

HYDROGEN FLUORIDE OBTAINING FROM URANIUM HEXAFLUORIDE IN THE COMBUSTION MODE

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Currently, there are no effective industrial technologies to return fluorine into a technological cycle. The authors have proposed a method for processing uranium hexafluoride depleted in the U-235 (DUHF) isotope in a hydrogen-oxygen flame that can be used as a basis for obtaining hydrogen fluoride and uranium oxides. Using own devising program code and complex ASTRA.4, performed thermodynamic calculations in the U-F-H-O elements system and it was shown that if the number of hydrogen atoms exceeds the number of fluorine atoms, then at temperatures above 1150 K, the only fluorine-containing substance in the thermodynamically equilibrium mixture was HF, while the main uranium-containing was UO₂. The proposed method was experimentally investigated at a pilot plant and it showed that the composition of its products was close to thermodynamic equilibrium. The results can become the basis for industrial technology of the hydrogen fluoride production from DUHF.

Keywords: depleted uranium hexafluoride, uranium dioxide, hydrogen fluoride, combustion

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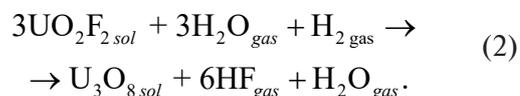
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Introduction

Uranium hexafluoride is a ²³⁵U-depleted by-product of isotopic separation of natural uranium. Uranium hexafluoride is a Class 1 hazardous substance, so its accumulation and storage is an environmental threat. Uranium hexafluoride (DUHF) is also a source of pure ²³⁵U-depleted uranium, which can be effectively used to produce mixed-oxide (MOX) fuel for fast-neutron reactors and fluorine. DUHF is currently stored at enrichment facilities of the Rosatom State Atomic Energy Corporation.

The methods for processing DUHF developed in Russia have a number of serious drawbacks, making it impossible to use them commercially [1–4].

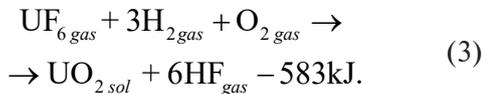
The only known industrial technology for processing DUHF is two-stage hydrolysis yielding an aqueous solution of hydrogen fluoride and triuranium octaoxide, developed by Orano (France) [5, 6]:



An excess of water is used for complete regeneration of fluorine by this method, with hydrogen fluoride and its azeotropic aqueous 40% solution acting as the main fluorine-containing products, which does not allow to recover fluorine in the nuclear fuel cycle.

In Russia, this technology is used by Electrochemical Plant JSC at the W-ECP facility. Notably, producing hydrogen fluoride at this facility is costlier than producing hydrogen fluoride by the traditional method (sulfuric acid decomposition of high-quality fluorite): the facility however has greater environmental safety [7].

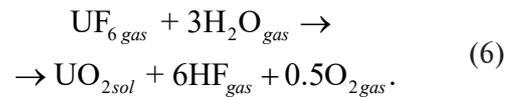
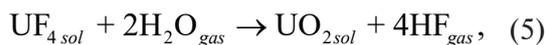
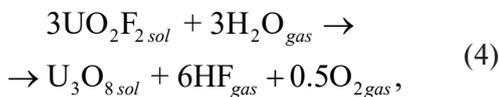
We have proposed a method for regeneration of fluorine in the form of hydrogen fluoride from DUHF by processing it in the flame of a hydrogen-containing fuel and an oxygen-containing oxidizer, for example,



Calculations indicate that process (3) is thermodynamically allowed, its thermal effect is that the adiabatic temperature of the products can reach about 2500 K, i.e., the process can proceed under combustion. Calculations also established that if the number of hydrogen atoms in a system of U-F-H-O elements exceeds the number of fluorine atoms, the main fluorine-containing substance at temperatures above 1150 K in a mixture in thermodynamic equilibrium is hydrogen fluoride, and the main uranium-containing substances are uranium oxides. These conclusions are confirmed by experiments on a test setup that we have constructed.

