



SAFETY IN MINING AND PROCESSING INDUSTRY AND ENVIRONMENTAL PROTECTION

Research article

<https://doi.org/10.17073/2500-0632-2021-3-181-191>**Chemical reactions and conditions of mineral formation at tailings storage facilities of the Russian Far East**V. P. Zvereva¹ , K. R. Frolov² , A. I. Lysenko¹ ¹ Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russian Federation² Far Eastern Federal University, Vladivostok, Russian Federation zvereva@fegi.ru**Abstract**

Cassiterite-sulfide and polymetallic deposits of the Far Eastern Region (FER) were mined by both open-pit and underground methods. This resulted in the emerging numerous mine workings and tailings storage facilities (TSFs) (abandoned without reclamation in latest decades) and the formation of mining technogenic mineralogical systems. Sulfide component of minerals in the mining technogenic system is subjected to hypergenic and technogenic processes (oxidation and hydrolysis reactions). As a result, highly concentrated technogenic solutions are formed, from which minerals of various classes precipitate. In this connection the purpose of this study was formulated as follows: to show the possibility of crystallization of technogenic minerals from micropore technogenic solutions. In achieving this goal the following tasks were solved: to demonstrate the possible reactions of oxidation and hydrolysis of technogenic minerals at the tailings storage facilities; to identify Eh-pH parameters of their precipitation from highly concentrated solutions; to determine their possible associations. The studies involved field observations and computations with the use of “Selector” software package. The study findings allow demonstrating possible chemical reactions and physico-chemical conditions of mineral formation for the following elements: Fe, Cu, Pb, Zn, Sb, Mg, Al, and Ca, including the following classes of minerals: oxides and hydroxides, sulfates, carbonates, arsenates and silicates. The paper presented for the first time the crystallization reactions of secondary minerals (37 ones) and their physico-chemical conditions. It was found that secondary minerals: jarosite, pitticite, siderite, tenorite, poznyakite, antlerite and ktenasite crystallize in the interval of positive temperatures, while scorodite, chalcantite, brochantite, cerussite, starkeyite, epsomite and rostitite originate in cryogenic conditions (below 0 °C). All other minerals, the possibility of precipitation of which was shown in the paper, crystallized in the whole considered temperature interval, from –25 °C to +45 °C. Field studies and modeling data on formation of technogenic waters (solutions) and crystallization of secondary minerals on the surface of and inside tailings at the tailings storage facilities of the Far East showed high intensity of technogenic processes. Since the tailings storage facilities were not reclaimed, the process of environmental pollution, including the hydrosphere, would last for many decades.

Keywords

mining, minerals, beneficiation, wastes, tailings storage facility, technogenic minerals, hypergene minerals, sulfides, association, paragenesis, slime and drainage waters

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ТЕХНОЛОГИЧЕСКАЯ БЕЗОПАСНОСТЬ В МИНЕРАЛЬНО-СЫРЬЕВОМ КОМПЛЕКСЕ И ОХРАНА ОКРУЖАЮЩЕЙ СРЕДЫ

Научная статья

Химические реакции и условия минералообразования на хвостохранилищах Дальнего Востока РоссииВ. П. Зверева¹ , К. Р. Фролов² , А. И. Лысенко¹ ¹ Дальневосточный геологический институт ДВО РАН, г. Владивосток, Российская Федерация² Дальневосточный федеральный университет, г. Владивосток, Российская Федерация zvereva@fegi.ru**Аннотация**

Касситерит-сульфидные и полиметаллические месторождения дальневосточного региона отрабатывались как открытым, так и подземным способами, что привело к появлению многочисленных горных выработок и хвостохранилищ (в период перестройки брошены без рекультивации), а также к



формированию горнопромышленных техногенных систем. Сульфидная составляющая полезных ископаемых в горнопромышленной техногенной системе подвергается гипергенным и техногенным процессам (реакциям окисления и гидролиза). В результате формируются высококонцентрированные техногенные воды, из которых выпадают минералы из различных классов. В связи с этим сформулирована цель данной работы – показать возможность кристаллизации техногенных минералов из микропорowych растворов техногенных вод. При достижении данной цели решались следующие задачи: показать возможные реакции окисления и гидролиза техногенного минералообразования на хвостохранилищах; выявить Eh–pH параметры их выпадения из высококонцентрированных растворов; определить их возможные ассоциации. Исследования проведены с помощью натурных наблюдений и программного комплекса «Селектор». Полученные результаты позволяют продемонстрировать возможные химические реакции и физико-химические условия формирования минералов: Fe, Cu, Pb, Zn, Sb, Mg, Al и Ca из различных классов: оксидов и гидроксидов, сульфатов, карбонатов, арсенатов и силикатов. В статье впервые показаны реакции кристаллизации вторичных минералов (37 наименований) и их физико-химические условия. Установлено, что в интервале положительных температур кристаллизуются вторичные минералы: ярозит, питтитит, сидерит, тенорит, познякит, антлерит и ктенасит, а в криогенных условиях: скородит, халькантит, брошантит, церуссит, старкеит, эпсомит и ростит. Все остальные минералы, возможность выпадения которых показана в статье, кристаллизуются во всем рассматриваемом интервале – от –25 до +45 °C. Натурные наблюдения и полученные при моделировании данные по формированию техногенных вод и кристаллизации вторичных минералов на поверхности и в толще хвостов обогащения на хвостохранилищах Дальнего Востока позволили показать высокую активность техногенных процессов. Так как хвостохранилища не рекультивированы, то процесс загрязнения окружающей среды, включая гидросферу, продлится на многие десятилетия.

