Power-efficient mode of the electrolytic fluorine production process control

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Abstract

Generalized functionality of the fluorine production manufacturing efficiency developed for determination of optimum values of temperature and hydrogen fluoride concentration according to the method of multiparametric optimization allowed calculating the optimum process performance and develop the optimum fluorine production process control by maintaining electrolyte solution temperature and hydrogen fluoride concentration in the electrolyte depending on the value of the current load in the electrolyzer.

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1. Main text

Research of the causes of high energy consumption and search for new engineering solutions and modes for increasing operation efficiency of fluorine electrolyzers is very important nowadays1–4. The ranges of electrolyte optimum composition have been obtained experimentally by Caddy in 19341. With the increase of hydrogen fluoride content in electrolyte from 36% to 42% wt, and temperature increasing from 90 to 120 °С, the efficient fluorine yield can increase from 27% up to 40%, while the content of hydrogen fluoride (HF) in the product grows from 6% to 18% vol.4.

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As a result, the need to form a generalized criterion for optimality of the manufacturing process operational mode expressing efficiency in terms of the main technological control variables and to develop efficient control mode on its bases appeared.

Operational ranges of the electrolytic content experimentally obtained by Caddy have some limitations such as electrolyte crystallization and the HF vapor pressure above the melt of 50 mm Hg which corresponds to the upper permissible value of HF concentration in the manufactures fluorine. It is well known that when HF content in electrolyte $C_{HF}$ increases from 36% to 42% wt, in the interval of the electrolyte temperature change $T_E = 90 \ldots 120^\circ C$, the efficient fluorine yield can increase from 27% to 40% [3], and the content of HF in the product can grow from 6% to 18% vol. $^1$. The production cost of fluorine is mainly determined by expenditures connected with HF (58%) and energy sources (16%), hence, cost savings, in case when 10 and more production units are used, is a very important task.

Electric power losses depend on the value of voltage drop on electrolyte and polarization$^{1,3,4}$. The decrease of the electrolyte temperature results in the increase of the electric power cost. The decrease of HF concentration in the melt leads to the decrease of electrolytic conductivity. This also leads to the increase of energy costs.

The quality of the produced fluorine is characterized by the presence of admixtures. The main component is HF (up to 95%) which evaporates from the electrolyte surface in the anode portion of the electrolyzer. Concentration of HF above the electrolyte surface is conditioned by a saturated vapor pressure. HF, evaporating from the electrolyte surface in the cathode portion and hydrogen go to ventilation and get lost. According to the above stated, the requirements and restrictions to the ranges of operation mode optimal values have been formulated. The bounds of this range determine: partial pressure of the saturated vapor of HF over the electrolyte melt which characterizes the product quality and raw material losses; electrolyte voltage drop which shows the power consumption; dissociation rate and electrolyte viscosity as the efficiency fluorine yield. According to the method of multi parametric optimization, the generalized efficiency functional $F$ with weight coefficients takes the form of $^5$:

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

Generalized functional the expert evaluation method has been used $^6$ to determine weight coefficients of the process efficiency. The functionality has been formed from the optimality criteria by using energy and materials resources and quality of produced fluorine which allows determining optimal values of controlled variables. Energy efficient mode of the fluorine production process means variability of controlled variables values depending on current load, specification of permissible quality of the produced fluorine, according to calculation results of the functional to achieve the minimum power costs.

The researches of the generalized efficiency criterion (1) in the range of working values of controlled variables have shown that the developed functional had been at its highest point in the range of 36…39% wt. of HF concentration and 99…103 $^\circ C$ of the electrolyte temperature.

The developed generalized efficiency functional can be used to determine optimal values of HF temperature and concentration from the point of view of the technology, resources conservation, product quality for the manufacturing process of technological fluorine production. The performed researches allowed developing the energy-efficient mode of the fluorine production process management.

While researching current voltage characteristic of the electrolyte (Fig. 1) $^5$, it turned out that when the values of HF concentration and temperature changed within the regulated range, the increment of voltage change begins with the current increase to 2.5V at maximum load.

Taking into account that the voltage drop on electrolyte can be explained by the HF concentration and electrolyte temperature can be described by a linear function with accuracy sufficient for control, and there is rather accurate temperature and HF concentration automated control, it is possible to adjust these variables at the load current change:

$$ C_{HF} = 0.2 \cdot I + 35.9, $$

(2)
The efficiency of changing HF concentration and temperature in electrolyte specified by an optimal relation during the fluorine production process according to equations (2) and (3) is in the range of HF concentration values of 37% ... 40% wt. and electrolyte temperature of 98 ... 103 °C at current load changes from 6 to 20 kA.

