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MODERN METHODS OF SEPARATING ZIRCONIUM AND HAFNIUM

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I. INTRODUCTION

The separation of the chemical elements zirconium and hafnium, which are encountered in nature only in the presence of one another in isomorphous crystals and whose chemical properties are extremely similar, was carried out by de Hevesy and Coster more than forty years ago[1], but the industrial application of processes for the separation of zirconium and hafnium and the production of these metals began much later, in the nineteen-fifties, in connection with the development of nuclear weapons (particularly naval weapons) and the production of nuclear energy[2]. Unlike most other fields of application of zirconium and its compounds—in ferrous and non-ferrous metallurgy, chemical plant construction, the manufacture of ceramics, refractories, glass, and enamels, industrial catalysis, etc.[2-6]—where it is possible to use zirconium without the expensive preliminary purification from hafnium, the chain reactions of nuclear fission require "reactor grade" zirconium, with the minimal possible hafnium concentration. "Reactor grade" zirconium is used chiefly in the form of alloys, as constructional material for nuclear reactors. Here use is made of the exceptionally favourable combination of properties shown by zirconium—the low effective capture cross-section for thermal neutrons, equal to 0.18 barn, compared with a figure of up to 3.5 barn for the natural mixture of zirconium and hafnium containing 1–3 wt. % of the latter, and the high mechanical strength and corrosion resistance at temperatures of up to 550°C in aggressive media.

Although the properties of hafnium and its compounds have been insufficiently studied, it is to be expected, by analogy with zirconium, that hafnium should find fairly extensive application in such fields of modern technology as electrical engineering, radio engineering, metallurgy, the optical industry, etc. The small scale of world production (several dozen tons per year) and the comparatively high cost of hafnium, however, together with the possibility of replacing it in most instances by the more readily available zirconium, has meant that up to the present most hafnium is used in nuclear technology. In contrast to zirconium, hafnium is capable of intensive absorption of thermal neutrons (capture cross-section 115 barn), and this, together with the high corrosion resistance and mechanical strength of the metal and its alloys at both low and elevated temperatures and with exposure to radiation, makes it valuable as a material for the control rods of nuclear reactors. The use of hafnium in assemblies providing protection against irradiation by thermal neutrons is also of considerable importance. The possibility of using hafnium dioxide and boride in the field of nuclear energy has recently been studied.

With increase in the scale of production and decrease in the cost, hafnium and its compounds are beginning to be used in the other branches of industry and technology noted above; the consumption of hafnium for these purposes is still relatively low, however. Extremely promising applications are the use of hafnium as constructional material for jet engines and guided missiles, in view of the ability of hafnium to absorb and give up heat more than twice as rapidly as zirconium or titanium, and also its use for alloying with refractory metals[2]. With time, hafnium will probably find application in the manufacture of chemical apparatus, and hafnium compounds may be used as catalysts. At the present time, numerous studies are being carried out to find new branches of modern technology, in which the use of hafnium might be promising. In connection with the features described above, the scale of the production of "reactor grade" zirconium and hafnium is increasing rapidly. Thus in 1950 the largest producer of these metals—the United States industry—produced 9 tons of "reactor grade" zirconium and several kilogrammes of hafnium, whereas the corresponding figures for 1959 were 1350 tons and 30 tons respectively[2].

A large number of methods for the separation of zirconium and hafnium have been proposed and tested, such as fractional crystallisation, precipitation, sublimation, distillation, or rectification; selective dechlorination of the oxides, reduction of the chlorides, or electrolysis; adsorption; ion exchange; selective liquid extraction; etc. It should, however, be noted that up to the present, even the best of the methods which are described in the literature and used in industry are comparatively complex due to the extensive difficulties associated with the problem of separating elements whose properties are so similar†.

Several fairly extensive reviews have been devoted to the problems of separating zirconium and hafnium, but one of the most complete Soviet reviews[7] appeared more than ten years ago and is naturally somewhat out of date. Works

† The similarity in the properties of zirconium and hafnium is due to the similarity in their atomic dimensions (the atomic radii are R_{Zr} = 1.45 Å and R_{Hf} = 1.44 Å) and the similarity in the configuration of the valency electrons ($4d^25s^2$ for zirconium and $5d^26s^2$ for hafnium)[4].

by foreign authors[5,6,8-11] say little about results obtained by Soviet research workers, so that it has become necessary to compile a new review containing information on the present state of this problem in the Soviet Union and abroad.

Modern technology, for the industrial separation of mixtures of zirconium and hafnium, uses chiefly the methods of liquid extraction, and also in some instances the methods of cation exchange and fractional crystallisation of potassium fluorozirconates and fluorohafnates. In the present review, most attention is paid to these methods, particularly the extraction method. The description of many other methods, chiefly older versions of methods for separating zirconium and hafnium, is omitted. This material can be found elsewhere[5-10], together with bibliographies of the original papers on these methods. In view of the extensive nature of the topic and space restrictions, the present paper gives only the fundamental principles and a brief description of the technological processes for the separation of zirconium and hafnium. More detailed information on the theory of these processes is given in a number of monographs and original papers, to which reference is made at appropriate points in the text. General information on the present state of the chemistry of aqueous solutions of zirconium and hafnium, necessary for an understanding of the hydrometallurgical processes involved in the separation of these elements, together with bibliographies, can also be found elsewhere[12-15].

II. METHODS FOR SEPARATING ZIRCONIUM AND HAFNIUM

1. Fractional Crystallisation

This method of separation makes use of comparatively small differences in the solubilities of individual compounds of zirconium and hafnium[4-6,11]: the oxide chlorides or oxide bromides, citrates, acetylacetonates, and the double oxalates, sulphates, or fluorides with ammonium or potassium. The efficiency of separation by fractional crystallisation is therefore low. Systems containing the double fluorides (fluorozirconates or fluorohafnates) of potassium or ammonium were the first to be used for the separation of zirconium and hafnium, and these methods, as noted above, have to some extent retained their importance to the present day.

In the fractional crystallisation of the double fluorides (fluorozirconates and fluorohafnates) of potassium or ammonium, the hafnium salts, which are more soluble than the zirconium salts, concentrate in the mother-liquors, and the zirconium in the crystals is gradually purified from hafnium. Several hundred recrystallisations are required in order to obtain pure hafnium from the usual raw material. On the other hand, modern versions of this method make it possible to obtain a "reactor grade" zirconium salt, containing not more than 0.05% hafnium impurity, in a much smaller number of recrystallisations (12–18). Thus this method, despite the simplicity of the individual crystallisations, is now used only for the preparation of "reactor grade" zirconium.

In a version of the method developed in the Soviet Union by Sazhin and Pepelyaeva[16] for the preparation of "reactor grade" zirconium dioxide and hafnium concentrates by recrystallising the fluorozirconates and fluorohafnates, the finely ground zirconium concentrate is sintered with potassium fluorosilicate at 650–700°C to give a sinter of potassium fluorozirconate and fluorohafnate with silicon dioxide. The sinter is finely ground, the fluorozirconate and fluorohafnate are leached out with dilute hydrochloric acid at 85°C, and the extract is left to stand. Cooling of the clarified solution gives crystals of K_2ZrF_6 containing 1.5–2.5% K_2HfF_6; the crystals are compressed, washed with water, and subjected to fractional crystallisation. This is carried out using a countercurrent scheme with 16–18 stages; the hafnium is concentrated in the mother-liquors, and the zirconium in the crystals. The original potassium fluorozirconate crystals containing hafnium impurity are passed to the first stage of the crystallisation and are successively recrystallised from mother-liquors containing an ever-decreasing percentage of hafnium impurity. The crystals are dissolved at 80–90°C, and recrystallise on cooling. In the last two stages, distilled water is used for the dissolution. The mother-liquors from the first and second stages are removed from the crystallisation cycle; precipitation with ammonia from these mother-liquors gives a 6% hafnium concentrate, which is taken for subsequent enrichment by extraction or ion exchange. The final K_2ZrF_6 crystals contain down to 0.01% K_2HfF_6. Similar processes for the separation of zirconium and hafnium were tested by Kawecki[17] in the USA and by the Knaaks[18] in the German Democratic Republic. The development of the theory of these processes is still continuing. Recently, Egerev and coworkers[19] published new data obtained in physicochemical studies of the K_2ZrF_6–K_2HfF_6–H_2O system by the solubility method; these data give more complete information on the regular features of the processes involved in the separation of zirconium and hafnium by fractional crystallisation of potassium fluorozirconates and fluorohafnates.

A new version of the method of fractional crystallisation was recently patented in Japan[20]. Dissolution of pyridinium chlorozirconate in chlorine water at 60°C with subsequent cooling and separation of the resulting crystals increases the hafnium concentration (calculated on the sum Zr + Hf) by a factor of 3 compared with the original concentration.

