DETERMINATION OF OPTIMAL CONDITIONS THE PHASE TRANSITION FOR INDUSTRIAL UNIT FOR PRODUCTION OF TUNGSTEN HEXAFLUORIDE

S.V. Chernigovskiy

Scientific Supervisor: PhD Smolkin P.A.

Linguistic Advisor: Teacher Shaykina O.I.

Tomsk Polytechnic University, Russia, Tomsk, Lenin Avenue, 30, 634050

E-mail:chernigovskiy.s@mail.ru

ABSTRACT

A mathematical model has been developed to calculate the optimal temperature of desublimation metal fluorides and the number of stages desublimation that allows bring the recovery of the desired product from the gas mixture to almost 100%. Experienced test results have been obtained with desublimation of tungsten hexafluoride and tungsten that showed a good convergence with theoretical data. The proposed method of calculating the parameters of the process desublimation can be applied to similar calculations desublimation processes (condensation) of other substances, for maximum efficiency.

Key words: phase transitions, condensation and desublimation, volatiles metal fluorides

Introduction

In the technology of getting a number of pure substances and intermediates, including technology and nuclear fuel, sublimation-desublimation redistribution is of particular importance being a refiner operation. All the existing methods for allocating desublimers solids from the gas stream can be divided into three groups: surface, volume and mixed. [1] However, these devices have a significant disadvantage that is a low yield in desublimat main product (70 ... 90%), the cause of which is the formation of aerosols at strong supercooling steam desublimaiting substances and their entrainment from the system.

In industrial processes of condensation and desublimation VF_5, ZrF_4, TiF_4, WF_6, UF_6, ReF_6, and other volatile metal fluorides are usually conducted at temperatures which are considerably below the initial temperatures of desublimation that causes formation of nuclei in the bulk nucleation device and as a consequence, the loss of a product in the form as aerosols. For example, at titanium tetrafluoridedesublimation , the reduction of sublimation temperature below the initial of 250 ° gives fluffy, crystal desublimat of a needle type; 150 ° -the layer of a bulk material partially covered with elastic film; 100 ° - solid glassy product throughout the layer. Thus, the loss of the product at the outlet of desublimator comprised 27, 12 and 5% wt. respectively. Therefore the greatest desublimation effective way would be the one in which the process of aerosols appearance has been able to suppress in a changing thermal conditions and monitor the growth of the layer desublimat, while maximizing the filling of apparatus and its permeability.

The purpose of this work is to determine the conditions of supersaturation and the critical supersaturation of tungsten hexafluoride, as well as the influence of these parameters on the process of condensation (desublimation).

Development, methodology.

The process of hexafluoride desublimation metals significantly affect the temperature of cold surfaces apparatus, partial pressures of the components of the process gas, the physical chemical properties of the components of the gaseous mixture, as well as a number of other factors.

In this paper we proposed and tested a method for calculating the temperature of the condensation process (desublimation) of tungsten hexafluoride, ensuring maximum yield in the condensed phase and minimal losses in the form of aerosols.

1) Calculation of temperature desublimation.

The degree of supersaturation of the vapor-gas mixture essentially depends on the difference between the temperatures of the gas-vapor mixture entering the apparatus and a surface desublimator. If we denote the temperature of the gas mixture entering the desublimator through T_1 , “cold” surface - T_2, the distance that takes gas mixture, cooing at the temperature from T_1 toT_2, is l, then, assuming that as the distance x from the entry point of gas into the machine to the exit point of the gas mixture has a temperature T to decrease linearly from T_1 to T_2. It is obtained:

$$T = T_2 + \frac{T_1 - T_2}{l} \cdot x. \qquad (2.24)$$

Then the pressure P changes in a similar manner

$$P = P_2 + \frac{P_1 - P_2}{l} \cdot x. \qquad (2.25)$$

Degree of supersaturation S can be calculated as follows:

$$S = \frac{P_T}{P_{\infty(T)}}, \qquad (2.26)$$

Where, P_T , $P_{\infty(T)}$ is a vapor pressure drop over and above the flat surface of a desublimaiting substance.

Substituting the values of pressure and temperature in the expression (2.26), we can define the degree of supersaturation at a given temperature

$$S = \frac{T - T_2}{T_1 - T_2} \cdot \frac{P_1 - P_2}{P_{\infty(T)}} + \frac{P_2}{P_{\infty(T)}}. \qquad (2.28)$$

A significant role in the processes of tungsten hexafluoride desublimation plays the heat exchange between the gas and the cooled surface. Coolant Temperature usually remains constant with increasing desublimat layer having a high thermal resistance (low thermal conductivity), the surface temperature desublimation increases and the desublimation degree decreases monotonically. Therefore desublimation of hexafluorid tungsten is carried out on a moving surface in unsteady conditions. For the stabilization process, the heat removal from the gas mixture and, in fact, different methods use varios methods of cleaning the surface from desublimat (scrapers, thermal sludge of discharge, etc.).

