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Separation of Hafnium from Zirconium by Vapour Phase Dechlorination

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The zircon sands of India contain about 3 per cent hafnium expressed as Hf × 100/Hf + Zr. As a consequence of the very close similarity between the chemical behaviour of zirconium and hafnium, the problem of their separation is attended with unusual difficulties, although several methods have been proposed for this purpose from time to time. The recognition of the importance of hafnium-free zirconium as a structural and cladding material for reactor applications has accentuated interest in this problem during recent years.

Among the methods of separation which have shown promise, mention may be made of fractional crystallisation, fractional precipitation, fractional sublimation, solvent extraction, and adsorption methods such as ion-exchange and chromatography. De Boer and van Arkel[1] obtained zirconium-enriched crystals by fractional crystallisation of the diammonium hexafluoro salts of hafnium and zirconium, and Hevesy and Madsden[2] extended the procedure to obtain zirconium-free hafnium compounds. Based on the relative instability of the hafnium coordination complexes, Prandtl[3] suggested and Schumb and Pittman[4] developed a procedure for effecting the separation by fractional precipitation of the ferrocyanides from aqueous solutions containing oxalate and sulphate ions. Larsen, Ferneleus and Quill[5] found that fractional precipitation of the phosphates from strongly acid solutions resulted in progressive enrichment in hafnium in the first precipitates. Fractional sublimation of the addition compounds of the tetrachlorides of zirconium and hafnium with phosphorus oxychloride was the means adopted by Gruen and Katz[6] to effect a separation. More recently, solvent extraction, ion exchange and other adsorption methods have come into prominence for this application. Thus Fischer and collaborators[7], in studying the distribution of the thiocyanate complexes of zirconium and hafnium between ether and water, have found that the zirconium complex gets preferentially extracted by ether. Huffman and Beaufait[8] investigated the distribution of thenoyltrifluoro acetone complexes, and Schultz and Larsen[9] of the trifluoroacetyl acetone complexes between benzene and water, and both investigations have shown that organic phase. For ion-exchange separation, both the zirconium complexes preferentially enter the anionic and cationic exchange resins have been investigated. Thus Kraus and Moore[10], and Huffman and Lilly[11] have separated hafnium from zirconium by fractional elution of the zirconium adsorbed on the anion exchange resins Dowex-1 and Amberlite (IR-400). Cation-exchange resins have been used by Street and Seaborg[12] and later by Newnham[13] for selective elution of the impregnated hafnium. Lister[14] has determined the conditions required for selective elution of zirconium instead of hafnium. Hansen and co-workers[15] have observed that activated silica gel preferentially adsorbs hafnium from a methanol solution of the chlorides. Another attempt at adsorption separation by paper-strip chromatography has been described by Kember and Wells.[16]

Among the methods reviewed, fractional crystallisation, fractional precipitation and sublimation have the disadvantage of requiring laborious multiple-step treatments. Adsorption separation on silica gel would require solvents of high purity. Solvent extraction and ion exchange seem applicable, in principle, to continuous flow operation and are therefore quite promising.

In India, investigations on the separation of hafnium from zirconium, have been directed towards examining the feasibility of (*a*) ion exchange, and (*b*) vapour-phase dechlorination, as means of separation. The process and the main conclusions of the investigation on the ion-exchange process[17] which was undertaken at the National Chemical Laboratories of India, are summarised below:

"Zircon from the Travancore sands was converted into potassium fluoro-zirconate and the fluoro complexes of zirconium and hafnium equilibriated with the anion-exchange resin Amberlite-IR-400, either in the chloride or sulphate form. Thereafter, the impregnated resin was eluted with 1.0*N* sulphuric acid at a flow rate of 0.3 to 0.4 cm³ per minute when hafnium got preferentially leached. Under optimum conditions, a maximum of 90 per cent hafnium-free zirconium was recovered."

The investigation reported here deals with attempts to devise a separation process based on the selective decomposition of zirconium tetrachloride to its oxide which would leave hafnium as a readily volatile chloride.

