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Determining the Optimal Process Conditions for Volatile Metal Fluoride Desublimation

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Abstract

A mathematical model is presented for the calculation of optimal temperature values for the desublimation of metal fluorides and the number of desublimation steps those allow achieving the level of target product extraction from the vapour and gas mixture to almost 100 %. Results of modelling desublimation of uranium hexafluoride are presented.

Key words: desublimation, supersaturation, critical supersaturation, aerosol, mathematical model, modelling

INTRODUCTION

In the technology for obtaining a number of pure substances and intermediates including the technology of nuclear fuel, of particular importance is a sublimation-desublimation redistribution representing a refining operation.

All the existing desublimators could be divided into three groups: surface, volume, and mixed ones, according to the method of separating the solid phase (desublimate) from the gas flow containing a sublimed product [1]. However, all of these devices have a significant disadvantage consisting in a low yield of a main product into the desublimate (80–90 %), which is caused by the formation of aerosols at a high supercooling level of the source vapour. In particular, industrial processes of VF_5, ZrF_4, TiF_4, WF_6, UF_6, ReF_6 desublimation and other volatile metal fluorides are usually carried out at the temperature values well below the conditionally true temperature of desublimation. (The conditionally true temperature of desublimation means the temperature when the current pressure of vapour under desublimation is equal to the vapour pressure of the desublimate). Under such conditions, there are prerequisites appearing for the formation of nuclei in the nucleation volume unit and for the product loss in the form of aerosols.

The studies we earlier carried out concerning the effect of the unit surface temperature on the process of titanium tetrafluoride desublimation demonstrated [2] that when the desublimation temperature drops 250 °C lower than the true value, a fluffy, crystalline desublimate of needle type is formed. When the desublimation temperature is 150 °C lower than the true value, a layer of granular solid products is formed, covered by an elastic film, whereas at 100 °C a solid glassy product is formed throughout entire layer. And the loss of the product at the outlet of the desublimator is equal to 27, 12 and 5 mass %, respectively.

The most efficient desublimation method is such a method considered whereat under changing thermal conditions it is possible to suppress the process of aerosol formation and to monitor the growth of a layer of desublimate to maximize filling the apparatus and its permeability.

AEROSOL FORMATION UNDER VAPOUR SUPERSATURATION

One of the stage in the desublimation process consists in delivering the molecules of the initial product (sublimate) from the bulk of the gas-vapour mixture to the cold surface of the desublimator. This process can take place at a high rate only under the following conditions [1]:

$$S = P/P_{\infty(T)} \le S_{\mathrm{cr}} \quad (1)$$

where S is the level of supersaturation of the vapour source; S_{cr} is the critical level of supersaturation above which beginning the process of solid phase nucleation takes place within the volume of the unit; P and $P_{\infty(T)}$ are the current pressure of initial vapour and the vapour pressure over a flat desublimate surface at a given temperature, respectively.

Depending on how the process is organized, there are two possible versions of its occurrence. When the condition $S > S_{\mathrm{cr}}$ is achieved only on the surface of desublimator, the product undergoes reducing the partial pressure down to $P_{\infty(T)}$ to be precipitated onto the surface. In this case, with increasing the temperature of the surface, the rate of the desublimation would increase. However, it was experimentally established [2] that when S is higher than S_{cr} in the bulk of the gas, the yield of desublimate is abruptly reduced due to its homogeneous (bulk) desublimation and the carryover of arising aerosols from the apparatus (Fig. 1).

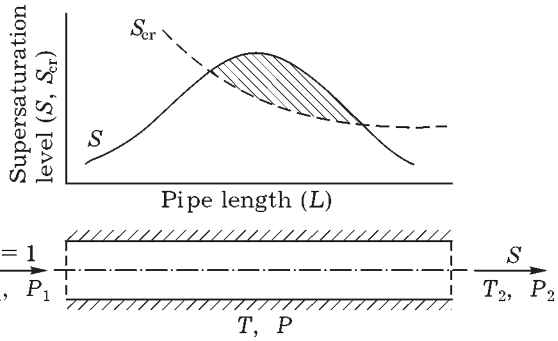

Fig. 1. Changing the supersaturation level of the vapour flow moving through the pipe.

