ГИАБ. Горный информационно-аналитический бюллетень /
MIAB. Mining Informational and Analytical Bulletin, 2021;(3-1):330—337
ОРИГИНАЛЬНАЯ СТАТЬЯ / ORIGINAL PAPER

УДК 66.08, 622.7 DOI: 10.25018/0236_1493_2021_31_0_330

КИСЛОТНОЕ ВЫЩЕЛАЧИВАНИЕ ТЯЖЕЛЫХ ЦВЕТНЫХ МЕТАЛЛОВ ИЗ ЗОЛОТОСОДЕРЖАЩИХ КАТОДНЫХ ОСАДКОВ

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Аннотация: Химическое обогащение концентратов, промпродуктов и катодных осадков является одним из перспективных направлений получения более высококачественной готовой продукции — сплава золота лигатурного. Большинство золотоизвлекательных фабрик используют цианистую технологию получения драгоценных металлов, с последующей угольно-сорбционной переработкой. В связи с низкой селективностью к золоту и серебру активных углей, образующиеся катодные осадки содержат большое количество примесей тяжелых цветных металлов, которые необходимо удалять перед последующими операциями плавки и аффинажа. Одним из способов очистки катодных осадков является солянокислое выщелачивание примесей. Для выявления возможности протекания кислотного выщелачивания примесей из катодных осадков, подбора реагента и определения оптимальных параметров выщелачивания была построена физико-химическая модель процесса с помощью программного комплекса «Селектор». В результате установлено, что использовании растворов соляной кислоты концентрацией 200 кг/м3 и более можно перевести в раствор: медь – 85,6 % свинец – 98,4 %, цинк – 99,0 %, также был установлен химический состав растворов и кеков выщелачивания. Проведенные экспериментальные исследования по солянокислому выщелачиванию примесей из катодных осадков показала достоверность физико-химической модели. Извлечение меди при этом составило 69,06%, свинца – 93,9 %, цинка – 79,5%, железа – 47%. При последующей плавке катодных осадков с флюсами в индукционных плавильных печах после солянокислого выщелачивания с получением сплава золота лигатурного удалось достичь увеличения массовой доли драгоценных металлов в сплаве на 23,5%, снижения содержания меди на 16,5% и свинца на 6,6%. Для определения химического состава катодных осадков и промпродуктов выщелачивания использовались методы рентгеноспектального микроанализа, рентгенофлуоресцентной спектрометрии.

Ключевые слова: катодные осадки, физико-химическое моделирование, выщелачивание, примеси, соляная кислота, драгоценные металлы.

Для цитирования: *Жмурова В. В., Абдусаломов А. Г.* Кислотное выщелачивание тяжелых цветных металлов из золотосодержащих катодных осадков // Горный информационно-аналитический бюллетень. — 2021. — № 3-1. — С. 330–337. DOI: 10.25018/0236_1493_2021_31_0_330.

Acid leaching of heavy nonferrous metals from gold-bearing cathode deposit

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Abstract: The cathode deposit after gold-bearing ore processing using the carbon–adsorption technology contains a large amount of heavy base metal impurities which should be removed before the subsequent smelting and affinage operations. One of the methods for refining the cathode deposit is hydrochloric acid leaching of impurities. The physicochemical process model is developed in Selector software to identify the potential for acid leaching of impurities from the cathode deposit, to select reagents and to optimize leaching. The model reveals that the use of hydrochloric acid solutions at concentration of 200 kg/m3 or higher allows base metals to be transferred to solution as follows: copper—85.6%, lead—98.4% and zinc—99.0%. The chemical composition of leach solutions and residues is also determined. The experimental tests of hydrochloric acid leaching of impurities from the cathode deposit have proven validity of the physicochemical model. Experimental extraction values are: copper—69.06%, lead—93.9%, zinc—79.5% and iron—47%. After hydrochloric acid leaching, smelting of the cathode deposit with fluxes in induction furnaces makes it possible to obtain alloyed gold with 23.5% higher weight content of precious metals at the decreased content of copper and lead by 16.5% and 6.6%, respectively. To determine the chemical composition of the cathode deposit and leaching products, the methods of X-ray spectral microanalysis and X-ray fluorescence spectrometry is used.

Key words: nonferrous metallurgy, cathode deposit, physicochemical modeling, leaching, impurities, hydrochloric acid, precious metals.

For citation: Zhmurova V. V., Abdusalomov A. G. Acid leaching of heavy nonferrous metals from gold-bearing cathode deposit. *MIAB. Mining Inf. Anal. Bull.* 2021;(3-1):330—337. [In Russ]. DOI: 10.25018/0236_1493_2021_31_0_330.

