

Research Article

Mathematical Model for Definition of Thermal Conditions in Desublimation Process of Volatile Metal Fluorides

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Abstract

Towards optimization of process parameters and creating of automatic control system for desublimation process a mathematical model for the process of desublimation of volatile metal fluorides in surface devices has been created (by the example of uranium hexafluoride). Optimal modes for the process of desublimation calculated with the developed model have been estimated in experimental tests and they showed reasonable convergence with the experimental data.

Keywords: Mathematical Model, De-sublimation Process

Introduction

From proper organization of desublimation process of thermal conditions of volatiles in surface desublimators often not only stability and efficiency of desublimation equipment depend, but also environmental safety of production. Thus, with production of uranium hexafluoride by fluorination process of uranium oxides, uranium hexafluoride during desublimation process is able to accumulate in certain areas of device's surface, where the most efficient conditions for this process are formed (Lazarchuk V.V et al,2006), which often leads to clogging of the device or the case when a non-condensed phase passing through the device, therefore maximum filling of industrial desublimators by based product (G_{max}) rarely exceeds 80% and for devices of complex geometry, such as annular desublimators, this value is only 30-50%.

As a solid layer is formed, free cross section of desublimation device is reduced, and accordingly, gas velocity increases, surface temperature of desublimation and conditions of heat transfer from the product to the surface of desublimation device change (Gromov B.V, 1978). This leads to changing of surface temperature of desublimation which may lead to breakthrough of gaseous uranium hexafluoride through device, so gases which contain uranium hexafluoride, oxygen and surplus of fluorine pass through two or more serially connected desublimators after the fluorination step. In each subsequent device along the gas flow, the surface of desublimation increases. So the vital task is definition of optimal desublimation conditions of uranium hexafluoride from gas mixture for the purpose of control the front of

desublimation in the device and increment of filling of desublimator by solid product due to its equal distribution in the device avoiding losses of the product associated with inefficiencies on the desublimation surface and prevention of sudden clogging of the device by solid uranium hexafluoride.

These problems can be solved assisted by the mathematical model for the process of desublimation, which has been developed by us, describing mass, thermal and hydrodynamic flows inside the device. This model allows to determine:

- mass flow of gas-vapor mixture and solid uranium hexafluoride in the device (material flows);
- coefficients of heat and mass transfer from gas-vapor mixture to solid surface;
- cooling time of gas-vapor mixture from initial temperature to the temperature of desublimation of uranium hexafluoride;
- velocity and mass of uranium hexafluoride producing from gas flow to solid phase per unit surface of desublimator;
- alteration of thermal and hydrodynamic flows within the device occurring due to increasing of thickness of product layer on the walls during desublimation process.

Calculation of annular-shape devices or flat plates is very complicated, so consider the mathematical model for determining of optimum thermal conditions for annular desublimation devices.

Material calculation for the process of desublimation of uranium hexafluoride

Material calculations were based on configuration of the flows in annular desublimator which enter and go out,

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taking into account desublimation process of uranium hexafluoride (figure 1). The data will continue to be used for calculating of cooling process of gas-vapor mixture containing uranium hexafluoride.

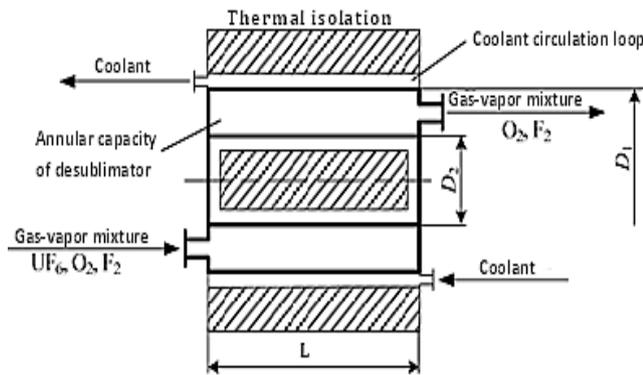


Fig 1. Scheme of the flows going out and entering in desublimator, where L – length of annular capacity of desublimator; D_1 and D_2 – external and internal diameters of the device

Gas-vapor mixture leaving the reactor for fluorination of uranium oxides has a complex composition. Together with the based product of the reaction (uranium hexafluoride), it contains surplus of F_2 and HF due to interaction of fluorine gas with moisture which unavoidable presents in gas phase (before entering the reactor for fluorination, process of cleaning of initial fluorine from HF is performed). Moreover, impurities presenting in uranium oxides and OF_2 and NOF vapors get into gas mixture. Due to low content of the least in gas mixture, concentrations of HF, OF_2 and NOF can be neglected.

