Modeling of uranium oxides hydrofluorination process with AREVA firm technology (Malvési, France)

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Abstract

The analysis of hydrofluorination process at AREVA plant in Malvési was carried out as part of the development algorithm aimed at building self-consistent models for chemical technology processes. This algorithm was developed within the framework of the contract for creating a computer-assisted system of simulation and optimization of chemical technology processes on behalf of State Atomic Energy Corporation “Rosatom”. The hydrofluorination process was selected due to uranium tetrafluoride (UTF) being the main precursor in the process of uranium hexafluoride (UHF) production.

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1. Introduction

The analysis of hydrofluorination process at AREVA plant in Malvési was carried out as part of the development algorithm aimed at building self-consistent models for chemical technology processes. This algorithm was developed within the framework of the contract for creating a computer-assisted system of simulation and optimization of chemical technology processes on behalf of State Atomic Energy Corporation “Rosatom”. The hydrofluorination process was selected due to uranium tetrafluoride (UTF) being the main precursor in the process of uranium hexafluoride (UHF) production. To intensify the UTF production and improve cost efficiency, the

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authorities of Joint Stock Company “TVEL” are interested in the technology of anhydrous hydrofluorination of uranium dioxide.

The hydrofluorination process at AREVA plant in Malvési is equivalent to the process in devices of combined type (DCT) that are widely used in Russia. The main principle of such device is described by the counterflow of the particles of solid uranium compounds down from the top of the column in the mode of hindered falling and gaseous hydrogen fluoride flow which is underfed. (See Fig. 1).

2. Thermodynamic Assessment of Hydrofluorination Process

Thermodynamic assessment of probability value of hydrofluorination behavior was carried out based on data. The reaction of uranium dioxide hydrofluorination is described by equation:

\[ \text{UO}_2 + 4\text{HF} \rightarrow \text{UF}_4 + 2\text{H}_2\text{O} \]  

The main thermodynamic functions of hydrofluorination process (\( \Delta H^\circ_T \), \( \Delta S^\circ_T \) and \( \Delta G^\circ_T \)) were calculated using Vant Hoff’s equation (See Table 1). The temperature after \( \Delta G^\circ_T \) reverses its sign is calculated with the help of thermodynamic functions: it is \( T=910 \text{K} \) or \( 637 \text{°C} \). Fig.2 \( \Delta G^\circ_T - t \) presents the relation in the hydrofluorination process. The data were taken from different references.
The analyzing of the data \(^2\) revealed a number of inaccuracies: ordinary heat effect of hydrofluorination was first declared as \(\Delta H^{\circ} _{298} = -164000 \text{ J/mol}\); then as \(\Delta H^{\circ} _{873} = -169000 \text{ J/mol}\). Furthermore temperature dependence was indicated to determine Gibbs free energy change:

\[
\Delta G_T = -RT \ln (K_p) = 224988 + 239.709 \cdot T
\]

Generally, in the work \(^2\) the temperature when \(G\) becomes zero (938 K, Fig.3) is calculated close to true value. However, page 26 of the work indicates that for the zones heating higher than 750°C it is possible to lose the quantity of end product obtained at lower temperatures.
\[
\Delta G^*_T = -RT \ln \left( \frac{(H_2O)^2}{(HF)^4} \right)
\]

(3)

\[
-R \ln K_p = \frac{\Delta H^*_T}{T} - \Delta S^*_T
\]

(4)

\[
\Delta H^*_T = \Delta H^*_T(UF_4) + 2 \cdot \Delta H^*_T(H_2O) - \Delta H^*_T(UO_2) - 4 \cdot \Delta H^*_T(HF)
\]

(5)

\[
\Delta H^*_{298} = -1910 - 2 \cdot 241.8 + 1085 + 4 \cdot 270.7 = -225.8 \text{ kJ/mol}
\]

(6)

\[
\Delta S^*_{298} = 248 \text{ kJ/mol}
\]

(7)

\[
T \approx 910 K \text{ or } 637^\circ C
\]

(8)

### 3. Shrinking core model

The model of reactive “shrinking core” is applies well to the blowing process of uranium dioxide granules compacted in pellets by gaseous constituents. Since there is an extremely weak dependency between the reaction rate and the temperature, and activation energy is close to zero, we can conclude that the rate of the entire process is limited by diffusion of gaseous compounds through the layer of ashes from the burnt solid uranium compound. At the same time the rate of chemical conversion itself is rather high and doesn’t influence the resulting conversion rate. Another conclusion is that it’s possible to ignore the rate of counter reaction because the process occurs in the temperature range lower than the point of free energy sign inversion. Fig. 4 presents calculation of the relationship between the diameter (or radius) of unreacted part of solid granule with the corresponding time.

![Fig. 4. a – shrinking core model; b – dependence of diameter (or radius) of the unreacted part on time](image)

### 4. Basic Equations

*Darcy’s law* describes the flow rate of substance (gas or liquid) through porous medium similar to that formed by uranium dioxide granules compacted in pellets. The flow rate is directly proportional to the level difference (or pressure difference) between two points and is inversely proportional to the distance between them:

\[
P = -\frac{\eta}{K} \bar{u} + \rho \bar{f},
\]

(9)

where \( P \) – pressure; \( \bar{u} \) – rate; \( \eta \) – dynamic viscosity; \( K \) – porosity factor; \( \rho \) – density; \( \bar{f} \) – vector force field including gravitation.

