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PRODUCTION OF NUCLEAR-GRADE ZIRCONIUM AND HAFNIUM TETRAFLUORIDES

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This paper presents the results of industrial-scale trials of a technology for producing high-purity zirconium and hafnium tetrafluorides. Nuclear-grade purity of the zirconium and hafnium nitrate salts is achieved through the high extraction kinetics enabled by the EC-250 and CET-125 centrifugal extractors. It was demonstrated that, to ensure complete conversion of zirconium and hafnium into insoluble fluorides, the solutions must first be concentrated to saturation by vacuum evaporation at 70…95 °C. The tetrafluoride monohydrates of zirconium and hafnium were precipitated using 40% HF and anhydrous hydrogen fluoride as the precipitating agents. The lowest residual content of zirconium and hafnium in the mother liquor was obtained when using anhydrous hydrogen fluoride. Removal of the water of crystallization was accomplished by drying at 120 °C, followed by thermal treatment of the salts at 650 °C under a flow of hydrogen fluoride and dry argon. The resulting fluorides, obtained in the β-phase, exhibited a purity of 99.9% and a moisture content below 0.05%. They fully met the requirements for the standard electrolysis process based on K_2ZrF_6 and K_2HfF_6. Both salts successfully completed a full cycle of process validation, during which zirconium and hafnium powders with a purity of no less than 99.85% were produced.

INTRODUCTION

The advancement of nuclear power in support of sustainable economic development has necessitated a shift in the approach to the quality of structural materials for the cores of thermal-neutron reactors, including the WWER-type reactors operated in Ukraine. A common limitation of all zirconium alloys used in nuclear fuel cladding is their insufficient radiation resistance – no more than 4 years – under conditions of high temperatures, high pressures, and intense neutron and gamma irradiation.

The primary cause of this limitation is the unsatisfactory purity of zirconium alloys with respect to critical impurities. Zirconium–niobium alloys produced from electrolytic powder obtained from a K_2ZrF_6-based electrolyte have elevated levels of hafnium (≤ 0.035%), silicon, carbon, nickel, and titanium, because fractional crystallization processes cannot achieve higher purity without compromising techno-economic performance. A key indicator is the low zirconium recovery (50%) after 18 crystallization stages.

Improvements in the quality of zirconium fluoride salts – K_2ZrF_6 and ZrF_4 – were achieved through alkaline decomposition of zircon, yielding zirconium and hafnium oxynitrates [1]. Their deep separation by extraction using a tributyl phosphate–kerosene mixture in EC-250 and CET-125 centrifugal extractors was first implemented in Ukraine at the PChZ plant in the 1970s [2]. This enabled the most complete separation of zirconium and hafnium, reducing hafnium in zirconium to ≤ 0.005% and zirconium in hafnium to ≤ 0.5%, while purifying transition metal impurities to ≤ 0.05% [3]. The ZrF_4 and HfF_4 salts were successfully used in the production of electrolytic powders of both metals for nuclear applications [4].

Replacing K_2ZrF_6 (32.3% Zr content) with the more zirconium-concentrated ZrF_4 (54% Zr) improves the techno-economic parameters of the electrolysis process [5]. A similar effect is achieved when replacing K_2HfF_6 with HfF_4 [6].

Research on fluoride glasses has been conducted in virtually all developed countries [7–13]. Compositions based on zirconium and hafnium fluorides became the foundation for optical components operating in the infrared range. Signal losses in such glasses are about 0.022 dB/km, compared to 0.2 dB/km for silica-based glasses.

The aim of this work is to study the production processes of zirconium and hafnium tetrafluorides, optimizing process parameters and reagent recovery.

MATERIALS AND METHODS

To obtain zirconium and hafnium tetrafluorides, nitrate solutions of zirconium and hafnium with a concentration of 30…40 g/l and acidity of up to 300 g/l HNO_3 were used. Two process flowsheets were proposed for the experiments (Figure).

The fluorides were analyzed for impurity content, and the mother liquor after precipitation was analyzed for zirconium, hafnium, fluorine, and nitric acid content.