Thermodynamic study of hydrolysis of uranium fluorides

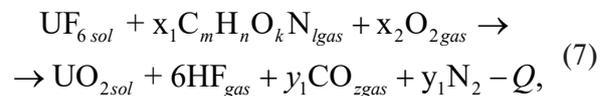
According to the data given in monograph [8], hydrogen fluoride can be obtained from uranium fluorides by hydrolysis:



To estimate the temperature range where it is optimal to carry out processes (1), (2) and (4)–(6), the values of the Gibbs energy change ΔG were calculated depending on the temperature T (Fig. 1).

Analyzing the data in Fig. 1, we can conclude that a high degree of fluorine recovery from uranium hexafluoride without excess water can be achieved via hydrolysis at a temperature above 1150 K.

This temperature can be obtained by treating UF_6 in the flame of a hydrogen-containing fuel and an oxygen-containing oxidizer:



where $\text{C}_m\text{H}_n\text{O}_k\text{N}_l$ is a volatile hydrogen-containing substance, $n > 0$, $m \geq 0$, $k \geq 0$, $l \geq 0$; $nx_1 \geq 6$, $2x_2 > 2$, $Q \approx 10^2\text{--}10^3$ kJ, $T > 10^3$ K.

The amount of fuel and oxidizer is chosen so that fluorine is completely recovered as hydrogen fluoride, without water produced, and the main uranium-containing substance is uranium dioxide.

Notably, the method we propose implies that heat is supplied to the reaction zone as a result of chemical heat release rather than from the reactor wall, so the temperature of the reactor walls can reach about 100°C.

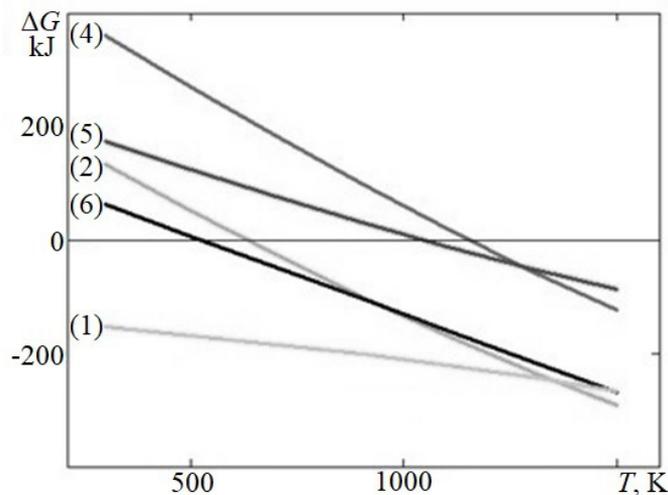
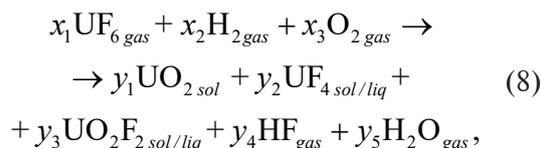


Fig. 1. Gibbs energy changes for hydrolytic reactions of uranium fluorides depending on temperature (curve numbers correspond to reaction numbers)

If hydrogen is used as a hydrogen-containing fuel (reaction (3)), the adiabatic temperature of the products, as well as the temperature accounting for the corrections for radiant heat transfer [9], calculated on the basis of the Kirchhoff law, are 2540 K and 1670 K, respectively. Thus, it is possible to recover fluorine from DUHF as hydrogen fluoride without excess water via scheme (3) in combustion mode.

Thermodynamic equilibrium composition of substances in the system of U-F-H-O elements

The thermodynamic equilibrium composition of substances in the system of U-H-F-O elements was calculated using the method for minimizing the Gibbs energy for a mixture of substances, assuming that the most stable compounds are uranium dioxide, uranium tetrafluoride, uranyl fluoride, hydrogen fluoride and water [10, 11]:



where x_i, y_i are the stoichiometric coefficients.