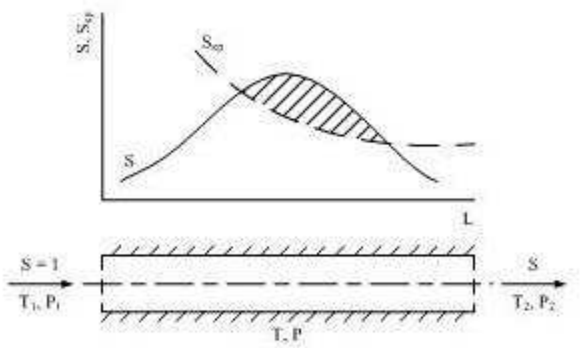

Figure 2.1 - Change of supersaturation of the vapor stream when moving through the pipe.

Speed ratio of mass transfer and heat transfer are such that the supersaturation increases initially, reaches a maximum and then decreases. In the region where it exceeds the critical value (hatched portion), the volumetric desublimation flows. If mass transfer predominates over the heat exchange, the tungsten hexafluoride diffuses the deposit before the gas mixture cools. Then supersaturation does not reach a critical value and the volumic product desublimation from gas mixture does not occur. If the stage of heat exchange is dominated, then the desublimat does not have an opportunity to diffuse to the surface of desublimation and the dominant process is the volume desublimation. For heavy molecules of tungsten hexafluoride, second model desublimation probability are much higher.

2) The rate of nucleation.

The work spent on the nucleus (equal change in the free energy), is formed by the work of transfer of particles from the gaseous phase in a liquid or solid (in the case of a supersaturated vapor, this work will be negative), and work related to the formation of the nucleus. For the complex located in unstable equilibrium with the available supersaturated vapor, the total work of formation is associated with Gibbs energy:

$$\Delta G = \frac{1}{3}\sigma F, \quad (2.36)$$

where F is surface of forming phase m^2.

for spherical drops $F = 4\pi r^2$, (2.37)

therefore, substituting the value of F in (2.36), we obtain:

$$\Delta G = 4/3\pi r^2 \sigma. (2.38)$$

$$\Delta G = \frac{16\pi m^2 \sigma^3}{3\rho^2 \kappa^2 T^2 (\ln S)^2}. (2.39)$$

2) Criterion determining the nature of the process desublimation.

The question of where desublimation product takes place on the surface or in the bulk desublimator of vapor-gas mixture is determined by the ratio of speeds heat and mass transfer desublimaiting product that can be evaluated using the criterion of Lewis Le

$$\mathrm{Le} = \frac{\alpha_{ñì}}{\mathrm{c}_{\mathrm{p}_{ñì}}\,\rho_{ñì}\,\beta}$$

where

α_{cm} - heat transfer coefficient, kJ / ($m^2 \cdot h \cdot k$);

c_{pcm}- specific heat of the gas-vapor mixture, kJ / (kg · K);

ρ_{cm} cm - gas mixture density,$^{kg}/_{m^3}$;

β- mass transfer coefficient, $^{m}/_{h}$

If Le is under these conditions is greater than one, then the heat transfer rate is higher than the intensity of a mass transfer. As a result, the desublimaiting product does not have time to be delivered to the surface in the form of steam, so the predominant is process of a volume desublimation. In view of the difficulty of determining the coefficients of mass and heat transfer for the various conditions of the organization of the process , criteria values Lewis hardly is not almost applicable to assess the effectiveness of the process.

The presented analysis of tungsten hexafluoride desublimation process allows us to identify those groups of parameters that determine, ultimately, its effectiveness, and to understand the mechanism of the process. However, these relationships as well as in most of the heat and mass transfer processes are not always applicable for practical design calculations of the desublimator and its parameters because of the difficulty of determining the coefficients of heat and mass transfer in terms of constant characteristics of the fluctuations of heat transfer surface, and the flow of the initial gas mixture. Therefore, to determine the optimum processing characteristics and parameters of desublimator their experimental verification is required, both at the stage of individual elements of machines and structures as a whole, drawing on mathematical modeling.