RESULTS AND DISCUSSION

A study of the chemical properties of zirconium compounds – oxynitrate and tetrafluoride – allowed us to select vacuum evaporation as the method for concentrating the process solution. Evaporation was carried out in two stages: the first to a zirconium concentration of 120 g/l and a density of 1.4 g/cm³; in the second stage, the zirconium concentration was increased to 170 g/l and nitric acid to 450 g/l. The solution temperature rose to 70 °C, ensuring concentration under vacuum. In the first stage, vacuum was maintained by a steam-jet ejector; in the second, by a VN-12 vacuum

pump. The condensate, containing 80 g/l HNO_3, held up to 3 g/l zirconium.

The evaporated solution had a zirconium concentration in the range of 140…180 g/l, HNO_3 400…450 g/l, and contained a solid phase of zirconium oxynitrate crystals in the amount of 150…300 g/l. The solution density was 1.5…1.6 g/cm³. The HNO_3: Zr ratio varied from 10:1 to 3:1. The nitrate-ion concentration after evaporation increased from 340 to 680 g/l.

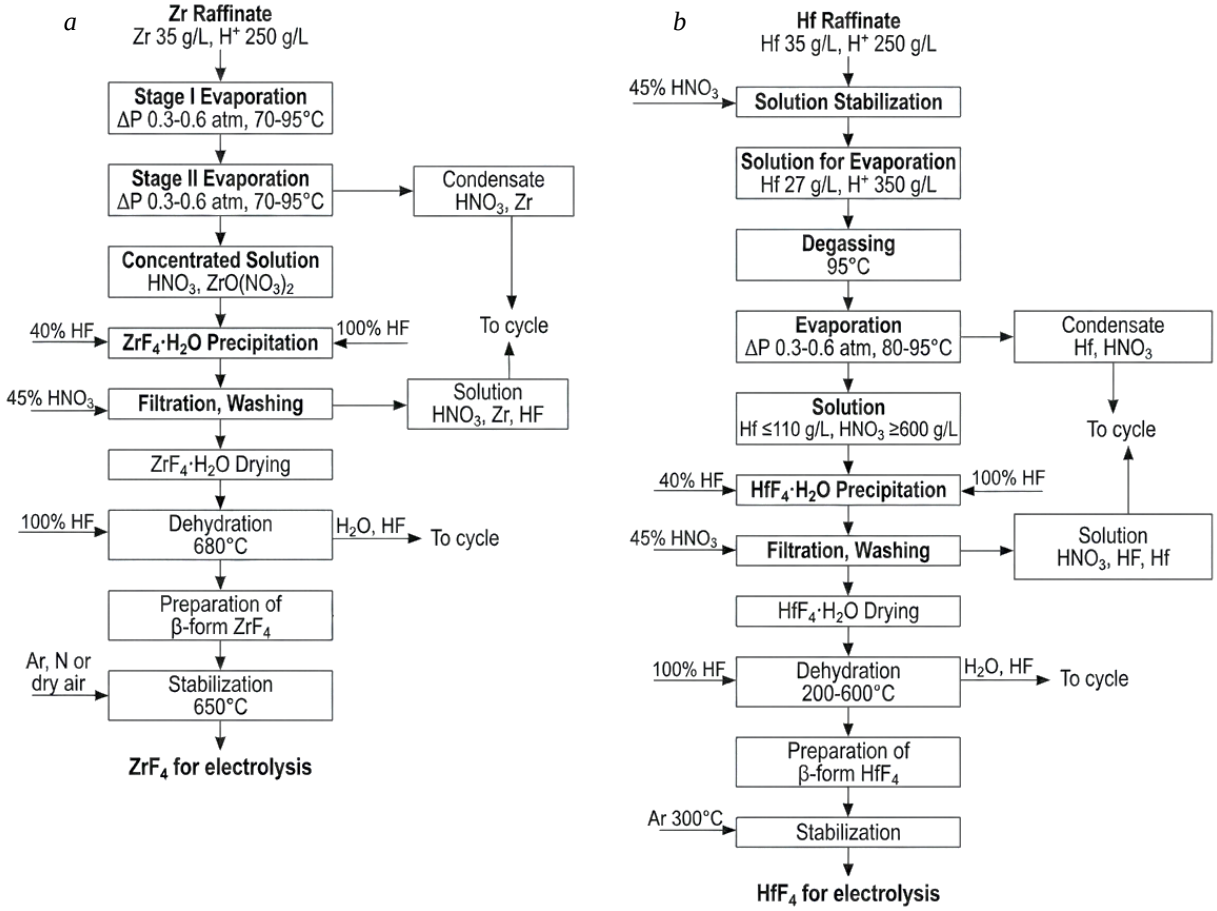
Precipitation of ZrF_4 was carried out using 40% hydrofluoric acid and anhydrous hydrogen fluoride according to the equation:

$$ZrO(NO_3)_2 + 4HF \rightarrow ZrF_4 \cdot H_2O + 2HNO_3. \quad (1)$$

The yield of zirconium into the monohydrate was 96% when using hydrogen fluoride and 90% when using 40% hydrofluoric acid. The zirconium concentration in the mother liquor after separating the $ZrF_4 \cdot H_2O$ crystals reached 10 g/l, necessitating additional zirconium recovery. The crystals were fine-grained and had a moisture content of up to 30%.

In investigating various drying methods for the monohydrate – which must ensure a product moisture content of ≤0.05% – the best results were obtained in a fluidized-bed dryer at 400…500 °C. This maintained a drying-zone temperature of (230±50) °C. The product was collected in cyclones.

The dried monohydrate was then fed to a standard rotary kiln with a retort made of EP-797 steel for dehydration. The process was conducted at 400...650 °C under a flow of hydrogen fluoride. Adsorbed HF was removed from the tetrafluoride using dry air at 680 °C.



Process flow diagram for experiments to obtain ZrF_4 (a) and HfF_4 (b)

Obtaining a fine-grained $ZrF_4 \cdot H_2O$ powder requires choosing an effective drying method. Both a shelf dryer with hot air drawn through the wet product and a microwave dryer gave unsatisfactory results. The best performance in process trials was achieved with a fluidized-bed dryer featuring 100% product carryover. Hot air is supplied by an electric air heater at a temperature of (650±30) °C. The product is fed into a cyclone and then to a tray scrubber. The optimal process parameters for the fluidized-bed furnace were as follows:

Air temperature under the grate: (440±20) °C.
Air temperature in the drying zone: (220±20) °C.
Drying time: (36±6) h.
Gas velocity in the furnace: 1.5 m/s.
Draft, mm H_2O:
– at the top of the furnace: 20;
– after the cyclone: 360.
Suction gas flow rate: 320 m³/h.
Moisture content of the feed product: ≤ 25%.
Throughput on wet product: 60 kg/h.
Specific capacity, kg/(m²·h):
– on dry product: 1000;
– on moisture: 300.

The drying study validated the efficiency of the chosen fluidized-bed method with full product entrainment and established the furnace capacity matching the overall throughput of the process train from feed preparation to dehydration.

As a result of optimizing all process parameters, ZrF_4 was obtained with the following major impurity content (wt.%): Fe – 0.008…0.018; Ni – 0.006…0.011; Al – 0.003…0.005; Si – 0.005…0.009; Cr – 0.003…0.006; Ti – 0.001; Mn – 0.001; Cu – 0.001; O – 0.05; N – 0.002.

Optimization of the dehydration step in the rotary kiln yielded ZrF_4 with a bulk density of 2.3 g/cm³ and volatile impurity content of ≤ 0.05 wt.%, meeting the requirements for the electrochemical production of nuclear-grade zirconium as specified in ASTM B349-16.

These results provided the basis for revising the process parameters of the vacuum evaporation of the zirconium oxynitrate nitrate solution and establishing their optimal values. The precipitation of $ZrF_4 \cdot H_2O$ must take into account the principles of crystallizing large product particles from a saturated rather than supersaturated solution. It was necessary to determine the kinetics of hydrogen fluoride feed and the endpoint parameters, based on optimal density to obtain coarser crystals. All these conditions were tested in the production of the zirconium tetrafluoride analogue – HfF_4.

The chemical composition analyses of the zirconium and hafnium tetrafluorides at the monohydrate production stage are presented in Tables 1 and 2.

