UDC 553.41

Efficiency increase for gold-bearing ore deposits with respect to the influence of sulfide surface nanobarrier on metal adsorption

A.E. Vorobyov

Doctor of Technical Sciences, Professor
Institute of Continuous Education Top Managers and
Specialists of Fuel and Power Industries,
Ramenskoye, the Russian Federation

V.I. Lyashenko

Candidate of Technical Sciences, senior research scientist,
Ukrainian Research and Design Insitute for Industrial Technology»
(SE «Ukr R&D Institute for IndTech»),
Zhovti Vody, Ukraine

Tcharo Honore

post-graduate student, head of laboratory,
Department of Oil-field Geology, Mining, Oil & Gas Engineering
RUDN University, Moscow, the Russian Federation

K.A. Vorobyev

bachelor
Engineering Academy
RUDN University, Moscow, the Russian Federation

Abstract
With this publication we introduce the summarized scientific and application results of our theoretical explorations, laboratory researches and experiments within the industrial full-scale production, carried out for gold, namely, for finely dispersed gold or so-called nanogold, which is unseeable by optical microscope but has good recovery perspectives. With our research we demonstrate that some of world's gold ore reserve with thereof type of gold in the form of pyrite and arsenopyrite disseminated mineralization is located in Bakyrchik gold deposit in Kazakhstan. Upon that, the part of the ore in this deposit contains two varieties of arsenopyrite (needlelike and elongated prismatic ones), and pyrite pentagonal dodecahedron habit. We study the problem how to increase the efficiency of operational cycle for gold deposits taking into account the influence of sulfide surface nanobarriers on metal adsorption. In this context, we also address extraction technology development for finely dispersed gold.

A wide range of methods were used for the current research: the analysis of the earlier conducted researches, the observations and their control, the mathematical and physical simulation, the analysis and statistical processing of the results, determination of dependences, the calculations and the control, the experimental studies and measurements in accordance with the conventional standard and the new techniques.

We consider and explain our point of view that the further researches of gold-containing reliefs are expected to allow determining the gold absorption degree in pyrite and arsenopyrite.

The current article deals with the new results of the comparative analysis on the properties of the nanorelief containing different gold-bearing sulfides. Morphology, microtopography of auriferous pyrites and arsenopyrites are described in it. Based on oxidation and reduction reactions, we have also revealed the mechanism of gold adsorption on sulfide surfaces.

It has been determined that gold is adsorbed on the surface of arsenopyrite rather than on pyrite. The new system of principle testing has been developed and implemented at the gold-processing plant, it allows a remarkable improvement on the results trustworthy, reduction in labour requirement and decrease in the number of tests commonly conducted by the laboratory for this operation as much as 6 times.

Key words: EFFICIENCY, GOLD ORE DEPOSITS, NANOBARRIERS, GOLD ADSORPTION, SURFACE OF SULFIDES, PYRITE, ARSENOPYRITE, MICROTOPOGRAPHY

Introduction

The present-day tendencies in the gold industry are certainly in searching and developing finely dispersed gold, invisible through optical microscope or so called nanogold. In some world's gold ore deposits, the gold of such type is included in pyrite and arsenopyrite disseminated mineralization, in particular, in gold deposit of Bakyrchik, Kazakhstan. The part of the ore in this deposit is arsenopyrite of two varieties (needlelike and elongated prismatic), the other is pyrite pentagonal dodecahedron habit. The ores of all the known gold deposits bear gold of different sizes, associated not only with sulfide but also with rock-forming minerals, for instance, quartz and others. Indeed, in association with quartz, gold usually settles in its free or native form into the existing microcracks and pores. The studies of gold-containing reliefs are expected to allow determining the degree of gold adsorption in pyrite and arsenopyrite. For this reason, based on scientific and practical results of theoretical studies, the laboratory researches and the industrial control experiments, the increase in operational cycle efficiency for gold deposits with respect to the influence of sulfide surface nanobarriers on metal adsorption and the development of the extraction technology for finely dispersed gold, unseeable by optical microscope, so called nanogold, are an important scientific, technical and practical problem, which requires immediate solution [1–5].

In order to solve the indicated problem, the authors used the complex method, which includes analysis of the earlier publications, the methods of theoretical generalization of physical properties of ores, the development of machines, the physical and mathematical simulation, and also the laboratory research and the industrial implementation with the conventional, the standard, and the new techniques [6–11].