2. Fractional Precipitation

Methods for separating zirconium and hafnium by fractional precipitation for the most part make use of differences in the solubilities of compounds of these elements, and also of differences in the stabilities of their complexes. In the large number of versions of these methods[4-11], studies have been made of separation by organic compounds (benzoic, tartaric, salicylic, and mandelic acids, and their derivatives) and by inorganic compounds—phosphoric acid, sodium hexacyanoferrate(II), hydrogen peroxide, ammonia, etc. The results of studies carried out over many years have shown that the methods of fractional precipitation are tedious and that the separation process is time-consuming; the degree of enrichment achieved in one stage of the fractionation is comparatively small. Thus even the most effective of these methods—certain versions of the phosphate and hexacyanoferrate(II) methods—are not now used in large-scale industrial production, although under certain conditions they can still be used in preparative laboratory work for the separation of zirconium and hafnium. Some versions of the phosphate and hexacyanoferrate(II) methods of separation are described below.

Phosphate method. (a) In Larsen's method[21], a 2–5% solution of phosphoric acid in 10% sulphuric acid, and a 2–5%—calculated as $(Zr, Hf)O_2$—solution of zirconium and hafnium sulphate in the same acid are added from spray jets with constant stirring to a 10% solution of sulphuric acid at 70–75°C. This gives a compact phosphate precipitate which settles readily, and in which the hafnium is concentrated. The precipitate is filtered off and washed with water. The resulting liquid paste is cooled with ice and treated with a cold solution of sodium hydroxide and sodium peroxide. The mixture is heated at 50–70°C until all the zirconium and hafnium is precipitated as the hydrated peroxides of these elements. The precipitate is filtered from the sodium phosphate solution and dissolved in sulphuric acid, and a new cycle of the phosphate precipitation is carried out. After seven successive cycles of this process, with precipitation of 55% of the total $(Zr, Hf)O_2$ from solution in each cycle, the concentration of HfO_2 in the concentrates is increased by a factor of more than 7, from 13% to 93%. With raw material containing 2–3% HfO_2, zirconium dioxide almost free from hafnium is left in the mother-liquor after two successive fractional precipitations of the phosphates from solution.

(b) In Peters' method[22], the zirconium and hafnium hydroxides are dissolved with heating in dilute (1 : 3) hydrochloric acid, and the resulting solution is treated with $NH_4H_2PO_4$ solution at 40°C. The resulting precipitate of zirconium and hafnium phosphates is washed with distilled water to remove phosphate ion, and dissolved with stirring in 10% oxalic acid solution at room temperature. The resulting solution is heated to 40–60°C and treated with a quantity of oxalic acid equal to that used for the dissolution. The solution is then heated on the water-bath at 40–60°C for a prolonged period varying from several days to several weeks. This is necessary for "aging"—the formation of a stable oxalato-complex of zirconium and hafnium. This complex is then subjected to fractional decomposition by the dropwise addition, with stirring at 70°C, of a solution of the precipitant—a mixture of hydrochloric acid and a solution of ammonium oxalate saturated in the cold. After some time an opalescence appears; this is eliminated by adding ammonium oxalate solution, after which the addition of the precipitant solution is continued until a turbidity appears. The addition of the precipitant is then stopped and the solution is stirred for a further 2 h. To increase the efficiency of the separation of zirconium and hafnium, a "seed" consisting of a fine crystalline nucleus of freshly-precipitated hafnium phosphate is added to the solution before the start of crystallisation. The resulting precipitate is separated from the mother-liquor, filtered, washed, and dissolved in 10% oxalic acid, from which the zirconium and hafnium hydroxide is precipitated.

The degree of separation of zirconium and hafnium by this method, when the "aging" of the complex is effective, is fairly high: from ~ 9% hafnium concentrates the first fraction gave 85% concentrates, and the sixth or seventh fractions gave zirconium dioxide containing down to 0.01% HfO_2. The chief disadvantage of the method is the time required for "aging" of the oxalato-complex.

The hexacyanoferrate(II) method. In the fractional precipitation of zirconium and hafnium hexacyanoferrate(II) from acid solutions of their mixtures in the presence of complex-forming reagents, hafnium is concentrated in the precipitate, since its hexacyanoferrate(II) complexes are less stable and less soluble than the zirconium complexes. The compositions of zirconium and hafnium hexacyanoferrates(II) were studied by Ionova and Tananaev[23], Savenko and Sheka[24], and others; the compositions depend on the conditions of preparation.

In Prandtl's method[25], freshly precipitated zirconium and hafnium hydroxides are dissolved in dilute sulphuric acid, the solution is boiled, and treated with ammonium sulphate and a solution of oxalic acid, saturated in the cold. The resulting solution, containing zirconium and hafnium in the form of anionic complexes, for example, $[ZrO(SO_4)_2]^{2-}$ and $[HfO(SO_4)_2]^{2-}$, is treated with sufficient sodium hexacyanoferrate(II) solution to give partial precipitation of zirconium and hafnium hexacyanoferrates(II). The precipitation is carried out at room temperature (according to Aleksandrov and coworkers[26], it is better to carry out the precipitation at 60°C). The hexacyanoferrate(II) precipitate, which is enriched in hafnium, is left to stand for a prolonged period and then separated from the solution; treatment with hot NaOH solution is then carried out to precipitate zirconium and hafnium hydroxides. These are washed with hot water, dissolved in dilute sulphuric acid, and passed to the next stage of the hexacyanoferrate(II) concentration of hafnium. According to Prandtl, 1% raw material after 6 precipitation cycles gives 95% hafnium concentrates.

Although stable results on the separation of zirconium and hafnium were not achieved in Prandtl's experiments, the higher efficiency of the hexacyanoferrate(II) process compared with most other processes based on fractional precipitation led to further studies of this method. Schumb and Pittman[27] put forward a slightly modified version of the hexacyanoferrate(II) process, the chief difference being that the precipitation of the hexacyanoferrates(II) is carried out from a solution of zirconium and hafnium oxide chlorides to which concentrated sulphuric acid has been added (the other components of the reaction mixture are the same as those in Prandtl's version). The sodium hexacyanoferrate(II) solution is added even more slowly—dropwise; the hexacyanoferrate(II) precipitates are filtered off and decomposed not with NaOH but with ammonia. When this version of the hexacyanoferrate(II) method is used, a 12% hafnium concentrate gives an 80% concentrate after four precipitation cycles.

Thus the hexacyanoferrate(II) method makes it possible, after a comparatively small number of fractional precipitations, to obtain high-percentage hafnium concentrates. One specific disadvantage of this method is that partial decomposition of sodium hexacyanoferrate(II) by sulphuric acid during the hexacyanoferrate(II) precipitation leads to the liberation of HCN vapour into the atmosphere, so that the process must be carried out with efficient ventilation, and also to contamination of the precipitates with iron.

3. Fractional Distillation

This method of separation is based on the use of the difference in the boiling points of various zirconium and hafnium compounds. Earlier, tests were carried out on methods for separating these elements by sublimation of their tetrafluorides and tetrachlorides[28] or by distillation of the tetrafluorides from solution in molten potassium fluorozirconate and fluorohafnate[28], or of the tetrachlorides at an elevated pressure of ~ 10 atm.[29] Although the efficiency of these methods was found to be comparatively low, the idea of using sublimation to separate zirconium

and hafnium has not been abandoned completely: comparatively recently, a sublimation separating apparatus of the column type was patented[30].

More effective methods of separation are those based on fractional distillation of complex compounds—products of the reaction of zirconium and hafnium tetrachlorides with phosphorus(V) chloride and, more particularly, phosphoryl(V) chloride. The compositions of the zirconium complexes are as follows—with PCl_5: $ZrCl_4.PCl_5$ and $2ZrCl_4.PCl_5$ [31,32]; and with $POCl_3$: $ZrCl_4.2POCl_3$, $ZrCl_4.POCl_3$ [33,34], and $2ZrCl_4.POCl_3$.[31] The compositions of the hafnium complexes are analogous to those of the zirconium complexes, for example: $HfCl_4.2POCl_3$ and $HfCl_4.POCl_3$ [34,35]. It has also been suggested[36] that the products of the reaction with $POCl_3$ are not individual chemical compounds, but only azeotropic mixtures.

