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## OPTIMIZATION OF FLUORINE OBTAINING PROCESSING

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*Integrated efficiency functional of fluorine obtaining processing for determining optimal temperature and concentrate magnitudes by the method of multiparameter optimization has been developed. Analytic dependences of HF vapor pressure over the melt KF-HF, activation energy of specific conductivity and viscosity in operating range of controlled variable were obtained.*

The reasons of low capacity of fluorine electrolytic cells and optimization of fluorine obtaining process have been studied from the moment of their functioning [1–4]. The attempt of process optimization from various particular stands: resource conservation, product quality, device construction, time increase of distance run between overhauls of the device, technology, fluorine energy output etc., increase efficiency of device operation but does not solve the general problem of process optimization.

In this connection there is a necessity to form a generalized criterion of process operating mode optimality expressing efficiency through the main controlled technological variables.

It is known that increasing hydrogen fluoride content in electrolyte from 36 to 42 wt. %, in the range of temperature change of electrolyte 90...120 °C fluoride current output may increase from 86 to 99 %, and HF content in the product from 6 to 18 rev. %. Ranges of optimal electrolyte composition were obtained experimentally by Cady in 1934 [1].

Solving the problem of optimization, the aim of optimization and the degree of optimized object freedom – quantity of controlled variables which allow changing its state according to the demands of optimality criteria should be revealed first of all.

The main input and output variables characterizing electrolysis process in the device, Fig. 1:  $G_{HF}$  is the consumption of hydrogen fluoride (control action), m<sup>3</sup>/h;  $I$  is the electric current flowing through electrolyte is specified depending on the required capacity, kA;  $G_B$  is the consumption of cooling water (control action), m<sup>3</sup>/h;  $T_{BX}$ ,  $T_{BbIX}$  are the cooling water temperature at the input and output of cooling pipe heater, respectively, °C;  $C_{HF}$  is the HF concentration in electrolyte (controlled variable), wt. %;  $\alpha$  is the ionic forms concentration in electrolyte melt (or dissociation degree of molecules into ions), g-ion/l;  $\mu$  is the electrolyte viscosity, mPa·c;  $G_{HF^*}$  is the HF consumption in anode and cathode gas, m<sup>3</sup>/h;  $\sigma$  is the specific electrolyte conductivity, Cm/m;  $T_3$  is the electrolyte temperature (controlled variable), °C;  $L$  is the level of electrolyte, mm;  $U$  is the general voltage drop at electrolytic cell, V;  $B$  is the fluoride energy output, %.

In tolerance range of controlled variables that is hydrogen fluoride content in electrolyte  $C_{HF}$  from 36 to 42 wt. % and electrolyte temperature change  $T_3$  in the range of 90...110 °C, fluoride current output can increase from 86 to 95 %, and HF content in the product from 6 to 18 %.

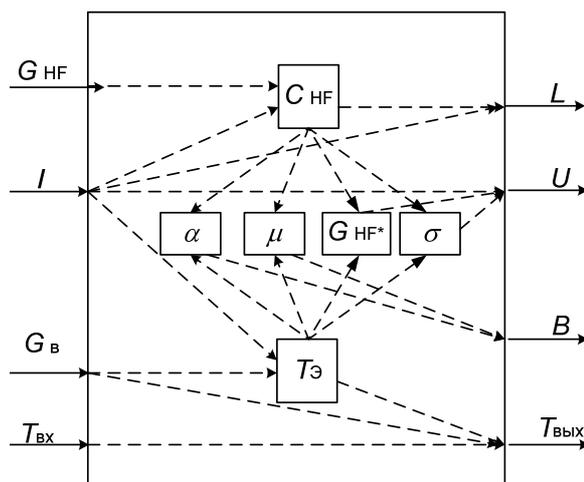


Fig. 1. Process block diagram

Fluoride cost is mainly determined by expenditures for HF 58 % and energy supply 16 % and using more than 40 devices for their saving is actual.

On the basis of above-stated the demands and limits for optimal region of operating mode are stated. The boundaries of this region determine: principle value of saturated vapor HF over electrolyte melt characterizing product quality and raw material consumption; voltage drop at electrolyte as an index of electric energy consumption; dissociation degree and viscosity of electrolyte as indices of fluoride energy output.

### Criteria of power inputs efficiency

Electric power losses mainly depend on the magnitude of voltage drop at electrolyte and polarization [1]. Decrease of electrolyte temperature results in increase of electric energy expenditures. Decrease of HF concentration in the melt results in decrease of specific electrolyte conductivity that is increase of energy expenses.