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THEORETICAL CONSIDERATIONS

The conversion of the tetrachlorides of zirconium and hafnium to their respective oxides by reaction with oxygen may be represented by the following equations:

$$ZrCl_4\ (g) + O_2 \rightleftharpoons ZrO_2 + 2\,Cl_2 \qquad (1)$$

$$HfCl_4\ (g) + O_2 \rightleftharpoons HfO_2 + 2\,Cl_2 \qquad (2)$$

The standard free energy change for the two reactions, as a function of temperature, has been calculated from thermodynamic data available in literature.[18,19] These calculations lead to the following relationships:

$$(\Delta F^\circ)_{Zr} = -58{,}525 - 8.956T \log T - 1.041 \times 10^{-3}\, T^2 + 1.3915 \times 10^5\, T^{-1} + 50.75T$$

and,

$$(\Delta F^\circ)_{Hf} = +21{,}642 - 10.68T \log T - 1.181 \times 10^{-3}\, T^2 + 1.4515 \times 10^5\, T^{-1} + 58.86T$$

From the above expression, the free energy change, equilibrium constant (K_P), and equilibrium $P_{Cl_2} : P_{O_2}$ ratios were calculated for different temperatures, and the data for the two reactions are presented in Table I.

These calculations show that the conversion of zirconium tetrachloride to the oxide is highly feasible whereas the conversion of hafnium tetrachloride is not. Thus at 1200°C, as will be observed from Table I, the equilibrium $P_{Cl_2} : P_{O_2}$ ratio for oxide formation is 114 for the zirconium reaction and it equals 6.97×10^{-5} for the hafnium reaction. The spread of the equilibrium ratios is even greater at lower temperatures. If, therefore, the chlorides in the vapour state are reacted with a gas mixture composed of chlorine and oxygen, in a ratio intermediate between the values for the two reactions, zirconium chloride should form the oxide and the more stable hafnium chloride should distil over unchanged. Alternately, the mixed oxides could be chlorinated under the above conditions when hafnium oxide would be expected to form the volatile chloride, leaving zirconium oxide behind. For accomplishing such a fractionation, it is necessary that the two oxides should have the same thermodynamic properties in the mixture as they have individually. This is not a justifiable assumption in this case because the two oxides probably form solid solutions. For this reason and because direct gas-solid chlorination of the refractory oxides would require a high temperature, vapour phase dechlorination was preferred. Though chlorination of the mixed oxides could be carried out in the presence of carbon, thermodynamic calculations show that under these conditions, selectivity of separation is greatly reduced.

EXPERIMENTAL METHODS AND RESULTS

The process for the separation of hafnium from zirconium in the zircon sands consisted of the following steps: (*a*) production of anhydrous zirconium chloride from zircon; (*b*) purification of the chloride to free it from contaminants other than hafnium; (*c*) vapour phase dechlorination for hafnium removal.

Production of Zirconium Chloride

The anhydrous chloride may be prepared by chlorination of zircon-carbon[20] or zirconia-carbon briquettes or by chlorination of zirconium carbide. Direct chlorination of zircon-carbon compacts, however, requires high temperatures of the order of 1000°C and the presence of silica in the zircon leads to excessive consumption of chlorine. The chlorination of zirconia-carbon compacts, though readily achieved, would require the preparation of zirconium oxide from the mineral zircon by relatively costly procedures. In this investigation, therefore, the chloride was prepared via the carbide.

A direct arc furnace was fabricated for the reduction of zircon to the carbide. The charge which consisted of zircon and charcoal in the proportion of 4:1 by weight was fed continuously into the furnace through a screw-conveyor at the top. During arcing, voluminous fumes of silicon monoxide (which oxidised in air) were produced and the carbide was obtained as a residue in the form of dense, bluish-grey blocks having a metallic lustre. The furnace made about one pound of carbide per hour.