*Ergun equation* – for the rate of gas flow in the conditions of fluidized bed in the column:
\[
\Delta P = \frac{150\mu (1 - \varepsilon)^2 V_s L}{\varepsilon^3 D_p^2} + \frac{1.75(1 - \varepsilon) \rho V_s^2 L}{\varepsilon^3 D_p} \tag{10}
\]

where \(\Delta P\) – pressure difference, \(L\) – thickness of fluidized bed, \(D_p\) – equivalent to spherical diameter of particle parking; \(\mu\) – media dynamic viscosity; \(V_s\) – visible surface rate (i.e. the rate of the flow in empty tube with the same volume flow); \(\varepsilon\) – volume ratio of column filling (i.e. media porosity factor).

Equation of mass transfer:

\[
\left\{ \frac{d Q_{U02}}{dz} = - \frac{d Q_{UP4}}{dz} \right\}_{solid} = W; \tag{11}
\]

\[
\left\{ \frac{d Q_{HF}}{dz} = - 2 \frac{d Q_{H2O}}{dz} \right\}_{gas} = 4W. \tag{12}
\]

where \(Q_U = Q_{U02} + Q_{UF4} = \text{const}\) are the flows of solid uranium dioxide and tetrafluoride through the unit cross section area of the reactor, mol/m²sec; \(W\) – the rate of chemical reaction determined according to molar conversion of uranium in reactor volume units, (mol/m³sec).

Enthalpy fluxes carried by solid-phase particles while they move throughout the height, mol/m³sec):

\[
H_{solid} = Q_{U02} \cdot C_{P_{U02}} \cdot T_s + Q_{UF4} \cdot C_{P_{UF4}} \cdot T_s = T_s \cdot \left[ Q_{U02} \cdot C_{P_{U02}} + (Q_0 - Q_{U02}) \cdot C_{P_{UF4}} \right] \tag{13}
\]

\[
\frac{d h_{solid}}{dz} = \frac{d (Q_{U02} C_{P_{U02}} T_s + Q_{UF4} C_{P_{UF4}} T_s)}{dz} = \Delta H \cdot W + a_{gas, exchange} \cdot (T_S - T_g) \tag{14}
\]

In similar manner for gas phase:

\[
\frac{d h_{gas}}{dz} = \frac{d (Q_{HF} C_{P_{HF}} + Q_{H2} C_{PH2O})}{dz} = \Delta H \cdot W + a_{gas, exchange} \cdot (T_S - T_g) + b_{wall, exchange} (T_0 - T_g). \tag{15}
\]

It is assumed that solid phase (granules) has very shot surface contact with reactor wall, that’s why all the heat transfer outward is realized in gas phase.

The next important stage is numerical analysis of chemical reaction conversion level as function of the height over the bottom of reaction column. We do not observe the possible particle size distribution, and consider that all the particles have approximately the same size for simplicity.

5. Simplified and “Cleaned” Mathematical Equations

Within the framework of the recommended model we were able to fulfill integration in quadratures of chemical kinetics equations and to get analytical expression in elementary functions (however, implicitly) for the conversion of unknown deepness (or the level of process incompleteness in the range from 0 to 1). This variable is determined only by vertical coordinate throughout the height of the reactor:

\[
\frac{d}{dz} \left(\frac{4}{3} \pi R^3 \cdot \rho \right) = - \frac{1}{t} \cdot \pi R^2 \cdot \rho \cdot [HF] \tag{16}
\]

\[
\frac{dR}{dt} = - \frac{1}{t} \cdot [HF] = const \tag{17}
\]

\[
\frac{dR(z)}{dz} = - \lambda_1 \cdot X(z) \tag{18}
\]

\[
\frac{dX(z)}{dz} = - \lambda_2 \cdot X(z) \cdot R^2 \tag{19}
\]
where $\xi$ – degree of radius change, $\xi = R/R_0$; $R$ - radius of unconverted nuclei of uranium dioxide granules; $z$ – vertical coordinate along the column, $k_{\text{eff}}$ - effective rate constant of radius “compression”; $\gamma$ – combination of numerical parameters of the model.

Computational solutions of initial differential equations in MATLAB environment as well as in self-designed software environment specially dedicated to simulate multistage chemical processes with complicated mechanism were held to test the adequacy of obtained equations to required set of chemical equations (taking the diffusion into account).

\[
z_0 - z = \gamma \cdot \int \frac{dR}{R^3 - a^3} = \frac{\gamma}{6a^2} \cdot \ln \left( \frac{(\xi - a)^2}{\xi^2 + a^2} \right) - \frac{\gamma}{\sqrt{3} R_0^2 a^2} \arctg \left( \frac{2\xi + a}{\sqrt{3} a R_0} \right) + b \quad (20)
\]

\[
z = z_0 - \frac{\gamma}{R_0^2 a^2} \cdot \left\{ \frac{1}{6} \ln \left( \frac{(\xi - a)^2}{\xi^2 + a^2} \right) - \frac{1}{\sqrt{3}} \arctg \left( \frac{2\xi + a}{\sqrt{3} a} \right) + b \right\} \quad (21)
\]

\[
z = z_0 - \frac{3u_y}{16n K_{\text{eff}} R_0} \cdot \left\{ \frac{1}{a^2} \{ \frac{1}{6} \ln \left( \frac{(\xi - a)^2}{\xi^2 + a^2} \right) - \frac{1}{\sqrt{3}} \arctg \left( \frac{2\xi + a}{\sqrt{3} a} \right) + b \} \right\} \quad (22)
\]

Fig. 5. A – Ideal mixing of the components. Stoichiometry [UO$_2$]:[HF] = 4:1. 100% conversion; B – Low-temperature and low-rate mode. Incomplete conversion of reactants (not enough time for phase contact – the column is too short). Approximately 30% UO$_2$ and half of HF remain unreacted.
We studied the modes of operation providing practically full interconversion of gaseous and solid components (to the depth of 99%); situations of stoichiometric excess of one of the components were studied and simulated too. The modes corresponding to excess and poor height of the column were calculated to determine its optimal size.

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