At given weight output of desublimator with the based product and composition of reaction gases before desublimation it is necessary to determine sequentially:

1. Volumetric flow rate of uranium hexafluoride:

$$V_{UF_6} = \frac{M_{UF_6}^m}{\rho_{UF_6}} \quad (1)$$

where $M_{UF_6}^m$ – weight output, kg/hr; ρ_{UF_6} – vapor density at the temperature of input gas-vapor mixture, kg/m^3 ; V_{UF_6} – volumetric flow rate, m^3/hr .

- 2) Volumetric flow rate for each component of gas mixture:

$$V_i = \frac{V_{UF_6} M_i}{M_{UF_6}} \quad (2)$$

where V_i – volumetric flow rate of i-component in mixture, m^3/hr .

- 3) Mass flow of each component of gas mixture:

$$M_i^m = V_i \cdot \rho_i \quad (3)$$

where ρ_i – density of i-component in mixture at given temperature T and pressure P , kg/m^3 (Galkin P.P et al, 1961), determined as:

$$\rho_i = \frac{M_i}{22,4} \cdot \frac{273 \cdot P}{T_g^{in} \cdot P_0} \quad (4)$$

where M_i – molar mass of i-compound of gas, $kg/kmol$; P – partial pressure of components in the system, Pa; P_0 – common pressure of gas mixture, Pa; T_g^{in} – temperature of i-component of gas, K.

Mass flow ratio of components in gas mixture after desublimator is defined from the material balance equation:

$$\sum M_{in} = \sum M_{out} \quad (5)$$

where M_{in} and M_{out} – mass flow ratios of compounds before and after desublimation, kg/hr , which are defined as:

$$\sum M_{in} = M_{UF_6}^m + M_{F_2}^m + M_{O_2}^m \quad (6)$$

$$\sum M_{out} = (M_{F_2}^m) + (M_{O_2}^m) + M_{UF_6(s)} \quad (7)$$

Common mass flow rate after desublimation is:

$$\sum M_g^m = (M_{F_2}^m) + (M_{O_2}^m) = \sum M_{in} - M_{UF_6} \quad (8)$$

Taking into account complexity and ambiguity of the explanation of desublimation process of uranium hexafluoride and behavior of impurities accept the following assumptions:

- the process of desublimation of uranium hexafluoride goes one hundred per cent;
- impurities containing in uranium hexafluoride (F_2 and O_2), do not undergo chemical transformations and remain in gas phase.

Thermal and hydrodynamic calculations

In calculating of cooling and desublimation of uranium hexafluoride for the flows shown on figure 1 the following values are consistently determined:

- integrated physical and chemical characteristics of gas-vapor mixture at the inlet and at the outlet of desublimator;
- heat transfer for the axially symmetric purpose.

Density of gas-vapor mixture ρ_{mix} is defined from the equation:

$$\rho_{mix} = x_{UF_6} \rho_{UF_6} + x_{O_2} \rho_{O_2} + x_{F_2} \rho_{F_2} \quad (9)$$

where x_i – mass fractions of mixture components, which equal to:

$$x_{UF_6} = \frac{M_{UF_6}}{M_{mix}} \quad (10)$$

$$x_{O_2} = \frac{M_{O_2}}{M_{mix}} \quad (11)$$

$$x_{F_2} = \frac{M_{F_2}}{M_{mix}} \quad (12)$$

Dynamic viscosity coefficient μ_{mix} , mass specific heat at constant pressure $c_{p\ mix}$ and thermal conductivity coefficient λ_{mix} of gas-vapor mixture are defined by the analogical equations:

$$\mu_{mix} = x_{UF_6}\mu_{UF_6} + x_{O_2}\mu_{O_2} + x_{F_2}\mu_{F_2} \quad (13)$$

$$c_{p\ mix} = x_{UF_6}c_{pUF_6} + x_{O_2}c_{pO_2} + x_{F_2}c_{pF_2} \quad (14)$$

$$\lambda_{mix} = x_{UF_6}\lambda_{UF_6} + x_{O_2}\lambda_{O_2} + x_{F_2}\lambda_{F_2} \quad (15)$$

Annual flow velocity of gas-vapor through cross-section of the device W , m/sec is defined by the equation:

$$W = \frac{Q}{S} \quad (16)$$

where S – cross-section area of the device, m^2 .

