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Review of Anhydrous Zirconium-Hafnium Separation Techniques

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom
atm	atmosphere
°C	degree Celsius
cm	centimeter
cm^3/mol	cubic centimeter per gram mole
cm/h	centimeter per hour
ft	foot
g	gram
$g/cm^3 \cdot h$	gram per cubic centimeter per hour
h	hour
in	inch
K	Kelvin
kcal/mol	kilocalorie per gram mole
kg/cm^2	kilogram per square centimeter
kJ	kilojoule
kJ/mol	kilojoule per gram mole
kPa	kilopascal
lb	pound
lb/h	pound per hour
m	meter
mm	millimeter
µm	micrometer
mm Hg	millimeter of mercury
min	minute
mol pct	mole percent
pct	percent, usually weight percent
ppm	part per million
psi	pound per square inch

REVIEW OF ANHYDROUS ZIRCONIUM-HAFNIUM SEPARATION TECHNIQUES

By Robert L. Skaggs,[1] Daniel T. Rogers,[2] and Don B. Hunter[3]

ABSTRACT

Sixteen nonaqueous techniques conceived to replace the current aqueous scheme for separating hafnium and zirconium tetrachlorides were reviewed and evaluated by the Bureau of Mines. The methods are divided into two classes: separation by fractional volatilization of the tetrachlorides, which takes advantage of the higher volatility of hafnium tetrachloride; and separation by chemical techniques, based on differences in chemical behavior of the two tetrachlorides.

The criteria used to evaluate separation methods were temperature, pressure, separation factor per equilibrium stage, complexity, compatibility with existing technology, and potential for continuous operation. Three processes were selected as being most promising: (1) high-pressure distillation, (2) extractive distillation from a molten salt, and (3) preferential reduction of gaseous $ZrCl_4$. Any of the proposed nonaqueous Hf-Zr separation schemes must be supplemented with additional purification to remove trace impurities.

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INTRODUCTION

This Bureau of Mines report focuses on one aspect of the problem of producing nuclear-grade zirconium, via zirconium tetrachloride, in a nonaqueous system. In 1981, reports of promising, nonaqueous Hf-Zr separation work in France and Japan led the Bureau to initiate a project to reexamine the field. During 1982 a literature search covering 1955-82 was conducted. The search included $HfCl_4$-$ZrCl_4$ separation techniques and related thermodynamic data and phase equilibria. Sixteen separation processes were critically evaluated and rated by a semiquantitative method based on cost parameters. On the basis of this evaluation, three processes were identified as promising candidates for commercial-scale separation. The three processes are--

1. High-pressure liquid-vapor distillation.

2. Extractive distillation at 1 atm.

3. Separation by the preferential reduction of $ZrCl_{4(g)}$ to $ZrCl_{3(s)}$.

The techniques reviewed were limited to Hf-Zr separation. In no case was the problem of the removal of trace elements considered. The evaluation is incomplete in that it does not address this important question. Any nonaqueous Hf-Zr separation scheme will entail the use of additional purification to achieve trace element removal. The most promising technique for accomplishing this is molten-salt scrubbing.

Zirconium, once considered a rare element, is actually common in the earth's crust. Current estimates indicate that zirconium makes up 0.028 pct of the lithosphere and is about as plentiful as carbon and much more abundant than the less expensive metals copper, nickel, lead, and zinc (37).[4] Zirconium is always accompanied by hafnium in its natural deposits, with Zr:Hf ratios averaging about 50 to 1 (40). The most common sources of zirconium are zircon ($ZrO_2 \cdot SiO_2$) and baddeleyite (ZrO_2). Zircon, the more abundant of the commercially important minerals, occurs domestically in beach sands of Florida but is also imported from Australia and South Africa (40).

The cost of nuclear-grade zirconium ingot, \$11.60/lb in January 1983, is considered high for such a plentiful element, but there are several reasons for the high cost:

1. The zircon ore is very stable. Although a number of techniques have been proposed for unlocking the ore, only three have achieved widespread use:

    a. Conversion to ZrCN in an electric arc furnace followed by chlorination.

    b. Direct carbochlorination in a gas-solid reactor.

    c. Caustic fusion.

In the process used by Teledyne Wah Chang, OR, and by Western Zirconium, UT, carbochlorination is employed twice: first to unlock the ore, and a second time to convert the oxide back to the chloride form after aqueous solvent extraction separation of hafnium.

2. The hafnium content of nuclear-grade zirconium must be less than 100 ppm. Hafnium has no perceptible effect on strength, ductility, or corrosion resistance, but it negates the utility of zirconium in a nuclear reactor. Nuclear-grade zirconium must have a low neutron absorption cross section (σ_c = 0.18 barn in zirconium), but the presence of even small amounts of hafnium (σ_c = 105 barns) greatly increases absorption of neutrons. Separation of these two metals is costly because their chemical properties are nearly identical.

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

3. The presence of other minor impurities not only affects the ductility and corrosion resistence of zirconium, but also increases neutron absorption. Fissionable elements such as uranium and thorium are particularly detrimental because of the degradation of mechanical properties that can occur on exposure to radiation.

Since mineral acids other than Hf will not attack zircon (6, 60), traditional extraction processes rely on high-temperature treatment in the presence of carbon and chlorine. In these processes zircon is reacted with carbon in an arc furnace at 3,500° C to form zirconium carbonitride, while silicon is driven off as SiO gas. The carbide then reacts exothermally with Cl_2 to form zirconium tetrachloride ($ZrCl_4$), which is condensed in a separate nickel-lined chamber.

The present commercial process (carbochlorination) involves treatment of zircon sand-carbon mixtures with chlorine at 1,150° C in a fluidized-bed reactor (59, 61). The silicon tetrachloride byproduct is readily separated from the less volatile $ZrCl_4$. Table 1 shows a typical analysis of the crude $ZrCl_4$ product.

TABLE 1. - Typical analysis of crude $ZrCl_4$,[1] percent

Element	$ZrCl_4$	Zr metal basis
Zr...............	38.3	Balance
Hf...............	.84	2.2
Al...............	.09	.23
Fe...............	.19	.5
P................	.03	.08
Si...............	.08	.2
Th...............	.01	.03
Ti...............	.008	.02
U................	.03	.08
Insoluble in H_2O.	.5	NAp
Cl^-..............	Balance	NAp

NAp Not applicable.

[1] Supplied by Teledyne Wah Chang, Albany, OR, Dec. 1981.

In another commercial method used to obtain aqueous process solutions, the zircon ore is reacted with dry NaOH in a steel vessel at 600° to 650° C to form a frit:

$$ZrO_2 \cdot SiO_2 + 4\ NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2\ H_2O. \qquad (1)$$

The solid frit is washed with water to remove soluble silicates. Nitric or sulfuric acid is added to dissolve the zirconium values. Caustic fusion has been used for unlocking the zircon ore by Columbia National in Pensacola, FL, in conjuction with the tributyl phosphate(TBP)-nitric acid separation process. TBP in n-hexane is used as the organic solvent for removing zirconium from the nitric acid solution.

Another aqueous method used commercially for achieving Hf-Zr separation is the methyl isobutyl ketone (MIBK)-thiocyanate process. Thiocyanate solutions in MIBK are used for removing hafnium from the aqueous phase. The less commonly used TBP-nitric acid process produces reactor-grade hafnium oxide as a byproduct only with great difficulty and is not being used commercially at present. Hafnium production is important because its high neutron absorption cross section makes it valuable as a control rod in nuclear reactors. Hence the MIBK-thiocyanate process is preferred.

After removal of the hafnium, hydrous zirconium oxide must be precipitated from solution, washed with water to remove impurities, and calcined to the oxide, and the oxide must be rechlorinated to the tetrachloride. Thus, removal of hafnium from zirconium by solvent extraction is a costly, energy-inefficient process.

Reduction of the tetrachloride to produce zirconium (or hafnium) metal must be carried out in the absence of air, because the absorption of oxygen or nitrogen renders these metals brittle. Before the invention of the Kroll process, the only practical way of preparing ductile zirconium metal was to decompose ZrI_4 on a hot tungsten wire. This is a slow, expensive process. The Kroll process was developed in the mid-1940's, and commercial production of zirconium metal was achieved in 1953.

The Kroll process is a batch technique and consists of the following steps:

1. Sublimation of impure $ZrCl_4$ in an inert atmosphere such as argon, to leave behind undesirable oxides and other nonvolatile impurities.

2. Reduction of the $ZrCl_4$ vapor with excess magnesium metal at 825° to 875° C to produce zirconium sponge.

3. Vacuum treatment at 920° to 960° C to remove Mg and $MgCl_2$. This step is carried out with the container inverted to allow partial drainage of liquid Mg and $MgCl_2$ from the solid zirconium sponge, which clings to the container wall.

Zirconium sponge produced in this way meets impurity limits of ASTM specification B 349-73 (2), shown in table 2. Standards for hafnium are not as strict, although 2 to 5 pct Zr content is the accepted upper limit for hafnium metal. The chemical requirements for reactor-grade hafnium metal are given by Goodwin (25) and are listed in table 3.

After the zirconium sponge is compacted and melted into ingots by the consumable electrode method, it is fabricated and used as cladding for the fissonable uranium in nuclear reactors (39). Zirconium and zirconium alloys are also used for structural components within such reactors.

