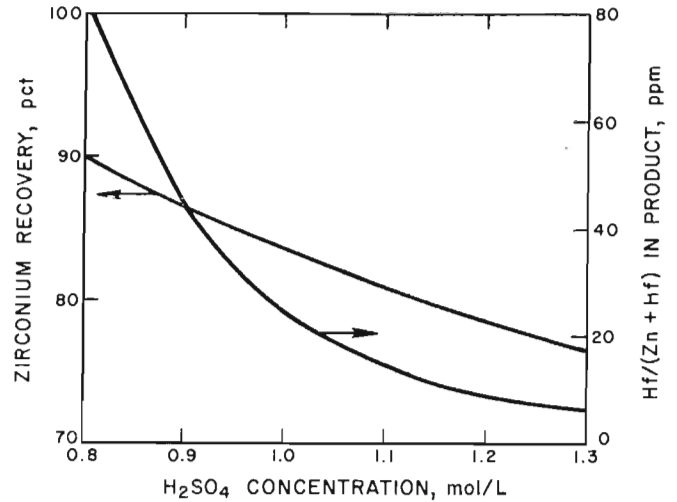
FIGURE 5. - Recovery and product purity versus H_2SO_4 concentration in aqueous feed and scrubbing agent solution, for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/L, $[Hf]_{feed} = 0.201$ g/L, $Q_{feed} = 12$ mL/min, and $Q_{org} = 45$ mL/min. $[H_2SO_4]_{feed}$ and $[H_2SO_4]_{scr}$ are assumed equal.
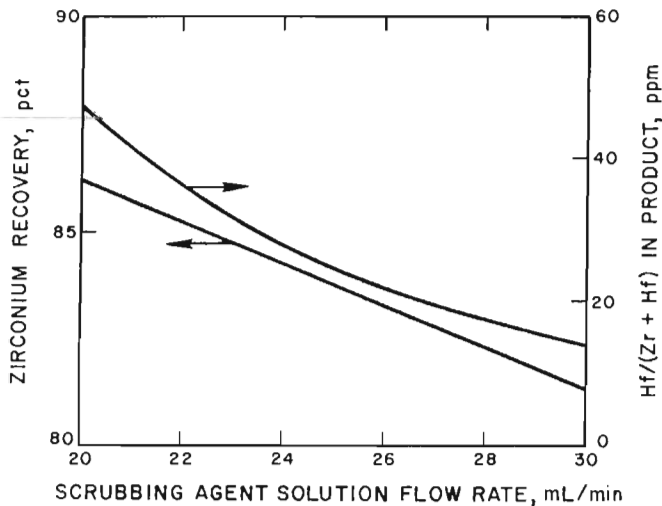
FIGURE 6. - Recovery and product purity versus scrubbing agent solution flow rate (Q_{scr}), for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/L, $[Hf]_{feed} = 0.201$ g/L, $[H_2SO_4]_{feed} = 1.0$ mol/L, $[H_2SO_4]_{scr} = 1.0$ mol/L, $Q_{feed} = 12$ mL/min, and $Q_{org} = 45$ mL/min.
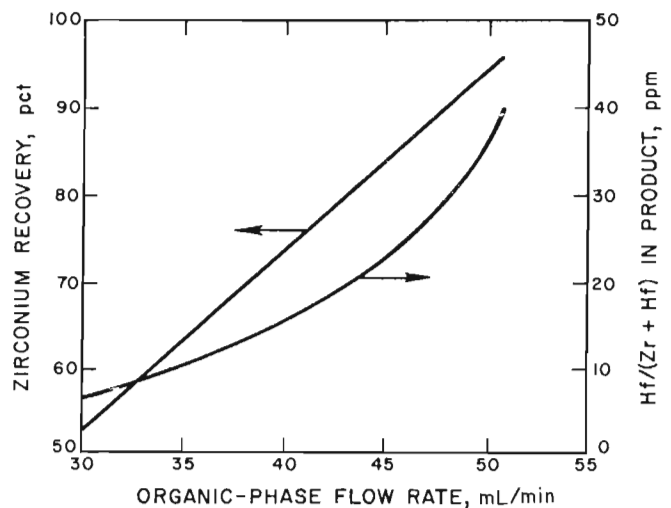
FIGURE 7. - Recovery and product purity versus organic-phase flow rate (Q_{org}), for conditions $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/L, $[Hf]_{feed} = 0.201$ g/L, $[H_2SO_4]_{feed} = 1.0$ mol/L, $[H_2SO_4]_{scr} = 1.0$ mol/L, $Q_{feed} = 12$ mL/min, and $Q_{scr} = 25$ mL/min.

($[H_2SO_4]_{feed}$) and scrubbing agent solution ($[H_2S)_4]_{scr}$) (treated as a single variable), scrubbing agent solution flow rate (Q_{scr}), and organic-phase flow rate (Q_{org}); other factors were held constant. Variables other than these can affect process economics, but only these influence purity and recovery.

Recovery of zirconium is affected strongly by $[Zr]_{feed}$ and by Q_{org}, and is relatively unaffected by $[H_2SO_4]$ and by Q_{scr}, as shown in figures 4, 7, 5, and 6, respectively. Higher recovery of zirconium correlates with lower values of $[Zr]_{feed}$, lower values of $[H_2SO_4]_{feed}$ and $[H_2SO_4]_{scr}$, lower Q_{scr}, and higher Q_{org}. In general, it is not possible to economize on consumption of H_2SO_4 without impairing product purity. The organic-phase flow rate, Q_{org}, can be increased to the point at which zirconium recovery just exceeds 95 pct; however, the amount of hafnium impurity relative to zirconium in the product stream is likely to increase rapidly with any further increase in Q_{org}.

Product purity is unaffected by $[Zr]_{feed}$, moderately affected by Q_{scr} and by Q_{org}, and strongly affected by $[H_2SO_4]$, as shown in figures 4, 6, 7, and 5, respectively. Improved purity correlates with higher values of $[H_2SO_4]$, higher Q_{scr}, and lower Q_{org}. There is a trade-off between recovery and purity. For a fixed number of separative stages, enhanced recovery can be achieved only by sacrificing product purity, and vice versa.

Since zirconium recovery is increased by decreasing the concentration of scrubbing agent (fig. 5), one might hope to minimize cost by using a lower H_2SO_4 concentration in the scrubbing solution and increasing the number of separative stages to maintain a desired level of purity. But the computer simulation indicates that this approach would fail if scrubbing agent concentration were significantly less than 1.0M. At a constant phase ratio, if H_2SO_4 concentrations were as low as 0.5M, organic-phase concentrations of zirconium and hafnium would be too high relative to their aqueous-phase concentrations, and separative efficiency would be seriously impaired, offsetting the benefit of using additional stages.

Conditions predicted by the computer simulation that are suitable for practical application 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 mL/min, Q_{scr} = 25 mL/min, and Q_{org} = 50 mL/min. These conditions yielded the computer-simulated results shown in table 5. For contrast, computer-simulated results for the same conditions of concentration and flow rate, but with different numbers for scrubbing (N_{sc}) and extraction (N_{ex}) stages are also shown in table 5. Data in the table demonstrate the principle that superior separative efficiency is achieved when the ratio Hf/(Zr+Hf) of the aqueous phase in the first extraction stage (EX1) is close to the ratio Hf/(Zr+Hf) in the aqueous feed solution,

TABLE 5. - Calculated effect on zirconium recovery and product purity of differing numbers of separative stages

Stages		Zr recovery,	Product Hf,	Ratio Hf/(Zr+Hf) in
N_{sc}	N_{ex}	pct	ppm	aqueous phase of EX1
8	4	95	41	0.0120
9[1]	3	94	36	.0145
10	2	94	70	.0366
9	4	94	30	.0119
10[2]	3	94	28	.0144
11	2	94	55	.0357

[1]Best 12-stage combination. [2]Best 13-stage combination.

assumed for this calculation to be 0.0134. The data also show that using a greater number of stages produces greater purity.