Although the difference in the boiling points of the complexes formed by phosphoryl(V) chloride with zirconium and hafnium tetrachlorides is comparatively small (360° and 355°C respectively)[31], effective separation of zirconium and hafnium can be achieved when the number of plates in the fractionating column is sufficiently large. Litton[37] carried out the fractional distillation of a mixture of commercial zirconium tetrachloride and phosphoryl(V) chloride in columns, each containing 50 plates; the hafnium concentrated in the distillate. Four successive fractional distillation cycles gave concentrates containing 98.5% HfO_2 in $(Zr, HF)O_2$, with a direct yield of hafnium equal to 25%. The concentration of HfO_2 in the residues in the still, calculated on the total $(Zr, Hf)O_2$, was 1.5–2%. The final distillate was dissolved in methanol, and hafnium hydroxide was precipitated with ammonia. The method involving fractional distillation of the complex compounds (or mixtures) of zirconium and hafnium tetrachlorides with phosphorus chlorides has now been fairly well studied. Thus Nisel'son[38], in one column with 50 plates, obtained zirconium containing less than 0.05% hafnium from a starting material in which the concentration was 1%; the yield of zirconium amounted to ~ 40%.

It has been reported[6] that an assembly has been planned for separating zirconium and hafnium by this method, with a continuously operating packed column of stainless steel, capable of an annual production of 18 tons of metallic zirconium containing less than 0.1% hafnium.

Ogburn and Fischer[39], using a high-efficiency glass apparatus, obtained zirconium containing ~ 0.01% hafnium from an original concentrate containing 3% hafnium.

The study of the possibility of separating mixtures of zirconium and hafnium tetrachlorides without the addition of phosphorus compounds is also of considerable interest. A satisfactory solution of this problem would make it possible to use the products of the separation of zirconium and hafnium for direct conversion into the metals. Thus in recent years, papers on the separation of zirconium and hafnium tetrachlorides by fractional distillation under pressure[40-42] or by extractive fractional distillation[40,43,44] have again appeared, at a higher technical level than earlier papers.

Extractive fractional distillation is carried out in columns irrigated with melts in which $ZrCl_4$ and $HfCl_4$ are readily soluble (NaCl, KCl, $SnCl_2$, $ZnCl_2$, etc., and their mixtures). The vapour in the upper part of the columns is enriched in hafnium; zirconium is concentrated in the melt leaving the section of the column adjoining the still. The temperature conditions for some systems are as follows: 350–500°C in the lower section of the columns and 330–350°C in the upper section (melt of NaCl and KCl); 470°C in the lower section of the columns and 250–450°C in the upper section of the columns ($SnCl_2$ melt). The efficiency of extractive fractional distillation is still comparatively low, however. For example, for an $SnCl_2$ melt, the separation factor in the column is only 2.

Laboratory experiments on fractional distillation under pressure have been carried out at 20–30 atm [31] at temperatures of ~ 450°C in the rectifying section of the columns; under these conditions the $ZrCl_4$ and $HfCl_4$ in the column are present partly in the liquid state and partly in the vapour state‡. The properties of gaseous and liquid zirconium and hafnium tetrachlorides have been studied[41,42]. The fractional distillation of a mixture of zirconium and hafnium tetrachlorides containing ~ 0.3% $HfCl_4$ gave 69–88% $ZrCl_4$ containing less than 0.03% hafnium, together with 7–11% hafnium concentrates in the first distillate fraction. In large-scale experiments in a column with metal packing[45], fractional distillation of mixtures of zirconium and hafnium tetrachlorides with an initial $HfCl_4$ concentration of ~ 1.5–2.5% gave zirconium containing less than 0.05% hafnium, in yields of more than 50%.

Advantages of the fractional distillation method for separating zirconium and hafnium are the comparatively high capacity of the apparatus and the possibility of achieving extensive purification of the products and establishing a continuous process. The introduction of this method in industry, however, particularly the version involving fractional distillation under pressure, first requires the solution of a number of complex problems, associated chiefly with the development of apparatus for carrying out the process—the selection of materials resistant to aggressive media at high temperatures and pressures, the design of fairly complex apparatus, etc.

4. Selective Dechlorination of Zirconium Tetrachloride

Thermodynamic calculations[46,47], carried out for the conversion of zirconium and hafnium tetrachlorides into the corresponding oxides by reaction with oxygen according to the equations

$$ZrCl_{4\,(gas)} + O_2 \rightleftarrows ZrO_2 + 2\,Cl_2$$

$$HfCl_{4\,(gas)} + O_2 \rightleftarrows HfO_2 + 2\,Cl_2$$

showed that the conversion of zirconium tetrachloride into the dioxide is possible, whereas the analogous process for hafnium tetrachloride is almost unrealisable. On this basis, Prakash and Sundaram[47] proposed a method for separating zirconium and hafnium by the selective dechlorination of zirconium tetrachloride with oxygen. A mixture of zirconium and hafnium tetrachlorides containing 2.54% HfO_2 in $(Zr, Hf)O_2$, previously purified from traces of silicon, iron, and titanium, was placed in a tubular quartz furnace from which it was sublimed at 300–325°C and carried by a stream of dry chlorine into the upper part of a vertical tubular furnace, into which a mixture of dry chlorine and oxygen was also passed. The mixture of gases entered the furnace from above; the white zirconium dioxide powder formed in the reaction was deposited in a collector connected to the foot of the reaction tube in the

‡ At atmospheric pressure, however, the sublimation temperatures of $ZrCl_4$ and $HfCl_4$ (335° and 314°C) are lower than the melting points (434° and 432°C respectively), and there is no need for rectification of the liquid phase.

furnace. The gas mixture passed into a condenser, where the unreacted chlorides—the hafnium concentrates—were deposited. At a chlorine: oxygen ratio of 1 : 1, a temperature of 500°C, and a duration of reaction equal to 2 h, the concentration of HfO_2 in the zirconium oxide deposited was 1.29% (half of the initial value) and the yield of zirconium oxide 90–97%; the volatile fraction contained more than 25% HfO_2.

It was thus shown possible to achieve partial separation of zirconium and hafnium in a single cycle by this method; a tenfold enrichment of the hafnium concentrates was achieved, but the purification of zirconium from hafnium was much less efficient.

Koemon Funaki and Kotaro Uchimura[48] studied the kinetics of the dechlorination of zirconium and hafnium tetrachlorides by oxygen. Their experiments confirmed that selective dechlorination of $ZrCl_4$ takes place. Contrary to the views previously expressed[46,47], however, these authors state that appreciable dechlorination of $HfCl_4$ also takes place, reducing the efficiency of the separation.

Later, it was suggested[49] that the selective dehalogenation be carried out in a continuously operating apparatus, preferably using zirconium and hafnium tetrachlorides as starting materials; the tetrabromides and tetraiodides can also be used. The process was carried out at 500–900°C, which is higher than the temperature in the first version of the method.

5. Selective Reduction of the Tetrachlorides by Metals

Although methods for the reduction of zirconium halides by aluminium and zirconium were developed fairly early[50–53], it was only some years later that research workers turned their attention to the marked difference in the abilities of $ZrCl_4$ and $HfCl_4$ to undergo reduction[54–57]. This indicated the possibility of using selective reduction of the tetrachlorides to separate zirconium and hafnium. This process was first developed by Newnham[55,56]; the original mixture of (Zr, Hf)Cl_4 containing 1.5% HfO_2 in (Zr, Hf)O_2 was reduced with zirconium in an evacuated vessel at 300–550°C. $ZrCl_4$ was reduced to $ZrCl_3$; the extent of the reduction of $HfCl_4$ was several times smaller. The hafnium tetrachloride and unreduced zirconium tetrachloride were sublimed off. A reduction temperature of 420°C and a duration of reaction equal to 8 h gave the sublimate with highest hafnium content—5.7%. It was found that the rate of reduction decreases considerably due to the formation of a sinter of the trichloride and unreacted zirconium powder. The reaction vessels were therefore subjected to repeated intensive agitation during the reduction; it was found that for the above temperature and duration of the process, this increased the concentration of hafnium in the sublimate to 29.4%, with a 95% yield of this element. The concentrates obtained were converted into hafnium dioxide by ion exchange or liquid extraction. The degree of reduction of $ZrCl_4$ to $ZrCl_3$ also amounted to 95%; the concentration of hafnium in the latter was reduced to 0.05%. The zirconium trichloride obtained was heated in a vacuum; disproportionation took place according to the reactions

$$2\,ZrCl_3 \rightleftarrows ZrCl_2 + ZrCl_4$$

$$2\,ZrCl_2 \rightleftarrows Zr + ZrCl_4.$$

A temperature of 540°C was found to be sufficient for complete disproportionation of $ZrCl_3$, but the disproportionation of the dichloride is more difficult. The $ZrCl_4$ was distilled off, and the $ZrCl_2$ was used as reducing agent in subsequent cycles.

