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MATHEMATICAL MODELING OF THE EQUILIBRIUM BETWEEN NITROGEN(II) AND (IV) OXIDES IN THE COMBINED PROCESS OF METALS EXTRACTION FROM THE SPENT CATALYSTS

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The paper gives the results of the study of equilibrium between nitrogen(II) and (IV) oxides under the conditions of the combined process of nitrogen oxides chemisorption from their mixtures with air and the extraction of metals from spent catalysts by an aqueous solution that contacts with the catalyst and the extractant. The mechanism of the combined process was established and the mathematical model was created that takes into account the interaction between nitrogen oxides and water with the formation of nitric acid, its subsequent interaction with the reactive component of the spent catalyst and the extraction of the formed metal nitrates. The investigation was performed and the mathematical model was developed for the determination of the equilibrium composition of nitrogen oxides in the production of nitric acid and the calculation of the equilibrium concentration and conversion degree of nitrogen oxides in the combined process. DIAP-3-6N catalyst was used as an example and the algorithm was proposed for the calculation of the time variation of the composition of a three-phase system «solid–liquid–gas». A mathematical model of the process was created that takes into account the dependence of the equilibrium conversion degree of nitrogen oxides on the consumption rate of the produced nitric acid in the extraction of metals from the catalyst.

Keywords: chemisorption, extraction, combined process, nitrogen oxides, equilibrium conversion degree, calculation method.

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Introduction

Metal nitrates are commonly used as precursors in the catalysts production for the fabrication of active nanostructured components by coating them on the inert matrix with a developed specific surface. They are highly soluble in water, which allows them to be applied by impregnation, and are easily oxidized forming the metal oxide. However, during the subsequent thermal-oxidative treatment ~59% of the mass of metal nitrate in the form of NO_x removes with flue gases at the calcination stage. In addition, when metal nitrates are produced by dissolving the corresponding metals or their oxides in nitric acid, nitrogen (II) and (IV) oxides are released into the gas phase in an amount equivalent to the decomposition of at least one-fourth of the nitric acid necessary for the dissolution process [1–4]. The concentration of nitrogen (II) and (IV) oxides in the exhaust gases of the calcination or dissolution stages is variable and, as a rule, does not exceed 2 vol.% at the oxidation degree of 65–85% [3].

The absorption and catalytic methods are the most common industrial methods for the capture of nitrogen oxides. The nitrate component of the catalyst raw material in both cases of neutralization is completely removed from the production cycle. For example, the resulting degree of use of raw materials in the production of catalysts for methane conversion does not exceed 66% (with reference to the cost of NO_x elimination) [1–4].

Analysis of the methods for the preparation of traditional catalyst raw materials shows [3–5] that the joint utilization of waste nitrous gases and spent catalysts to obtain commercial solutions of metal nitrates allows both increasing the utilization rate of raw materials up to 87% and reducing the cost of catalysts up to 30%. To create industrial combined processes, it is necessary to develop a mathematical model for the determination of the equilibrium concentration of nitrogen(II) and (IV) oxides in the combined chemisorption-extraction process, which includes two stages: the formation of nitric acid from nitrogen oxides and water vapor contained in exhaust gases, and its interaction with catalyst metal to form metal nitrates.

Results and discussion

The following system was used in our study: 1) gas phase: air (N_2 and O_2), nitrogen (II), (IV) oxides and H_2O vapors; 2) liquid phase: H_2O and HNO_3; and 3) solid phase: NiO, CoO, PdO, and Ag_2O. The study was carried out in a bubbling apparatus of the column type; it was equipped with irrigated nozzle, a part of which was chemically interacted with a liquid phase.

