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A. N. BERKINBAYEVA[1], Z. D. DOSYMBAYEVA[1], R. Kh. SHARIPOV[1], B. T. ZHEKSEMBIYEVA[2]*

*[1]Kazakh-British Technical University, Almaty, Kazakhstan, *e-mail: ainur_kbk@mail.ru*
[2]Kazakh State Women's Pedagogical University, Almaty, Kazakhstan

ELECTROCHEMICAL LEACHING OF REFRACTORY SULFIDE ORE WITH AN APPLICATION OF THE SULPHUR-GRAPHITE ELECTRODE

Abstract: The article presents results of the study on extraction of non-ferrous and precious metals from refractory sulphide ores using sulphur- graphite material as a source for obtaining the leaching agent. To conduct experiments, sulphur- graphite electrode was made containing 65 % sulphur. It is found that under the anodic polarization of sulphur- graphite electrode in a solution of sodium hydroxide, sulphide ore is well-opened with selective gold recovery. Among the non-ferrous metals, the following are passing into the solution: copper, manganese, chromium and zinc in minor amounts. The optimal process parameters: current density i - 180 A/m^2, the concentration of sodium hydroxide - 1.0 M - 2.0 M, stirring the solution at a speed of 480 rev/min. Under cathodic polarization of sulphur- graphite electrode, gold, copper, manganese, chromium and zinc extracted well into the solution. Thus, the leaching in the presence of sulphur- graphite electrode in a solution of sodium hydroxide allows to combine the preparation of the leaching agent and recovering of non-ferrous and precious metals from ores in a single reactor volume. Moreover, the use of sulphur-graphite electrode allows gradual leaching in a single reactor. In the first step of under anodic polarization of sulphur- graphite electrode, an extraction of gold in the solution occurs. After replacing a solution, which is rich in gold, with the fresh sodium hydroxide solution, extraction of non-ferrous metals can be carried out (copper, manganese, chromium and zinc) by cathodic polarization of sulphur- graphite electrode. Electro leaching is carried out with high efficiency at relatively low temperatures, which saves energy and expensive reagents in the organization of technological processes.

Keywords: The electrochemical leaching, noble and non-ferrous metals, the electrode extraction degree

Introduction. Refractory ores amount up to 75-80 % of the mineral resource base of non-ferrous metallurgy in Kazakhstan. Existing technologies do not provide sufficiently efficient recovery of noble and non-ferrous metals from these ores.

Analysis of the patent studies and scientific literature demonstrates that the problem solving oriented research related to the individual types of raw materials and a special reagent regime of technological processes dominate among others, while the most relevant objective is the topic of the complex processing of raw materials with differentiated extraction of precious and non-ferrous metals.

Solving the problem of waste from gold ore mining and enrichment production is constrained by lack of research in the field of technologies for extracting gold from low-grade raw materials. The issues in obtaining gold from the accumulated waste of mining and ore processing at the final stage of development of gold deposits form a separate major problem of mining science and practice [1–3].

It is known that the most common used method of cyanide leaching of gold is not environmental friendly, moreover, it is ineffective to extract the gold from the carbon and organic material, and it is sensitive to the presence of copper, zinc, nickel, antimony and arsenic.

Modern alternative to cyanide leaching and thiosulfate is thiocarbamide leaching. It is well known that thiosulfate tends to form complex compounds with metals. For example, the process of thiosulfate leaching of gold proceeds by the following reaction:

$$4Au + O_2 + 8S_2O_3^{2-} + 4H^+ = 4[Au(S_2O_3)_2]^{3-} + H_2O$$

The resulting gold thiosulphate complex is extremely durable (instability constant $4.0 \cdot 10^{-30}$) [4].

Thiosulphates of alkali metal are safe and biodegradable, which allow their use in geotechnologies underground and heap leaching; they are cheaper than cyanides and more effective in the case of refractory ores containing carbonaceous and copper [5 - 7].

