В случае многозарядных ионов (рис. 1-б.) выщелачиваемость в почве не более 50 %, хотя величина ионного потенциала очень высока. Это объясняется тем, что содержание многозарядных ионов в почве очень низкое (10^{-4}-10^{-3}% вес), что видно из рис. 2 для ионов Br^{7+}, Cr^{4+}, Co^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Se^{5+}, Sc^{3+}, Th^{4+}, Yb^{3+} и т.д.

Линейная зависимость между ионным потенциалом и растворимостью с коэффициентом корреляции r_{xy}=0,85 для переходных элементов, Th, РЗЭ, Sc показывает, что комплексообразование, по-видимому, в общем случае, более устойчивое, хотя имеются некоторые тенденции роста выщелачиваемости (несмотря на низкие концентрации элемента в почве) с увеличением величины ионного потенциала и сродства их с кислородом, что приводит к превращанию в устойчивые анионные комплексы через ряд простых превращений. В зависимости от pH среды, степень растворимости оксидов и гидрооксидов элементов меняется от устойчивого до растворимого.

Полученные данные показывают, что в условиях сильного засоления почв (pH=7-9) процессы выщелачиваемости одновалентных ионов (например Na^{1+}, K^{1+}, Cs^{1+}, Rb^{1+}) относительно слабее, чем двухвалентных ионов (Ba^{2+}, Ca^{2+}). Двухвалентные катионы меньшие по размеру, образуют несколько слаборастворимых соединений с различными анионами. Трех и многозарядные ионы, которые при различных природных условиях образуют комплексные растворимые соединения, по-видимому, мало переходят в раствор, поскольку они легко осаждаются в виде окислов и гидроокислов на геохимических барьерах (в частности глине).

Таким образом, в условиях сильного засоления почв зоны Приаралья, геохимические процессы развиваются разными путями с образованием комплексных соединений химических элементов, которые по степени выщелачиваемости ионов находятся в интервале от растворимых до труднорастворимых соединений.

Как показывают экспериментальные результаты, при выщелачивании элементов дистиллированной водой из сильнозасоленных почв в течение различных промежутков времени имеются определенные предпосылки для оздоровления экологической ситуации агропочв региона Южного Приаралья. Для этого, в первую очередь, следует заниматься вопросами реконструкции существующих дренажно-коллекторных систем и созданием новых систем по современным технологиям.

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COMPACTING CARBON COMPOSITES BY PYROCARBON FROM PRODUCIS OF NATURAL GAS PYROLYSIS IN THE TERMOCHEMICAL FLOW-TYPE REACTORS

Abstract. The mathematical modelling natural gas pyrolysis and compacting carbon composites by pyrocarbon from a gas phase in the thermochemical flow-type reactors is performed. A model takes into account the processes of transporting gaseous hydrocarbons in the porous structure of composite, their subsequent decomposition and deposition of pyrocarbon on the heated surfaces of pores.

Keywords: carbon composite, natural gas, pyrolysis, isothermal compacting, pyrocarbon, flow-type reactor, modelling

Introduction. At the production of carbon composites one of the important stages is a compacting their porous structure with the use of natural gas (methane) [1]. When homogeneous reactions occur, the complex of paraffinic and unsaturated hydrocarbons and a number of radicals appears [2-5]. Products of homogeneous reactions and initial hydrocarbon diffuse to the heated surfaces of composite and then into its porous structure where subsequently decomposite he heated walls of pores and form a solid phase, namely pyrocarbon.

The assemblage of volume chemical reactions of methane pyrolysis can be presented as system of equations:

$$\begin{aligned} CH_4 &\xrightarrow{k_1} CH_3^\bullet + H^\bullet\ ; \\ 2CH_4 &\xrightarrow{k_2} C_2H_2 + 3H_2\ ; \\ H^\bullet + C_2H_2 &\xrightarrow{k_3} C_2H^\bullet + H_2\ ; \\ C_2H_2 &\xrightarrow{k_4} C_4H_2 + H_2\ ; \\ C_2H_2 &\xrightarrow{k_5} C_2 + H_2\ ; \end{aligned} \qquad (1)$$

Carbon composite samples and reactor walls have an almost identical temperature. Near the heated surfaces of composites the temperature of reaction gases corresponds the temperature of reactor walls, but with distance from walls the temperature of gases decreases and in area of mainlines of its flow has a minimum value.

