PLASMA HYDROLYSIS TECHNOLOGY FOR CONVERSION OF DEPLETED URANIUM HEXAFLUORIDE: SCIENTIFIC BASIS AND APPLICATION.

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1. Abstract.

Scientific and technical concepts of plasma steam process for conversion of uranium hexafluoride depleeted on isotope U-235 to uranium oxides and hydrogen fluoride are reported including thermodynamics, reaction kinetics, mechanism of the process, apparatus equipment and results of the experimental test

2. Introduction.

Plasma steam process for conversion of uranium hexafluoride to uranium oxides and hydrogen fluoride is the basis of the most promoted industrial technology for solving one of essential social, technical and ecological problems at all the countries experiencing in uranium isotopes separaton technology - elimination of the stockpiles of uranium hexafluoride depleted on isotope U-235. The technology aforesaid has a basis in plasma steam conversion of depleted uranium hexafluoride at stoichiometric ratio (or close to it) of UF_6 and steam (H-OH) plasma. The process has been experimentally tested on several levels: laboratory research, verification on experimental stands, testing at a pilot plant, development of equipment. Some fragmentary data relating to the process have been published /1 /, now we present the principal scientific and technical concepts of the process and the results of its testing at the level of a pilot plant.

3. High temperature thermodynamics of interaction of UF_6 with (H-OH)-plasma.

The thermodynamic system "UF_6 – HOH" contains 4 chemical elements and 22 components: 17 are gaseous, 5 are condensed: UF_6(g), UF_5(g), UF_4(g), UO_2F_2(g), UO_2(g), F_2(g), O_2(g), HF(g), H_2O(g), H_2(g), H(g), UF_4(c), UO_2F_2(c), UO_3(c), U_3O_8(c), UO_2(c), UO(g), U(g), U(c), O(g), F(g), OH(g). Pressure range is $1.03 \cdot 10^4$ -$1.03 \cdot 10^5$ Pa; temperature range - 800 -4000 K; initial reactants ratios are within 3 (stoichiometric ratio) - 12. According to calculation of equilibrium composition of reacting mixture UF_6 + 3HOH at pressures 53-101 kPa at T=850 C the system does not contain UF_6 /1/. At temperatures exceeding 1000 K predominant portion of fluorine is in hydrogen fluoride, HF; some portion of fluorine is in UO_2F_2: first as UO_2F_2(c), then as UO_2F_2(g). Gaseous UO_2F_2 is a stable compound which retains some content of fluorine up to 2000 K. At T~1450 K predominant quantity of U is in uranium oxide U_3O_8. Increase of temperature above 1450 K results in decomposition of U_3O_8 to uranium oxides with lower element content of oxygen; above 2500 K - predominantly UO_2.

Therefore, according to thermodynamics of the system "UF_6 –(H-OH)", the most probable products at conversion of UF_6 by (H-OH)-plasma within1500-2500 K are U_3O_8 and HF; other products like UO_2F_2 etc observed in the experiments on plasma steam conversion of

UF_6 arise both as residual products of the primary conversion of UF_6 and as a result of recombination. As a result, the overall process taking into account all the feasible recombination reactions at the exit from the reactor can be described by the next gross-equation:

$$UF_6 + 3(H\text{-}OH)\text{-plasma} \longrightarrow 1/3\ U_3O_8 + 6\ HF + 1/6\ O_2. \quad (1$$

At further increase of temperature all the uranium compounds dissociate so that uranium valency falls from 6 to 4.

4. Mechanism of the process and reaction kinetics.

Chemical and X-ray analysis of the products of plasma steam conversion of UF_6 in combination with the data of thermodynamic analysis shows that the mechanism of the conversion includes ~ 20 homogenous and heterogenous chemical reactions and physical processes of congruent and incongruent condensation. Nevertheless all the chemical reactions and physical transitions in this reacting mixture are limited by three chemical reactions and two processes of congruent and incongruent condensation described by the next equations:

$$UF_6(g) + H\text{-}OH\ (g) \rightarrow UOF_4\ (g) + 2\ HF\ (g),\ \Delta H = 54.8\ kJ, \quad (2)$$

$$UOF_4(g) + H\text{-}OH\ (g) \rightarrow UO_2F_2\ (g) + 2\ HF\ (g),\ \Delta H = 123.0\ kJ, \quad (3)$$

$$UO_2F_2\ (g) + H\text{-}OH\ (g) \rightarrow UO_3\ (g) + 2\ HF\ (g),\ \Delta H = 250.5\ kJ, \quad (4)$$

$$UO_2F_2\ (g) \rightarrow UO_2F_2\ (c),\ \Delta H = -300.0\ kJ, \quad (5)$$

$$UO_3(g) \rightarrow 1/3U_3O_8\ (c) + 1/6\ O_2\ (g),\ \Delta H = -392.4\ kJ. \quad (6)$$

