

A Physicochemical Model of Gold Transformation in the Wastes of Processed Pyrite–Polymetallic Ores (Salair Ridge, Russia)

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Abstract—Gold-bearing dumps of processed pyrite–polymetallic ores of the Ursk ore field (Novo-Urskoe and Beloklyuchevskoe deposits, Salair Ridge) have been studied. Physicochemical modeling of the gold behavior in wastes allowed us to describe quantitatively the gold precipitation process in different horizons of the dumps. In the upper part of the sulfide-rich section, sulfide minerals undergo intense oxidation accompanied by the dissolution of structural and surface-bound gold. Gold redeposition on the pyrite surface (sorption reduction barrier) as a result of electrochemical processes is accompanied by the formation of heavy-metal sulfates and barite. Under the sorption barrier, there is a loose leaching horizon with high humidity, where gold is present in pore solutions as thiosulfate, hydrosulfide, and hydroxo complexes; its content reaches 68 mg/L. In the middle part of the section, composed of compact siliceous sandstones (hardpan), high-grade (up to 973‰) gold forms through the disintegration of thiosulfate complexes, but its content decreases to 10⁻⁶ mg/L (lithologic reduction barrier). No visible gold was found in the lower part of the section (soil bed), but its high contents (up to 0.35–0.42 g/L) might be due to the sorption by organic high-molecular compounds, such as humic acids. The morphology and chemical composition of native gold from the gold-containing dumps of processed pyrite–polymetallic ores have been first studied. It is shown that the gold surface has traces of supergene transformations, e.g., gold nano- and microparticles as sponge overgrowth on the gold or barite particle surface or as newly formed gold phases in Fe, Mn, and Al hydroxide films.

Keywords: technogenic mineral phases; horizon of secondary enrichment; supergene gold; physicochemical model

INTRODUCTION

Studying the behavior of noble metals in supergene processes, namely, the degree of their aggregation and differentiation in weathering crusts, oxidation zones and technogenic-mineral formations (TMF), is extremely important for the reconstruction of physical-chemical conditions for the formation of ore concentrations in natural and technogenic objects. Published research and our own materials on various supergene gold-bearing objects (Kalinin et al., 2009; Yanchenko et al., 2019) enable us to talk about the appearance of a new supergene geochemistry of gold due to its sufficiently high mobility, the ability to change its mineral and soluble species and concentrate on geochemical barriers. A distinctive TMF feature is that they are analogues of natural systems in which, however, all chemical reactions occur faster (Kirillov et al., 2018). The horizons of second-

ary enrichment have been formed over decades, allowing us to consider them as potential (and often real) ore objects.

At the same time, questions about the consolidation mechanisms of native gold particles and the reasons for the change in its fineness in supergene media, the chemistry and the scale of the processes of dissolution, migration, and precipitation of noble metals, and their migration distance remain not fully clarified. The gold consolidation from the process of local chemogenic redistribution comes at the expense of the association of small native gold particles into larger aggregates by the mechanism of interdiffusion at the boundaries of contacting particles (Kalinin et al., 2009). Also, the role of the biogenic factor in the processes of gold transformation in various supergene media is not fully appreciated, since this process has even more parameters. Reith et al. (2010) described biofilms living on native gold, playing a key role in its biogeochemical cycle, contributing to dispersion through the formation of nanoparticles, as well as the formation of secondary biomorphic Au. Bacterial colonies of *C. Metallidurans* can accumulate gold in the form of spherically shaped particles (Southam et al., 2009).

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Bacillus bacteria are known to dissolve gold (Korobushkina et al., 1983) and then precipitate gold colloids from solutions intracellularly and extracellularly (Karthikeyan and Beveridge, 2002). In (Amosov and Vasin, 1993; Kuimova and Moiseenko, 2006) it is shown that supergene gold can be formed both in biotic and abiotic processes during low-temperature mineral formation.

According to the data of the microbiological study of the Novo-Ursk tailing, representatives of the genus *Bacillus* and the genus *Micrococcaceae sp.* dominate here, and their number increases with depth (Rihvanov et al., 2017). It is shown that at least 26% of sulfate sulfur is produced due to the activity of microorganisms, and microbial oxidation is much more effective. These authors found that representatives of the genus *Bacillus* dominate in soils, and the representative's number of group *B. Subtilis* significantly exceeds the representative's number of group *B. Cereus*.

The aim of this work is (1) to study the morphology and composition of native gold from the cyanidation tailings of pyrite-polymetallic ores of the Novo-Ursk and Belokluch deposits, (2) to characterize the secondary enrichment zones with supergene gold and to classify geochemical barriers, (3) taking into account mineral and the chemical composition of the substance and the solutions interacting with it, create a thermodynamic model and explain the conditions of transfer and deposition of gold.

OBJECTS OF INVESTIGATION

The Ursk mine has been known since the beginning of the 19th century (Kemerovo Region, Russia, the Northeast Salair Ridge). Initially, from 1893 to 1896 years, deposits were developed in an open way for flux mining. Then the Belokluch and Novo-Ursk deposits were discovered in 1931 and 1932, respectively. On the deposits gold and silver from the oxidation zone were predominantly mined, namely from quartz-barite and quartz-pyrite sypuckies. The noble metals were extracted by leaching with cyanide. After extraction, the gold-bearing waste ores were stocked on the soil on the tailing. The structure, morphology, and composition of the ore bodies, the sequence of mineral formation, and the history of mining have been studied and described by many researchers; thus, a brief description of the ore field is given in these articles (Bolgov, 1937; Cherepnin, 1957; Kovalev, 1969).

For the deposits of the Ursk ore field, endogenic gold mainly is in a bound form, in sulfides (Bolgov, 1937; Cherepnin, 1957; Distanov, 1977), as well as in low-thickness quartz veins (Roslyakova et al., 1983). The sizes of gold grains are ~ 0.015 mm, gold is associated with chalcopryrite, pyrite, and fahlite (Zerkalov, 1962; Kovalev, 1969), as well as with argentite in quartz (Cherepnin, 1953). The gold concentration is 5.8 ppm (Roslyakova et al., 1983). However, tellurides of Au and Ag are insignificantly developed – altaite and hessite; in the ores of the Belokluch deposit it is geocronite (Distanov, 1977). As the result of the chemical weathering, gold was liberated, forming the gold

native particles in the zone of oxidation. The Belokluch deposit distinctive feature is the oxidation zone with a gossan, which directly lies on barite and pyrite loose material (Bolgov, 1937). The maximum concentration of gold belongs to the gossan zone. Compared to primary ores, gold enrichment is 7–20 times, silver 5–7 times and arsenic 2–3 times (Bolgov, 1937; Debrikov, 1937). Besides, in the oxidation zone, mercury has a high concentration. Mercury is found as native form and in the form of cinnabar. Fahlite and sphalerite can be a source of mercury (Kovalev, 1969).