The plan area of the settling chamber for each mixer-settler stage must be large enough to provide adequate time for phase disengagement. Hazen Research, Inc., performed experiments to determine the settler area requirement (12). Hazen's experiments used an aqueous solution containing 0.5 g/L Zr in 1.0M H_2SO_4 and an organic solution containing 2.8 g/L Zr in a mixture of 10 pct Alamine 336, 5 pct decanol, and 85 pct kerosine. These solutions were equilibrated with each other to simulate solutions occurring in scrubbing and extraction stages during typical operation of the process. Hazen's standard test was based on measurement of the rise of the coalescing interface as a function of time following cessation of mechanical mixing, and it indicated that total specific flow rates, i.e., aqueous and organic, should be 1.4 $gal \cdot min^{-1} \cdot ft^{-2}$ for a phase ratio of 1.25 or 1.2 $gal \cdot min^{-1} \cdot ft^{-2}$ for a phase ratio of 1.5. The flow rates are one-half those that would cause flooding in the standard test. Phase separation was faster in all stages other than the scrubbing and extraction stages.

IMPURITY ELEMENTS OTHER THAN HAFNIUM

Nuclear and metallurgical factors combine to require that a typical purity specification for nuclear-grade zirconium include a total of 24 elements that may occur in the strip liquor from which reactor-grade ZrO_2 would be made. The elements and their maximum permissible levels in product ZrO_2 are listed in table 6.

Most of the elements are excluded by one stage of extraction with Alamine 336. Hafnium can be removed to any extent desired, as described in the previous section. Thorium is not extracted (30), although uranium is partially extracted with zirconium into Alamine 336 solution. Uranium can be separated from zirconium by scrubbing under conditions of high chloride ion activity.

Impurity elements may be introduced into the strip liquor by corrosion of materials of construction or as adventitious impurities in the reagents or water from which the stripping agent solution is made. Two such elements, aluminum and boron, were found at higher levels in reactor-grade ZrO_2 produced by this process (87 ppm and >5 ppm, respectively) than in representative samples of

TABLE 6. - Typical purity specifications[1] applicable to strip liquor from which reactor-grade ZrO_2 is produced

Element	Maximum permissible relative to Zr, ppm	Element	Maximum permissible relative to Zr, ppm
Aluminum............	75	Nickel.............	70
Boron..............	.5	Niobium (columbium).	100
Cadmium............	.5	Phosphorus.........	20
Chromium...........	500	Samarium...........	10
Cobalt.............	20	Silicon............	100
Copper.............	40	Tantalum...........	200
Gadolinium.........	5	Thorium............	7
Hafnium............	60	Titanium...........	50
Iron...............	2,000	Tungsten...........	50
Lead...............	100	Uranium............	3
Manganese..........	50	Vanadium...........	50
Molybdenum.........	50	Zinc...............	100

[1]Private communication from an industry source.

reactor-grade ZrO_2 produced by the hexone-thiocyanate process (54 ppm and 1 ppm, respectively). Aluminum was found at 43 ppm in the NaCl from which stripping agent solution was made. Since 18 g NaCl was used per gram of ZrO_2 produced, NaCl was probably the source of aluminum in the ZrO_2. Origin of the boron is not known.
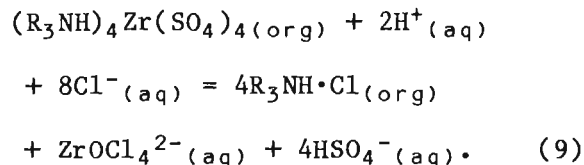
Chlorination of ZrO_2 to make $ZrCl_4$ for use in the Kroll process for making zirconium metal converts aluminum and boron to chlorides more volatile than $ZrCl_4$ and diminishes the concentrations of aluminum and boron in the final product. The presence of aluminum and boron in ZrO_2 at these levels is tolerable, according to an expert in the zirconium industry.

With regard to other significant impurity elements, ZrO_2 made by the Bureau process was purer than representative samples of ZrO_2 made by the hexone-thiocyanate process. Thorough discussion of impurities is not possible because several of the impurity elements in strip liquor cannot be determined with the required sensitivity, but they can be determined in solid ZrO_2, the final product of strip liquor treatment.

STRIPPING

Passage through the combination of scrubbing and extraction stages produced an organic extract typically containing Zr, 3.3 g/L; Hf, 0.0001 g/L; U, 0.002 g/L; and SO_4^{2-}, 18 g/L. Stripping the organic extract to produce an aqueous strip liquor high in purified zirconium is accomplished by countercurrent contacting with NaCl-HCl solution. Sulfuric acid or soda ash solution may be used for stripping, but they are much less effective than chloride solutions. A NaCl-HCl solution gives the best combination of completeness of stripping, low cost, and absence of impurities that would be undesirable in the product.

The reaction involved in stripping with chloride approximates

$$(R_3NH)_4Zr(SO_4)_{4(org)} + 2H^+_{(aq)}$$
$$+ 8Cl^-_{(aq)} = 4R_3NH \cdot Cl_{(org)}$$
$$+ ZrOCl_4^{2-}_{(aq)} + 4HSO_4^-_{(aq)}. \quad (9)$$

The reaction removes at least 4 moles of chloride from the aqueous phase for each mole of zirconium stripped. Stripping would be incomplete in a stage in which the organic phase enters first, unless the mass flow rate of chloride was sufficient relative to the zirconium.

Using two countercurrent stripping stages with a stripping solution initially 3.0M in NaCl left approximately 0.005 g/L Zr in the stripped organic phase. By using three countercurrent stripping stages, complete stripping of zirconium was accomplished with a 1.5M NaCl stripping solution.

In stripping, higher aqueous-phase zirconium concentrations correlated with higher organic-phase concentrations, although the relation was not directly proportional, as shown by data in table 7. The relation may be influenced by concentrations of sulfate and chloride.

These conditions, however, would not suffice to remove uranium. References in the patent literature (14, 24-26) describe the use of chloride stripping for recovery of zirconium from a loaded tertiary amine organic phase, but do not show the significance of chloride stripping for eliminating uranium impurity.

URANIUM SCRUBBING

Although extraction with Alamine 336 separates zirconium from most other elements, it does not separate zirconium from uranium. Most of the uranium occurring in the zircon sand remains in the zirconium-loaded organic phase, from which it could enter the strip liquor, and would constitute an unacceptable contaminant. If the aqueous-phase chloride ion activity were high enough during

TABLE 7. – Representative concentrations in stripping stages[1]

Run	Stage	Initial stripping agent solution [NaCl], mol/L	$[Zr]_{org}$, g/L	$[Zr]_{aq}$, g/L	$[SO_4^{2-}]$, g/L	$[Cl^-]$, g/L
17	2	1.5	0.006	3.1	16.9	43.5
16	2	1.5	.007	3.6	17	42
13	2	3.0	.009	1.5	8.63	94
9	1	3.0	.03	10	73.5	81
10	1	3.0	.04	12	64.8	56.6
13	1	3.0	.31	14	72.8	71
16	1	1.5	.80	16	66	22
17	1	1.5	.80	13	72.2	24
18	1	1.5	.86	14	75.5	25

[1]Equilibrium concentrations of zirconium in the organic phase and of zirconium, sulfate, and chloride in the aqueous phase for multistage countercurrent stripping with stripping agent solution initially 1.5M or 3.0M in NaCl.

stripping, uranium would remain in the organic phase while zirconium was stripped. This is analogous to the behavior of uranium(VI) with anion exchange resin (34). Uranium remaining in the zirconium-depleted organic stream was removed by contact with Na_2CO_3 solution in the regeneration stages.

