Development and identification of a mathematical model of the process of continuous autoclave desorption of noble metals in moving-bed apparatus

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Abstract. The process of continuous autoclave desorption is the most promising for the intensification of coal-sorption technology for extracting noble metals by active carbons from solutions and pulps. The article presents a mathematical model of continuous autoclave desorption of gold from active carbons, which is based on the physicochemical regularities of the process and describes its dynamics. The developed mathematical model of the dynamics of the continuous desorption process allows analyzing the influence of the main parameters on the degree of extraction of gold and silver from activated carbons. It has been established that such parameters as temperature, phase ratio, processing time and pH of the elution solution have the greatest influence. Identification of the mathematical model showed satisfactory agreement between the experimental and the data obtained as a result of the simulation, which confirms the possibility of using it for analyzing and optimizing the process.

1. Introduction
Continuous autoclave desorption of gold from active carbons is the most promising for sorption technologies for extracting noble metals by active carbons from solutions and slurries of hydrometallurgical processing of enrichment industries. The process of desorption is carried out in the apparatus of a continuous principle of action with a counter-current of the liquid and solid phases of the work area under conditions of elevated temperatures and pressures.

Earlier researchers studied the periodic desorption process [1-4]. In the course of studying the patterns of percolation and optimization of the autoclave desorption process, a number of factors complicating the work were identified. On the one hand, diffusion of valuable components from sorbent grains affects. On the other hand, under certain conditions, the decomposition of cyanide complexes of noble metal anions proceeds in parallel. As a result of decomposition of the complex, non-eluted compounds are formed in the coal phase. In this regard, it is necessary to determine the optimal characteristics of the process of continuous autoclave desorption. The method of mathematical modeling was used as an instrumental method for determining the optimal characteristics.

2. Development of a mathematical model
When developing a mathematical model of the dynamics of continuous countercurrent desorption, the following assumptions were made [5-7]:
- saturated active charcoal continuously moves the dense isotropic layer;
-...
grains of activated carbon have the same size;
- isothermal conditions of desorption;
- desorption isotherm linear;
- there is no near-wall effect;
- longitudinal diffusion is absent [8].

The elution solution is introduced at the speed $w$ at the bottom and, after passing through a layer of saturated active carbon, is removed from the top of the apparatus. Saturated active carbon is fed into the upper part of the apparatus and in a dense layer of height $H$ under the action of gravity with a speed of $v$ goes down towards the flow of the elution solution.

The desorption process can be described by a system of differential equations of gold (silver) balance in the solid and liquid phases for the elementary part of the apparatus $dh$:

$$
\begin{cases}
\frac{\partial \alpha}{\partial t} + v \frac{\partial \alpha}{\partial h} = - \frac{\beta_e}{G} \cdot \alpha \\
\frac{\partial C_e}{\partial t} + w \frac{\partial C_e}{\partial h} = \frac{\beta_e}{G} \cdot \alpha \\
\alpha = G \cdot C_e
\end{cases}
$$

$h$ - height of the layer; $\alpha$ - concentration of gold in coal; $G$ - Henry coefficient; $C_e$ - concentration of gold in the eluate; $t$ - time; $v$ - speed of movement of the active carbon; $w$ - flow rate of the eluting solution; $\beta_e$ - effective mass transfer coefficient.

The left parts of the first two equations (1) include the non-stationary terms $\partial \alpha/\partial t$ and $\partial C_e/\partial t$, which are essential only for the starting and transient modes of operation of the apparatus. In stationary conditions of the apparatus, equations (1) are simplified, transforming from partial differential equations into ordinary differential ones:

$$
\begin{align*}
\frac{\partial \alpha}{\partial h} &= -\frac{\beta_e}{G} \cdot \alpha \\
\frac{\partial C_e}{\partial h} &= \frac{\beta_e}{G} \cdot \alpha.
\end{align*}
$$

Boundary conditions for the bottom ($h = 0$) and upper ($h = H$) section coal layer:

$$C_e(0) = 0|_{h=0}; \alpha(0) = \alpha_0|_{h=H}. \quad (4)$$

From equations (2) and (3), it follows that:

$$-v \frac{\partial \alpha}{\partial h} = w \frac{\partial C_e}{\partial h} = \frac{\beta_e}{G} \cdot \alpha$$

or

$$-v \cdot \partial \alpha = w \cdot \partial C_e. \quad (5)$$

After integrating equation (5) under appropriate boundary and initial conditions, we obtain the equation for the gold concentration in the interacting flows in any section of the apparatus, that is:

$$C_e = -\frac{v}{w}(\alpha - \alpha_0). \quad (6)$$

Equations (4) and (5) are not bound to the inner coordinate of the layer and do not depend on the nature of mass transfer.