TABLE 2. - ASTM specification B349-73 for nuclear-grade zirconium sponge (2)

Element	Max conc, ppm	Element	Max conc, ppm
Al........	75	Mn........	50
B.........	0.5	Mo........	50
C.........	50	N.........	50
Cd........	0.5	Ni........	70
Cl........	1,300	O.........	1,400
Co........	20	Si........	120
Cr........	200	Ti........	50
Cu........	30	W.........	50
Fe........	1,500	U (total).	3.5
Hf........	100		

TABLE 3. - Chemical requirements for reaction-grade hafnium metal (25)

Element	ppm[1]	Element	ppm[1]
Al...........	50	Mo...........	<10
B............	<5	N............	20
C............	50	Ni...........	<10
Cd...........	<1	O............	500
Co...........	<10	Pb...........	<10
Cr...........	<10	Si...........	<10
Cu...........	<50	Sn...........	<10
Fe...........	100	Ti...........	<10
H............	[2]<30	W............	50
Mg...........	<10		
Mn...........	<10	Zr......pct..	2.25

[1] Except zirconium.

[2] Vacuum melting would result in 5 to 10 ppm H.

SEPARATION TECHNIQUES BASED ON RELATIVE VOLATILITY

The close similarity between hafnium and zirconium is reflected in the physical constants of their chlorides, shown in table 4.

TABLE 4. - Physical constants of hafnium and zirconium tetrachlorides

Properties	$HfCl_4$	$ZrCl_4$	Properties	$HfCl_4$	$ZrCl_4$
Sublimation temp[1]..°C..	317	331	Critical point:		
Triple point:			Temperature......°C..	449.2	505.0
Temperature......°C..	432.0	437.0	Pressure........kPa..	5,776.12	5,766.31
Pressure........kPa..	4,501.3	2,235.92	Volume......cm^3/mol..	303.6	319.3

[1] Lange (37).

Source: Denisova (14) for all except sublimation temperature.

Three separation concepts (7-8, 24, 29-32, 58-59) based on the relative volatility of $HfCl_4$ and $ZrCl_4$ have been studied:

1. Thin-film sublimation at atmospheric pressure.

2. Molten-salt distillation at 1 atm (101.3 kPa).

3. High-pressure fractional distillation at 40 to 60 atm (4,050 to 6,080 kPa).

THIN-FILM SUBLIMATION

$HfCl_4$ and $ZrCl_4$ have a relative volatility P_{HfCl_4}/P_{ZrCl_4} of 1.9 at 250° C, enabling separation at 1 atm. However, sublimation columns do not operate as efficiently as countercurrent fractionation columns, because the solids adhere to the surfaces and thus do not flow countercurrent to the gas. To overcome this problem, mechanical transfer of solids down the column must be accomplished.

The vapor pressures of solid $ZrCl_4$ and of $HfCl_4$ may be represented by equations 2 and 3 (13):

$$\log P_{ZrCl_4} = 11.4632 - \frac{5,191}{T} \qquad (2)$$

(below 426° C),

$$\log P_{HfCl_4} = 11.6726 - \frac{5,148}{T} \qquad (3)$$

(below 412° C),

where P is in mm Hg and T is in kelvins.

As the relative volatility of these two tetrachlorides is nearly constant over the temperature range 150° to 350° C, the Fenske-Underwood equation (51) can be used to estimate the number of theoretical plates needed to achieve the desired separation, under a condition of total reflux:

$$n \log \alpha = \log \frac{(X_1/X_2)_p}{(X_1/X_2)_o}, \qquad (4)$$

where α = relative volatility (approximately 2 in the range of interest, 150° to 350° C),

n = number of theoretical plates required,

X_1/X_2 = ratio of mole fraction of more volatile component (1) to mole fraction of less volatile component (2) on a lower plate o and an upper plate p, respectively.

This approach predicts approximately 30 theoretical plates for the separation.

The concept was explored in 1949 by Plucknett, Hansen, and Duke (54), who attempted to separate zirconium and hafnium tetrachlorides in a 10-plate column with mechanical transfer of the solid material down the column. Practical separation was not accomplished because only the surface of the solids came into equilibrium with the traveling gases.

The opposite situation, stationary solids and an inert gas as a carrier for the volatilized tetrachlorides, was investigated by Jacqué and Dumez (32) in 1967. Temperature of the heated column was 300° to 400° C at the bottom, decreasing to 150° to 230° C at the top; column height was 2 m, and column ID was 16 mm. The authors stated that $ZrCl_4$ with an $HfCl_4$ content of 250 to 1,000 ppm could be produced by repeating the batch process several times. The authors postulated a process capable of producing 0.3 kg of "dehafniated" $ZrCl_4$ in a 4-h cycle. A bundle of parallel columns, 8 m long and 10 mm in ID, with a total cross section of approximately 80 cm^2, was required.

A process was devised by Goldberger and Gillot (22, 24) to overcome the disadvantages of the two solid-gas fractionation concepts described above. A column 4.5 cm in ID by 1 m long, maintained at

280° C, was filled with inert glass spheres of 0.42- to 0.59-mm diam, which moved down the column by gravity at a controlled rate of 50 cm/h. A drawing of the apparatus is shown in figure 1. The crude $ZrCl_4$ was vaporized in a chamber at the bottom of the column and carried upward by a stream of nitrogen gas. The $HfCl_4$-rich vapor was condensed at the top of the column. Fresh inert material was fed into the top of the column as replacement for that withdrawn at the bottom; the purified $ZrCl_4$ was vaporized from the glass spheres and condensed in a separate chamber. The patent by Goldberger and Gillot also covered separation by means of a temperature gradient without the nitrogen gas stream.

In this patent (24), it is stated that a mixture of 2.64 g $ZrCl_4$ and 2.51 g $HfCl_4$ (59.3 mol pct $ZrCl_4$), after fractionation for 3 h in the column described, had the following compositions:

Height of sampling point above bottom of heating jacket, cm	Composition of sample, mol pct $ZrCl_4$
12	68.7 ± 0.8
32	57.3 ± 3.0
52	38.5 ± 4.0

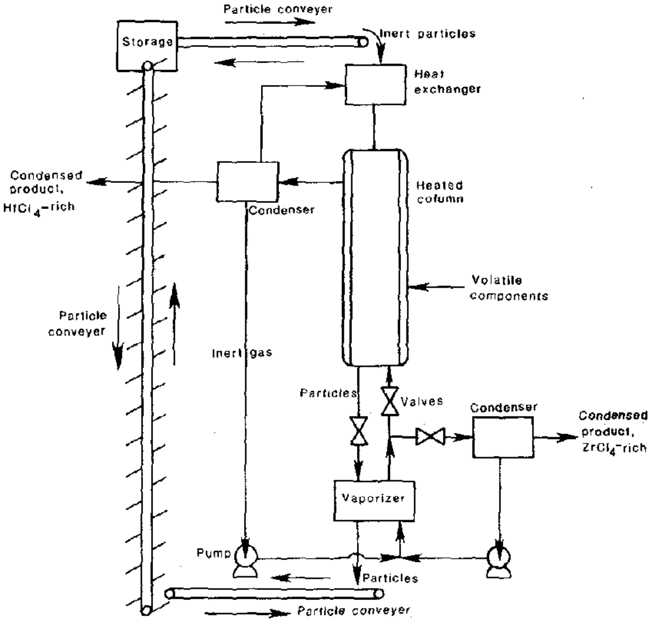

FIGURE 1. - Diagram of fractional sublimation apparatus used by Goldberger and Gillot (24).

The repeated sublimation and condensation of the tetrachlorides concentrates the more volatile $HfCl_4$ in the upper part of the column. Goldberger and Gillot found a height equivalent to a theoretical plate of 22 cm and postulated that the column length would have to be 4.2 m to achieve the desired purification of the $ZrCl_4$, but no practical work was done to confirm this. The process has the following advantages and disadvantages:

1. Process operates at atmospheric pressure; the need for high-pressure process components such as valves and seals is eliminated.

2. Temperatures do not exceed 350° C. Thus, material requirements are less stringent.

3. Process is simple in operation and could be operated continuously if required.

4. No process reagents are used, and no byproduct streams are created.

5. The main disadvantage is temperature control, particularly if larger diameter columns are used, because of the difficulty in achieving uniform radial temperature.

6. Secondary operations are required for stripping the inert solids exiting the bottom of the column, so that carrier material can be recycled.

7. The diffusional nature of the process requires that the uniform film thickness be less than 1 µm in order to achieve equilibrium between the solid and vapor within a realistic time period. This implies a very inefficient utilization of column volume. The mass throughput per equilibrium stage for the work described was approximately 0.004 $g/cm^3 \cdot h$, compared to a corresponding value of 5,800 times greater for the liquid-vapor separation of Ishizuka (29).

8. The need to protect the hydroscopic solid from contact with the atmosphere

complicates the problem of column operation.

EXTRACTIVE DISTILLATION FROM MOLTEN SALTS

Researchers (15-16, 24, 43) have pointed out the technical difficulties associated with the high-pressure liquid-vapor distillation of $ZrCl_4$-$HfCl_4$ mixtures. The operating pressures needed to achieve liquid-vapor distillation are in the range of 40 to 60 atm and require the use of special high-pressure components. A serious drawback associated with high operating pressure is the difficulty in achieving continuous operation that involves feeding a solid into the system. Only a narrow operational temperature range exists between the triple point (437° C) and the critical point (505° C) of $ZrCl_4$. This condition places a stringent temperature control requirement on the separation system.

A number of attempts have been made to achieve distillation using solutions of $(Zr,Hf)Cl_4$ in molten salts. The use of molten salts decreases the activity of the tetrachlorides and permits separation at atmospheric pressure and at temperatures below 400° C.