Discussion and assessment of the research

A coarse or visible gold often occurs within intergranular areas, microcracks and microdislocation discontinuities in ore-forming minerals; this gold has rounded (Fig.1) isometric and irregular shape [4–8]. However, the spread of this visible gold in ores (in gold deposit of Bakyrchik in Kazakhstan) is rather limited while finely dispersed gold is more common within the

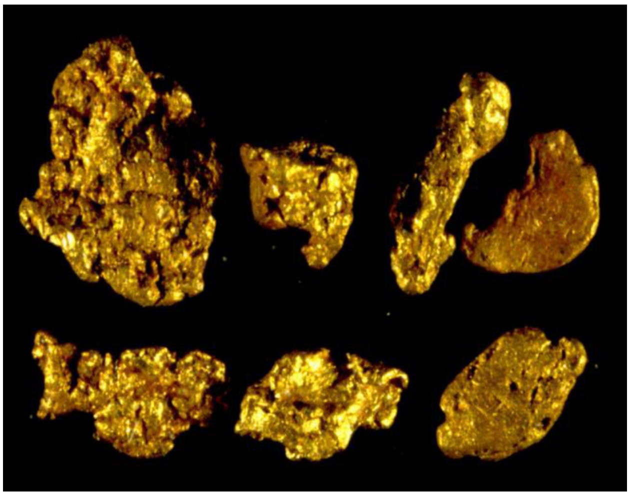


Fig. 1. Morphology of gold grains (photo, general view)

deposits like Bakyrchik, where principle ore minerals are arsenopyrite and pyrite and where the maximum content of gold is found in the rewarding mineral association [9]. Upon this, a larger proportion of gold is present as “invisible”, “colloidal” or nanogold (particles of which are less than 0.1 μm).

The term of “colloidal gold” was introduced into scientific discourse for describing discrete submicron gold (500 nm), included into sulfide minerals, almost invisible for both optical and conventional electronic microscopy, but found by the technology of microfocused ion beam and also detected by the technology of transmission electronic microscopy [2]. Moreover, colloidal gold is an intermediate form between optically visible gold and its solid solution. At this, colloidal gold can be the product of nanoliberation of gold-bearing solid solution or that of the first phase of its formation, adsorbed “surface” gold.

Furthermore, “surface” gold is a result of sorption, reducing settling and, possibly, ion exchange settling from gold-containing solutions. This type of gold exists in three chemical forms of Au^0, $AuCl_{2-}$ and $Au(SCN)_{2-}$. It is believed [2] that formation of “surface” gold is an initial phase of gold introduction into arsenic pyrite in the form of solid solution, and also into non-arsenic pyrite as microinclusions.

According to the scientific researchers, “invisible” gold is represented mainly as ultrafine metal particles born as decomposition products of solid solution or captured as mechanical impurities [3]. The others sources consider that this gold occurs in sulfides as atomic and molecular scattering, isomorphically replacing iron, copper, arsenic, zinc and lead in the structures of minerals [9–11]. Earlier, the main focus of the researchers of gold-bearing rock (both geo- and technology-related) was mostly on the studies of general properties of mineral grain liberations, and also on the data of their granulometry, internal structure properties, chemical composition, physical properties, etc. [12, 13]. Regarding a particular example, the gold-bearing pyrites of Bakyrchik deposit generally have pentagonal dodecahedral habit, which in weak gold-bearing differentials is changed by pentagonal dodecahedrons with accurately developed cube faces (Fig. 2).