Common thermal and hydrodynamic similarity criterions (Reynolds number Re , Prandtl number Pr , Peclet number Pe) are equal to (Perry D, 1969; Kasatkin A.G,1971):

$$Re = \frac{W\rho_{mix}d_e}{\mu_{mix}} \quad (17)$$

$$Pr = \frac{c_{p\ mix}\mu_{mix}}{\lambda_{mix}} \quad (18)$$

$$Pe = RePr \quad (19)$$

where d_e – equal diameter of annular cross-section of the device, m.

Calculation of physical and chemical properties of gas-vapor mixture at the outlet of the device is performed analogically by the equations 10-15.

The equation of heat transfer for axially symmetric laminar flow is defined as:

$$\frac{\partial T}{\partial \tau} + W \frac{\partial T}{\partial x} = a \left(\frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) \quad (20)$$

Consider approximately as:

$$W = \text{const},$$

$$\frac{\partial T}{\partial x} = \frac{T - T_0}{x} \quad (21)$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{T - T_0}{x^2} \quad (22)$$

and take into account the relation:

$$\left(W \frac{\partial T}{\partial x} \right) / \left(a \frac{\partial^2 T}{\partial x^2} \right) = \frac{Wx}{a} = \frac{Wd_e v x}{\nu a d_e} = RePr \frac{x}{d_e} = Pe \frac{x}{d_e} \gg 1 \quad (23)$$

where $W \frac{\partial T}{\partial x}$ – convection heat transfer; $a \frac{\partial^2 T}{\partial x^2}$ – diffusion heat transfer; $a = \frac{\lambda_{mix}}{c_{mix}\rho_{mix}}$ – temperature conductivity coefficient of gas mixture, m^2/sec .

The assessment shows that the ratio between convective heat transfer and heat transfer by conductivity $\gg 1$ throughout the calculated area. Therefore, heat transfer along the longitudinal axis (x) by thermal conductivity compared to transfer by convection is negligible.

As the result the approximate equation of boundary layer has been made. Taking into account the relationship between values of thermal conductivity and heat transfer, as well as geometric dimensions of flow area of gas-vapor mixture in annular desublimator, it can be assumed that gas stream is cooled to a constant temperature equal to the desublimation temperature of uranium hexafluoride and entire heat flow generated in the process of desublimation is discharged through the side surfaces (figure 2).

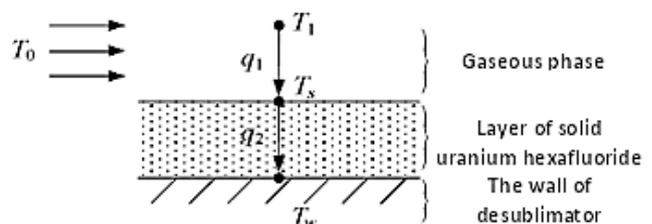


Fig. 2. Scheme of cooling and desublimation processes of uranium hexafluoride from gas-vapor mixture

The following nomenclatures have been taken: T_0 , T_1 , T_s , T_w – temperatures of gas mixture at the entrance to desublimation cooled zone; of the front of desublimation; of the desublimation surface and of the cold wall of desublimator; q_1 , q_2 - heat flows withdrawn from gas stream to the surface of desublimation and through layer of desublimation product to the wall of the device.

To estimate the length of initial transient flow area of gas-vapor mixture l_i the following formula is used (Frank-Kameneckiy D.A, 1978; Levich V.G, 1959; Grigorev V.A, 1982):

$$\frac{l_i}{d_e} = 0,055Re \quad (24)$$

Heat balance in the system is described by the equation:

$$dQ = dm\Delta H = adTdFdt \quad (25)$$

where ΔH – heat energy of desublimation of uranium hexafluoride, KJ/mole; dF – square of elementary unit (surface) of desublimation, m^2 which equals to:

$$dF = \frac{\pi}{4}(D_1^2 - D_2^2)dx \quad (26)$$

where D_1 , D_2 – diameters of inside and outside rings of the cylindrical device, figure 1, m; dx – length of elementary unit, m.

