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Evaluation of sorption properties of «sodium oleate – sulfhydryl collectors» mixtures on copper-lead ore samples

The kinetic and thermodynamic parameters of the sorption process for mixtures of oxy-hydryl and sulf-hydryl collectors on the Ayak-Kodzhan deposit ore samples were determined in this paper. An analysis of sorption isotherms oxy-hydryls and sulfhydryls howed a tendency to the formation of the adsorption layer is not the entire surface of the particles. Preferably in the micropores (macro and mesopores), energy interaction «adsorbate-adsorbent» is defined as the structure of the adsorbent and adsorbate structure (sulfur — and oxygen-collectors), and hence, value of parachor and molear volume.

Key words: oxy-hydryl and sulfhydryl collectors, sodium oleate, adsorption, Gibbs energy of adsorption, adsorbate, molar volume, sorption isotherms, thermodynamic parameters.

Introduction

Currently, the mining and metallurgical cluster in connection with the depletion of the main large deposits of ore minerals at the fore front enhancement processing refractory materials that require the use of new technological methods and reagent modes [1]. Consequently, the current is the assessment of the sorption properties of mixtures reagents that are individually able to allow to extract minerals containing hard and soft cations.

Experimental

According to elemental analysis of Ayak-Kodzhan deposit ore is mixed (oxydized and sulfide). The main useful component is copper, is essential as lead, and from impurities — molybdenum, titanium, present in minor amounts any cadmium, nickel and manganese. From the data of X-ray analysis shows that Ayak-Kodzhan deposits ore represented mainly chalcocite, galena, cuprite, pyrite and gangue — silica, aluminum silicates. Elemental analysis was performed on the ore grade instrument (Spektrolab) and X-ray analysis was performed X-ray diffractometer (XRD-7000 Shimadzu).

Working solutions of collectors mixtures (in a ratio of 1: 1 for two-component, in a ratio of 1:1:1 ternary mixture) were prepared by diluting the concentrated solutions of the individual collectors to a concentration of 10^{-4} mole·l^{-1}. Determination sorption properties of collector's mixtures surface polymetallic Ayak-Kodzhan deposit ore is carried out according to the method described in [2].

Adsorption equilibrium constants were calculated by the formula

$$C_L = C_M \frac{V_M}{V_L}, \tag{1}$$

where C_L and C_M are respectively, the concentration of the ligand and metal; V_L, V_M — are their volumes.

Adsorption values are calculated according to the equation:

$$A = \frac{\left(C_0 - C_p\right)V}{m}, \tag{2}$$

where C_0, C_p — are the initial and the equilibrium concentration of the individual collectors in mole·l^{-1}; V — is the volume of individual collectors in which the adsorption process, ml; m — amount of adsorbent, g.

$$\lg A = \lg K + {}^{1}\!/_{n} \lg C_p. \tag{3}$$

$\lg A$ and C_p values determine the constants of Freundlich – Bedekker′sequation (3) or the graphical method of least squares.

Results and discussion

The energy characteristics the sorption of sodium oleate, and other phosphorus collectors based on the adsorption data for potassium butyl xanthate and sodium dibutyldithiophosphates were calculated (Table 1).