The contact of a mixture of nitrogen oxides and air with a catalyst in the presence of water leads to the chemisorption of NO and NO_2 with the formation of HNO_3:

$$3NO_2+H_2O\leftrightarrow 2HNO_3+NO,\ \Delta G^0_{298}=2.0\ \text{kJ}. \quad (1)$$

The achievement of a maximum chemisorption degree of nitrogen oxides (60–70% at the NO_x concentration in the range of 0.1 and 1 vol.% at 298–308 K) in reaction (1) is limited by a nitric acid concentration of 15–25 wt.%. The equilibrium constant K_p of the reaction (1) is usually represented as a product of partial constants K_1 and K_2, which are the functions of temperature and concentration of HNO_3 in solution [6]:

$$K_p = K_1 \cdot K_2 = \frac{p_{NO}}{p^3_{NO_2}} \cdot \frac{p^2_{HNO_3}}{p_{H_2O}}. \quad (2)$$

The value of the partial equilibrium constant K_2, which depends both on the temperature and on the concentration of nitric acid, is determined based on data of the vapors composition over the HNO_3 solutions. The partial equilibrium constant K_1, which characterizes the partial pressure of NO and NO_2 over aqueous solutions of nitric acid and nitrogen oxides, is usually determined experimentally. The performance of an absorber of nitrous gases is classically considered using the concept of a theoretical stage. The height of the nozzle is an equivalent to one theoretical level; it is calculated based on a specified hydrodynamic conditions. In the gas phase, under the stage, it is assumed that the oxidation reaction of NO occurs in the kinetic region according to the stoichiometric equation:

$$2NO+O_2\leftrightarrow 2NO_2. \quad (3)$$

NO_2 dimerization reaction has a significant effect on the vapor phase composition at high partial pressures of nitrogen oxides:

$$2NO_2\leftrightarrow N_2O_4. \quad (4)$$

The equilibrium constant of reaction (4) is determined by the Bodenstein equation [4].

Mathematical models of this process and algorithms for their solution are successfully used in the design of large-tonnage nitric acid production. Therefore, the results of the mathematical modeling of this process were used for the development of the mathematical model of a combined chemisorption-extraction process.

In the system under consideration, simultaneously with reactions (1)–(3) during the extraction of, for example, nickel nitrate from spent nickel containing catalysts, the reaction takes place, which in general form can be written as follows [4,5]:

$$Me_nO_m+2mHNO_3\rightarrow nMe(NO_3)_m+mH_2O. \quad (5)$$

This reaction is also correct for CoO, PdO, and Ag_2O-containing catalysts.

The first stage of the combined process of the metals extraction from spent catalysts by an aqueous solution via bubbling nitrous gases through the suspension is similar to the process of absorption of the nitrous gases in the production of nitric acid. A part of the formed nitric acid is bound at the second stage with the corresponding salt by reaction (4) and does not participate in the equilibrium absorption. In mathematical modeling, it is usually thought of as an internal system drain [8,9]. In these salts, the nitrogen and oxygen atoms that are taken out of the equilibrium are in a 1:3 ratio (NO_3^- ion is formed in the course of the dissociation of salt).

The mathematical description of the equilibrium transformation was developed based on the Temkin-Horiuti's stationary reactions theory. In accordance with this theory, an atomic-molecular matrix was formed. For the five components of the reactions (NO_2, H_2O, HNO_3, NO, N_2O_4, and NO_3^-), consisting of three different chemical elements (H, O, N), one can compile a chart (Table 1).

The number of atoms in the molecules

Atom	Number of atoms					
	H_2O	HNO_3	NO_2	NO	N_2O_4	drain (NO_3^-)
H	2	1	0	0	0	0
O	1	3	2	1	4	–3
N	0	1	1	1	2	–1

The data of the table can be represented as a matrix:

$$A=\begin{pmatrix}2 & 1 & 0 & 0 & 0 & 0\\ 1 & 3 & 2 & 1 & 4 & -3\\ 0 & 1 & 1 & 1 & 2 & -1\end{pmatrix}. \tag{6}$$

The equations for the conversion of elements during the transformation of the matrix have the following form:

$$A\times X=A\times X^0, \tag{7}$$

where $X(n(H_2O)$, $n(HNO_3)$, $n(NO_2)$, $n(NO)$, $n(N_2O_4)$, $n(drain))$ is the equilibrium vector; $X^0(n^0(H_2O)$, $n^0(HNO_3)$, $n^0(NO_2)$, $n^0(NO)$, $n^0(N_2O_4)$, $n^0(drain))$ is the input vector.