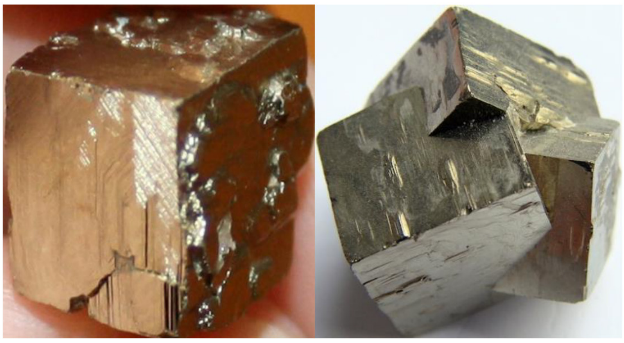
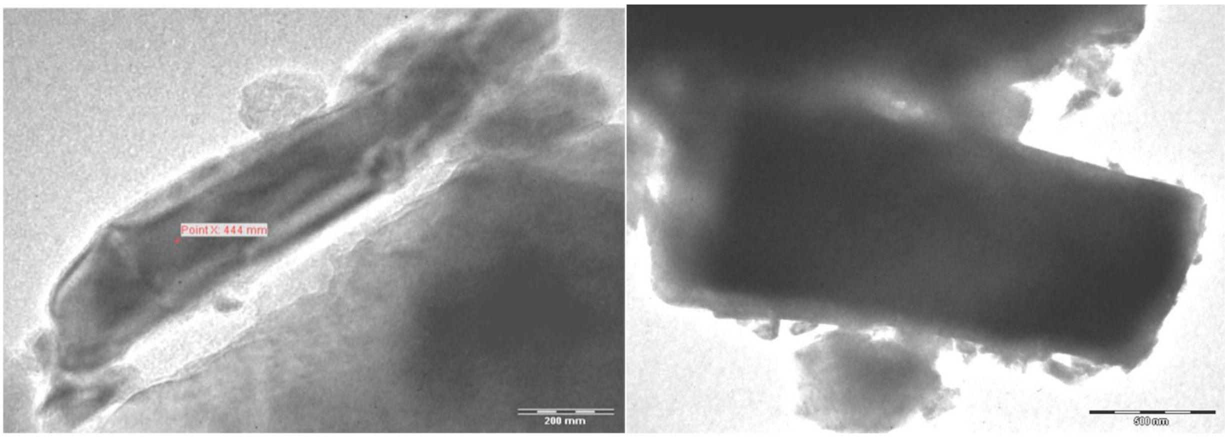


Fig. 2. Crystals of pyrites (photo, general view)

In a point of fact it should be noted that in Bakyrchik ores, minerals with cube shape contain less gold than the others. On the contrary, the gold-bearing arsenopyrite crystals of this ore deposit are typically of fine-needlelike and elongated prismatic appearance (Fig.3) and they show significant deviation from the stoichiometry of the crystal lattice of the mineral matrix.

Based on the materials of the earlier researchers [12], it becomes obvious that the following has attracted the least of the scientific attention in the analyzed publications: the study of gold grains surface structure (Fig.4), the detailed description of micro- and nanoreliefs of gold grain surfaces (for example, nanobumpiness, nanofracturing, nanoporosity, and also presence of different nanofilms, nanoinclusions, nanochannels, etc). Moreover, it was established that for the sulfides of earlier generation, sorption capacity can be determined primary by geochemical affinity of gold for the elements included into the composition of these sulfides (for instance, arsenic has rather high affinity for gold, and this reason explains why arsenopyrite adsorbs gold well enough). However, for the sulfides of the later generation the geochemical affinity factor does not have such dominating value, but the electrostatic phenomenon and the physics of crystals. [14]. This explains why an important feature of Bakyrchik ores is the significant concentration of nanogold in their arsenic pyrite (Fig.5) [9].

Here, the content of As in gold-bearing pyrite is 1.2 - 4 % (refer to the table below).



3a) 3b)

Fig. 3. Image of needlelike (a) and elongated prismatic (b) arsenopyrite: transmission electronic microscopy; TEM (photo, general view)

