MATHEMATICAL MODEL OF DETERMINING HEAT CONDITION IN DESUBLIMATION PROCESS OF VOLATILE METAL FLUORIDES

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To optimize the technological parameters of the process and to create the automatic regulation system of desublimation process the mathematical model for desublimation process of volatile metal fluorides in surface devices (by the example of uranium hexafluoride) has been developed. Optimal conditions for desublimation process designed with the use of the model developed were tested and showed good agreement with the experimental data.

Introduction

Not only stability and efficiency of desublimation equipment operation but also manufacturing environmental safety often depend on proper organization of heat conditions in desublimation process of volatile substances in surface desublimators. So obtaining uranium hexafluoride (UHF) by uranium oxides fluorination, UHF at desublimation may be accumulated on certain areas of device surface where the most efficient conditions for the given process are formed [1]. It often results in device packing or breakthrough of residual phase into solid product due to its uniform distribution on the surface. Additionally, the increase of device packing may adversely affect its operation. Therefore determination of optimal conditions of desublimation process and of changes of heat- and hydrodynamic flows inside the device occurring due to increasing thickness of product layer on its walls is very important.

Computational model for determining optimal heat conditions of desublimation for annular devices. These tasks may be solved using the developed mathematical model for determining optimal conditions of desublimation from gas-vapor mixture to solid surface; velocity and mass of UHF segregated from gas flow into solid phase per unit surface; cooling time of gas-vapor mixture from initial temperature to the temperature of UHF desublimation; change of heat- and hydrodynamic flows inside the device occurring due to increasing thickness of product layer on its walls in desublimation process.

1. Material computation of UHF desublimation process

Material computation was carried out on the basis of the scheme of annular desublimator flows entering and escaping it subject to uranium hexafluoride desublimation (Fig. 1). The obtained data will be further used at thermal design of cooling process of gas-vapor mixture containing UHF.

Gas-vapor mixture escaping the reactor of uranium oxides fluoridation has a complex composition. Together with desired product of the reaction (UHF) there is an excess of F, and HF forming as a result of interaction of fluorine with moisture inevitably attending in gaseous phase (before entering into fluoridation reactor initial fluorine is purified from HF). Besides, mixtures attending in uranium oxides as well as vapors of OF, and NOF enter into gaseous mixture. Due to low content of the latter in gas-vapor mixture HF, OF, and NOF concentrations may be neglected.

At specified mass efficiency of desublimator by the main product and reaction gases composition before desublimation the following things are determined subsequently:

1) volume flow of UHF

\[ V_{UF} = \frac{M_{UF} \cdot V_{UF}}{\rho_{UF}} \]

where \( M_{UF} \) is the volume flow, kg/h; \( \rho_{UF} \) is the density of vapors at the temperature of entering gas-vapor mixture, kg/m³; \( V_{UF} \) is the volume flow, m³/h.

2) volume flow of each component in gas mixture

\[ V_i = \frac{V_{UF} \cdot M_i}{M_{UF}} \]
where $V_i$ is the volume flow of $i$ mixture component in composing, m³/h;

3) mass flow of each component in gas mixture

$$M_i^{mass} = V_i \cdot \rho_i,$$

where $\rho_i$ is the density of $i$ mixture component at specified temperature $T$ and pressure $P$, kg/m³ [3] determined as

$$\rho_i = \frac{M_i}{22.4 \cdot T_i^{0.9}} \cdot P_i,$$

where $M_i$ is the molar mass of $i$ gas component, kg/mole; $P_i$ is the total pressure of gas mixture, Pa; $T_i$ is the temperature of $i$ gas component, K.

Mass flows of the gas mixtures components after desublimator are determined from the equation of material balance

$$\sum M_{prev} = \sum M_{post},$$

where $\sum M_{prev}$ and $\sum M_{post}$ are the mass flows of substances before and after desublimation, kg/h, equal to

$$\sum M_{prev} = M_{F_1}^{mass} + M_{O_2}^{mass} + M_{O_3}^{mass};$$

$$\sum M_{post} = (M_{F_1}^{post}) + (M_{O_2}^{post}) + M_{UHF}^{post}. $$

Total mass flow of gas mixture after desublimator equals to

$$\sum M_{num} = (M_{F_1}^{num}) + (M_{O_2}^{num}) = \sum M_{prev} - M_{UHF}. $$

Taking into consideration the complicity and ambiguity of explanation of UHF desublimation process and admixtures behavior at it let us accept the following assumptions:

- UHF is desublimated for 100 %;
- Mixtures contained in UHF ($F_2$ and $O_2$) do not undergo chemical transformations and stay in gaseous phase.

