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Modern mineral formation and thermodynamic modeling of secondary concentration formation processes in sludge waters of a gold concentration plant tailings dump

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Abstract. The article deals with the features of mineral composition of gold-bearing waste from the gold concentration plant. The tailings material consists primarily of a finely dispersed, silty fraction. The structure of the accumulated tailings resembles a layered pie: three horizons of different compositions are distinguished. They were formed during the processing of mixed, and primary (sulfide) ores oxidized in different years. The most common ore minerals in the tailings dump deposits are pyrrhotite, arsenopyrite, pyrite, stibnite, magnetite, and iron hydroxides. In addition, native bismuth, native gold, bismuth and tellurium sulfides, scheelite, and secondary antimony and arsenic minerals (valentinite, tripugiite, and scorodite) are also noted. The composition of the tailings dump's recirculating water and sludge was studied. Vertical variability in the chemical composition of the tailings storage facility's recycled waters was established. Sharp variability in water composition is observed at depths of 6–8 meters. To study the direction and rate of dissolution and precipitation of substances in the liquid phase of the tailings dump field experiments were conducted. During the experiments, samples of minerals and man-made materials including rubber, sulfur, mercury amalgam on copper, copper, steel, graphite, native gold in quartz, pyrite and pyrrhotite, arsenopyrite were placed in recycled sludge water at various depths to be extracted in batches with the exposure times of 1, 2, and 3 months. The experiment revealed the etching traces of native gold and a diverse range of newly formed mineral phases including gypsum, iron hydroxides, scorodite, iron and manganese cyanides, copper sulfates and thiocyanates, and others. The Selector-Windows software package was selected for physicochemical modeling of the hypergene processes occurring in the tailings sludge waters. The Selector-Windows software package features a system of built-in thermodynamic databases and a module for generating models of varying complexity and architecture. Performed thermodynamic modeling using the software package allowed the authors to calculate the parameters and direction of technogenic processes occurring in the concentration tailings, determine the elemental and ionic composition, Eh-pH parameters of forming solutions, crystallizing minerals, and their associations as well as to propose a mechanism for secondary gold concentrations in the silt fraction of tailings.

Keywords: experimental mineralogy, gold deposit, tailings dump, technogenic deposits, gold concentration plant, thermodynamic modeling, Selector software package, secondary concentrations of gold

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УДК 550.8

Современное минералообразование и термодинамическое моделирование процессов формирования вторичных концентраций в шламовых водах хранилища хвостов золотоизвлекающей фабрики

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Резюме. Целью проведенного исследования являлось рассмотрение особенностей минерального состава золотосодержащих отходов фабрики. Материал хвостов представлен преимущественно тонкодисперсной, пылевой фракцией. По своему строению толща накопленных хвостов напоминает слоеный пирог: выделяются три горизонта разного состава, образовавшихся при переработке в различные годы окисленных, смешанных и коренных (сульфидных) руд. Из рудных минералов в отложениях хвостохранилища чаще всего встречаются пирротин, арсенопирит, пирит, стибнит, магнетит и гидроксиды железа. Кроме того, отмечаются самородный висмут, само-

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родное золото, сульфиды висмута и теллура, шеелит, вторичные минералы сурьмы и мышьяка (валентинит, трипугиит, скородит). Изучен состав оборотных вод и илов хвостохранилища. Установлена изменчивость химизма оборотных вод хвостохранилища по вертикали. Резкая изменчивость состава вод отмечается на глубине 6–8 м. С целью изучения направленности и скорости протекания процессов растворения и осаждения вещества в жидкой фазе хвостохранилища выполнены натурные эксперименты. В ходе экспериментов в оборотные шламовые воды на различные глубины помещались образцы минералов и техногенных материалов: резина, сера, ртутная амальгама на меди, медь, сталь, графит, самородное золото в кварце, пирит и пирротин, арсенопирит, которые устанавливались и извлекались партиями с экспозицией 1, 2 и 3 месяца. По результатам экспериментов выявлены следы травления самородного золота и разнообразный спектр новообразованных минеральных фаз – гипс, гидроокислы железа, скородит, цианиды железа и марганца, сульфаты и тиоцианаты меди и другие. Для физико-химического моделирования гипергенных процессов, протекающих в шламовых водах хвостохранилища, был выбран программный комплекс «Селектор-Windows», снабженный системой встроенных баз термодинамических данных и модулем формирования моделей различной сложности и архитектуры. В результате выполненного термодинамического моделирования рассчитаны параметры и направленность техногенных процессов, протекающих в хвостах обогащения, определены элементный и ионный составы, Eh-pH параметры формирующихся растворов, кристаллизующиеся минералы и их ассоциации, а также предложен механизм вторичных концентраций золота в илистой фракции хвостов.