Efficiency functional of energy expenses  $f_1$  is made in such a way that in prescribed limit of controlled variable change its maximal value tends to unit and minimal one to zero

$$f_1 = 1 - \frac{U - U_{\min}}{U_{\max} - U_{\min}}, \quad (1)$$

where  $U_{\min}$  and  $U_{\max}$  are voltage drops at minimal controlled parameters, electrolyte temperature and HF concentration, and maximal, respectively.

To determine voltage drop at electrolyte the static mathematic model of the object was developed [5], according to which HF concentration in electrolyte is defined by the expression:

$$C_{\text{HF}} = 0,65 \cdot \frac{I \cdot l}{(U - U_0) \cdot S} + 50,34 - 0,22 \cdot T_3,$$

where:  $U_0$  is the initial value of voltage at electrolytic cell, V;  $I$  is the current, A;  $l$  is the distance between electrodes, m;  $S$  is the electrolyte area of section between electrodes,  $\text{m}^2$ .

Then from (1) voltage drop at electrolyte:

$$U = U_0 + \frac{0,65 \cdot I \cdot l}{(C_{\text{HF}} - 50,33 + 0,22 \cdot T_3) \cdot S}.$$

### Criterion of quality optimality

Quality of the obtained fluoride is characterized by impurity content. The main component of impurity is hydrogen fluoride (up to 95 %) removed with finished product from anode space of electrolytic cell. HF concentration over electrolyte surface is determined by pressure of saturated vapors of hydrogen fluoride  $P_{\text{HF}}$ . Then the criterion of quality optimality  $f_2$  is of the form:

$$f_2 = \frac{A \cdot P_{\text{atm}}}{P_{\text{HF}}},$$

where  $A$  is the coefficient selected in such way that maximal value of  $f_2$  amounts to unit,  $P_{\text{atm}}$  is the atmospheric pressure;  $P_{\text{HF}}$  is the pressure of HF saturated vapors.

The results of measuring HF vapor pressure over KF-HF melt [1] in effective range of controlled variables allowed obtaining analytic expression of dependence on temperature and HF concentration in electrolyte. The data are given in [1] approximated to an accuracy of 6 % by the equation of the form:

$$P_{\text{HF}} = 4 + \left( \frac{C_{\text{HF}} - 36,5}{2,4} + \frac{T_3 - 70}{13,5} \right)^3. \quad (2)$$

### Criterion of HF consumption efficiency

It is necessary for consumption of hydrogen fluoride to be minimal at standard process behavior. Then similarly to the efficiency functional of energy consumption the criterion of HF consumption efficiency  $f_3$  is described by the following equation:

$$f_3 = 1 - \left( \frac{G_{\text{HF}} - G_{\text{HFmin}}}{G_{\text{HFmax}} - G_{\text{HFmin}}} \right),$$

where  $G_{\text{HF}}$  is the consumption of hydrogen fluoride defined according to the reaction and HF pressure in gas (2) over electrolyte surface:

$$G_{\text{HF}} = \frac{P_{\text{HF}}}{P_{\text{atm}} - P_{\text{HF}}} \cdot 2G_{\text{F}_2}.$$

where  $G_{\text{HF}}$  is the consumption of the product determined in its turn by the formula:

$$G_{\text{F}_2} = \frac{\left( 22,4 \frac{m_{\text{F}}}{M(\text{F}_2)} \right)}{1000 \cdot t},$$

where  $M(\text{F}_2)$  is the fluoride molar mass;  $m_{\text{F}}$  is the amount of fluoride  $\text{F}_2$  extracted at anode determined according to summary reaction and Faraday law [6]:

$$m_{\text{F}} = k_{\text{3F}} \cdot I \cdot t,$$

where  $t$  is the time of electric current transmission, s;  $k_{\text{3F}}=0,709$  g/A·h is the electrochemical equivalent of fluoride.

### Criterion of process efficiency by the degree of dissociation

One of the main characteristics of KF-HF melt is ionic form concentration (or the degree of molecule dissociation into ions) [7]:

$$\alpha = \exp\left(\frac{W_\theta - W_\eta}{R \cdot (T_3 + 273)}\right) \cdot 100\%, \quad (3)$$

where  $W_\theta$ ,  $W_\eta$  is the activation energy of specific conductivity and viscosity respectively, kJ/mole;  $R$  is the universal gas constant.