Weight losses of uranium hexafluoride are defined by the equation:

$$dm = dV\rho_s = dFd\delta\rho_s \tag{27}$$

where $d\delta$ – thickness alteration of uranium hexafluoride layer on the cooled surface of desublimator during time $d\tau$, m; dV – value of solid part of uranium hexafluoride, m^3 , which equals to:

$$dV = dFd\delta \tag{28}$$

Hence

$$\Delta Hd\delta\rho_s dF = \alpha dT dF d\tau \tag{29}$$

$$\frac{dm}{d\tau} = \frac{\alpha dT dF}{\Delta H} = \dot{m} \tag{30}$$

$$\frac{\dot{m}}{\rho_s} = \dot{V} = dF\beta = \frac{\alpha dT dF}{\Delta H \rho_s} \tag{31}$$

where \dot{m} – speed of mass discharge, kg/sec; \dot{V} – speed of uranium hexafluoride discharge, m^3 /sec.

Hence

$$\beta = \frac{d\delta}{d\tau} = \frac{\alpha dT}{dH\rho_s} \tag{32}$$

where β – coefficient of mass transfer from gas to the cool surface, m/sec (Perry D., 1969; Kasatkin A.G, 1971; Frank-Kameneckiy D.A, 1987).

From Newton's law of heat transfer it is possible to define the heat flow transmitted by gas to the surface of desublimation:

$$q_1 = \alpha(T_s - T_1) \tag{33}$$

and from Fourier's law of heat transfer it is possible to define the heat flow transmitted through solid layer of uranium hexafluoride to the wall of device:

$$q_2 = -\lambda_s \frac{T_s - T_w}{\beta} = -\frac{\lambda_s}{\beta} (T_s - T_w) \tag{34}$$

Based on the above consider that $q_1 = q_2$, hence:

$$\alpha(T_s - T_1) = -\frac{\lambda_s}{\beta} (T_s - T_w) \tag{35}$$

Extracting from the equation 35 temperature of desublimation surface we get:

$$T_s = \left(\alpha + \frac{\lambda_s}{\beta} \right) = \alpha T_1 + \frac{\lambda_s}{\beta} T_w \tag{36}$$

Hence

$$T_s = \frac{\alpha T_1 + \frac{\lambda_s}{\beta} T_w}{\alpha + \frac{\lambda_s}{\beta}} = \frac{T_w}{1 + \frac{\alpha\delta}{\lambda_s}} + \frac{\frac{\alpha\delta}{\lambda_s} T_1}{1 + \frac{\alpha\delta}{\lambda_s}} \tag{37}$$

So Nusselt number is equal to (Perry D, 1959):

$$Nu_s = \frac{\alpha\delta}{\lambda_s} \tag{38}$$

Placing the equation 38 to the equation 37 we get:

$$T_s = \frac{T_w}{1 + Nu_s} + \frac{Nu_s T_1}{1 + Nu_s} \tag{39}$$

Calculation of hydrodynamic mode in working volume of the device has been carried out on the basis of the system of complete stationary axially symmetric averaged Navier-Stokes differential equations of elliptic type (Frank-Kameneckiy D.A, 1987; Levich V.G,1959; Samarskiy A.A,1989), written in the parameters of vorticity Ω , current function Ψ (the equations 40 and 41) which are written in cylindrical coordinate system, where r – radial and z – axial coordinates:

$$u_r \frac{d\psi}{dr} + u_z \frac{d\psi}{dz} = \frac{1}{Re} \frac{1}{r} \left[\frac{\partial}{\partial r} \left(r v_t \frac{d\psi}{dr} \right) + \frac{\partial}{\partial z} \left(r v_t \frac{d\psi}{dz} \right) \right] + F_j \tag{40}$$

$$\frac{d^2\psi}{dr^2} + \frac{d^2\psi}{dz^2} = \Omega r^2 + \frac{1}{r} \frac{d\psi}{dr} \tag{41}$$

where

$$\Omega = \frac{1}{r} \left[\frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r} \right] \tag{42}$$

$$u_r = \frac{1}{r} \frac{d\psi}{dz} \tag{43}$$

$$u_z = \frac{1}{r} \frac{d\psi}{dr} \tag{44}$$

The left side of the equation 40 describes convective transfer of the substance (gaseous uranium hexafluoride) using velocity of the medium (gas-vapor mixture). The first term on the right side of the equation 9 describes diffusive transfer of the substance using viscosity of the medium v_t on coordinates r and z . The member of F_j describes addition source components established by alteration of flow rate of the medium in the cross-section as a result of mass decrease of uranium hexafluoride from gas-vapor mixture during desublimation. Poisson's equation 10 for definition of current function Ψ is obtained from the continuity equation (Frank-Kameneckiy D.A,1987; Levich V.G, 1959).

