тотықсызданғыштығын төменгі окидке дейін төмендетеді, оны қиын тотықсызданатын натрий титанатына байланыстыратыны белгіленді.

Түйінді сөздер: титанмагнетитті концентрат, қаттыфазалық тотықсыздандыру, кальцийленген сода, жартылай кокс, шикіқұрам, қыздыру қисықтары, температура, термиялық эффект, натрийлеу үрдесі, натрий ферриті

Summary

Influence of the calcinated soda additives on phase transformations at solid phase reduction of titaniferrous magnetite concentrate wais studied in the interval of temperatures 200-1450^{o}C. Thermogravimetric researches of process of titaniferrous magnetite concentrate carbothermic reduction at the ratio of Fe/C=0,25, in flux-free mode and with addition of the calcinated soda showed catalytic influence of soda. So the temperature of the rapid stage of reduction decreased from 790 down to 658°C, i.e. for 132°C, and the depth of iron metallization considerably increased. It is shown that at the increase of calcinated soda consumption (Na_2O) up to 10% and at consumption of 18,3% of semicoke all of solid phase iron metallization process flows within an interval 672-956°C, thereupon joint reduction of iron and titanium from a slag phase and successive melting of eutectic compositions of slag phase take place. It is established that the calcinated soda decreases reducibility of TiO_2 down to lower oxides and binds it into more hard reducing sodium titanates.

Keywords: titaniferrous magnetite concentrate, solid phase reduction, soda calcinated, semicoke, charge, thermoeffects, sodium, sodium ferrite

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Комплексное использование минерального сырья. № 1. 2013.

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DEVELOPMENT OF BIOTECHNOLOGY FOR GOLD RECOVERY FROM RESISTANT ORES AND SLIMES BY USING MINERAL ACIDS

Possibility in principle of gold recovery from resistant ores and slimes of one of Kazakhstani deposits (gold content - 5.6 and 2.6 g /t respectively) is discussed in the article. Bioleaching method was used in the investigation for resistant sulfide ores and production's waste processing. This method has significant advantages, because it is characterized by simple process scheme due to cancellation of high temperatures and pressures and more complete opening of ores by bio-reagents. Complex inorganic solvent (H_2SO_4) with an organic additive (timber fungi of *Phellinus* genus) were used in the experiments for gold recovery. Experiments showed that at bioleaching of slime samples with sulfuric acid and an organic additive (timber fungi of *Phellinus* genus) - 75,0 % of Au was extracted into solution at 20 ^{o}C. At bioleaching of samples of Akbakaj resistant sulfide gold-bearing ores - 70,0 % of Au was extracted into solution at same conditions. Thus, the presented results of the studies show that the introduction of organic additives into the solution of sulfuric acid intensifies the leaching of gold without using high temperatures and the pressure.

Key words: slime, sulfuric acid, *Phellinus* genus fungi, resistant sulfide ores, gold-bearing ores, bioleaching, organic additives

Introduction. Substantial composition and natural forms of gold-bearing ores are varied in wide range. The individual technology of their processing is necessary in each concrete case. Characteristic feature of gold-bearing ores is the lowest content of the basic valuable component in them. Even ultrafine milling of a material does not allow getting necessary degree of opening.

Hydrometallurgy of processing gold-bearing ores with transferring of noble metals into a solution in the form of soluble salts and complexes is complicated heterogeneous process [1-3]. The scope of gold solvents is very wide, more than 20. However not all of them are interesting in view of technology i.e. simultaneously meet such requirements, as nontoxicity, selectivity in relation to the noble metals, the moderate cost, an opportunity of commercial operation.

One of actual problems of a modern gold mining is involving into production low-grade raw material and raw material with complicated composition (complex, persistent, overburden, stale slime of benefication, etc.). That allows essentially increase a raw-material base and gold production quantity in the country. The standard methods of gold recovery from such kind of the raw material, based on processes of mechanical, gravitational or flotation benefication are inefficient in this case. Thus, for this problem solving the nonconventional approach with essentially new scientific and technical developments is required.

Now bioleaching technology becomes widespread due to its effectiveness for resistant sulfide ores and production's waste processing. This technology has significant advantages providing an increase of gold recovery, and the economic efficiency of ores processing. Also this technology is characterized by simple process scheme because of cancellation of high temperatures and pressures use due to more complete opening of ores by bio-reagents. Application of bioleaching processes allows achieving high degree of gold dissolution during cyanidation [4].

Now works on finding and application of cheap and widely accessible waste of the microbiological industry are conducted. One of perspective directions of increasing efficiency of noble metals recovery from depleted ores is use of bioreagents such as biological liquid, containing amino acids, on the base of products of life processes of yeasts of Saccharomyces, Klupxoromycos or Pichiaspecies [5].

