Studies of the rate of gold sorption by the AM-2B anionite from cyanide-alkaline solutions

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ABSTRACT
The paper presents the results of studies on the sorption leaching of gold-containing ore of the Vasilkovskoye deposit. Kinetic dependences of the sorption of gold and associated metals from cyanide-alkali solutions under different physical and chemical factors were obtained. It was found that gold on the AM-2B resin sorbed at a higher rate than, for example, copper and zinc. The solutions were analyzed using modern devices of a new generation: FT-IR spectrometer "Avatar 370". Laboratory studies were performed to determine the gold sorption rate by the AM-2B anionite from cyanide-alkaline solutions. It was found in the process of sorption of gold from multicomponent cyanide-alkali solutions on AM-2B anionite of mixed basicity, with the macroporous structure containing benzyl dimethylamine and dibenzyl dimethyl ammonium functional groups, that an important factor of qualitative and quantitative separation of gold and impurity metals is the concentration of cyanide and hydroxyl ions in solution. The temperature effect on the sorption rate of gold from cyanide-alkali solutions was studied with the temperature dependences F of t, Bt, ln (1 - F) of t, and D of t that show that the sorption process of dicyanoaurate ions is controlled by mixed diffusion.

Keywords: ore, gold, sorption leaching, anionite AM-2B, cyanidation.

Introduction
The Republic of Kazakhstan is one of the most important gold-producing provinces in the Central Asian region in terms of gold reserves and production. The most important problem of gold hydrometallurgy is the search for rational methods of its extraction from low-grade refractory ores. It is becoming increasingly important as new deposits are discovered and exploited, allowing the gold reserve of the Republic of Kazakhstan to be increased. Theoretical and technological results of the research performed, tests of the main processes intended to process gold-bearing raw materials - leaching of the material, sorption of gold on ion-exchange resins can be used to design and construct production facilities at various gold-bearing deposits in Kazakhstan.

Kazakhstan has significant potential reserves of gold-containing minerals [1]. Geotechnological
methods, in particular heap leaching, are currently considered the most suitable for gold-containing raw materials.

The kinetic characteristics of the process were studied with the purpose to develop a technology intended for the sorption extraction of the target metal (gold). Anion exchanger AM-2B, an effective, easily regenerated sorbent with high mechanical strength and macroporous structure widely used in metallurgy has been applied as sorbents [2, 3].

The search for rational ways to increase the gold extraction completeness is an urgent task due to the annual growth in the processing amount of poor, refractory gold-bearing ores and secondary raw materials.

Modern technology for extracting gold and silver from leach solutions widely uses processes of sorption of cyanide complexes of these metals. Two principal directions were developed: a) sorption with activated carbons [2, 3, 4], b) sorption with synthetic ion-exchangers [5].

The study is relevant, since the concentration of the recovered metal in the external solution and the temperature of the solution are the main factors affecting the ion-exchange sorption rate.

The study of the sorption kinetics is of practical interest, since the rate that determines the ion exchange stage revealed during the experiment, plays a major role with the purpose to solve such practical problems as the choice of conditions for the ion exchanger synthesis or the finished sorbent type.

The objective of this work was to study the gold sorption rate with the AM-2B anionite from cyanide-alkaline solutions

**Experimental part**

The ion exchange process has been actively developed in the CIS countries and is the most promising for the mining industry in Kazakhstan. Gold was one of the first metals that people tried to extract from dilute solutions using ion exchange.

The object of research was the cyanide-alkaline solutions for leaching ore from the Vasilkovskoye deposit.

Experiments intended to obtain productive solutions and sorption extraction were performed under the standard methods. The chemical composition of the test solution is represented by the following main components, mg/dm³: 0.6-2.0 Au; 8.3-40 Cu; 1.1-6.2 Zn; 0.4-8.5 Fe; 0.1-0.5 Co; 0.1-0.5 Ni; 0.07-0.94 Stot. g / dm³; 0.1-0.2 CN- mg/dm³; 0.9-1.2 OH- mg/dm³. The initial cyanide-alkaline solutions were obtained by leaching gold-bearing ores of the Vasilkovskoye deposit, containing 1.4 - 3.4 g/t of gold. Sorption products. i.e. solution and cake were subjected to atomic adsorption and assay types of analysis, respectively. The research used AM-2B grade resin. produced by “Resins” State Enterprise, Ukraine.

Before sorption, the resin was pre-saturated with OH-ions, by treatment with a 5% NaOH-solution to convert the sorbent into the OH-form. The process was controlled by the solution pH

**Discussion of the results**

Productive gold-containing solutions obtained from agitation leaching are sent for sorption extraction. Ion-exchange resins or activated carbons are used as sorbents in industrial practice [6], [7], [8], [9], [10], [11], [12].

The ion exchange process in the anionite solution system was studied in a static mode in thermostated Plexiglas cells equipped with a mechanical stirrer. Sampling was performed periodically. The total number of samples taken for analysis did not exceed 5% of the initial amount of the solution.