A disadvantage of the reduction by zirconium is that $ZrCl_3$ begins to disproportionate even at 300°C, as a result of which the $HfCl_4$ being sublimed off is diluted with unreduced $ZrCl_4$. This disadvantage is eliminated if the reduction is carried out with aluminium powder at 300°C.[55] Moreover, at this temperature a melt of $ZrCl_3$ in $AlCl_3$ is obtained, and this prevents the formation of a sinter. Versions of this method, in general differing little from one another, were patented in several countries. The starting materials were (Zr, Hf)Cl_4 [58–61] or (Zr, Hf)I_4 [62,63] mixtures.

In the Soviet Union, the separation of zirconium and hafnium by selective reduction of their tetrachlorides was studied under laboratory conditions by Emel'yanov and coworkers[64,65], by Kozhemyakin and coworkers[66,67], and by others. The thermodynamic principles and kinetics of the process were studied, and the optimal conditions for carrying it out were determined. The results of the studies made it possible to develop a laboratory method for separating zirconium and hafnium. Using this method, it is possible to reduce the concentration of hafnium in (Zr, Hf)Cl_4 from 1–1.5% to 0.05% in one cycle, but the degree of reduction is comparatively low—not more than 70–75%; the concentration of hafnium in the concentrates obtained reaches 3–4%. With further increase in the degree of reduction, the concentration of hafnium in the purified $ZrCl_4$ and the hafnium concentrates increases; thus for 99% reduction of zirconium, the $ZrCl_4$ obtained contains 0.3–0.5% HfO_2, and the concentrates contain 25–29% HfO_2 (calculated on the total oxides).

Thus this method is of undoubted interest for further studies, particularly since its further development might make it possible to eliminate completely the hydrometallurgical processes of converting the (Zr, Hf)Cl_4, obtained by the chlorination of zirconium, into pure $ZrCl_4$ and $HfCl_4$, and then into the corresponding metals.

6. Electrolysis of Melts

After it had been shown, in the nineteen-twenties, that methods for separating zirconium and hafnium, based on the small difference in the mobilities of the ions of the two metals, had a low efficiency[68,69], the electrolysis method was not tested further for this purpose for a long time. It was only when the industrial production of zirconium by electrolysis was successfully developed that the attention of research workers was again drawn to this problem. The possibilities provided by the electrolytic separation of zirconium and hafnium can be illustrated by a recent paper devoted to the study of this problem[70]. The electrolysis vessel contained a mixture of 65% NaCl and 35% K_2ZrF_6. The electrolysis was carried out at 850°C in an atmosphere of argon previously purified from traces of nitrogen and oxygen. The initial current density at the cathode was 2 A cm^{-2}; the current strength was 10 A, and the potential difference 5 V. The graphite crucible in which the melt was placed was used as the anode, and the cathode consisted of rods of heat-treated molybdenum, nickel, and low-carbon steel. Metallic zirconium powder containing 0.05% hafnium was obtained in one cycle from fluorozirconate containing 0.6% hafnium. When the duration of electrolysis exceeded 2 h, the degree of separation began to decrease sharply; within this period, 40% of the metal taken was extracted. It was possible to extract a further 25% of the metal in additional cycles.

Smirnov and coworkers[71] showed that an even greater degree of purification of zirconium from hafnium can be achieved by the electrolysis of K_2ZrF_6 in an NaCl–KCl melt. The concentration of hafnium in zirconium is decreased by a factor of 20 at 700°C and by a factor of 70 at 650°C. The hafnium is concentrated in the electrolyte.

Although the efficiency of electrolysis as an independent method for the separation of zirconium and hafnium is comparatively low, the results obtained indicate the possibility of additional incidental purification of reactor zirconium during its industrial preparation by electrolysis.

Electrolytic refining in NaCl–KCl or LiCl–KCl melts can also be used to purify $HfCl_4$ from traces of iron, aluminium, etc.[72]

7. Adsorption and Ion Exchange

Sorption (chromatographic) methods for separating zirconium and hafnium are based on differences in the behaviour of these elements in molecular or ionic forms in processes of sorption or desorption on adsorbents or ion-exchange resins. The general theoretical principles of these processes are given in many papers and monographs[73,74].

(a) Partition chromatography. In the original version of this method[75,76], a cellulose mass impregnated with aqueous zirconium nitrate solution was treated with an eluant consisting of a mixture of diethyl ether and nitric acid (7 : 1). As a result of the difference in the constants for distribution between the aqueous and organic phases, zirconium was eluted more rapidly than hafnium. The degree of extraction of purified zirconium, containing less than 0.01% HfO_2, amounted to ~ 70%; the hafnium was concentrated in the last fractions. In a method developed by Chou and Tao[77] for the separation of zirconium and hafnium by paper chromatography, the combustible and explosive diethyl ether was replaced by less dangerous eluants consisting of mixtures of tributyl phosphate (TBP) with butanol and xylene (or benzene) in 8–10 M HNO_3. The authors reported complete separation of zirconium and hafnium.

Data on the separation of these elements by reversed-phase chromatography were published recently. Crawley[78] passed a solution of zirconium and hafnium in an eluant consisting of a mixture of 25% HNO_3 and 50% NH_4NO_3 through a column containing kieselguhr and TBP; up to 88% hafnium passed into the eluate. Better results were obtained by Fritz and Frazee[79], who used a stationary phase consisting of polytetrafluoroethylene (Teflon-6) treated with isobutyl methyl ketone previously brought into equilibrium with 3 M HSCN solution. A hydrochloric acid solution of the mixture of zirconium and hafnium was mixed with the eluant and placed in the upper part of the column, after which the zirconium was eluted with an aqueous solution of a mixture of NH_4SCN and $(NH_4)_2SO_4$. The hafnium was then eluted with a solution of $(NH_4)_2SO_4$ or H_2SO_4. Quantitative separation of zirconium and hafnium was achieved.

The methods of partition chromatography described above are unsuitable for industrial use. These methods, however, particularly those involving reversed-phase chromatography, can apparently be used for the laboratory preparation of small quantities of pure zirconium and hafnium, and for the analytical determination of the concentrations of these elements in their mixtures.

(b) Adsorption on silica gel. Methods for separating zirconium and hafnium on silica gel are based on differences in the degree of adsorption and desorption of various compounds of these elements. A recent paper[80] described a study of the mechanism of the sorption of zirconium from nitric acid medium on silica gel; the kinetics of sorption are determined by the rate of diffusion. There are no data indicating that the separation of zirconium and hafnium may take place by an ion-exchange mechanism (as has been shown for the sorption of various metals on silica gel[81]).

Work on the separation of zirconium and hafnium on silica gel was first published by Hansen and coworkers[82,83], and later by Beyer and coworkers[84]. In Beyer's method, a 20% methanol solution of $ZrCl_4$ containing 2–2.5% $HfCl_4$ was passed through a column of silica gel previously activated at 300°C. Hafnium was selectively sorbed by the silica gel, as a result of which the concentration of hafnium in the zirconium in the solutions leaving the column was reduced to ~ 0.3%. Subsequent elution with a 1.9–2.5 *N* solution of HCl in methanol also eluted chiefly zirconium. 7 *N* sulphuric acid was then passed through the column to elute the enriched hafnium concentrate. This was converted into the tetrachloride and the cycle was repeated. Two cycles of this process gave a 90% hafnium concentrate with a yield of hafnium equal to ~ 70%; pure hafnium was not obtained.

Zirconium and hafnium were also separated from solutions of their oxide chlorides in methanol by a frontal chromatographic process on silica gel[85]. From the original 3–15% hafnium concentrates the authors obtained purified zirconium dioxide containing $\leq$ 0.01% HfO_2, with a yield of zirconium equal to 70–75% of the original quantity (~ 0.23 kg ZrO_2 per kg silica gel) and hafnium concentrates containing more than 20% HfO_2.

The method of separation by adsorption was also tested in continuously operating columns[86]; zirconium dioxide containing only 0.01% HfO_2 was obtained from a raw material containing 2% HfO_2. On the basis of these results, a pilot-plant separating assembly was designed, capable of an annual production of 5 tons of zirconium, purified to a hafnium content of less than 0.01%.