The coefficient of energy efficiency is suggested to evaluate efficiency of the specified mode in the current change range. It characterizes the efficiency product yield and is defined by the following formula:

$$\eta_U = \frac{t}{U_p} \int_0^U \frac{I}{I} dt,$$

(4)

where $U_p$ – decomposition voltage, V; $U$ – electrolyzer voltage, V.

Materials yield efficiency criterion is used as a condition which limits the increase of specified values for control systems which limits the HF concentration in the product at a permissible level.

$$\eta_{HF} = \frac{\int_0^t G_{HF} \cdot dt - \int_0^t 0,53 \cdot G_{HF}(I) \cdot C_{HF}^* \cdot dt}{\int_0^t G_{HF} \cdot dt},$$

(5)

where $G_{HF}$ – HF consumption rate; $C_{HF}^*$ – HF concentration above electrolyte.

The principle of fluorine production process optimal control includes the maintaining process specified by the optimal relation between the HF concentration and temperature in electrolyte in automatic mode, that is depending on current and evaluation of the manufacturing unit operation efficiency according to (4) and (5), calculated automatically during a definite process period of the process.

Economic efficiency of the control algorism is achieved by savings on the costs of primary products and energy resources. At the same time improving quality of the end product and increasing the run between repairs of the manufacturing equipment. Let us consider in detail each of the stated arguments.

Increase of the material yield of fluorine and reduction of HF spending is expected due to maintaining controlled variables at the optimal level. On average, during fluorine production the loss of HF due to evaporation is from 6 to 8%. According to Table 1, presenting experimental data of the dependence of the saturated vapor pressure above the electrolyte melt on temperature and HF concentration, it follows that significant HF losses appear when the temperature of electrolyte is above 105 °C and the HF concentration is more than 40% wt.

Accordingly, when controlled variables are maintained at the optimal level, the loss value can decrease by 1..2% which is more than 1% relative to the full cost.

Energy losses can be reduced either if the energy yield of fluorine increases or the electrolyzer voltage decreases. The results of the average cost calculation of the electric energy at different current values are presented in Table 2.
Table 1. HF losses at specified operation mode maintenance, %

| Concentration HF, % wt | Electrolyte temperature, °C |
|------------------------|-----------------------------|
|                        | 90  | 95  | 100 | 105 | 110 |
| 37                     | 2   | 3   | 3   | 4   | 5   |
| 38                     | 2   | 3   | 4   | 5   | 6   |
| 39                     | 3   | 4   | 5   | 6   | 7   |
| 40                     | 4   | 5   | 7   | 8   | 10  |
| 41                     | 6   | 6   | 9   | 11  | 14  |

Table 2. Energy indicators of electrolyzer operation

| Average values          | Current (I), kA |
|-------------------------|-----------------|
|                         | 6   | 10  | 20  |
| Costs U, V              | 6.9 | 8   | 12.2|
| Losses U, V             | 0.75| 1.25| 2.5 |
| Energy consumption, W, kW| 41.4| 80  | 244 |
| Energy losses, W, kW     | 4.5 | 12.5| 50  |

When controlled variables are maintained at the optimal level, savings in terms of the power consumption can be up to 13% which is more than 2% relative to the full cost. Besides, optimization of the costs and increase of the run between repairs of the technological equipment has significant importance. In patent it is suggested to increase the equipment service life not less than by 1.5…2 times by the special cyclic variation of the level (± 40 mm) by electrolyte dumping and adding.

The research results of the level change at the electrolyte concentration change are shown in Fig. 2.

![Fig. 2. Dependence of the electrolyte concentration on its level](image)

The reason for scatter of the readings is the influence of the current on the level due to change of the gas component. It follows from the results that simultaneous periodic temperature and HF concentration change when optimum is maintained. It allows changing the level up to ± 30 mm which in its turn increases the life time of the bell without interfering with the process. This allows increasing the efficiency of the optimal control and reducing the costs by at least 1% due to increase of the equipment lifetime.
As a research result of the technological fluorine production in electrolyzers from different efficiency aspects of economic and technological character, the functionality in terms of optimality has been obtained. It allows calculating the optimal mode of the fluorine production process and serves as the basis of the developed algorism of the fluorine production process optimal control, as the required HF concentration and temperature in the electrolyte are specified depending on the electrolyzer current load value. The evaluation of the energy efficient mode of the process management on the technological process computer model of electrolytic fluorine production (partially presented in [9-11]) has shown the possibility to reduce the full production cost by 4% per year only by reducing the energy consumption at the same time keeping the required product quality.

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