The model was verified by comparing the results obtained by experiment and by calculations in the ASTRA.4 software package. The latter is based on the method for calculating the thermodynamic equilibrium composition by searching for the maximum entropy [11, 12]. The calculated results are given in Table 1. The discrepancy between the calculated results obtained by minimizing the Gibbs energy and

maximizing the entropy at temperatures above 1150 K is less than 20%, at temperatures above 1150 K. A possible reason for this discrepancy is that the reference books used give differing values for the thermodynamic functions of the substances considered. For example, the data for calculations by the method for minimizing the Gibbs energy were taken from [10], giving 1854 kJ/mol for the standard enthalpy of formation for UF_4 , while the value of the same parameter in [11], used in calculations by the ASTRA.4 software package, was 1920 kJ/mol. Discrepancies of several percent are also observed for other parameters (heat capacity, standard entropy of formation), which is what results in the 20% difference for uranium dioxide and 6% for hydrogen fluoride. Thus, the developed model is suitable for calculating the thermodynamic equilibrium composition.

It follows from the results in Table 1 that HF is the main fluorine-containing substance in the thermodynamic equilibrium mixture at temperatures above 1100 K, and the main uranium-containing substance is UO_2 . The content of uranium fluorides is less than 5%, and less than 0.5% at temperatures above 1700 K; the water content at temperatures above 1300 K is several percent.

Thus, apparently, complete recovery of fluorine from DUHF via reaction (3) is not thermodynamically prohibited.

The results of thermodynamic analysis lead us to conclude that the process of obtaining hydrogen fluoride during the interaction of uranium hexafluoride with hydrogen and oxygen in combustion mode deserves further consideration.

Table 1

Calculated thermodynamic equilibrium composition of substances in system of 1U-6F-6H-2O elements

T, K	Compound concentration, C, mol%									
	UO ₂		UF ₄		UO ₂ F ₂ UOF ₃		H ₂ O		HF	
	G	Astra	G	Astra	G	Astra	G	Astra	G	Astra
700	< 0.1	< 0.1	20.0	19.5	< 0.1	< 0.1	40.0	39.1	40.0	40.9
900	1.0	< 0.1	19.0	17.8	< 0.1	< 0.1	40.0	35.1	40.0	47.1
1100	17.0	10.3	0.9	4.1	< 0.1	< 0.1	1.5	8.1	80.6	77.6
1300	16.9	13.8	0.8	< 0.1	< 0.1	< 0.1	2.7	1.9	79.6	84.3
1500	16.7	13.4	0.3	0.6	< 0.1	< 0.1	3.5	2.2	79.5	83.8
1700	16.3	12.9	0.3	0.7	< 0.1	0.8	3.9	2.7	79.5	82.9

Note. The calculations were carried out using the in-house program code (G) and the ASTRA.4 software package.