The purpose of the work was determination of technological methods for processing Kazakhstani persistent gold-bearing ores in dependence on their phase and chemical composition and choice optimal conditions for their effective using, including selection of a solvent.

Structurally-phase transformations of the basic components of gold-silver-bearing raw materials in mineral acids at leaching are studied with use of a complex of modern physical and chemical methods of the analysis.

Experiments. *Leaching of noble metals from persistent ore and slimes after flotation.* Persistent gold-bearing ore from vein "Main" of Akbakaj deposit with composition, mass. %: SiO_2 - 56,8; Al_2O_3 - 11,5; Fe_2O_3 - 6,7; CaO - 0,51; S_{total}- 1,2; MgO - 1,98; Zn -

0,016; Cu - 0,10 and Au - 5,6 g/t, Ag - 3,8 g/t was used for leaching. Ore was averaged and crushed up to 0,071 mm. Granulometric composition of ore, %: (1,0 mm) - 13,65; (0,5 mm) - 37,84; (0,4 mm) - 10,52; (0,2 mm) - 8,79; (0,1 mm) - 8,35; (0,071 mm) - 20,85.

Chemical composition of quartering and crushed up to size 0,074 mm samples of slimes after flotation was as follow, mass. %: SiO_2 - 60,11; Al_2O_3 - 6,2; Zn - 0,016; Cu 0,10; Fe - 2,5; S - 0,50; Au - 2,6 г/т, Ag - 3,2 g/t.

The ore bodies of deposit Akbakai are folded from various quartz- rocks on which the thin crack-interspersed sulfide mineralization is imposed. Total amount of sulfides (table 1) does not exceed 5-15 %.

Table 1 - Mineralogical structure of raw material of Akbakai deposit

Minerals	Main	Minor	Rare
Hypogenic			
Ore	Pyrite, arsenopyrite	Gold, sphalerite, chalcopyrite, pyrrhotite	gray copper ore, marcasite, rutile, scheelite, electrum
Nonmetallic	Quartz	Sericite, chlorite, calcite	biotite, muscovite
Hypergenic			
Ore	limonite		chalcocite, malachite, covellite
Nonmetallic	Clay minerals	Calcite	gypsum

Physical and chemical researches of initial raw material have shown that among sulfides pyrite and arsenopyrite sharply prevail. Ores contain 70-75 % of silica, 10-12 % of alumina, 0,5 % of sulfide sulfur. The content of copper, zinc, lead, antimony is very low – minor part of percent. Substantial composition of the deposit is classed as gold-quartz moderately sulfide formation.

Sulfides often contain gold, and evolving native gold in quartz is seldom. Concretion of gold with sphalerite, gray copper ore, pyrite, arsenopyrite, and also location in intervals between arsenopyrite crystals without forming concretions are most widespread. The grains size is 0,001-0,05 mm. Gold in the form of electrum is frequently observed in the form of inclusions with size of 0,001-0,003 mm inside pyrite. In quartz gold is observed in the form of octahedral crystals.

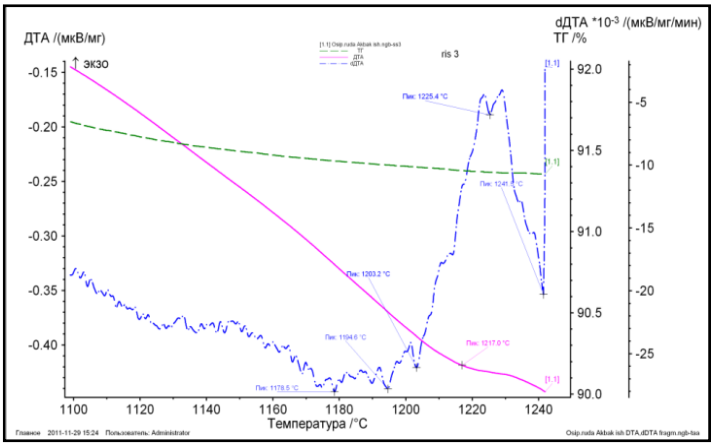
In researches on persistent ore and slimes after flotation leaching the inorganic solvent (H_2SO_4 - 75,0 g/dm^3) and the organic additive (timber fungi of Phellinus genus) at ratio S:L = 1:3 were used as solvents of gold and silver. Experiments were carried out in flask with mechanical stirrer (by the agitation method), speed of mixing was 300 rev/min.