Table 1

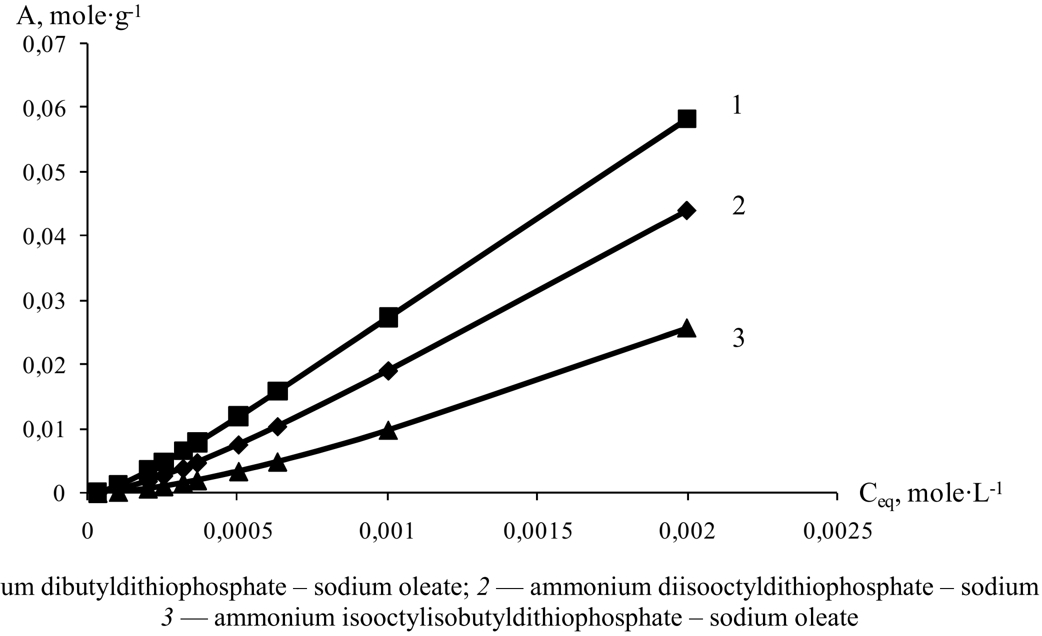
The sorption characteristics of sulfur and oxygen containing collectors for Ayak-Kodzhan deposit ore

Collector	C_s, M	a_m, mole / g	E_a, kJ·mole^{-1}	V_n, cm^3 / g	P, g$^{1/4}$·cm^3··s$^{1/2}$·mole^{-1}	lgK_s	$-\Delta G_{\text{ads}}$, kJ·mole^{-1}
$C_4H_9OCS_2K$	5.32	1.21	8.568	204.72	1144	2.44	13.92
$(C_4H_9O)_2PS_2Na$	2.72	1.64	9.590	271.05	1046	2.09	11.93
$C_{17}H_{35}COONa$	0.17	1.60	7.838	276.77	1280	3.11	17.75
$(C_4H_9O)_2PS_2NH_4$	2.69	1.47	4.508	249.19	601.7	8.92	50.9
$(i\text{-}C_8H_{17}O)_2PS_2Na$	1.99	1.64	10.15	278.21	1354.21	1.95	11.13
$(i\text{-}C_8H_{17}O)_2PS_2NH_4$	1.96	1.57	6.815	266.49	909.7	4.06	23.17
$(i\text{-}C_4H_9O)(iC_8H_{17}O)PS_2NH_4$	1.87	1.53	5.634	259.27	752.1	5.84	33.32
$(i\text{-}C_4H_9O)(iC_8H_{17}O)PS_2Na$	1.78	1.61	8.010	271.75	1196.62	3.00	17.12

Analysis of the data in Table 1 provides an indication of the capacity for adsorption is observed, which of sodium oleate is maximum, sodium dibutyldithiophosphates is minimum. Since, in this case, a mixture of collectors is sorbed (but its not individual is collector, there is a competition for the formation of a complex adsorption center — adsorbate).

It is also shown that the minimum activation energy formation of a sorption complex is observed for ammonium dibutyldithiophosphates, and the maximum for ammonium diisooctyldithiophosphates. Consequently, in the first case will be the most durable layer adjacent to the surface of the ore particles and the second layer is formed mainly of the adsorptive molecules and located at the interface between the solution-gas, which confirms the high foaming properties of sodium diisooctyldithiophosphates.

Further, based on the energy parameters listed in Table 1, equilibrium constants of sorption process diisooctyldithiophosphates collectors mixtures on the surface of the Ayak-Kodzhan deposit ore were calculated. Analysis of sorption curves (Fig. 1) showed that the mixture of sodium dibutyldithiophosphate — sodium oleate on the micropores was adsorbed, and for the adsorbate characterized by the formation of complexes in the pores smaller than for mixtures of ammonium isooctylisobutyldithiophosphates and ammonium diisooctyldithiophosphates. Next, changes of adsorption values the for mixtures of sodium diisooctyldithiophosphate — sodium oleate and potassium butyl xanthate — sodium oleate (Fig. 2, 3), were calculated.