In 1976, Spink (58) obtained a patent covering the distillation of a feed mixture of 63 mol pct tetrachlorides, 29 mol pct KCl, and 8 mol pct NaCl. This is the ternary eutectic composition with an invariant freezing temperature of 218° C. As shown in figure 2, the crude feed eutectic solution is fed into a distillation column operating between 325° C at the top and 400° C at the bottom. Fifty theoretical plates are specified in order to obtain the desired end products, nuclear-grade $ZrCl_4$ and commercially pure $HfCl_4$. This number of plates corresponds to a relative volatility of 1.7, which is assumed constant over the entire range of operating temperature. Reflux of the $HfCl_4$-rich overhead vapor stream and recycle of the stripped $ZrCl_4$-rich salt bottoms are included in the scheme. This necessitates the handling of hot molten-salt streams; the feed and reflux flows can be transferred by gravity, but the recycle stream must be pumped. Pumping of molten salts in the range of 300° to 400° C requires special consideration. Alternatively, the molten salts could be transferred using inert gas pressure. A variation that avoids molten salt is to add the solvent salt at the top of the column as a granular solid. To eliminate the need to crush the solidified salt, Spink has experimented with "prilling" or dropwise solidification.

Removal of the product tetrachloride from the overhead and bottom streams is a major problem in molten-salt distillation. Spink and Jonasson (59) concluded that a combination of high temperature and vacuum was necessary to completely remove $ZrCl_4$ from the bottoms salt because of the high stabilities of K_2ZrCl_6 and Na_2ZrCl_6.

Three possible approaches for removal of the $ZrCl_4$ from the bottom stream will be considered in the following paragraphs:

1. Molten-salt electrolysis.—Electrowinning of zirconium from the $ZrCl_4$-rich bottoms stream is an attractive approach in that the solvent salt mixture would be returned to the mixing tank with its original composition. Spink and Vijayan (60), however, have demonstrated that the tetrachloride-rich solution is unsuitable for electrowinning because of the high vapor pressure exerted. For this reason, only dilute $ZrCl_4$ solutions are used in electrowinning. Martinez and Couch (41) were able to produce ductile zirconium crystals from NaCl melts, but the level of zirconium was only 2 pct. It is apparent that the bottom stream of the distillation column cannot be treated directly on a commercial scale by molten-salt electrolysis. Dilution is a possibility, but an extremely large electrolytic recovery vessel would be needed.

2. Partial thermal stripping with recycle.—Spink and Jonasson (59) have suggested that the addition of $MgCl_2$ to the solution salt might increase the activity of $ZrCl_4$ according to the reaction

$$K_2ZrCl_6 + MgCl_2 \rightarrow K_2MgCl_4 + ZrCl_{4(g)}, \qquad (5)$$

as reported by Tverskov and Morozov (63). Examination of the KCl-NaCl-$MgCl_2$ ternary system (32) shows three double salts: KCl•$MgCl_2$ (mp ≈ 490° C), NaCl•$MgCl_2$ (dec ≈ 465° C) and 2NaCl•$MgCl_2$ (dec ≈ 485° C) (36) (mp = melting point; dec = decomposition point.) A ternary eutectic point occurs at 385° C and approximately 46 mol pct $MgCl_2$, 21 mol pct KCl, and 33 mol pct NaCl. $ZrCl_4$ and $MgCl_2$ form a simple eutectic system with the invariant point at 426° C and 94 mol pct $ZrCl_4$. Thus, the addition of $MgCl_2$ to the metal chloride solvent not only increases the activity of $ZrCl_4$ by incorporating KCl and NaCl into double salts, but also lowers the melting point of the $ZrCl_4$-depleted return solvent salt.

Dutrizac and Flengas (15-16, 18) made a systematic study of the stabilities of double salts of zirconium and hafnium with alkali and alkaline-earth chlorides and found a relationship between decomposition temperature and the radius of the metal ion. Decomposition temperature was defined as the temperature at which the vapor pressure of the $ZrCl_4$ over the double salt was equal to 1 atm. Figure 3 shows a plot of decomposition temperature versus metal ion radius. The smaller metal ions are more able to pull a covalently bonded Cl^- ion from the octahedral $ZrCl_6{}^{2-}$ ion. The addition of Li^+, Mg^{2+},

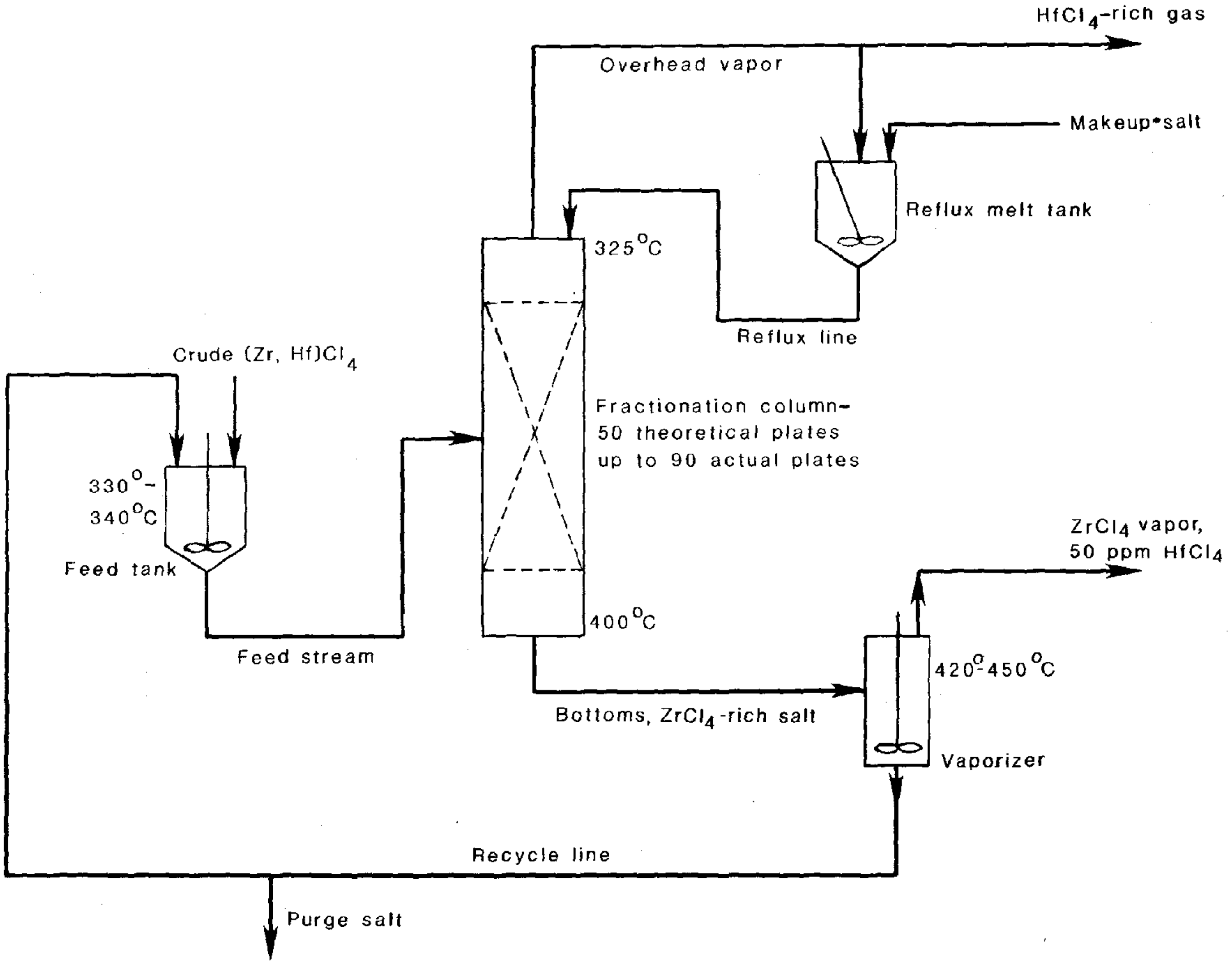

FIGURE 2. - Diagram of Spink extractive distillation process (58).

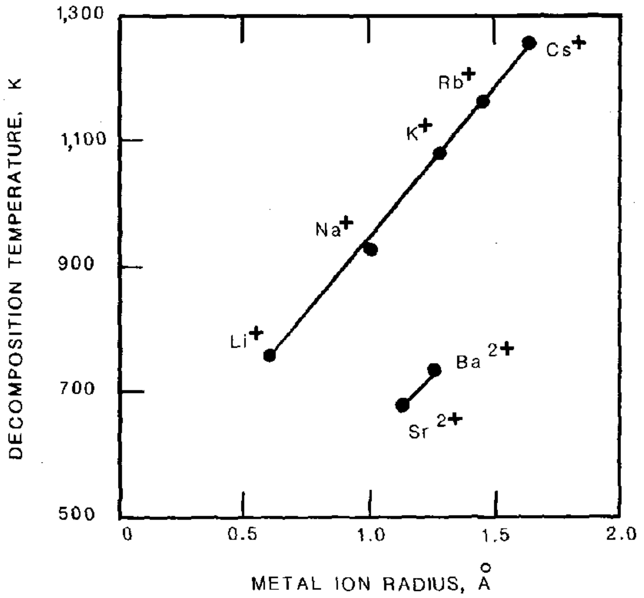

FIGURE 3. - Relationship between decomposition temperature of hexachlorozirconates and metal ion radius for selected alkali and alkaline earth elements. (After Morozov and Sun (45))

or Ca^{2+} to the melt breaks up the $ZrCl_6{}^{2-}$ ion and increases the activity of $ZrCl_4$. Such a solvent melt, high in LiCl and $MgCl_2$, should be easily stripped at moderate temperature.