Results and discussions. Experiments have shown, that at leaching by a solution of a sulfuric acid with the organic additive (timber fungi) from flotation slimes into a solution of 75,0 % Au and 68,0 % Ag were recovered, and from persistent sulfide ore of Akbakai gold-bearing deposits 70,0 % Au and 65,5 Ag were recovered into a solution (table 2).

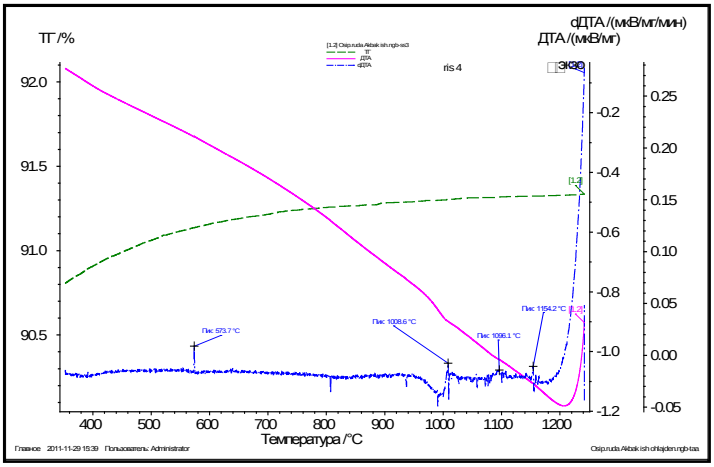
In figure 1 (a, b) thermogravimetric curves ДТА– change of enthalpy, dДТА - speed of weights change received during sample cooling are resulted. On curve ДТА is one peak of crystallization - at 1159 °C. On dДТА curve it is possible to see already three peaks.

Table 2 – Recovery of noble metals from Akbakaj deposit persistent sulfide ore and slimes after flotation

Leaching agent	Concentration Au/Ag, mg/dm^3	Recovery Au/Ag, %
Persistent sulfide ore		
H_2SO_4	0,69/0,61	65,7/60,2
H_2SO_4 + fungi	0,75/0,70	70,0/65,5
slimes after flotation		
H_2SO_4	0,71/0,67	68,9/61,0
H_2SO_4 + fungi	0,82/0,78	75,0/68,0



a



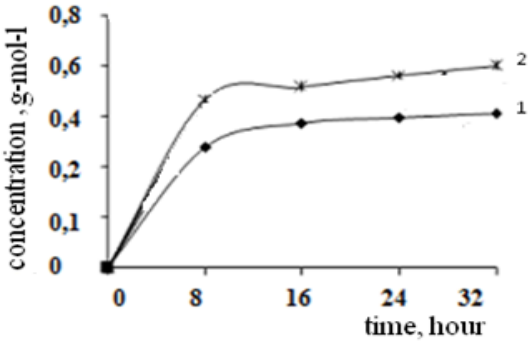
b

Figure 1 - Thermogram of samples (a) initial sample and (b) cake after leaching by sulfuric solution

On a curve dДТА even more peaks of crystallization of primarily molten phases appear. In figure 1 curves ТГ - change of weight and dТГ together with change of weight during heating in percentage, according to minima on dТГ are shown. Effects in curves ДТА and dДТА in the field of temperatures 500 - 600 °С reflect processes of pyrite decomposition. Weak endothermal effect with an extremum at 344 °С, probably, reflects polymorphic transformation of a small amount of pyrrhotite. Effects on curves ДТА and dДТА in the field of temperatures 700 - 800 °С display of calcite decomposition. Weak endothermal effect with an extremum at 671 °С on a curve dДТА, possibly, reflects process of polymorphic transformation of hematite. Hematite could contain in sample initially besides it is an end-product of pyrite decomposition. Weak endothermal effect with the maximal development at 839 °С on a curve dДТА can reflect smelting small quantity of argentite - Ag_2S. Exoenergic effect on a curve dДТА with peak at 935 °С can display crystallization of a small amount of metamictorthite - $(Ca, TR)_2 (Al, Fe^{2+}, Fe^{3+})_3 [SiO]_4 [Si_2O_7]O(OH)$ or a clay mineral collyrite - $mAl_2O_3nSiO_2pH_2O$. Minima on a curve dТГ at 1038 and 1097 °С can display dehydration and decomposition of small amounts of micaceous minerals or rhombic and alkaline amphiboles (alkaline hornblende, anthophyllite).

Endothermal effects on a curve dДТА in the field of temperatures 1100 - 1250 °С (b) reflect stage-by-stage sample smelting. Not strongly expressed endothermal effect on curve ДТА with the maximal development at 1217 °С is probably resulting effect of low-intensity effects reflected on dДТА.