1 — sodium dibutyldithiophosphate – sodium oleate; *2* — ammonium diisooctyldithiophosphate – sodium oleate; *3* — ammonium isooctylisobutyldithiophosphate – sodium oleate

Figure 1. Adsorption isotherms of mixtures sulfur- and oxygen containing collectors on the surface of Ayak-Kodzhan deposit ore

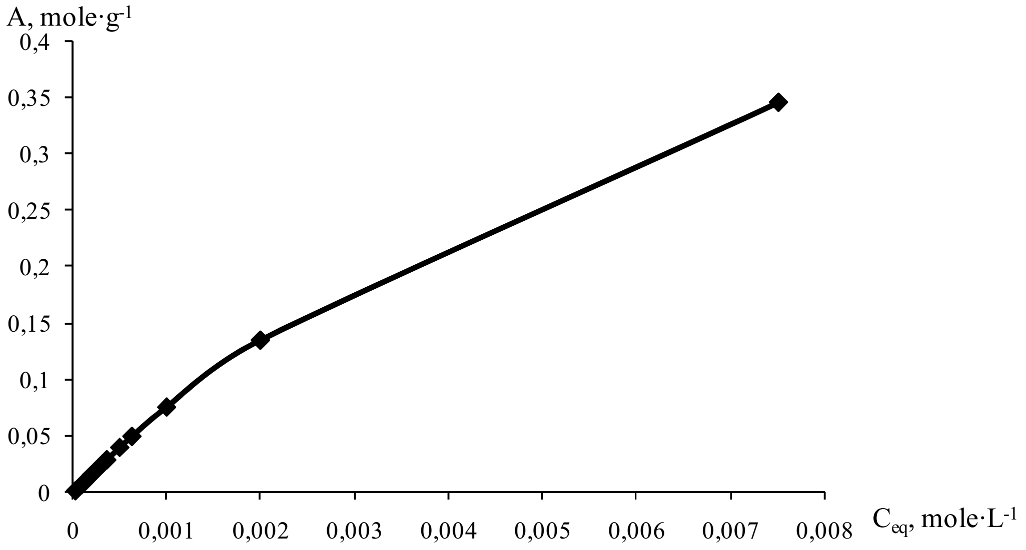


Figure 2. Sorption isotherms sodium diisooctyldithiophosphate – sodium oleate on samples of copper-lead ore

It is shown that the change in the adsorption of the adsorbate concentration in the solution can be attributed the interaction of sorbate to the Langmuir type on microporous adsorbents having macro-pores in its structure. Typical sor mixtures potassium is sodium oleate. The specific interaction on sulfides of transition metals (copper in this case), and oxydation products shouwed (Fig. 3).