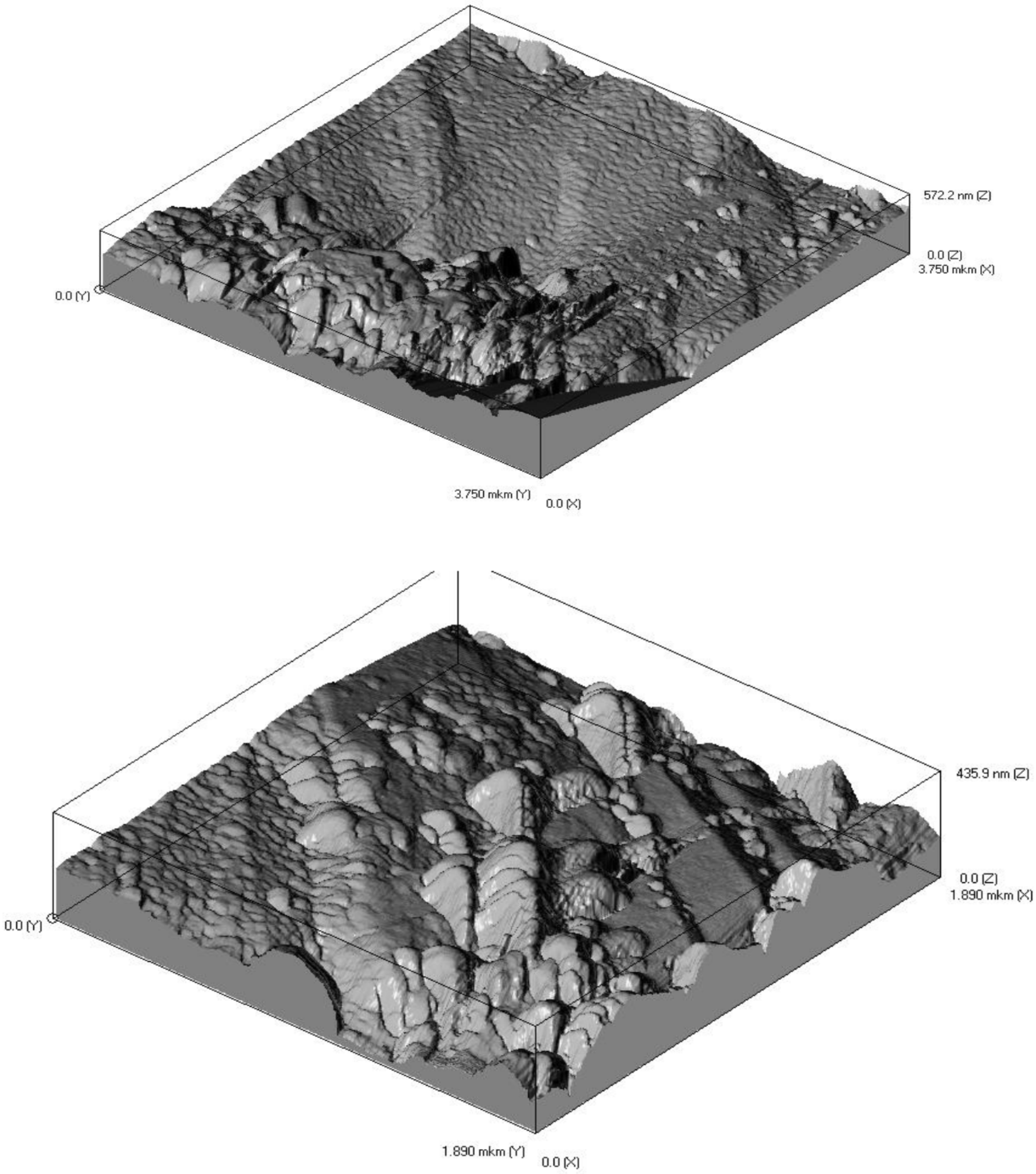


Fig. 4. Nanosurfaces of pyrite (2.5*5*1 µm), according to L.V. Tauson (photo, general view)