Ключевые слова

горное дело, полезные ископаемые, обогащение, отходы, хвостохранилище, техногенные минералы, гипергенные минералы, сульфиды, ассоциация (associare), парагенезис, шламовые и дренажные воды

Для цитирования

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Introduction

Mining industry in the Far Eastern Region (FER) developed rather intensively in the last 60–120 years. This produced significant impact on the Region's environment. Cassiterite-sulfide and polymetallic deposits were mined by both open-pit and underground methods. The main ore minerals in the deposits are cassiterite, chalcopyrite, galena, and sphalerite, and, among the sulfides – pyrite, pyrrhotite, and arsenopyrite are common, and, for the Dalnegorsk district, argentite, acanthite, pyrargyrite, and jamesonite should be added [1, 2]. The main extractable ore elements are: Sn, Cu, Pb, Zn, and associated (minor ones): Ag, In, Bi. It is known that not more than 2 % of the extracted ore volume are transformed into concentrate, while the residual 98 % belong to concentration waste (tailings) stockpiled in tailings storage facilities. In the Komsomolsky district, the processing tailings are stored in three tailings storage facilities with total area of 130.5 ha and volume of 37.3 million tons, in the Kavalеровsky district, in six TSFs: 18 hectares and 49 million tons, respectively. In the Dalnegorsk district, there are two tailings storage facilities of the Central processing plant (CPP) with area of 825,000 m² and amount of tailings of 56.6 mln tons, and two tailings storage facilities at the Krasno-rechenskaya processing plant (KPP): 300,000 m² and

6.8 million tons. In the processing tailings, sulfides account for about 4% of the total volume, and the rest is represented by silicate and carbonate minerals of the host rocks. In Komsomolsky and Kavalеровsky districts, the host rock minerals include quartz, chlorite, sericite, tourmaline, epidote, calcite, etc., and, in Dalnegorsk district, they include potassium feldspar, micas, garnets, calcite, etc. The host rock minerals contain the following elements: K, Na, Ca, Al, Mg, and Si. At different points of the tailings storage facilities the percentage contents of sulfides and host rock minerals differ and range from 5 to 95 % and vice versa from 95 to 5 %. It should be noted that the ratio between the sulfides themselves and the host rock minerals at different points in the tailings storage facilities varies both horizontally and vertically.

The processing tailings are permanently exposed to various climatic factors, such as changes in daily and seasonal temperature, precipitation in the form of rain and snow. Hypergene processes in the form of oxidation and hydrolysis reactions of the sulfide component, which are accompanied by the formation of sulfuric acid and destruction of minerals of the host rocks, actively occur in them. This leads to the appearance of highly concentrated micropore solutions and the formation of slime and drainage waters. A number

of technogenic minerals precipitate from them (Figures 1–4). Acidic solutions can be partially neutralized by the carbonate components of processing tailings. The creation of a mining technogenic system (adits, pits, trenches, clearings, and tailings storage facilities) promotes the transition of hypergenic processes to the technogenic stage. Over time, technogenesis can lead to the complete destruction of tailings storage facilities (technogenic deposits) and their loss.

The process of technogenic minerals crystallization is clearly seen not only in the underground mine workings, but also in the pit (see Fig. 1) of recycled tailings (on TSF wall), on the vertical cut (clearing) surface (see Fig. 2) and on the surface of tailings (see Fig. 3, 4). 35 technogenic minerals of Fe, Cu, Pb, Zn, Sb, Mg, Al, Ca of different classes: oxides and hydroxides, sulfates, carbonates, arsenates and silicates were found by different mineralogical methods in the Far East Region [2].

Research objectives and tasks

The purpose of this study was formulated as follows: to show the possibility of crystallization of technogenic minerals from micropore technogenic solutions (slime and drainage waters). In achieving this goal, the following tasks were solved: 1 – to demonstrate the possible reactions of oxidation and hydrolysis of technogenic minerals at the tailings storage facilities; 2 – to identify Eh-pH parameters of their precipitation from highly concentrated solutions; 3 – to determine their possible associations.