3. Reduction in the salt solution with electrolysis of the product salt.--The entire bottoms stream may be fed directly into a vessel, where zirconium is recovered from the molten salt by reducing the $ZrCl_4$ to the metal, which precipitates. The zirconium-depleted salt is drained from the reduction vessel. During the reduction step, the original eutectic salt composition is altered due to the generation of either $MgCl_2$ or NaCl, depending on the reducing metal agent used. Electrolysis of the resulting NaCl-KCl-$MgCl_2$ salt solution could be used to restore the composition and at the same time generate reductant metal. Based on the relative oxidation potentials, the resulting metal would be predominately magnesium.

The above practice would provide a completely closed system. The distillation column becomes an integral component in a closed system consisting of extractive distillation column, reduction reactor, and a molten-salt electrolysis cell for the recovery of the high-magnesium alloy. Opportunities exist for energy conservation by the use of hot metal and hot salt transfer from stage to stage. However, it is not consistent with existing practice, which involves reduction of the pure tetrachloride with magnesium. New techniques and equipment would be required if reduction in molten-salt solution were adopted.

The process developed by Besson (5) for Pechiney Ugine Kuhlmann, whose subsidiary Cezus is reported by Brun (8) to be using it commercially, is based on mixing $ZrCl_4$ and $HfCl_4$ with molten aluminum chloride and potassium chloride and distilling the mixture at atmospheric pressure. It is referred to as the Cezus-Pechiney process. The resulting $ZrCl_4$ contains less than 50 ppm $HfCl_4$. This process has been termed "extractive distillation" by its developers and is similar to the process investigated by Spink. Two critical differences are evident:

1. The ratio of $AlCl_3$ and $FeCl_3$ to KCl in the melt must be maintained above 0.94:1, and preferably between 1.04 to 1.10:1, by periodic addition of $AlCl_3$ or $FeCl_3$.

2. After the $HfCl_4$ has been removed from the $ZrCl_4$, the latter is stripped out of the solvent salt by a nitrogen stream and condensed. The molten solvent salts are recirculated to the top of the column so that the operation is continuous. Figure 4 shows a schematic representation of the process.

Although the patent claim of Besson (5) cites use of either $FeCl_3$ or $AlCl_3$ in the solvent salt, in the process described by Brun (8) only $AlCl_3$ is used.

Based on the correlation of Dutrizac and Flengas (15), $FeCl_3$ or $AlCl_3$ should be quite effective in unlocking the $ZrCl_6{}^{2-}$ complex. They have shown that the stability of the metal chlorozirconate will vary as $(r_m + r_{Cl})^2/q_m$, where r_m is the ionic radius of the metal, r_{Cl} is

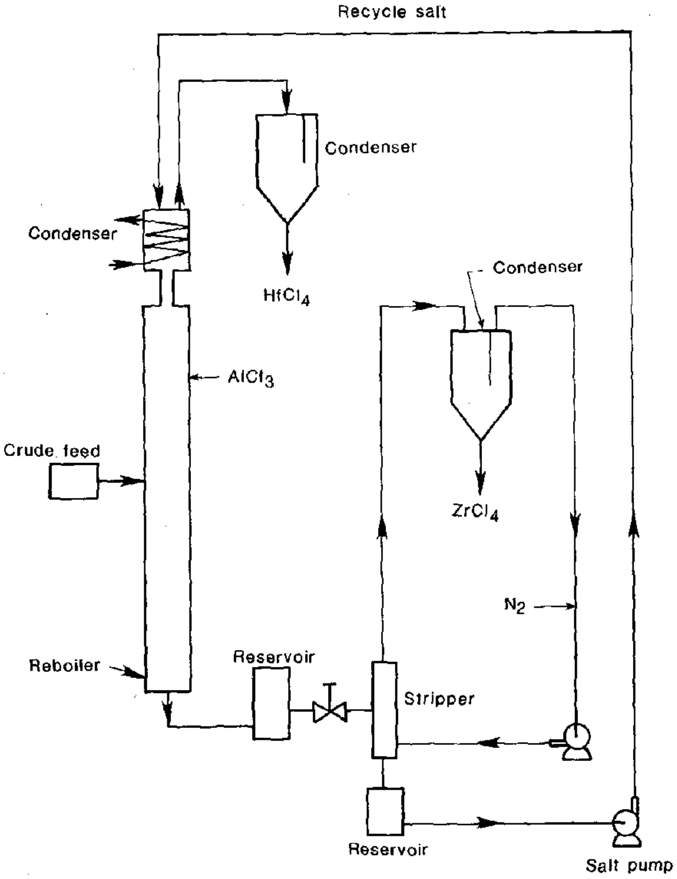

FIGURE 4. - Pechiney process for extractive distillation (5).

the covalent radius of chlorine in the $ZrCl_6^{2-}$ complex, and q_m is the charge on the metal ion. Table 5 shows the decomposition temperatures of several alkali chlorozirconate and chlorohafnate compounds. Because of the relatively small size and trivalency of Fe^{3+} or Al^{3+}, the removal of $ZrCl_4$ should be accomplished readily. Besson (5) reports that at 500° C and 13 mm Hg (1.7 kPa), the residual $ZrCl_4$ was reduced to 0.6 g/100 g $KAlCl_4$. No mention was made of $FeCl_3$ or $AlCl_3$ contamination of the product tetrachloride. This should occur because of the volatilities of these two substances, but the product reported by Brun (8) yields a nuclear-grade sponge.

TABLE 5. - Comparison of the thermal stability of the alkali chlorozirconate and chlorohafnate compounds

Compound	Decomposition temperature,[1] °C	Reference
Li_2ZrCl_6....	501	3
Li_2HfCl_6....	513	3
Na_2ZrCl_6....	634	3
Na_2HfCl_6....	~648	35
K_2ZrCl_6.....	831	3
K_2HfCl_6.....	863	34
Rb_2ZrCl_6....	904	3
Cs_2ZrCl_6....	1,040	3
Cs_2HfCl_6....	953	3

[1] $P_{(Zr,Hf)Cl_4}$ = 1 atm.

This extractive distillation process, termed by its inventors the "S" process, is being used in a pilot plant, replacing the MIBK-thiocyanate process. However, nothing in either the patent claim by Besson or the article by Brun indicates how contamination of the purified $ZrCl_4$ by $AlCl_3$ is prevented. There must be a practical reason for using $AlCl_3$ instead of $FeCl_3$, because ASTM specifications permit 1,500 ppm Fe but only 75 ppm $AlCl_3$ in the zirconium metal.

The role of trace impurity chlorides must be considered in any molten-salt extraction process. The main impurities are the chlorides of Fe, Al, Si, P, and Ti (table 1); in the Cezus process (7), these are removed by a preliminary sublimation of the crude $ZrCl_4$-$HfCl_4$. An alternative method is molten-salt scrubbing of the $ZrCl_4$, described by Spink (53). Greenberg (26) and Frey (20) describe other patented methods for selective impurity removal. Greenberg claims that aluminum halides can be removed by distilling the $ZrCl_4$ through $CaCl_2$. Frey states that the use of highly viscous oil that carbonizes below the sublimation points of $ZrCl_4$ and $HfCl_4$ will remove $FeCl_3$. A patent was issued to Ross (55) for removal of CO, $COCl_2$, and Cl_2 from crude $ZrCl_4$. The impure $ZrCl_4$ was dissolved in a KCl-NaCl bath partitioned into chambers, and the purified tetrachloride was removed as a vapor.

HIGH-PRESSURE LIQUID-VAPOR DISTILLATION

Distillation techniques require heavy-duty components necessary to withstand pressures of 587.6 to 881.4 psi (4,050 to

6,080 kPa) and temperatures up to 505° C. Materials of construction must be resistant to $ZrCl_4$, $HfCl_4$, and impurity chlorides. Despite these requirements, several processes have been devised for the high-pressure liquid-vapor separation of $ZrCl_4$ and $HfCl_4$.

In 1958, Bromberg (7) patented a method for purification of $ZrCl_4$ by fractional distillation. The patent claims that the temperature should be between 455° and 520° C at the bottom of the column and a minimum of 440° C at the top. The critical temperature for $ZrCl_4$ was probably not known in 1958 when the Bromberg patent was written because 520° C is above the critical temperature for $ZrCl_4$ (505° C). A line leading from the top of the column enables the more volatile $HfCl_4$ to be condensed in a receiving vessel. The purified condensed $ZrCl_4$ is collected in a receiving vessel at the bottom. The impure $ZrCl_4$ (1.6 pct $HfCl_4$) is vaporized from a boiler at the side of the fractionation column. Valves on all three storage vessels enable the $HfCl_4$-rich distillate (92 pct $HfCl_4$) and the purified $ZrCl_4$ (60 ppm $HfCl_4$) to be withdrawn at intervals, and fresh, impure $ZrCl_4$ to be added periodically. Preferred operating temperatures were 495° C at the bottom and 460° C at the top. The column was constructed of type 316 stainless steel, and was 26 ft high by 3 in. in ID. Either a plate or packed-column design is claimed to be effective. Bromberg claimed that a 36-ft column, operating at a reflux ratio of 100:1, would produce nuclear-grade $ZrCl_4$ in the bottom receiver, while purified $HfCl_4$ would be taken off from the top.