Several stripping agent solution compositions were tested in combination with several configurations of flow through the stripping stages. Data in table 8 show how the uranium contained in a zirconium-bearing organic solution entering a three-stage countercurrent stripping operation was distributed between the strip liquor and the regenerator waste for a series of compositions of stripping agent solution. Even the

lowest strip liquor uranium content found in that series was not low enough to satisfy a reactor-grade specification. Improvement was sought by providing for the strip liquor to be scrubbed with a separate organic-phase stream that had been loaded with chloride before use. This was done with the flow sequence shown in figure 8. A lean organic solvent stream was loaded with chloride in a pair of countercurrent chloride-loading stages by contact with an aqueous stripping agent solution. The organic stream was used in a pair of countercurrent uranium-scrubbing stages, in which trace amounts of uranium were transferred from raw strip liquor to organic solvent. No transfer of zirconium occurred in the uranium-scrubbing stages. In the stripping stages, zirconium and part of the

TABLE 8. – Uranium in strip liquor and regenerator waste for three-stage countercurrent stripping with a series of stripping agent solution compositions[1]

Stripping agent solution		[U], mg/L	
[NaCl], mol/L	[HCl], mol/L	Strip liquor	Regenerator waste
2.0	0.0	4.2	0.94
2.5	.0	3.5	1.1
3.0	.0	2.6	1.9
3.5	.0	2.4	2.8
4.0	.0	1.7	2.7
4.0	.1	1.4	3.6
4.0	.5	.33	3.9

[1]$[U]_{feed}$ = 6.9 mg/L, Q_{feed} = 12.0 mL/min, Q_{st} = 12.3 mL/min, Q_{org} = 45.2 mL/min, Q_{reg} = 14.8 mL/min.
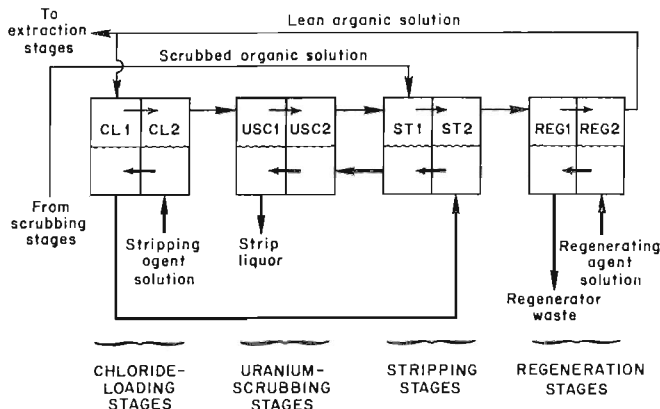
FIGURE 8. - Flowsheet for uranium-scrubbing treatment of zirconium-bearing strip liquor. Heavier lines denote aqueous-phase flows.

uranium entering with the scrubbed organic solution were transferred to the aqueous phase and formed the raw (uranium-contaminated) strip liquor. In the stripping stages, chloride concentrations in the organic phase were not high enough to cause all the uranium to be retained in the organic phase, as it was in the uranium-scrubbing stages. The stripped organic solution, laden with chloride, a lesser amount of sulfate, and minor amounts of zirconium and uranium, was treated with excess Na_2CO_3 solution in a pair of countercurrent regeneration stages, where it was restored to a lean, neutralized condition. Uranium impurity borne by the scrubbed organic solution entering the stripping step emerged with

the regenerator waste. Table 9 shows the resulting zirconium and uranium concentrations significant to the flow scheme.

The best mode of uranium removal used a stripping agent solution consisting of $4.0\underline{M}$ NaCl and $0.5\underline{M}$ HCl. Lower concentrations of chloride were inadequate. Stripping agent solutions having less than $4.0\underline{M}$ NaCl or less than $0.5\underline{M}$ HCl did not adequately remove uranium. Successful uranium scrubbing requires a chloride ion activity higher than can be obtained with NaCl alone, even up to the highest NaCl concentration that can be maintained without precipitating zirconium salts from the strip liquor prematurely. Hydrochloric acid added to NaCl solution provides the needed enhancement of chloride ion activity without exceeding solubility limits. For example, a stripping agent solution of $4.0\underline{M}$ NaCl and $0.5\underline{M}$ HCl produced a U/Zr ratio in strip liquor of 2 ppm, but a stripping agent solution of $4.0\underline{M}$ NaCl and $0.25\underline{M}$ HCl produced a U/Zr ratio of 14 ppm, which is not good enough to make reactor-grade zirconium. Although two countercurrent stages were adequate for each step, three stages for each step would be desirable.

As shown in table 10, the chloride content of the zirconium-depleted organic phase (and by implication, its effectiveness in uranium scrubbing) depended on the chloride concentration of the

TABLE 9. - Zirconium and uranium concentrations resulting from uranium-scrubbing operations, with stages and flow sequence shown in figure 8[1]

Stage or stream (aqueous phase)	Stripping agent solution: $4.0\underline{M}$ NaCl in $0.5\underline{M}$ HCl		Stripping agent solution: $4.0\underline{M}$ NaCl in $0.25\underline{M}$ HCl	
	[Zr], g/L	[U], mg/L	[Zr], g/L	[U], mg/L
Aqueous feed............	16	8.5	16	8.5
Extractor raffinate.....	1.0	.70	.92	.46
Regenerator waste (REG1)	.10	5.3	.11	3.9
Strip liquor (USC1).....	14	.03	14	.19
USC2....................	NA	1.3	NA	.41
ST1.....................	NA	1.0	13	1.3
ST2.....................	NA	.05	1.7	.09

NA Not available.

[1][Zr]$_{feed}$ = 16 g/L, [U]$_{feed}$ = 8.5 mg/L, Q_{feed} = 11.7 mL/min, Q_{st} = 12.06 mL/min, Q_{org} (to ST1) = 45 mL/min, Q_{org} (to CL1) = 18 mL/min, Q_{reg} = 16.7 mL/min.

aqueous phase previously in contact with it. Data refer to an organic solution containing 10 pct Alamine 336 and 5 pct decanol in kerosine. Temperature was 25° C.

TABLE 10. – Chloride concentration in organic solution as a function of aqueous-phase concentration of NaCl

$[NaCl]_{aq}$, mol/L	$[Cl]_{org}$, mol/L	$[NaCl]_{aq}$, mol/L	$[Cl]_{org}$, mol/L
1.0......	0.249	2.0......	.289
1.5......	.275	3.0......	.326

REGENERATION

After being loaded with chloride during the stripping operation, the organic solution cannot accept zirconium. Therefore, chloride must be removed before the organic solution is returned to the last extraction stage, and uranium must be removed before the organic solution is returned to the chloride-loading and uranium-scrubbing stages. This was done by contact with Na_2CO_3 solution in the regeneration stages. The regeneration reaction is

$$2R_3NHCl_{(org)} + CO_3^{2-}{}_{(aq)} = 2R_3N_{(org)}$$

$$+ 2Cl^-_{(aq)} + H_2O + CO_{2(g)}. \qquad (10)$$
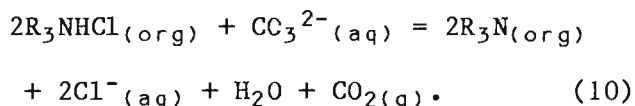
More than 0.5 mol of carbonate must be used per mole of Alamine 336, or regeneration would be incomplete and would result in a gradual buildup of chloride in the extraction and scrubbing stages. Evolution of CO_2 caused frothing in the first regenerating stage, but the froth was not persistent and did not cause an operating problem.

FLOWSHEET FOR LIQUID-LIQUID EXTRACTION

Figure 9 is a flowsheet of the liquid-liquid extraction section of the process, showing the paths of the components passing through the unit operations of extraction, scrubbing, stripping, chloride-loading, uranium scrubbing, and regeneration, and showing how the unit

operations are related. The streams are numbered to correlate with those of figure 1 and table 5 in RI 8718 (21).

Five flows are involved. The organic phase circulates at a steady rate of flow from a sump to the last extraction stage (stream 17), from there stage by stage to the first extraction stage, and thence to the last scrubbing stage (stream 19). It emerges from the first scrubbing stage (stream 21), passes to the first stripping stage, then stage by stage to the first regeneration stage (stream 25), and from the last regeneration stage back to the sump (stream 28). A separate organic stream is pumped from the sump to the first chloride-loading stage (stream 33), flows from the last chloride-loading stage to the first uranium-scrubbing stage (stream 32), and then from the last uranium-scrubbing stage (stream 23) to the first stripping stage, where it blends with the zirconium-laden organic stream (stream 21) coming from the first scrubbing stage. The sump is located downstream from the regeneration stage because phase separation is least effective in the regeneration stage. The sump serves as an auxiliary settling chamber and as a means for accommodating the effect of fluctuations in settling chamber interface levels throughout the system. Entrained aqueous matter settling out in the sump amounted to approximately 1 mL per liter of organic-phase flow. The organic phase is the less dense phase throughout the system. The organic-phase inventory in bench-scale experiments amounted to approximately 900 mL/g Zr processed per hour.