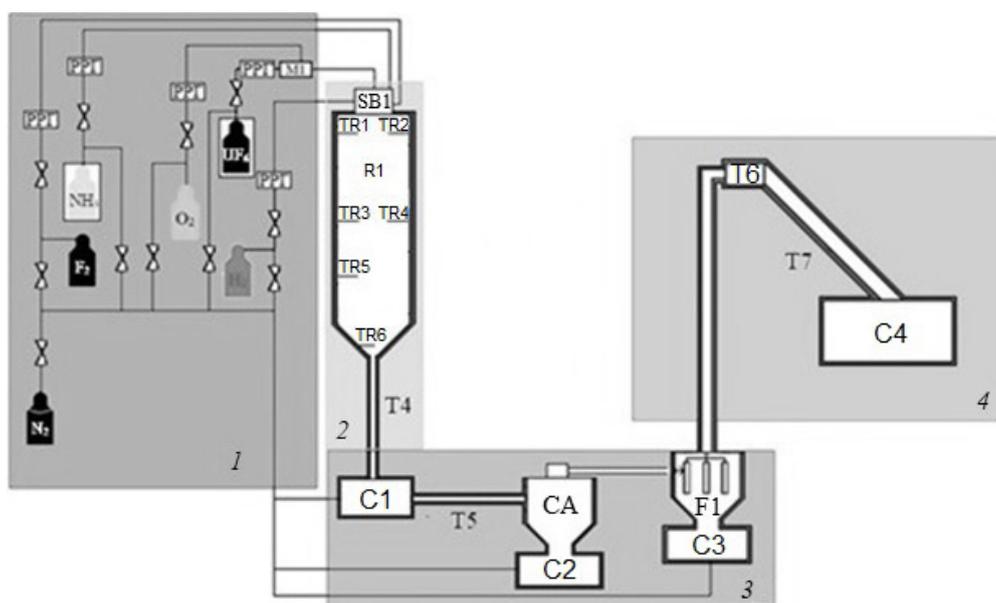


Fig. 2. Schematic of pilot plant:

unit 1 for preparing and supplying initial gaseous substances, reactor unit 2, unit 3 for separating solid and gas phases, unit 4 for condensing hydrogen fluoride and water; nozzle SB1, thermocouples TR1–TR6, solid phase collectors C1–C4, heat exchangers T4–T7, cyclone separator CA, sintered metal filter F1

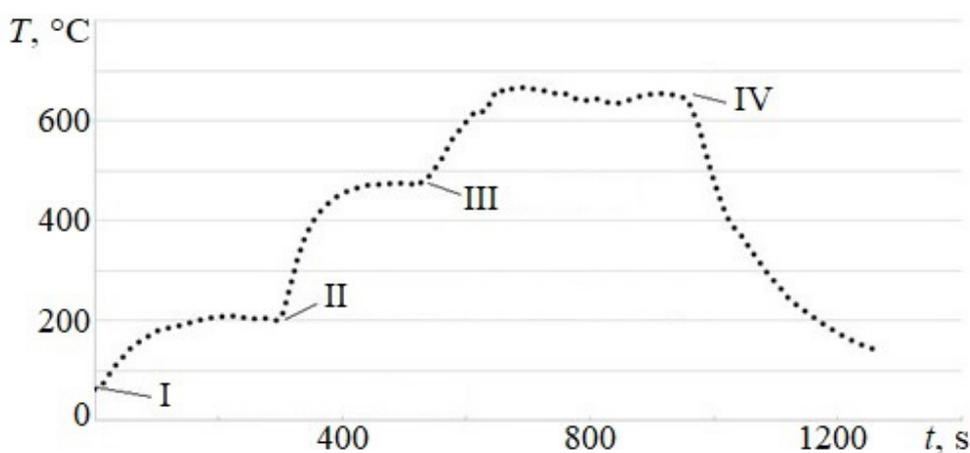


Fig. 3. Time dependence of junction temperature of thermocouple TR2 (see Fig. 2) in the reactor.

The following stages of the process are shown: NH₃ and F₂ are supplied (I), H₂ and O₂ are supplied (II), DUHF is supplied (III), supply of components is stopped (IV)

Gas flow rates, g/s: 0.010 for F₂, 0.014 for NH₃, 1.50 for DUHF, 0.05 for H₂, 0.27 for O₂

Experimental study of interactions of uranium hexafluoride with hydrogen and oxygen in combustion mode

A pilot plant was constructed to experimentally study the composition of the products resulting from processing DUHF in the flame of a hydrogen-containing fuel and an oxygen-containing oxidizer,

The setup (Fig. 2) consists of four main units.

Unit 1 for preparing and supplying the initial gaseous substances is intended for feeding DUHF, hydrogen, ammonia, fluorine, and nitrogen into the reactor. Ammonia and fluorine were used as a self-igniting mixture to initiate combustion of the main flame. Flow controllers by Bronkhorst were used to monitor the flow rates of all gases.