The narrow operating range of this process was made clear in 1967 when Denisova, Safronov, Pustil'nik, and Bystrova published their study of liquid-vapor phase equilibria of $ZrCl_4$ and $HfCl_4$ (14). In figure 5, solid-vapor and liquid-vapor behavior are shown. The authors' extension of the log P versus $10^3/T$ plot into the supercritical region is unexplained. Figure 6 shows the densities of coexisting liquid and vapor phases at constant temperature. The temperature at

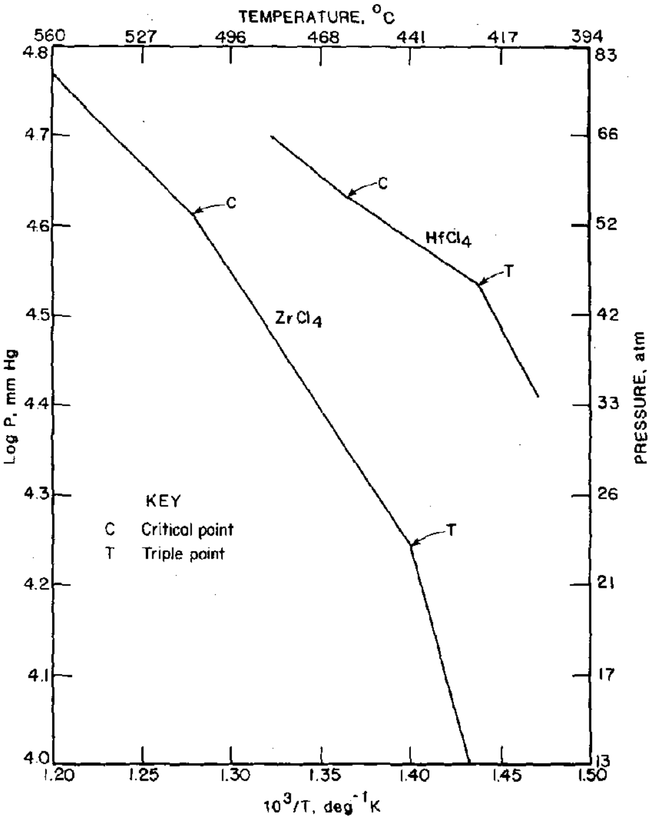

FIGURE 5. - Vapor pressure of $ZrCl_4$ and $HfCl_4$. (After Denisova (14))

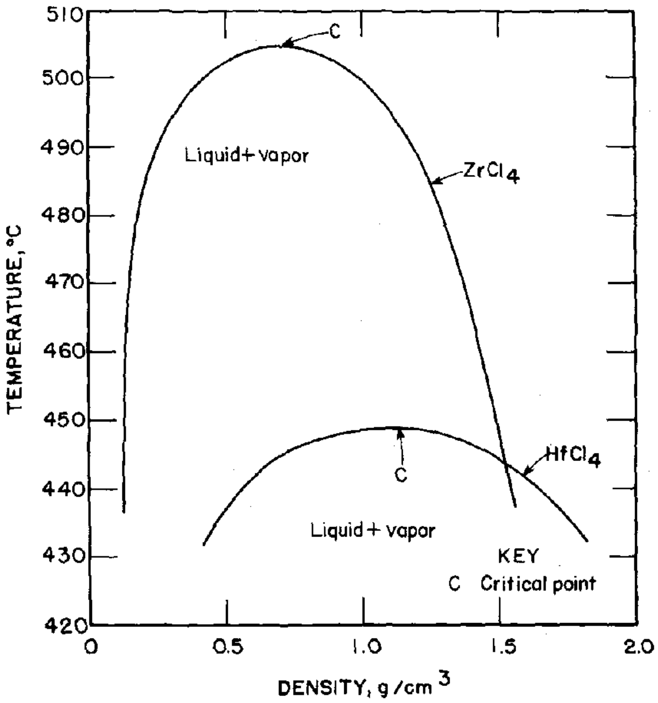

FIGURE 6. - Density of coexisting liquid and vapor phases of $ZrCl_4$ and $HfCl_4$. (After Denisova (14))

the bottom of the column is limited by the critical conditions for $ZrCl_4$ (5,766.3 kPa and 505.0° C). The lower temperature limit of operation is the triple point for $HfCl_4$, 432° C.

The necessity for a narrow range of operating conditions was also reported by Ishizuka (29). The 1974 patent application stated that the temperature of the boiler was 469° C, bottom rectifier 466° C, top rectifier 461° C, and condenser 454° C, at an operating pressure of 40 kg/cm^2 (3,900 kPa). Column height and ID were 700 mm and 20 mm, respectively. Figure 7 shows the type of apparatus used by Ishizuka. The crude feed to this batch process contained 2 pct $HfCl_4$ and produced, after 24 h of operation, a condenser product with 32 pct $HfCl_4$ and a $ZrCl_4$ boiler product with 50 ppm $HfCl_4$. Before the column was frozen to collect product fractions, the boiler product contained only 8 ppm $HfCl_4$. Although specification $HfCl_4$ (<5 pct $ZrCl_4$) was not obtained, extrapolation to the 26-ft column used by Bromberg (7) indicated that the Ishizuka column was more efficient.

Operation of a unit for processing 5 tons of crude $ZrCl_4$ is reported in a European patent application by Ishizuka (30). A mild steel column was good for 20 to 50 runs before it needed substantial repairs. A second distillation was necessary to convert hafnium-rich overhead chloride to nuclear-grade $HfCl_4$. Removal of impurity chloride was achieved by adding of small amounts of NaCl or KCl to form nonvolatile complexes with $AlCl_3$ and $FeCl_3$.

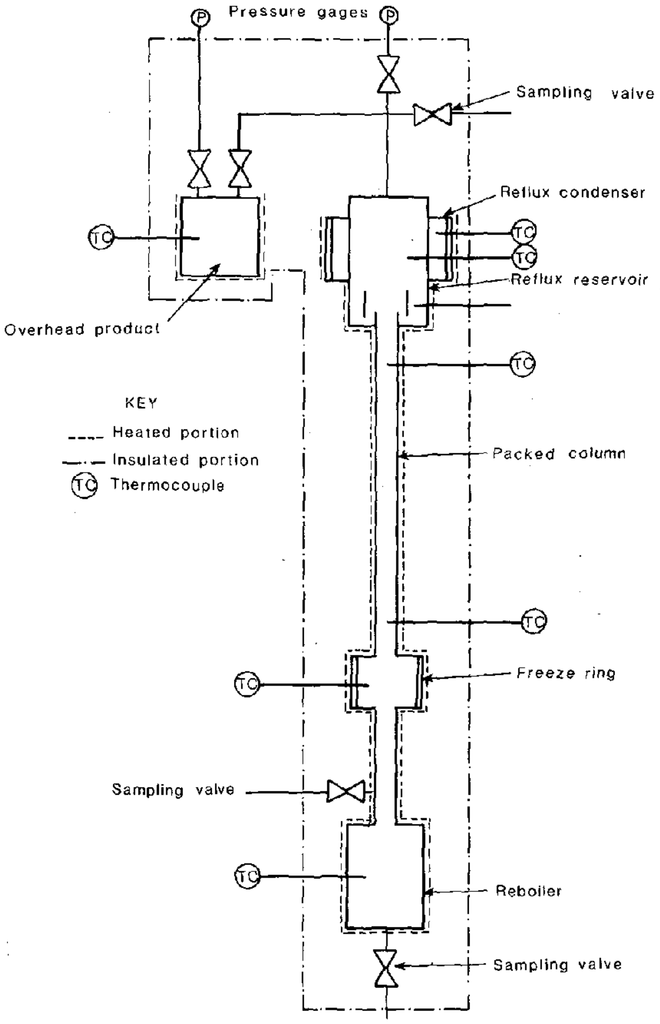

FIGURE 7. - Apparatus used by Ishizuka to separate $HfCl_4$ from $ZrCl_4$ (29).

The narrow operating range for fractional distillation shown in these patents would require close temperature control for successful separation of zirconium and hafnium tetrachlorides.

CHEMICAL METHODS OF SEPARATING HAFNIUM FROM ZIRCONIUM

Because of the difficulty of separating hafnium from zirconium by sublimation or fractional distillation, chemical methods have been investigated. Unlike the methods based on relative volatility, chemical separation techniques cannot be easily categorized. As a broad generality, hafnium compounds are slightly more stable than the corresponding zirconium analogs. This is probably because the Hf-X bond is stronger and displays a more covalent character than the Zr-X bond. These small differences have been exploited in the separation of hafnium from zirconium by chemical methods.

A number of schemes have been proposed. Each is unique, so the chemical separation methods must be treated individually. Several of the most promising candidate processes follow:

Preferential reduction of $ZrCl_4$ (Newnham - 1957) (46).

Fluoride-redox equilibrium (Megy - 1979) (44).

Chloride-oxide exchange (Chandler - 1966) (9).

Preferential decomposition of salts (Flengas and Dutrizac - 1977) (18).

Differential oxidation of chlorides (Berl - 1961) (4).

Each process has inherent advantages and disadvantages. The high separation factor and closed cycle nature of the Newnham process are offset by the necessity of handling pyrophoric solids. The Megy process has the highest separation factor, but the use of fluoride and the lack of compatibility with existing Kroll or electrolytic technology are serious disadvantages.

PREFERENTIAL REDUCTION OF $ZrCl_4$

In 1957, Newnham (46) obtained a patent for the separation of $HfCl_4$ from $ZrCl_4$ based on the observation that $ZrCl_4$ is more easily reduced to the lower chloride form than is $HfCl_4$. For example, at 427° C (700 K) the Gibbs energy change for the reaction (23)

$$HfCl_{3(s)} + ZrCl_{4(g)} \rightarrow HfCl_{4(g)} + ZrCl_{3(s)} \quad (6)$$

is -22 kcal/mol (-92 kJ/mol). The lower chloride of zirconium remains in the condensed form, while $HfCl_4$ and unreacted $ZrCl_4$ may be sublimed. The separation is much more effective than one based on the relative volatilities of $HfCl_4$ and $ZrCl_4$.