In subsequent studies it was found possible to obtain higher degrees of separation under optimal laboratory conditions by altering the method of preparing the silica gel. Thus Koemon Funaki and coworkers[87] used silica gel, treated with alkali solution, to purify zirconium from hafnium. Waltenberger-Raźniewska[88] obtained an 80% yield of purified zirconium dioxide (HfO_2 content $\leq$ 0.01%) by using silica gel obtained by neutralising Na_2SiO_3 solution with hydrochloric acid in the presence of a considerable quantity of $Ni(NO_3)_2$.

c. Cation exchange. The differences in the stabilities of zirconium complexes and the corresponding hafnium compounds in sulphuric and certain other acids have been used successfully to separate these elements on cation-exchange resins. The first paper on the separation of zirconium and hafnium by cation exchange appeared in 1948.[89] Finely divided Dowex-50 resin—a polystyrene resin with active sulphonic acid groups—was treated with a solution of zirconium and hafnium oxide chlorides in 2 M perchloric acid; at this acidity, zirconium is present in solution chiefly in cationic form[90-92]; recently, the same has been proved for hafnium. About 80% of each metal was sorbed by the resin, which was then transferred to the

upper part of a column of the same resin (without metal) and eluted with 6 *N* hydrochloric acid. 99.9% HfO_2 was isolated from the first fraction of eluate in 66% yield relative to the original quantity. In this first work, milligramme quantities of zirconium and hafnium were used; Newnham[93], however, used this method to separate several grammes of the mixture. The yield of 99.9% HfO_2 amounted to only 42%.

Several versions of the cation-exchange process for separating zirconium and hafnium were subsequently developed in a series of papers by Lister and coworkers[94-97]. The efficiency of desorption by hydrochloric, perchloric, nitric, oxalic, and sulphuric acids was first studied; best results were obtained using sulphuric acid. Later, Benedict and coworkers[98] showed that a mixture of dilute nitric and citric acids is an effective desorbent, but sulphuric acid is much cheaper and is therefore more promising for preparative and particularly industrial use. The separation of zirconium and hafnium on desorption by sulphuric acid is due chiefly to the marked difference in the stabilities of the sulphato-complexes of hafnium and zirconium in solution. Thus according to Ryabchikov and coworkers[99,100], the stability of the sulphato-complexes of zirconium in solution under certain conditions is three times that of the hafnium complexes. Almost no separation of zirconium and hafnium takes place during sorption on cation-exchange resins from nitric acid solutions. This was confirmed by a study of the isotherms and kinetics of the cation-exchange sorption on the strongly acidic KU-2 sulphonic acid cation-exchange resin§ produced in the Soviet Union[101,102].

In Lister's method, to obtain zirconium purified from hafnium from a raw material containing 20% HfO_2 in $(Zr, Hf)O_2$, the original 0.01 M solution of zirconium oxide chloride in 2 *N* hydrochloric, nitric, or perchloric acid was passed through a column of Dowex-50 or Zeocarb-225 cation-exchange resin. 0.8–1.2 *N* H_2SO_4 was used for the subsequent elution. The first fraction contained 98–99% of the original quantity of zirconium, containing 0.01% hafnium. The hafnium remaining in the column was extracted with 0.05 *N* hydrofluoric or oxalic acid.

In another version of the method, the sorption of zirconium and hafnium was carried out from 0.8–1.2 *N* H_2SO_4 solution. Zirconium containing less than 0.05% hafnium was obtained from the first fractions of eluate. The separation of hafnium from zirconium on Wofatit[103] was found to be less efficient.

Lister also tested a semicontinuous separation process in a battery of two columns. A 0.01 M solution of zirconium nitrate in 2 *N* HNO_3 was passed through the first column, after which 0.8–1.5 *N* H_2SO_4 was passed successively through both columns. Up to 90% of the sorbed zirconium and less than 0.05% of the hafnium was extracted in the first fraction. Hafnium was then extracted by dilute hydrofluoric or oxalic acid in good yield, in the form of a high-percentage concentrate.

Other papers describe various versions of the cation-exchange method—separations on KU-2 resin using various mixtures as eluants: 0.025 M citric acid and 1 M perchloric or nitric acid[99], or hydrochloric acid containing organic solvents (acetone, isopropyl alcohol, ethyl methyl ketone, diethyl ketone, and acetylecetone[104]); separations by Lister's method have also been carried out using ion-exchange membranes[105]. Laskorin and coworkers[106] developed a new version of the ion-exchange process using the KU-2 sulphonic acid cation-exchange resin produced in the Soviet Union; the separation factors for zirconium and hafnium reached values of 5. The original sulphuric acid solutions contained 20–30 g litre^{-1} $(Zr, Hf)O_2$ and 0.65–0.75 M H_2SO_4; fluoride ions were added to the solution to give a ratio F : Zr = 0.7–1.0. When this solution was passed through a layer of KU-2 resin, as a result of the marked difference in the stabilities of the fluorosulphato-complexes of zirconium and hafnium, the hafnium and part of the zirconium were sorbed by the cation-exchange resin, and the remainder of the zirconium was left in the solution leaving the column. The elution was carried out with 0.65 M sulphuric acid. Zirconium hydroxide containing 0.01–0.08% HfO_2 in $(Zr, Hf)O_2$ was isolated from the first fraction of the eluate, and the second fraction gave a mixture of zirconium and hafnium, which was returned to a new separation cycle. The third fraction, containing hafnium, was passed through a column of RF phosphate cation exchanger¶; the hafnium was sorbed, and the dilute sulphuric acid solution was used for elution in a new ion-exchange cycle. The hafnium was washed from the RF exchanger with ammonium oxalate solution, from which hafnium hydroxide containing 99% HfO_2 in $(Hf, Zr)O_2$ was precipitated with ammonia. Further studies of the fluorosulphate process were carried out by Pepelyaeva and coworkers[107]. An advantage of this method over other ion-exchange methods is that partial separation of hafnium from zirconium also takes place in the ion-exchange sorption process; this makes it possible to increase considerably the capacity of the ion-exchange columns.

Laskorin and coworkers[108,109] also studied the separation of zirconium and hafnium in a moving layer of ion-exchange resin, in a continuously operating countercurrent chromatographic column. The cation-exchange resin with particle size 20–50 mesh moves down the column, and the original solution and eluant solutions move up the column. The cation-exchange resin suspension is moved from the lower to the upper sections of the column by means of an airlift. The concentrations of the original solution and the eluant solution (for the desorption of hafnium), because of subsequent dilution in the column, are greater than those for the batch process; the original solution contained 65 g litre^{-1} $(Zr, Hf)O_2$ and had a total acidity of 150 g litre^{-1}; 0.8–0.9 M H_2SO_4 was used as desorbent solution. Hafnium containing down to 1% zirconium passed to the lower section of the column, and zirconium containing less than 0.03% hafnium moved into the upper section. According to the authors, the capacity of the columns in the continuous countercurrent process is three times that for the batch process.

(d) Anion exchange. At sufficiently high concentrations of hydrofluoric acid, zirconium and hafnium form anionic complexes with different stabilities. This has provided the starting point for the development of most methods for separating these elements by anion exchange. Kraus and Moore[110] sorbed zirconium and hafnium from solutions of a mixture of fluorozirconates and fluorohafnates on the strongly basic resin Dowex-1; on elution with a mixture of acids (1 M HCl + 0.5 M HF) at a rate of flow

§ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

¶ RF is a strongly acid cation-exchange resin with $-PO_3H_2$ functional groups (Ed. of Translation).

of eluant equal to 0.3 ml cm^{-2} min^{-1}, zirconium was concentrated in the first fractions, and more than 95% of the hafnium was concentrated in the last fractions. Better results were obtained by Huffman and Lilly[111] using Amberlite IRA-400 resin in the chloride form, at lower concentrations of eluant (0.2 M HCl + 0.01 M HF): the yield of purified zirconium was 70%, and that of purified hafnium containing 0.03% zirconium was 83%. Forsling[112], who studied the optimal conditions for the purification of zirconium from hafnium by anion exchange, achieved even better results on Amberlite IRA-400 resin by eluting with a mixture of 0.00008 M HF and 0.22 M HCl at a rate of flow equal to 0.04–0.15 ml cm^{-2} min^{-1}; the degree of extraction of purified zirconium amounted to 98%.

A number of papers describe the use of dilute sulphuric acid as desorbent. According to the data of Rajan and Gupta[113-115], who used finely divided Amberlite IRA-400 resin in the chloride form, the degree of extraction of zirconium dioxide purified from hafnium amounted to 94%, and the yield of spectroscopically pure hafnium amounted to 75%; the use of Dowex-2 resin gave 91.2% zirconium and 75% hafnium with the same purity; thus the efficiency of separation was approximately the same for these resins. Slightly less satisfactory results were obtained when resin fractions with a larger particle size were used. When hafnium concentrates were sorbed in a column of Amberlite IRA-400 resin in the SO_4^{2-} form and subsequently eluted with dilute sulphuric acid with varying concentration (first 0.25–0.5 N H_2SO_4 and then 3 N H_2SO_4), purified hafnium (less than 0.1% zirconium) was eluted first, followed by purified zirconium. The yield of purified hafnium was 93–95%. Huré and coworkers[116,117] also achieved effective separation of zirconium and hafnium from sulphate solutions using Dowex-2 and Amberlite IRA-400 resins, and also using Dowex-1 resin[118].