In the research [8] a possibility of obtaining an electrode for sulphur- graphite electrode for obtaining the sulphur-containing compounds (thiosulfate, sulphate, sulphides, polysulfides and hydrogen sulphide, sulphite) in a solution of alkaline electrolytes. It is shown that when the polarization of the cathode electrode, sulphur sulphide, polysulfide or sulphide ions can occur and, during anodic polarization - sulphite, thiosulfate- and sulphate ions which promote the formation of complex compounds with most metals present in refractory ores and thereby facilitate the transition of the liquid phase.

Thus, it was of interest to investigate the effect of sulphur-containing, obtained during the dissolution of the sulphur- graphite electrode, on the processes of extraction of non-ferrous and noble metals from persistent sulphide ores.

Experimental procedure. The degree of extraction of metals in the solution as a function of the electrolyte concentration and the composition of cakes obtained after leaching were determined by chemical analysis and atomic absorption spectrometer "contrAA 300".

Studies of the dissolution of sulphide ore were carried out in a specially designed three-electrode cell, including a working electrode- sulphur- graphite, a reference electrode-silver chloride and auxiliary electrode-graphite.

Optimal parameters of the leaching process were preliminarily determined: the current density is 180 A/m^2, the speed of mixing the solution is 480 rpm, the phase ratio S:L is 1:10.

The degree of extraction of metals from ore depending on the different concentration of sodium hydroxide - 0.1 M, 0.5 M, 1.0 M and 2.0 M when using a sulphur-graphite electrode as an anode and a cathode was studied.

Experimental part and discussion of results. In the study of electro leaching of nonferrous and noble metals using a sulphur- graphite electrode, the sulphide ore was used, the content of which was, %: Au (g/t) –1.12; Ag (g/t) – 33.61; Pb – 2.08; Fe – 5.1; Cu – 0.2; Zn – 0.34; $S_{total.}$ - 15.05; $S_{sulfide}$ – 14.45; Ca - 1.08; C_{total} – 6.9; C - 4.7; SiO_2 – 30.22; Al_2O_3 – 1.4; $BaSO_4$ – 27.8; Sb – 0.007; Mn – 0.08.

In the first series of experiments, the sulphur-graphite electrode was used as the anode, and the cathode was a graphite electrode. Leaching was carried out at various concentrations of sodium hydroxide: 0.1 M, 0.5 M, 1.0 M and 2.0 M.

Figure 1 presents data on gold recovery depending on the different electrolyte concentrations.

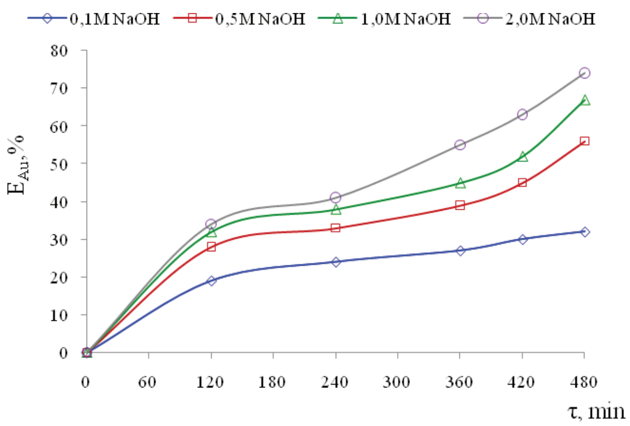

Figure 1 – Extraction of gold from persistent sulphide ore as a function of the electrolyte concentration

As can be seen from Figure 1, the highest degree of gold recovery into the solution occurs at a concentration of 2.0 M. It is shown that during 8 hours of leaching with an increase in the concentration of sodium hydroxide in the solution from 0.1 to 2.0 M gold recovery rises from 32 to 74 %.

It has been established that gold is recovered well into the solution, and the extraction degree of copper, manganese, chromium, zinc does not exceed 1.5–2.0 %. Thus, it has been established that in the anodic polarization of the sulphur-graphite electrode, sulphide ore is well opened with selective gold recovery.

The results of the study of the dissolution of metals from ore using a sulphur–graphite electrode as a cathode are shown in Figures 2 – 6. The degree of extraction of metals from ore (at a current density of 180 A/m^2, a solution agitation speed of 480 rpm, a phase ratio of 1: 10) depending on the electrolyte concentration.