Among TMF of gold-bearing ore deposits, tailings dump of high-sulfide ores, such as Belokluch and Novo-Ursk (pyrite-polymetallic) deposits located in the village of Ursk are of most interest. Because the sulfides have high gold concentration, their oxidation can result in the release of significant amounts of dispersive Au that forms larger native-form grains. Depending on the scale, intensity and process durations, horizons of secondary gold enrichment are formed, which have not only scientific but also applied significance. For example, in 1969 the Salair mine researched the tailings of Novo-Ursk and Belokluch deposits as a technogenic deposit on the gold and barite extraction. The total reserves of two dumps in categories B + C₁ amounted to Au – 641 kg (average contents varied in the range 0.4–0.7 ppm); Ag – 37.8 t (average content 26.5 ppm). Significantly higher concentrations of gold (up to 11.9 ppm) and silver (up to 350.7 ppm) were recorded in the underlying soil horizon and, probably, in the lower parts of the dumps. The concentration ratio for individual Au profiles was 10.8, varying from 2 to 24. For Ag, the concentration ratio variations were wider, from 0.5 to 12.6 (average 3.5), that is silver behaves like a much more mobile element, concentrating in some cases, and others moving outside the dump.

Since for many years the objects considered above have been the reference for the study of various aspects of the geochemical behaviour of elements in supergene conditions, they traditionally receive much attention (Gas'kova et al., 2000; Bortnikova et al., 2006; Shcherbakova et al., 2010; Myagkaya et al., 2013, 2016a,b; Olenchenko et al., 2016; Saryg-ool et al., 2017; Rihvanov et al., 2017; Yurkevich et al., 2017b; Gustaytis et al., 2018; Lazareva et al., 2019).

The tailings of the Novo-Ursk deposit are heaps of oxidized ores cyanidation. Heaps of quartz-barite and quartz-pyrite tailings are separated by a stream formed as a result of flushing from the surface and seeping of atmospheric water through rocks up to the base of the dump. The drainage stream water is salty (TDS up to 7 g/L), strongly acidic (pH 1.8–2.7, Eh 665–760 mV), mainly sulfate, Al–Fe–Ca. The molar concentration of Mn and Zn reach 1% in these solutions (Shcherbakova et al., 2010; Olenchenko et al., 2016). In the drainage stream water, the concentration of the noble metal depends on the season, namely, Au from 0.2 to 1.2 mg/L; Ag from 0.01 to 0.3 mg/L. With increasing distance from the dumps in the drainage stream, the pH increases, and Au concentrations decrease to 0.003 mg/L, Ag to 0.008 mg/L (Myagkaya et al., 2013).

The tailings of the Belokluch deposit is also represented by heaps of the same composition and origin (quartz-barite and quartz-pyrite composition), up to 10 m height. These pH of the solutions varies from 1.9 to 3.0, Eh 500+800 mV (Yurkevich et al., 2017a).

In this article, the accent has been done on the following research aspects: (1) identification of localization and zonation of secondary gold enrichment in the body of ore cyanidation dumps; (2) studying the mineral composition and internal structure of the waste heaps, determining the forms and composition of gold in these zones (typomorphic features of Au); (3) explaining the mechanisms of gold transfer and deposition in specific environments using calculations of thermodynamic equilibria using physical-chemical computer modeling.

METHODS

This work is based on materials selected during the field-work of 2015–2018. On the dump of the Novo-Ursk deposit, the lower part section of oxidation ores (2 m from bedrock exit) was exposed. This was chosen because the research of 1969 has shown, that the high gold concentration belongs to the lower part cut. The samples were collected from vertical sections in different “lithological” interlayers (top-down, Fig. 1a): 1) a gray-bluish quartz-barite-pyrite horizon ($h = 40$ cm) with silica geodes; 2) a brown iron horizon ($h =$

40 cm); 3) a schist horizon ($h = 50$ cm), lying directly on the ground. The total number of samples is 19, with a volume of 15 kg each.

At the dump of the Belokluch enriched ores, a 5 m section was opened. The section can be divided to the follow interlayers (top-down, Fig. 1b): 1) an upper horizon, which consists of rust-red quartz-barite sypuchka (0–220 cm); 2) a middle horizon – a quartz-pyrite sypuchka of grey color (220–350 cm); 3) a lower horizon – an oxidation zone of rust-red color to a depth of 500 cm. Samples were collected at regular intervals to determine the chemical composition. The total number of samples is 17. For research of the native golds, 8 samples were selected with a volume of 15 kg each.

For 17 samples from the Belokluch dump pore solutions were squeezed under a pressure of 100 atm. The concentration of noble metals was determined by the method of ICP-MS in the HATs “Plazma” (Tomsk).

Studies of the chemical composition of samples were conducted in the Analytical Center for Multielemental and Isotopes Research, SB RAS (Novosibirsk). The concentration of gold and silver was determined by atomic absorption analysis (analyst V.N. Il’ina).

The samples were enriched by the gravity method by using a rocker. The gold particles were selected under a binocular microscope.

The main results were obtained by scanning electron microscopy (SEM) a TESCAN MIRA 3LMU (Carl Zeiss,