Usually, the critical supersaturation (S_{cr}) is understood as the supersaturation level whereby the rate of nuclei formation capable of further

TABLE 1

Initial data for the mathematical modelling

Parameters	Unit	Value for the calculation example
Gas temperature at the desublimator input	°C	80
Target product vapour pressure at the desublimator input (relative content)	mmHg	230
Universal gas constant	J/(mol · K)	8.314
	cm^3 · mmHg/(mol · K)	$6.24 \cdot 10^4$
Boltzmann constant	erg/K	$1.38 \cdot 10^{-16}$
	J/K	$1.38 \cdot 10^{-23}$
Molecular mass of desublimate	g/mol	350
Desublimate density	g/cm^3	5.06
Molar volume of the substance	cm^3/mol	69.17
Molecular mass of the substance	g	$5.814 \cdot 10^{-22}$
Number of missed neighbours in the surface monolayer of the crystal lattice	–	1
Coordination number of uranium atom	–	6
Thickness of the monolayer of the substance molecules (was determined *via* the calculation of the bond length in l, which is equal to $4/3 \cdot l$ for UF_6)	nm	$0.1996 \cdot 4/3$
Change in the enthalpy of evaporation	J/mol	48 148.2
Desublimation coefficient (the fraction of vapour molecules remaining of on the solid surface of the desublimator due to collisions)	–	0.8

growth, equal to unity, *i. e.*, $I = 1\ \text{cm}^{-3} \cdot \text{s}^{-1}$. Such an assumption, of course, is relative since the nucleation occurs at $I < 1$, but the rate of this process is low. Taking into account this assumption, the value of critical supersaturation can be calculated by means of the equation [1, 3]

$$\log\ S_{\text{cr}} = \sqrt{\frac{1.44}{\lg K}} M / \rho\left(\sigma / T\right)^{3/2} \qquad (2)$$

where M is the molecular mass of the substance under desublimation, g/mol; σ is the surface tension, J/cm^2; ρ is the desublimate density, kg/m^3; T is the temperature in the system, K; K is the kinetic coefficient. The latter is determined from the following model:

$$K = \gamma/\rho(2m\sigma/\pi)(P/\kappa T)^2 \qquad (3)$$

where γ is the desublimation coefficient expressing the fraction of vapour remaining due to the collisions on the solid surface of the desublimator; m is the molecular mass of the vapour of the substance under desublimation, g; κ is Boltzmann constant, equal to $1.38 \cdot 10^{-23}$ J/K. Depending on the nature of the substance under desublimation, on the level of contamination by impurities, on the presence of inert gas molecules on and a number of other factors, the value of γ can vary from 0 to 1.0.

The surface tension (σ) is determined by the equation

$$\sigma = (\Delta H - RT)/V^0(\Delta n/n)h \qquad (4)$$

where ΔH is the enthalpy change under evaporation, kJ/mol; R is the universal gas constant, equal to 8.314 J/(mol · K); n is the coordination number; Δn is the number of missing neighbours in the surface layer; h is the monolayer thickness (for fluorides h = 0.2–0.3 nm), m; V_0 is the molar volume of the solid equal to M/ρ, cm^3/mol.

The supersaturation level occurring in the system at any moment of time corresponds to a certain critical particle size. The critical radius of a spherical nucleus (r_{cr}) can be determined from the Thomson equation [3, 4]:

$$r_{\text{cr}} = 2\sigma M/(\rho RT \ln S) \qquad (5)$$

When reaching a certain critical size of the nucleus (10^{-4}–10^{-3} μm), it is stabilized to becomes a centre of crystal formation [3, 4].

The mass concentration of the fog (G, in g/cm^3) formed in this case can be calculated by means of the equation [3]

$$G = MP/RT_{\infty(T)}(S - 1) \qquad (6)$$

The desublimation of the product may occur on the surface of the desublimator or in the bulk of the gas mixture, which is determined by a ratio between the rates of mass and heat exchange for the desublimating product those could be evaluated using the Lewis criterion [4, 5]:

$$\text{Le} = \alpha/(C_p\rho\beta) \qquad (7)$$

where α is heat transfer coefficient, $\text{W/(m}^2 \cdot \text{K)}$; C_p is the specific heat the gas at constant pressure, J/(kg · K); β is the mass transfer coefficient, m/s.

When Le > 1 under these conditions, the heat transfer rate is higher than that for mass transfer. As a result, the desublimating product does not have time to be delivered to the surface of desublimator in the form of vapour; in this case, the bulk desublimation process should prevail.