According to this scheme, kinetics of the reactions and phase transitions 2-6 can be described by the set of kinetic equations:

$$d(UF_6)/dt = k_2\ (UF_6)(HOH), \quad (7)$$

$$d(UOF_4)/dt = k_2\ (UF_6)(HOH) - k_3\ (UOF_4)(HOH), \quad (8)$$

$$d(UO_2F_2)/dt = k_3\ (UOF_4)(HOH) - k_4(UO_2F_2)(HOH) - k_5\ (UO_2F_2), \quad (9)$$

$$d(UO_3)/dt = k_4(UO_2F_2)(HOH) - k_6\ (UO_3). \quad (10)$$

Kinetic constants of the reactions 2-4 are evaluated on the basis of the transition state theory: an equilibrium distribution function of an activited complex and of free molecules determine kinetic constant of chemical reactions /2/:

$$k_2 = 4.98 \cdot 10^{13} \cdot \exp(-228434/RT), \quad (11)$$

$$k_3 = 5.01 \cdot 10^{13} \cdot \exp(-240173/RT), \quad (12)$$

$$k_4 = 5.07 \cdot 10^{13} \cdot \exp(-271506/RT). \quad (13)$$

Kinetic constants of the processes 5-6 are rate constants of congruent condensation of UO_2F_2 and incongruent condensation of UO_3. These values can be evaluated using thre principal theses of Frenkel's condensation theory. The values of the condensation rate constants were evaluated by the expression:

$$J_c = N_1 \cdot (2p/KT\rho_c) \cdot (\sigma_0 \cdot M/2\pi A_0)^{0.5} \cdot \exp[-4\pi r_*^4 \cdot \sigma_0 / 3KT(r_*^2 + 2\delta)^2], \quad (14)$$

where N_1 - density of gas particles; p - pressure, T - temperature, K; K-Boltzmann's constant; σ_0-surface tension on plane surface, M - molecular weight, A_0 - Avogadro's number; r_* - critical radius of condensation nucleus. ; δ-a correction to surface curvature ($\delta = 0.5\ r_*$).

The formula enables to calculate a rate of formation of nucleus of condensed phase from neutral molecules. Supersaturation of the gas phase on uranium oxides and oxyfluorides is reduced both because of formation of new nucleus of condensed phase and of growing off nucleus. The growth rate of a nucleus, at assumption that condensation rate is a minor function of reducing supersaturation, is described by the formula /3/:

$$d(r_c^{*2})/d\tau = C, \quad (15)$$

where C is a constant. By the time τ mass of condensate m(t) is equal to

$$m(t) = 4\pi/3 \int_0^t J_c \cdot \rho_c [C(t-\tau) + r_c^{*2})^{3/2} d\tau , \quad (16)$$

When $m(t) = 1$ kg/m^3, $J = 10^{29}$ m$^{-3}\cdot$s^{-1}, ρ_c=5 kg/м^3, $r_c^* = 10^{-9}$ m, $\tau \approx 4.8\cdot10^{-4}$ c. If a value $r_c^{*2} << C\tau$, at integration of (16) we have the expression

$$t_c \approx [15m(t)/8\pi J \cdot \rho_c [C^{5/2} \cdot \rho_c)^{2/5}, \quad (17)$$

which is used as a rough approximation based on assumption that J=const as supersaturation decreases. So far as there is deficiency of data necessary for precise calculations of kinetics of conversion and condensation of uranium compounds at conversion of UF_6 in steam plasma we made comparative evaluation of time values of proceeding above enumerated reactions and phase transitions and comparing them with residence time of reacting molecules in the zone of a plasma reactor defined by velocities of chemically reacting plasma we determined the optimal conditions where the conversion of UF_6 proceeds completely and ends in gas phase before condensation of uranium oxyfluorides.