2. Heat and hydrodynamic computations

Calculating UHF cooling and desublimation the following things are determined subsequently for the flows, showed in Fig. 1:

1) integral physical-chemical characteristics of gas-vapor mixture at input and output of desublimator;

2) heat transfer for axially symmetric problem.

Density of gas-vapor mixture $\rho_{st}$ may be found from the equation

$$\rho_{st} = x_{UHF} \rho_{UHF} + x_{O_2} \rho_{O_2} + x_{F_1} \rho_{F_1},$$

where $x_i$ is the mass fractions of mixture component, equal

$$x_{UHF} = \frac{M_{UHF}}{M_{st}}; \quad x_{O_2} = \frac{M_{O_2}}{M_{st}}; \quad x_{F_1} = \frac{M_{F_1}}{M_{st}}.$$ (1)

Coefficient of dynamic viscosity $\mu_{st}$, specific mass heat capacity at constant pressure $c_{p,st}$ and coefficient of heat conductivity $\lambda_{st}$ of gas-vapor mixture are calculated by the similar equations

$$\mu_{st} = x_{UHF} \mu_{UHF} + x_{O_2} \mu_{O_2} + x_{F_1} \mu_{F_1};$$ (2)

$$c_{p,st} = x_{UHF} c_{p,UHF} + x_{O_2} c_{p,O_2} + x_{F_1} c_{p,F_1};$$ (3)

$$\lambda_{st} = x_{UHF} \lambda_{UHF} + x_{O_2} \lambda_{O_2} + x_{F_1} \lambda_{F_1}. $$ (4)

Average rate of moving gas-vapor mixture along the section of the device $W$, m/s is determined by the formula

$$W = \frac{Q}{S},$$

where $S$ is the cross-sectional area in the device, m².

The main criteria of heat and hydrodynamic similarity (Reynolds Re, Prandtl Pr and Peklet Pe) equal [4, 5]:

$$Re = \frac{W \rho_{st} d_e}{\mu_{st}}; \quad Pr = \frac{c_{p,st} \rho_{st}}{\lambda_{st}}; \quad Pe = Re Pr.$$

where $d_e$ is the equivalent diameter of the device cross-section, m.

Physical-chemical properties of gas-vapor mixture at the device output are calculated similarly by the formulas (1)–(4).

Thermal-transport equation for the case of axial-symmetric laminar flow has the form [6, 7]:

$$\frac{\partial T}{\partial t} + W \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left( \frac{\mu_{st}}{\rho_{st}} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial r} \left( \frac{\mu_{st}}{r} \frac{\partial T}{\partial r} \right).$$

Let us write down approximately:

$$W = \text{const}, \quad \frac{\partial T}{\partial x} = \frac{T - T_0}{x}; \quad \frac{\partial^2 T}{\partial x^2} = \frac{T - T_0}{x^2},$$

and consider the ratio:
Mass loss of UHF at desublimation may be determined by the formula
\[ dm = \frac{dV}{\rho_m} \rho_m = dF \delta \rho_m, \]
where \( d\delta \) is the change of UHF layer thickness on desublimator cooling surface for the time \( d\tau \), m; \( dV \) is the volume of extracted UHF into solid phase, m³, equal
\[ dV = dF \delta. \]

Hence:
\[ \Delta H \delta \rho_m \frac{dF}{d\tau} = \alpha dT dF d\tau, \]
\[ \frac{dm}{dt} = \frac{\alpha dT dF}{\Delta H} = m, \]
\[ \frac{m}{\rho_m} = \dot{V} = dF \beta = \frac{\alpha dT dF}{\Delta H \rho_m}. \]

where \( m \) is the rate of mass release, kg/s; \( \dot{V} \) is the rate of UHF volume release, m³/s.

Then
\[ \beta = \frac{d\delta}{dt} = \frac{\alpha dT}{dH \rho_m}, \tag{5} \]
where \( \beta \) is the coefficient of mass transfer from gas to cool surface, m/s \([4–6]\).

Heat flow transferred by desublimation surface gas may be expressed from Newton law for heat transfer:
\[ q_1 = \alpha (T_s - T_w), \]
and heat flow transferred through the layer of solid UHF to the device wall may be stated by Fourier law for heat transfer:
\[ q_2 = \frac{\alpha \delta}{\lambda_m} (T_s - T_w). \tag{6} \]

On the basis of the above we accept \( q_1 = q_2 \), then
\[ \alpha (T_s - T_w) = \frac{\alpha \delta}{\lambda_m} (T_s - T_w). \tag{6} \]

Having stated the temperature of desublimation surface from the equation (6) we have:
\[ T_s = \left( \alpha + \frac{\lambda_m}{\rho_m} \right) = \alpha T_1 + \frac{\lambda_m}{\rho_m} T_1. \]