Table 1

Chemical composition of zirconium and hafnium fluoride compounds

Compound	Content, mol.%								
	Zr/Hf	F	N	Fe	Al	Ni	Cr	Ti	Si
$ZrF_4 \cdot H_2O$	49.9	38.0	0.03	0.03	0.002	<0.001	<0.001	<0.001	<0.001
$HfF_4 \cdot H_2O$	66.0	27.5	0.02	0.02	0.001	0.001	0.001	0.001	0.004
ZrF_4	54.5	45.5	<0.02	0.013	0.004	0.008	0.004	0.001	0.007
HfF_4	70.0	30.0	0.1	0.02	0.015	0.001	0.001	0.003	0.005

The content of adsorbed gases in the zirconium and hafnium tetrafluorides is given in Table 2.

Table 2

Content of adsorbed gases in zirconium and hafnium tetrafluorides

Compound	T, °C	Content, mol.%					
		N_2	H_2O	H_2	CO_2	CH_4	Other gases
HfF_4	363	29.7	32.4	28.1	4.3	3.2	2.3
	550	34.7	33.7	22.1	5.8	3.5	0.0
ZrF_4	370	51.1	33.5	35.0	6.8	4.5	3.0

During the experiments, it was determined that the initial ratio of nitric acid to hafnium concentrations should be increased to ≥12. A 45% HNO_3 solution must be introduced into the strip solution. To reduce the hafnium concentration from 35 to 25 g/l, the nitric acid concentration was raised to 400…440 g/l. Given the high vapor pressure of nitric acid at temperatures ≥100 °C, evaporation was carried out under vacuum in the range of 0.3…0.6 atm at a temperature of 80…95 °C.

The optimal evaporation factor was 4, at which the hafnium concentration increased to 105 g/l and nitric acid to 650 g/l, corresponding to the solution saturation limit. This kept the solution stable and prevented the formation of hafnium oxynitrate crystals. The results of the evaporation of the hafnium nitrate solution are given in Table 3.

Table 3

Composition of hafnium nitrate solutions

No	Initial hafnium strip solution, g/l			Evaporated solution, g/l			Condensate, g/l	
	Hf	HNO_3	HNO_3/Hf	Hf	HNO_3	HNO_3/Hf	Hf	HNO_3
1	27.3	446	16.3	106	644	1.45	0.1	185
2	29.6	423	14.8	110	643	1.50	0.2	175
3	27.5	469	17.0	105	650	1.49	0.2	180
4	29.7	404	13.6	110	570	1.41	0.2	160
Avg.	28.7	434	15.4	107	625	1.49	0.15	175

The vacuum in the evaporator was increased twofold, to 0.6 atm, which lowered the evaporation temperature from 110 to 95 °C without reducing throughput. To reduce gas evolution during evaporation, the hafnium strip solution was preheated to 95 °C. This reduced hafnium losses in the condensate by a factor of 15, down to 0.15 g/l, and increased its yield in the tetrafluoride.

After evaporation, the concentration of nitrate ions – both free and bound to hafnium – was raised to 775 g/l, i.e., to 13 mol. The stability of the solution prevented solids from clogging the heating chamber tubes.

The main step in the production of hafnium tetrafluoride is the reaction of hydrogen fluoride with hafnium nitrate, which is described by the equation:

$$HfO(NO_3)_2 + 4HF \rightarrow HfF_4 \cdot H_2O + 2HNO_3. \quad (2)$$

The process efficiency is determined by the minimum residual hafnium content in the mother liquor (≤1 g/l) at a minimum fluoride ion content (3…5 g/l). Using hydrogen fluoride in gaseous form gave the best results. To improve crystal quality, a molar F:Hf ratio of ≥4.2:1 is maintained during the reaction, which ensures minimal hafnium solubility.

The crystal size of $HfF_4 \cdot H_2O$ depends on the hydrogen fluoride feed rate into the solution. It was determined that fluorination should be carried out in two stages. The first stage should be performed by feeding 50% of the calculated HF amount in the shortest possible time to obtain a saturated solution of the well-soluble intermediate salt $HfOF_2$. This provides maximum hafnium saturation of the solution and initiates the precipitation of $HfF_4 \cdot H_2O$ crystals at an optimal rate, preventing spontaneous formation of fine crystals. To this end, pulp density was continuously monitored with an automatic densitometer. The endpoint corresponded to a solution density of 1.34 g/cm³. The results of the $HfF_4 \cdot H_2O$ precipitation study are given in Table 4.