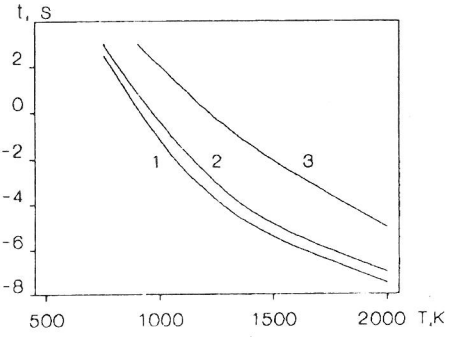

Fig.1. The 99.99 % conversion time values of UF_6, UOF_4,UO_2F_2 in the reactions (2 - 4) as a function of temperature: 1 -conversion of UF_6; 2 - conversion of UOF_4; 3 - conversion of UO_2F_2

The time values of conversion of UF_6, UOF_4, UO_2F_2 in (H-OH) -plasma depending on temperature for stoichiometric ratio of reactants are shown in Fig.1. When the mole ratio HOH/ UF_6 increases to 12, i.e. by a factor of 4 as compared to the stoichiometry of the reactions 2-4, the values of the conversion time decrease by factors of 2-4. The results of the calculations are tested for adequacy to the experimental data; the results of the comparison showed that the data of the experiments and the calculations correspond to each other with the accuracy of 10-15%.

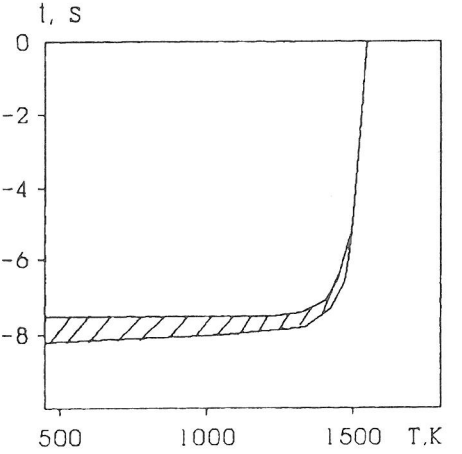

Fig.2. The values of condensation time of UO_2F_2 as a function of temperature.

As a result, we found that gaseous conversion of UF_6 in (H-OH)-plasma to 99% and more proceeds by no means not momentary, as it can be imagined by the sources of reader character. Even the primary conversion $UF_6 \rightarrow UOF_4$ в (HOH)-plasma proceeds at little surplus of steam during 0.01s. only at T~1000K. For secondary conversion $UOF_4 \rightarrow UO_2F_2$ in (HOH)-plasma to 99% at 1000K it is necessary more long time (by factors of 2-3). As it concerns the third stage UO_2F_2 (g)$\rightarrow UO_3$(g), the conversion to 99% proceeds during 0,01s only at T~1350K. Firstly it is connected with the activation energy at extending the

conversion (the reaction 2-4); secondly it is caused with dilution of the reactants by the conversion products (HF, O_2, UO_3).

The results of the calculations and the experiments show that for proceeding the reactions 2-4 at least to 99,99 % within 10^{-4}-10^{-6}s. necessary temperature is of ~1500-1600K. For preventing condensation of UO_2F_2 (the equation 5) and obtaining U_3O_8 (the equation 2-4, 6) it is necessary to ensure the conditions at the plasma reactor when condensation time of UO_2F_2 is longer than conversion time of this compound to U_3O_8. Approximating the thermophysical properties and the surface tension of UO_2F_2 by the properties of UF_4 we calculated the condensation time values of UO_2F_2 depending on temperature (Fig.2). We calculated the time values necessary for falling partial pressure of UO_2F_2 from $3.4 \cdot 10^4$ Pa to $3.4 \cdot 10^2$ Pa. The scatter of points for $\tau_{0,99}$ in the temperature range 500-1400K is explained by the appropriate scatter of the values of vapor pressure of UO_2F_2 in this temperature range. Comparing this dependence in Fig.2 with the calculation results of the conversion time values of UF_6, UOF_4, UO_2F_2 in Fig.2 shows that time of condensation of UO_2F_2 in this temperature range is longer than the conversion time of UOF_4 and UO_2F_2 in (H-OH)-plasma. Secondly we found that owing to approaching the mixture of reactants the temperature to the boiling point of UO_2F_2, the condensation time of UO_2F_2 increases extremely rapidly. As a matter of fact, condensation of UO_2F_2 is forbidden because of absense of supersaturation of UO_2F_2. One can see in Fig.2 that it takes place at the temperatures higher than 1500K. It means that keeping temperature1600K in the conversion zone of UF_6 by (H-OH)-plasma one can realize the reaction 4 in gas phase and prevent the process 5. As a result the only U-containing product of conversion of UF_6 in (H-OH)-plasma will be gaseous uranium trioxide(UO_3), which should be condensed on the termination of the reactions 2-4. The analysis of the temperature dependences of pressure vapor of uranium oxides and dioxyfluoride showed that incongruent condensation of uranium oxide as a function of temperature proceeds at more low temperature than condensation of intermidiate products of the conversion of UF_6. It means that the end product of the conversion of UF_6 in (H-OH)-plasma-UO_3 will condense incongruently at T~1600K when uranium oxyfluorides are in gas phase.