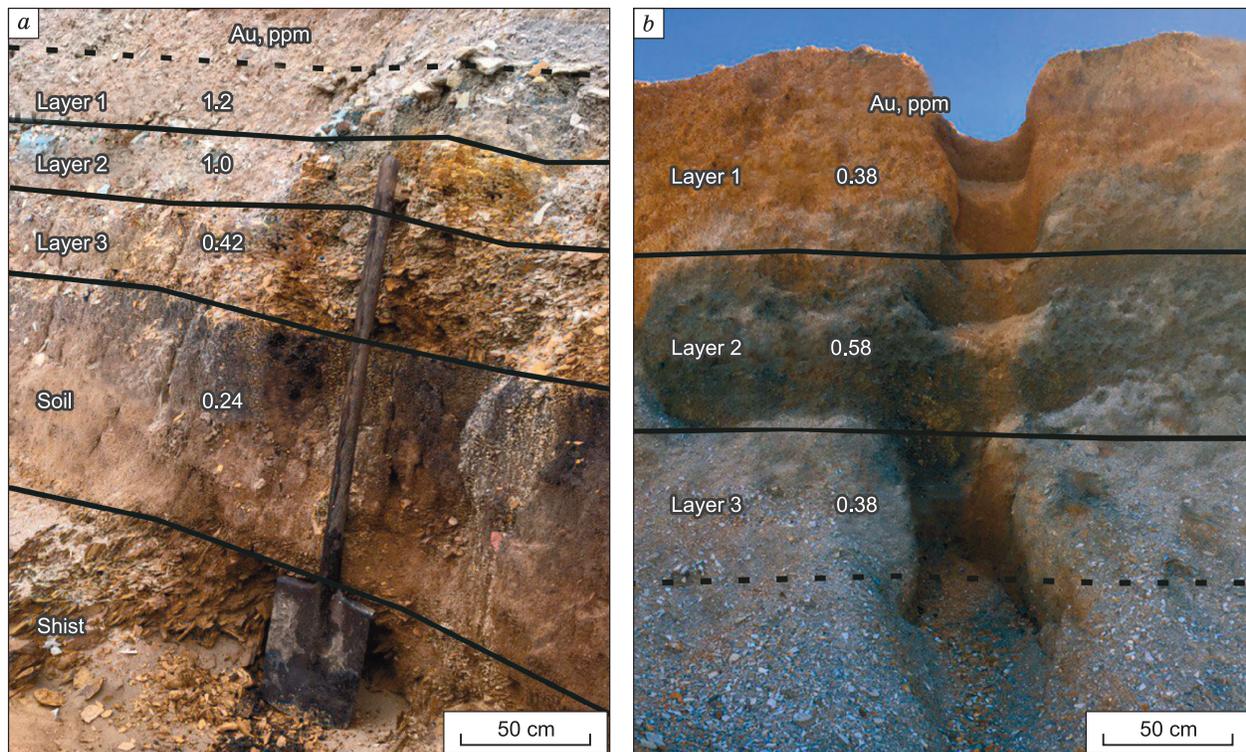


Fig. 1. The common view of the cuts with sampling horizons and distribution of the gold concentration (data of atomic absorption analysis). a, The dump of Novo-Ursk deposits; b, the dump of Belokluch deposits.

Table 1. Physical and chemical modelling scheme based on the composition mineralogical and chemical analysis of oxidation zones samples for the dump of the Novo-Ursky deposit

Layers of the cut	The composition of solid phases	Major oxides, wt.%
The upper part of Layer 1	Barite, pyrite, quartz, sulfates of Fe, Cu	SiO ₂ 14.35; Fe ₂ O ₃ 3.47; BaO 55.05; SO ₃ 24.19; LOI 2.32
The lower part of Layer 1	Quartz, pyrite, barite, sulfates of Fe, Cu, CaCO ₃	SiO ₂ 7.11; Fe ₂ O ₃ 8.05; BaO 4.22; SO ₃ 18.29; Al ₂ O ₃ 1.2; CaO 34.2; LOI 25.29
Layer 2	Quartz, hydroxides of Fe, jarosite, barite, clay minerals, gypsum	SiO ₂ 40.19; Fe ₂ O ₃ 13.26; BaO 10.88; SO ₃ 10.92; Al ₂ O ₃ 6.22; CaO 5.86; LOI 10.42
Layer 3	Quartz-albite-chlorite schists, clay minerals, the abundant hydroxides of Fe, a soil	SiO ₂ 63; Fe ₂ O ₃ 10; BaO 0.3; SO ₃ 0.3; Al ₂ O ₃ 12; CaO 0.7; Na ₂ O 1.6, K ₂ O 1.8; LOI 9 (mean)

Germany), spectrometer in the JEOL JXA-800. The finenesses of gold, as well as its impurities, was obtained by microprobe analysis.

Physicochemical modeling was carried out at 25 °C and 1 bar total pressure using the “HCh” software (Shvarov, 2008) and the consistent thermodynamic database “UNITHERM”. We modelled the heterophase 19-component system H₂O–Na–Ca–Mg–K–Sr–Ba–Si–Al–Cl–C–S–Fe–Mn–Ag–Au–Cu–Zn, including species in solution, minerals and gases. The initial information was analytical data on the mineral and chemical composition of the substances deep into the dump cross-sections (Table 1). Oxidation-reduction conditions (Eh) were assessed by opening the system to oxygen (the chemical potential of the mobile component was specified). Acidity was maintained by the degree of sulfide oxida-

tion at different Eh, alkalinity was corrected by the presence of carbonate and bicarbonate ions in the solution in equilibrium with the atmospheric CO_{2(gas)}, i.e., 10^{-3.5} atm.

RESULTS

The typomorphic characteristics of gold

The Novo-Ursk dump. According to the atomic absorption analysis, the gold content for oxidized ore varies in the range of 0.4–1.2 ppm. We have found about 68 particles of nugget gold from horizons 1 and 2 (Fig. 1). The gold is fine, of 0.25–0.1 mm (60%) in size, <0.1 mm (25%), 0.5–0.25 mm (10%), 1–0.5 mm (5%). Predominant grains are the grains of the crystalline form, elongated and rarely flattened (Fig. 2). According to the microprobe analysis, in Ho-

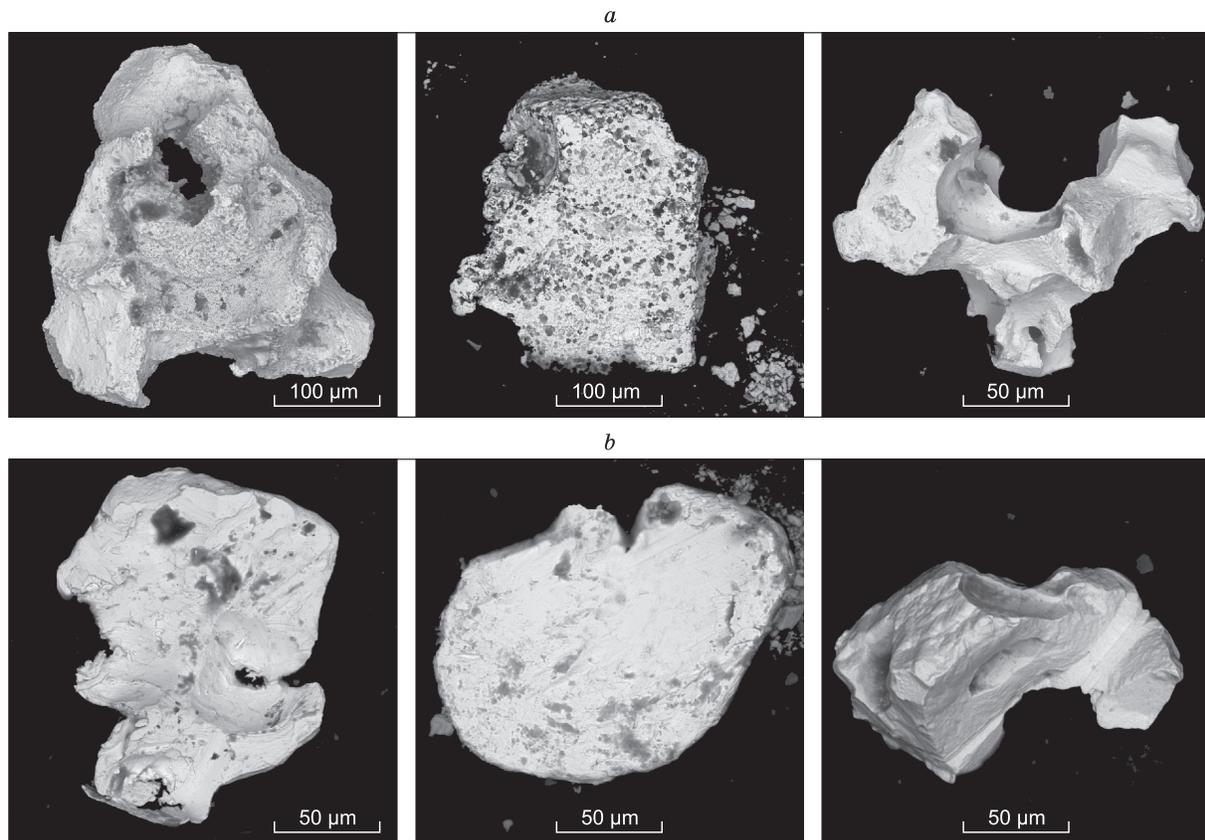


Fig. 2. Morphology gold particles from the secondary enrichment horizon of Novo-Ursk dump. *a*, layer 1; *b*, layer 2.