Using the methods of linear algebra, we may multiply the system (6) from the left by the inverse minor M^{-1} of the matrix A, then we get the following system:

$$\begin{pmatrix}1 & 0 & 0 & 1 & 0 & 1\\ 0 & 1 & 0 & -2 & 0 & -2\\ 0 & 0 & 1 & 3 & 2 & 1\end{pmatrix}\times X=$$

$$=\begin{pmatrix}1 & 0 & 0 & 1 & 0 & 1\\ 0 & 1 & 0 & -2 & 0 & -2\\ 0 & 0 & 1 & 3 & 2 & 1\end{pmatrix}\times X^0. \tag{8}$$

For this particular case, system (8) gives three invariants (balance equations) for hydrogen, oxygen, and nitrogen, respectively:

$$n_{H_2O}+n_{NO}+n_{Stoc}=n^0_{H_2O}+n^0_{NO}+n^0_{Stoc}, \tag{9}$$

$$n_{HNO_3}-2n_{NO}-2n_{Stoc}=$$
$$=n^0_{HHO_3}-2n^0_{NO}-2n^0_{Stoc}, \tag{10}$$

$$n_{NO_2}+3n_{NO}+2n_{N_2O_4}+n_{Stoc}=$$
$$=n^0_{NO_2}+3n^0_{NO}+2n^0_{N_2O_4}+n^0_{Stoc}, \tag{11}$$

where n_i is the equilibrium amount of the i-th substance, mol; n_i^0 is the initial amount of the i-th substance, mol.

In accordance with the results of work [7], equilibrium condition for the reaction (4) is given as:

$$p_{N_2O_4}=\frac{p^2_{NO_2}}{K_3}. \tag{12}$$

If we further take into account Eq. (2), then we get the equations:

$$p_{HNO_3}=(K_2p_{H_2O})^{1/2}, \tag{13}$$

$$p_{NO}=K_1p^3_{NO_2}. \tag{14}$$

The amount of nitrogen and oxygen, which are removed from equilibrium reaction (1) due to the model reaction (5), can be defined as:

$$n_{Stoc}=\frac{U_{MeO}v_{HNO_3}}{W_G}, \tag{15}$$

where W_G is the gas mixture specific consumption, $m^3/(m^3\cdot h)$; U_{MeO} is the metal oxide dissolution rate, mol/h; $\nu(HNO_3)$ is the stoichiometric coefficient of HNO_3 in the reaction (5).

Further, we can neglect a decrease of the system volume due to the NO_2 dimerization and a physical solubility of these components in the liquid phase, multiply both parts of the invariants (9)–(11) by the ratio P/N (where P is the system pressure and N is the total amount of the reaction mixture, mol) and take into account the amount of nitrogen and oxygen, which are released from equilibrium reaction (1). Then, we obtain the following expressions for determination of the equilibrium gas composition during absorption [7]:

$$p_{H_2O}+p_{NO}+S=d+a+S^0, \tag{16}$$

$$p_{HNO_3}-2p_{NO}-2S=e-2a-2S^0, \tag{17}$$

$$p_{NO_2}+3p_{NO}+2p_{N_2O_4}+S=b+3a+2c+S^0, \tag{18}$$

where $a=\frac{n^0_{NO}}{N}P$, $b=\frac{n^0_{NO_2}}{N}P$, $c=\frac{n^0_{N_2O_4}}{N}P$, $d=\frac{n^0_{H_2O}}{N}P$ and $e=\frac{n^0_{HNO_3}}{N}P$ are the partial vapor pressure of

NO, NO_2, N_2O_4, H_2O and HNO_3 before absorption, respectively; $S = \frac{22.4 P n_{Stoc} \cdot 10^3}{V_L}$; V_L is the suspension volume, m^3, ($S^0=0$).