Ключевые слова: экспериментальная минералогия, золоторудное месторождение, хвостохранилище, техногенные месторождения, золотоизвлекающая фабрика, термодинамическое моделирование, программный комплекс «Селектор», вторичные концентрации золота

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Introduction

The article presents the results of studying the mineral composition of tailings from an operating tailings dump of a gold concentration plant located in the Severo-Yeniseysky district of the Krasnoyarsk Territory [1, 2]. Modern tailings dumps of gold concentration plants represent complex natural-technogenic systems where, alongside the processes of tailings material accumulation, intensive processes of their chemical transformation and technogenic mineral formation occur¹ [3, 4]. Based on field observations, experimental data, and computer physicochemical modeling, the nature of the variability in the chemical composition of recirculating waters, the scale and rate of formation of secondary (technogenic) minerals, the modes of occurrence of residual gold concentrations and associated elements, as well as the pattern of their distribution within the liquid and solid phases of the tailings dump, were assessed. The relevance of this study is determined by the fact that the scale of gold ore processing in this region is extremely large (placer and primary gold have been actively mined for over a hundred years), and, consequently, a large volume of mining waste has been accumulated. The latter, while posing a certain environmental hazard, often contain precious metals and other useful components in concentrations

close to industrial grades [5]. Their re-extraction is impossible without knowledge of the mineral forms and an understanding of the processes of modern mineral formation occurring in the tailings dump [6, 7].

Materials and methods

Objects and methods of analytical research. To study the mineral composition of the alluvial tailings deposits, sludge, recirculating waters, and experimental products, the authors employed a wide range of methods: optical study of heavy fraction minerals of the tailings, scanning electron microscopy, energy-dispersive X-ray spectrometry, X-ray fluorescence analysis, X-ray diffraction analysis, fire assay, analysis of samples using inductively coupled plasma mass spectrometry and atomic absorption spectrometry, as well as chemical analyses of recirculating waters.

The tailings material was obtained from the core of 5 wells drilled to the full depth of the tailings dump. The sludge was sampled by dredging along a profile within the flooded part.

Methods of field experiments. To directly study the processes of dissolution and precipitation of substances in the tailings dump environment, two field experiments were conducted. In the first experiment, samples of minerals and technogenic materials – rubber, sulfur, mercury amalgam on

¹ Alekseenko V.A. *Ecological Geochemistry: a textbook*. Moscow: Logos; 2000, 627 p.



copper, copper, steel, graphite, native gold in quartz, pyrite and pyrrhotite, arsenopyrite (Fig. 1) – were placed in recirculating waters at a depth of 9–10 m. The samples were fixed on an insulated aluminum wire in the form of garlands, which were installed and extracted in batches with exposure times of 1, 2, and 3 months.

The second experiment was conducted with a modified composition of samples: chemically pure gold, copper, mercury amalgam on copper, steel, sulfur, graphite. The samples were placed at a shallower depth (2–3 m) in close proximity to the pumping station, which ensured intensive water exchange and made it possible to observe a higher rate of secondary mineral formation processes.

Thermodynamic modeling method. To model the hypergene processes of sludge water formation, the Selector-Windows software package, featuring a system of built-in thermodynamic databases, was used. The algorithm of the package allows for the calculation of chemical equilibria in multisystems that include aqueous electrolyte solutions, gas mixtures, solid phases, and melts. Modeling was conducted for a system consisting of the atmosphere, water, and concentration tailings under isobaric-isothermal conditions in the temperature range from 5 to 30 °C at a pressure of 1 bar. The calculations accounted for the chemical composition of the tailings (based on the data in Table 1) and the recirculating waters. The equilibrium phase composition was de-

termined by the method of minimizing the Gibbs free energy [8].

Results and discussion

Mineral and chemical composition of tailings and sludge. The tailings material consists primarily of a finely dispersed, silty fraction. The structure of the accumulated tailings resembles a layered pie: three horizons of different compositions are distinguished, formed during the processing of oxidized, mixed, and primary (sulfide) ores in different years. The color varies from light gray, greenish-gray (products of processing unoxidized ores) to light brown (tailings from oxidized ore processing). The mineral composition of the tailings dump deposits is presented in Table 1. It is in good agreement with the mineral composition of the host rocks and ores of the deposit – quartz-mica and garnet schists. Among the non-ore minerals, as seen in Table 1, the most common are quartz, micas (muscovite, biotite), and chlorite. Carbonates, amphiboles of the tremolite-actinolite series, tourmaline, zircon, rutile and anatase, monazite, and gypsum are present in subordinate amounts.

Among the ore minerals, the most common in the tailings dump deposits are pyrrhotite, arsenopyrite, pyrite, stibnite, magnetite, and iron hydroxides. In addition, native bismuth, native gold, bismuth and tellurium sulfides, scheelite, and secondary antimony and arsenic minerals (valentinite, tripuhyite, and scorodite) are also noted.