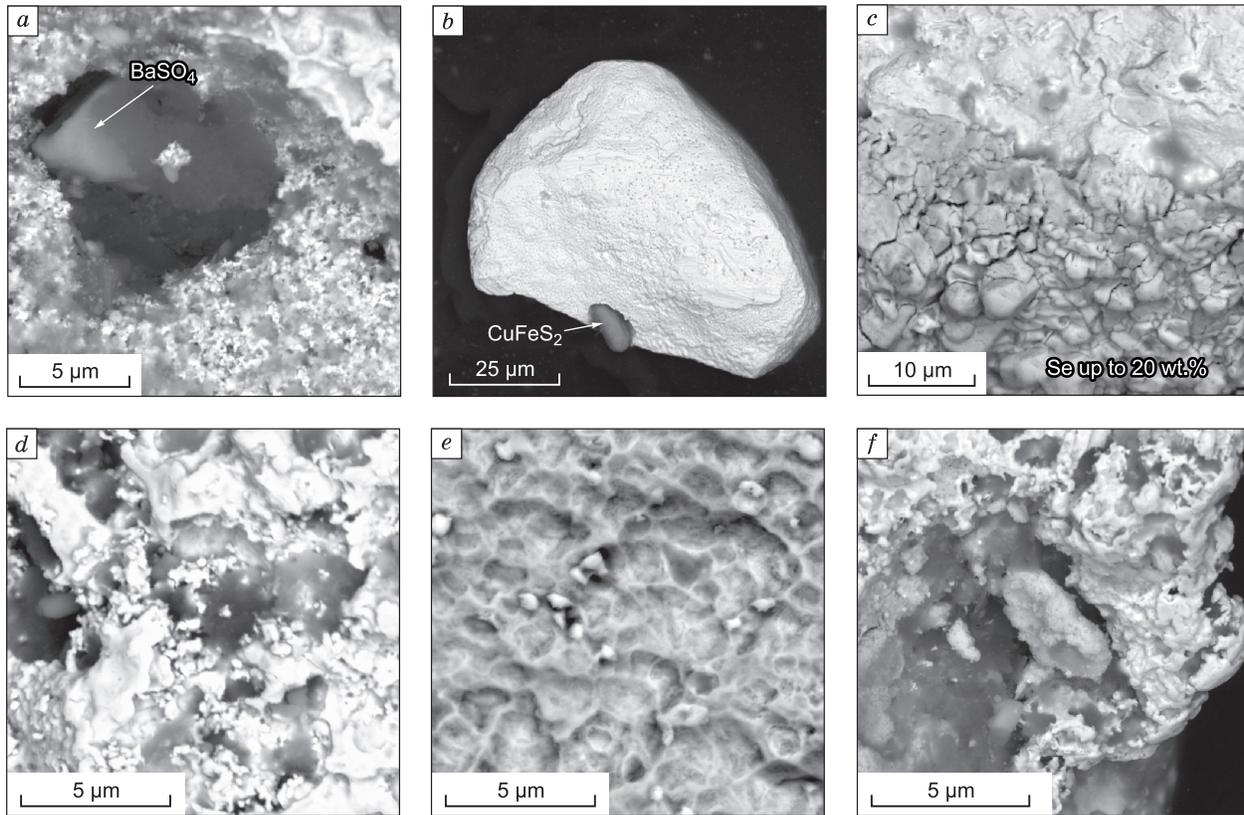


Fig. 3. Surface sculpture of gold from the dump of Novo-Ursk deposit. *a*, Association of sponge (the new-formed) gold, a massive gold and trapped barite grain; *b*, inclusion of chalcopyrite grain; *c*, Ag-Au-Se-phase overgrowth on the gold surface; *d*, the micron size cluster of gold particles on the gold surface; *e*, the micron-size single particles of gold with mesh structure of surface; *f*, the various size and form overgrowths on the gold surface.

rizon 1, the gold has the following composition: 1) gold with a medium fineness (~840‰) with impurities of Hg (1.2–3.0 wt.%), Ag – 13.3–16.7 wt.%; 2) gold with a low fineness (~730‰) with impurities Hg (3.4–5.0 wt.%), Ag – 19.8–27.1 wt.%.

In Horizon 2, we found about 9 particles with a size of <0.25 mm. Predominant grains have isometric- (60%) or flattened form (40%). Fineness varies from 727 to 973‰ with the separation of the same two groups. Besides, we found the gold particle with a fineness of 973‰. The gold has a uniform inner structure; no zonal structure or residual cores were noted. At the same time, the surface combines a variety of sculptures.

By SEM we found supergene transformation on the gold surface morphology, for example, growth and dissolution structures (Fig. 3). The nano- and microparticles of gold in the form of spongy growths and/or single rounded grains. They were located in films, depressions, surface irregularities, or, conversely, on elevations. Also new-formed phases of gold are present on the surface of gold particles (Fig. 3*a*, *d-f*), on the surface of the grain of other minerals (Fig. 3*a*) or on the surface of native gold itself (Fig. 3*d-f*). In addition, the presence of mineral inclusions, such as barite (Fig. 3*a*),

chalcopyrite (Fig. 3*b*), the overgrowth of Ag-Au-Se-phase (Fig. 3*c*) were noted.

Another characteristic of grains is the step structure of growth or imprints of minerals on the surface of the particles (Fig. 4).