Research techniques

Modeling is one of the methods for analyzing the processes of alteration of sulfide-containing processing tailings in the course of interaction with oxygen and water at tailings storage facilities, formation of drainage waters and precipitation of technogenic minerals from them. Similar studies were conducted



Fig. 1. Technogenic formations on the wall of the tailings storage facility (Komsomolsky district)



Fig. 3. Technogenic formations on the surface of the tailings storage facility (Kavalerovsky district)



Fig. 2. Technogenic formations on the vertical surface of the clearing (TSF in Kavalerovsky district)



Fig. 4. Technogenic formations on the surface of the tailings storage facility (Dalnegorsk district)



in Namibia [3], Slovakia [4], Brazil [5] and many other countries [6–9]. Computer physicochemical modeling is used to solve various environmental problems in hydro-geochemistry.

These studies were carried out by the authors using “Selector” software package (its development leader was I.K. Karpov in A.P. Vinogradov Institute of Geochemistry of SB of RAS). The software package implements a convex programming approach to the calculation of equilibria in heterogeneous systems by minimizing thermodynamic potentials. One of the key features of this package is the possibility of implementing calculation of complex chemical equilibria in isobaric-isothermal, isochoric and adiabatic conditions in multisystems, where an aqueous electrolyte solution, gas mixture, liquid and solid hydrocarbons, minerals as solid solutions and one-component phases, melts and plasma can be present simultaneously [10]. The calculation of thermodynamic properties of the components in the “Selector” is performed for various temperatures, pressures and activity coefficients. In the calculation of isothermal changes of thermodynamic functions the following is used: equations of dependence of changes in the volume of condensed phases on temperature and pressure; semiempirical equations of gas states at the given parameters. Thermodynamic properties of aqueous solution components in the region up to 1000 °C and 5000 bar are calculated using the modified HKF (Helgeson-Kirkham-Flowers) model [11, 12]. The activity coefficients of the components of the aqueous electrolyte solution are calculated using the Debye-Hückel equation modified by Helgeson [11].

Initial thermodynamic information (Gibbs energy, enthalpy, entropy, and coefficients for the heat capacity equation) was taken from publications¹ [13–20]. The missing parameters were calculated and provided by V.A. Bichinsky and A.A. Tupitsyn, employees of the Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences.

The following unified thermo-barometric conditions were used in the modeling: T from –25 to +45 °C and $P = 1$ atm. The systems under consideration were open to the atmosphere. The chemical composition of the atmosphere was calculated on the basis of the study of R. Horn [21]. The composition of 10 kg of the atmosphere in moles includes: Ar – 3.2, C – 0.10, N – 539.48, O – 144.85. Composition of rainwater is as follows [22]: N_3^- , N_2^- , NH_4^+ , NH_4N_3 , HNO_2 , NH_4NO_3 ,

NH_4OH , NH_4NO_2 , NH_3 , H_2CO_3 , NCO_3^- , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, CH_4 , O_2 , H_2 , N_2 , Ar, He, Kr, Ne, OH[–], H⁺, H_2O , NO_3^- , HNO_3 (pH = 5.66). In each version of the models, independent components were included in the calculations: the most probable gases, dissolved species, and hypogene and hypogene minerals. Oxidation of the processing tailings was modeled for the association of sulfide minerals and host rock minerals taking into account their percentage ratio. The sulfide/host rock ratio was taken at 5:95, 10:90, 20:80, 40:60, 80:20, and 95:5. More than 500 model variants were simulated and analyzed for each of the considered districts [23–25].

The study findings allowed demonstrating possible chemical reactions and physico-chemical conditions of mineral formation for the following elements: Fe, Cu, Pb, Zn, Sb, Mg, Al, and Ca, including the following classes of minerals: oxides and hydroxides, sulfates, carbonates, arsenates and silicates.

Chemical reactions and physico-chemical parameters of recent mineral formation at the tailings storage facilities of the Far Eastern Region

The study findings showed that the following secondary Fe minerals can crystallize at the tailings storage facilities: goethite, hydrogoetite, fibroferrite, jarosite, pitticite, siderite, and scorodite. For their formation, the presence of iron-containing sulfides: pyrite, pyrrhotite, arsenopyrite or chalcopyrite is required, and these minerals are constantly present in the processing tailings. Where the oxidation reactions of sulfides and crystallization of minerals from slime and drainage waters coincide with those published earlier [26], they will not be presented here for mine waters.

The temperature conditions and Eh-pH parameters of goethite precipitation in tailings are as follows: 0.5–0.97 V, 5.4–13.7, and 0.42–0.95 V, 5.1–13.3 (hereafter, Eh-pH parameters will be given for two temperature intervals of formation, first for temperatures from –25 to 0 °C and then from 0 to 45 °C). Goethite can occur in thermodynamically stable association (paragenesis) with all minerals whose crystallization conditions are given below. It was identified in the whole considered temperature range and practically at any values of sulfides/host rock minerals ratio in the processing tailings. Hereinafter, the term “association” (or “associates with” when a mineral occurrence is described), is used within the meaning of “thermodynamically stable association” as a synonym of term “paragenesis”. Besides, only thermodynamic stability of minerals was analyzed, while the questions of reaction kinetics were out of scope of this study.