The four aqueous-phase flows consist of (1) feed solution (stream 16) merging with the scrubbing agent flow (stream 20) on entry into the first extraction stage, (2) scrubbing agent solution (stream 22) entering the first scrubbing stage, (3) stripping agent solution (stream 34) entering the last chloride-loading stage, then going from the first chloride-loading stage to the last stripping stage (stream 26), and from the first stripping stage to the last uranium-scrubbing stage

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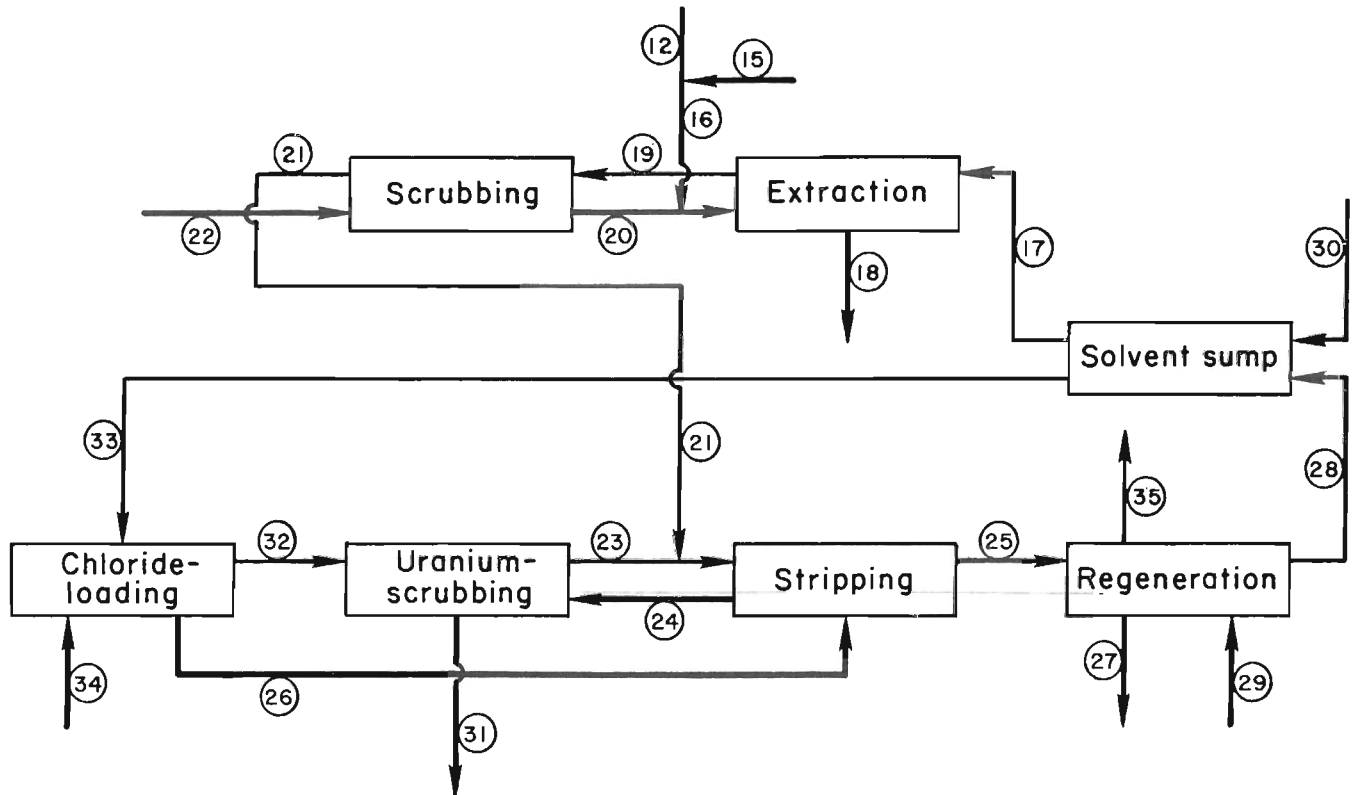
KEY TO STREAM NUMBERS

12 Acid leaching filtrate (18)
13 Water vapor (18)
14 Recycle (dry) zircon sand (18)
15 Dilution water (optional)
16 Aqueous feed
17 Lean organic solution to extraction stages
18 Extractor raffinate
19 Extract (loaded solvent)
20 Scrub product solution
21 Scrubbed organic solution (scrubbed solvent)
22 Scrubbing agent solution
23 Uranium-bearing organic solution

24 Raw strip liquor
25 Stripped organic solution
26 Postloader stripping agent solution
27 Regenerator waste
28 Lean organic solution (solvent)
29 Regenerating agent solution
30 Organic solution (solvent) makeup
31 Strip liquor (strip product solution)
32 Chloride-loaded organic solution
33 Lean organic solution to chloride-loading stages
34 Stripping agent solution
35 Regeneration vapor (CO_2)

FIGURE 9. - Flowsheet for identification of process streams. Heavier lines denote aqueous-phase flows. (Streams 1 through 14 are described in reference 21.)

(stream 24), and (4) the regenerating agent solution (stream 29) entering the last regeneration stage. Aqueous-phase flows move countercurrent to organic-phase flows throughout the system.

Aqueous flows emerging from the extraction stages, uranium-scrubbing stages, and regeneration stages are designated extractor raffinate, strip liquor, and regenerator waste, respectively. Variations of this flow scheme were used in the 29 mixer-settler runs.

WASTE DISPOSAL

Extractor raffinate may be regarded as waste or as a raw material for producing

hafnium. If extractor raffinate is to be discarded, it may be blended with regenerator waste to partly neutralize both streams before disposal. The resulting mixture would contain excess H_2SO_4. Grinding extractor raffinate with excess limestone chips was effective, but slow, in neutralizing the H_2SO_4 and converting the dissolved zirconium, hafnium, and other impurities to a filterable precipitate consisting predominantly of $CaSO_4 \cdot 2H_2O$.

Nothing in these wastes would cause eutrophication of natural waters. Extractor raffinate and regenerator waste contained uranium, a low-level radioactive material. Restrictions on disposal of uranium-bearing materials may differ from one local jurisdiction to another.

OPERATION OF MIXER-SETTLER APPARATUS

By observation of electrical conductivity, the continuous phase in the scrubbing- and extraction-stage mixers was determined to be the organic phase. The aqueous phase was the dispersed phase.

Operating with the organic phase continuous is not necessarily desirable. Primary phase disengagement in the settlers would probably be faster if the aqueous phase, which is the less viscous phase, were continuous. But on the other hand, the organic-continuous mode of operation helps minimize entrainment of organic matter in aqueous effluents (15).

The organic-continuous mode of operation was a consequence of the design of the mixer-settler units. In these units, an uninterrupted slug of the organic phase was drawn through the shear zone under the impeller of the mixer cell during startup. This might have been avoided by operating at startup with only aqueous material available to the impeller's shear zone, but doing so would have imposed an undesired offset from previously established steady-state conditions.

In the bench-scale apparatus used, all mixer-settler units were the same size and shape and were made of clear polyvinyl chloride (PVC). The mixers were square in section, 57 by 57 mm, and 57 mm deep, and had a mixer volume of 185 mL. The settlers were 57 mm deep by 57 mm wide by 122 mm long, and had a settling chamber volume of 396 mL. Impellers were 31 mm in diameter, with six radial slots each 3 mm square in section on the surface facing the mixer-cell inlet, and were run at 1,200 to 1,600 rpm. Residence time for each phase in a mixer is inversely proportional to its flow rate. Residence time of a given phase in the settling chamber is inversely proportional to its flow rate and proportional to the depth of that phase in the settler as determined by the position of the interface. Interface levels were adjusted to make the organic-phase depth two to four times the aqueous-phase depth. This was done to provide a greater residence time for the organic phase, the phase in which greater cloudiness (implying greater counterphase entrainment) was observed. Typical settler residence times are given in table 11. Steady, controlled flow rates were obtained with adjustable rotating-reciprocating pumps made by Fluid Metering, Inc.