Tests on sorption extraction of gold from multicomponent solutions obtained by leaching-filtration scheme were performed in laboratory conditions. Gold was leached with the cyanide-alkali solution. AM-2B anionite was used as sorbents. Anionite AM-2B is a macroporous ion-exchange resin based on a copolymer of styrene with divinylbenzene, containing strong and weakly basic functional groups in its structure. The presence of bifunctional tertiary groups containing nitrogen atoms capable of forming active groups with metals (i.e., forming complexes) in combination with a high exchange capacity and a good (due to the macroporous matrix) exchange rate makes it possible to selectively extract anionic metal complexes.

Obtaining the kinetic characteristics is necessary to justify the regime of the proposed sorption technology for the extraction of gold from solutions.

One of the main factors affecting the rate of ion-exchange sorption is the concentration of extractable metal in the external solution and solution temperature.

**Effect of the concentration of gold in the solution on the sorption rate.** Rate changes during sorption under static conditions were studied depending on gold concentration, temperature, and the presence of impurities in the solution. In the experiments
presented, the concentration of gold in the initial solutions varied within the range of 0.005-0.11 mg-eq / dm³; the concentration of CN⁻ and OH⁻ was constant and amounted to 0.04 and 0.56, respectively; the same amount of sorbent (V, ml) was added to the sorbent weight (m, g) V: m = 2000.

Sampling was performed in 30 minutes, then in an hour during the day. The gold concentration in the solution after sorption was determined by atomic absorption spectrometry.

Experimental data on the effect of the concentration of dicyanoaurate ions on the degree of gold exchange are presented in the form of curves in Figure 1, and the rate of gold sorption on Figure 2. It is noted that the degree of exchange (F) of dicyanoaurate ions increases depending on the time of contact of the phases and the concentration of gold in the initial solution; the sorption rate increases proportionally with an increase in the concentration of the external solution concerning the extracted ion. The experimental data obtained indicate that the sorption process is limited by both external and internal diffusion, that is, the process proceeds in a mixed region with the predominance of either external diffusion or intra-diffusion limitations at each stage of sorption.

The temperature dependences F of t, Bt of t, ln(l-F) of t, and D of t were determined when studying the effect of temperature on the sorption rate of gold from cyanide-alkali solutions that show that the sorption process of dicyanoaurate ions is controlled by mixed diffusion (Figures 3 and 4). Curvilinear relations F on t, ln(l-F) on t and W on t confirm the mixed nature of the gold sorption kinetics (Table 1).

Studies on the temperature effect on the gold sorption from cyanide-alkaline solutions with a low content of cyanide and hydroxyl ions have found that the most favorable temperature for the dicyanoaurate ions sorption is 298 K. An increase in temperature to 308 - 318 K, as well as a decrease to 288 K is negative affects the gold sorption rate and depth [[13], [14], [15], [16]].

As can be seen from the data obtained, with an increase in temperature to 303 K, the exchange degree insignificantly but evenly increased during 6 sorption hours at a temperature of 288; 294; 303 K and was 0.85; 0.98 and 1.0, respectively. The exchange degree begins to decrease and in 6 hours of sorption reaches only 0.93 with an increase in temperature over 303 K.
It can be stated that an increase in temperature to 303 K slightly increases the process of gold sorption on the AM-2B anionite from cyanide-alkaline solutions, and with a further increase in temperature (more than 303 K), the rate of gold sorption decreases.

Changes in the rate during sorption were studied depending on the concentration of cyanide and hydroxyl ions in the solution, as well as gold and temperature.

The results are presented in tables 2 and 3. The sorption rate is directly proportional to its concentration in the solution: the higher the concentration of the external solution increases, the higher the penetration of counterions of the boundary layer into the inner layers of the sorbent also increases as well. Similar dependencies were obtained when studying the effect of temperature on the sorption rate of gold (Table 3).

As the temperature increases, the sorption rate decreases that can be explained by the following reasons. A dynamic equilibrium between the ions entering and leaving the resin at each period is established in the sorption process. Probably, as the time increases above a certain temperature, the rate of reverse desorption of gold ions increases reducing the rate of direct sorption.

The IR-spectroscopic method of studying the materials was performed using an "Avatar 370" IR-Fourier spectrometer. According to the results, the infrared spectroscopy analysis showed that absorption bands of valence ν(OH) - 3439 cm⁻¹, strain δOH-1647 cm⁻¹, and librational ν L H2O - 632 cm⁻¹ vibrations of molecular water were recorded in the spectrum (Figure 5) [17]. Group [NCS]⁻ vibrational ν OH was 1.452; δ OH, ν L H2O were measured. Optical density at the maxima of absorption bands corresponding to stretching vibrations of water ν OH was 1.452; deformational vibrations of water δ HOH - 0.548; librational water fluctuations ν L H2O - 0.495. The optical density at wave number 1118 cm⁻¹ was 0.034 at the maximum absorption band that characterizes the ν4(E) fluctuation of the cyanide ion. The optical density at the absorption band maximum at wave number 995 cm⁻¹ that characterizes the ν1(A1) cyanide ion vibration, was 0.035.