The main element of reactor unit 2 was a 'tunnel burner' type reactor with a cooling

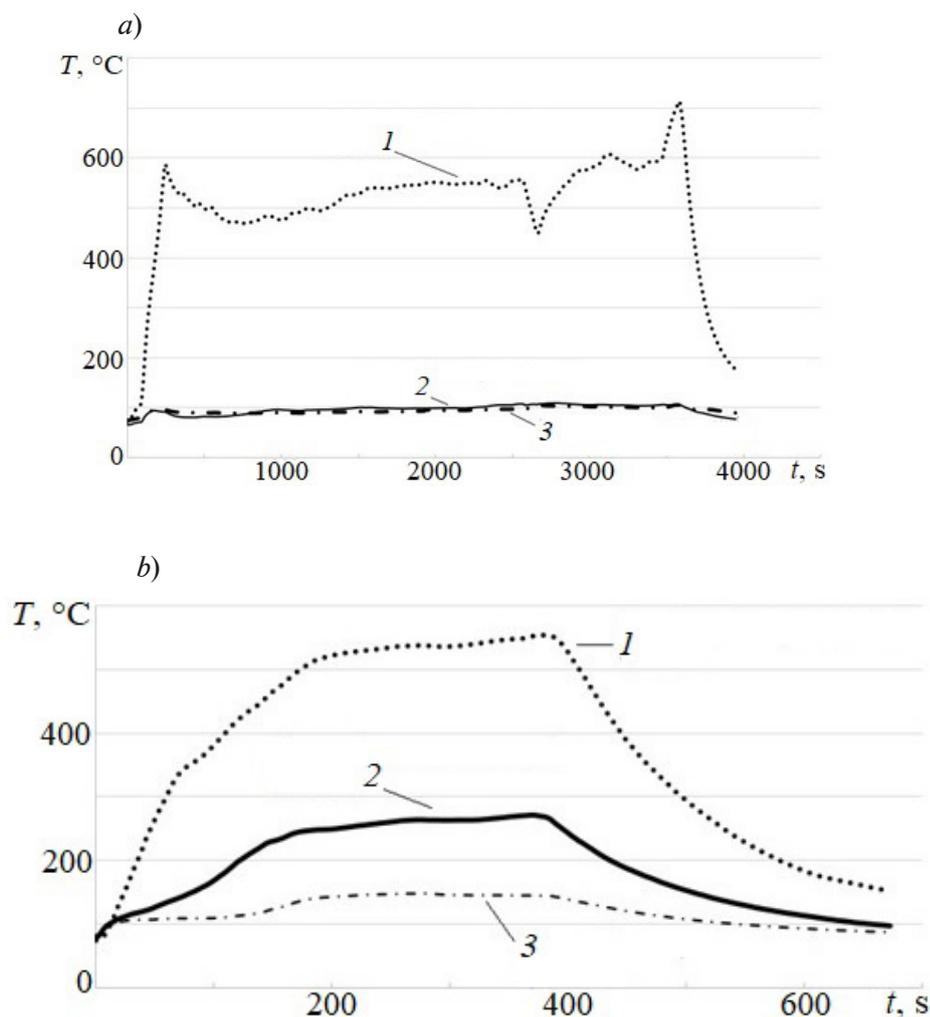


Fig. 4. Time dependences for temperature of thermocouple junctions in the reactor for two cases of component flow rates, g/s: 1.5 DUHF, 0.04 H₂, 0.016 O₂ (a) and 7.0 DUHF, 0.14 H₂, 0.76 O₂ (b); the flow rate of other components remains the same, g/s: F₂ 0.010, NH₃ 0.014. Data from thermocouples mounted on top (1), middle (2), and bottom (3) flanges are given

jacket, where water with a temperature of about 90°C was supplied to prevent condensation of hydrogen fluoride. The length and diameter of the reactor were 2650 and 142 mm, respectively. The reactor consisted of two cylindrical sections 1.00 m long and one conical section 0.65 m long. Measuring flanges were mounted between the sections in the reactor, with chromel-alumel thermocouples in protective covers and pressure sensors installed. The components were fed into the reactor using two nozzles installed in nozzle assembly SB1.

Unit 3 for separating the solid and gas phases consisted of solid phase collectors C1, C2, C3, heat exchanger T5, where the flow was cooled to a temperature of 120°C, cyclone separator CA and a sintered metal filter F1 separating particles with the size of more than 0.15 μm.