TABLE 2

Calculation of the optimum desublimation temperature for uranium hexafluoride at $S = S_{\text{cr}}$

Temperature of “cold” surface, K (°C)	Supersaturation level	Aerosol mass concentration, g/cm^3	Residual pressure of UF_6, mmHg (Pa)	Trapping efficiency, %
		First stage of desublimation		
288 (15)	4.1	$3.4 \cdot 10^{-3}$	55.3 ($7.37 \cdot 10^3$)	76.05
		Second stage of desublimation		
267 (−6)	5.3	$9.4 \cdot 10^{-4}$	10.4 ($1.38 \cdot 10^3$)	19.51
		Third stage of desublimation		
246 (−27)	7.3	$2.0 \cdot 10^{-4}$	1.4 ($1.86 \cdot 10^2$)	3.90
		Fourth stage of desublimation		
224 (−49)	12.3	$3.2 \cdot 10^{-5}$	0.1 (13.3)	0.50

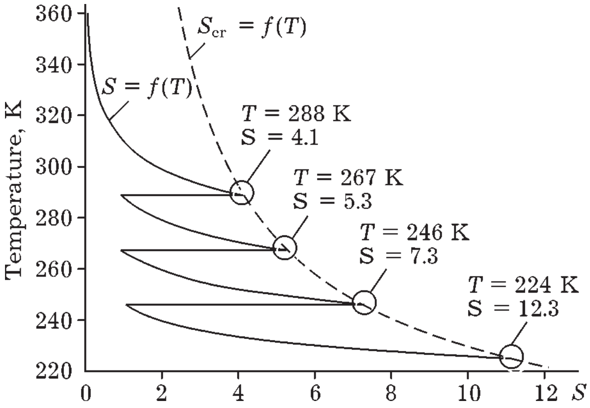

Fig. 2. Level of supersaturation (S) and the critical level of supersaturation (S_{cr}) depending on the desublimator wall temperature.

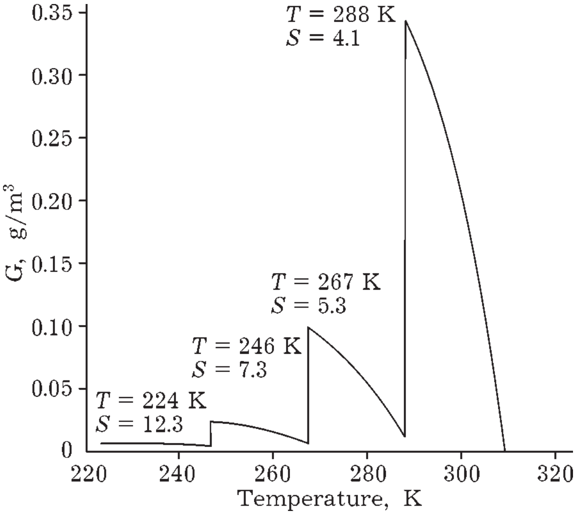

Fig. 3. Mass concentration of aerosols in the unit volume of the desublimator (G) depending on the wall temperature.

MODELLING THE PROCESS OF DESUBLIMATION

Thus, with the help of the mathematical model described by equations (1)–(7) in the presence of background information concerning the parameters required one can determine the number of desublimation stages, the optimum temperature of the desublimating surface at each stage that prevents the formation of aerosols at the maximum rate of the desublimation process. As an example, let us consider the results of the mathematical modelling of uranium hexafluoride (UHF) desublimation originating from the processing gas of triuranium octoxide fluorination. The initial data for the calculation of the number of stages and their temperature values for complete UHF desublimation are demonstrated in Table 1 [8], the results of the calculation are presented in Table 2 and Figs. 2, 3.

The total trapping efficiency of UHF after the four stages of desublimation could amount up to more than 99.96 %.

It should be noted that the number of desublimation stages required in order to reach a necessary residual value of the partial pressure of the component under isolation can be achieved using a single unit, however this requires performing the calculation of the mass, thermal, hydrodynamic parameters of the environment at every point.

We are going to present an example of such a calculation in next publications.

CONCLUSION

The mathematical model developed for calculating the effective desublimation temperature of substances allows revealing the parameters whereby a maximum rate of the surface desublimation and minimum in the bulk formation of aerosols is observed. So, for the most complete trapping of UHF from the processing gas in the case of triuranium octoxide fluorination it is required for organizing four stages of desublimation at 15, −6, −27 and −49 °C. In this case, the overall efficiency of UHF trapping at the output of the last stage would be at least 99.96 %.

The method for calculating the temperature values of UHF desublimation process proposed and tested in this paper could be used for similar calculations of desublimation processes (condensation) for any other substances, in order to provide the maximum efficiency of the process.

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