TABLE 11. - Typical settling chamber residence times, minutes

Stage type	Organic phase	Aqueous phase
Scrubbing.............	6	5
Extraction.............	6	4
Chloride-loading.......	14	10
Uranium-scrubbing......	14	10
Stripping.............	4	10
Regeneration..........	4	8

Cell-to-cell connections were made of Pyrex glass tubing inserted into PVC compression fittings, with polyethylene tubing fitted over the glass tubing. Polyethylene tubing provided the flexibility needed for vertical adjustment of glass Y-tubes whose elevation controlled the interface levels. Heating

the polyethylene tubing in boiling water made it soft enough to slip over glass tubing and sufficiently annealed it to prevent cracking from unrelieved hoop stress. Tygon tubing of R-3603 composition was not suitable for this application because it contains a phthalate ester as plasticizer. The plasticizer is leached by kerosine and hydrolyzed by H_2SO_4 to produce free phthalate, which forms a precipitate with zirconium. The zirconium phthalate precipitate would interfere with phase separation. But Tygon-brand tubing designated "formulation F-4040-A" was found satisfactory in this application.

Phase separation in the stripping stages was rapid because of the large difference in density between the Alamine-kerosine solution (epiphase) and the NaCl-HCl stripping agent solution (hypophase). In the scrubbing and extraction stages, a substantial density difference alone was not sufficient. Phase separation failed when the aqueous-phase concentration of zirconium was less than 0.5 g/L, even when the aqueous phase was $\underline{2M}$ in H_2SO_4. The mixer-settler system could not be started without having a moderate concentration of zirconium present in the aqueous phase of each of the scrubbing and extraction stages.

At startup, a mixer-settler extraction system undergoes a dynamic readjustment of concentrations in each stage as the steady-state condition is gradually achieved. The same is true if any alteration in operating conditions is made after steady state has been established. Since concentrations in the two phases are interrelated, the approach to steady state is slower than would be predicted by assuming plug flow for each phase. For example, in an experiment using flow rates that would have required 24 min for plug flow of the aqueous phase from the first of four extraction stages (the feed point) to the last (where the extractor raffinate emerges), 4 h or more was required for concentrations in the last extraction stage to come within 10 pct of new steady-state concentrations after a

step-function increase in feed concentration was imposed on a system initially at steady state.

Figure 10 shows the behavior of a system having eight separative stages (N_{sc} = 4, N_{ex} = 4), whose mass flow rate of feed solution was increased by 25 pct at time zero. Residence time, assuming plug flow, would have been 20.7 min in the four stages between the feed point and the sampling point. The delayed response occurred because the effects of phase-to-phase mass transfer are propagated backward from their point of origin via countercurrent flow of one phase relative to the other. The parameter monitored for this purpose was the ratio of concentrations of hafnium tracer in the aqueous and organic phases, which was selected because it could be measured precisely. Temporal variation of other parameters is assumed to be similar. In other experiments, an abrupt *decrease* in feed concentration produced a transient consisting of an asymptotic approach to steady state, in contrast to the oscillatory transient produced by an abrupt *increase*
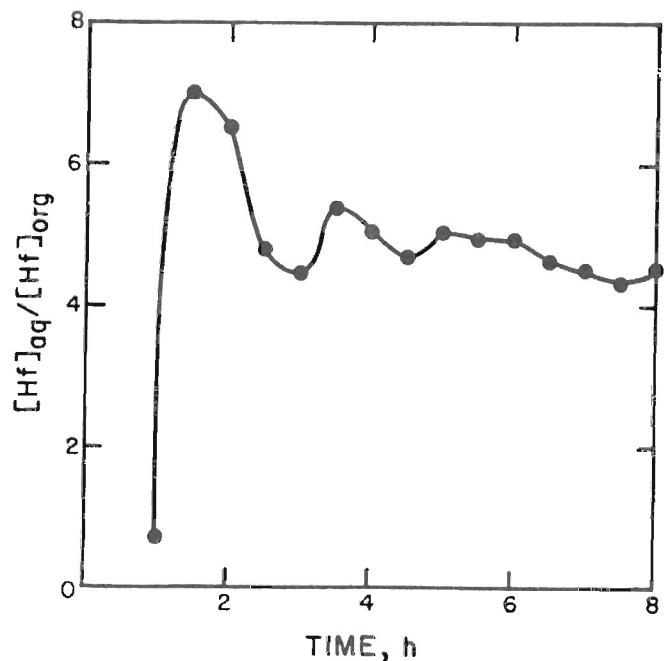

FIGURE 10. - Transient response of a countercurrent extraction system comprising four scrubbing stages and four extraction stages, following a 25-pct increase in feed concentration.

in feed concentration. Since the oscil-latory behavior might make zirconium con-centrations swing low enough to cause a failure of phase separation, it is desir-able to prepare for startup by loading each extraction and scrubbing stage with solutions having zirconium concentrations higher than the expected steady-state concentrations for that stage.
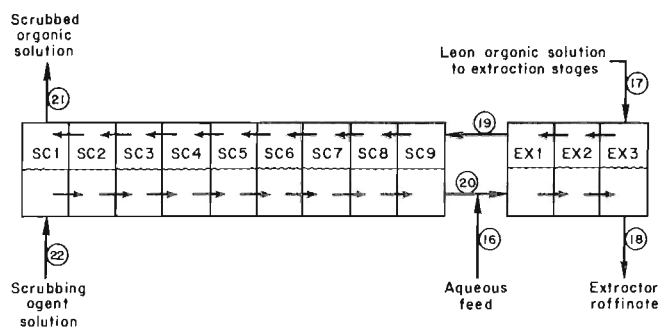

FIGURE 11. - Flowsheet for scrubbing and extrac-tion steps, showing nine scrubbing stages and three extraction stages.
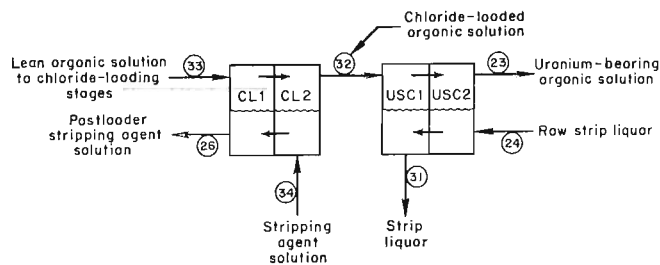

FIGURE 12. - Flowsheet for chloride-loading and uranium-scrubbing steps, showing two chloride-loading stages and two uranium-scrubbing stages.
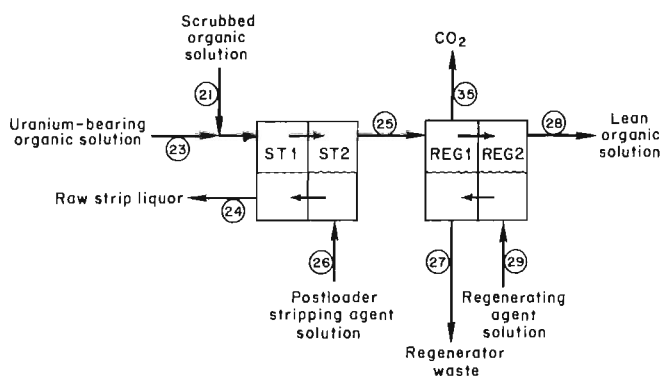

FIGURE 13. - Flowsheet for stripping and regener-ation steps, showing two stripping stages and two regeneration stages.

Flowsheets illustrating flow paths through typical numbers of stages for each of the six steps are shown in fig-ures 11, 12, and 13. In the 29 experi-mental runs conducted, various numbers of stages were used. The numbers of stages shown in the figures are illustrative, but not necessarily optimal.

Flowsheets containing mass flow rates for the components in each process stream are shown in figures 14 through 19. Vol-ume flow rates are included. The flow rates shown pertain to a process using zircon sand starting material at a rate of 10 tpd. Data in the flowsheets corre-late with data given in table 5 of refer-ence 21 and are based on an assumption of 81.5-pct recovery of zirconium. The as-sumed recovery is not related to a spe-cific number of mixer-settler stages.

ECONOMIC FACTORS

The computer simulation includes an es-timate of costs that would be incurred in operating a plant-scale multistage mixer-settler system for zirconium-hafnium sep-aration with strip liquor as its product. Table 12 shows the values assumed for cost factors in the estimate.