Using the above equations we have developed a program for calculation of cooling and desublimation of uranium hexafluoride gas mixture.

Numerical implementation of the mathematical model

Numerical implementation of the mathematical model is made in the following order:

1. It is necessary to take initial data: initial geometry of the calculated area (D_1, D_2, L); physical properties and parameters of each of the consumable components of initial gas mixture ($\rho, \mu, \lambda, c_p, dm$)_{UF₆, O₂, F₂}; crystal uranium hexafluoride ($\rho_s, \lambda_s, \Delta H$); boundary temperature and velocity conditions (Q_0, T_0, T_w), time of the technological process (τ_{con}).

2. Global calculation cycle ought to be organized for a period of time with a defined step δ and then relevant to this interval mass flow parameters ought to be calculated dm_{UF_6} (Samarskiy A.A, 1988);

3. Inside calculation cycle ought to be arranged with the condition that ($x \leq L$ and $dm_{UF_6} > 0$), where x – current coordinate of calculated area, varying in the range $0 \leq x \leq L$; L – length of the cooling part of desublimator. Within these cycle physical and chemical characteristics of gas mixture, similarity criteria for the process of flowing mixture Re , Pr , Nu , and heat transfer, coefficient α is calculated.

Consider that on initial part the cooling process of gas-vapor mixture goes in transient mode, calculation of desublimation mass of uranium hexafluoride is defined using the ratio:

$$K = \frac{T_0 - T_i}{T_0 - T^*} \quad (45)$$

where T_i – current temperature, K; T^* – temperature of desublimation, K.

Amendment K is taken into account up to the time until $T_i > T^*$, in the following we assume that $K = 1$ and temperature of gas mixture remains constant and equal to T^* , while $dm_{UF_6} > 0$.

Based on the obtained parameters, mass transfer coefficient β is calculated taking into account K . From the values of W and $d\tau$ the released material of uranium hexafluoride is placed over the side surface of the calculated area and by this amount dm_{UF_6} decreases, and x increases.

4. After closure of the outer loop, diagrams of functions are plotted $\beta = f(x)$.

As an example, on figures 3 and 4 the graphs of temperature changes in gas mixture are shown depending on transverse (y) and longitudinal (x) coordinates in the annular area of desublimator in the primary cooling region for the case of filling of desublimator with initial mixture with mass flow rate $M_{UF_6}^m$. The graphs show that length of

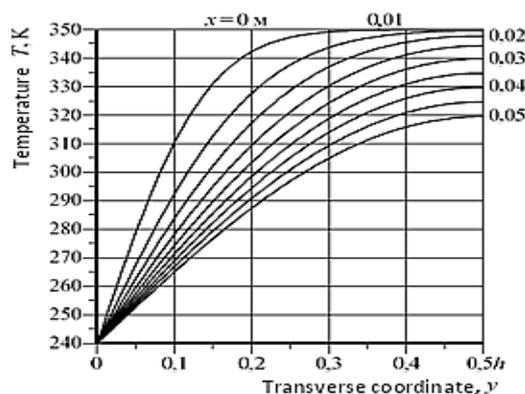


Fig.3. Dependence of gas-vapor mixture temperature from transverse coordinate at different values of x

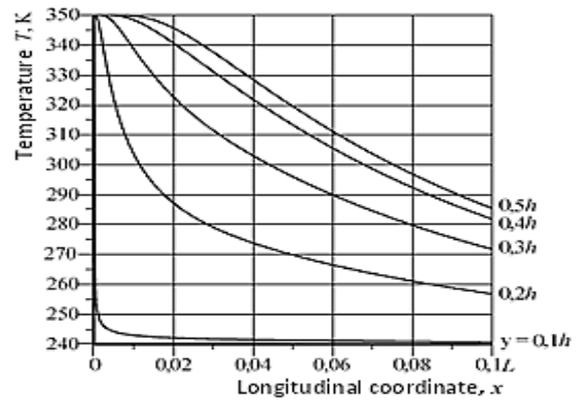


Fig.4. Dependence of gas-vapor mixture temperature from longitudinal coordinate at different values of y .