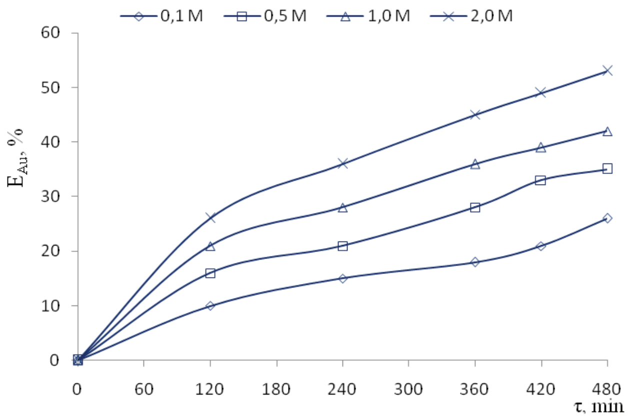

Figure 2 – Extraction of gold from persistent sulphide ore as a function of the electrolyte concentration

Figure 2 shows that an increase in the concentration of electrolyte leads to an increase in the degree of gold recovery. The maximum gold recovery is 53 %, which is 1.4 times lower than the gold extraction rate under similar conditions for the anodic polarization of the sulfur-graphite electrode.

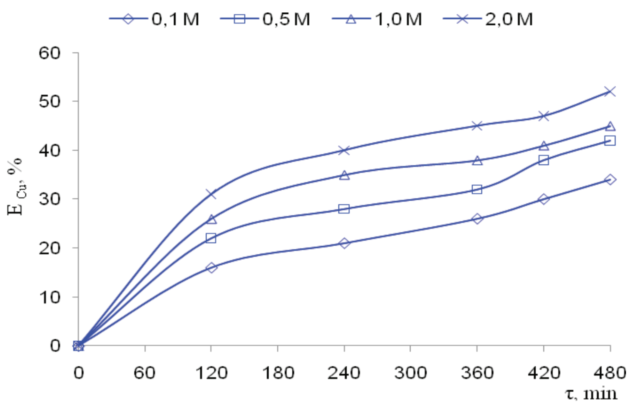

Figure 3 – The degree of recovering copper from persistent sulphide ores depending on the electrolyte concentration

The degree of copper recovery reaches within 8 hours of leaching 34 % at a sodium hydroxide concentration of 0.1 M and 52 % with a sodium hydroxide concentration of 2.0 M (Figure 3).

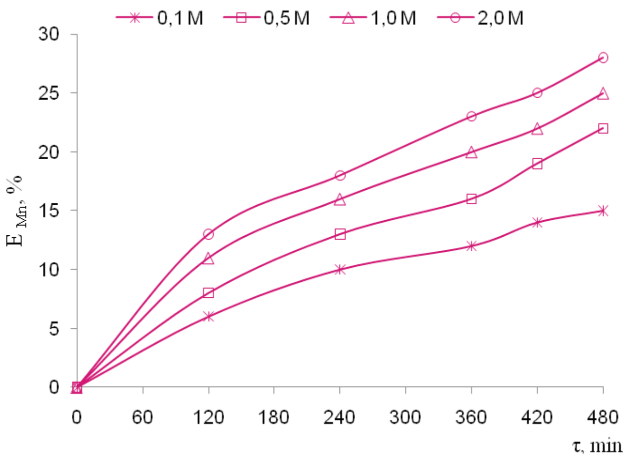

Figure 4 – Extraction of manganese from persistent sulphide ore as a function of the electrolyte concentration

For manganese (Figure 4), the extraction rate for 8 hours of leaching at different concentrations of electrolyte is, respectively: 0.1 M – 15.2 %, 0.5 M – 22.1 %, 1.0 M – 25.3 %, 2.0 M – 28 %.