Yagodin and Orlov[119], using the weakly basic EDE-10P resin† and elution with 0.5 N sulphuric acid at a rate of 0.5 ml cm^{-2} min^{-1}, obtained in the first fraction a 30% hafnium concentrate, with 52% yield of the element, from an orginal 4% concentrate; zirconium dioxide containing less than 0.05% HfO_2 was obtained from the subsequent fractions. With the addition of KCl to the original fluorozirconate solutions, the order of elution of zirconium and hafnium was altered: 40–50% hafnium concentrates, with a hafnium yield of 60–90%, were obtained in the last fractions of the eluates from 8% hafnium concentrates.

In addition to the original fluorozirconate complexes, solutions of chloro-containing complexes of zirconium and hafnium in concentrated hydrochloric acid were also tested[120]. On desorption by the slow passage of 9 M hydrochloric acid, hafnium was eluted first in a fraction with extremely small volume, and effective separation of zirconium and hafnium was achieved.

Vinarov and Shul'gina[121] studied the conditions of separation of zirconium and hafnium on anion-exchange resins produced in the Soviet Union—the weakly basic AN-2F‡ and EDE-10P resins and the strongly basic AV-16§ and AV-17¶ resins. The best separation was achieved using AV-16 resin. Concentration of hafnium in the aqueous phase was observed during sorption on this resin from hydrochloric acid solutions. With sorption on these resins from hydrofluoric acid solutions and subsequent elution with dilute hydrochloric or sulphuric acid, the hafnium is concentrated in the eluates. Thus by sorption on AV-16 and elution with 1 N H_2SO_4, hafnium concentrates with a mean concentration of 50% and a direct yield of hafnium equal to 69% were obtained from the original 29% concentrates.

Thus it has not yet been possible to achieve on anion-exchange resins the high degree of separation of zirconium and hafnium achieved on cation-exchange resins. The good results recently obtained[122] by a combination of chromatography on silica gel and anion exchange on IRA-400 or Dowex-2 are therefore of interest. A two-stage chromatographic process gives purified zirconium dioxide containing less than 0.01% HfO_2, and an enriched hafnium concentrate (Hf: Zr = 40%), which is refined in an anion-exchange resin column to a zirconium concentration of 0.1%.

8. Selective Extraction by Solvents

The methods for separating zirconium and hafnium by selective extraction by solvents (liquid extraction) are the most common in modern technology. Many versions of these methods have been proposed. Examination of the mechanisms of the various extraction processes on the basis of Fomin's classification[123] shows that the methods which are most widely used in industry are those based on extraction by neutral organic reagents, with the formation of the corresponding solvates—selective extraction of hafnium thiocyanates by solvents, chiefly isobutyl methyl ketone (IBMK) and of zirconium nitrates by TBP. We shall examine these versions in most detail. Extraction processes taking place by cation-exchange or anion-exchange mechanisms are also being studied.

(a) Thiocyanate extraction. This method of separation is based on the difference in the distribution constants of the thiocyanato-complexes of zirconium and hafnium between aqueous and organic phases. The technological processes have been developed chiefly by empirical selection of conditions close to the optimal conditions, since there is very little information on the composition and properties of the thiocyanato-complexes of zirconium and hafnium in solution. The composition of the thiocyanato-complexes of zirconium and hafnium was established only recently. According to Golub and Sergun'kin[124], the composition of the thiocyanato-complexes of zirconium and hafnium in aqueous solutions is given by the formula $M(SCN)_n^{4-n}$, where $n = 1-8$. Vinarov and coworkers[125,126] established that the thiocyanato-compounds of zirconium

† EDE-10 is a polyfunctional strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines with epichlorohydrin, and contains $-N(CH_3)_3$ groups (Ed. of Translation).

‡ AN-2F is a polyfunctional, weakly basic anion-exchange resin containing tertiary and secondary nitrogen groups. It is obtained by polycondensation of methyl derivatives of phenol with polyethylenepolyamines and formaldehyde (Ed. of Translation).

§ AV-16 is a polyfunctional, strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines, pyridine, and epichlorohydrin. It contains secondary, tertiary, and quaternary (pyridinium) nitrogen groups (Ed. of Translation).

¶ AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen-groups. It is based on styrene and trimethylamine (Ed. of Translation).

and hafnium which are most readily extracted by acetophenone (APH) from perchloric acid solutions contain the complex anion $[M(SCN)_6]^{2-}$, or under certain conditions have the formula $M(SCN)_4$. The extraction takes place by a solvate mechanism. Sinegribova and Yagodin[127] reported the compositions of the zirconium and hafnium compounds extracted by diisopentyl methylphosphonate (DPMP) from sulphuric acid solutions: $M(OH)_2(SCN)_2.2DPMP$, or $M(OH)_2(SCN)_2.2(DPMP.HSCN)$.

In the original version of the thiocyanate extraction proposed by Fischer and Chalybaeus[128], ammonium thiocyanate and sulphate were added to an aqueous solution of the mixture of zirconium and hafnium sulphates, and the mixture was shaken with diethyl ether in a separating funnel; the hafnium concentrated in the ether phase. Later, a repeated stepwise fractionation was developed[129]. The ether extract obtained as described above was washed with a solution of a mixture of ammonium sulphate and thiocyanate to achieve further selective removal of zirconium into the aqueous phase, after which the zirconium and hafnium were re-extracted with ammonium sulphate solution acidified with sulphuric acid. Zirconium sulphate enriched in hafnium was obtained from the re-extract and passed to the next stage of the fractional extraction. 70–90% concentrates were obtained after 6–8 fractionation stages from a raw material containing 0.5% HfO_2, and 99.6% hafnium specimens were obtained from 60–95% concentrates in an eight-stage extraction scheme.

The process described above for the thiocyanate extraction of hafnium from sulphate solutions is in general fairly efficient, but it also has a number of disadvantages: it is impossible to extract hafnium completely from the raffinates; formation of precipitates is often observed, leading to a decrease in the distribution constants; equilibrium is not established during the experiment in the sulphate scheme, so that the course of the process is influenced to a significant extent by the time for which the original solutions have been left to stand. The first attempts to carry out the thiocyanate extraction from hydrochloric acid solutions[128], however, led to a decrease in the efficiency of separation of zirconium and hafnium, since diethyl ether extracts zirconium preferentially from solutions of the chlorides, so that the presence of chloride ion decreases the degree of enrichment of hafnium in the extract. The use of ether as organic solvent also restricted the possible utilisation of the method on a larger scale, in view of the appreciable solubility of ether in water, its volatility, combustibility, and ability to form explosive mixtures with air.

Because of these features, Fischer and coworkers[130] patented another version of the thiocyanate extraction, in which the distribution of the thiocyanato-compounds of zirconium and hafnium was carried out in the absence of sulphate ions at a low concentration of chloride ions in the original solutions, as a result of which reproducible equilibrium was established in the system and precipitates were not formed. Although the authors, as before, used chiefly diethyl ether, they also noted the possibility of using certain other solvents for this process: n-butanol, cyclohexanone, n-butyl acetate, pentyl acetate, methyl propyl ketone, ethyl isopropyl ketone, and benzaldehyde. The distribution and separation of thiocyanato-compounds of zirconium and hafnium during extraction by hexanone was studied in detail[131].

The separation of zirconium and hafnium in a multistage countercurrent continuously operating apparatus has also been described[132]. The liquid phases are solutions of thiocyanic acid in water and in hexane. The solid salts—mixtures of zirconium and hafnium tetrachlorides or oxide chlorides—are introduced continuously into the middle stage of the distribution cascade. The aqueous phase or raffinate obtained contained purified zirconium with an Hf concentration down to 3×10^{-4}%,

Hoshino Yoshio[133] studied the distribution constants for zirconium and hafnium between an aqueous phase containing NH_4SCN, $(NH_4)_2SO_4$, and HCl, and 80 oxygen-containing solvents: ketones, alcohols, esters, and ethers. The highest distribution constants were obtained using alicyclic ketones. In some papers by Hoshino Yoshio and Ito Takuii[134,135], preference is given to extraction by cyclohexanone, which gives high values for the separation factor (β) for zirconium and hafnium (up to 250). The same solvent was previously used by Motov and Leshtaeva[136,137] to obtain zirconium dioxide purified from hafnium, together with hafnium concentrates (the values of β reached 140).

Yagodin, Kaplan, and coworkers[138-140] successfully separated thiocyanato-compounds of zirconium and hafnium by selective extraction by diisopentyl methylphosphonate (DPMP), diluted with benzene or xylene, from sulphuric or nitric acid solutions of zirconium and hafnium. Diviš[142] studied the selective extraction of the thiocyanato-compounds by methylcyclohexanone. No data on the industrial application of the above versions of the thiocyanate extraction have been published, however. We shall therefore not deal with these in more detail, but shall consider the method of separating zirconium and hafnium by selective thiocyanate extraction using isobutyl methyl ketone (IBMK, hexone), which is widely used at the present time[8,11,143-149]. Using this method, conditions have been found for effective extraction from hydrochloric acid solutions; this proved difficult in the first years after the development of the thiocyanate extraction by Fischer.