The inner loop of the program continues with calculation taking into account growth of uranium hexafluoride layer and temperature changes on the surface of this layer T_s (figure 2);

the non stationary cooling zone of gas mixture up to the temperature of uranium hexafluoride desublimation along the device's axis does not exceed $0,1L$.

Because of low gas velocity ($w = 0,06$ m/sec) and laminar flow of gas mixture in the annular desublimator section ($Re = 20$) there is no mixing of gases transverse direction (along axis y). Therefore, heat transfer in lateral direction of gas flow occurs only by conduction.

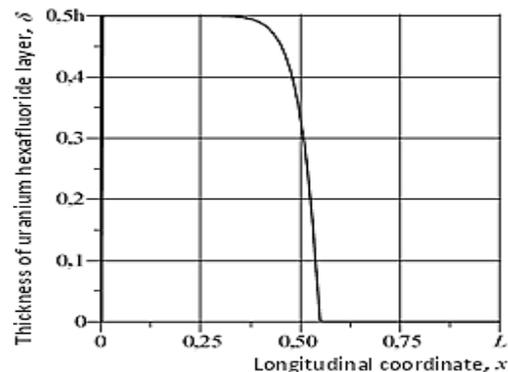


Fig 5. Dependence of thickness of desublimed uranium hexafluoride layer from longitudinal coordinate in the case of absence of transient cooling area of gas-vapor mixture at the wall temperature of 243 K

Length of device's zone, in which all uranium hexafluoride is desublimed at the wall temperature of 243 K and loading of desublimator by uranium hexafluoride up to $0,5G_{max}$ is $0,5L$ in the case of absence of transient cooling area of gas-vapor mixture (figure 5) and $0,8L$ - in the case of presence (figure 6), and total length of desublimation area is L . Thickness of uranium hexafluoride layer on the both annular walls of the cavity is $0,5h$, $0,4h$, respectively.

The graphs of desublimator zones in which all uranium hexafluoride is desublimed at the wall

temperatures of 243, 253, 263 and 273 K in the case of presence of non-stationary cooling area of gas mixture are shown on figure 6.

Figure 6 shows that length of the area in which all uranium hexafluoride is desublimed with loading of desublimator by uranium hexafluoride up to $0,5 G_{max}$ in the case of presence of transient cooling area at the wall temperatures of 253, 263 and 273 K is $0,83L$, $0,88L$ and $0,98L$ respectively considering total length of the device as L . At such temperatures of desublimation thickness of uranium hexafluoride layer on the both annular walls of the cavity is $0,77h$, $0,70h$ and $0,65h$ respectively considering thickness of annular space as h .

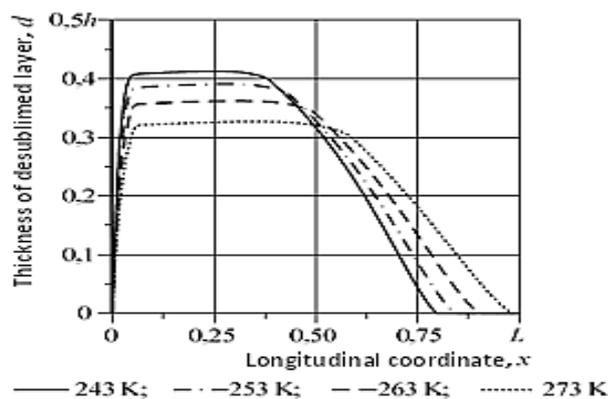


Fig.6. Dependence of thickness of desublimed uranium hexafluoride layer from longitudinal coordinate in the case of presence of transient cooling area of gas-vapor mixture at various wall temperatures

Conclusions

The mathematical model of cooling and desublimation

processes of uranium hexafluoride gas-vapor mixture which goes into desublimator from reactor of fluorination is developed which allows qualitatively and quantitatively

determine the influence of mass and heat transfer and hydrodynamic characteristics on the considered processes, thereby allows to optimize technological parameters of the process and develop a system of automatic control of desublimation process.

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