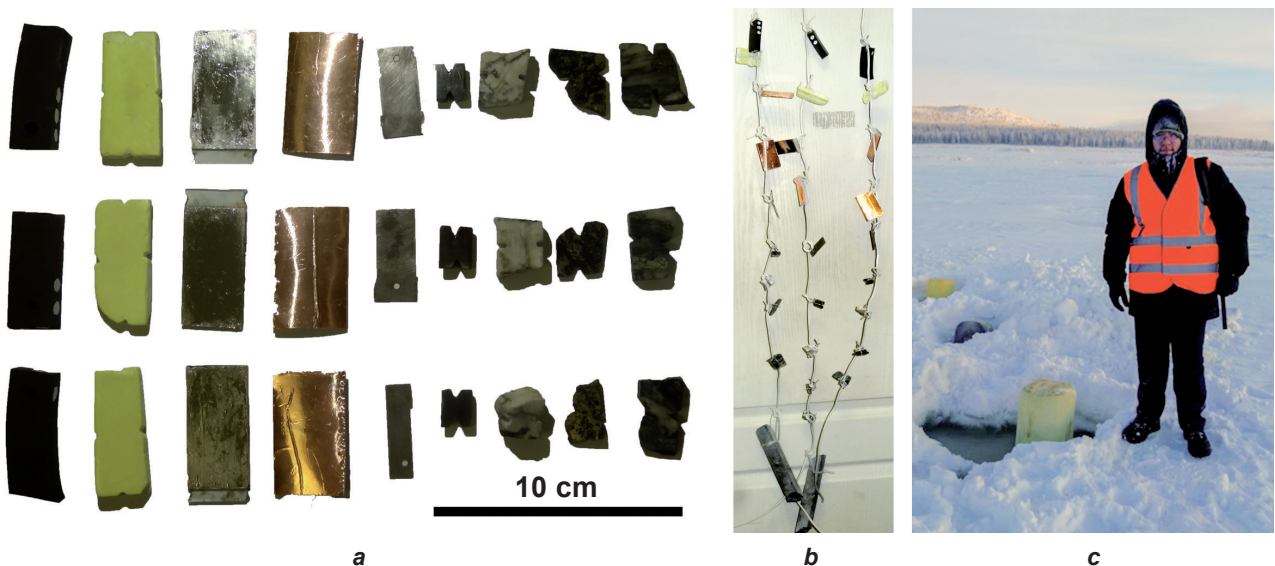


Fig. 1. Samples of materials used in the experiment:

a – as packings; *b* – as garlands; *c* – placed on the ice of the recycled water settling pond

Рис. 1. Образцы материалов, используемых в эксперименте:

a – в качестве закладок; *b* – связанные в гирлянды;

c – размещенные со льда пруда отстойника оборотных вод



In total, about 40 mineral species were identified in the tailings dump deposits. The average gold content is 0.3 c. u. in tailings from oxidized ore processing and 0.6 c. u. in tailings from primary ore processing.

The mineral and chemical composition of the tailings dump sludge, sampled by dredging along a profile within the flooded part of the tailings dump, differs significantly from the tailings studied from core samples. An increased gypsum content (up to a maximum of 14 %) is recorded in the sludge. Also characteristic are elevated contents of iron (up to 7.12 % compared to the tailings average of 3.52 %), arsenic (1.14/0.13 %), sulfur (2.73/0.44 %), zinc (0.033/0.009 %), potassium (2.80/2.42 %), and lower silicon (19.55/29.58 %). Gold content also increases with depth: from 0.3 c. u. in the beach zone to 1.5 c. u. at depths greater than 8 m. This correlates well with both a decrease in the proportion of quartz in the silt fraction and a corresponding increase in the amount of micas, as well as with the accumulation (in addition to gypsum) of newly formed X-ray amorphous finely dispersed phases of iron and arsenic, which sorb less common components (zinc, selenium, etc.) onto their active surfaces. The X-ray amorphous nature of the newly formed phases is indicated by the absence of diagnosed iron and arsenic minerals by X-ray diffraction analysis, while the high contents of these elements were determined by inductively coupled plasma mass spectrometry.

Chemical composition of recirculating waters. Vertical variability in the chemical composition of the tailings dump's recirculating waters was established. Sharp variability in water composition is observed at depths of 6–8 meters. A change

in pH from 7.5 (near the surface) to 6.6 was noted; the thiocyanate content increases significantly from approximately 1400 mg/l near the surface to 1600 mg/l; iron is not detected in the near-surface water layer (< 0.1 mg/l), but its content with depth averages 0.88 mg/l; the contents of copper (from 6 to 8 mg/l) and calcium (from 650 to 750 mg/l) also increase.

Results of field experiments. As noted above, to study the dynamics of processes occurring in the tailings dump (dissolution – precipitation of substances), two field experiments were conducted by placing various materials in the recirculating waters of the settling pond.

In the first experiment, three sets of samples were submerged to a depth of 9–10 m, with exposure times of 1, 2, and 3 months, respectively. The sample placement point was chosen taking into account the movement of recirculating waters – it was intended to be a non-stagnant zone – so the samples were installed approximately between the pulp discharge points and the water intake.

In the second experiment, the samples were placed in close proximity to the pumping station at a depth of about 2–3 m, which also allowed for more intensive water exchange around the samples. As it turned out, this solution made it possible to observe a very high rate of mineral formation processes. An important objective of the experiment was to observe the effect of recirculating water on native gold. It was found that the native gold particle had practically not changed morphologically after one month, despite the rather high content of residual cyanides in the tailings dump's recirculating waters. Upon detailed examination of the gold grain surface in the first ex-