Table 4

Chemical composition of hafnium tetrafluoride crystals and moisture content

No.	Hf	F	HNO_3	Moisture, %
1	1.0	4.6	870	17.8
2	1.5	1.5	840	16.1
3	1.8	1.7	800	24.0
4	1.9	5.6	792	30.0
5	2.0	9.1	832	19.5
6	2.4	2.1	888	10.8
7	2.9	4.0	793	25.0
Avg.	1.8	4.1	830	23.0

A crystal moisture content of ≤15% was achieved by increasing the filtration time to 4 h.

The precipitation of $HfF_4 \cdot H_2O$ was carried out in equipment made of PTFE (fluoroplastic-4) due to the

highly corrosive nature of the process solution. Other materials could not ensure the hafnium salt purity required for nuclear-grade metal production.

Selective dehydration was achieved under optimal conditions. The process was performed in a rotary drum retort made of EP-797 steel. A moisture content of ≤ 0.05% was ensured by preheating the argon and hydrogen fluoride feed to 300 °C. The adsorbed HF was stripped from the HfF_4 powder surface with a gas stream at (650±50) °C. During the trials, the optimal product feed rate (5 kg/h), temperature, and hydrogen fluoride flow rate were determined. The optimized throughput allowed a monthly output of up to 3 t of HfF_4. This reduced the oxygen content in HfF_4 by a factor of 20, down to 0.2…0.3%.

By optimizing the process parameters for producing the β-modification of hafnium tetrafluoride, the conversion of hafnium into the insoluble HfF_4 salt reached 98…99.6%. The resulting salt successfully passed a full test cycle in electrochemical metal production and calciothermic reduction processes, yielding hafnium suitable for nuclear applications.

The physical properties of hafnium tetrafluoride are primarily determined by its particle size, which dictates the specific surface area and sorption characteristics. The crystal size of HfF_4 ranged from 1 to 10 μm, with a maximum density of 1.45 g/cm³ and a specific surface area of (1.6±0.1) m²/g.

The mother liquor after filtration of $ZrF_4 \cdot H_2O$ had the following chemical composition, g/l: Zr – 5…10; F – 5…10; HNO_3 – 640.

In the production of Zr-Nb alloy products, metallic waste is generated and must be reprocessed. Combined processing of these streams reduces the consumption of fresh nitric acid and allows $ZrF_4 \cdot H_2O$ to be obtained according to stoichiometry, balancing the total zirconium content (mother liquor + waste) and total fluorine content (mother liquor + hydrogen fluoride).

Analysis of the Zr^{4+}–HF–HNO_3 system showed that zirconium dissolution should be carried out at a molar ratio of F : Zr = 2.5. Hydrated zirconium tetrafluoride is then formed when hydrogen fluoride is introduced to achieve F : Zr = 4.0…4.2. Under these conditions, the solubility of zirconium in the nitric-fluoride mixture can reach 250 g/l, with a yield of up to 98% into the monohydrate.

Ionic equilibrium calculations and thermodynamic analysis indicated that the main fluorinating agents are the $[ZrF_n]^{4-n}$ complexes. Dissolving zirconium in the acid mixture can generate hydrogen-containing gases, creating an explosion hazard. A study of the off-gas composition showed that dissolving 1 mol of zirconium in 5…11 M HNO_3 with 1.6 mol of fluorine at 100 °C produces up to 1.5 mol NO_2, up to 0.5 mol NO, up to 0.25 mol N_2O, and up to $5 \cdot 10^{-3}$ mol N_2. The amount of hydrogen depends on the nitric acid concentration and the F : Zr ratio; hydrogen evolution reaches up to $100 \cdot 10^{-3}$ mol/g for Zr-1% Nb alloy and up to $15 \cdot 10^{-2}$ mol/g for pure zirconium.

At nitric acid concentrations of 7…9 M and a temperature of 100 °C, the following reactions can occur:

$$Zr + (2+x)HNO_3 + (4-x)HF \rightarrow ZrF_{4-x}(NO_3)_x + 1.5NO_2 + 0.25NO + 0.25N_2O + 5H_2O, \quad (3)$$

$$Zr + 0.5ZrF_3NO_3 + 4.5HNO_3 \rightarrow 0.75Zr_2OF_2(NO_3)_4 + 1.25NO_2 + 0.25NO + 0.25N_2O + 2.5H_2O, \quad (4)$$

where x = 0–2.