Introduction

One of the ways of obtaining alloyed gold with a high content of the precious component is improving the quality of intermediate products which include cementing cyanic precipitates, gravity concentrates, anodic slimes of copper production, nonferrous metal alloys, cathode deposit of cyanic adsorption technology, etc. Impurities of heavy nonferrous metals in gold-bearing products increase the cost of affinage, initiate affinage differences between supplier and refineries because of nonuniform gold and silver distribution in the material, and lead to formation of matte phases in the first smelting in case of high content of precious metals, which causes uncertainty of assaying.

Removal of such impurities from gold-bearing materials by means of acid leaching utilizes the chemical stability property of precious metals [1]. As it is known, gold is inoxidizable in the air, moisture-resistant, and irresponsive to acids, alkalies and salts. Sulphuric, hydrochloric and nitric acids are strong reagents and easily dissolve various metal impurities. However, special literature lacks information on the methods of acid leaching of gold-bearing materials. In general, such methods were applied at gold refineries on a low scale due to their cumbersomeness and complexity. Acid leaching of impurities from the gold-bearing cathode deposit is one of the promising areas of enhancing the quality of gold ingots.

The known method (No. 2351667 as of 10.10.2007) for processing of zinc-bearing gold-and-silver cyanic precipitates is characterized by production of the extremely high content of silver (30–80%), relatively low contents of gold (0.2–4%) and zinc (5–15%), selenium and tellurium (up to 2%), lead (up to 30%), copper (0.1 — 5.0%), silicon oxides, calcium and aluminum. Leaching of an initial product in nitrogen acid removes zinc, a greater part of acid-soluble impurities, as well as silver to solution (the risk of formation of the explosive air–hydrogen mix is impossible in the process). The insoluble precipitate contains gold, silicon and aluminum oxides [2].

Another approach to obtaining a higher-quality finished product in processing of low-grade and complex gold-bearing ore is selective dissolution using various acids, with gold concentrated in the insoluble residue to be subjected to cyanidation later on. This approach can be implemented using three methods: NITROX process, ARSENO process and REDOX process.

NITROX process utilizes nitric acid to leach gold-bearing ore in the air under the atmospheric pressure, with pulp heating to 80–90 °C. This process ensures total oxidation of iron, arsenic, sulphide sulfur and nonferrous metals. This method is advantageous for the simplicity, while its disadvantage is elemental sulfur formation in case of high content of sulfides in the ore, which impedes further cyanidation.

ARSENO process utilizes nitrous acid HNO_2 as a dissolver for sulfides. This acid is more chemically active than nitric acid. In this processes, the rate of oxidation of sulfides is very high. As a result, iron, sulfur and arsenic remain in solution, which ensures production of the higher-quality cathode deposit in further recovery of precious metals.

REDOX process is autoclave leaching at the temperature of 180 °C. Arsenic and sulphide sulfur remain in solution and can be extracted later on if necessary. This technology eliminates formation of elemental sulfur.

Melting of copper electrolytic slime to produce silver-and-gold alloy features loss of precious metals with slag and dust. The process of melting can be avoided using acid leaching of impurities from anode slime.

During processing of copper sulfide ore containing some gold and silver, the bulk of precious metals concentrate in anode slime after electrolytic copper refining. The chemical composition of slime varies in a wide range, % mass: Cu – 10–80; Ag – 1–45; Au – 0.2–1.5; Se – 2–15; Te – 0.1–8; As – 0.5–10; Sb – 0.2–15; Bi – 0.2–1; Pb – 1–25; Ni – 0.2–10; Fe – 0.2–2; S – 2–10; SiO_2 – 0.5–15; Al_2O_3 – 0.5–1.5.

Copper is prevented from getting into the gold-and-silver alloy by decoppering in diluted 10–15% sulfuric acid solution. Dissolution is carried out under heating up to 80–90 °C and intensive aeration of pulp. Metallic copper dissolves. Decoppering reduces the copper content of slime to 1–3%.

The promising technology for processing high-grade and difficult gold-bearing gravity concentrates is treatment of the initial concentrate in nitric acid solution, with melting of solid residue (cake).

The cathode deposit in gold refinery by cyanide adsorption in activated carbon also contains some impurities (to 70%) due to low selectivity of carbon and owing to complex composition of gold-bearing ore [3, 4]. Subsequent smelting and affinage require that the cathode deposit meets the standard content of heavy nonferrous metals (Technical Specifications TU 117-2-3-78): their total content is not to be higher than 10%. The X-ray microanalyzer JXA-8200 (JEOL, Japan) showed that the cathode deposit mainly contained Au, Ag, Cu, Pb, Fe, Zn, CaO, SiO_2 etc. [5, 6]. It is proposed to remove impurities of heavy nonferrous metals by acid leaching with hydrochloric acid as a dissolver [7].