Table 1. Mineral composition of tailings
Таблица 1. Минеральный состав хвостов

Abundance	Mineral composition of tailings	
	Tailings from primary ore processing	Tailings from oxidized ore processing
Major	Quartz (75.9–36.0/54.3) Muscovite + Biotite (29.1–8.57/18.3) Calcite (14.8–6.6/9.93) Chlorite (16.3–2.38/10.1)	Quartz (90.4–60.0/81.2) Muscovite + Biotite (17.7–5.25/11.83)
Minor	Dolomite (3.76–0/2.05) Albite (6.7–0/2.89) Gypsum (4.4–0.16/1.52)	Calcite (4.8–0/1.15) Dolomite (0.96–0/0.36) Chlorite (19.3–0/4.1) Albite (3.76–0/0.65)
Rare	Rutile (0.9–0.11/0.2)	Scheelite (0.16–0/0.01) Rutile (0.79–0/0.23) Gypsum (1.6–0/0.16)

Note: The parentheses show the content range from maximum to minimum (numerator) and the average content (denominator), %.



periment, crystals of newly formed gypsum were discovered (Fig. 2, a). No significant changes were observed on the gold grain surface. In the second experiment, traces of partial etching were observed, manifested as fine rippling even after the first month of exposure (Fig. 2, b).

Other manifestations of modern mineral formation include the following. Arsenopyrite underwent significant changes. On its surface, islands (patches) of aggregates of secondary minerals were encountered – mainly scorodite (an oxidation product of arsenopyrite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), the newly formed crystals of which have a cubic appearance (Fig. 3, a). On the native sulfur sample, small (first microns) cubic crystals formed, presumably of iron and manganese cyanide (Fig. 3, b).

The crystal sizes in both the first and second experiments ranged from the first microns up to 5, rarely up to 10 microns across. This is presumably iron and manganese cyanide. Its unambiguous identification is difficult, but it can be done based on a number of features. Unfortunately, due to the uneven surface of the sample, it was

not possible to determine the stoichiometry, but based on a large number of analyses, the following statistics were accumulated: nitrogen – 15–20 %, oxygen – 18–22 %, sulfur – 0.5–1.5 %, iron – 8–14 %, manganese – 5–10 %, and an unknown amount of carbon, the quantity of which cannot be accurately determined due to the coating of the studied samples with a conductive carbon layer. Based on indirect evidence – a sharply higher amount of carbon in the actual spectrum than in the theoretical one – a significant carbon content in the sample can be inferred.

A considerable amount of copper thiocyanate formed on the copper plate (Fig. 4, a).

In addition, large accumulations of tiny (from hundreds of nanometers to the first microns across) globules of iron hydroxides are observed on the surface of metallic copper. A distinctive feature of the latter is the constant presence of arsenic – 2.5–2.8 wt %. The same was noted in the aggregates of iron hydroxides that formed on the iron plate. This may indicate both the high sorption properties of iron hydroxides and the significant amount of arsenic dissolved in the tail-

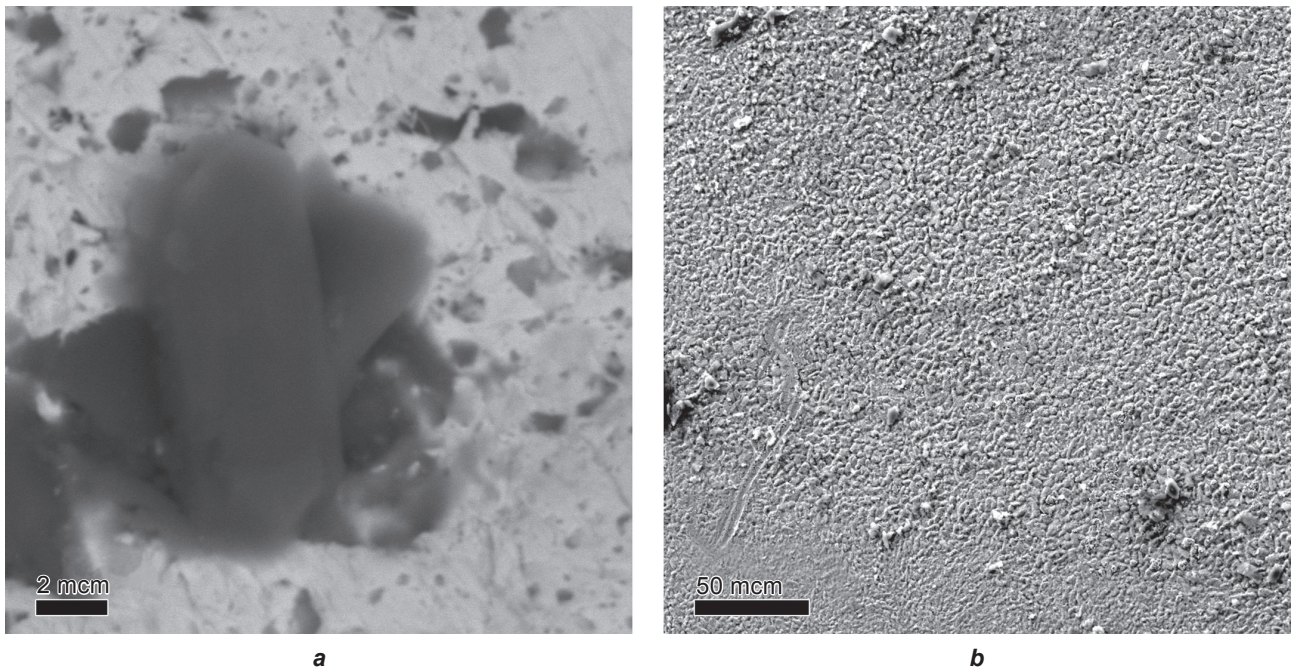
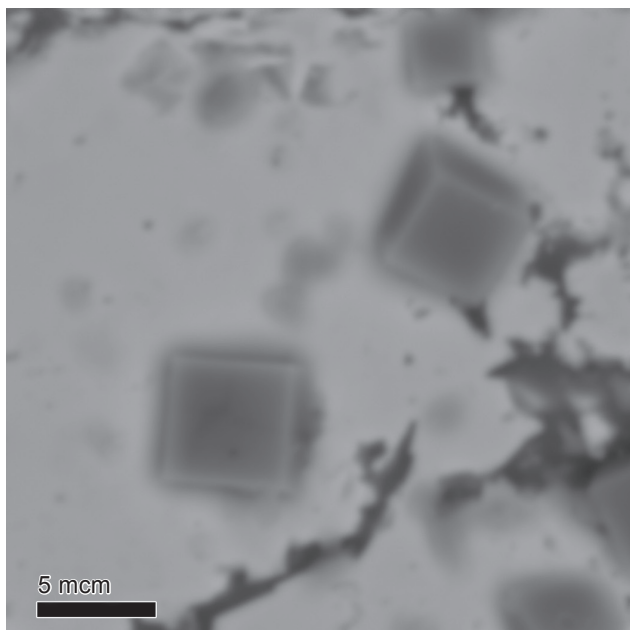