Then, the balance equations (16)–(18), considering equations (12)–(14), can be written in the following form:

$$p_{H_2O} + K_1 p_{NO_2} + S = d + a, \tag{19}$$

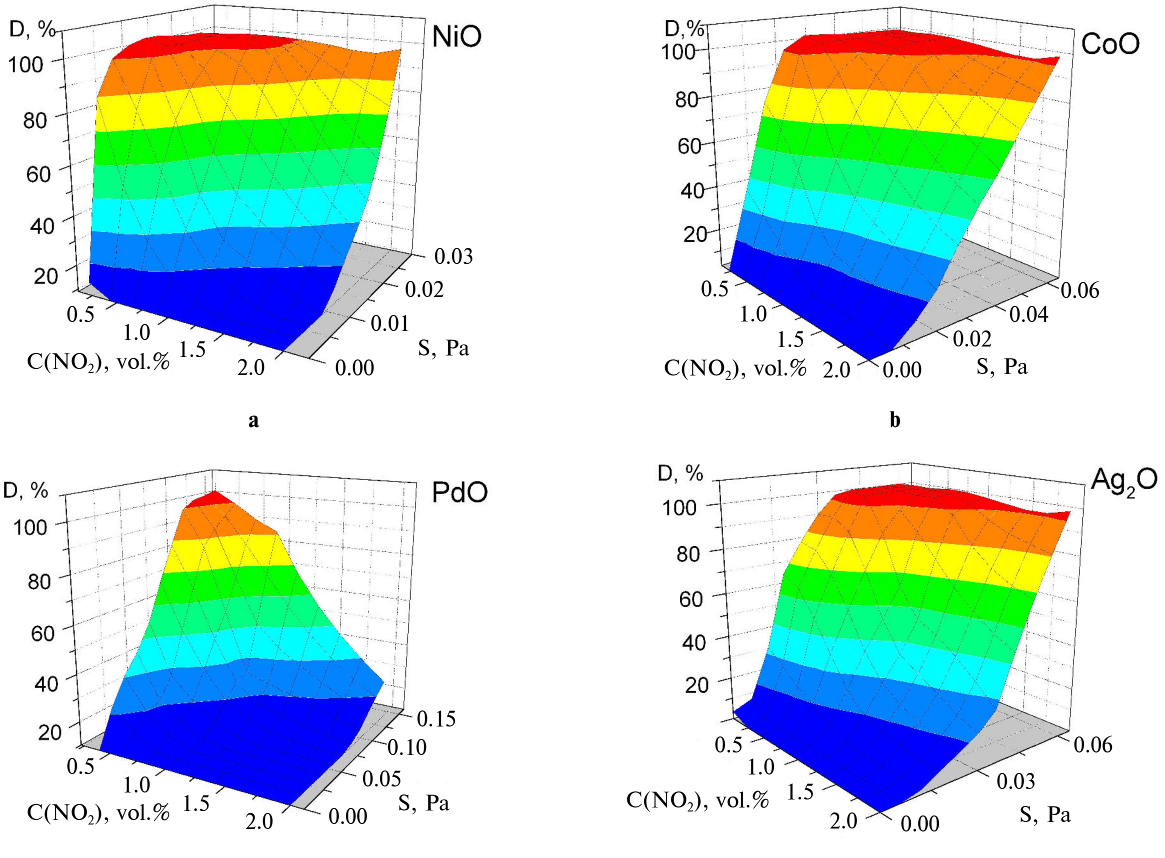
$$(K_2 p_{H_2O})^{1/2} - 2K_1 p_{NO_2}^3 - 2S = e - 2a, \tag{20}$$

$$p_{NO_2} + 3K_1 p_{NO_2}^3 + 2\frac{p_{NO_2}^2}{K_3} + S = b + 3a + 2c. \tag{21}$$

To determine the residual nitrogen oxides amount and calculate their equilibrium conversion degree, the balance equation (21) is commonly used [7]; its solution determines the reaction mixture composition after one absorption step. Equation (21) contains three parameters: (i) the parameter K_1 which depends on the concentration of nitric acid; (ii) the parameter Y=b+3a+2c which depends on the initial composition of nitrous gases; and (iii) the parameter S which depends on the concentration of nitric acid, the initial content of the extracted metal oxide, the suspension volume and the consumption of nitrous gases.