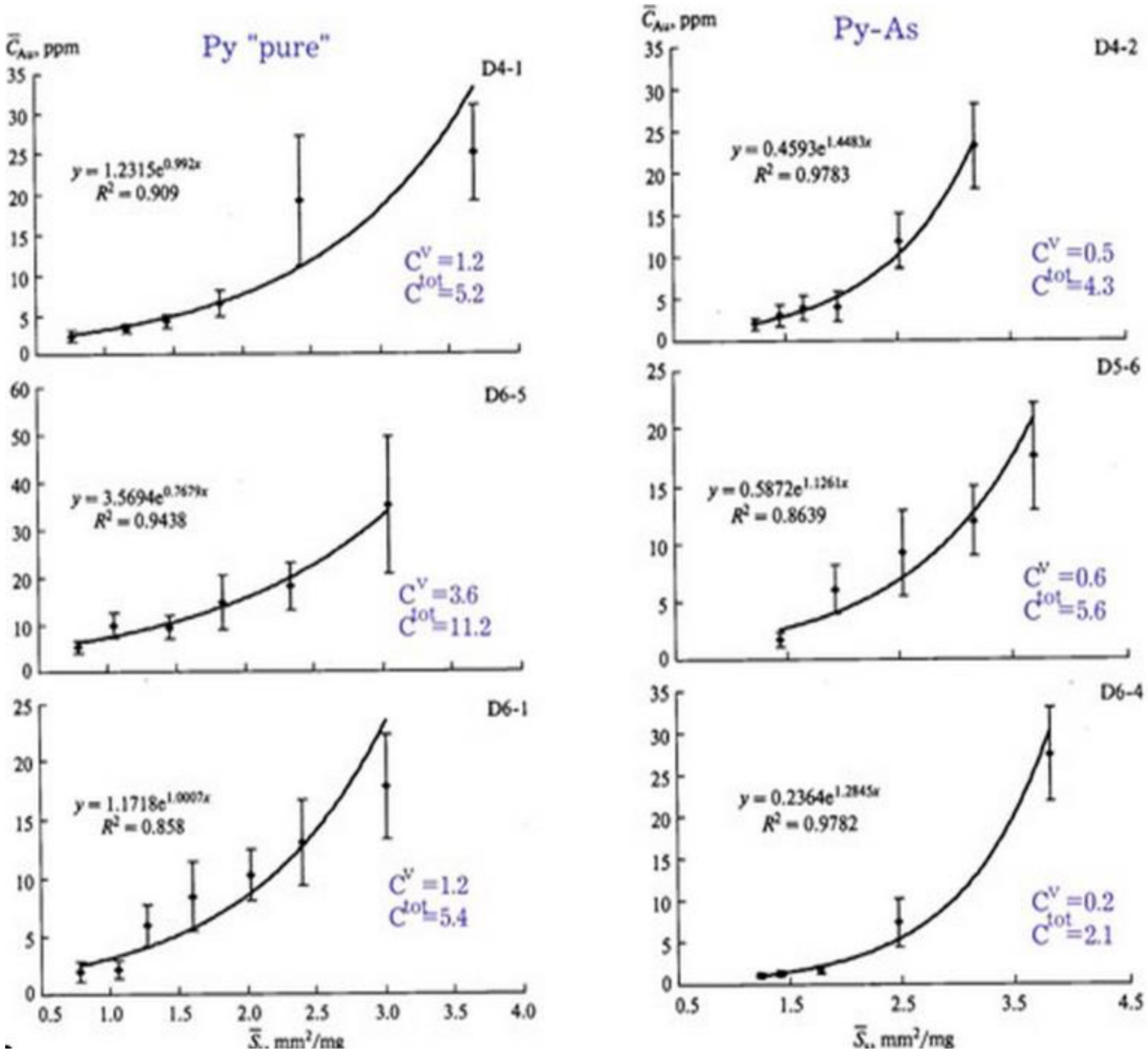


Fig. 5. Dependence of the average equally distributed gold in pyrite on the specific surface area of the average crystal (according to L.V. Tauson)

Table. Chemical composition of gold-bearing pyrite of Bakyrchik deposit

Number of sample	Content, mass. %			
	Fe	S	As	Ag
L-71 (sulfide ore)	26.15	32.77	2.02	1.12
	22.57	29.76	1.26	1.89
L-67(Concentration of rougher floatation)	19.84	17.01	1.79	-
	40.95	46.36	3.12	-
	33.23	64.S4	1.86	0.02
	45.72	50.04	4.05	0.05
	45.09	50.6S	2.89	0.05
	45.40	50.96	2.68	0.04
	44.59	49.94	3.35	0.06
	44.75	50.64	2.44	0.06
Tva 96 (monomineral fracture)	41.15	54.31	2.32	-
Tva 98 (monomineral fracture)	56.93	36.48	3.72	-

Nowadays, the mechanism of gold adsorption on the sulfide surface can be explained from the perspective of the existing concepts of the special physical and chemical properties of the nanoparticles, their relation to the huge specific surface energy and their great chemical activity (especially at their size decrease to the value of 5 nm and less) [1]. The mechanism of this process is grounded mainly on oxidation and reduction reactions: the reduction of gold in the areas with the minerals rich in arsenic (As) is accompanied with its oxidation on the neighbouring areas, which are rich in sulphur (S).

In order to reveal the gold adsorption by the sulfide surfaces, the experiments with application of the instruments were carried out for the research. The grounded samples of FeS_2 and FeAsS were put for 24 hours into the solution of $KAuCl_4$ / 1 molal mass NaCl in the amount of 100 ppm per the solution. As a result of substances interaction, the FeAsS surface sample became somewhat darker, and its solution turned less yellow, whereas there were no similar changes observed with sample of FeS_2. The samples of the sulfides treated in such a way were analyzed with the help of scanning electron microscope (SEM) and energy-dispersive spectrometer (EDS). Thus, the images obtained by SEM-analysis (Fig.6) demonstrate that the FeAsS sulfides had much larger area of gold cover if compared against FeS_2.

EDS analysis has indicated the chemical element capable to have greater gold sorption while the absence of chlorine peaks in the spectrum means that gold was deposited in the reduced form. The polished plain (roughness of <0.1 μm) samples of sulfide minerals were subjected to further x-ray fluorescent spectrometer (hereinafter referred as X-RayFL) analysis, recognized as the efficient method for analyzing the surface composition of a mineral and the oxidation degree of its chemical elements. In our research, X-rayFL analysis was used to determine the way how Au (III) was adsorbed on FeS_2 and FeAsS.