Unit 4 for condensing hydrogen fluoride and water was a pipe-in-pipe heat exchanger, where the temperature was maintained at 40°C.

The pilot plant was used for studying the interaction of DUHF with hydrogen and oxygen in combustion mode at a ratio of components close to that given in reaction (3). The flow rate of DUHF was varied from 1 to 7 g/s in the experiments, which corresponded to the rate of 0.02–0.20 m/s of the mixture of initial materials in the reactor at 90°C.

Thermocouples were used to observe the formation of the flame front. A typical thermogram of the experiment is shown in Fig. 3, showing the time dependence of the junction temperature for thermocouple TR2 (first measuring flange, 40 mm from the axis) in the reactor. The temperature clearly increases when ammonia

and fluorine (self-ignition), hydrogen and oxygen (combustion of an oxygen-hydrogen flame) and DUHF are supplied; the variation of temperature amounts to hundreds of degrees.

Thus, it was found that a three-component flame consisting of DUHF-hydrogen-oxygen is reliably produced and burns steadily upon initiation by a fluorine-ammonia flame with the flow rate of DUHF varying from 1 to 7 g/s and a component ratio close to that in reaction (3).

Fig. 4 shows thermograms for the thermocouples installed in three measuring flanges for DUHF flow rates close to minimum and maximum.

We can conclude from the data shown in Figs. 3 and 4 that the length of the flame in the reactor did not exceed 1 m in the given range of flow rates.

The main uranium-containing product of process (3) was a powder of uranium oxides, primarily uranium dioxide and triuranium octaoxide. More than 97% of the powder gravitated downwards to collector C1.

The contents of fluorine, covalently bound to uranium and determined using instrumental methods, i.e., X-ray phase analysis and FTIR spectroscopy, varied from 0.1 to 3%.

The liquid phase of reaction products (3) was hydrofluoric acid, with the hydrogen fluoride concentration of more than 90 wt%.

The degree of fluorine recovery from DUHF was calculated by the formula

$$R_F = \left(1 - \frac{1}{6} \sum_i C_{UF_i} N_{UF_i} \right) \cdot 100\%, \quad (9)$$

where C_{UF} is the molar concentration of uranium fluorides and oxyfluorides, N_{UF} is the number of fluorine atoms in uranium fluorides and oxyfluorides.

The value of the parameter R_F reached 99%.

Table 2 shows the results of experiments determining the concentration of covalently bound fluorine, the degree of fluorine recovery and the concentration of hydrogen fluoride in hydrofluoric acid, depending on the flow rate of DUHF and the molar ratio of the initial components.

Table 3 gives the composition of solid products resulting from processing DUHF, the amount of hydrogen fluoride, water and hydrogen per 1 mole of DUHF; all values were calculated from the solid composition.

It can be concluded from the experimental results in Tables 1 and 2 that using the proposed method for processing DUHF makes it possible to recover more than 95% of fluorine from DUHF in the form of hydrogen fluoride with a slight excess of oxygen and hydrogen relative to the stoichiometry of process (3). The concentration of the obtained hydrofluoric acid (an aqueous solution of hydrogen fluoride) exceeds 90%. The main uranium-containing substances are uranium oxides, and the uranium dioxide content typically exceeds 90%. Impurity

Table 2

**Dependence of concentration of fluorine-containing compounds
and degree of fluorine recovery on flow rate of DUHF
and molar ratio of initial components**

#	W_{UF_6} , g/s	Ratio of initial components	C_F , wt%	C_{HF} , wt%	R_F , %
1	3.0	$UF_6 + 3.4H_2 + 1.2O_2$	3.28	94.9	87.9
2	4.4	$UF_6 + 3.1H_2 + 1.0O_2$	1.86	96.3	92.0
3	3.0	$UF_6 + 3.3H_2 + 1.2O_2$	1.35	94.6	93.8
4	6.0	$UF_6 + 3.4H_2 + 1.0O_2$	1.18	100.0	95.3
5	3.0	$UF_6 + 3.4H_2 + 1.3O_2$	1.17	96.2	95.3
6	7.0	$UF_6 + 3.4H_2 + 1.2O_2$	0.98	94.2	95.8
7	6.0	$UF_6 + 3.4H_2 + 1.0O_2$	0.91	98.2	96.0
8	1.5	$UF_6 + 4.7H_2 + 1.2O_2$	0.12	98.5	99.5