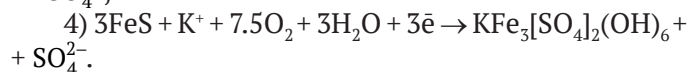
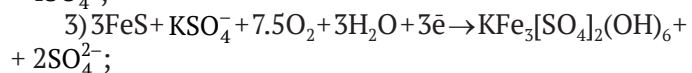
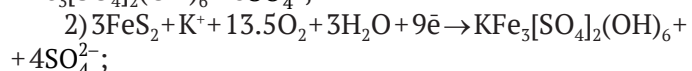
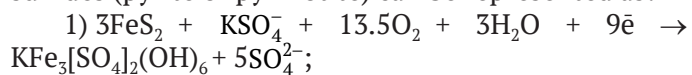
¹ Shock E. SUPCRT 1992–1998 Database Database. Geopig, Arizona State University. URL: <http://geopig.asu.edu/sites/default/files/slop98.dat>



Hydrogoethite was identified only in the wastes of the old tailings storage facility of Krasnorechenskaya processing plant, where it was formed at negative temperatures in the range of Eh–pH parameters from 0.6 to 0.7 V and pH 9.7–13.7 in paragenesis with valentinite, gypsum, fibroferrite, calcite and cerussite. In addition, it was identified at sulfide content in the system of 5 to 20 % at 35–45 °C at the system parameters of Eh = 1.06–1.07 V and pH 2.3–2.4, but in association with goethite, plumbojarosite, and fibroferrite.

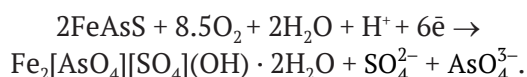
Fibroferrite at the tailings storage facilities precipitates throughout the whole temperature range under consideration at Eh = 0.58–1.15 V and pH 1.3–13.7.

The precipitation of *jarosite* requires potassium, which was identified in the solution in the form of KSO_4^- and K^+ ions. Consequently, the reactions of its formation due to oxidation of main iron-containing sulfides (pyrite or pyrrhotite) can be represented as:



It crystallizes in the range of positive temperatures at the following solution parameter: Eh = –0.82–1.16 V and pH 1.1–8.0 and associates (hereinafter this means “thermodynamically stable association” or “paragenesis”) with goethite, gypsum, plumbojarosite and adamine in the Pb–Zn ore processing tailings of the Central Processing Plant and in the 3rd tailings storage facility in the Komsomolsky district. In the latter case, the paragenesis also comprises the following minerals: alunogen, antlerite, ktenasite, vudvardite, pitticite, magnesite, siderite, smithsonite, olivenite, clinoclase, vivianite, allophane, and nontronite.

The next Fe mineral is *pitticite*, for the formation of which oxidation of arsenopyrite is sufficient by the following reaction:



It was identified in the processing tailings in the 3rd tailings storage facility in the Komsomolsky district in the paragenesis described above for jarosite. The mineral precipitates in the interval of 15–45 °C from solutions with parameters Eh = 0.76–0.84 V and pH 5.9–8.0.

For the formation of *siderite* during the oxidation of pyrite and pyrrhotite, calcite must be present in the system: $\text{FeS}_2 + \text{CaCO}_3 + 4\text{O}_2 + 2\text{H}_2\text{O} + 2\bar{e} \rightarrow \text{FeCO}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{SO}_4^{2-}$ or/and $\text{FeS} + \text{CaCO}_3 + 2\text{O}_2 +$

$+ 2\text{H}_2\text{O} \rightarrow \text{FeCO}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Eh = 0.76–0.84 V and pH 5.85–7.98 in the temperature range of 15–45 °C). It was found in the tailings of the 3rd tailings storage facility in Komsomolsky district in association with jarosite and gypsum.

Scorodite in the processing tailings was found only at low temperatures from –25 to 0 °C and the following solution parameters: Eh = 0.6–0.97 V, pH 5.3–12.5. Scorodite can occur in paragenesis with the majority of the minerals of the technogenic system.

Among the technogenic Cu minerals in the tailings storage facilities, the following ones were identified: tenorite, chalcantite, poznyakite, wroewolfeite, antlerite, broshantite, olivenite and clinoclase, and, if Cu and Zn are present in the system, ktenasite; Cu and Al, vudvardite; Cu and Pb, duftite and baydonite.