Fig. 2. Surface of gold samples after exposure to tailings pond recycled water using scanning electron microscopy:

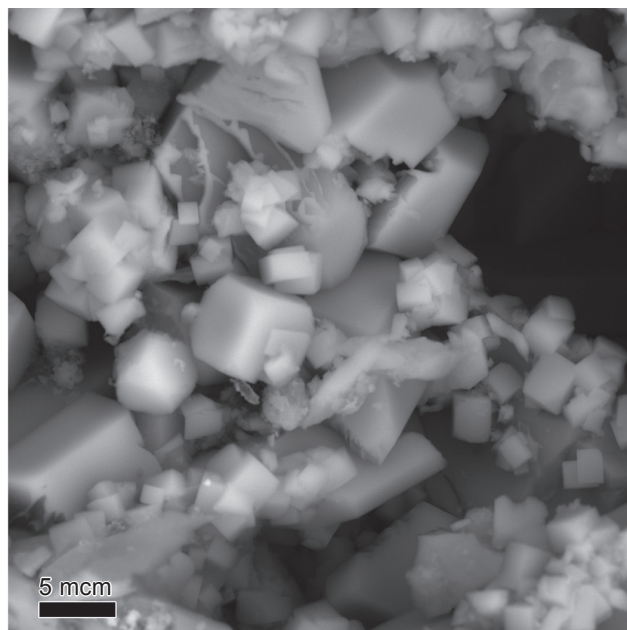
- a – gypsum crystals on natural native gold – experiment 1 (a backscattered electron image);
b – etching traces on the surface of a plate of chemically pure gold – experiment 2 (a secondary electron image)

Рис. 2. Поверхность образцов золота после экспозиции в оборотных водах хвостохранилища методом сканирующей электронной микроскопии:

- a – кристаллы гипса на природном самородном золоте – эксперимент 1 (изображение в обратно-отраженных электронах);
b – следы травления на поверхности пластины химически чистого золота – эксперимент 2 (изображение во вторичных электронах)



a



b

Fig. 3. Newly formed phases on the surface of samples obtained by scanning electron microscopy:

- a – crystals of presumed iron cyanide on arsenopyrite (a backscattered electron image);
b – aggregate of crystals of presumed iron and manganese cyanide on the surface of sulfur
(a secondary electron image)

Рис. 3. Новообразованные фазы на поверхности образцов, полученные методом сканирующей электронной микроскопии:
а – кристаллы предположительного цианида железа на арсенопирите
(изображение в обратно-отраженных электронах);

- б – агрегат кристаллов предположительного цианида железа и марганца на поверхности серы
(изображение во вторичных электронах)

ings dump's recirculating waters. Copper sulfate, repeatedly encountered in the sample, does not form good crystals, only thin films found in aggregates with other phases.

New mineral phases were found on the mercury amalgam on the copper plate. There was virtually no mercury left – only isolated tiny (tens of microns in size) mercury-containing phases (close to copper-mercury) in lacy aggregates composed of copper oxides and sulfate (Fig. 4, b). Occasionally, minor (up to 1 %) contents of oxygen (thin oxide films on the surface) and sulfur are noted.