| Table 1 - Effect of temperature on the exchange degree, diffusion coefficient and sorption rate of gold (CAu = 0.025 mg-eq/dm³) |
|-----------------|----------------|-----------------|----------------|
| Temperature, K  | Time, h         | Exchange degree, F | ∆F/∆t, mg-eq/s |
| 288             | 0.5            | 0.14            | 6.9-10⁻⁷      |
|                 | 1.0            | 0.33            | 9.98-10⁻³     |
|                 | 2.0            | 0.56            | 3.5-10⁻⁷      |
|                 | 4.0            | 0.78            | 9.94-10⁻³     |
|                 | 6.0            | 0.85            | 5.5-10⁻⁶      |
|                 | 8.0            | 0.92            | 9.0-10⁻⁶      |
|                 | 10.0           | 1.0             | 9.0-10⁻⁶      |

The results are presented in tables 2 and 3. The sorption rate is directly proportional to its concentration in the solution: the higher the concentration of the external solution, the more ions penetrate deep into the sorbent. The rate of penetration of counterions of the boundary layer into the inner layers of the sorbent also increases as well. Similar dependencies were obtained when studying the effect of temperature on the sorption rate of gold (Table 3).

As the temperature increases, the sorption rate decreases that can be explained by the following reasons. A dynamic equilibrium between the ions entering and leaving the resin at each period is established in the sorption process. Probably, as the time increases above a certain temperature, the rate of reverse desorption of gold ions increases reducing the rate of direct sorption.

| Table 2 - Change in the gold sorption rate over time at different concentrations in solution, mg-eq / dm³ |
|-----------------|----------------|----------------|
| Time, h         | CAu = 0.005    | CAu = 0.025    | CAu = 0.110   |
| 0.5             | 5              | 15             | 150           |
| 2.0             | 13             | 28             | 122           |
| 4.0             | 6              | 18             | 74            |
| 6.0             | 3              | 10             | 41            |
| 8.0             | 3              | 8              | 30            |

| Table 3 - Change in the gold sorption rate over time at different process temperatures mg-eq / s |
|-----------------|----------------|----------------|
| Time, h         | 288 K          | 294 K          | 303 K         | 313 K         |
| 0.5             | 12             | 12             | 14.5          | 21.9          |
| 1.0             | 15             | 17             | 20.8          | 22.6          |
| 2.0             | 13.6           | 14.8           | 15.7          |               |
| 4.0             | 8.8            | 9.5            | 9.2           |               |
| 6.0             | 6.7            | 7.2            | 7.3           |               |
| 8.0             | 4.7            | 5.3            | 5.3           |               |
Thus, it can be concluded based on the studies performed to determine the rate of gold sorption by the AM-2B anion exchanger from alkaline cyanide solutions that the amount of gold in the ion exchanger after treatment does not change and decreases with the use of alkaline cyanide solutions. Anionite of mixed basicity AM-2B shows high selectivity for gold [18, 19, 20, 21].

**Conclusions**

Laboratory studies to determine the gold sorption rate by the AM-2B anion exchanger from cyanide-alkaline solutions were performed. It was found in the process of gold sorption from multicomponent cyanide-alkaline solutions on AM-2B anionite of mixed basicity with the macroporous structure containing benzyl dimethylamine and dibenzyl dimethyl ammonium functional groups, that an important factor of qualitative and quantitative separation of gold and impurity metals is the concentration of cyanide and hydroxyl ions in solution. The temperature effect on the gold sorption rate from cyanide-alkali solutions was studied with the temperature dependences F of t, Bt, of t, ln (1 - F) of t, and D of t that shows that the sorption process of dicyanoaurate ions is controlled by mixed diffusion.

**Conflict of interests.** On behalf of all authors, the correspondent author declares that there is no conflict of interest.

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Исследования скорости сорбции золота анионитом AM-2B из цианидно-щелочных растворов

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АННОТАЦИЯ
В работе представлены результаты исследований по сорбционному выщелачиванию золотосодержащей руды Васильковского месторождения. Получены кинетические зависимости скорости сорбции золота и сопутствующих металлов из цианидно-щелочных растворов при различных физико-химических факторах. Установлено, что золото на смоле AM-2B сорбируется с большей скоростью, чем, например меди и цинк. Рассчитывали с использованием современных приборов нового поколения: ИК-спектрометра «Avatar 370». Проведены лабораторные исследования по определению скорости сорбции золота анизонитом AM-2B из цианидно-щелочных растворов. В процессе сорбции золота из многокомпонентных цианидно-щелочных растворов на анизонит AM-2B, смешанной основности, макропористой структуре с бензилдиаминамиами и дин-диаминами-аммониевыми функциональными группами, установлено, что важным фактором качественного и количественного разделения золота и примесных металлов являются концентрации цинка и гидроксили-ионов в растворе. При изучении влияния температуры на скорость сорбции золота из цианидно-щелочных растворов установлены температурные зависимости F от t, Bt от t, ln (t - F) от t и D от t, которые показывают, что процесс сорбции дицианоаурат-ионов контролируется смешанной диффузией.

Ключевые слова: руда, золото, сорбционное выщелачивание, анизонит AM-2B, цианирование.
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