At a basic condition of $N_{sc} = 9$, $N_{ex} = 3$, $[Zr]_{feed} = 15$ g/L, $[Hf]_{feed} = 0.201$ g/L, $[H_2SO_4]_{feed} = 1.0$ mol/L, $[H_2SO_4]_{scr} = 1.0$ mol/L, $Q_{feed} = 12.0$ L/min, $Q_{scr} = 25.0$ L/min, $Q_{st} = 12.0$ L/min, $Q_{org} = 45.0$ L/min, and $Q_{reg} = 12.0$ L/min, and using a 6-pct Na_2CO_3 regenerating agent solution and a stripping agent solu-tion of 4.0$\underline{M}$ NaCl and 0.5$\underline{M}$ HCl, the cost was estimated to be \$3.$\overline{14}$ per pound of zirconium produced in the form of strip liquor. Variations in the parameters would produce partial derivatives of cost, shown in table 13. Above-mentioned flow rates are relative, and do not rep-resent actual flowrates required for a 10-tpd zircon sand throughput.

Using more stages would decrease the overall cost, capital included. For example, a change from $N_{sc} = 9$ and $N_{ex} = 3$ to $N_{sc} = 14$ and $N_{ex} = 4$ would

TABLE 12. – Bases for estimates of operating cost of zirconium-hafnium separation to produce zirconium-bearing strip liquor

Factor	Cost
Zr in feed solution[1]......................................	$0.99/lb Zr contained in feed.
HCl, 18° Be′ acid, C.P.[2].................................	$0.22/lb.
NaCl[2]..	$2.67/80 lb.
H_2SO_4[2]...	$80.00/ton.
$Na_2CO_3 \cdot H_2O$[2]...	$56.00/ton.
Capital and labor for a system of 17 mixer-settler units and 10-tpd throughput of zircon sand[1].........	$0.096/lb Zr produced.
Incremental capital and labor for 1 additional mixer-settler unit and 10-tpd throughput of zircon sand[1]..	$0.001/lb Zr produced.

[1]Estimated by Process Evaluation Group, Bureau of Mines, Avondale, MD.
[2]Reagent costs published in Chemical Marketing Reporter, October 1980.

TABLE 13. – Partial derivatives of cost of zirconium contained in strip liquor relative to operating parameters

Parameter	Cost derivative
$[Zr]_{feed}$......	+0.058 ($/lb Zr)/(g/L).
$[H_2SO_4]$[1]......	+1.98 ($/lb Zr)/(mol/L).
Q_{scr}...........	+0.044 ($/lb Zr)/(L/min).
Q_{st}............	+0.23 ($/lb Zr)/(L/min).
Q_{org}...........	-0.079 ($/lb Zr)/(L/min).
Q_{reg}...........	+0.034 ($/lb Zr)/(L/min).

[1]Assuming $[H_2SO_4]_{feed}$ and $[H_2SO_4]_{scr}$ are equal.

decrease the cost from $3.14 per pound of zirconium produced to $2.81 per pound of zirconium produced while maintaining the same product purity, and in spite of increased capital costs for the additional stages.

Some changes leading to decreased cost tend toward conditions of unstable operation or production of an impure product. For example, if Q_{org} were too high, the product would be grossly impure or operation of scrubbing stages might be unstable. If Q_{st} were too low, the product's uranium content would be too high or stripping would be incomplete and would lead to formation of a precipitate that would clog the regeneration stages. If Q_{reg} were too low, an upset of the regeneration stages would occur because of failure of phase separation caused by precipitation. Conditions for lowest cost were not determined.

SUMMARY AND CONCLUSIONS

Conditions necessary for the production of strip liquor containing zirconium of reactor-grade purity by liquid-liquid extraction in a tertiary amine-H_2SO_4 system were determined in bench-scale experiments. Suitable conditions were—

Organic solution composition: 10 pct Alamine 336, 5 pct decanol in kerosine.

Number of scrubbing stages: at least nine.

Number of extraction stages: at least three.

Feed solution composition: 15 g/L Zr, in 1.0M H_2SO_4.

Scrubbing agent solution composition: 1.0M H_2SO_4.

Number of chloride-loading stages: at least two.

Number of uranium-scrubbing stages: at least two.

Number of stripping stages: at least two.

Number of regeneration stages: at least two.

Stripping solution composition: 4.0$\underline{M}$ NaCl in 0.5$\underline{M}$ HCl.

Regeneration solution composition: 6 to 10 pct Na_2CO_3.

Relative feed solution flow rate: 12.

Relative scrubbing solution flow rate: 25.

Relative stripping solution flow rate: 12.

Relative regeneration solution flow rate: 16.

Relative organic solution flow rate to extraction stages: 45.

Relative organic solution flow rate to chloride-loading stages: 18.

These conditions are predicted to yield strip liquor with an Hf/(Zr+Hf) ratio of less than 40 ppm and with a U/Zr ratio of less than 2 ppm at a zirconium recovery of 90 pct or more, and assume no loss of zirconium except in extractor raffinate.
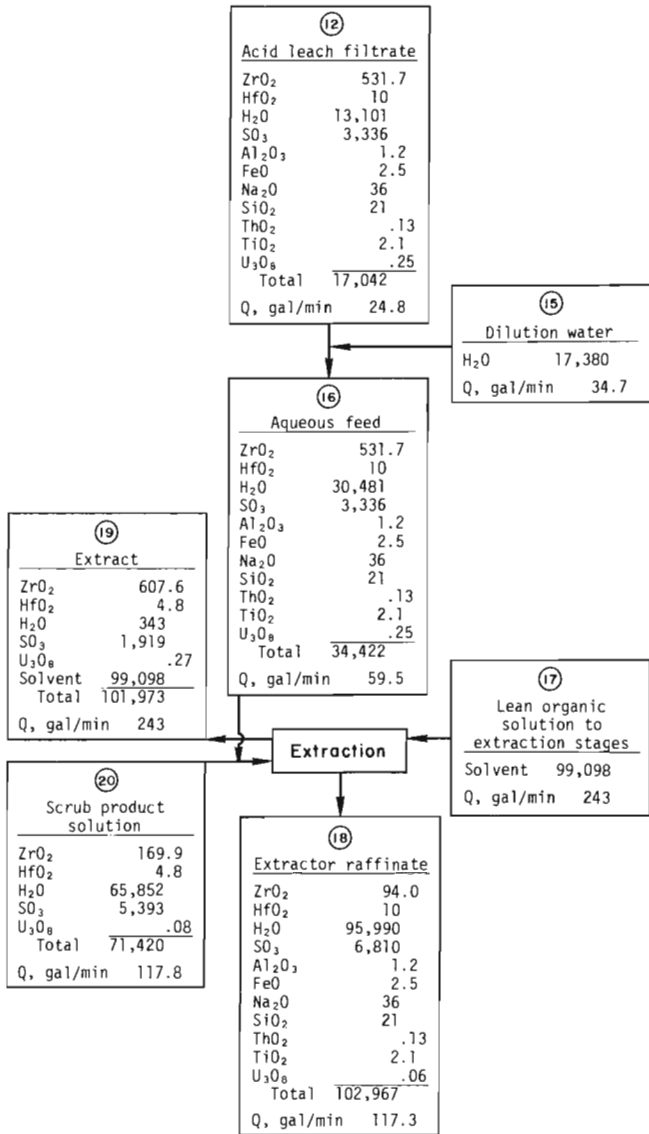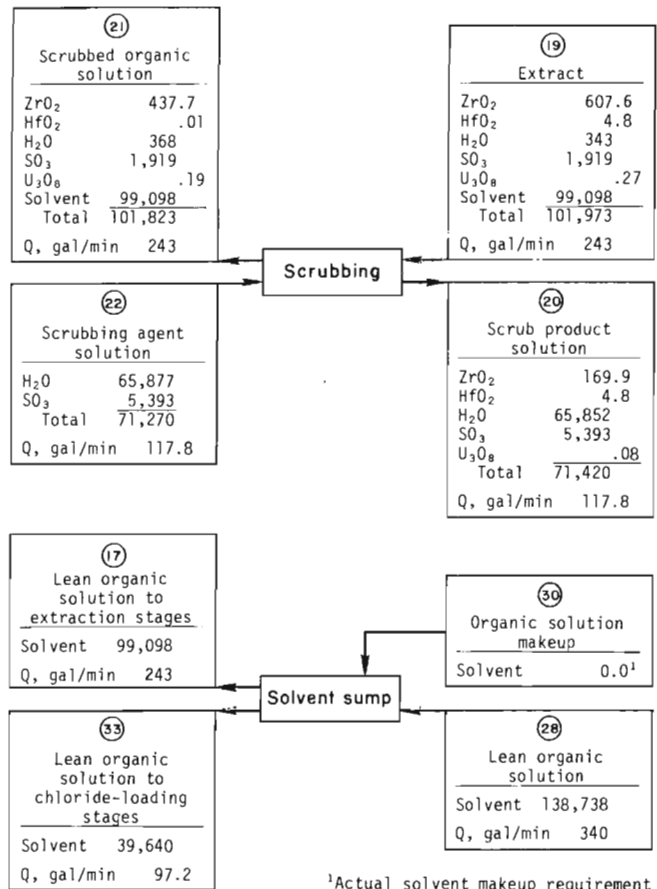