The Belokluch dump. The gold distribution is subject to certain laws in the cut. Average gold contents are 0.38 ppm (Fig. 5) both in the upper and lower layers of the oxidation horizons. In the upper layer, concentration varies from 0.23 to 0.60 ppm, the lower layer – from 0.34 to 0.46 ppm. This is a consequence of the active redistribution of gold in the surface layers compared to deeper horizons. For the horizon of quartz-pyrite sypuchka in the middle part of the cut, the average concentration of gold equals to 0.58 ppm and varies from 0.50 to 0.66 ppm. The gold content of the horizons depends on the concentration of gold in the sulfide substance of the deposit. Measured gold concentrations were found in the pore waters of each layer, reaching high values in some layers. It should be noted that the presence of gold in the pore waters of the dump is determined by the processes of dissolution/re-deposition that occur after its formation. It is logical that in the upper oxidized horizon, the concentrations of gold in pore solutions are

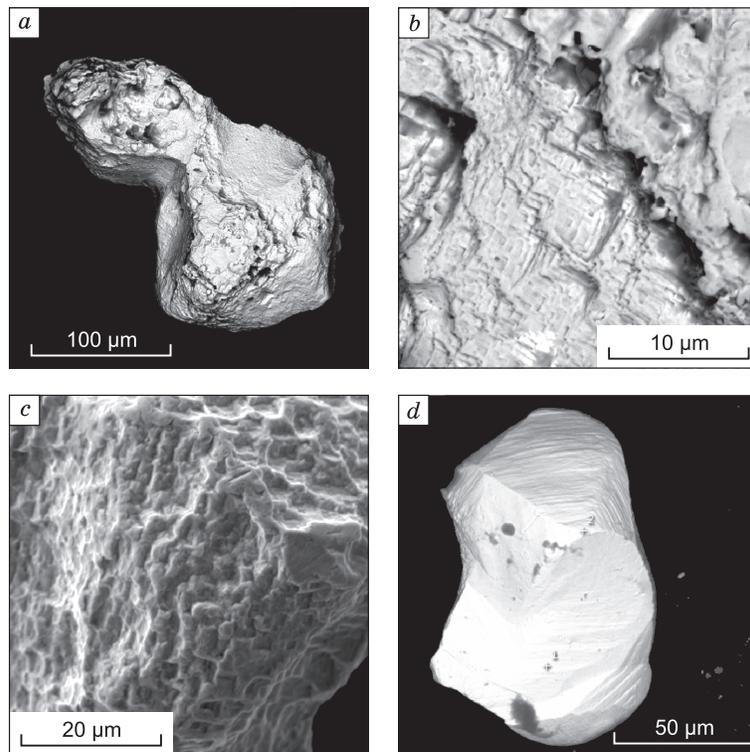


Fig. 4. Step growth structure of gold from the dump of Novo-Ursk deposit. *a*, The common view of particle crystal gold with elements of growth or imprints (?); *b*, enlarged fragment «*a*» with micro-layers; *c*, rougher stepping; *d*, a gold particle with nano-layers.

highest: on average 0.024 mg/L with fluctuations from 0.0013 to 0.083 mg/L. Moreover, the maximum content is determined in the layer at a depth of 37 cm, where it accumulated, gradually increasing from the surface itself. Then, with some fluctuations, the gold concentration in the pore waters of the oxidized layers gradually decreased. In the upper horizons, the distribution curves of bulk and gold concentrations in pore waters are identical (up to depth 87 cm). But then this correlation is disturbed: in the quartz-pyrite supychka, the content is significantly higher than in the oxidized layers, and in pore solutions, it decreases radically on average to 0.00027 mg/L and remains approximately at this level to deep horizons (470–500 cm), where there is a slight increase in the concentration of gold in pore waters (0.0021 ppm).

Thus, it is possible to characterize the process of gold redistribution due to the action of acidic aggressive solutions. The initial gold concentration in the tailings was determined by its content and forms in the two types of processed ores. Apparently, in the oxidized quartz-barite ores, a large proportion of gold was in the native, recoverable by cyanide solutions form. It corresponds to relatively low Au content in the oxidized waste material. In a quartz-pyrite ores, where Au mainly is the impurity in sulfide minerals, gold content is higher. It is known that sulfides inhibit the cyanidation process and reduce its effectiveness.

During the existence of the tailing, the acid drainage water dissolved the various minerals. The gold content depends

on its bulk concentration and native gold forms in the pore solution in the upper part of the cut. In the horizon of quartz-pyrite supychka the gold came to the pore solution from the sulfide minerals. Note, that in the pore solution the distribution of silver differs from gold.

We found 18 particles of gold from the lower part of the cut (Horizon 3) (Fig. 1*b*). The gold is fine, size of 0.5–25 μm (39%), 1–0.5 mm (33%), 0.25–0.1 mm (22%), <0.1 mm (6%). It is presented by crystalline gold particles with distinct edges, elongated prismatic crystals of tabular form. Morphological types of native gold, represented by aggregates of lumpy grains, have an irregular shape (Fig. 6). The vertices of the faces are smoothed, and the edges of the particles are curved.

A specific characteristic of the studied particles is the presence of mineral inclusions inside them, both on the surface and particles trapped inside. Sculptures of particles' surfaces are very diverse. Almost all particles of gold have an overgrowth of micron size (Fig. 7*a*), microlayers (Fig. 7*b*, *c*) and tuberosity (Fig. 7*d*). Furthermore, imprints of minerals and cross-hatching on the grains were noted (Fig. 7*e*, *f*). In addition, a grain with a porous surface was found, which is filled with rounded aggregates of gold (Fig. 7*k*, *l*).

Gold has a homogeneous composition. The fineness varies from 847 to 899‰, Ag impurities are presented – 9.6–15.7 wt.%; Hg – up to 0.4 wt.%; Cu – до 0.2 wt.%. The inner (central) part of the gold has, predominantly, a fineness higher than the edges. The fineness of gold decreases

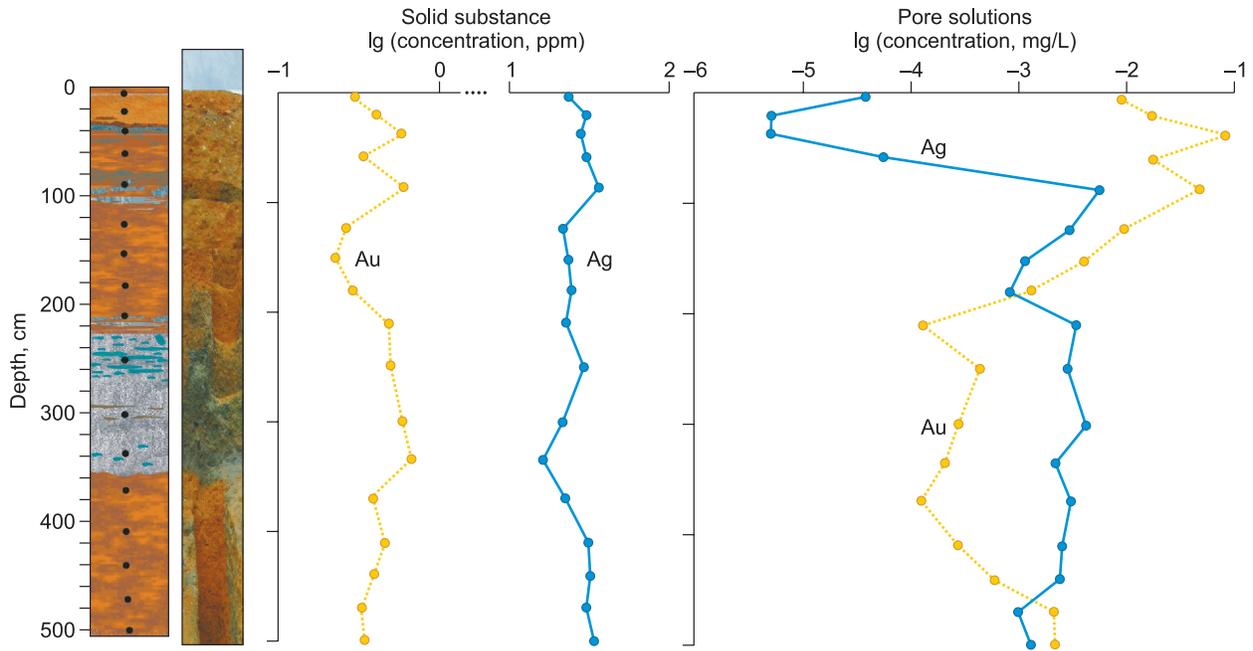


Fig. 5. Gold and silver distribution in solid substance and pore solutions.