In one of the latest industrial versions of this method[8,11], a mixture of zirconium and hafnium tetrachlorides or oxide chlorides, obtained from "ore" raw material containing 2% HfO_2 in $(Zr, Hf)O_2$, is dissolved in water to which ammonium thiocyanate has been added. The concentrations of the components in the original solution are as follows: 1.3 M metal, 2.8 M NH_4SCN, and 1 N free acid; the IBMK extracting agent contains 2.8 M HSCN. The extraction, washing, and re-extraction are carried out in continuously operating countercurrent columns. The extract containing enriched hafnium concentrate and thiocyanic acid is washed with 3.5 M HCl; this is accompanied by additional removal of part of the zirconium. The hydrochloric acid wash solution is combined with a new portion of the original solution. The washed extract passes to a system of re-extraction columns, where the hafnium product is washed out with 5 N sulphuric acid. Ammonia is added to precipitate hafnium hydroxide containing small quantities of zirconium, titanium, boron, cadmium, etc.; if a pure product is required, further purification is carried out by re-pulping the product in hydrochloric acid, precipitating hafnium phthalate, re-pulping with aqueous ammonia, drying, and heating the hafnium hydroxide residue. The extracting agent and NH_4SCN (after regeneration from the ammoniacal solution) are used again.

The thiocyanic acid present in the raffinate is also extracted in a countercurrent system with pure IBMK, from which it is then re-extracted with water; the solution obtained is used for the preparation of the original solution for extraction, or the IBMK and HSCN are used

in a new extraction. Zirconium is regenerated by diluting the raffinate to a (Zr, Hf)O_2 concentration of ~ 12 g litre^{-1}, precipitating zirconium sulphate at pH 1.4–1.8 and 60–70°C, re-pulping the basic sulphate precipitate with aqueous ammonia, and heating the zirconium hydroxide. Purified zirconium dioxide and hafnium dioxide are obtained on the industrial scale by this method.

(b) Extraction by TBP and other alkyl phosphates. The method of extraction by TBP, first developed and used in France, is now being developed and extended on an increasing scale[8,11]. The method is based on the difference in the distribution constants of zirconium and hafnium nitrates in extraction by dilute TBP. Zirconium is extracted much more readily than hafnium, so that zirconium is concentrated in the extract, and hafnium in the raffinate. The theoretical principles of the separation of zirconium and hafnium by extraction using TBP are dealt with in a large number of papers by Huré, Korovin, Rozen, and others[75,76,150-154]. The extraction takes place by a solvate mechanism. The composition of the solvates formed during extraction may be different under different conditions. For the conditions usually employed in the separation of zirconium and hafnium, the mechanism of extraction can be represented as follows[75,76]:

$$(Zr, Hf)O^{2+} + 2H^+ + 4NO_3^- + 2\,TBP \rightleftarrows (Zr, Hf)(NO_3)_4 \cdot 2\,TBP + H_2O$$

or, with allowance for the hydration of zirconium and hafnium in the aqueous phase[150]:

$$[(Zr,Hf)(OH)_2]^{2+} + 2H^+ + 4\,NO_3^- + 2\,TBP \rightleftarrows (Zr,Hf)(NO_3)_4 \cdot 2\,TBP + 2H_2O\ .$$

From this it follows that the Zr : Hf ratio in the equilibrium organic phase in extraction from their mixtures is greater than that in the aqueous phase.

In the original version of the method, developed by Huré and Saint-James[155], the extraction was carried out with a mixture of TBP and white spirit (volume ratio 60 : 40), acidified to 1.6 M HNO_3; the original solution contained 30 g litre^{-1} Zr(Hf), 3 M HNO_3, and 3.5 M $NaNO_3$. The separation factor for the extraction was ~ 10. The washing was carried out with a mixture of 3 M HNO_3 and 3.5 M $NaNO_3$. The process was carried out in a system of mixing and settling vessels. Four extraction theoretical plates and two washing theoretical plates were required in order to obtain zirconium containing less than 0.02% hafnium, in 90% yield from the original ore raw material. The final aqueous phase contained 20–40% hafnium, relative to the total hafnium and zirconium.

The principles of the technology of the separation of zirconium and hafnium by extraction using TBP, developed at Harwell (England), are given in reviews by Hudswell and Hutcheon[75,76]. The extraction was carried out from an original solution of the nitrates, containing 80 g litre^{-1} zirconium and 1.6 g litre^{-1} hafnium in 8 M HNO_3. A 50% solution of TBP in xylene was used as extracting agent. A system of 4 extraction plates and 6 washing plates gave a high yield of zirconium with low hafnium concentration, together with ~ 25% hafnium concentrate. When kerosene (or decalin[156]) was used as diluent for the TBP, a third phase appeared, complicating the process.

Various extractors have been described[156-159] for the separation of zirconium and hafnium by extraction using TBP (vibrational columns, mixing and settling vessels, etc.). Much information has been published[147,159-173] on various versions of the extraction using these solvents. There are also a few data on extraction by TBP from sulphuric acid solutions[170]; the presence of thiocyanate ion is necessary. Hafnium is concentrated in the organic phase, but the separation factors are low.

Let us consider in slightly more detail one modern version of the extraction by TBP (the "nitrophos process"), developed in the USA. Initially, Cox and coworkers[159] used for the extraction a mixture of TBP and heptane (60 : 40), acidified to 0.65 *N* HNO_3; the original solution of zirconium and hafnium nitrates did not contain salting-out agents, and its acidity corresponded to ~ 5 M HNO_3. The separation factor was ~ 15. 14 working stages of the mixing and settling vessels (equivalent to 12 theoretical plates) gave zirconium containing less than 0.01% hafnium, together with a ~ 44% hafnium concentrate. The separation of zirconium and hafnium was carried out on the pilot-plant scale under slightly modified technological conditions[160].

An original solution of 1 M zirconium nitrate, with acidity 8 M HNO_3, and Hf : (Hf + Zr) ratio = 2%, was prepared. The solution was passed to the middle section of the column and moved downwards, in the opposite direction to a mixture of TBP and n-hexane (1 : 1), saturated beforehand with nitric acid by mixing with 8 M HNO_3. The extract then passed into the upper half of the column, where it was washed in a countercurrent process with 5 M HNO_3. The re-extraction was carried out in a special countercurrent column using de-ionised water. The re-extract contained purified zirconium with ≤ 0.006% hafnium, and the raffinate contained a 90–95% hafnium concentrate. The ratio of the volumes of solutions entering the system, the original organic solvent, the wash solution, and the re-extracting water was 1 : 3.6 : 0.6 : 0.9.

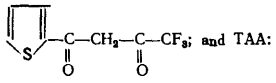
On the industrial scale, the "nitrophos process" is carried out in stainless steel columns. The concentration of zirconium nitrate in the original solution is 0.6 M, and the ratio of the volumes of the above solutions is 1 : 2.8 : 1.8 : 1.2. A mixture of saturated and unsaturated hydrocarbons is used to dilute the TBP.

Approximate calculations of the main data for extraction apparatus for the separation of zirconium and hafnium by extraction with TBP are given by Benedict and Pigford[174]. Granovskii, Komissarova, Nalimov, and others[175-177] have begun the development of a mathematical model for this process in order to determine its optimal conditions. The use of modern mathematical methods of optimisation in such complicated processes as the separation of zirconium and hafnium is undoubtedly extremely promising.

In addition to the improvement of the method of extraction by TBP, the search for other equally effective extracting agents is of interest. In particular, it has been suggested that zirconium and hafnium may be separated by extraction from nitrate solutions using other alkyl and aryl phosphates[166]. Separation by oxygen-containing solvents such as 3-methylbutanol, n-hexanol, methyl propylketone, etc. has been tried[178]; from 4 *N* HNO_3, these solvents extract 50–60% zirconium and hafnium, with separation factors of 6–9. In extraction by acetophenone from hydrochloric acid solutions with an acidity of 10 M, the maximal separation factors for zirconium and hafnium reach the value 5. All of these methods have as yet been little developed and are of no industrial importance.

(c) Extraction by fluorinated β-diketones. Thenoyltrifluoroacetone or thiophencarbonyltrifluoroacetone (TTA), trifluoroacetylacetone (TAA), and various

other fluorinated β-diketones react with zirconium and hafnium to form inner-complex compounds (chelates), soluble in benzene and various other solvents. The general formula for the fluorinated β-diketones can be written: $R-COCH_2-CO-CF_3$, where R represents various radicals; for example, TTA is:



; and TAA: is $CH_3-C(=O)-CH_2-C(=O)-CF_3$ [180].