Under irradiation of the treated samples of FeS_2 and FeAsS, the peaks of Au4f were located near the same energy bond as those for Au (0). Therefore, the amount of Au (III) has somewhat decreased on the surface of sulfide minerals (Fig.7). Upon that, the peaks obtained at irradiation of processed FeS_2 samples show protrusions, coming out in the areas of Au (III). This means that on the surface of FeS_2 there possibly occurred reduction of Au (III) or partial reduction of Au (I). The absence of the protrusions on the peaks of FeAsS evidences that FeAsS facilitates reducing adsorption to be substantially easier in the comparison with FeS_2. The peaks of As3d belonging to FeAsS sample are compared with those of the sample to have been subjected to processing earlier. This aimed at defining whether As was oxidized and respectively whether gold deposition had the easier ways (Fig. 8).

The difference in the intensiveness of the peaks evidences that the higher degree of oxidation is prevailing within material after processing. The results of analysis conducted with atomic–force microscope (hereinafter referred as AFM) were used in order to receive the images of the gold growth on the polished surfaces of FeS_2 and FeAsS sulfides in the form of the functions of time. At the beginning of the experiment, the surfaces of both FeS_2 and FeAsS were relatively smooth. In 10 minutes of the experiment duration the adsorbed gold was noticeable on the surfaces of the both types of samples, but on the FeAsS surfaces it was to a greater extent. In 60 minutes, all the the FeAsS surfaces turned out to be almost completely covered by the adsorbed gold, whereas the FeS_2 surfaces had less

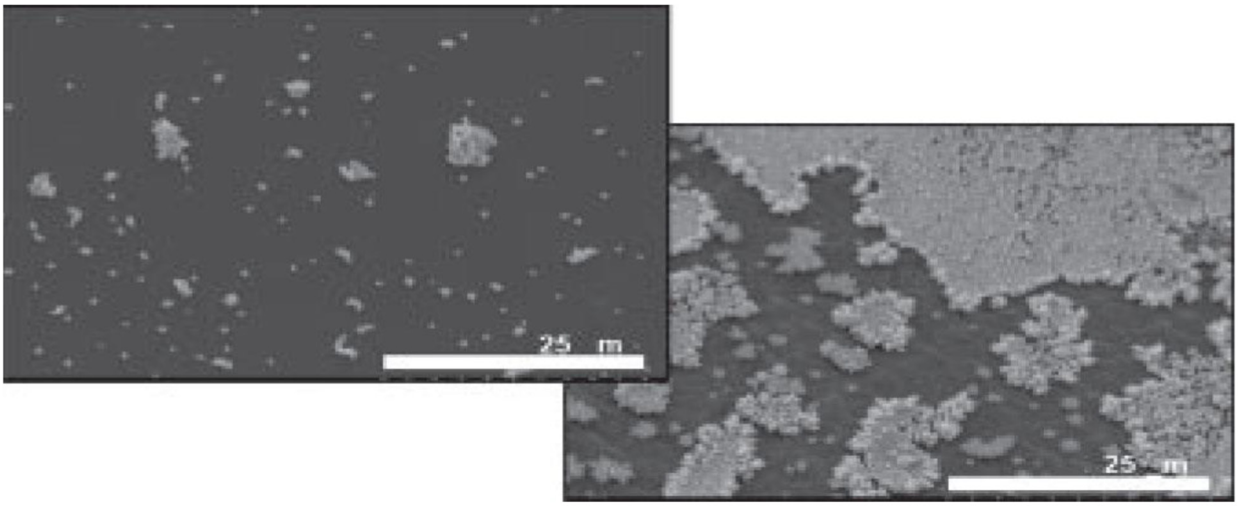


Fig. 6. SEM–images of FeS_2 gold-bearing samples (left) и FeAsS (right) after 24 hours of treatment (photo, general view)