The results of the calculations and the experiments enable to evaluate a necessery length of plasma reactor for conversion of UF_6 in (H-OH)-plasma to U_3O_8 and HF. This results of the calculation provide a point of start of condensation of the end product U_3O_8 and the conditions of necessary separation of U_3O_8 and HF.

5. Experiment tests of conversion of UF_6 to U_3O_8 and HF in (H-OH)-plasma.

The experimental test reported had the next goals: to obtain U_3O_8 with minimal content of residual fluorine and to attain maximal concentration of the second product-HF. The general flow sheet of the pilot plant for conversion of depleted UF_6 is shown in Fig.3. The plasma reactor consists of the reactor itself 6 in combination with DC steam plasmatron 4 supplied with a magnetic coil 5. Power source is a high voltage rectifier 3. Depleted UF_6 was fed from the containers 1 with use of the compressor 2 for injection of UF_6 into (H-OH)-plasma. The technological line after the plasma reactor consists of vortex separator 8, metal cloth filter 9, cermet filter 10, screw conveyor for unloading uranium oxides 11, transport container for uranium oxides 12; condenser of HF 13; transport container for liquid hydrogen fluoride 14 supplied with heating 15. Depleted UF_6 is fed to the plasma reactor 6 and mixed with steam plasma generated by plasmatron 4. Products of conversion- U_3O_8 and HF are separated at the system of separation consisting of metal cloth 9 and metal-ceramic10 filters. The U -oxides are unloaded into a transport container 12. A portion of HF and water condensed in the con-

denser 13 as the azeotrope HF-HOH (further named as HF-acid) and collected in the container 14. The latter was heated and operates as a simplest rectification column. The most part of HF moves after the condenser as a gas phase intended for utilization of fluorine as a concentrated hydrofluoric acid.

Some technical characteristics of the equipment used:

4.1.Containers with depleted UF_6 having capacity of 2.5 m^3.

4.2. Compressor.

UF_6 pressure at the sucking tube of compressor P_{gage}=0.1 kgc/cm^2; in the compressor the pressure is raised to a gage pressure P=0.8-1.5 kgc/cm^2; then UF_6 is transported into the reactor through flow-metering membrane.

4.3. Dry steam generator.

The steam from the workshop communication liberated in the receiver of water droplets in transported into the plasmatron through flow metering disk and the over-heater heated by electrical current to 503-523 K. The W-cathode of the steam plasmatron is protected by N_2 (~5 % of the steam feed rate).

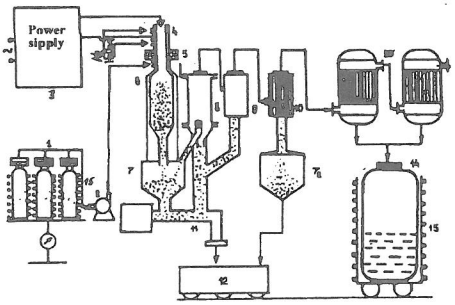

Fig. 3 Plasma apparatus for conversion of depleted UF_6 to U_3O_8 and concentrated HF:1-containers with UF_6; 2-compressor; 3-power source; 4-steam plasmatron; 5-magnetic coil; 6-plasma reactor; 7-receiver; 8-centrifugal separator; 9-metal cloth filter; 10-metal ceramic filter; 11-screw conveyor; 12-transport container for U_3O_8; 13-condenser; 14-transport container for HF; 15-heater.

4.4 Steam plasmatron ЭДП-145.

The plasmatron is equipped with water-cooled butt W-thermocatode, with the water-cooled Cu-anode and the interelectrode insert (IEI). Gas stabilization is steam vortex. For protection of W-cathode of steam there is the interelectrode insert where N_2 is pumped. Between the IEI and the anode there is the main swirl ring where steam is fed. The rear electrode (anode) is equipped with a solenoid creating magnetic field for rotation of radial portion of the electric arc. For start-up of the plasmatron we used high frequency oscillator. After intiation of the discharge the IEI is electrically neutral. Technical characteristics of the plasmatron: electrical power - 350 W; current - 600 A; voltage - 600 V; steam feed rate - up to 9 g/s; protective gas: to 12 g/s at start-up; to 0.3-0.4 g/s at operation.