The reduction reaction may be represented by

$$Zr_{(s)} + 3\ ZrCl_{4(g)} \rightarrow 4\ ZrCl_{3(s)}. \quad (7)$$

A number of reducing agents may be used, but zirconium metal is preferred because no impurities are introduced into the system. The more volatile $HfCl_4$ and the unreacted $ZrCl_4$ remain in the gaseous form.

$ZrCl_3$ is subsequently heated to 420° to 460° C, where it disproportionates:

$$2\ ZrCl_{3(s)} \rightarrow ZrCl_{2(s)} + ZrCl_{4(g)}. \quad (8)$$

The low-hafnium $ZrCl_4$ product is recovered, and the resulting $ZrCl_2$ solids are recycled as a reducing agent in subsequent stages:

$$ZrCl_{2(s)} + ZrCl_{4(g)} \rightarrow 2\ ZrCl_{3(s)},\quad 340^\circ \text{ to } 420^\circ \text{ C}. \quad (9)$$

The patent proposes a process that is closed and cyclic.

In 1959, Newnham obtained a second patent (47) that extended the original concept to carry out the reduction in a molten-salt medium, such as $AlCl_3$-NaCl, LiCl-KCl, or other mixtures containing at least one alkali chloride salt. The molten-salt medium keeps the temperature close to the optimum required for selective reduction. In addition to separation of $ZrCl_3$ and $HfCl_4$ by volatility, the patent claims that this separation can be carried out through decantation or filtration, as $ZrCl_3$ is a solid in a liquid medium.

A related patent was issued in 1973 to Larsen and Gil-Arnao (38). In this case the crude $ZrCl_4$ is reacted with a metallic reducing agent (Al or Zr) in a pure molten $AlCl_3$ medium. Whereas Newnham insisted on the presence of an alkali chloride salt to maintain atmospheric pressure, Larsen implies that the resultant advantage of a faster reaction at lower temperature (260° C) is more important than avoiding higher pressure, which could be as high as 8 atm (810 kPa) for pure $AlCl_3$ at 260° C (12). Recycling of $ZrCl_2$ recovered is the same as in the Newnham method. Separation factors demonstrated by Larsen vary from 5.7 to 19.8, while Newnham (48) demonstrated values up to 200. Frampton and Feldman (19) report separation factors from 6.6 up to 22 for the technique. Separation factor (SF) is defined by

$$SF = \frac{\text{Hf in feed, pct}}{\text{Hf in product, pct}}. \qquad (10)$$

Larsen points out that the liquid-phase reaction mechanism overcomes the disadvantages of the solid-gas reaction of Newnham, where the $ZrCl_3$ coats the surface of the zirconium metal and impedes the reaction. With molten $AlCl_3$, the $ZrCl_4$ first forms a blue intermediate phase that is soluble in the melt, so that the melt turns blue. Brown $ZrCl_3$, which is insoluble in molten aluminum chloride, forms later, and the molten bath becomes colorless, which indicates the end of the reaction. Related patents are claimed by Newnham (48-49).

The disproportionation of $ZrCl_3$ to regenerate $ZrCl_2$ is complicated by a series of reactions to form nonstoichiometric compounds. Shelton and others (10, 54) summarize the reactions and their temperatures of occurrence, as follows:

$$12\ ZrCl_{3(s)} \rightarrow 10\ ZrCl_{2.8(s)} + 2\ ZrCl_{4(g)},\ 115° \text{ to } 300° \text{ C.} \qquad (11)$$

$$10\ ZrCl_{2.8(s)} \rightarrow 5\ ZrCl_{1.6(s)} + 5\ ZrCl_{4(g)},\ 310° \text{ to } 450° \text{ C.} \qquad (12)$$

$$5\ ZrCl_{1.6(s)} \rightarrow 4\ ZrCl_{(s)} + ZrCl_{4(g)},\ 500° \text{ to } 600° \text{ C.} \qquad (13)$$

$$4\ ZrCl_{(s)} \rightarrow 3\ Zr_{(s)} + ZrCl_{4(g)},\ 570° \text{ to } 700° \text{ C.} \qquad (14)$$

The equilibrium $ZrCl_4$ pressures for the first two of these reactions are given by Copley and Shelton (10):

$$\log P = -6{,}138/T + 13.288, \qquad (15)$$

$$\log P = -9{,}870/T + 15.555 \qquad (16)$$

respectively, where P is given in mm Hg and T in kelvins. The latter two reactions are not important in the currently conceived reduction process cycle.

Shown in figure 8 is a plot of log P versus $10^3/T$ for the sublimation of solid $HfCl_4$ and $ZrCl_4$ (56). On the same plot is shown the decomposition pressure of $ZrCl_{4(g)}$ over lower chlorides of zirconium. The stability of the lower chlorides of zirconium as a function of temperature and pressure is shown in figure 9 (56).

In 1968, Mauser (42) studied the selective reduction reaction occurring in a rotating stainless steel reactor filled with stainless steel balls. The rolling balls crush the particles and break up the $ZrCl_3$ coating that forms on the reductant and quenches the reaction. From this gas-solid reaction study, the following conclusions were drawn:

1. The reactor grinding balls were effective in eliminating sintering (agglomeration) of the reacting particles.

2. The dichloride ($ZrCl_2$) was not an effective reductant for $ZrCl_4$. Zirconium in the form of sponge, minus 325-mesh fines, or machine turnings had to be used. Regeneration was carried out at 900° C in order to drive the disproportionation reactions to completion and yield finely divided metallic zirconium. Improved yields and separations were reported with recycled zirconium. This was attributed to the increased surface resulting from repeated reduction and disproportionation. The zirconium became increasingly pyrophoric with each cycle.

3. Zirconium sponge and fines were equally effective reductants, but the turnings were less effective.

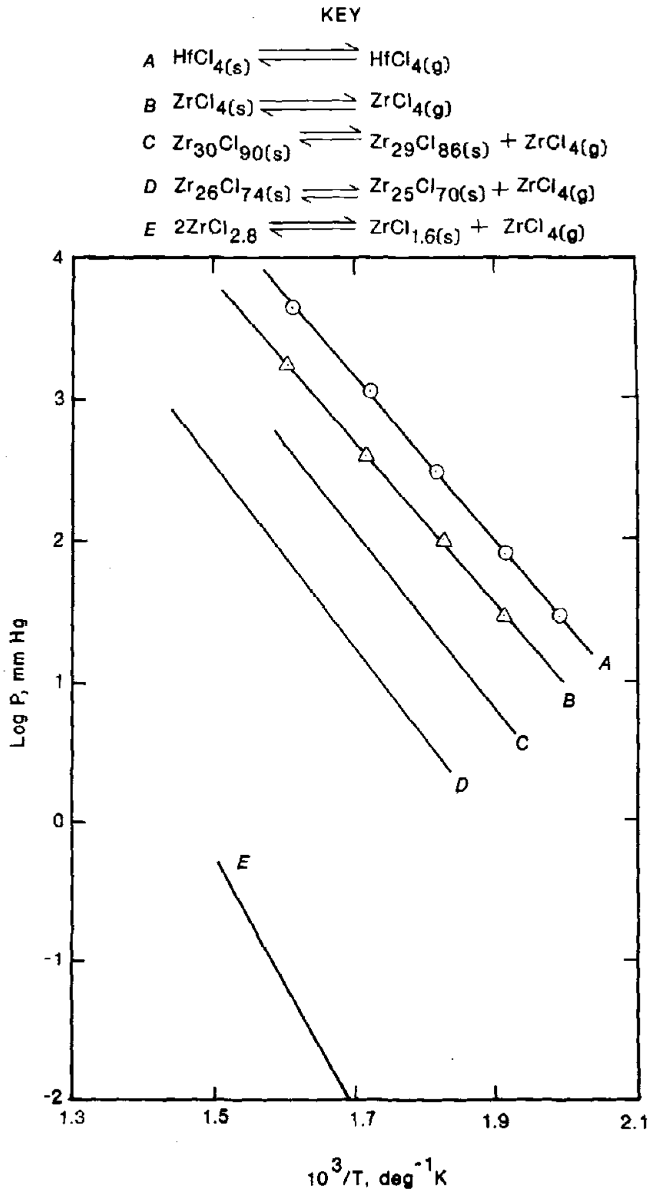

FIGURE 8. - Pressure of the tetrachloride gas over $HfCl_{4(s)}$, $ZrCl_{4(s)}$, and lower chlorides over Zr. (After Copley and Shelton (10))

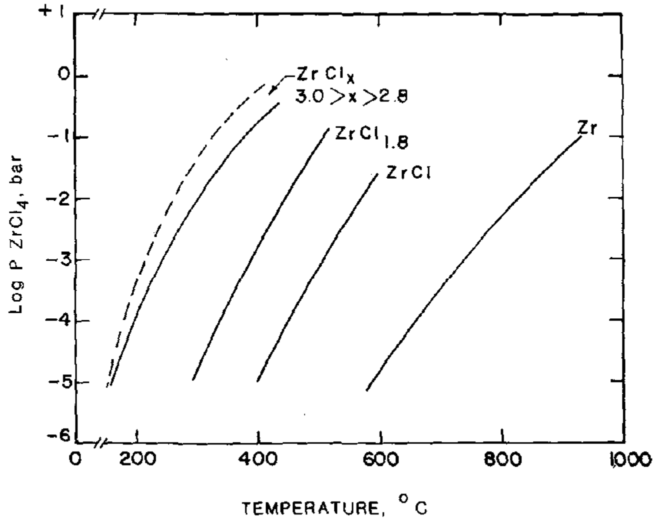

FIGURE 9. - Thermal stability of the lower chlorides of zirconium. (After Shelton (56))