Modeling of the condensation process (desublimation) of tungsten hexafluoride

As above, to eliminate the bulk desublimation it is necessary that the magnitude of the degree of supersaturation is close to the critical value, but does not exceed its entire range of temperature from a temperature of the sublimation of the substance (gas flow entrance temperature to desublimator) to a temperature coefficient at any desublimation.

The temperature of the cold wall, that is desublimaiting surface temperature, is in the condition that it must be the lowest temperature at which the volume desublimation is excluded but ensured the maximum temperature difference between the temperature of the incoming gas in desublimaiting camera (or a hot surface desublimator) and a cold surface, causing the maximum rate of sublimation processing.

To determine these conditions, a computer program has been developed. The results of calculations for the desublimation process of tungsten hexafluoride are shown in Table 2.5

Table 2.5 - Calculation of temperature the desublimation tungsten hexafluoride provided S = Skr

hot walltemperature , K	cold wall temperature, K (° C)	supersaturation degree	aerosols mass concentration, g/cm3	capture degree, %	residual pressure WF_6, mm Hg.
The first stage of desublimation					

333	264 (– 9)	3,5	0,0098	71,4	217
The second stage of desublimation					
333	241 (– 32)	5,3	0,0035	81,1	41

The total capture degree of tungsten hexafluoride after two stages of condensation is equal to 94.6%.

Results

Desublimated purification of tungsten hexafluoride from impurities is the least researched stage of the production technology of fluoride. Therefore, the results should be considered as one of the stages of development of this technology. Studies show the effectiveness of the use of desublimation processes for extraction of tungsten hexafluoride from the process gas generated after its synthesis by the gas fluoride technology.

Analytical calculations establish that at the hot wall temperature of the vessel (inlet temperature of gas in the desublimation area) 333 K (333 K) the calculated value of the surface temperature of sublimation (hot surface) of tungsten hexafluoride is 333 ... 293 K.

The cold surface temperature at tungsten hexafluoride desublimation should be maintained within 253 ... 245 K, because at such a high temperature desublimation residual pressure of tungsten hexafluoride is large 217 mm Hg. and it may lead to the loss of the product due to aerosol formation and their entrainment from the system. Therefore, the second step of desublimation is required.

To prevent the formation of aerosols the minimum temperature of tungsten hexafluoride desublimation at the second stage should be 241 K. The residual vapor pressure of tungsten hexafluoride at this temperature is small (41 mm Hg. Tbsp.), so the loss of the product would be negligible - 0.0035 g/cm3, which allows get the product outlet in the desublimat at I and II stages of the desublimation 0.95.

Conclusion

In this paper the role of the desublimation processes in the industry is considered in general and radiation area in particular. The critical parameters of tungsten hexafluoride have been calculated, such as temperature, a specific volume, a density and a compressibility factor.

A mathematical model has been developed to determine the conditions of critical supersaturation of metal fluorides and conditions excluding the formation of aerosols at the desublimation. The program for determining these conditions has been created.

References

1. AG Gorelik, A.V. Amitin (1986) Desublimation in the chemical industry . - Moscow: Khimiya , 272 .

2. Pishchulin V.P, V.P Trochkine (2000) Processing of weapons-grade uranium into fuel for nuclear power plants Energy: Textbook. - Seversk TPU Publisher, 36.

3. Technical Dictionaries (1998). Editorial Board: A. ISHLINSKII (Editor), etc. - 3rd ed. rev. and add.
M.: «Great Russian Encyclopedia», 656 p.

4. Klogina L.I., Chekhov A. Bulatov S.N. etc (1975). Mass crystallization. - Moscow: IREA, (1975), № 1, 119 p.

5. Buynovskiy A.S., Sofronov V.L., Rusakov I.Y. (1987) Calculation - sublimation desublimatsionnyh devices. - Tomsk: TPI, 121.

6. Buynovskiy A.S., Velikoselsky N.D., P.A. Smolkin (1999) Computer calculations of the nucleation rate, growth and deposition of particles: A Practical Guide for Students. - Seversk STI TPU, 29 p.

7. Hausen H. (1981) Heat transfer in countercurrent, cocurrent and cross- currents: Per. from English. Énergoizdat, 383 p.

8. Volinets A.Z., Skachko A.M., A.V. Chernyak (1984) and other continuous process of sublimation purification dispersion of substances / / Theoretical Foundations of Chemical Engineering, V. 15, № 5. S.615.

9. K.P. Shumsky (1974) Vacuum apparatus and instruments chemical engineering. - M.: Mechanical Engineering, 576.

10. Pat. (1960) 93773 Czechoslovakia MKI3 In 01 D 7/00. Sublimation apparatus for cleaning substances: Publ