Both K_1 and S simultaneously depend on the concentration of nitric acid. The effect of the nitric acid concentration on K_1 is determined by the well-known dependence, which is given elsewhere [7]. Calculations performed using the shrinking sphere model [10,11] and the kinetic data given in refs. [10,12–14] and some other papers showed that the dissolution rate of Me_nO_m oxide can be written as follows:

$$U_{Me_nO_m} = k_{Me_nO_m}\left(C_{HNO_3} \cdot 10^{-2}\right)^{1.03} M^0_{Me_nO_m} \times$$
$$\times (1 - \alpha_{Me_nO_m})^{2/3}, \tag{22}$$



a b

c d

Fig. 1. The area of displacement of the equilibrium conversion degree of nitrogen oxides when combining the processes of chemisorption of NO_x and extraction of the corresponding metal nitrates from the solid phase: (a) – NiO; (b) – CoO; (c) – PdO and (d) – Ag_2O

where $k_{Me_nO_m}$ is the rate constant of metal extraction from solid phase into solution (h^{-1}). It is equal 1.07, 1.05, 1.103 and 0.022 for NiO, CoO, PdO and Ag_2O, respectively.

Figure 1 presents typical results of the calculation of the equilibrium NO_2 partial pressure displacement due to the process of metal extraction from the catalyst. The abscissa axis shows the values of the parameter S, which characterizes the ratio of the consumption rate of nitric acid to the supply rate of nitrous gas. The ordinate axis shows the parameter D:

$$D=\left(1-\frac{p_{NO_2,\,S\neq0}}{p_{NO_2,S=0}}\right)\cdot100,\%, \qquad (23)$$

where $p_{NO_2,\,S\neq0}$ and $p_{NO_2,S=0}$ are the partial pressures of NO_2 in solutions with $S\neq0$ and $S=0$, respectively (i.e. with and without the extraction process).

The calculations were carried out with the simultaneous change of the parameters K_1 and S using the following experimental data: T=293–298 K; W_G=0.01–0.12 m^3/h (W_G is the specific flow rate of the gas mixture), $C(NO_x)$=0.01–2.00 vol.% (oxidation degree of 80%), the mass of nickel oxide (according to the State Standard No. 17607-72) of 200 g (the solid phase of suspensions is represented by unrestored catalysts with the content of extractable components NiO, CoO and PdO – 0.1 mol/kg, Ag_2O – 0.2 mol/kg), the mass ratio of $H_2O/NiO=6/1$ (in general, $H_2O/kat=6/1$).

The excess HNO_3 concentration in nitrate solutions of catalytically active metals is sought to be minimized in the catalysts production, since an increase in its excess leads to an overrun of reagents-precipitators in the co-precipitated catalysts production and dissolution of supported metal oxides during subsequent impregnations in the supported catalysts production [15]. Therefore, the range of nitric acid concentration variation was limited to 28 wt.% in our study.