Of particular scientific interest was determining the conditions under which hydrogen cannot evolve. Electrochemical studies showed that for the Zr-1% Nb alloy, at HNO_3 concentrations > 6 M, there is a concentration range where hydrogen evolution is suppressed. Based on these data, the following mechanism for zirconium dissolution can be proposed:

$$Zr + 2H_2O \rightarrow ZrO_2 + 4H^+ + 4e^-; \quad (5)$$

$$ZrO_2 + [ZrF_n]^{4-n} + 4H^+ \rightarrow [ZrF_3]^+ + [ZrF_{n-1}]^{(3-n)} + 2H_2O; \quad (6)$$

$$ZrO_2 + nHF \rightarrow [ZrF_n]^{4-n} + H_2O, \quad (7)$$

where n = 5–6.

Monitoring the chemical reactions in solution using a fluoride-selective electrode for the Zr^{4+}–HF–HNO_3 system is essential. This ensures the most complete transfer of zirconium from solution into the monohydrate. Acidity was controlled with a tungsten metal-oxide electrode. Redox potential (ORP) measurements were performed using a glassy carbon electrode. The electromotive force of the electrode systems was recorded with laboratory fiber-optic millivoltmeters. During the experiments, a correlation was established between the pH measured by the fluoride-selective electrode and the F : Zr molar ratio. The ORP data provided additional kinetic information. In practice, this method proved to be the most reliable and accurate in nitric-acid solutions, and it was therefore also applied to the Hf^{4+}–HF–HNO_3 systems.

CONCLUSIONS

As a result of the study on the production of nuclear-grade zirconium and hafnium tetrafluorides, the optimal process parameters were established: the acidity-to-metal concentration ratios before and after evaporation, the evaporation factor, the metal content in the condensate, the saturation level of the solution with zirconium and hafnium prior to precipitation, and the HF feed rate required to obtain large monohydrate crystals.

It was determined that obtaining the β-modification of ZrF_4 and HfF_4 requires removal of adsorbed gases and stabilization of the phase composition with argon at 650 °C. The high purity of ZrF_4 and HfF_4 (99.9%) makes them suitable for use in electrochemical and calciothermic reduction processes to produce nuclear-grade metals.

Zirconium alloy products derived from this ZrF_4 have undergone a full cycle of radiation testing under actual WWER-1000 and WWER-400 operating conditions and have shown results identical to standard products obtained from K_2ZrF_6 salt produced by fractional crystallization [14].

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ОТРИМАННЯ ТЕТРАФТОРИДІВ ЦИРКОНІЮ ТА ГАФНІЮ ЯДЕРНОЇ ЧИСТОТИ

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Викладено результати промислових випробувань технології високочистих тетрафторидів цирконію та гафнію. Ядерна чистота нітратних солей цирконію та гафнію досягається завдяки високій кінетиці процесу екстракції, досягнутій у відцентрових екстракторах ЕЦ-250 та ЦЕТ-125. Показано, що для повного переходу цирконію та гафнію в нерозчинні фториди, необхідно отримати насичені за цирконієм та гафнієм розчини після їх упарювання у вакуумі за 70…95 °С. Моногідрати тетрафторидів цирконію та гафнію було отримано із застосуванням як осаджувача 40% HF та 100% фтористого водню. Мінімальний вміст цирконію та гафнію в маточному розчині було отримано при використанні фтористого водню. Видалення кристалізаційної води забезпечувалося після сушіння за температури 120 °С та термічної обробки солей за температури 650 °С у потоці фтористого водню та сухого аргону. Отримані в β-фазі фториди цирконію та гафнію мали чистоту 99,9% та вологість менше 0,05%. Вони повністю відповідали вимогам процесу штатного електролізу на основі K_2ZrF_6 та K_2HfF_6. Обидві солі пройшли повний цикл технологічних випробувань, у ході яких було отримано порошки цирконію та гафнію з чистотою не менше 99,85%.