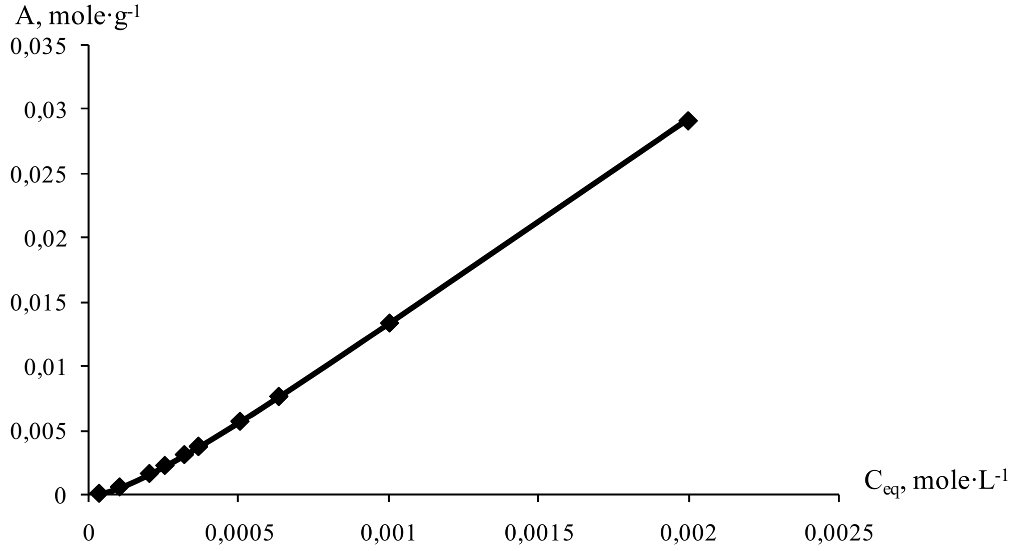


Figure 3. Sorption isotherms potassium butyl xanthate – sodium oleate

According to the BET theory convex portions of II and IV types isotherm (Langmuir adsorption) indicate the presence of micropores in the sorbent, but, moreover, sorbents II and IV also have macroporosity. Isotherms III and V types are less common and represent a strong intermolecular interaction in the material sorbate. The slope of the isotherm of type I characterizes the size of the micropores of sorbents: *a* — ultra microporous, *b* — microporous. Isotherm IV *b* belongs transitional porous sorbent; IV *b* — homogeneous macroporous and IV *a* — with a mixed structure. The steeper the isotherm, the finer micropores. The limit value of such a adsorption A_{lim} corresponds covering the surface monolayer. Concave portions indicate the presence of macropores [3].

Isotherm of monomolecular adsorption on microporous adsorbents usually takes the form shown in Figure 1. This curve has two straight segments — small and large values of the equilibrium concentration of adsorbate. As the vapor adsorption and adsorption is carried out from solutions in pores with a radius 0.5–1.6 nm.

It is shown that the sorption process of a mixture is preferably at an exchange mechanism, with the strongest collector reacts with the active sites of the surface, while the less active or collector forms complexes with metal ions of the crystal lattice, or interacts with another collector via hydrogen bonds. Those, in this case it is necessary to consider the change of energy in the process of breaking the bonds «adsorbent adsorbent» and «adsorbate – adsorbate» and the formation of compounds «adsorbent – adsorbate» that quantitatively described by the Aranovich-Tolmachev equation for monolayer adsorption. However, the sorption analysis data gives an indication of the presence of multiple layers of material on the surface of the ore particles. The results are shown in the Table 2.

Table 2

The sorption characteristics for mixtures of sulfur and oxygen containing collectors for Ayak-Kodzhan deposit ore

Sorbate	lg$K$	N	$-\Delta G_{ads}$, kJ·mole^{-1}
$(C_4H_9O)_2PS_2Na - C_{17}H_{33}COONa$	2.85	0.78	16.24
$C_4H_9OCS_2K - C_{17}H_{33}COONa$	8.07	0.42	46.06
$(i\text{-}C_8H_{17}O)_2PS_2Na - C_{17}H_{33}COONa$	29.40	0.13	167.76
$(i\text{-}C_8H_{17}O)(\text{i-}C_4H_9O)PS_2NH_4 - C_{17}H_{33}COONa$	10.36	0.33	59.11
$(i\text{-}C_8H_{17}O)_2PS_2NH_4 - C_{17}H_{33}COONa$	3.38	0.71	19.25
$C_4H_9OCS_2K - (i\text{-}C_8H_{17}O)_2PS_2Na - C_{17}H_{33}COONa$	11.36	0.26	64.84
$(i\text{-}C_8H_{17}O)(C_4H_9O)PS_2NH_4 - C_4H_9OCS_2K - C_{17}H_{33}COONa$	1.70	1.00	9.69

From the literature [3] it is known that for a quantitative thermodynamic characteristics of adsorption is used to reduce the value of the standard free energy adsorption. Since dispersion forces causing physical adsorption additive. A.V.Kiselev [3] reduced payment to reduce the free energy of adsorption of molecules to the calculation of the standard increments to reduce the free energy of adsorption, due to certain structural elements of the adsorbate molecules [4]. Those, under this assumption, the value of the Gibbs energy of adsorption for individual collectors must contribute at adsorption mixture. It is shown that the most intensive process of sorption proceeds to mixture of sodium diisooctyldithiophosphate- sodium oleate, followed by a decrease in the sorption capacity of the mixture located potassium butyl xanthate — of sodium diisooctyldithiophosphate — sodium oleate, sodium oleate — potassium butyl xanthate, for other mixtures collectors sorption process is dynamic in nature and is associated with the occurrence of the reverse reaction (desorption), or the destruction of the sorption complex.