National Distillers and Chemical Corp. obtained the rights to the Newnham patents and devoted considerable effort to bring the dry process to commercial practice. Frampton and Feldman (19) have described this work. Although $ZrCl_2$ is reported to be a satisfactory reducing agent, the temperature at which the preferential reduction is carried out is critical. In the temperature range 330° to 370° C, a nonselective lower chloride complex ($Zr_3Cl_8 \cdot HfCl_4$) is formed and decreases the separation factor. Above 420° C, the disproportionation of $ZrCl_3$ occurs at an appreciable rate. The $ZrCl_4$ formed mixes with $HfCl_4$, and the separation factor is decreased. These two conditions restrict the temperature of the reduction operation to 400°±20 ° C. The close temperature control was obtained by immersing the apparatus in a bath of molten tin; the authors suggested using molten sodium-potassium alloy (NaK) for large-scale operations. The equipment was constructed of type 316 or 347 stainless steel. To insure thorough mixing of the reactants, an anchor-type stirrer that scraped the bottom and sides of the container and prevented any buildup of solids was used.

Disproportionation of $ZrCl_3$ was carried out in the range 420° to 460° C and yielded product $ZrCl_4$ and regenerated $ZrCl_2$. The initial $ZrCl_2$ bed was prepared by reacting finely divided zirconium sponge with $ZrCl_4$ vapor at 430° C for an extended time and subsequently increasing the temperature to 460° C to cause disproportionation.

The authors proposed a pilot plant in which the reactions would be carried out in horizontal tube, screw-fed reactors that would produce 25 lb/h of hafnium-free $ZrCl_4$. The separation factor used in the hafnium concentration stage is a very conservative 1.6; three to four stages of separation were required to produce $ZrCl_4$ containing <100 ppm Hf/(Hf + Zr).

Frampton and Feldman report a three-stage separation using solid feed. Operating conditions and results are given in table 6. The solid-gas process (19, 46) studied by Frampton and Feldman has the following advantages:

1. The process is closed and cyclic and does not require reagents. The only raw materials are crude $ZrCl_4$ and makeup zirconium sponge.

2. The National Distillers work has already provided a process scheme with material balances and a tentative cost estimate.

3. The process lends itself to continuous countercurrent operation.

Disadvantages are--

1. Extremely close temperature control is required.

2. Reducible impurities, such as $FeCl_3$, will collect in the $ZrCl_2$ ($ZrCl_{1.6}$) bed and shorten its useful life.

3. Although the process is potentially continuous, initial designs will probably be batch with considerable manual handling of equipment and materials.

4. Mechanical agitation is necessary to expose fresh zirconium surface to vapor. Several techniques are available to accomplish this:

a. Stirred reactor.

b. Rotating ball mill reactor.

c. Fluidized-bed reactor.

5. The effectiveness of $ZrCl_2$ as a reducing agent is questionable. If Mauser's observations are correct, a considerably higher regeneration temperature (900° C) will be required in order to produce metallic zirconium.

TABLE 6. - Operating conditions and results for a three-stage separation of $HfCl_4$ from $ZrCl_4$ by the method of Frampton and Feldman (19)

Results	Temperature range, °C		
	301-328	302-319	318-338
Time..........h..	1.1	0.9	3.2
Hf content, pct:			
Feed...........	2.4	0.29	0.05
Product........	0.31	0.05	0.01
Yield, pct:			
Per stage......	65	54	77
Net............	65	35	27
Separation factor per stage.......	7.7	5.5	4.8

FLUORIDE REDOX EXCHANGE

In 1978, Megy (43) improved yields on the exchange reaction

$$ZrF_6^{2-} + Hf \rightleftarrows HfF_6^{2-} + Zr \qquad (17)$$

by the addition of molten zinc to dissolve the zirconium metal produced. The zinc shifted the reaction to the right because zirconium is preferentially dissolved in molten zinc and also increased the reaction rate by improving transport in the molten zinc so that conversion was essentially complete in 5 min.

The equilibrium constant (K_e) for the reaction as a function of temperature (T in kelvins) is

$$\log K_e = -1.565 + 4{,}320/T \qquad (18)$$

for systems using Na_2ZrF_6, plus NaCl and KCl to lower salt phase melting temperatures (700° to 900° C).

A reductant, preferably aluminum metal, must be used to convert hafnium and zirconium salts to the metal so that the exchange reaction can occur. The presence of aluminum salts does not interfere with the separation.

A similar reaction using chlorides rather than fluorides has the disadvantage of producing intermediate oxidation states (2+, 3+) for hafnium and zirconium.

Operating in the temperature range with molten zinc and fluoride salts poses formidable containment problems. Megy and Freund (44) found that during screening tests employing temperatures of 800° C for 1 h, vitreous quartz, boron nitride, alumina, and glassy carbon were attacked. Even tungsten and graphite were only marginally adequate. Graphite containers contributed 100 ppm C to the metal phase in a 1-h test (44). For this reason the Megy process is of limited interest.

CHLORIDE-OXIDE EXCHANGE REACTION

In 1966 Chandler (9) patented a method of separating $HfCl_4$ from $ZrCl_4$ by preferential conversion of $HfCl_4$ to HfO_2:

$$ZrO_{2(s)} + HfCl_{4(g)} \rightarrow HfO_{2(s)} + ZrCl_{4(g)}. \qquad (19)$$

This is achieved by passing the mixture of tetrachloride gases over a bed of ZrO_2 and HfO_2, where the hafnium preferentially enters the solid phase.

Hafnium is removed from the gas phase because HfO_2 is more stable than ZrO_2 relative to the respective chlorides. This is a thermodynamic rather than a kinetic effect (4, 21). Equilibrium constant calculations show little change (K_e = 2.3 to 2.8) between 25° and 950° C. K_e is determined from

$$K_e = \frac{[HfO_2]\,[ZrCl_4]}{[ZrO_2]\,[HfCl_4]}. \qquad (20)$$

The constant agrees approximately with that estimated from Chandler's experiments (K_e = 5).

In the limited work that Chandler performed, crude $ZrCl_4$ freshly prepared by carbochlorination was passed through a 15-in bed of crude ZrO_2 and removed two-thirds of the hafnium from the tetrachloride vapor stream (at 950° C over a 2-h period). No impurity removal was reported.

PREFERENTIAL DECOMPOSITION OF ALKALI METAL SALTS

Most physical methods for separating anhydrous hafnium and zirconium tetrachlorides make use of the higher volatility of $HfCl_4$.

Flengas and Dutrizac (16, 18) have discovered a separation method in which $ZrCl_4$ is the more volatile species. The chlorides are converted to alkali metal salts, M_2ZrCl_6 and M_2HfCl_6. The salts are heated, and preferential decomposition of the less stable zirconium salt occurs at >450° C:

$$M_2ZrCl_{6(s)} \rightarrow 2MCl_{(s)} + ZrCl_{4(g)}. \qquad (21)$$

Table 5 shows the decomposition temperatures of the double alkali metal chlorides that were compiled by Flengas and and others. Recent studies show that potassium is the preferred alkali metal cation for the reaction because all others show lower separation factors (34-35). The method used (16, 18) involves equilibration of 1 mol of $HfCl_4$-$ZrCl_4$ at 330° C with slightly more than 2 mol of KCl held at 450° C. Equilibration takes up to 3 days before a separation factor of 1.6 is achieved. If the $ZrCl_4$:KCl ratio is increased, the separation factor decreases. If the reaction time is decreased, the tendency of the zirconium salt to form more quickly than the hafnium salt (49) greatly decreases efficiency.

The disadvantages are--

1. The 3-day reaction time required for static equilibration greatly reduces production rates.

2. Small separation factors (1.6 to 1.9) for KCl systems require a large number of separation stages.

3. Continuous processes in a packed-salt column, where $ZrCl_4$ reacts quickly and decomposes quickly at low separation efficiency, are plagued by the problem of salt swelling; that is, volume change associated with the cyclic formation and decomposition of the double salt. The swelling causes plugging of the column (18).

Although both the reaction kinetics and the material throughput might be improved by development work, this process is not particularly promising.

DIFFERENTIAL OXIDATION OF CHLORIDES

Berl (4) has suggested a novel method for separating zirconium and hafnium compounds in a fluidized-bed reactor at temperatures above 600° C. The basis for separation is that the following exothermic reaction for $ZrCl_4$:

$$ZrCl_{4(g)} + O_{2(g)} \rightarrow ZrO_{2(s)} + Cl_{2(g)} \qquad (22)$$

proceeds more rapidly than the corresponding reaction for $HfCl_4$. ZrO_2 preferentially builds up in the solid phase, while enriching the hafnium content in the gas phase. $HfCl_4$ is easily separated from product Cl_2 by selective condensation at 0° to 300° C.

Funaki and Uchimura (21) confirmed the selective reactivity and measured the rate constants (k_r, mm Hg/h) as a function of absolute temperature. For zirconium,

$$\log k_r = 4.25 - 5{,}300/T, \qquad (23)$$

and for hafnium,

$$\log k_r = 2.9 - 4{,}100/T. \qquad (24)$$

Calculations show that the rates are equal at 615° C. Berl (4) ran tests at temperatures where rate differential is small (620° to 800° C) and obtained a maximum separation factor of 2.5 at 620° C.