in the peripheral part of the gold, having a smooth, gradual transition.

For the Belokluch dump, for inner gold structure, the large gold particles have hollows and holes, as well as barite inclusions (Fig. 8a). For grains of smaller classes (0.25–0.10 mm), curved edges (Fig. 8b) were noted. For the Novo-Ursk dump, there is the presence of gold microparticles at the boundary with the surface (Fig. 8c). Also, the contact of intergrowth of massive (main gold particle) with new-formed (sponge) gold (Fig. 8d) was noted.

Sculptures of gold clearly reflect the processes of redistribution of gold described above. The cellular surface relief is apparently the result of the etching of grains and crystals of native gold. And micron growths on the surface appear during the deposition of new-formed particles from pore solutions.

THERMODYNAMIC MODELING

Based on the above data, Table 1 shows the calculation scheme of the model associations equilibria, which are a macro-system that determines the processes of migration and deposition of gold in the dumps of the Novo-Ursk processed ores. In general, the scheme is as follows. In the upper part of the pyrite rich section, intense oxidation and the formation of sulfate solutions begin (Horizon 1). The first reaction is characteristic of very acidic solutions with $\text{pH} < 2$, and the second one for $\text{pH} > 3$.

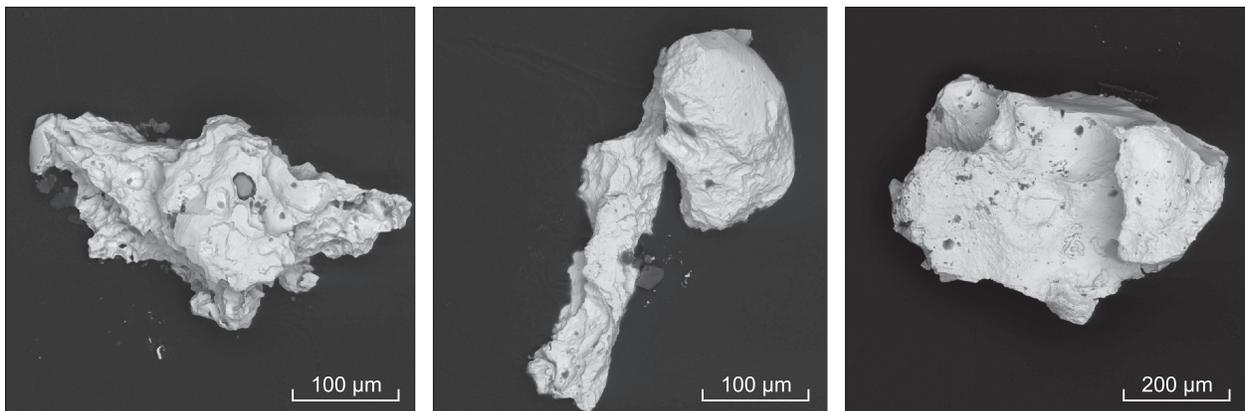
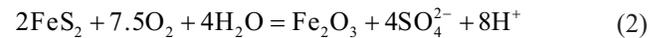
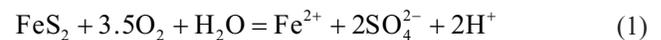


Fig. 6. Morphology of gold particles from the Belokluch dump.

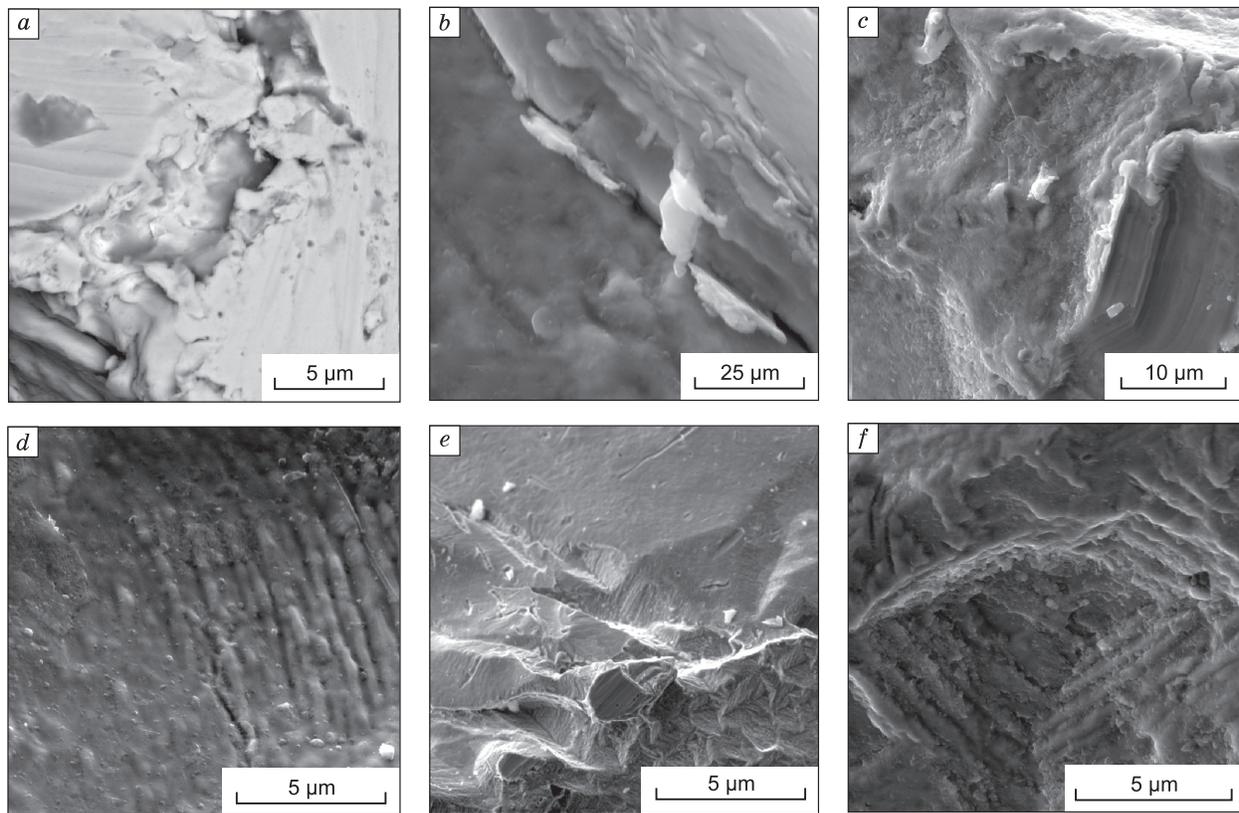
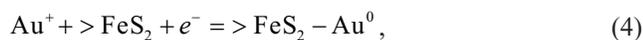
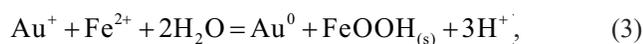