Tenorite was identified in the processing tailings in the Kavalеровsky district. It was formed as a result of oxidation of chalcopyrite through the following reaction: $\text{CuFeS}_2 + 5.5\text{O}_2 + \text{H}^+ + 5\bar{e} \rightarrow \text{CuO} + \text{FeO} \cdot \text{OH} + 2\text{SO}_4^{2-}$, in the range of positive temperatures, at Eh = 0.42–0.53 V and pH 11.8–13.3, and the ratio sulfide/host rock of 5:95 and 10:90. It occurs in paragenesis with goethite, gypsum, fibroferrite, alunogen, vudwardite, anglesite, magnesite, duftite, allophane, and montmorillonite.

The parameters of the solutions from which chalcantite precipitates are as follows: Eh = 0.51–1.15 V and pH 1.9–13.2, in the temperature range from –25 to –5 °C. It associates with goethite, gypsum, fibroferrite, vudvardite, wroewolfeite, antlerite, starkeyite, alunogen, magnesite, allophane, and montmorillonite.

Poznyakite was established when simulating the oxidation process of processing waste of Vysokogorskoe deposit, Kavalеровsky district, in the absence of arsenopyrite in them, in the range of 25–35 °C. It is formed from the solution with parameters Eh = 0.98 V and pH 3.9, at the ratio sulfide/host rock of 80:20, in paragenesis with gypsum, antlerite, wroewolfeite, fibroferrite, alunogen and anglesite.

Wroewolfeite was observed in temperature interval of 0–25 °C in association with poznyakite, where it precipitated from solutions with the following parameters: Eh = 0.98–1.1 V and pH 3.9–4.0. In addition, it was identified in the interval from –25 to 0 °C at Eh = 1.0–1.1 V and pH 2–4. In this case, posnyakite and antlerite disappeared from the paragenesis, but starkeyite and chalcantite were added.

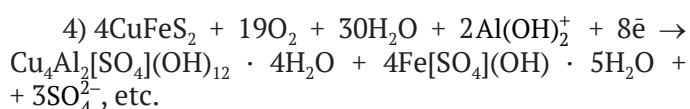
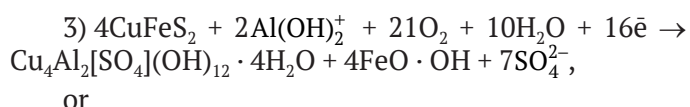
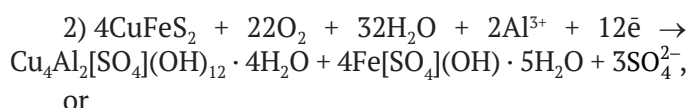
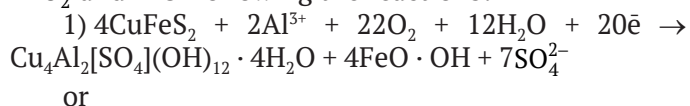
Antlerite in the tailings of TSFs in Komsomolsky district occurs in association with jarosite, where it originates at Eh = 0.78–0.84 V and pH 5.9–7.4, T = 25–45 °C. In Kavalеровsky district, it was identified in association with poznyakite at Eh = 0.98–1.0 V and pH 3.4–3.9, T = 35–45 °C.



The following conditions are typical for *broshantite* crystallizing at the tailings storage facility of the Central Processing Plant in Dalnegorsk district: temperature: -25 to 0 °C, $Eh = 0.6$ – 0.7 V and pH 9.5 – 13.0 , the ratio sulphide/host rock of $5:95$ and $10:9$, and the paragenesis: goethite, gypsum, calcite, adamine, montmorillonite.

Ktenasite crystallizes in the processing tailings (3rd tailings storage facility, Komsomolsky district) when oxidizing chalcopryrite and sphalerite by reaction: $5CuFeS_2 + 5ZnS + 30.5O_2 + 11H_2O + H^+ + 27\bar{e} \rightarrow (Cu, Zn)_5[SO_4]_2(OH)_6 \cdot 6H_2O + 5FeO \cdot OH + 13SO_4^{2-}$. The conditions for its existence are as follows: $T = 15$ – 20 °C, $Eh = 0.76$ – 0.77 V and pH 7.8 – 8.0 . It occurs in the association with jarosite described above.

Vudvardite precipitates together with goethite or fibroferite in the presence of chalcopryrite and aluminum ions in processing tailings: Al^{3+} , $Al(OH)_2^+$, AlO_2^- and AlO^+ following the reactions:



It associates practically with all minerals of technogenic and hypergenic mineralization, and Eh - pH parameters of its crystallization are as follows: $Eh = 0.5$ – 1.15 V, pH 1.8 – 13.2 and 0.42 – 0.99 V, pH 4.9 – 13.3 .