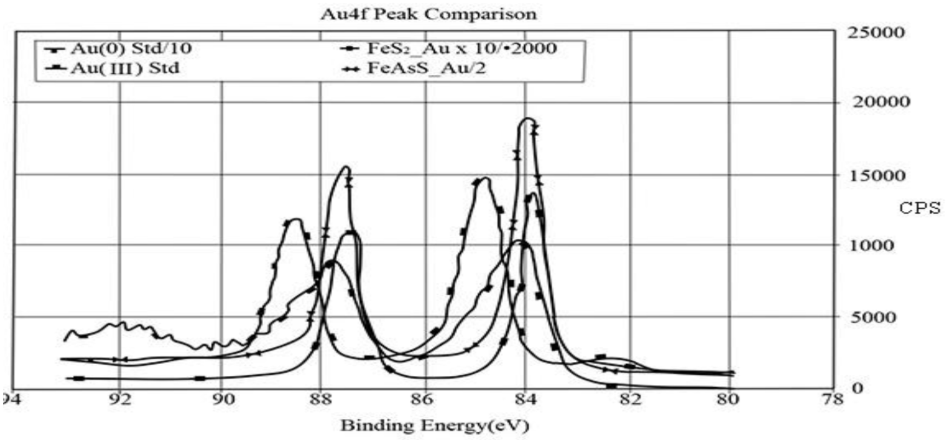


Fig. 7. Results of comparative studies by XrayFS analysis: the peaks of standard Au (0) and Au(III) and irradiated samples of FeS_2 and FeAsS

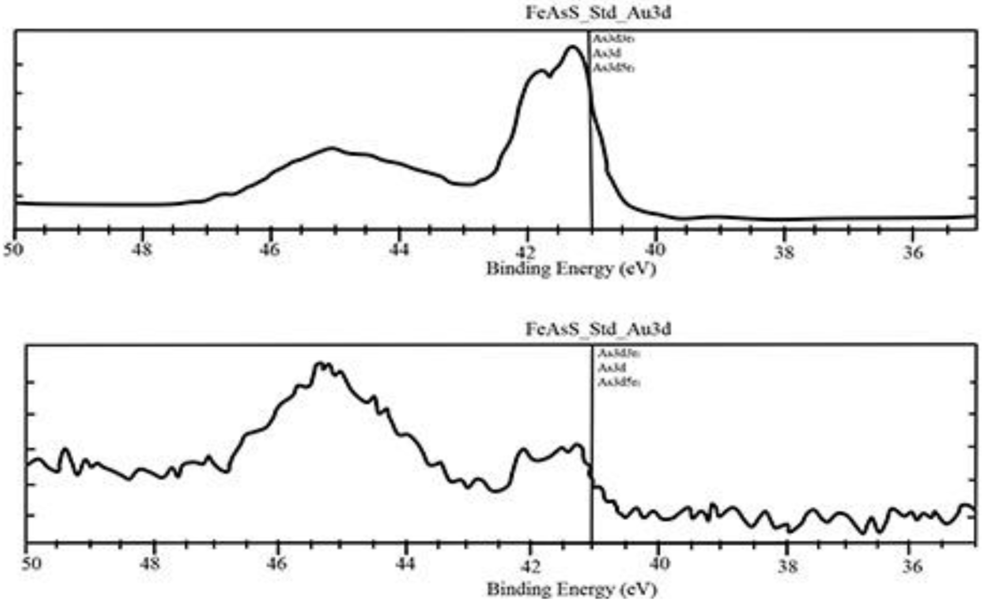


Fig. 8. The peaks of the FeAsS sample (top) and the FeAsS sample after processing (bottom) for PS As 3d comparative analysis

of that. The AFM analysis was also used to consider whether there was observed the influence of micro- and nanotopology of the mineral surface on selective gold adsorption. The results of AFM analysis for FeS_2 and FeAsS surfaces after 10 minutes treating with Au (III) solution are introduced in Fig. 9. The both types of samples show the selective gold adsorption on the different defects of the minerals surfaces, but to a greater extent these changes are seen on FeAsS sample.

Therefore, it has been revealed that Au (III) adsorbs on the FeAsS surface in a greater extent that on $FeS_{2.}$ Particularly, Au (III) reduces to Au (0) on the FeAsS surface while the surface of FeS_2 shows the characteristics of Au (III) and Au (0) sorption, and also partially reduced Au (I). Moreover, the gold adsorption turned out to be associated with certain physical imperfections of sulfide crystal structure, namely as follows: boundaries of grains, strains, twin boundaries and interphase boundaries of minerals [8]. Such surface imperfections of minerals lead to significant distortion of their perfect lattice. Furthermore, in the areas of the imperfections, the interatomic spaces within the crystal lattice in most cases are enlarged, which simplifies the diffused drain of gold atoms in these zones as the element possessing large size (Fig. 10).