FIGURE 14. - Flowsheet for material balance around the extraction step, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.

FIGURE 15. - Flowsheet for material balance around the scrubbing step and the solvent sump, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.

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FIGURE 16. - Flowsheet for material balance around the chloride-loading step, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.

FIGURE 17. - Flowsheet for material balance around the uranium-scrubbing step, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.
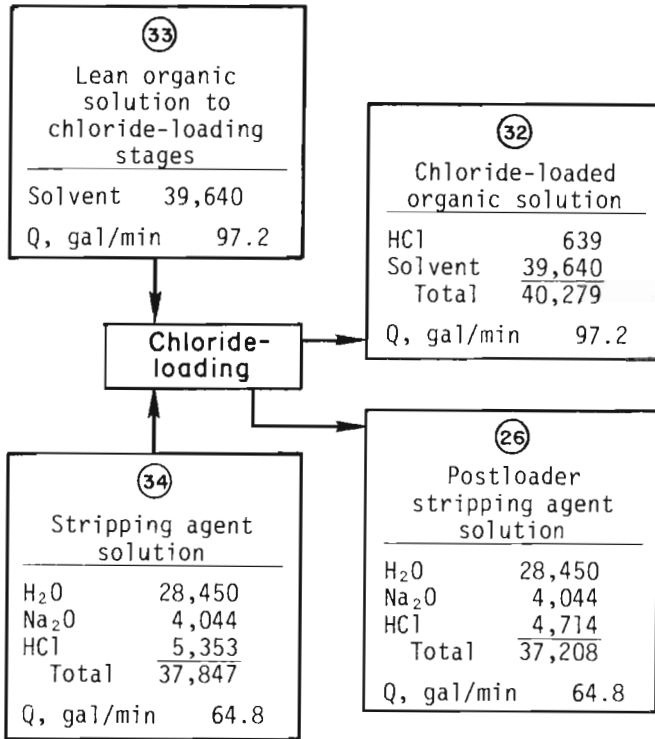

FIGURE 18. - Flowsheet for material balance around the stripping step, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.

FIGURE 19. - Flowsheet for material balance around the regeneration step, with flow rates in pounds per hour, for plant capacity of 10 tpd zircon sand. Q refers to volume rate of flow.
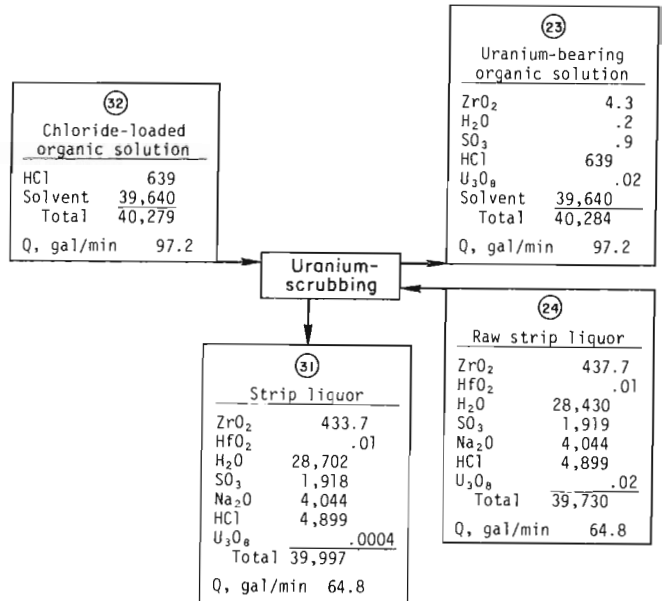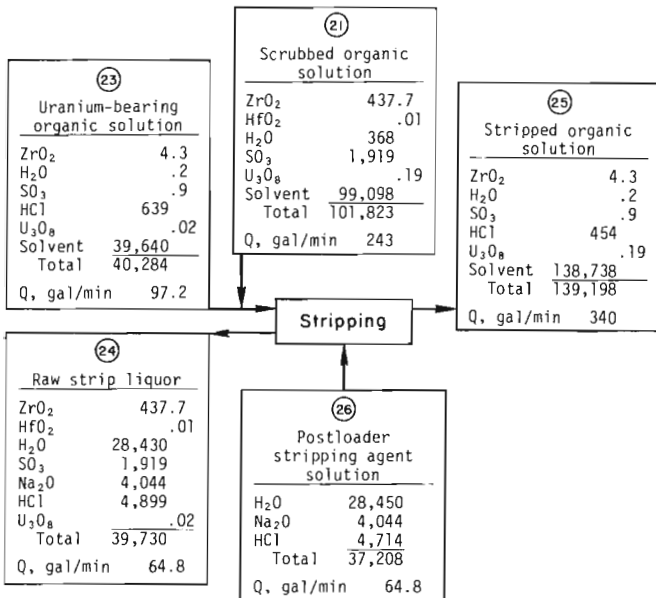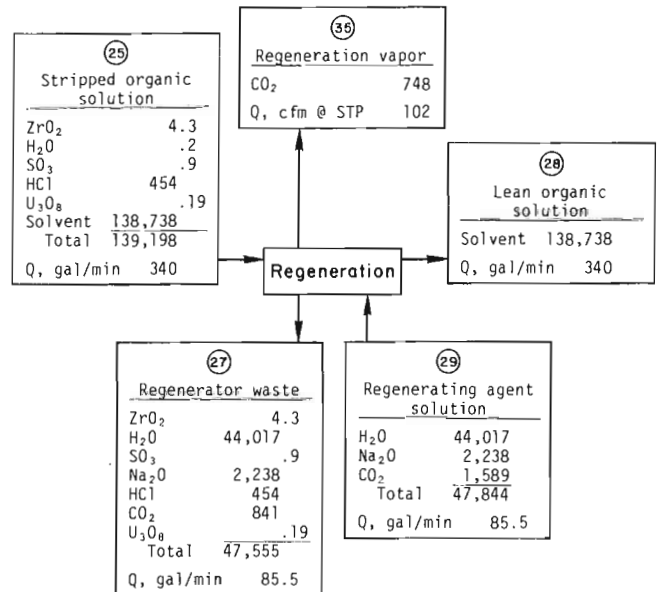
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APPENDIX A.--SYMBOLS