Olivinite, *duftite*, *bayidonite*, and *clinoclase* are Cu minerals of the arsenate class, which are characteristic of cassiterite-sulfide ore processing tailings in the Komsomolsky and Kavalerovsky districts. Chemical reactions of olivinite, duftite, and bayidonite formation are given earlier in [26], and those for clinoclase are as follows: $FeAsS + 3CuFeS_2 + 18O_2 + 23H_2O + H^+ + 7\bar{e} \rightarrow Cu_3[AsO_4](OH)_3 + 4Fe[SO_4](OH) \cdot 5H_2O + 3SO_4^{2-}$. Olivinite and bayidonite crystallize from the simulated solutions throughout the whole temperature range under consideration. Under cryogenic conditions (negative temperatures) their crystallization parameters coincide: $Eh = 0.5$ – 1.1 V, pH 2.4 – 13.8 . In the interval of positive temperatures, their crystallization parameters are as follows: $Eh = 0.86$ – 1.0 V, pH 3.9 – 6.5 and $Eh = 0.86$ – 1.09 V, pH 2.5 – 6.5 , respectively. At negative temperatures, duftite crystallization parameters are as follows: $Eh = 0.5$ – 1.1 V, pH 2.5 – 12.5 , and in the interval of 0 – 45 °C, duftite and clinoclase were established

at $Eh = 0.42$ – 1.09 V, pH 2.5 – 13.3 and $Eh = 0.76$ – 0.83 V, pH 6.2 – 8.0 , respectively. They were found in association with many technogenic minerals.

Then let us consider the precipitation of Pb technogenic minerals from the solutions formed due to the oxidation of processing tailings: anglesite, cerussite, plumbojarosite (Pb and Fe) and corresponding Zn minerals: adamine and smithsonite.

Anglesite is more often identified in polymetallic ore processing tailings. It was found throughout the whole studied temperature range at the following Eh - pH parameters: $Eh = 0.51$ – 1.2 V, pH 0.9 – 13.2 and $Eh = 0.57$ – 1.15 V, pH 1.3 – 10.6 . It occurs in association with valentinite, gypsum and fibroferite in the Krasnorechenskaya Processing Plant (KPP) tailings storage facility, and with goethite, fibroferite, vudvardite, starkeyite, alunogen, gypsum, chalcantite, wroewolfeite, allophane and montmorillonite in the Kavalerovsky district's TSFs.

Plumbojarosite was identified in simulated solutions of tailings oxidation with the following parameters: $Eh = 0.7$ – 1.2 V, pH 0.9 – 10.4 , and $Eh = 0.76$ – 1.38 V, pH 1.1 – 8.0 . It is present in paragenesis with most of the technogenic minerals.

Cerussite is carbonate, and its formation from solutions requires calcite presence in the system. The reaction of its crystallization is as follows: $PbS + CaCO_3 + 2O_2 + 2H_2O \rightarrow PbCO_3 + CaSO_4 \cdot 2H_2O$. It was identified in cryogenic conditions in the temperature range from -25 to -20 °C, at $Eh = 0.6$ V and pH 13.4 – 13.7 , in the association with valentinite, hydrogoetite, gypsum, fibroferite at the KPP tailings storage facility, at the simulated ratio sulfide/host rock of $5:95$ and $10:90$.

Adamine was found only in the presence of sphalerite and arsenopyrite in the processing tailings and was identified at the Central Processing Plant (CPP)'s tailings storage facility: $Eh = 0.6$ – 1.2 V, pH 0.9 – 13.0 and $Eh = 0.65$ – 1.2 V, pH 0.9 – 10.5 , where it associated with goethite, gypsum, epsomite, broshantite, chalcantite, anglesite and plumbojarosite.

Smithsonite was identified in the models of tailings oxidation at TSF's of the Komsomolsky district. The chemical reaction of its crystallization in conditions of oxidation of sphalerite in the presence of calcite is as follows: $ZnS + CaCO_3 + 2O_2 + 2H_2O \rightarrow ZnCO_3 + CaSO_4 \cdot 2H_2O$, at conditions: $Eh = 0.79$ – 0.97 V, pH 5.3 – 6.8 (-25 °C), $Eh = 0.75$ – 0.84 V, pH 5.7 – 8.0 . It can associate with most of the technogenic minerals.

The only Sb mineral was *valentinite*, which crystallized in the tailings storage facilities of Kavalerovsky district. The solution Eh - pH parameters for valentinite crystallization were as follows: $Eh = 0.56$ – 1.1 V, pH 2.6 – 13.7 , and $Eh = 0.66$ – 0.98 V, pH 3.7 – 10.0 . It was present in the association mentioned above for calcite.



Since the oxidation of the sulfide components of processing tailings and the generation of sulfuric acid leads to decomposing minerals of host rocks, and the solutions are enriched with Mg, Al and Ca ions, it is expedient to consider the chemical reactions of formation of starkeyite, epsomite, magnesite, gibbsite (hydrargillite), alunogen, rostitite, allophane, kaolinite, nontronite, montmorillonite, gypsum and calcite.