On the basis of the data on specific conductivity and viscosity of KF-HF melt [7] the empirical equations for activation energy of specific conductivity and viscosity in the range of compositions 38...46 wt. % HF were obtained in the course of the given researches:

$$W_\theta = 73,78 - 1,23 \cdot C_{\text{HF}}, \quad (4)$$

$$W_\eta = 85,77 - 1,68 \cdot C_{\text{HF}}. \quad (5)$$

Thus, at substitution (4) and (5) into (3) criterion of process efficiency by the dissociation degree  $f_4$  is described by the expression:

$$f_4 = \exp\left(\frac{11990 - 450 \cdot C_{\text{HF}}}{R \cdot (273 + T_3)}\right).$$

### Criterion of process efficiency by viscosity

As melt viscosity defines finished product energy output, calculated through the main controlled variables and reflects process efficiency then the efficiency criterion by viscosity of electrolyte  $f_5$  may be made:

$$f_5 = 1 - \left( \frac{K - K_{\text{min}}}{K_{\text{max}} - K_{\text{min}}} \right),$$

where  $K$  is liquid viscosity determined by the character of molecule thermal motion in liquids [7]. Viscosity of KF-HF melt decreases at temperature increase by linear dependence at HF concentration growth also decreases but dependences are of more complicated, S-shaped character with deflection in points corresponding to stoichiometric composition of KF-HF compound. Taking into account (5) we obtain:

$$K = A_1 \cdot \exp\left(\frac{8577 - 1680 \cdot C_{\text{HF}}}{R \cdot (273 + T_3)}\right).$$

where  $A_1$  is obtained by parameters varying with minimization of mean-square value of an error up to 5 %.

By the method of multiparametric optimization the integrated efficiency functional  $F$  weighting factors has the form [8]:

$$F = \sum_{i=1}^5 k_i \cdot f_i.$$

To determine weighting factors of integrated functional of process efficiency from various positions the judgment method was used [9]. As in our case there is no possibility to express integrated functional of process efficiency in price equivalent let us divide all criteria into economic and technological then economic efficiency criteria:  $f_1$  and  $f_3$  take up a half of the sum of all weights as well as criteria determining technological efficiency:  $f_2$ ,  $f_4$  and  $f_5$ .

According to the contribution into prime cost as well as maximum possible economy of energy consumption for voltage drop decrease at certain current and HF consumption, fraction  $d_1$  of the criterion  $f_1$  and fraction  $d_3$  of the criterion  $f_3$  are determined respectively:

$$d_1 = 0,16(U_{\text{max}} - U_{\text{min}}),$$

$$d_3 = 0,59(G_{\text{HFmax}} - G_{\text{HFmin}}).$$

Then weighting factors for  $f_1$  and  $f_3$ :

$$k_1 = \frac{0,5d_1}{d_1 + d_3},$$

$$k_3 = \frac{0,5d_3}{d_1 + d_3}.$$

Dissociation degree and viscosity determine energy output of finished product being the indices of process engineering efficiency as there is no opportunity to express them through economic indicator owing to inaccessibility of some data and limits of process measured variables. Dissociation degree influences the process up to the total capacity decrease at the same time viscosity is of considerable value as when it increases the internal friction at ion motion increases. Therefore, ratio between weighting coefficients, determining efficiency depending on the degree of dissociation and viscosity, amounts to 2:1. In spite of the fact that viscosity may be changed up to electrolyte freezing moment and complete process shutdown, in the given case the efficiency is considered in the boundaries of controlled variables

operating range therefore, electrolyte viscosity contributes to polarization process.

Quality criterion is referred to technological efficiency as in the given case product quality influences the technology of further manufacturing cycle using industrial fluoride. Therefore, degradation of industrial fluoride quality due to increasing HF content in it does not involve considerable increase of expenditures and decreasing HF concentration in fluoride does not result in any significant resources economy. The given criterion could play a significant role in the case of selling industrial fluoride as finished product at profit earning or at its known cost. In this case increasing «purity» of manufactured product the cost increases exponentially. In the same case the tenth of all technological criteria falls on the efficiency fraction due to the quality. Thus, criteria of technological efficiency have the following weight:  $k_2=5$ ,  $k_4=30$  and  $k_5=15$ .

Extreme investigation of quality functional  $F$  (9) was made by the method of gradient descent [9] in the package Mathematica 6.0.

Studying integrated efficiency criterion in working values range of controlled variables showed that the developed functional has maximum in the range of values 36...39 wt. % of HF concentration and 99...103 °C electrolyte temperature (Fig. 2) the position of which also depends on other measured variables of the process.