A	a constant in equation 5
B	a constant in equation 5
CL1, CL2, etc.	numbered stages of chloride-loading
D_1, D_2	distribution ratio for components 1 and 2, dimensionless
D_{Hf}	distribution ratio for hafnium, dimensionless
D_{Zr}	distribution ratio for zirconium, dimensionless
EX1, EX2, etc.	numbered stages of extraction
N_{ex}	number of extraction stages
N_{sc}	number of scrubbing stages
Q_{aq}	volume rate of flow of aqueous phase, mL/min
Q_{feed}	volume rate of flow of aqueous feed, mL/min
Q_{org}	volume rate of flow of organic phase, mL/min
Q_{reg}	volume rate of flow of regenerating agent solution, mL/min
Q_{scr}	volume rate of flow of scrubbing agent solution, mL/min
Q_{st}	volume rate of flow of stripping agent solution, mL/min
REG1, REG2, etc.	numbered stages of regeneration
SC1, SC2, etc.	numbered stages of scrubbing
ST1, ST2, etc.	numbered stages of stripping
USC1, USC2, etc.	numbered stages of uranium-scrubbing
$[Cl]_{org}$	concentration of chloride in organic phase, mol/L
$[H_2SO_4]$	concentration of H_2SO_4 in aqueous phase, mol/L
$[H_2SO_4]_{feed}$	concentration of H_2SO_4 in feed solution, mol/L
$[H_2SO_4]_{scr}$	concentration of H_2SO_4 in scrubbing agent solution, mol/L
$[Hf]_{aq}$	concentration of Hf in aqueous phase, g/L
$[Hf]_{feed}$	concentration of Hf in feed solution, g/L
$[Hf]_{org}$	concentration of Hf in organic phase, g/L
$[NaCl]_{aq}$	concentration of NaCl in aqueous phase, mol/L
$[Zr]_{aq}$	concentration of Zr in aqueous phase, g/L
$[Zr]_{feed}$	concentration of Zr in feed solution, g/L
$[Zr]_{org}$	concentration of Zr in organic phase, g/L
α	separation factor, dimensionless

APPENDIX B.—EFFECT OF CARBOXYLIC ACIDS ON ZIRCONIUM-HAFNIUM SEPARATION FACTOR

The separation factor can be affected by water-soluble carboxylic acids (16)[1] and is affected most favorably by certain α-hydroxy carboxylic acids (20). These presumably act by selectively altering the complexation of zirconium relative to that of hafnium, thereby altering their relative extractability. The effects of several water-soluble substances on the separation factor and organic-phase loading of zirconium are shown in tables B-1 and B-2. Table B-1 gives the zirconium-hafnium separation factor for 10 pct Alamine 336 and 5 pct decanol in kerosine contacted at a 1:1 phase ratio with aqueous solutions initially bearing 6.0 g/L Zr (0.065 mol/L Zr and with tracer amounts of radioisotope hafnium). Table B-2 shows organic-phase loading of zirconium for 10 pct Alamine 336 and 5 pct decanol in kerosine by extraction at a 1:1 phase ratio from aqueous solutions initially bearing 6.0 g/L Zr (0.065 mol/L Zr). Lactic acid was the most effective of the substances for improving zirconium-hafnium separation. The presence of 2 to 6 mol of lactic acid per mole of zirconium in the aqueous phase, together with H_2SO_4 in a concentration range of 0.5M to 2M H_2SO_4, increased the separation factor by more than 50 pct. Although the effect was demonstrated in single-stage experiments using separatory funnels, carboxylic acid additives were not used in multistage mixer-settler experiments.

[1] Underlined numbers in parentheses refer to items in the list of references preceding appendix A.

TABLE B-1. – Separation factor (α) in the presence of additives at various H_2SO_4 concentrations

Additive (0.26M)	0.10 mol/L	0.25 mol/L	0.50 mol/L	0.75 mol/L	1.00 mol/L	1.25 mol/L	1.50 mol/L	1.75 mol/L	2.0 mol/L	3.0 mol/L
None...............	NA	6.02	8.27	8.98	9.32	NA	9.10	NA	9.10	NA
NaHSO4............	NA	NA	NA	NA	NA	NA	NA	NA	9.2	NA
Formic acid.......	NA	1.02	4.48	9.32	10.9	NA	10.3	NA	9.49	NA
Acetic acid.......	NA	1.16	8.18	10.55	10.47	NA	10.1	NA	10.0	NA
Chloroacetic acid	NA	1.79	6.40	10.0	9.72	NA	9.46	NA	8.77	NA
Glycolic acid....	1.60	5.52	8.15	11.9	10.9	11.4	10.9	10.5	7.39	9.76
Malonic acid.....	NA	1.46	8.53	9.71	10.2	NA	10.4	NA	9.34	NA
Oxalic acid......	NA	1.47	1.49	1.56	1.53	1.62	1.67	1.73	1.85	NA
Citric acid......	1.06	.99	1.24	NA	4.96	NA	11.9	NA	10.9	9.9
Lactic acid......	NA	8.55	12.2	13.4	14.4	NA	12.9	NA	11.8	NA
Salicylic acid[1]..	NA	2.73	8.87	10.0	9.49	NA	9.05	NA	7.33	NA

NA Not available.   [1] Used at 0.13M because of limited solubility.

TABLE B-2. – Organic-phase loading of zirconium, in grams per liter, in the presence of additives at various H_2SO_4 concentrations

Additive (0.26M)	0.10 mol/L	0.25 mol/L	0.50 mol/L	0.75 mol/L	1.00 mol/L	1.25 mol/L	1.50 mol/L	1.75 mol/L	2.0 mol/L	3.0 mol/L
None...............	NA	5.45	4.15	4.00	3.75	NA	3.25	NA	2.50	NA
NaHSO$_4$............	NA	NA	NA	NA	NA	NA	NA	NA	3.61	NA
Formic acid......	NA	3.58	3.74	3.64	3.78	NA	3.22	NA	2.47	NA
Acetic acid......	NA	4.27	4.13	4.13	3.88	NA	3.31	NA	2.55	NA
Chloroacetic acid	NA	1.65	2.15	2.40	2.25	NA	1.95	NA	1.60	NA
Glycolic acid....	4.11	4.04	3.88	3.87	3.60	3.32	3.11	2.72	2.34	0.93
Malonic acid.....	NA	3.58	4.01	3.91	3.66	NA	3.12	NA	2.29	NA
Oxalic acid......	NA	4.44	4.29	4.16	3.99	3.62	3.43	3.13	3.20	NA
Citric acid......	5.52	4.60	2.16	NA	2.72	NA	2.76	NA	3.20	4.66
Lactic acid......	NA	3.74	3.49	3.56	3.42	NA	2.77	NA	2.05	NA
Salicylic acid[1]..	NA	3.97	2.80	2.77	2.59	NA	2.35	NA	2.04	NA

NA Not available.   [1]Used at 0.13M because of limited solubility.

APPENDIX C.--DENSITY, SURFACE TENSION, AND VISCOSITY OF SOLUTIONS

TABLE C-1.- Density, surface tension, and viscosity of solutions of Alamine 336 and
decanol in kerosine[1] at 25° C, after conditioning by contact with 1.0M H_2SO_4

Alamine 336, pct	Decanol, pct	[Zr], g/L	Density,[2] g/mL	Surface tension,[3] dyn/cm	Viscosity,[4] cP
0	0.0	0	NA	[5,6]44.8	NA
10	5	0	0.814	23.4	2.70
20	10	0	.831	24.6	6.95
25	12.5	0	.838	22.4	9.8
30	15	0	.841	24.2	14.5
35	17.5	0	.853	26.6	19.2
40	20	0	.861	NA	NA
10	5	4	.817	23.6	2.5
35	17.5	10	.868	24.9	15.9

NA Not available.
[1]Chevron Pearl Kerosene, Standard Oil Co. of California.
[2]Measured with a pycnometer.
[3]Relative to air, and measured by the capillary rise method.
[4]Measured with an Ostwald viscometer.
[5]Surface tension relative to water.
[6]Reference 6.

TABLE C-2. - Density, surface tension, and viscosity of selected aqueous
solutions at 25° C

Composition	Density,[1] g/mL	Surface tension,[2] dyn/cm	Viscosity,[3] cP
NaCl, 2.0 mol/L......................	1.112	73.3	1.34
NaCl, 4.0 mol/L; and HCl, 0.5 mol/L..	1.56	NA	NA
NaCl, 3.0 mol/L; and Zr, 20 g/L......	1.168	53.6	1.59
H_2SO_4, 1.0 mol/L......................	1.058	71.8	1.18
H_2SO_4, 1.0 mol/L; and Zr, 10 g/L.....	1.084	72.7	1.17
Na_2CO_3, 10 pct......................	1.102	74.4	1.57

NA Not available.
[1]Measured with a pycnometer.
[2]Relative to air, and measured by the capillary rise method.
[3]Measured with an Ostwald viscometer.