Table I. Thermodynamic Data on the Dechlorination of the Chlorides of Zirconium and Hafnium

Temp. °C	Calories $(\Delta F^\circ)_{Zr}$	Calories $(\Delta F^\circ)_{Hf}$	$(K_p)_{Zr}$	$(K_p)_{Hf}$	$\left(\frac{P_{Cl_2}}{P_{O_2}}\ Zr\right)$	$\left(\frac{P_{Cl_2}}{P_{O_2}}\ Hf\right)$
500	−39,740	+42,780	1.70×10^{11}	8.13×10^{-13}	4.12×10^5	9.02×10^{-7}
600	−37,850	+44,880	2.99×10^9	5.75×10^{-12}	5.46×10^4	2.40×10^{-6}
700	−36,080	+46,880	1.24×10^8	2.95×10^{-11}	1.11×10^4	5.43×10^{-6}
800	−34,260	+48,850	9.48×10^6	1.13×10^{-10}	3.08×10^3	1.06×10^{-5}
900	−32,550	+50,730	1.16×10^6	3.53×10^{-10}	1.08×10^3	1.88×10^{-5}
1000	−30,900	+52,540	2.02×10^5	9.55×10^{-10}	4.50×10^2	3.09×10^{-5}
1100	−29,300	+54,310	4.60×10^4	2.27×10^{-9}	2.15×10^2	4.76×10^{-5}
1200	−27,740	+56,040	1.30×10^4	4.85×10^{-9}	1.14×10^2	6.97×10^{-5}

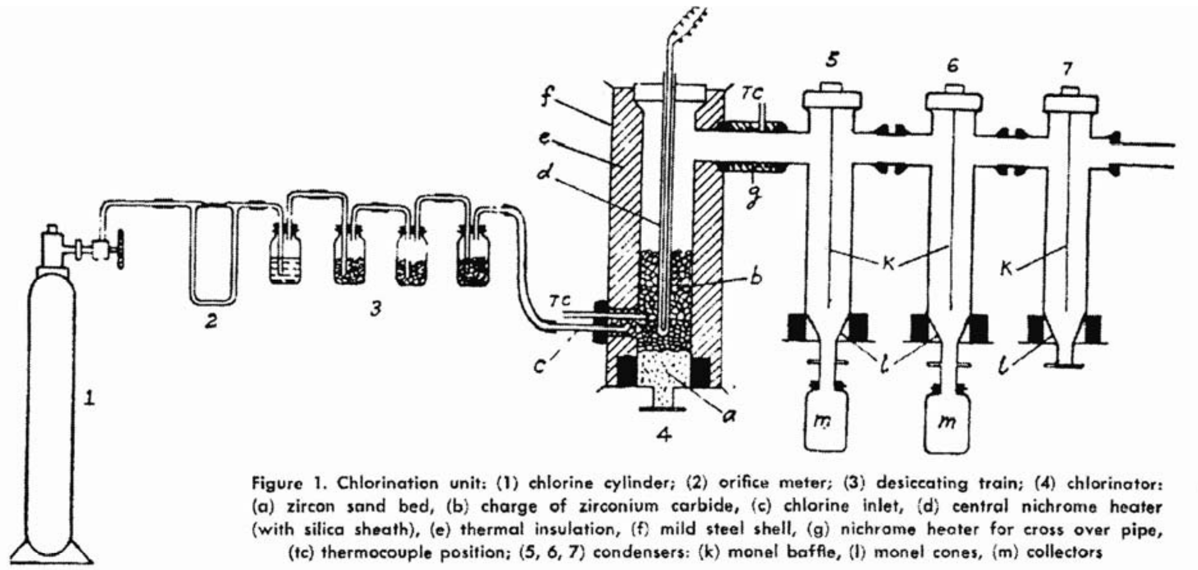

Figure 1. Chlorination unit: (1) chlorine cylinder; (2) orifice meter; (3) desiccating train; (4) chlorinator: (a) zircon sand bed, (b) charge of zirconium carbide, (c) chlorine inlet, (d) central nichrome heater (with silica sheath), (e) thermal insulation, (f) mild steel shell, (g) nichrome heater for cross over pipe, (tc) thermocouple position; (5, 6, 7) condensers: (k) monel baffle, (l) monel cones, (m) collectors