Previous studies have revealed that simultaneously with desorption in the phase of active coal, irreversible thermal decomposition of gold (silver) cyanocomplexes occurs with the formation of non-desorbed compounds in the form of simple cyanides and metals.

The reaction of the decomposition has the greatest influence on temperature and alkali concentrations in the eluting solution.

The decomposition rate constant $K_d$ can be expressed by the equation:

$$K_d = K_0 \cdot e^{-\frac{E_d}{RT} \cdot \ln C^{'}}$$

$E_d$ - activation energy of the decomposition reaction; $C'$ - alkali concentration in the eluent; $n$ -
empirical coefficient (for Au - 1, for Ag – 0.5); \(K_0\) – pre-exponential factor of the decomposition rate
constant dependence on temperature.

Taking into account the thermal decomposition reaction of cyanocomplexes, equation (2) takes the form:

\[
v \cdot \frac{\partial \alpha}{\partial h} = - \left( \frac{\beta_e}{G} + K_d \right) \cdot \alpha.
\]  

(7)

Thus, the process of continuous autoclave desorption with the foregoing can be described by a system of equations:

\[
\begin{cases}
v \cdot \frac{\partial \alpha}{\partial h} = - \left( \frac{\beta_e}{G} + K_d \right) \cdot \alpha \\
\frac{\partial C_e}{\partial h} = \frac{\beta_e}{G} \cdot \alpha \\
\alpha = G \cdot C_e
\end{cases}
\]

under boundary conditions:

\[C_e(0) = 0 \mid_{h=0}, \alpha(0) = \alpha_0 \mid_{h=H}.
\]

The solution of this system of equations makes it possible to determine the degree of gold (silver)
extraction from active coal depending on the height of the coal
layer in the apparatus, the temperature
regime and the feed rates of coal and the elution solution, as well as the distribution of gold (silver)
concentrations in the coal and in the eluate according to the height of the layer coal.

The velocity \(v\) entering into equation (6) is the volumetric velocity of moving the layer of active
carbon \(H\) through the total cross-section \(S\) of the apparatus:

\[
v = \frac{F}{S} = \frac{H \cdot S}{S \cdot t} = \frac{H}{t}.
\]

\(t\) - time of the coal being in the machine.

We transform the equation (6) to the form:

\[
\frac{\partial \alpha}{\alpha} = - \left( \frac{\beta_e}{G} + K_d \right) \cdot t \cdot \frac{\partial h}{h}
\]

and integrate the right and left parts in the range from \(\alpha_0\) to \(\alpha\) and from \(H_0\) to \(H\), respectively:

\[
\int_{\alpha_0}^{\alpha} \frac{\partial \alpha}{\alpha} = - \int_{H_0}^{H} \left( \frac{\beta_e}{G} + K_d \right) \cdot t \cdot \frac{\partial h}{h}.
\]  

(8)

In the right side of equation (8), the integral sign contains a factor, all members of which do not depend
on the height of the layer of active carbon in the apparatus and can be calculated. Therefore, taking this
factor out of the integral sign and solving the equation, we get:

\[
\alpha = \alpha_0 \left( \frac{H}{H_0} \right)^{\frac{\left( \beta_e + K_d \right) t}{\alpha_0}}
\]  

(9)

\[
H = H_0 \left( \frac{\alpha_0}{\alpha} \right)^{\frac{1}{\left( \beta_e + K_d \right) t}}.
\]  

(10)

The equation (9) includes the rate of the eluting solution, which can be expressed as:

\[
w = \frac{H}{t} \cdot f = v \cdot f
\]

\(f\) - the ratio of the phases of the elution solution and activated carbon.

Substituting the current value of the desorption \(\alpha\) (equation (8)) and the velocity of the eluting solution
(equation (3)) and integrating the right and left parts from \(C_0\) = 0 to \(C_e\) and from \(H_0\) to \(H\), respectively, we get:

\[
w \cdot \frac{\partial C_e}{\partial h} = \frac{\beta_e}{G} \cdot \alpha_0 \left( \frac{H}{H_0} \right)^{\frac{\left( \beta_e + K_d \right) t}{\alpha_0}}
\]

\[
C_e = \frac{1}{f} \cdot \frac{\beta_e}{\beta_e + G \cdot K_d} \cdot \alpha_0 \cdot \left[ 1 - \left( \frac{H}{H_0} \right)^{\frac{\left( \beta_e + K_d \right) t}{\alpha_0}} \right].
\]