Gold recovery from flotation slimes dependence on leaching time is presented in figure 2. So the maximal values of recovery are observed during the first 8 hours.



1 – H_2SO_4; 2 - H_2SO_4 + fungi

Figure 2 –Dependence of gold recovery from slimes on leaching time

Thus, the presented results shown, that introduction of organic additives into a solution of a sulfuric acid intensifies process of noble metals leaching [6]. It occurs due to passing of concomitant metals sulfides into soluble sulfates and the subsequent chelation of gold with formation of organic-mineral soluble complexes under the influence of a bioorganic reagent and a sulfuric acid. These processes proceed with participation of the amino acids capable to complexing with gold and containing in a biomass of crushed timber fungi of *Phellinus* genus. It is known, that amino acid composition of fungi (timber fungi) is almost identical and variates within the limits from 7 up to 18 and includes representatives of

replaceable and irreplaceable amino acids, among which: leucine, serine, etc. It is known, that use of amino acids in hydrometallurgy leads to substantial increase of noble metals recovery. However, pure amino acids are very expensive reagent. Therefore crushed timber fungi - a rich source of a mix of amino acids – are applied instead of them. So this biomass - cheap reagent - has allowed to achieve simplification of a method at a high degree of noble metals recovery. As result efficiency of one-phase without cyanide gold leaching increases up to 75 % and silver up to 68 % and ecological safety of process raises, also the technological scheme of persistent gold-silver ore processing becomes considerably simpler.

In figure 3 IR-spectra of cake after leaching by a sulfuric acid are presented on which all changes are well visible. Quartz α-SiO_2 - 1163, 1082, 798, 779, 694, 518, 470, 397, 371 sm^{-1} [6, 7]. Albite type plagioclase Na [$AlSi_3O_8$] - 1163, 649, 470 sm^{-1}. Muscovite KAl_2 [(OH, F) $_2$ | $AlSi_3O_{10}$] - 3614, 1620, 1031, 694 sm^{-1}. Calcite $CaCO_3$ - 1798, 1422, 876, 713 sm^{-1}. Absorption bands of valent fluctuations ν (OH) - 3614, 3551, 3401 sm^{-1}, deformation fluctuations δ HOH - 1620 sm^{-1}. In long-wave area where links Me–O Me - S, Me - X were observed absorption bands at wave numbers 371, 320, 278 sm^{-1} are fixed, conformity to valent fluctuations of links of type Fe^{2+}-O (in oxide) - 371 sm^{-1} is possible.

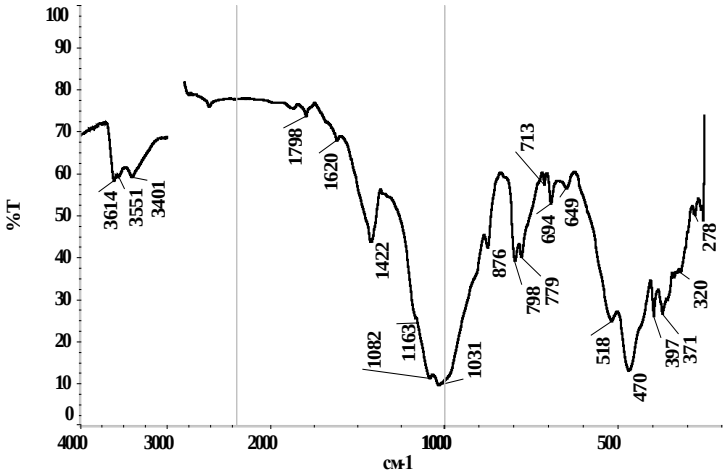


Figure 3 - IR-spectrum of cake after leaching flotation slimes by sulfuric solution

Valent fluctuations Fe^{3+} - O are shown in a range of 400-300 sm^{-1}. There is a band of valent fluctuations ν (OH) - 3401 on a spectral curve that indicates formation of its sulfuric salt.

The IR-spectral analysis in a solution after leaching by sulfuric acid at presence of timber fungi (figure 4) bands of stretching vibrations ν (OH) - 3408 sm¯1, deformation δHOH-1651 sm¯1 and libration νL H_2O - 682 sm¯1 fluctuations of molecular water are fixed. The wide dim band with a maximum at 1212 sm^{-1}, possibly, relates to fluctuation ν_{as} (O … H …) of proton H_5O_2 $^+$dehydrate [7, 8]. The IR-spectroscopic analysis of sulfuric solutions at presence of timber fungi after leaching has shown increase of such oxygen and hydrogen-containing groups, as carboxyl and hydroxyls.