Then
\[ T_s = \frac{\alpha T_1 + \frac{\lambda_m}{\rho_m} T_1}{\alpha + \frac{\lambda_m}{\rho_m}} = \frac{T_1}{1 + \frac{\alpha \delta}{\lambda_m} + 1 + \frac{\alpha \delta}{\lambda_m}} \tag{7} \]

As Nusselt number equals \([4–6]\]
\[ Nu_m = \frac{\alpha \delta}{\lambda_m}, \tag{8} \]

then substituting equation (8) into expression (7) we may obtain:
Hydrodynamic regime in the effective volume of the device was calculated on the basis of the system of Navier-Stokes complete steady-state axial-symmetric averaged differential equations of elliptic type \[6, 7, 9\] written in variables of vorticity \(\Omega\), stream function \(\Psi\). Equations (9), (10) were written in cylindrical coordinate system, where \(r\) is the radial and \(z\) is the axial:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial z} \left( \frac{\partial \Psi}{\partial z} \right) = F_j, \tag{9}
\]

\[
\frac{\partial^2 \Psi}{\partial r^2} + \frac{\partial^2 \Psi}{\partial z^2} = \Omega r^2 + \frac{1}{r} \frac{\partial \Psi}{\partial r}, \tag{10}
\]

where \(\Omega = \frac{1}{r} \frac{\partial u_r}{\partial z} - \frac{1}{r} \frac{\partial u_r}{\partial r}\).

Left part of equation (9) describes convective transport of a substance (gaseous UHF) due to the medium speed (gas-vapor mixture). The first member of the right part of equation (9) describes diffusion substance transfer due to medium viscosity \(v\) by the coordinates \(r\) and \(z\). Member \(F_j\) describes additive source constituent stabilized by the change of volume medium flow by the section as a result of UHF mass loss from gas-vapor mixture in the process of desublimation. Poisson equation (10) for determining stream function \(\Psi\) is obtained from the equation of continuity \[6, 7\].

Using the above mentioned equations the program of calculating cooling process and uranium hexafluoride desublimation process from gas-vapor mixture is developed.

3. Numerical implementation of mathematical model

Numerical implementation of mathematical model is carried out in the following order:

1) specified with initial data: initial geometry of computed area (\(D_i, D_o, L\)); physical properties and consumable parameters of each component in initial gas-vapor mixture (\(\rho, \mu, \lambda, c, \Delta H\)) crystal UHF (\(\rho_{\mu}, \lambda_{\sigma}, \Delta H\)); rate and temperature boundary conditions (\(Q, T_i, T_o\)), technological process time (\(t_{\text{trans}}\));

2) global calculation cycle is organized by the time with a specified stage \(\delta\) and values of mass flow corresponding to this interval are searched out \(dm_{\text{uf}}\) \[10\];

3) inner calculation cycle is organized by the condition (\(x \leq L \) and \(dm_{\text{uf}} > 0\)), where \(x\) is the current coordinate by calculated area changing in the range of \(0 \leq x \leq L\); \(L\) is the length of desublimator cooled part \[10\].

Physical-chemical characteristics of gas mixture, similarity criteria for the flow process of mixture \(Re, Pr, Nu\) are computed and heat-transfer coefficient \(\alpha\) is determined inside this cycle.

Taking into account the fact that at the initial cooling area of gas-vapor mixture the process occurs in unstable conditions the calculation of desublimated UHF mass is found out subject to the ratio:

\[
K = \frac{T_0 - T}{T_0 - T'},
\]

where \(T_i\) is the current temperature, \(K\); \(T'\) is the temperature of desublimation, \(K\).

\(K\) deduction is taken into consideration to the moment while \(T' > T\) in the sequel it is supposed that \(K = 1\) and gas mixture temperature remains steady and equal to \(T\) while \(dm_{\text{uf}} < 0\).

On the basis of the obtained parameters the mass-transfer coefficient \(\beta\) is calculated subject to \(K\). According to the values \(\beta\) and \(\alpha\) the released UHF material is distributed on the lateral surface of calculated area and \(dm_{\text{uf}}\) is decreased by this value and \(x\) is increased.

Inner loop of the program continues computing subject to UHF layer growth and change of temperature on the surface of this layer \(T_i\) (Fig. 2).

4) after finishing outer loop the function graphs \(\delta = f(x)\) are plotted.

Temperature curves of gas-vapor mixture depending on transverse \((y)\) and longitudinal \((x)\) coordinates in an-nular desunlimator space in initial nonsteady cooling area for the case of feeding base mixture with mass rate of \(M_{\text{uf}}\) to desublimator are presented in Fig. 3, 4 as an example. It is seen from the curves that the length of nonsteady cooling zone of gas-vapor mixture to UHF desublimation temperature along the device axis does not exceed 0,1L.