Berl (4) used hafnium-free zirconium or zirconium oxides as catalysts (seed crystals). In consideration of Funaki's (21) work, the catalyst must be essential to the separation at 620° C, where $ZrCl_4$ and $HfCl_4$ react at equal rates.

The method offers no advantages over other methods that require numerous stages to produce reactor-grade zirconium. As in other methods, prepurification to remove $AlCl_3$, $FeCl_3$, etc., is necessary. The most serious problem is the requirement that the zirconium catalyst be hafnium-free, which makes the approach self-defeating. If a countercurrent purification process is set up, with $ZrCl_4$ containing 2 pct $HfCl_4$ fed into one side and O_2 + ZrO_2 (2 pct HfO_2) into the other side, the steps using high-hafnium ZrO_2 will be highly inefficient, especially at 620° C, where rates are nearly equal. This result contradicts the results of Chandler (9), where preferentially oxidized HfO_2 concentrated in the solid phase. The separation method is not worthy of further study.

RANKING OF PROCESSES

All process options must be judged on the basis of relative costs. To prepare realistic production cost estimates on which to base process selection is not now possible. It is possible to identify critical process characteristics and to relate them to costs in a qualitative manner. Six characteristics were rated for each of the processes studied as follows: (--) very unfavorable, (-) unfavorable, (0) neutral, (+) favorable, (++) very favorable. The results are summarized in tables 7 and 8. Caution should be exercised in the use of the tables because the parameters are not equally important. The assignment of relative weights would imply an unjustified precision for the method. It is not intended that the processes be compared quantitatively on the basis of point totals. The tables should be viewed as a systematic attempt to consider identifiable factors that contribute to processing cost.

TABLE 7. - Comparison of the distillation processes for separating $HfCl_4$ from $ZrCl_4$[1]

Process (year of patent)	Description	Temp, °C	Press, atm	Separation factor per equilibrium stage	Complexity	Kroll compatibility	Continuous potential	Comment
Fernelius (1954): PCl_5 complex distillation.	Conversion to complex distillation--recovery of PCl_5.	364-416 (+)	1 (++)	1.1 (--)	(--)	(0)	(--)	Combines both distillation and chemical treatment.
Eaton (1956).....	Distillation in a chloride solvent--NaCl, KCl, or NaCl-KCl.	330-400 (+)	1 (++)	1.7 (-)	(-)	(++)	(+)	Solvent salt introduced at top of column as a solid.
Plucknett (1957).	Distillation in a volatile chloride solvent--$SnCl_2$.	250-450 (+)	1 (++)	1.7 (-)	(-)	(++)	(+)	2 parts $SnCl_2$: 1 part $ZrCl_4$. Some removal of Fe claimed. $SnCl_2$ losses, costs unknown.
Spink (1976).....	Distillation in a nonvolatile chloride solvent--eutectic NaCl-KCl.	350-600 (-)	1 (++)	1.7 (-)	(+)	(++)	(++)	Removal of $ZrCl_4$ from bottom salt difficult. Salt recirculation difficult.
Spink (modified) (1981).	Distillation in a nonvolatile chloride solvent--$MgCl_2$-NaCl.	350-500 (0)	1 vac. (+)	1.7 (-)	(+)	(++)	(++)	$MgCl_2$ aids $ZrCl_4$ removal. Salt added as solid at top.
Besson (1977)....	Distillation in a modified chloride solvent.	350-500 (0)	1 (++)	1.7 (-)	(-)	(++)	(++)	$AlCl_3$:KCl>1:1 facilitates $ZrCl_4$ removal. Commercial application claimed.
Bromberg (1958)..	High-pressure liquid vapor distillation.	450-520 (--)	30-70 (--)	1.7 (-)	(++)	(++)	(--)	Equipment expensive; corrosion problems.
Ishizuka (1976)..	High-pressure batch distillation.	400-500 (-)	50 (--)	1.7 (-)	(++)	(++)	(--)	Pilot plant operation claimed.
Goldberger (1969)	Sublimation fractionation.	280-340 (++)	1 (++)	2.0 (-)	(+)	(++)	(+)	Process limited by diffusion in solid; problems.
Ishizuka (1972)..	Combined double-salt formation and distillation.	420-700 (--)	1-20 (--)	1.1-2.5 (--)	(--)	(++)	(-)	Wide range of operating conditions; elaborate equipment.

[1] Rating system: (--) very unfavorable; (-) unfavorable; (0) neutral; (+) favorable; (++) very favorable.

TABLE 8. - Comparison of the chemical processes for separating $HfCl_4$ and $ZrCl_4$[1]

Process (year of patent)	Description	Temp, °C	Press, atm	Separation factor per equilibrium stage	Complexity	Kroll compatibility	Continuous potential	Comment
Chandler (1966): Chloride-oxide exchange.	Gas-solid reaction; preferential conversion $HfCl_4 \rightarrow HfO_2$.	300-950 (--)	1 (++)	3.0 (+)	(+)	(+)	(+)	Good candidate for fluosolids reactor.
Flengas-Dutrizac (1977): Double-salt exchange.	Gas-solid reaction; formation of K_2ZrCl_6; decomposition.	330-450 (+)	1 (+)	1.7-2.0 (-)	(+)	(+)	(-)	Slow kinetics; possible candidate for fluosolids reactor.
Newnham (1957), (1959), and (1966): Preferential reduction $ZrCl_4$.	Gas-solid reaction; $ZrCl_4 \rightarrow ZrCl_3$ $2ZrCl_3 \rightarrow ZrCl_2 + ZrCl_4$.	375-450 (+)	1 (++)	2.0-9.0 (+)	(+)	(++)	(++)	Mechanical agitation needed; stirred reactor, fluosolid or countercurrent horizontal kiln.
Larsen (1973): Preferential reduction $ZrCl_4$.	$ZrCl_4$ dissolved in $AlCl_3$ (Al reductant).	375-450 (+)	5 (-)	3.0-20.0 (+)	(-)	(+)	(-)	Poor kinetics; possible $AlCl_3$ contamination.
Megy (1979): Hf/Zr redox.	Conversion to fluoride; reduction with Al salt; metal equilibration; zinc recovery.	700-900 (--)	1 (++)	100.0-300.0 (++)	(--)	(--)	(-)	High-temperature corrosion problems; long-range prospect.
Berl (1961)......	$ZrCl_4$ converted by O_2 to ZrO_2 faster than $HfCl_4$ converted.	620-800 (--)	1 (++)	2.5 (-)	(+)	(--)	(++)	ZrO_2 product necessitates a rechlorination.

[1] Rating system: (--) very unfavorable; (-) unfavorable; (0) neutral; (+) favorable; (++) very favorable.

1. Temperature.--Elevated operating temperatures involve increased energy costs and the use of expensive materials of construction. Increased maintenance costs from corrosion and deterioration of mechanical equipment also occur.

2. Pressure.--High pressure requires the use of heavy-duty components and special fabrication techniques. Added inspection is needed, and an element of risk is added. Operation at pressure less than 1 atm requires special vacuum equipment and fabrication techniques.

3. Separation Factor.--Separation factor is important because it determines the number of equilibrium stages required to achieve separation. The number of equilibrium stages needed reflects on the amount of recycle, the number and size of reaction vessels, material inventory, energy, and operating costs. The cost per separation stage may not always be the same.

4. Compatability with Kroll Technology.--The inclusion of a separation process that does not mesh well with the Kroll process flow scheme would cause the premature loss of usable facilities. The design and construction costs for replacement equipment are a deterrent for such a choice.

5. Degree of Complexity.--Process complexity is reflected in the number of different steps required and in side streams that must be treated. Process complexity contributes to costs through energy consumption, material inventory, labor, and equipment.

6. Potential for Continuous Processing.--Although a batch or semibatch process is acceptable, a continuous process is more desirable. Improved quality control, efficient use of energy, and lower labor costs favor the continuous process. In some cases the potential for continuous operation is easy to assess. For instance, the continuous operation of a high-temperature, high-pressure distillation unit would be a difficult undertaking. The continuous or even intermittent introduction and removal of tetrachloride from the high-pressure unit is a formidable task and makes a batch operation a more attractive alternative. On the other hand, continuous operation is already claimed for the extractive distillation separation process described by Besson (5) and Brun (8).

CONCLUSIONS

At least one and possibly three nonaqueous Hf-Zr separation processes show promise for future commercial operation. The economic impact of this development on domestic zirconium producers who are using the aqueous solvent extraction process is unknown.

Only two separation processes are now being studied. Of these, the extractive distillation process of Cezus-Pechiney has greater potential for commercial application than the high-pressure distillation described by Ishizuka. This judgment is based on considerations of temperature, pressure, and potential for continuous operation. Commercial-scale production is already claimed for the Cezus process (8).

Two promising separation techniques are not being studied as far as can be determined. The Newnham process, based on the selective reduction of $ZrCl_4$, was studied extensively during the 1960's by both the Bureau of Mines and the National Distillers Corp. The process is simple and has high potential for continuous operation. The extractive distillation process described by Spink in Canada is similar to that used by Cezus, with variations that have promise for improved product purity and more reliable operation. This work was discontinued in 1981 because of lack of funding.

The removal of minor impurities from the products has not been solved. The Brun description of the Cezus-Pechiney process claims a nuclear-grade $ZrCl_4$ product but does not mention purification steps for removal of iron, aluminum, and other minor chloride impurities. The authors believe that additional purification is necessary regardless of the primary Hf-Zr separation process employed.

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