The obtained data showed that a simultaneous increase in the parameter S and the nitrogen oxides concentration (i.e. parameter Y) results in a decrease in the equilibrium partial pressure of NO_2 up to values limited by the value of S=0.05–0.08 in the considered range of the initial concentrations of nitrogen (II), (IV) oxides, which corresponds to the value of Y=0.001–0.100 and the initial concentration of nitrogen (II), (IV) oxides of 0.5–1.5 vol.% (Y=0.0001–0.0100). Within this area (S>>Y), the rate of equilibration in the part of the considered liquid-solid phase system is higher than in the part of the considered gas-liquid phase system. Moreover, nitrogen oxides entering into chemisorption do not compensate the consumption of nitric acid due to reaction (4). That is why, we should expect in this area the highest increase in the equilibrium conversion degree of nitrogen oxides due to the combination. The intersection of the curves with the abscissa axis corresponds to the condition Y=S, which corresponds to the equality of the velocities in parts of the liquid-solid phase and gas-liquid phase system and the complete conversion of NO_2 (the parameter D→100%). With a further increase in the parameter S, due to a decrease in the nitrous gases consumption and a simultaneous increase in the parameter Y resulted from an increase in the nitrogen oxides concentration, their equilibrium conversion degree will be determined by the known conditions of HNO_3 formation [7]. The dependences of the parameter S on the initial concentrations of nitrogen (II), (IV) oxides, at which D≈100% for various soluble components of catalysts, are shown in Fig. 2.

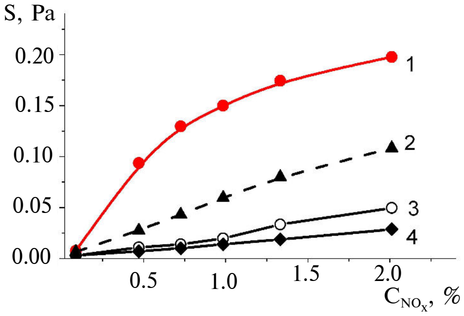


Fig. 2. The dependence of the parameter S on the initial concentration of nitrogen (II), (IV) oxides at which the parameter D≈100% for various soluble components of catalysts: (1) – Pd; (2) – Ag_2O; (3) – Ni; and (4) – Co

As an example, Figure 3 shows the experimental data on the change of the NO_2 conversion degree as a function of the concentration of nitric acid in a system with an inert nozzle and powdered NiO and an unreduced Al–Ni catalyst with a NiO content of 0.1 mol/kg.

At a nitric acid concentration of 6 wt.%, the degree of Ni^{2+} extraction is 12 wt.%, which corresponds to the parameter S=0.005. According to Fig. 1, the parameter D should theoretically be 67% due to the combination processes. The actually achievable value is D=63%.

At $C(HNO_3)$=26 wt.%, the degree of Ni^{2+} extraction reaches 97 wt.%, the parameter S=0.00013. Actually, the parameter D→0, i.e. the equilibrium

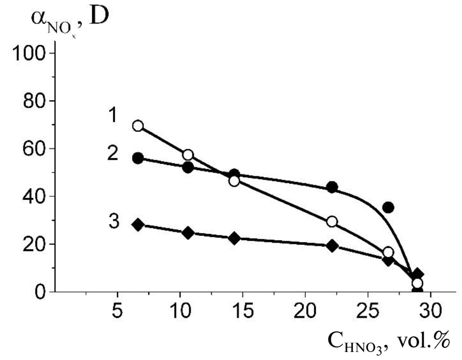


Fig. 3. Dependences of the chemisorption degree of nitrogen oxides (α_{NO_x}) and the parameter D on the nitric acid concentration: (1) – nozzle-catalyst containing 0.1 mol/kg NiO; (2) – the parameter D; (3) – inert nozzle. T=293–298 K, W_G=180 h^{-1}, C_{NO_x}=1 vol.%

conversion degree of nitrogen oxides is determined only by the concentration of nitric acid. This is confirmed by the calculations.

The sequence of calculations was as follows: first, by analogy with [7], the concentrations of nitric acid at the theoretical extraction stage at a known consumption, the composition of the nitrous gas, the extracted metal initial content, and the degree of metal extraction were calculated. Then, the parameters of K_1 and S were determined and equation (21) was solved. The resulting solution of this equation allowed specifying the concentration of nitric acid and the conversion degree of nitrogen oxides at this stage by the iterative method. After that, the next extraction stage was calculated.