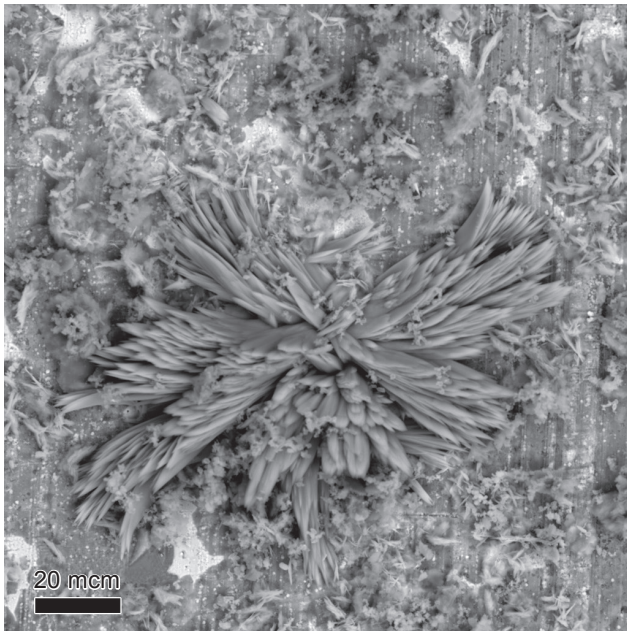
Results of thermodynamic modeling and their interpretation. To assess and predict the processes occurring in the tailings dump, identified during field and experimental studies, thermodynamic modeling was performed. The application of computer thermodynamic modeling made it possible to calculate the technogenic processes occurring in the concentration tailings, determine

the elemental and ionic composition, Eh-pH parameters of the forming solutions, crystallizing minerals, their associations, and the formation of secondary gold concentrations² [9, 10].

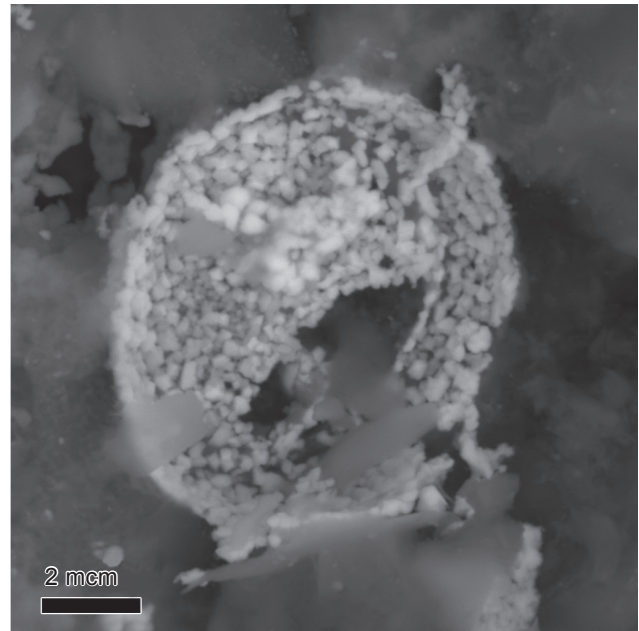
In this work, the Selector-Windows software package was selected for the physicochemical modeling of hypergene processes observed in the tailings sludge waters. The Selector-Windows software package features a system of built-in thermodynamic databases and a module for generating models of varying complexity and architecture [11].

Several scenarios of system evolution were calculated: in the first scenario, secondary (hypergene and technogenic) minerals did not form – their elements passed into solution; in the second, these secondary minerals precipitated from the solution. The process under consideration is the formation of sludge waters on the surface of tailings dumps as a result of the interaction of weathering agents with tailings from the pro-

² Frolov K.R., Zvereva V.P., Kostina A.M. *Modeling of technogenic and natural systems: a laboratory manual.* Vladivostok: Far Eastern Federal University; 2017, 72 p.



a



b

Fig. 4. New surface formations of copper samples obtained as a result of scanning electron microscopy:
a – a rosette of copper thiocyanate crystals surrounded by copper sulfate and copper oxides
(a backscattered electron image);

b – an aggregate of crystals of the phase of copper-mercury tetrathiocyanate composition
with gypsum and copper oxides in place of mercury amalgam (a backscattered electron image)

**Рис. 4. Новообразования на поверхности медных образцов,
полученные методом сканирующей электронной микроскопии:**

a – розетка кристаллов тиоцианата меди, окруженная сульфатом и оксидами меди
(изображение в обратно-отраженных электронах);

b – агрегат кристаллов фазы состава тетрацианата меди-ртути с гипсом и оксидами меди на месте
ртутной амальгамы (изображение в обратно-отраженных электронах)

cessing of primary and oxidized ores containing gold and silver. The chemical composition of the model forms the independent components of the system – stoichiometric constituents from which, through their linear combination, the compositions of all phases and components can be obtained. According to the methodology of physicochemical (thermodynamic) modeling [11], the models consisted of 10 kg of atmosphere, 1 kg of water, and 0.1 kg of concentration tailings. Uniform thermobarometric conditions were established: a temperature range from 5 to 30 °C and a pressure of 1 bar [12, 13]. The calculations considered dependent and independent components: dissolved species, minerals, and solid solutions, i. e., the most likely hypogene gases, as well as hypergene and technogenic minerals [14, 15]. Among other things, thermodynamic parameters from the software package and the relevant literature were used [8, 16–18]. The chemical composition of the atmosphere was calculated based on the work of R. Horne [19]. The composition of tailings from the processing

of primary and oxidized ores is given in Table 2 and was compiled based on X-ray diffraction and elemental analysis data of core samples. The models also account for the chemical composition of recirculating waters [2]. By minimizing the Gibbs free energy and in accordance with the algorithms embedded by the developers, the Selector-Windows program calculates the equilibrium composition of the gas, liquid, and solid phases of the systems [8]. The main modeling results represent qualitative and quantitative characteristics for all phases of the primary and oxidized ore systems in the temperature range of 5–30 °C.