Problem statement. To study the processes of mass transfer of reaction gases mixture and deposition of pyrocarbon in flow-type reactors at the compacting of carbon composite from a gas phase.

Basic part of researches. For conditions of gas flowing along the reactor axis and diffusion rate lower then flow rate, equations of mass transfer of *i*-th component of gas mixture and chemical transformation can be written as:

$$\frac{\partial C_i}{\partial \tau} = \mathrm{div}(\nabla C_i - D_{iN} \cdot \varDelta C_i) = k_i \cdot C_1^n \cdot C_2^n \ldots C_N^n\ , \quad (2)$$

where C_i is a concentration of *i*-th component of gas mixture; D_{iN} is a diffusion coefficient of *i*-th component from mixture of N components; ΔC_i is a concentration gradient; k_i, n are a rate constant of homogeneous reaction and reaction order on *i*-th component respectively.

A solving of the system of equations (2) is possible, if the initial and border conditions of the studied process are known.

Initial conditions determine the distribution of concentration for components of gas mixture in the reaction volume of reactor in start moment of process

$$C(\bar{x}, 0) = C(\bar{x})\ . \qquad (3)$$

As a rule, initial distribution of concentration for components of reaction gas mixture in the volume of reactor is accepted as a constant.

Border conditions determine the features of mass transfer on the interface between reaction gases and heated surfaces, i. e. conditions of chemical interactions on the interface, its gas permeability and activity.

It is known that the structure of surface for porous carbon composite has a distinct heterogeneity conditioned by the presence of solid phase and open porosity.

For such surface total mass density I_i of *i*-th component stream on a border a «gas-solid» is determined by correlation

$$I_i = (1 - \omega_i) \cdot I_i^S + \omega_i \cdot I_i^V\ , \qquad (4)$$

where I_i^S, I_i^V are a mass density of streams of *i*-th component on the surface of composite and in the volume of its pores, respectively; ω_i is relative porosity of composite surface.

The mass density of *i*-th component steam on the surface S of composite is calculated by a formula

$$I_i^S = D_i \frac{\partial C}{\partial \eta}\Big|_S = W_i^S\ , \qquad (5)$$

where η is a normal to the surface S; W_i^S is specific volume productively of chemical transformations that defined on the basis of postulates of chemical kinetics [6] and which is rate of heterogeneous reaction of *i*-th component of reaction gas mixture.

In a formula (5) the rate of heterogeneous reaction for *i*-th component is determined by means of correlation

$$W_i^S = k_i^S \cdot C_i^S\ , \qquad (6)$$

where k_i^s, C_i^S are a rate constant of heterogeneous reaction and concentration of *i*-th component on the surface of carbon composite, respectively.

For determination stream of reaction mixture density in the volume of the investigated composite, the problem of diffusive mass transfer in pores is considered.

In the conditions of stationarity equation of diffusive mass transfer of *i*-th component of reaction gases mixture along the length of pore can be written as:

$$\bar{r} \cdot D_i \frac{\partial c_i}{\partial \ell^2} = 2k_i^S \cdot f_i^S(C)\ , \qquad (7)$$

where $\bar{r}$, ℓ are a middle radius and length of pore, respectively; $f_i^S(C)$ is a kinetic function of heterogeneous processes.

In the case of sufficient thickness of the investigated carbon composite, border conditions for equation (7) are following

$$C_i|_{\ell\to\infty} = 0\ ; \qquad (8)$$

$$C_i|_{\ell\to 0} = C_i^S\ . \qquad (9)$$

A condition (8) demonstrates the absence of reaction gas in the end of endlessly long pore, and condition (9) sets the concentration of gas near the mouth of pore.

In the case of linearness of function, $f_i^S(C) \equiv C$ solution of equation (9) looks like

$$C_i = C_i^S \cdot \left[-\frac{2k_i^S}{r \cdot D_i}\right] \cdot \ell\ . \qquad (10)$$

The stream mass density for *i*-th component of reaction mixture in a pore is set by the first Fick law

$$I_i^V = D_i \cdot F \frac{dC}{d\ell}\Big|_{\ell=0}\ , \qquad (11)$$

where F is cross-sectional area of pore.