Problem formulation

A cathode deposit has a complex chemical composition with the presence of impurities both as elements and as compounds able to interact with each other during acid leaching and be in solution in various ionic states. Therefore, it is more appropriate to use mathematical modeling methods to estimate the thermodynamic probability of interactions between impurities and between impurities and a solvent [8, 9]. Different software packages have been created to simplify calculations: Solmneq, Phreq, Selector, Choice, Tranql, Balance, Gibbs, Protocol, Astra, etc.

Selector software widely used for studying metallurgical processes was chosen for development of a mathematical (physicochemical) process model [10, 11]. The mathematical model of acid treatment of the cathode deposit is based on the Gibbs energy minimization when calculating heterogeneous equilibria, as well as on physicochemical principles of impurities leaching [12, 13]. Selector software package is commonly used for modeling various processes to treat gold ores and concentrates [14, 15], e.g. when studying pressure oxidation processes for refractory sulfide gold ores and various types of flotation concentrates, as well as when developing an ultra-fine grinding technology for precious metals ores, etc. [16 – 22]. This approach suggests that a study object is replaced with a simple and available model; and the modeling results are assumed to be relevant for the object properties [23, 24].

In interaction of the cathode deposit with concentrated hydrochloric acid, Cu, Pb and Ag go to solution in the form of dichlorocuprate, tetrachloro-plumbite and dichloroargentates of Ca, Mg and Na, respectively. Alkali and alkali-earth metals contained in the cathode deposit generate chlorides in interaction with HCl, which than react with copper, lead and silver chlorides, and form dissoluble compounds. The chemical reactions are described below in terms of copper and lead:

$$CuCl_2 + 2NaCl = Na_2CuCl_4,\ \Delta G^0_{298} = -645.6\ \text{kJ/mole}; \quad (1)$$

$$PbCl_2 + 2NaCl = Na_2PbCl_4,\ \Delta G^0_{298} = -703.66\ \text{kJ/mole}; \quad (2)$$

$$CuCl_2 + CaCl_2 = CaCuCl_4,\ \Delta G^0_{298} = -626.68\ \text{kJ/mole}; \quad (3)$$

$$PbCl_2 + CaCl_2 = CaPbCl_4,\ \Delta G^0_{298} = -684.44\ \text{kJ/mole}. \quad (4)$$

All reactions are thermodynamically feasible.

Physicochemical model outcomes

The physicochemical model shows the interaction between two phases of the heterogeneous system: a cathode deposit (solid) and a solvent (liquid) at a constant temperature of -25 °C. This model helped predict the behavior of the cathode sediment components during acid leaching at different concentrations of hydrochloric acid [25]. The solvent concentration (kg/m^3) was used as a variable in the physicochemical model [26, 27]. Figure 1 demonstrates the mathematical modeling results of the acid leaching of impurities from the cathode deposit at various concentrations of hydrochloric acid solution.

It is obvious in fig. 1 that hydrochloric acid leaching of impurities from the gold-bearing cathode deposit is effective for copper, zinc, and lead, whereas the other elements pass poorly into the solution. According to the physicochemical model, the optimal concentration of hydrochloric acid is 200.6 kg/m^3 or higher, which allows copper extraction to be 85.52%, lead – 98.34% and zinc – 99%. Since the main impurities in the cathode deposit are copper and lead, hydrochloric acid leaching is the most appropriate process to leach these metals from the gold-bearing cathode deposit. Alongside with precious metals, the other major components of leach residues are Pb, Zn^2SiO^4, CuO, and $CuFeS^2$.

Fig. 2 shows the composition of solutions after leaching impurities from the cathode deposit.