Fig. 7. Surface sculpture of gold from the dump of Belokluch deposit. *a*, Groove on the surface of the gold grain, which is filled with gold particles of nano- and micron size; *b*, *c*, surface with thin layers; *d*, lumpy relief; *e*, the imprints (?) of crystals and their faces, which are filled with nanoparticles (the enlarged fragment *d*); *f*, the interstitial particle with captured inclusion of barite grain; *g*, the rounded gold with dissolution structures (the cellular relief), which is filled with a rounded gold particle (the enlarged fragment *i*).

Under these conditions, both structural and surface-bound gold is dissolved. In acidic solutions, reaction (3) can occur. However, the main process that proceeds in the upper horizon is the reduction of Au to its own solid species on the pyrite surface (4):

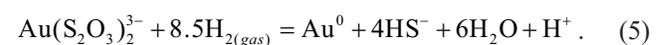


where $> \text{FeS}_2$ is sulfide with surface defects, and e^- is an electron. This phenomenon is more due to the electrochemistry of the process (sharp variations in Eh, V) and is associated with the influence of namely supergene processes (Tauson et al., 2014, Vorob'ev and Tcharo, 2016). The results of these authors allow us to conclude that these defects on the surface of the mineral matrix of sulfides are the site of capture of gold in various forms. The authors of the latest work suppose that surface gold can exist as 3 chemical forms, i.e., Au^0 , AuCl_2^- и $\text{Au}(\text{SCN})_2^-$. Complexes with chloride- and thiocyanate ions are not related to reductive deposition, but ion-exchange deposition from gold-containing solutions and will not be considered here. We will call the first stage as

reductive sorption, realizing that it was initially caused by the oxidation of pyrite.

Due to the percolation of acid sulfate solutions (from lat. Persolatio – filtering as opposed to surface flushing), the subzone of the upper part of the section (upper part of Horizon 1) is a leaching horizon with high humidity. Let's pay attention to high loss on ignition (LOI 25.29%). Water sulfates and organics accumulate over a dense brown-iron horizon (lower part of Horizon 1). Gold in pore solutions is in the form of various complexes, including thiosulfate-, hydrosulfide-, hydroxo- and chloride species. Sponge gold is determined here, which in nature and various technological processes is obtained by reduction from its salts. The deposition process is repeated, as evidenced by small growths on larger gold grains.

The middle part of the section is a dense iron-siliceous sandstone (Horizon 2), which in Western literature is called “hardpan”. Here 10 times fewer gold signs are found, but including the highest-grade gold 973‰. This zone is marked by limited oxygen availability and could be named as the lithological reductive barrier (5):



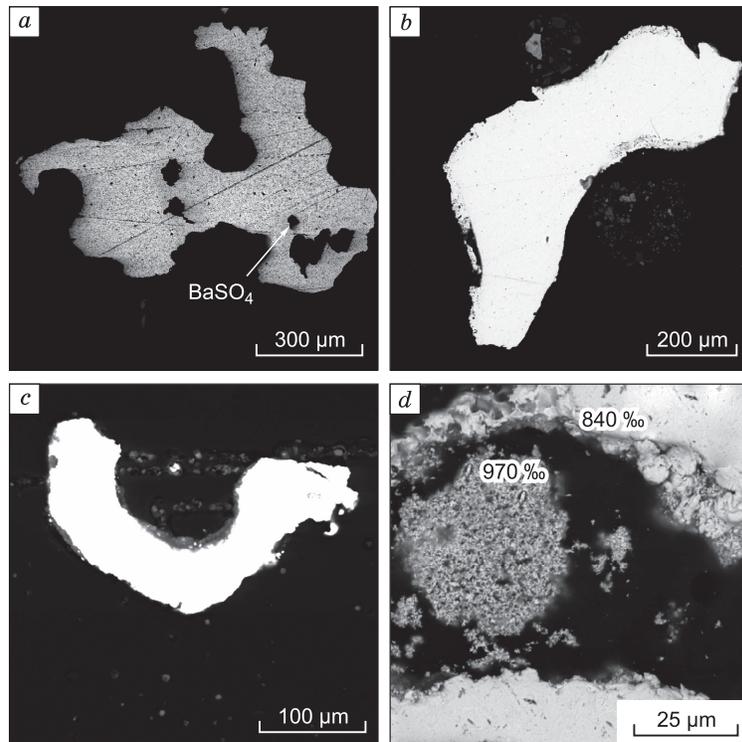
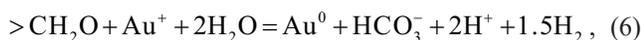


Fig. 8. The internal structure of gold from the dumps of Belokluch (*a, b*) and Novo-Ursk (*c, d*) deposits. *a*, The gold with the inclusion of barite particle; *b*, the openwork edges; *c*, the overgrowth gold nano- and micron size on the surface particle; *d*, contact of the basic (recrystallization) gold with sponge gold.

In the soil layer, the gold content reaches 0.42–0.35 g/L. Native visible gold is not found here. For example, in the layer pr.5 – SPP is 11.6 wt.% (82 wt.% accounted for oxides of Si, Fe, Al). In a recent work (Hadri et al., 2018), the huge role of soils in the irreversible retention of metal nanoparticles, which occurs immediately in the first hours, is shown. This process can be represented as follows (6):



where $>\text{CH}_2\text{O}$ is an organic molecule with acidic functional groups capable of reducing gold and to be oxidized to HCO_3^- ; and Au^+ can be initially complexed with one of the ligands (thiosulfate, chlorine or OH^-).