4.5. Plasma reactor was equipped with ring feed of UF_6 into the mixing chamber having two cooling jackets. The internal jacket is cooled by compressed N_2 with steam condensate; the external jacket is cooled by water having temperature of 15-20 C. At the top of the plasma reactor there is a ring nozzle for radial introducing UF_6 into the reactor and the ring nozzle for introducing N_2 screen between plasma and UF_6.

4.6. Technical chracteristic of metal cloth filter:

The metal-cloth filter - 19 holders wrapped around with 2 layers of Ni-sieve. A size cell is of 100 μ. Each holder is equipped with an individual valve for blow-back of filtering layer by compressed N_2. The total filter surface area — 8.7 m^2.

4.7. The first collector-7 t for U_3O_8 having bulk density of 4-5 g/cm^3. The second collector-7 t.

The main parameters of the process are as follows: power of the plasmatron is of 300 kW; production rate of the apparatus is up to 150 kg UF_6 /h; initial temperature of the (H-OH)-plasma stream is of 3500-4100 K. Mole ratio HOH / UF_6 is within 3.1 - 4.4 (stoichiometric mole ratio is of 3.0); specific expenditures of energy ~ 1.4 - 1.5 kWh/kg UF_6 ;

The results of commission tests are summarized as follows: conversion degree of UF_6~100 %;

concentration of HF downstreams of the plasma reactor at initial mole ratio HOH/ UF_6 of 3.4 before entering into the condenser is of 88.5 %; concentration of HF downstreams of the plasma reactor at initial mole ratio HOH/ UF_6 of 3.4 after the condenser is of 95.4 %; output of fluorine to the goal products ~98 %; content of residual fluorine in the U-oxides 0.02-1.44 % mass.; degree of catching uranium oxides at the system of dust catching-0.9999. By-product of a plasma conversion of UF_6 is gaseous O_2 liberating in a quantity of 10.61nm^3 /ton UF_6. It is an unique case when a gas exhaust of technological apparatus is useful for environment.

6. Plasma-rectification technology for conversion of depleted uranium hexafluoride.

Fluorine liberated from UF_6 as HF is intended for electrolytic producing fluorine. But HF for supply of fluorine electrolyzers must be anhydrous. According to experimental data on plasma steam conversion of deple-ted UF_6, it is rather difficult to produce anhydrous HF directly because of difficulty to keep stoichiometric ratio HOH/UF_6 and simultaneously to have low content of residual fluorine in U_3O_8. Therefore, one should have some surplus of steam plasma so that to provide a mole ratio of HOH/ UF_6 of ~3.4. In this case one should use counter-flow distillation (rectification) to obtain anhydrous HF from the product produced at the stage of plasma steam conversion. The flow sheet of plasma-rectification technology of conversion of depleted UF_6 is shown in Fig. 4. As a result of rectification of concentrated hydrofluoric acid (80-95 %) one has two products: anhydrous HF directed to fluorine electrolyzer and the remainder-azeotrope 40 % HF-60 % H_2O. The azeotrope can be used for two applications. Firstly, it can be used as hydrofluoric acid for any commercial or domestic applications. Secondly, it can be returned to the plasma reactor for use a water from the azeotrope for conversion of UF_6. Therefore, the process aforesaid is practical wasteless.

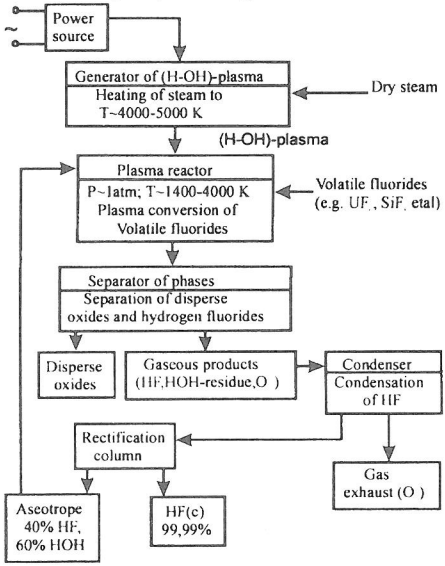

Fig.4. Rectification-plasma conversion of depleted UF_6 to U_3O_8 and anhydrous HF. U_3O_8

7. References.

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