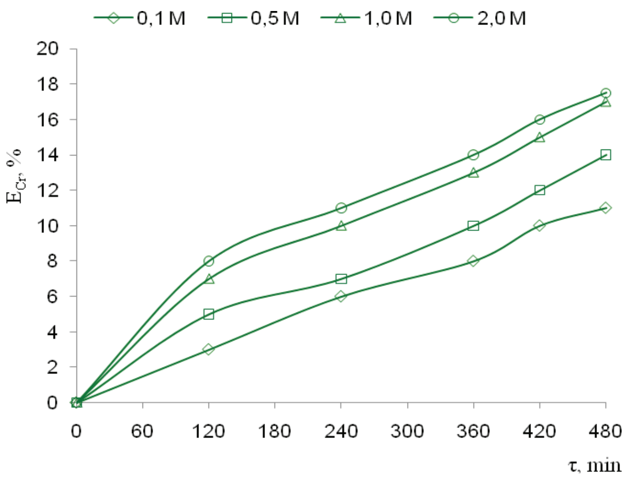

Figure 5 – Extraction of chromium from persistent sulphide ore as a function of the electrolyte concentration

With an increase in the electrolyte concentration from 0.1 to 2.0 M, the degree of chromium recovery rises – from 11.4 % to 17.2 % (Figure 5).

It should be noted from figure 6 that the maximum degree of zinc dissolution during the leaching process reaches up to 15 % within 8 hours.

It can be noted that in general, extraction of non-ferrous metals is lower than gold. Most likely, this is due to the fact that these metals are less prone to complex formation than gold.

As follows from the data of [8], the reduction of sulphur to polysulfide–, hydrosulphide–, sulphide– ions takes place on the cathode. All these anions can, to a greater or lesser extent, form complex compounds with noble and non-ferrous metals of variable valence.

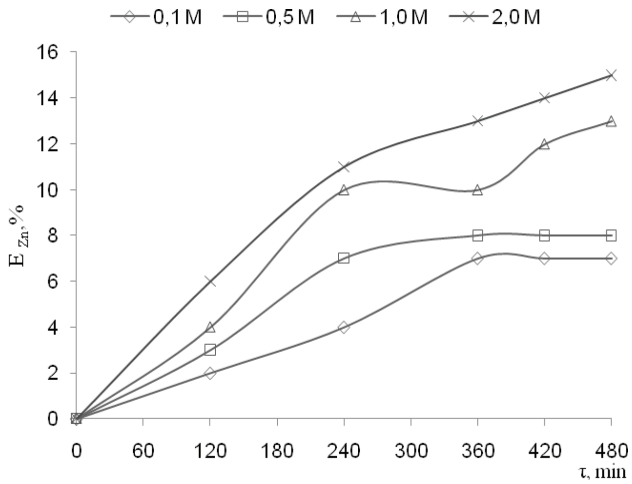

Figure 6 – Extraction of zinc from persistent sulphide ore as a function of the electrolyte concentration

Thus, the results of a study of electrochemical leaching using a sulphur– graphite electrode showed that this method is a fast and efficient way of extracting many valuable metals from persistent sulphide ores. The use of a sulphur– graphite electrode allows for a stepwise leaching in a single reactor. At the first stage, during the anodic polarization of the sulphur–graphite electrode, gold is extracted into the solution. After replacing the solution enriched with gold with a fresh solution of sodium hydroxide, it is possible to extract non-ferrous metals (copper, manganese, chromium and zinc) by cathodic polarization of the sulphur–graphite electrode. Electro leaching is carried out with high efficiency at relatively low temperatures, which saves energy and expensive reagents when organizing technological processes.

Conclusions. The results of the extraction of non-ferrous and precious metals using a sulphur-graphite electrode show that during the anodic polarization of the sulphur–graphite electrode, the resistant sulfide ore is well opened with selective gold recovery (73 %). Of the non-ferrous metals, copper, manganese, chromium and zinc are transferred to the solution in small quantities (1.5 - 2.0 %).

With the cathode polarization of the sulphur-graphite electrode, gold recovery in the solution is 53 %, copper – 34 %, manganese – 28 %, chromium – 17.2 % and zinc – 15 %.

Thus, electro-leaching in the presence of a sulphur-graphite electrode as an anode can be used, if necessary, to limit the yield of non-ferrous metals.