The following characteristics were considered in this work:

– for the aqueous phases: Eh-pH parameters, qualitative ionic and molecular composition of solutions, their quantitative elemental composition;

– for the solid phases: qualitative and quantitative composition of hypergene and technogenic minerals crystallizing in the systems.



Parameters of the Aqueous Environment.

Modeling showed that solutions with an oxidative redox potential (Eh) of about 0.83–0.84 V and a pH close to neutral values (6.36–6.98) are formed in the system. The solutions of the modeled system contain the following components:

– ions and molecules: $(Al(NO_3)_2)^+$, $(Au(OH)_2)^-$, $(HCO_3)^-$, AuOH, CO_2^* , $Ca(NO_3)_2^*$, $H_2CO_3^*$, $H_4SiO_4^*$, $KHSO_4^*$, KNO_3^* , $Mg(NO_3)_2^*$, $NaNO_3^*$, $Si(OH)_4^*$, SiO_2^* , CO_2^* , CO_3^{-2} , HCO_3^- , N_2^* , O_2^* , SO_4^{-2} , SiO_2^* ;

– elements of sulfide ores: $KHSO_4$, $NaAsO_4^{-2}$, $NaSO_4^-$;

– elements of ore-hosting rocks: $Ca(HCO_3)^+$, SiO_2 .

The concentration of sulfide ore elements in the solutions is, g/l: gold – up to 0.00043; nitrogen – up to 5.69 and 1.46; magnesium – up to 1.39 and 0.51; calcium – up to 4.72 and 5.64; oxygen – up to 22.7 and 7.87 (for primary and oxidized ores, respectively). These data are in good agreement with the results of chemical analyses of actual recirculating waters.

Composition of the solid phase. In the considered temperature range, the model predicts the crystallization from solutions of solid phases of

Table 2. Modeling results of ore processing tailings oxidation with the formation of technogenic minerals

Таблица 2. Результаты моделирования окисления хвостов переработки руд с образованием техногенных минералов

Primary ores							Oxidized ores					
T, °C	5	10	15	20	25	30	5	10	15	20	25	30
Independent components, mg/l												
C	6.14E+01	1.87E+01	6.57E+00	2.79E+00	1.50E+00	1.04E+00	4.59E+01	1.38E+01	4.73E+00	1.91E+00	9.43E-01	5.87E-01
N	5.62E+03	5.45E+03	5.72E+03	5.69E+03	5.67E+03	5.66E+03	1.46E+03	1.31E+03	1.46E+03	1.44E+03	1.42E+03	1.41E+03
S	7.47E+02	7.46E+02	2.00E-01	3.92E-02	1.04E-01	3.67E-01	4.81E+02	4.80E+02	1.41E-01	6.39E-02	1.38E-01	3.09E-01
Ag	5.05E-02	5.04E-02	5.05E-02	5.05E-02	5.05E-02	5.05E-02	5.03E-02	5.03E-02	5.04E-02	5.04E-02	5.04E-02	5.04E-02
As	9.01E-01	8.98E-01	8.95E-01	8.90E-01	8.77E-01	8.44E-01	8.25E+02	8.98E-01	8.98E-01	8.98E-01	8.98E-01	8.98E-01
Cu	6.75E-01	6.65E-01	6.54E-01	6.47E-01	6.54E-01	6.99E-01	6.67E-01	6.99E-01	6.65E-01	6.54E-01	6.47E-01	6.40E-01
Au	4.34E-01	4.34E-01	4.34E-01	4.34E-01	4.34E-01	4.34E-01	4.33E-01	4.33E-01	4.33E-01	4.33E-01	4.33E-01	4.33E-01
Al	1.30E+02	3.66E+01	1.12E+01	3.74E+00	1.31E+00	4.06E-01	9.87E+01	2.81E+01	8.62E+00	2.93E+00	1.13E+00	4.41E-01
Ca	4.72E+03	4.72E+03	4.73E+03	4.73E+03	4.73E+03	4.73E+03	5.64E+02	5.64E+02	5.65E+02	5.65E+02	5.65E+02	5.65E+02
Fe	3.80E-06	1.17E-06	4.14E-07	2.15E-07	2.03E-07	2.75E-07	3.78E-06	1.17E-06	4.13E-07	2.15E-07	2.03E-07	2.76E-07
K	9.10E+02	9.10E+02	9.11E+02	9.11E+02	9.11E+02	9.11E+02	5.86E+02	5.86E+02	5.86E+02	5.86E+02	5.86E+02	5.86E+02
Mg	1.39E+03	1.39E+03	1.39E+03	1.39E+03	1.39E+03	1.39E+03	5.14E+02	5.13E+02	5.14E+02	5.14E+02	5.14E+02	5.14E+02
Na	6.65E+02	6.65E+02	6.66E+02	6.66E+02	6.66E+02	6.66E+02	3.21E+02	3.21E+02	3.22E+02	3.22E+02	3.22E+02	3.22E+02
Si	9.95E+02	2.54E+02	7.23E+01	2.71E+01	1.67E+01	1.56E+01	1.00E+03	2.56E+02	7.29E+01	2.73E+01	1.68E+01	1.57E+01
H	1.71E+02	6.09E+01	1.04E+01	3.46E+00	1.71E+00	1.34E+00	1.63E+02	5.26E+01	1.03E+01	3.43E+00	1.69E+00	1.33E+00
O	2.27E+04	2.05E+04	1.96E+04	1.94E+04	1.94E+04	1.94E+04	7.84E+03	5.75E+03	4.99E+03	4.86E+03	4.82E+03	4.81E+03
System characteristics												
Eh, V	0.84	0.84	0.84	0.84	0.84	0.83	0.84	0.83	0.83	0.83	0.83	0.83
pH, units	6.86	6.76	6.66	6.55	6.44	6.40	6.98	6.88	6.78	6.66	6.50	6.36
Total dissolved solids, mg/l	37880	34586	33002	32786	32729	32716	12883	9762	8464	8262	8210	8199
Phases of the system, g												
Aqueous phase	1029	1026	1023	1023	1023	1023	1006	1004	1001	1001	1001	1001
Gas phase	9982	9983	9981	9982	9982	9982	9993	9994	9993	9993	9993	9993
Goethite FeOOH	5.98	5.98	3.93	3.93	3.93	3.93	1.77	1.77	0.44	0.44	0.44	0.44
Limonite Fe ₂ O ₃	4.57	4.57	4.58	4.58	4.63	1.41	1.68	1.61	1.62	1.69	1.57	1.48
Fibroferrite Fe[SO ₄](OH)·5H ₂ O	8.67	8.67	14.65	14.65	14.65	14.64	8.75	8.75	12.60	12.60	12.60	12.60
Allophane SiO ₂ ·2Al ₂ O ₃ ·8H ₂ O	16.03	16.38	16.47	16.50	16.51	16.51	8.26	8.53	8.60	8.62	8.63	8.63
Quartz SiO ₂	59.12	60.64	61.01	61.10	61.12	61.12	82.97	84.52	84.89	84.99	85.01	85.01