The obtained equations (8), (9) and (10) express the dependence of the gold (silver) concentration in
the eluate on the phase ratio \(f\) and the coal treatment time \(t\), the concentration of gold over the height of
the coal layer and are a mathematical description of the dynamics of the continuous autoclave desorption
process.
3. Mathematical Model Identification

To identify the mathematical model, we used experimental data from industrial tests of the continuous autoclave desorption process, as well as the constants previously calculated for the conditions of the periodic process. The preexponential factor for the temperature dependence of the Henry coefficient was $G = 0.2 \times 10^4$; differential heat of sorption $\Delta H = 50.6$ kJ/mol; the apparent activation energy of the decomposition of cyanocomplexes of gold is $E_a = 119.81$ kJ/mol; alkali concentration $C' = 0.2\%$.

In the working chamber of the industrial autoclave desorption apparatus, a dense isotropic layer of active carbon 1.3 m high with a volume of 0.05 m$^3$ was continuously moving. The maximum design capacity of the apparatus according to the eluent was taken to be 1 m/h, the phase ratio was 10:1, the residence time of saturated coal in the working chamber of the apparatus was 30 minutes. When the temperature of the elution solution is 150 °C, the Henry coefficient for saturated active carbon IPI-T is $G = 35.43$, $\beta_e = 0.013$ s$^{-1}$, and for 170 °C (while maintaining the other process parameters) $G = 18.5$, $\beta_e = 0.019$ s$^{-1}$.

According to the calculated model data, when gold concentration is 1 mg/g, in the above modes of process control, gold-containing eluates can be obtained: for 150 °C $C_e = 49.3$ mg/l, and for 170 °C $C_e = 56$, 7 mg/l. According to the results of industrial tests, the mean values of gold concentration in eluates were for temperature 150 °C $C_e = 44.7$ mg/l, and for 170 °C $C_e = 54.7$ mg/l.

Some difference between the data calculated by the model and the experimental ones can be explained by the instability of the temperature regime during the tests, caused by a small temperature gradient of the incoming and outgoing solutions. At the same time, the experimental data are in fairly good agreement with those calculated by the model, which confirms the possibility of using it to analyze and optimize the process of continuous autoclave desorption.

4. Conclusion

A mathematical model of the dynamics of the continuous desorption process has been developed, which allows analyzing the influence of the main parameters on the degree of extraction of gold and silver from active carbons. It has been established that such parameters as temperature, phase ratio, processing time and pH of the elution solution have the greatest influence.

Identification of the model showed satisfactory agreement between the experimental and the data obtained as a result of the simulation, which confirms the possibility of using it to analyze and optimize the process. The resulting mathematical model was used in practical calculations in the design of an experimental-industrial apparatus of continuous desorption of various capacities.

References

[1] Elshin V V, Mironov A P, Ovsvyukov A E 2016 Development of the mathematical model of dynamics of high-temperature desorption of gold with active coals based on physical and chemical representations of the process Nonferrous metals No 12 pp 27–32

[2] Van Deventer J S J, Van Der Merwe P F 1994 The mechanism of elution of gold cyanide from activated carbon Metallurgical and Materials Transactions (B Vol 25) No 6 pp 829–838

[3] Sun T M, Yen W T 1995 A reactor model for gold elution from activated carbon with caustic cyanide solution Canadian Metallurgical Quarterly (vol 34) No 4 pp 303–310

[4] Bhattacharyya D, Depci T, Elnathan F, Miller J D 2014 Effect of activated carbon particle size on the adsorption/desorption of gold from alkaline cyanide solution Proc of 2014 SME Annual Meeting and Exhibit (Salt Lake City 23–26 February) pp 418–420

[5] Korolkov N M, Mikhailov Y A 1987 Mass transfer processes in chemical technology Liquid sorption (Riga: Publishing House Riga polit Institute) pp 1-74

[6] Levenspiel O 1972 Chemical Reaction Engineering (2nd Edn John-Wiley, New York) chapter 15 p 684

[7] Romankov P G, Lepilin V N and Frolov V R 1973 Engineering Methods of Calculating Adsorption and Desorption Processes Kinetics and Dynamics of Physical Adsorption [in Russian] pp 231–237
[8] Elshin V V, Stramok V S 1998 Development and testing of continuous autoclave desorption equipment *Technological and environmental aspects of complex mineral processing* (Thesis of the Report of the International Scientific and Practical Conference, Irkutsk, June) p 132