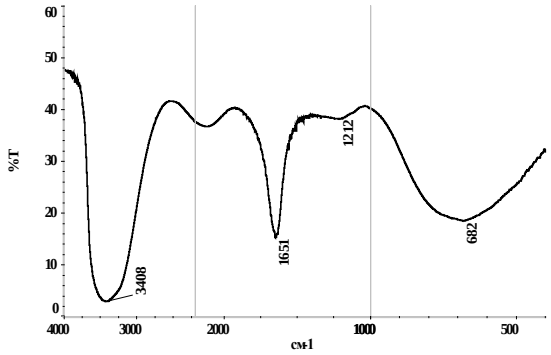


Figure 4 - IR-spectrum of sulfuric solutions after leaching flotation slimes at presence of timber fungi

Conclusions. The comparative analysis of the received results has shown that at leaching of flotation slimes and persistent ores by complex bio-reagent intensive destruction of crystal lattices of pyrite and arsenopyrite minerals is observed and depending on medium pH is distributed between liquid and solid phases. Finally favorable conditions for noble metals recovery by sulfuric solution are created. Thus, these results demonstrated that the introduction of organic additives into the solution of sulfuric acid increases gold recovery by the leaching without using high temperatures and the pressure.

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Резюме

В статье рассмотрена принципиальная возможность извлечения золота из упорной руды и хвостов флотации одного из казахстанских месторождений (содержание золота – 5,6 и 2,6 г/т). В исследованиях был использован метод биовыщелачивания как наиболее эффективный для переработки упорных сульфидных руд и отходов производств. Этот метод обладает существенными преимуществами и характеризуется простотой технологической схемы за счет отказа от высоких температур и давлений благодаря более полному вскрытию руд биореагентами. Для проведения экспериментов в качестве растворителей золота использовался неорганический растворитель (H_2SO_4) и органическая добавка (древесные грибы рода *Phellinus*). Эксперименты показали, что при выщелачивании раствором серной кислоты с органической добавкой (древесные грибы) из пробы хвостов извлекается в раствор 75,0 % Au при 20^{o}C, а из пробы упорной сульфидной руды акбакайского золоторудного месторождения в этих же условиях извлекается 70,0 % Au. Таким образом, представленные результаты исследований показали, что введение органических добавок в раствор серной кислоты интенсифицирует процесс выщелачивания золота без использования высоких температур и давлений.

Ключевые слова: хвосты флотации, серная кислота, древесные грибы рода *Phellinus*, упорная сульфидная руда, золотоносная руда, выщелачивание, органические добавки

Түйіндеме

Статьяда қазақстан жерінің (алтынның құрамы-5,6 г/т, 2,6 г/т) өңделуі қиын және флотация қалдықтарынан алтын алудың тікелей мүмкіндіктері қарастырылған. Тәжірибеде алтынды ерітуге бейорганикалық еріткіш ретінде (H_2SO_4), органикалық қоспа (*Phellinus* ағаш жаңқасы) қолданды. Тәжірибе нәтижесінде қалдықтардан күкірт қышқылы мен органикалық қоспамен (*Phellinus* ағаш жаңқасы) шаймалауда ерітінді бойынша алтын алу -75%, ақбақай өңделуі қиын алтынды сульфидті кенінен 20 ^{o}C- та 70 % алтын алынды. Сонымен, тәжірибе қорытындысы жоғарғы температура мен қысымсыз , күкірт қышқылы мен органикалық қоспамен шаймалауда алтын алу мөлшері жоғарылайды.

Түйін сөздер: қалдықтар, күкірт қышқылы, Phellinus ағаш жаңқасы, өңделуі қиын сульфидті кен, құрамында алтыны бар кен

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Комплексное использование минерального сырья. № 1. 2013.

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ТЕРМОДИНАМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ОБРАЗОВАНИЯ СИЛИЦИДОВ ЖЕЛЕЗА (Fe_mSi_n) В СИСТЕМЕ SiO_2-Fe_3C-C

Исследования в данной статье направлены на разработку ресурсо- и энергосберегающей технологии производства ферросилиция с сокращением до минимума расходов дефицитных составляющих сырья - кокса и железной стружки, а также на решение экологической проблемы - на утилизацию отходов цинковой промышленности. Приведены термодинамические исследования процесса образования различных модификаций ферросплава (FeSi, Fe_5Si_3, Fe_3Si,) в системе SiO_2-Fe_3C-C. Показана принципиальная возможность образования ферросилиция при взаимодействии Fe_3C и SiO_2 в присутствии углерода в условиях электротермической плавки.