Chemical reaction of *starkeyite* precipitation from the aqueous solution is as follows: $\text{Mg}^{2+} + \text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$. The solution parameters are as follows: $E_h = 0.5\text{--}1.14$ V and pH 1.9–13.2, the temperature range is from -25 to -5 °C. In the tailings of the Komsomolsky district, it occurs in association with gypsum, alunogen, fibroferite, anglesite, chalcantite, and nontronite, and, in the tailings of Kavalersky district, goethite, vudvardite, wroewolfeite, magnesite, olivenite, duftite, bayidonite, skodite, allophane and montmorillonite (instead of nontronite) should be added to the paragenesis.

Epsomite was established in the models at the Central Processing Plant tailings storage facility at low temperatures from -25 to -5 °C and the following Eh-pH parameters of the system: $E_h = 0.66\text{--}1.2$ V, 0.9–11.7, in the presence of sulfides above 20%, in association with goethite, gypsum, chalcantite, anglesite, plumbojarosite, calcite, adamine, and montmorillonite. The reaction of its crystallization is as follows: $\text{Mg}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Magnesite precipitates from the solution by the following reaction: $\text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MgCO}_3$. It is formed throughout the whole temperature range under consideration at the solution parameters: $E_h = 0.5\text{--}1.14$ V, pH 1.9–13.2 и $E_h = 0.42\text{--}0.86$ V, pH 5.7–13.3. In the interval of positive temperatures it associates with goethite, fibroferite, gypsum, alunogen, vudvardite, smithsonite, duftite, allophane and montmorillonite, while at negative temperatures the association is added with gibbsite, olivenite, bayidonite and scorodite.

Gibbsite (hydrargillite) can crystallize with involvement of different ion species: Al^{3+} , $\text{Al}(\text{OH})_2^+$, AlO_2^- , AlO^+ , existing in slime and drainage water solutions, by reactions:

- 1) $\text{Al}^{3+} + \text{H}_2\text{O} + \text{O}_2 + \text{H}^+ + 3\bar{e} \rightarrow \text{Al}(\text{OH})_3$;
- 2) $\text{Al}(\text{OH})_2^+ + \text{H}^+ + 0.5\text{O}_2 + 2\bar{e} \rightarrow \text{Al}(\text{OH})_3$;
- 3) $\text{AlO}_2^- + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Al}(\text{OH})_3$;
- 4) $\text{AlO}^+ + \text{H}_2\text{O} + 0.5\text{O}_2 + \text{H}^+ + 2\bar{e} \rightarrow \text{Al}(\text{OH})_3$.

It was identified in the processing tailings of the Komsomolsky district. The parameters of the simulated solutions were as follows: $E_h = 0.89\text{--}0.95$ V, pH 5.7–6.3, between -25 and -5 °C, and at $E_h = 0.77\text{--}0.8$ V, pH 6.5–7.4, $25\text{--}40$ °C. Its association coincides with the paragenesis for magnesite.

Alunogen crystallization requires presence of the same ions in the solution, which were established for the formation of gibbsite. 4 possible chemical reactions of the mineral crystallization are as follows:

- 1) $2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 17\text{H}_2\text{O} \rightarrow \text{Al}_2[\text{SO}_4]_3 \cdot 17\text{H}_2\text{O}$;
- 2) $2\text{Al}(\text{OH})_2^+ + 3\text{SO}_4^{2-} + 15\text{H}_2\text{O} \rightarrow \text{Al}_2[\text{SO}_4]_3 \cdot 17\text{H}_2\text{O} + \text{O}_2 + 4\bar{e}$;
- 3) $2\text{AlO}_2^- + 3\text{SO}_4^{2-} + 17\text{H}_2\text{O} \rightarrow \text{Al}_2[\text{SO}_4]_3 \cdot 17\text{H}_2\text{O} + 2\text{O}_2 + 8\bar{e}$;
- 4) $2\text{AlO}^+ + 3\text{SO}_4^{2-} + 17\text{H}_2\text{O} \rightarrow \text{Al}_2[\text{SO}_4]_3 \cdot 17\text{H}_2\text{O} + \text{O}_2 + 4\bar{e}$.

It was found throughout the whole studied temperature range at $E_h = 0.7\text{--}1.15$ V, pH 1.3–8.0 and $E_h = 0.53\text{--}1.16$ V, pH 1.3–13.2. Alunogen occurs in paragenesis with almost all technogenic minerals in cassiterite-sulfide tailings in TSFs of the Komsomolsky and Kavalersky districts.