![Dependence of gas-vapor mixture temperature on transverse coordinate at different values of x](image-url)

Due to low gas velocity (\(w = 0,06\ m/s\)) and laminar-flow conditions of gas-vapor mixture in desublimator ring section \(Re = 20\) gas mixing does not occur in transverse direction (along axis \(y\)). Therefore, in transverse direction heat transfer in gas flow occurs only due to heat conductivity.

The length of the device zone in which all UHF is desublimated at temperature of desublimator wall of 243 K and desublimator UHF load to 0,5\( \dot{G}_{\text{uf}}\) amounted.
to 0.5L without nonsteady cooling area of gas-vapor mixture (Fig. 5) and 0.8L with it (Fig. 6) and the total length of the device desublimation part is \( L \). In this case the thickness of UHF layer on both walls of annular cavity amounts to 0.5\( h \) and 0.4\( h \) accordingly.

The curves of desublimator zones in which all UHF is desublimated at temperature of the device wall of 243, 253, 263 and 273 K with the area of nonsteady cooling of gas-vapor mixture are presented in Fig. 6.

It is seen from Fig. 6 that the length of the device area in which all UHF is desublimated at desublimator UHF load to 0.5\( G_{\text{max}} \) with the area of nonsteady cooling at temperatures of desublimator walls of 253, 263 and 273 K amounts to 0.83\( L \), 0.88\( L \) and 0.98\( L \) correspondingly at total length of the device desublimation part \( L \). At such desublimation temperatures the thickness of UHF layer on both walls of annular cavity equals to 0.77\( h \), 0.70\( h \) and 0.65\( h \), 0.77\( h \), 0.70\( h \) and 0.65\( h \) correspondingly at the width of annular gap \( h \).

**Conclusion**

The mathematical model of UHF cooling and desublimation processes from gas-vapor mixture entering to desublimator from the fluoridation reactor which allows qualitatively and quantitatively defining the influence of mass- and heat exchange, hydrodynamic characteristics on the examined processes, thereby optimizing technological parameters of the process and creating the system of automatic controlling the desublimation process was developed.
REFERENCES


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ADSORPTION REFINEMENT OF WASTE TRANSFORMER OIL USING INDUSTRIAL MONTMORILLONITE-CONTAINING SORBENTS

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The possibilities of adsorption contact refining of waste transformer oil with active montmorillonite-containing sorbents of «Filtrol» series of BASF Catalysts LLC corporation and Zikeevsk M-80 deposit sorbent have been investigated. Usage of F-160 sorbents of «Filtrol» series in the refinement process allows achieving high quality degree of lean transformer oil, permitting its further use in the equipment with operating voltage to 750 kV.

Mineral oils step-by-step undergo deep changes in operating process as the result of accumulation oxidation products and degradation fragments of hydrocarbon base, products of resins firming, as well as products of wearing and corrosion of structural materials and fouling in them [1]. Oil purification and regeneration are the most perspective areas of resources recycling solving both economical and environmental problems.

For waste oils purification the same ways as for base oils purifications are used. They are distillation, acid-base purification, purification with solvent refining agents, contacting (adsorption refining), hydrotreating. Treatment of oils, containing dissolved aging products, with adsorbents, for example natural or activated discoloring clays, is technologically efficient and simple way of oil purification [2, 3].

Samples of waste mineral transformer oils, weakly-contaminated (OST-1) and strong-contaminated (OST-2) ones, unsuitable for further use by such quality indices as acid number, chromaticity, loss-angle tangent, breakdown voltage have been chosen as the objects of investigation.

On the basis of literary data analysis and products availability on domestic market the sorbents of domestic and imported manufacturing have been chosen for oils contacting investigation (Table 1).

Table 1. Base sorbents characteristic

<table>
<thead>
<tr>
<th>Name</th>
<th>Grade</th>
<th>Mineral composition</th>
<th>Manufacturer</th>
<th>Packed density, kg/m³</th>
<th>Specific surface, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanch soil of Zikeevsk deposit</td>
<td>M-80</td>
<td>Opal-cristobalite, montmorillonite, minor admixtures of silica and clinoptilite</td>
<td>«Sorbent» Russia</td>
<td>No data</td>
<td>80...200</td>
</tr>
<tr>
<td>Activated adsorbent of Filtrol series</td>
<td>F-1 F-160 F-1055 F-24 Mb LVMM</td>
<td>Main component montmorillonite</td>
<td>BASF Catalysts LLC corporation</td>
<td>500...800</td>
<td>250...400</td>
</tr>
</tbody>
</table>

Optional process variables of waste oils adsorption refining, recommended by sorbent manufacturer, are the following: after water removal by centrifuging 0,5...10 % of adsorbent is entered into oil at temperature 80...120 °C and the mixture is stirred during 30...60 min. Adsorbent is separated from oil by filtra-