Based on the results obtained, leaching in the presence of a sulphur–graphite electrode in a sodium hydroxide solution makes it possible to combine the production of leaching reagents and the extraction of non-ferrous and noble metals from ores in the volume of one reactor. At the same time, it allows to save energy and expensive reagents when organizing technological processes.

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ТҮЙІНДЕМЕ

Мақалада шаймалау агенті ретінде күкірт-графит материалын пайдалана отырып, өңделуі қиын сульфидті кендерден түсті және бағалы металдар бөліп алу мақсатында жүргізілген зерттеу нәтижелері ұсынылады. Бұл үшін құрамынды 65 % күкірт бар күкірт-графит электроды жасалды. Натрий гидроксиді ерітіндісінде күкірт-графит электродын анодтық поляризация нәтижесінде сульфидті кендерден алтын таңдамалы түрде ашылуына ықпал ететіндігі анықталды. Ал, түсті металдар мыс, марганец, хром, мырыш елеусіз мөлшерде ерітіндіге өтеді. Оңтайлы технологиялық параметрлері анықталды: ток тығыздығы i - 180 А/м², натрий гидроксиді концентрациясы - 1,0 М - 2.0 М, араластыру жылдамдығы 480 айн./мин. Күкірт-графит электродын катодтық поляризациялау кезінде ерітіндіге алтын, мыс, марганец, хром және мырыш жақсы өтеді. Осылайша, натрий гидроксиді ерітіндісінде күкірт-графит электрод қатысында шаймалау реагенттер алуға және кеннен түсті және асыл металдарды ерітуді бір реакторда жүзеге асыруға мүмкіндік береді. Сонымен қатар, пайдалану күкірт-графит электроды бір реакторда металлдарды сатылап шаймалауға мүмкіндік береді. Алдымен, күкірт-графит электродын анодтық поляризацияда алтынның еруі жүреді. Алтынмен байытылған ерітіндіні жаңа натрий гидроксиді ерітіндісімен ауыстырғаннан кейін, күкірт-графит электродын катодтық поляризациялай отырып түсті металдарды (мыс, марганец, хром, мырыш) ерітіндіге өткізуге болады. Электрошаймалау технологиялық процестерді төмен температурада жоғары тиімділікпен жүзеге асырылатындықтан, энергия және қымбат реагенттер үнемдеуге мүмкіндік береді.

Түйінді сөздер: электрохимиялық шаймалау, бағалы және түсті металлдар, электрод, еру дәрежесі

РЕЗЮМЕ

В статье представлены результаты исследования извлечения цветных и благородных металлов из упорных сульфидных руд с использованием серографитового материала в качестве источника получения выщелачивающего агента. Для этого был изготовлен серографитовый электрод с содержанием 65 % серы. Установлено, что при анодной поляризации серографитового электрода в растворе гидроксида натрия сульфидная руда хорошо вскрывается с селективным извлечением золота. Из цветных металлов в раствор переходят медь, марганец, хром и цинк в незначительных количествах. Установлены оптимальные параметры процесса: плотность тока i – 180 А/м^2, концентрация гидроксида натрия - 1.0 М - 2.0 М, перемешивание раствора со скоростью 480 об/мин. При катодной поляризации серографитового электрода в раствор хорошо извлекаются золото, медь, марганец, хром и цинк. Таким образом, выщелачивание в присутствии серографитового электрода в растворе гидроксида натрия позволяет совместить получение выщелачивающих реагентов и извлечение цветных и благородных металлов из руд в объеме одного реактора. Причем, использование серографитового электрода позволяет осуществлять поэтапное выщелачивание в одном реакторе. На первом этапе при анодной поляризации сераграфитового электрода происходит извлечение в раствор золота. После замены раствора, обогащенного золотом свежим раствором гидроксида натрия можно проводить извлечение цветных металлов (медь, марганец, хром и цинк) путем катодной поляризации серографитового электрода. Электровыщелачивание осуществляется с высокой эффективностью при сравнительно низких температурах, что позволяет экономить энергию и дорогостоящие реагенты при организации технологических процессов.

Ключевые слова: электрохимическое выщелачивание, благородные и цветные металлы, электрод, степень извлечения

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