Chlorination of the Carbide

A special chlorinator unit was designed for conversion of the carbide into zirconium chloride and is shown in Fig. 1. The unit consisted of a vertical shaft furnace (4) made from an acid- and heat-resistant stoneware pipe (height: 36 inches, inside diameter: 6 inches, and wall thickness: 0.75 inches). The furnace communicated with a system of three stoneware condenser pipes (5,6,7) (height: 24 inches, and inside diameter: 6 inches), arranged in sequence. The furnace was heated from the centre by means of a nichrome heating element, sheathed in a one-inch diameter silica tube (*d*) closed at the bottom. The inlet pipe from the furnace shaft to the condenser was electrically heated with nichrome in order to prevent clogging of the passage. The furnace and the cross-over pipes were enclosed in a mild steel shell and the space between the shell and the stoneware pipes was packed with asbestos lagging. The condenser pipes were provided with monel baffles (*k*) to facilitate condensation of the chloride, and monel cones (*l*) were fitted at their bottom to direct the condensed chloride into glass- collectors situated below. The whole unit was supported in a mild steel frame.

In order to start the operation, the shaft furnace was charged from the top with zircon sand to form a bottom-bed, and thereafter zirconium carbide, crushed to a size of ¼ to ⅛ inch, was charged into the furnace to a height of about 12 inches. The furnace was sealed at the top and chlorine gas introduced at the rate of one pound per hour from a chlorine cylinder, via a flow-meter and a desiccating train. After flushing the furnace and the condensers free of air, heat was switched on. Chlorination was observed to commence at about 500°C as indicated by a sudden rise in the furnace temperature due to exothermicity of the chlorination reaction. The chloride collected in the glass-collectors below the monel cones and was in the form of a yellowish-white, fluffy powder. The powder is very hygroscopic and therefore presents problems in collection and storage. The unit gave an output of about 1.5 pounds of zirconium chloride per hour. Analysis of a typical sample (expressed in terms of oxides) showed 0.10 per cent silicon, 0.06 per cent titanium, and 0.18 per cent iron.

Purification of Zirconium Tetrachloride

As the subsequent selective dechlorination gave zirconium oxide as the end-product, it was considered desirable to free the chloride of its associated impurities such as silicon, titanium and iron at this stage. On account of their low volatilization points, the chlorides of titanium and silicon (b. pts. 136°C and 57°C respectively) would be separable by fractional distillation, but the separation of iron would require prior reduction of ferric chloride (sb. pt.: 319°C) to the relatively non-volatile ferrous chloride. A batch-purification unit, as shown in Fig. 2, was therefore set up for this purpose. The crude zirconium chloride was charged into the Pyrex distillation flask (1) which was radiation-heated by nichrome elements carried on the asbestos insulation of oven (4). The condenser bulb (3) was maintained at 200°C by simmerstat control, so that the silicon and titanium chlorides might escape as volatiles. The elbow-ground-glass joint (2) was kept at 450°C to avoid condensation of the chloride in this region during distillation. The entire assembly was flushed with hydrogen and the crude chloride soaked for one hour at 250°C in the reducing atmosphere of hydrogen. The temperature was gradually raised to 500°C when the purified chlorides of zirconium and hafnium condensed as white and compact crystalline powder in the condenser (3). After one fractionation, the sublimate was found to be free from silicon and gave an average analysis of 0.011 per cent iron and 0.0024 per cent titanium. The chlorides initially contained 0.10 per cent silicon, 0.06 per cent titanium and 0.18 per cent iron.