Complex formation by zirconium and hafnium with β-diketones has been studied by many authors [181-183]. The extraction of zirconium and hafnium can be represented in general form as follows:

$$Zr\,(Hf)^{4+}_{aq} + 4HK_{org} \rightleftarrows (Zr,Hf)\,K_{4\,org} + 4H^{+}_{aq}$$

where HK represents the fluorinated β-diketone and the subscripts aq and org denote the aqueous and organic phases. These reactions are often complicated by hydrolysis and polymerisation of the zirconium and hafnium ions. The differences in the distribution constants of zirconium and hafnium complexes make it possible to separate these elements by selective extraction [183-187]; zirconium is concentrated in the organic phase. According to Huffman [187], the separation factors obtained using a solution of TTA in benzene amount to 25; figures of 13-18 are obtained for various other extracting agents of the same class. Despite the fairly high separation factors, extraction by β-diketones cannot find extensive industrial application until these extracting agents become much more readily available.

(d) Extraction by liquid sorbents. Laboratory experiments on the separation of zirconium and hafnium by extraction using liquid sorbents of the cation-exchange (alkyl hydrogen phosphates) and anion-exchange (amines) types have been described in recent years. The mechanism of these separation processes is in principle similar to those on solid ion-exchange resins.

In extraction by solutions of alkyl hydrogen phosphates in organic solvents, salts of the cations being extracted (zirconium or hafnium) with the anions of the organic acids are formed.

Extraction by the acid esters of orthophosphoric acid—dihexyl, diheptyl, dioctyl, and diphenyl hydrogen phosphates—from sulphuric acid solutions showed that hafnium is concentrated in the organic phase [140,188]. In extraction by 50% solutions of these acids in xylene from a solution containing 20 g litre^{-1} Zr(Hf) in 2 N H_2SO_4, the separation factor reaches the value 12. Better results—separation factors up to 20—were achieved by extraction using di-2-ethylhexyl hydrogen phosphate. Zirconium is extracted preferentially from hydrochloric acid solutions [189].

In the extraction of zirconium and hafnium by solutions of amines, salts of the anions being extracted with organic cations are formed. For example, the mechanism of the extraction of zirconium and hafnium from solutions of their fluoro-complexes by trioctylamine (TOA) can probably be represented [190]:

$$2\,(NR_3H)\,HSO_{4\,org} + K_2MF_{6\,aq} \rightleftarrows (R_3NH)_2MF_{6\,org} + 2\,KHSO_{4\,aq}$$

where $R = C_8H_{17}$.

The study of extraction from hydrochloric acid solutions using primary, secondary, and tertiary amines [191,192] has shown that zirconium is concentrated in the organic phase. The separation factors vary over a wide range, from 1 to 89, depending on the conditions. Tertiary amines are the most selective. In extraction by a 0.1 M solution of TOA in cyclohexane from 7-9 M HCl solutions of zirconium and hafnium, the separation factor had values of 22-29. Decrease in temperature to ~ 10°C increased the separation factor to 70-89, but the degree of extraction was reduced. A sharp increase in the separation factor to 65-77 was achieved by adding HNO_3 to the original solution. In extraction by trioctylamine in xylene from sulphuric acid solutions with an acidity greater than 1 N, [140] zirconium was also extracted preferentially, with a separation factor of 10. In extraction from acidic solutions of fluorozirconate and fluorohafnate, the separation factor did not exceed 5.

Thus the use of liquid sorbents for the separation of zirconium and hafnium has proved effective, and continuation of these studies appears desirable.

III. FUTURE PROSPECTS FOR THE APPLICATION OF THE MOST IMPORTANT METHODS FOR SEPARATING ZIRCONIUM AND HAFNIUM

The above data make possible a comparative estimate of the future prospects for the industrial application of various methods for separating zirconium and hafnium. Since the present review did not give detailed technical-economic calculations on individual technological methods (for a number of methods these calculations have not been carried out), such a comparative estimate can obviously be made here only in the most general form. The basic criteria for the selection of methods or a combination of methods should be as follows: the highest separation factors, highest specific capacity of the apparatus, simplicity in the technological process and in the apparatus required, the possibility of carrying out a continuous process, low cost of the raw material and reagents used, and the possibility of obtaining them in the required quantities. Another important problem concerns the most rational way of introducing the separation of zirconium and hafnium into the general scheme for the production of these metals from the ore raw material.

If we examine on this basis the future prospects for the application of the above processes for the separation of zirconium and hafnium in industry (most of them can be used for small-scale preparative laboratory separation), it immediately becomes necessary to reject almost all methods of fractional crystallisation or precipitation, because of the low separation factors and the tedious and time-consuming nature of the technological processes, and also the inefficient (in present form) methods of selective dechlorination and electrolysis. Here an exception is the method developed by Sazhin and Pepelyaeva for the fractional crystallisation of potassium fluorozirconates and fluorohafnates, where the simplicity of the technology of separation and its successful combination with the method for opening zircon will evidently enable it, within a short time, to compete successfully even with other more effective separation processes, for the production of zirconium dioxide purified from hafnium. The method of selective reduction of the chlorides by metals is of considerable interest, since it uses zirconium and hafnium chlorides, obtained in the opening of zircon by the efficient chlorination method, and eliminates completely the intermediate hydrometallurgical stages in the production of zirconium and hafnium. This method, however, apparently still requires further technological development. The same

is true of the effective method of separation by fractional distillation under pressure, but the rapid development of this method can take place only after the optimal solution has been found to the problems of selecting constructional materials and a rational design of apparatus for the process. The method of separation on silica gel, although in general fairly effective, has an important disadvantage which makes its extensive industrial application difficult, namely the use of methanol, which is very toxic.

Of the ion-exchange methods, cation exchange on the sulphonic acid cation-exchange resins Dowex-50, KU-2, etc. has found most extensive application, thanks to the high separation factors, the availability of the resins and reagents used, and the possibility of setting up a continuous countercurrent process. The specific capacity of the ion-exchange apparatus (calculated on unit cross-sectional area or volume) and the concentration of zirconium and hafnium in the solutions obtained are usually low, however. Thus on the industrial scale of production it is necessary to have batteries of large-scale columns and to pass comparatively large volumes of solutions through these columns, and this naturally restricts the possible application of the ion-exchange method. This method, however, may even become the predominant method for the industrial separation of zirconium and hafnium, when conditions are found for the highly selective sorption of hafnium by ion-exchange resins. At present, however, the most promising field of application of the ion-exchange method for the separation of zirconium and hafnium is evidently to be found in the treatment of high-percentage hafnium concentrates and the refining of hafnium and zirconium specimens.

The methods of selective extraction by solvents, particularly IBMK and TBP, are widely used in industry. The advantages of these methods are the high separation factors, the high concentrations of the zirconium and hafnium solutions, the high specific capacity of the apparatus, the possibility of using continuously operating countercurrent extractors, etc. By selecting a suitable version, extraction methods can be used for the treatment of hafnium concentrates obtained by any of the existing methods for opening ore concentrates (zircon, etc.). The chief disadvantage of extraction methods is the relatively high cost of the reagents. Thus one of the most important tasks facing industries producing pure specimens of zirconium and hafnium must be the further improvement of the technology of extraction separation processes, including the search for the most readily available and at the same time highly efficient complex-forming reagents and extracting agents.

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THE RADIOCHEMICAL PREPARATION OF ION-EXCHANGE MATERIALS

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The preparation of ion-exchange materials under the influence of ionising radiation is one of the few radiochemical processes which has found definite practical application. Thus homogeneous ion-exchange membranes have been obtained by grafting certain monomers on to various polymer-carriers under the influence of radiation[1-9]. These membranes have distinct advantages over those prepared by ordinary chemical methods. Moreover, ion-exchange resins prepared by the radiochemical method are in a number of instances not only better, but also cheaper, than ordinary standard ion exchangers[10].

The methods of radiation polymerisation, copolymerisation, and grafting have recently become fairly widespread, since they make it possible to prepare materials which differ from ordinary materials in their high purity, improved physicomechanical characteristics, and other valuable properties influencing their performance.

Grafting under the influence of radiation makes it possible in certain instances to obtain graft copolymers whose preparation is difficult or impossible by ordinary chemical methods. These copolymers can be used to prepare ion-exchange membranes with high mechanical strength, high selectivity, and low electrical resistance. All these features are responsible for the considerable interest in the radiochemical preparation of ion-exchange resins, the progress made in this field, and methods for its further development.