Thus, the sorption constants of individual collectors, namely potassium butyl xanthate, sodium dibutyldithiophosphates higher compared with other collectors. The energy characteristics of securing process of collectors on the surface of the ore, allowing to identify the most effective individual collector, namely ammonium dibutylditiophosphate were determined. The data are interpreted in terms of the theory volume filling of micropores. It is possible to calculate the amount of adsorption for a mixture of collectors and determine the nature of the consolidation process ore of the collectors molecules on the ore surface. The theoretical sorption isotherms in good agreement with the experimental data of sorption constants of Freundlich equation for a mixture of collectors.

References

1 *Игнаткина В.А., Бочаров В.А., Хачатрян Л.С., Баатархуу Б.* Флотация порфировых медно-молибденовых руд с использованием различных собирателей и вспенивателей // Горный журнал. — 2007. — № 7. — С. 321–329.

2 *Амерханова Ш.К., Шляпов Р.М., Уали А.С.* Физико-химические параметры процессов адсорбции дибутилдитиофосфатов щелочных металлов и аммония на границе твердое тело–жидкость // Сорбционные и хроматографические процессы. — 2011. — № 5. — С. 607–614.

3 *Теряева Т.Н., Костенко О.В., Исмагилов З.Р., Шикина Н.В., Рудина Н.А., Антипова В.А.* Физико-химические свойства алюмосиликатных полых микросфер // Вестн. Кузбасского гос. техн. ун-та. — 2013. — Т. 99, № 5. — С. 86–90.

4 *Когановский А.М., Клименко Н.А., Левченко Т.М., Марутовский Р.М., Рода И.Г.* Очистка и использование сточных вод в промышленном водоснабжении. — М.: Химия, 1983. — 288 с.

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Мыс-қорғасынды кен үлгілеріне натрий олеаты мен сульфгидрильді қоспалар жинағыштарының сорбциялық қасиеттерін бағалау

Мақалада Аяқ-Қоджан кен орнының кендерінің үлгілеріне оксгидрильді және сульфгидрильді жинағыштар қоспаларының сорбция процесінің термодинамикалық және кинетикалық параметрлері анықталды. Сорбция изотермінің талдауы адсорбциялық қабықтың бөлшектердің толық бетінде емес, тек микроқуыстарда (макро- және мезоқуыстарда) түзілетіні, «адсорбат – адсорбент» әрекеттесу энергиясы адсорбенттің және адсорбат құрылымымен (күкірт және оттегі бар жинағыштармен), яғни парахор және мольдік көлеммен, анықталатыны көрсетілді.

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Оценка сорбционных свойств смеси олеата натрия и сульфгидрильных собирателей на образцах медно-свинцовой руды

В статье определены кинетические и термодинамические параметры процесса сорбции для смесей оксгидрильных и сульфгидрильных собирателей на образцах руды месторождения Аяк-Коджан. Анализ изотерм сорбции показал склонность к образованию адсорбционного слоя не на всей поверхности частиц, а преимущественно в микропорах (макро- и мезопорах), энергетика взаимодействий «адсорбат – адсорбент» определяется как структурой адсорбента, так и структурой адсорбата (серо- и кислородсодержащих собирателей), а следовательно, величиной парахора и мольным объемом.

References

1 Ignatkina V.A., Bocharov V.A., Khachatryan L.S., Baatarhuu B. *Gorny zhurnal*, 2007, 7, p. 321–329.

2 Amerkhanova Sh.K., Shlyapov R.M., Uali A. *Sorption and chromatographic processes*, 2011, 5, p. 607–614.

3 Teryaeva T.N., Kostenko O.V., Ismagilov Z.R., Shikina N.V., Rudina N.A., Antipova V.A. *Bull. of the Kuzbass State Technical University*, 2013, 99, 5, p. 86–90.

4 Koganovsky A.M., Klimenko N.A., Levchenko T.M., Marutovsky R.M., Roda I.G. *Treatment and use of wastewater in industrial water supply*, Moscow: Khimiya, 1983, 288 p.