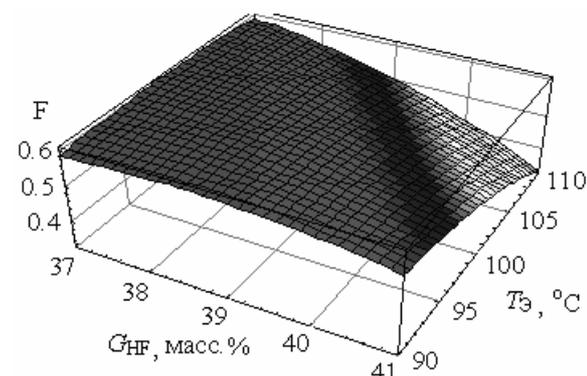


Fig. 2. Dependence of integrated functional  $F$  on controlled variables of the process

At the given stage the integrated efficiency functional was developed which may be applied for determining optimal values of temperature and concentration from the point of view of technology, resources conservation and product quality for technological process of obtaining industrial fluoride. The carried out researches allow passing to dynamic optimization that is automatic process maintenance in optimum condition.

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## PHASE EQUILIBRIUM LIQUID-VAPOR IN THREE-COMPONENT SYSTEM $UF_6$ - $IF_5$ - $BrF_3$ AT COMPLETE MUTUAL COMPONENTS SOLUBILITY

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*The results of studying phase equilibrium liquid-vapor at 353,15 K in the system of uranium hexafluoride, iodine pentafluoride, bromine trifluoride have been presented. The dependences of saturated vapor pressure on condensed phase composition, the results of analysis of studied system deviation from error-free behavior, the data on equilibrium vapor phase are given.*

Applying halogen-fluorides in processing materials of nuclear power engineering is of great importance. Use of halogen-fluoride mixture for fluoridation of uranium-containing compounds is rather actual. Applying gaseous mixture  $BrF_3$ - $IF_5$  for these purposes allows fluoridating uranium compounds at low temperatures and pressures in contrast to elemental fluoride [1]. In this case multi-component systems are formed. They contain uranium hexafluoride and halogen-fluorides which should be separated for extracting pure  $UF_6$  and regeneration of fluoridating agents. Besides, using halogen-fluorides and their mixtures at processing nuclear fuel improves significantly process variables and reduces production string and decreases considerably waste volumes.

Thermodynamics of phase equilibrium liquid-vapor of three-component system  $UF_6$ - $IF_5$ - $BrF_3$  at temperature 353,15 K was studied. As the given system at the specified temperature has unlimited reciprocal components solubility [2, 3] heterogeneous equilibrium between liquid and vapor was studied.

For researching phase equilibria in three-component systems the selection of changing technique of three-component system composition is of great importance [4, 5]. We selected the technique of composition changing by secant planes passing through the top meeting uranium hexafluoride. The triangle of Gibbs-Rosebum compositions of three-component system  $UF_6$ - $IF_5$ - $BrF_3$  indicating secants by which the compositions of condensed system were changed is presented in Fig. 1.

The composition was changed adding uranium hexafluoride to the mixture of iodine pentafluoride and bromine trifluoride the content of which in the mixture decreases at hexafluoride addition. However, the ratio of

concentrations  $x_{IF_5}$  to  $x_{BrF_3}$  remains constant along the whole secant and expressed by the coefficient  $a_i$ :

$$a_i = \frac{x_{IF_5}}{x_{BrF_3}} = \text{const},$$

where  $i$  is the number of the plane.

Thus, each secant may be presented in the form of pseudobinary system in which uranium hexafluoride is one of the components and another one is the mixture of iodine pentafluoride and bromine trifluoride at constant ratio of the components

According to the experimental data of the dependence of saturated vapor pressure on solution composition at constant temperature the dependence of saturated vapor pressure on liquid and vapor phases composition was calculated on the basis of Wilson equation [6]. The dependences of saturated vapor pressure on liquid phase composition for the system  $UF_6$ - $IF_5$ - $BrF_3$  by the secants with corresponding values of the coefficient  $a_i$  are given in Fig. 2.

One of the peculiarities of the system  $UF_6$ - $IF_5$ - $BrF_3$  is different character of deviations from Raoult law in binary system constituents. In three-component systems it should be taken into consideration that factors influencing the character of deviation from the ideal behavior act simultaneously in solution therefore the deviations observed in three-component systems are the result of overlapping deviations opposite in sign which are introduced by each component. As it was stated in the work [5] very often simultaneous action of opposite factors and deviation character are mainly defined by condensed system composition.