After differentiation of equation (10) on length of pore and its substitution in equation (11), we get

$$I_i^V = -\pi \cdot \frac{C_i^S \cdot k_i^S \cdot r}{D_i} . \qquad (12)$$

Taking into account equations (7) and (12) total stream mass density, given by correlation (4), it can be written as

$$I_i = C_i^S \cdot \left[(1-\omega_i) \cdot k_i^S - \pi \cdot \omega_i \cdot \frac{k_i^S \cdot r}{D_i}\right] . \qquad (13)$$

Equation (13) sets the discharge of components of reaction gas mixture on the surface of porous carbon composite. After the diffusion rate of reaction gases from the reactor volume and the rate of their discharge on the surface of composite will equal, the stationary concentration of reaction gases is set.

Assuming, that the concentration of i-th component from the volume of reactor to the surface of composite changes on a linear law, the size of its gradient can be defined with use of correlation

$$\frac{dC_i}{dn} = \frac{C_i^0 - C_i^S}{\delta} , \qquad (14)$$

where C_i^0 is a concentration of i-th component in the volume of reactor; δ is a thickness of diffusion layer.

The condition of stationarity can be written as

$$D_i \frac{dC_i}{dn} = I_i . \qquad (15)$$

Then correlation between the concentrations of i-th component in the volume of reactor (C_i^0) and on the surface of porous composite (C_i^S) is

$$C_i^0 = \frac{\beta \cdot C_i^S}{\beta + (1-\omega_i) \cdot k_i^S - \pi \cdot \omega_i \cdot (2k_i^S \cdot r / D_i)} , \qquad (16)$$

where β is diffusion rate constant, $\beta = D_i / \delta$.

Correlation (16) is end result of method of equally accessible surfaces, specified by the two-stream approximation for porous bodies [7].

To simplify the solution of the system of equations (2), we introduce a number of assumptions [8]:

– a circular axisymmetrical reactor is considered, for which a function describing the structure of gas streams does not depend on an azimuthal coordinate, and operating mode is stationary;

– rates of homogeneous and heterogeneous reactions on every individual component correspond to the first order;

– the Frank-Kamenetskij method of equally accessible surfaces is used.

Taking into account the accepted assumptions, the system of equations (1) can be written as:

$$\frac{d(UC_i)}{dz} + \frac{2k_i^S \cdot C_i^S}{R \cdot \langle \beta + (1-\omega_i) \cdot k_i^S - \pi \cdot \omega_i \cdot (2k_i^S \cdot r / D_i) \rangle} = W_i^S , \qquad (17)$$

where U is rate of gas stream on the axis of reactor; R is a radius of reactor; z is a coordinate along the axis of reactor.

The diffusion coefficients for i-th component are calculated on the Blank formula:

$$D_i = \frac{1 - x_i}{\sum (x_i / D_{ij})} , \qquad (18)$$

where x_i is a molar fraction of i-th component; D_{ij} is a diffusion coefficient.

The concentrations of products of homogeneous and heterogeneous reactions are determined with the use of correlations:

$$\begin{gathered} [CH_4] = \frac{A \cdot (1-X-B) \cdot P}{\theta}; \ [CH_3^{\bullet}] = \frac{A \cdot B \cdot P}{\theta} ; \\ [C_2H_2] = \frac{A \cdot (X-L-F=E) \cdot P}{\theta} ; \ [C_2H^{\bullet}] = \frac{A \cdot L \cdot P}{\theta} ; \\ [\sum_{n=2} \sum_{m=2} C_n H_m] = \frac{A \cdot F \cdot P}{\theta} ; \ [C_2] = \frac{A \cdot E \cdot P}{\theta} . \end{gathered} \qquad (19)$$

where A is a volume flow rate of methane; X, B, E, L, F are relative fractions of methane pyrolyzed to products of homogeneous reactions C_2H_2, $CH_3^{\bullet}$, $C_2H^{\bullet}$, C_nH_m, C_2, respectively; $\theta = K \cdot T \cdot M$; T, P are a temperature and pressure in the reactor; M is a common quantity of moles of gas passing through the given section of reactor per time unit; K is gas constant.