When the liquid phase is recirculating, the concentrations of nitric acid, entering the top of the column, and the concentrations of nitrogen oxides in the gas, leaving the column, were calculated at the next time step based on the obtained concentration of nitric acid in the solution, which flows from the catalyst layer.

Conclusions

Equilibrium concentrations of nitrogen (II), (IV) oxides were determined under the conditions of the combined chemisorption process of nitrogen oxides NO and NO_2 from their mixtures with air and the extraction of catalyst metals by an aqueous solution, which is in contact with the spent catalyst and the extractant. The mechanism of the combined process was established and the mathematical model was proposed, which takes into account the processes of the interaction between nitrogen oxides and water that resulted in the formation of nitric acid, its subsequent interaction with the reactive component of the spent catalyst and the extraction of the formed nickel nitrates into the solution.

Using the DIAP-3-6N catalyst, an algorithm for calculating the time variation of the component composition of a three-phase gas–solid phase–liquid system was proposed. A mathematical model of the process was created taking into consideration the dependence of the equilibrium conversion degree of nitrogen oxides on the rate of the consumption of the resulting nitric acid for the extraction of metals from the catalyst.

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МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ РІВНОВАГИ НІТРОГЕН(II), (IV) ОКСИДІВ В СУМІЩЕНОМУ ПРОЦЕСІ ВИЛУЧЕННЯ МЕТАЛІВ ІЗ ВІДПРАЦЬОВАНИХ КАТАЛІЗАТОРІВ

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Наведені результати досліджень рівноваги нітроген(II), (IV) оксидів в умовах суміщеного процесу хемосорбції нітроген оксидів із їх сумішей з повітрям і вилучення металів каталізатора в водний розчин, що знаходиться в контакті з відпрацьованим каталізатором та екстрагентом. Встановлено механізм суміщеного процесу та розроблена математична модель, що враховує процеси взаємодії нітроген оксидів і води з утворенням нітратної кислоти, її наступної взаємодії з реакційноздатним компонентом відпрацьованого каталізатора та вилучення металів, що утворились. Здійснено дослідження та створено математичну модель для визначення рівноважного складу нітроген оксидів у виробництві нітратної кислоти та розрахунку рівноважної концентрації і ступеня перетворення нітроген оксидів в суміщеному процесі. На прикладі каталізатора ДІАП-3-6Н запропоновано алгоритм розрахунку зміни з часом компонентного складу трифазної системи «газ–тверде–рідина». Створено математичну модель процесу, що враховує залежність рівноважного ступеня перетворення нітроген оксидів від швидкості витрачання нітратної кислоти, що утворилась, на вилучення металів із каталізатора.

Ключові слова: хемосорбція, вилучення, суміщений процес, нітроген оксиди, рівноважний ступінь перетворення, методика розрахунку.

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The paper gives the results of the study of equilibrium between nitrogen(II) and (IV) oxides under the conditions of the combined process of nitrogen oxides chemisorption from their mixtures with air and the extraction of metals from spent catalysts by an aqueous solution that contacts with the catalyst and the extractant. The mechanism of the combined process was established and the mathematical model was created that takes into account the interaction between nitrogen oxides and water with the formation of nitric acid, its subsequent interaction with the reactive component of the spent catalyst and the extraction of the formed metal nitrates. The investigation was performed and the mathematical model was developed for the determination of the equilibrium composition of nitrogen oxides in the production of nitric acid and the calculation of the equilibrium concentration and conversion degree of nitrogen oxides in the combined process. DIAP-3-6N catalyst was used as an example and the algorithm was proposed for the calculation of the time variation of the composition of a three-phase system «solid–liquid–gas». A mathematical model of the process was created that takes into account the dependence of the equilibrium conversion degree of nitrogen oxides on the consumption rate of the produced nitric acid in the extraction of metals from the catalyst.

Keywords: chemisorption; extraction; combined process; nitrogen oxides; equilibrium conversion degree; calculation method.

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