Selective Dechlorination

The purified chloride, obtained in the previous step, contained 2.54 per cent HfO_2 in terms of the hafnia plus zirconia content of the product. For effecting the separation by reacting the gaseous chloride with oxygen and chlorine under controlled $P_{Cl_2} : P_{O_2}$ ratios at selected temperatures, a number of experimental set-ups was devised. The results obtained demonstrated the feasibility of fractionation into (1) a zirconium oxide residue relatively low in hafnium, and (2) a volatile chloride which was high in hafnium. A design for one such apparatus is shown in Fig. 3. The hafnium-containing chloride was kept inside a silica tube-furnace (*S*) which was wound with nichrome and controlled by a simmerstat. The chloride was volatilised at a relatively low temperature of the order of 300–325°C in a current of dry chlorine and the vapour led into a vertical tube-furnace (*V*) where it reacted with a down-coming stream of chlorine and oxygen at selected temperatures. For conducting dechlorination at higher temperatures, silica was substituted for Pyrex glass in the vertical reaction-chamber. Zirconium oxide, formed as a result of reaction with oxygen, deposited as a white powder in the collector, (*M*) and formed one fraction, whereas the unreacted chloride was caught in the condensers (*C*). The condensate was subsequently leached with dilute hydrochloric acid, filtered, and the hydroxides precipitated from it ignited to oxide to give the second fraction. Both the fractions were analysed spectrographically for their hafnium-contents. It was thus found that with a chlorine to oxygen ratio of 1:2 and a furnace temperature of 800°C, the residue contained 1.4 per cent hafnia after reaction for one hour, and the volatiles contained ≈ 25 per cent hafnia; with a chlorine to oxygen ratio of 1:1, the temperature at 500°C and reaction-time as two hours, the hafnia content of zirconia was 1.29 per cent while the volatiles contained above 25 per cent hafnia. The recovery of zirconia was 90 to 97 per cent. Similar results on hafnium-separation were obtained over a wide range of $P_{Cl_2} : P_{O_2}$ ratios and temperatures.

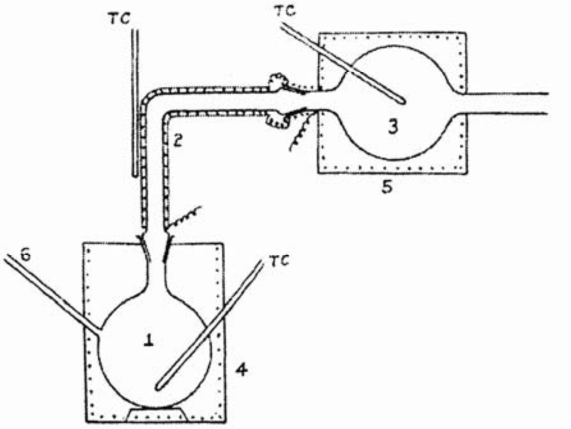

Figure 2. Distillation set-up for the purification of zirconium tetrachloride: (1) distillation flask; (2) elbow ground glass joint (heoted with nichrome); (3) condenser flask; (4, 5) box type ovens; (6) inlet for pure, dry H_2; (t.c.) thermocouple position

It will thus be observed that under optimum conditions, a single treatment results in lowering the hafnium content of the oxide by about 50 per cent. Further tests have been conducted in which briquetted zirconia-charcoal or zirconium carbide has been chlorinated in one step, and the resulting chloride directly led into the reaction-furnace for treatment with oxygen and chlorine under controlled conditions. The results of such tests have again confirmed the separation of the chloride into a low and a high hafnium-containing fraction. Further work is in progress.

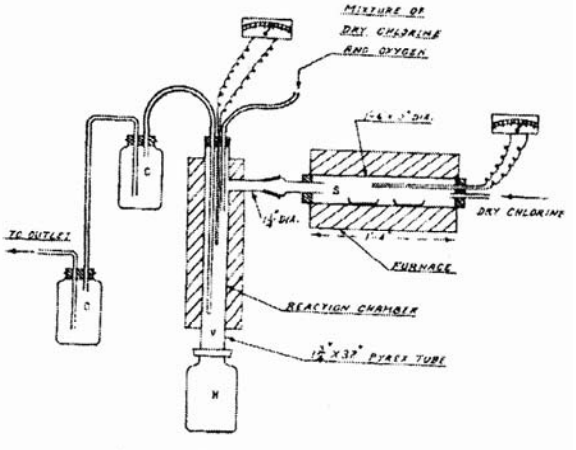

Figure 3. Vapour-phase dechlorination

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