The system of equations (16) for methane and products of its homogeneous decomposition in a reactor, taking into account correlations (18), looks like:

$$\begin{gathered} \frac{d(U \cdot S \cdot \varphi)}{dz} + \Psi_6 \cdot \varphi = S \cdot (k_1 + k_2) \cdot \phi ; \\ \frac{d(U \cdot S \cdot \phi)}{dz} + \Psi_3 \cdot \phi = S \cdot k_3 \cdot \varphi - (k_2 + k_4 + k_5) \cdot \varphi ; \\ \frac{d(U \cdot S \cdot B)}{dz} + \Psi_1 \cdot B = S \cdot k_1 \cdot \varphi ; \frac{d(U \cdot S \cdot L)}{dz} + \Psi_2 \cdot L = S \cdot k_2 \cdot \varphi \\ \frac{d(U \cdot S \cdot F)}{dz} + \Psi_5 \cdot F = S \cdot k_5 \cdot \phi ; \frac{d(U \cdot S \cdot E)}{dz} + \Psi_4 \cdot E = S \cdot k_4 \cdot \phi , \\ \text{where } \varphi = 1 - X - B ; \phi = X - L - F - E . \end{gathered} \qquad (20)$$

Rate constants for homogeneous reactions of formation of radicals, acetylene, heavy hydrocarbons and soot carbon k_1-k_5 in the system (1) are determined with the use of following correlations [9]:

$$\begin{gathered} k_1 = -\frac{B}{(X+B) \cdot t} \cdot \ln\left(\frac{A-X-B}{A}\right) ; \ k_2 = -\frac{L}{(L+E+F) \cdot t} \cdot \ln\left(\frac{\phi}{k_3 \cdot A \cdot t}\right) \\ k_3 = -\frac{X}{(X+B) \cdot t} \cdot \ln\left(\frac{A-X-B}{A}\right); \ k_4 = -\frac{F}{(L+E+F) \cdot t} \cdot \ln\left(\frac{\phi}{k_3 \cdot A \cdot t}\right); \\ k_5 = -\frac{E}{(L+E+F) \cdot t} \cdot \ln\left(\frac{\phi}{k_3 \cdot A \cdot t}\right) . \end{gathered} \qquad (21)$$

It is assumed that during processes of compacting porous structure of carbon composite the next conditions are fulfilled:

– deposition rate of pyrocarbon in the porous structure of composite is small enough;

– porosity of composite is the slowly changing function of time.

In this case, problem of mass transfer in single cylindrical pore of carbon composite is mathematically formulated by the system of equations (7)-(9), and also by the following correlations:

$$\vartheta \cdot \frac{d\rho}{d\ell} = \sum_{i=1}^{N} S_i \cdot k_i^S \cdot C_i\ ; \qquad (22)$$

$$\rho|_{\ell=0} = \rho_0\ , \qquad (23)$$

where S_i is a specific reactive surface of composite; ρ_0 is an initial density of material of composite; ϑ is rate of pyrocarbon layer growth.

Solution of equation (7) taking into account conditions (8)-(9) can be presented as correlations [10]:

$$C_i = \frac{C_i^0 \cdot \left\langle \exp[(2k_i^S/\bar{r}\cdot D_i)]^{0,5}\cdot(\ell-2h)] + \exp[-\ell\cdot(2k_i^S/\bar{r}\cdot D_i)^{0,5}] \right\rangle}{1+\exp[2\ell\cdot(2k_i^S/\bar{r}\cdot D_i)]}\ , \qquad (24)$$

where $2h$ is a thickness of carbon composite wall.

Because of the size of specific reaction surface area of carbon composite S_i corresponds the specific surface area of pores; it can be defined with the use of correlation:

$$S_i = \frac{2(\rho_r-\rho)}{\bar{r}\cdot\rho_r\cdot\rho}\ , \qquad (25)$$

where ρ_r is a real density of material of composite.