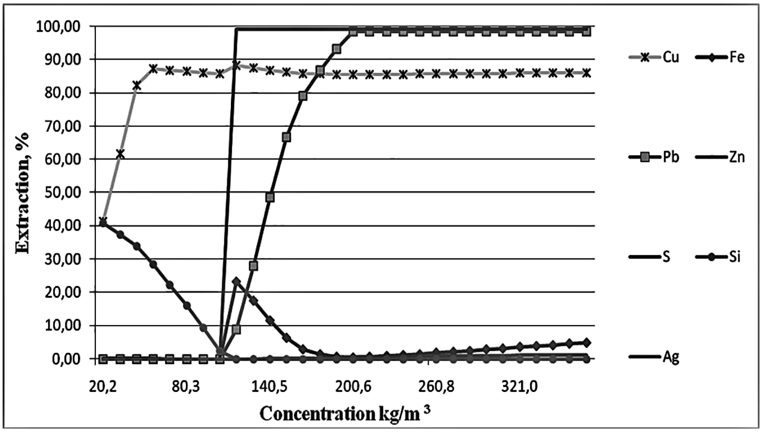

Fig. 1. Mathematical modeling: acid leaching of impurities from cathode deposit

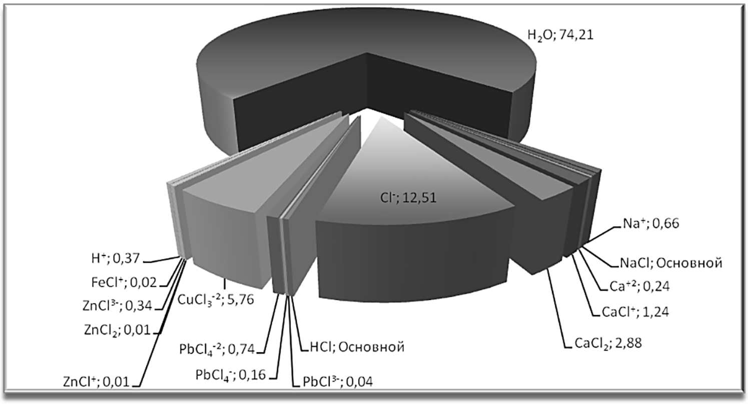

Fig. 2. Main components in solution in hydrochloric acid leaching, %

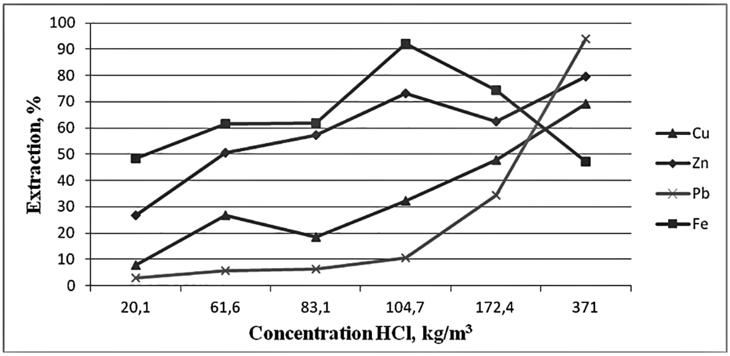

Fig. 3. Experimental results of hydrochloric acid leaching of impurities from cathode deposit

Основной — Basic

Experimental results

To confirm the model data, experimental studies were carried out into hydrochemical removal of impurities from the cathode deposit with the use of HCl as a solvent [28]. Figure 3 illustrates the experimental tests on removal of

Table 1
Chemical composition of alloyed gold

Au alloy type	Content of elements, [wt. %]										
	Au	Ag	Cu	Pb	Al	Zn	Si	S	Ca	Fe	ΣSb, As
Alloy from original cathode deposit	24	35.5	30	7.6	0.6	0.6	0.5	0.5	0.3	0.3	<0.1
Alloy from HCl leached cathode deposit	44	39	13.5	1	0.3	0.5	0.6	0.1	0.3	0.5	<0.1

impurities from the gold-bearing cathode deposit at various concentrations of hydrochloric acid solution.

According to fig. 3, the most complete removal of impurities from the cathode deposit is obtained at HCl solution concentration of 371 kg/m^3: copper extraction amounts to 69.06%, lead — 93.9%, zinc — 79.5% and iron — 47%. Removal of other impurities is under 1–2%. The experimental results confirm the mathematical modeling data on hydrochloric acid leaching of impurities from the deposit.

A cathode deposit is a feedstock for the downstream operation, i.e. production of alloyed gold. For this purpose, conventional smelting of the cathode deposit with fluxes is used [29]. Table 1 summarizes chemical compositions of alloyed gold produced from the original cathode deposit and from the hydrochemically treated cathode deposit. The chemistry data were obtained using X-ray fluorescence spectrometer Magnesium-1 (Yuzhpolimetall-Holding, Russia).

It can be seen that alloyed gold obtained from the HCl treated cathode deposit contains 23.5% more precious metals, while copper and lead contents reduce by 16.5% and 6.6%, respectively, and the content of other impurities undergoes minor changes.

Conclusion

The physicochemical modeling of the hydrochloric acid leaching process proves its efficiency in removal of impurities from the gold-bearing cathode deposit. The model has determined compositions of leach solutions and residues, optimal HCl concentration (at least 200 kg/m^3), as well as extraction of the main impurities (Cu — 85.52%, Pb — 98.34%, Zn — 99%). The physicochemical model has shown the efficiency of the leaching technology for removal of impurities from the cathode deposit [30]. The experimental testing data agree well with the mathematical modeling results. The experimental extraction values are: copper — 69.06%, lead — 93.9%, zinc — 79.5%, and iron — 47%. The subsequent smelting of the HCl leached cathode deposit with production of alloyed gold has allowed the increased mass percent of precious metals by 23.5% and reduction of copper and lead contents by 16.5% and 6.6%, respectively.

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Получена редакцией 15.10.2020; получена после рецензии 10.12.2020; принята к печати 10.02.2021.
Received by the editors 15.10.2020; received after the review 10.12.2020; accepted for printing 10.02.2021.