secondary (hypergene and technogenic) minerals of various classes:

- class of oxides and hydroxides, g: iron – goethite – up to 5.98 for primary ores and up to 1.77 for oxidized ores; limonite – up to 4.63 for primary ores and up to 1.68 for oxidized ores;

- class of silicates, g: aluminum – allophane – up to 16.51 for primary ores and up to 8.63 for oxidized ores;

- class of sulfates, g: fibroferrite – up to 14.64 for primary ores and up to 12.6 for oxidized ores.

The crystallization of these solid phases is possible only from saturated solutions containing high concentrations of sulfide ore elements, which indicates the formation of saturated solutions with high concentrations of iron, aluminum, and sulfate ions in the system as a result of sulfide oxidation.

Possibilities of secondary gold concentration.

The modeling results, which are consistent with experimental data (absence of massive gold dissolution, sorption of arsenic onto iron hydroxides), allow us to draw an important conclusion. At neutral pH values and oxidative Eh, the most likely mechanism for secondary gold concentration in the tailings dump sludges is its sorption and possible subsequent reduction onto the highly active surface of newly formed iron hydroxides (goethite, limonite). This explains the observed increase in gold content with depth in the silt fraction.

Conclusion

A comprehensive mineralogical and geochemical study of the gold concentration plant tailings dump has established that its deposits contain a wide range of minerals (about 40 spe-

cies) inherited from the ores and host rocks, and the average gold content is 0.3–0.6 c. u.

Using scanning electron microscopy and energy-dispersive X-ray spectrometry during field experiments, the processes of modern mineral formation were demonstrated for the first time under these conditions: the formation of gypsum on gold and arsenopyrite; the formation of presumed iron and manganese cyanides and copper thiocyanate; intensive oxidation of arsenopyrite to scorodite and of mercury amalgam to copper compounds.

It was established that the mineral and chemical composition of the sludges differs significantly from the original tailings and is characterized by the accumulation of X-ray amorphous phases of iron and arsenic, as well as elevated (up to 1.5 c. u.) gold concentrations, which increase with depth.

Using thermodynamic modeling with the Selector software package, it was shown that during the oxidation of tailings, neutral (pH ~6.4–7.0), oxidative (Eh ~0.83–0.84 V) solutions are formed, from which secondary minerals crystallize: goethite, limonite, fibroferrite, allophane.

The combination of experimental and modeling data indicates that the main mechanism of secondary gold concentration in the silt fraction of the tailings dump is its sorption onto the highly developed surface of newly formed nano- and microcrystalline iron hydroxides.

The obtained results have important applied significance for assessing the technogenic mineral resource potential of tailings dumps and developing technologies for recovering residual gold, as well as for predicting environmental risks associated with the migration of heavy metals and arsenic.

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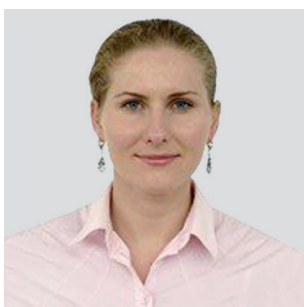
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