Performing the substitution of correlation (25) in differential equation (21), taking into account a formula $\vartheta = \frac{1}{\rho_0} \cdot \sum_{i=1}^{N} k_i^S \cdot C_i$ it can be written:

$$\frac{d\rho}{d\ell} = \frac{2(\rho_r-\rho)}{\bar{r}\cdot\rho_r\cdot\rho} \cdot \sum_{i=1}^{N} \frac{h_i\cdot C_i\cdot\rho_0}{\sum_{i=1}^{N} k_i^S}{}_i\ . \qquad (26)$$

After integration of correlation (26) on ρ (from ρ_0 to ρ) and on ℓ (from 0 to ℓ) we obtain transcendent equation in relation to a parameter ρ_r ρ_n which characterizes the change of apparent density for material of composite on the its wall thickness:

$$\rho_r \cdot \ln\left(\frac{\rho_r-\rho}{\rho_r-\rho_0}\right) = \frac{2\rho_0}{\bar{r}\cdot(2k_i^S/\bar{r}\cdot D_i)^{0,5}\cdot\rho_r\cdot\sum_{i=1}^{N} k_i^S} \cdot \sum_{i=1}^{N} k_i^S \cdot C_i^0 \cdot$$

$$\cdot \frac{\left\langle 1+\exp[(1-2h)\cdot(2k_i^S/\bar{r}\cdot D_i)^{0,5}] - \exp[-\ell\cdot(2k_i^S/\bar{r}\cdot D_i)] - \right.}{1-\exp[-2h\cdot(2k_i^S/\bar{r}\cdot D_i)^{0,5}]}$$

$$\cdot \frac{\left. -\exp[-2h\cdot(2k_i^S/\bar{r}\cdot D_i)] \right\rangle}{1-\exp[-2h\cdot(2k_i^S/\bar{r}\cdot D_i)^{0,5}]} \qquad (27)$$

Computing experiment with the use of the offered mathematical model was performed by means of the computer program in algorithmic language of «Turbo Pascal».

Initial data for the calculation are natural gas composition and flow rate; geometrical parameters of reactor; initial porosity and thickness of carbon composite wall; middle radius of pores; temperature and remaining pressure in reactor; duration of pyrocarbon deposition process.

Output parameters are distribution of individual hydrocarbons (radicals) concentration in the volume of reactor and in the porous structure of carbon composite; deposition rate of pyrocarbon; distribution of composite density on the wall thickness for its different areas.

As a numeral example the calculation of pyrolytic compaction of composite was executed for next conditions: composite on basis of graphitized carbon clothes with novolak-type binder; natural gas (96.50 % CH_4; 0.54 %; C_3H_8; 0.44 % C_2H_6; 0.20 % C_4H_{10}; 1.5 % H_2; 0.82 % N_2) at a temperature 1050-1100 °C; remaining pressure 1.0 kPa, open porosity of composite - 24 %; middle radius of pores 7.0 mcm).

Table 1

DISTRIBUTION OF DENSITY ALONG TO THE THICKNESS OF CARBON COMPOSITE AFTER ITS GASPHASE COMPACTING

Distance from surfaces, mm	Density, g/cm^3		
	initial	calculated	real
0	1.085	1.286	1.285
2	1.085	1.278	1.276
4	1.085	1.267	1.265
6	1.085	1.250	1.254
8	1.085	1.248	1.247

Authentication of the offered mathematical model was performed by comparison of calculated values of carbon composite density with real ones obtained during in optical and mechanical researches (see table

1). It was found that variance of theoretical and experimental values of density is, on average 0.5 %, that confirm to applicability of the offered model to the quantitative estimation of density distribution on thickness of composite wall at its compacting from a gas phase.

Conclusions. The model for natural gas pyrolysis process and mass transfer of reaction gas mixture at compacting of carbon composites by pyrocarbon deposited in flow-type reactor is developed. Offered model was successfully tested at practical calculations of pyrolytic compacting carbon composites` in reactors of different construction.

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MODELING OF WATER TREATMENT IN THE «AERATION TANK-SETTLER» SYSTEMS

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МОДЕЛЮВАННЯ ОЧИСТКИ ВОДИ В СИСТЕМАХ «АЕРОТЕНК–ВІДСТІЙНИК»