Directions for the future researches

Under present-day conditions, geotechnologies are expected to allow the efficient use of minerals on the basis of fundamental knowledge of their physical and chemical properties and skillfulness to change these properties purposefully at the nanolevel. These certainly encourage the further development for the radical departure from the conventional practice of minerals processing to the new methods, including broader horizons with mineral uncommon types, for example, minerals of nanosize parameters [11]. In this

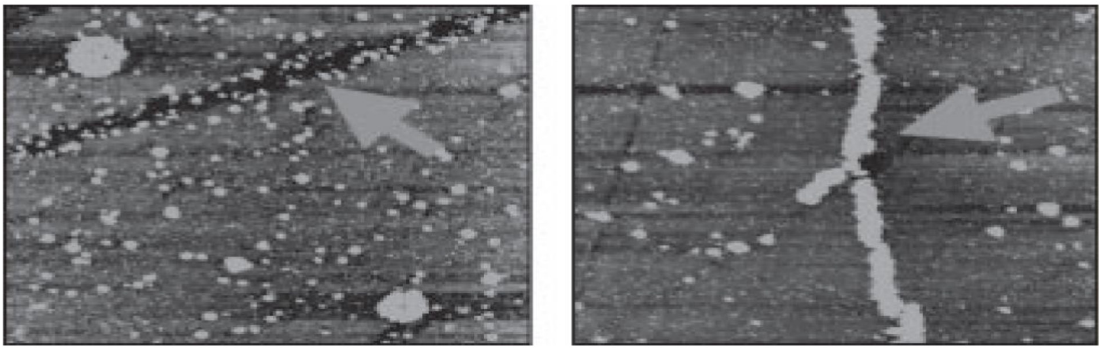
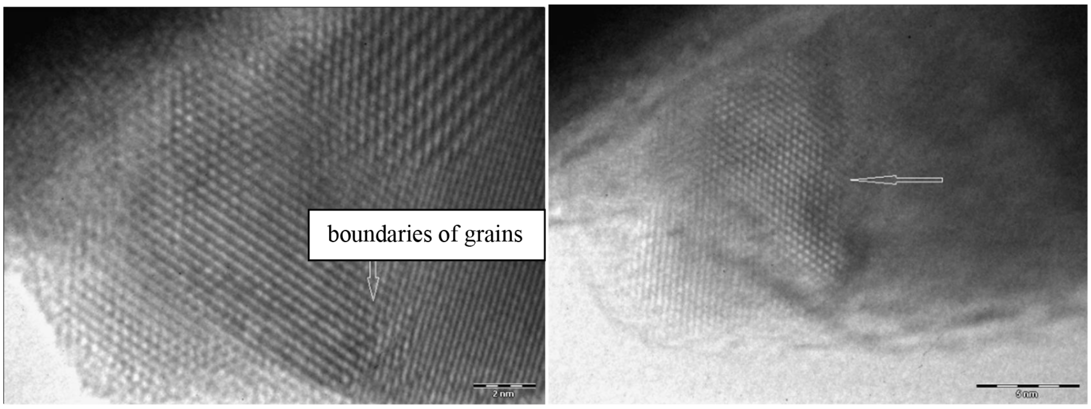


Fig. 9. AFM images of polished FeS_2 sample (left) and FeAsS sample (right) after 10 minutes of treatment (20 µm x 20 µm): the research results



10 a) 10 b)

Fig. 10. TEM images of nanoparticles [9]: 10 a) in arsenopyrite; 10 b) in pyrite

context, nanosize geotechnologies should be based on study and implementation of the valuable constituent extraction mechanisms on molecular, atomic and electronic levels, when the control of mineral processing procedures becomes possible already on the phase of valuable constituent formation [15–18].

The further publications are to contain more detailed examination of unique properties of nanoparticles with the objective to develop the efficient and rational means of gold nanoparticles recovery from the ores at heap leaching.

The results of the current research allow us to come to the conclusions that the imperfect subsystem of sulfide mineral matrix nanosurface is the place for gold adsorption in different forms. Some of them make a real challenge for the existing technologies used in the gold-processing plant [15]. Better understanding the properties of Fe, As and S in the sorption processes is important for the further development of efficient gold recovery technologies, for the control of mine acid drainage and for understanding the aftereffects of As release into the environment.

Results

The results of the comparative analysis conducted on the properties of the nanoreliefs of different gold-bearing sulfides are represented in the article. The morphology and the microtopography of the gold-bearing pyrite and the gold-bearing arsenopyrite are described.

Based on the oxidation and reduction reactions, the mechanism of gold adsorption is revealed. It is shown that gold to a greater extent is adsorbed by the surface of arsenopyrite than of that of pyrite. The gold adsorption mechanism is explained from the standpoint from the sulfide surface imperfections.

We have developed and implemented the new system of principle testing for gold-processing plant, which allows abrupt improvement of the results validity, reduces labour requirements and decreases the number of laboratory tests operations as much as 6 times.

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