Table 2 shows the results of model equilibrium conditions of the studied mineral associations and the amounts of gold and silver involved in migration. At negative Eh -0.36 V and pH 8–9, when barite, pyrite and other sulfides are stable, gold and silver in the solution remain below a geochemically significant level (column 1–2). Sulfur in the solution is in the form of HS^- and SO_4^{2-} (0.68 mg/L), Ba and Si concentrations are 3–4 mg/L. With little access to oxygen, Eh 0.2 V (pH 2.5–5.1 depending on the amount of Ca in the solid phase), pyrite disappears, and quartz, barite, chalcocite, and argentite are present in the solid phase. Barite and calcite may compose of up to 1%. Iron in solution is as Fe^{2+} and FeSO_4^0 species up to 2.6 g/L; the concentration

of sulfates is the same. These sulfate solutions contribute to the leaching of Al, Ca, Zn up to hundreds of mg/L. Gold and silver concentrations are about 10^{-6} – 10^{-8} mg/L. Gold enrichment due to accumulation in the residual phase is possible here, its intense dissolution is prevented by Fe^{2+} (4). Further, the solutions become strongly acidic, Eh 1.1, pH 1.6.

Only under such acidic, oxidizing conditions do jarosite and goethite appear in association with quartz and barite. Gold concentration in the superacid solution can be up to 68 mg/L, and silver up to 100 mg/L, respectively, in the form of AuCl^0 , $\text{Au}(\text{OH})^0$, Ag^+ and AgSO_4^- . Gold is instantly reprecipitated when solutions are alkaline or difficult access to oxygen, as described above, take place. At Eh 0.18, pH 7.8, there is in the solution of $6 \cdot 10^{-8}$ mg/l gold, silver is two orders of magnitude higher. In the mineral association, oxides, sulfates are stable, and carbonates (calcite and smithsonite) can be presented.

At the final stage, we calculated the stability conditions of quartz-albite-chlorite schists. Iron hydroxides appear there, as the clay mineral kaolinite; the mobility of gold and silver is limited. This mineral paragenesis (this layer) will keep gold from leaching solutions until the Eh-pH conditions are close to the natural ones.

The sulfur concentrations in solution changes due to a specific equilibrium (Table 2, third line from the bottom). The minimum values are in equilibrium with pyrite at Eh -0.36 V, then its content sharply increases up to 3.25 mg/L,

Table 2. Calculated stability conditions of mineral associations and the amounts of gold and silver involved in migration and deposition

pH	9.35		2.4		1.6		7.78		8.2	
Eh	-0.36		0.2		1.1		0.18		-0.22	
Silver	9.27E-04	0.21%	0	0	0	0	9.27E-04	0.17%	9.27E-04	1.60%
Gold	5.08E-05	0.02%	5.08E-07	0.00%	1.15E-07	0.00%	5.08E-04	0.17%	5.08E-04	1.60%
Quartz	1.66E-01	21.22%	1.78E-01	25.93%	1.82E-01	24.92%	1.66E-01	16.56%	4.84E-02	46.62%
Cuprite							2.72E-03	0.65%	0	0
Pyrite	4.17E-02	10.62%								
Sphalerite	1.03E-02	2.12%								
Chalcocite	0	0	2.72E-03	1.05%						
Chalcopyrite	5.45E-03	2.12%	0	0						
Argentite			4.64E-04	0.28%						
Goethite					2.79E-02	5.65%	4.71E-02	6.94%	1.67E-03	2.37%
Calcite							8.21E-03	1.36%		
Smithsonite							9.12E-03	1.90%		
Gypsum							7.91E-02	22.57%		
Baryte	1.29E-01	63.69%	1.29E-01	72.74%	1.29E-01	68.27%	1.29E-01	49.70%		
Kaolinite									3.81E-03	15.77%
Chlorite									3.59E-03	32.04%
Jarosite					1.01E-03	1.15%				
Solution, mg/l										
Ag	5.51E-08		2.27E-06		1.00E+02		4.65E-06		3.61E-12	
Al	0		3.39E+02		2.48E+02		0		2.10E-04	
Au	4.07E-11		2.40E-08		6.77E+01		5.49E-08		7.13E-14	
Ba	2.92E+00		3.90E-03		4.74E-03		4.80E-03		0	
Ca	0		1.44E+02		0		6.67E+02		0	
Cu	5.58E-11		1.33E-04		3.46E+02		2.78E-02		0	
Fe	1.39E-03		2.63E+03		9.03E+02		3.52E-05		6.17E-03	
S	6.84E-01		3.25E+03		3.29E+03		8.13E+02		1.07E+02	
Si	3.87E+00		2.82E+00		2.82E+00		2.85E+00		2.91E+00	
Zn	2.80E-06		6.71E+02		6.71E+02		7.44E+01		0	

where only poorly soluble barite (according to barium concentration in the solution) is present. The rest of the sulfur in the form of SO_4^{2-} is “excessive”. It will accumulate in the solution until the appearance of jarosite (pH 1.6), however, when the pH shifts to the neutral region (pH 7.8), the concentration of sulfates is already regulated by gypsum (by calcium, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In Fig. 5, there was shown a sharp difference in the behavior of gold and silver in solution in the upper part of the section. Calculations allow us to prove that this is due to the possibility of the formation of argentite As_2S , while gold is present only in the native form.

CONCLUSIONS

The gold-bearing pyrite-polymetallic ore treatment dumps of the Ursk ore field (Novo-Ursk and Belokluch deposits) were studied. Physicochemical modeling of gold behaviour inside wastes allowed quantitatively describing the

gold precipitation process on the different horizon of wastes. In the upper part of the sulfide-rich cross-section, sulfide minerals undergo intense oxidation while dissolution of structural and surface-bound gold takes place on the surface of pyrite. Gold deposition on reducing sorption barrier occurs due to the electrochemical processes, accompanied by the formation of heavy metals sulfates and barite. Under the sorption barrier, there is a loose leaching horizon with high humidity, where the gold in pore solutions is in the form of thiosulfate-, hydrosulfide- and hydroxocomplexes, its content reaches 68 mg/L. Finally, in the middle part of the section, composed of dense siliceous sandstones (hardpan), high-grade gold (up to 973‰) is formed due to the disintegration of thiosulfate complexes. The Au content again falls to 10^{-6} mg/L and this is lithological reduction barrier. No visible gold was found in the lower part of the cross-section (soil layer), but its increased contents to 0.42–0.35 g/L could be associated with the sorption by organic high-molecular compounds such as humic acids.

For the first time, the morphology and chemical composition of native gold from the gold-bearing dumps of pyrite-polymetallic ores have been studied. The gold surfaces have evident traces of supergene transformations, e.g., nano- and micron size gold particles as sponge overgrowth on the gold surface or barite particles, new-formed gold phases related with Fe, Mn, Al hydroxides.

On the dump of tailings of the Novo-Ursk and Belokluch deposits, physical-chemical processes led to a significant redistribution of native metals (Au, Ag) due to the active interaction in the water-rock system during 80 years. The presence of gold-bearing sulfide minerals, as well as the small dimension of their grains, contributed to faster processes of oxidation and deposition of gold when changing Eh-pH conditions. Physicochemical modeling demonstrated, that this process is possible and the proposed scheme explains the formation of supergene zoning. The variations in gold concentrations under different Eh-pH conditions were calculated, varying from geochemically insignificant values (below the determination level) to tens of mg/L (in acidic oxidized pore solutions).

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