Notations: W_{UF_6} is the flow rate of DUHF, C_F is the amount of fluorine covalently bound with uranium, R_F is the degree of fluorine recovery, C_{HF} is the concentration of hydrogen fluoride.

Note. The experimental values of C_F and C_{HF} were obtained on a pilot plant, the values of R_F were calculated by Eq (9).

Table 3

Composition of solid and gaseous products of DUHF processing

#	W_{UF_6} , g/s	Chemical composition of solid products, wt%								Gas, mol		
		UO ₂	U ₃ O ₈	U ₃ O ₇	UO ₃	UO ₂ F ₂	UOF ₄	UF ₄	UF ₅	HF	H ₂ O	H ₂
1	3.0	56.3	5.0	–	18.2	14.1	–	6.4	–	5.27	0.32	0.44
2	4.4	92.3	–	–	–	–	–	7.7	–	5.52	0.24	0.10
3	3.0	79.5	14.6	–	–	–	5.9	–	–	5.63	0.37	0.12
4	6.0	59.3	12.2	23.6	–	–	–	4.9	–	5.72	–	0.54
5	3.0	–	43.5	51.6	–	–	–	4.9	–	5.75	0.26	0.27
6	7.0	86.3	9.4	–	0.8	–	–	–	3.4	5.75	0.4	0.13
7	6.0	96.2	–	–	–	–	–	3.8	–	5.71	0.12	0.55
8	1.5	60.2	39.2	–	–	0.3	0.3	–	–	5.97	0.10	1.62

Notes. 1. All experimental data were obtained on a pilot plant. 2. The amounts of HF, H₂O and H₂ per 1 mole of DUHF were calculated from the composition of solid products.

uranium fluorides are mainly uranyl fluoride and uranium tetrafluoride whose concentrations vary from several percent to tenths of a percent.

Comparing the data in Table 1 with the data in Tables 2 and 3, we can conclude that the results of experiments on the composition of the products resulting from process (3) are in good agreement with the calculation results for the thermodynamically stable composition of substances in the system of U-F-H-O elements.

Conclusion

Thermodynamic calculations have confirmed that it is expedient to carry out hydrolysis of UF₆ aimed at obtaining uranium oxides and hydrogen fluoride in the absence of excess water at temperatures above 1150 K.

Furthermore, the calculations indicate that the main fluorine-containing substance in the system of U-F-H-O elements in a mixture in thermodynamic equilibrium at temperatures above 1150 K is hydrogen fluoride, and the main uranium-containing one is uranium dioxide.

Based on the experimental data obtained on the setup, we have found that the flame of UF₆-3H₂-O₂ is reliably generated and burns steadily in a 'tunnel burner' type reactor (its inner diameter is 142 mm) with combustion initiated by a

fluorine-ammonia mixture in the entire range of DUHF flow rates considered (from 1 to 7 g/s).

The main uranium-containing products of the process given an excess of fuel and oxidizer are uranium oxides (about 10%), primarily in the form of uranium dioxide and triuranium octaoxide, while the UF₄ and UO₂F₂ contents in uranium oxides vary from several percent to several tenths of a percent.

The main fluorine-containing substance is hydrogen fluoride, the concentration of the obtained hydrofluoric acid is about 95%.

The degree of fluorine recovery from DUHF reaches 99%.

The results of the experiments on finding the composition of the products resulting from processing DUHF in a hydrogen-oxygen flame are in good agreement with the calculated results of a thermodynamically stable composition of substances in the system of U-F-H-O elements.

Thus, production of hydrogen fluoride from DUHF can be recommended as the basis for an industrial method.

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