Rostite precipitates from solutions with the following Eh-pH parameters: $E_h = 0.58\text{--}0.6$ V, pH 11.8–12.0, in the temperature range from -10 to -5 °C, at the tailings storage facilities of Komsomolsky district through the following reactions:

- 1) $\text{Al}^{3+} + \text{SO}_4^{2-} + 5.5\text{H}_2\text{O} + 0.5\text{O}_2 + \bar{e} \rightarrow \text{Al}[\text{SO}_4](\text{OH}) \cdot 5\text{H}_2\text{O}$;
- 2) $\text{Al}(\text{OH})_2^+ + \text{SO}_4^{2-} + 4.5\text{H}_2\text{O} \rightarrow \text{Al}[\text{SO}_4](\text{OH}) \cdot 5\text{H}_2\text{O} + 0.5\text{O}_2 + \bar{e}$;
- 3) $\text{AlO}_2^- + \text{SO}_4^{2-} + 5.5\text{H}_2\text{O} \rightarrow \text{Al}[\text{SO}_4](\text{OH}) \cdot 5\text{H}_2\text{O} + \text{O}_2 + 3\bar{e}$;
- 4) $\text{AlO}^+ + \text{SO}_4^{2-} + 5.5\text{H}_2\text{O} \rightarrow \text{Al}[\text{SO}_4](\text{OH}) \cdot 5\text{H}_2\text{O} + 0.5\text{O}_2 + \bar{e}$.

It was identified in the following association: goethite, gypsum, alunogen, vudvardite, starkeyite, magnesite, scorodite, duftite, mimetosite, kaolinite, montmorillonite.

Allophane formation requires presence of Si in the system (in addition to Al), which exists in solution in the form of $[\text{Si}(\text{OH})_2]^{2+}$ ion; hence, it is possible to write 4 reactions of its crystallization:

- 1) $2\text{Al}^{3+} + [\text{Si}(\text{OH})_2]^{2+} + 7\text{H}_2\text{O} + 2\text{O}_2 + 8\bar{e} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$;
- 2) $2\text{Al}(\text{OH})_2^+ + [\text{Si}(\text{OH})_2]^{2+} + \text{O}_2 + 5\text{H}_2\text{O} + 4\bar{e} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$;
- 3) $2\text{AlO}_2^- + [\text{Si}(\text{OH})_2]^{2+} + 7\text{H}_2\text{O} + \bar{e} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O} + 0.5\text{O}_2$;
- 4) $2\text{AlO}^+ + [\text{Si}(\text{OH})_2]^{2+} + 7\text{H}_2\text{O} + \text{O}_2 + 4\bar{e} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$.

It was identified in paragenesis with all the considered technogenic minerals, at the following Eh-pH parameters of the simulated solutions: $E_h = 0.5\text{--}0.95$ V, pH 5.7–13.7, and $E_h = 0.42\text{--}0.87$ V, pH 5.4–13.3.

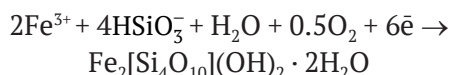
Kaolinite can precipitate from the solution by the following 4 reactions:

- 1) $2\text{Al}^{3+} + 2[\text{Si}(\text{OH})_2]^{2+} + 2.5\text{O}_2 + 10\bar{e} \rightarrow \text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$;
- 2) $2\text{Al}(\text{OH})_2^+ + 2[\text{Si}(\text{OH})_2]^{2+} + 1.5\text{O}_2 + 6\bar{e} \rightarrow \text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4 + 2\text{H}_2\text{O}$;
- 3) $2\text{AlO}_2^- + 2[\text{Si}(\text{OH})_2]^{2+} + 0.5\text{O}_2 + 2\bar{e} \rightarrow \text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$;

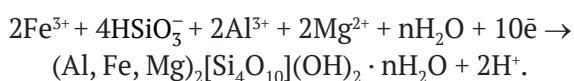


The conditions of its formation from solution are as follows: $E_h = 0.59\text{--}0.73$ V, pH 7.9–12.3, in the temperature range from -10 to $+45$ °C. It associates with most of the described technogenic minerals in the Komsomolsky and Kavalerovsky districts.

Among other minerals from the class of silicates established in conditions of oxidation of the tailings were *nontronite* and *montmorillonite*. Fe and Si ions are required for their crystallization from solution. The chemical reaction of nontronite formation is as follows:



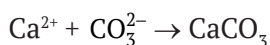
and montmorillonite



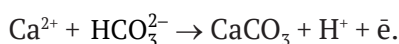
The solution parameters at which nontronite precipitates: $E_h = 0.79\text{--}1.15$ V, and $E_h = 0.75\text{--}1.15$ V, in the pH range of 1.3–8.0, and those for montmorillonite: $E_h = 0.5\text{--}1.1$ V, pH 2.7–13.9 и $E_h = 0.42\text{--}1.0$ V, pH 3.3–13.3. Nontronite is typical for the tailings of TSFs of Komsomolsky district, and montmorillonite, for the tailings of TSFs of Kavalerovsky and Dalnegorsk (Central Processing Plant) districts. They are present in paragenesis with most of the minerals under consideration.

Gypsum is one of the most common minerals in the ore mining-and-processing technogenic systems of the Far Eastern Region. It can occur in paragenesis with all the mentioned minerals. The reaction of its formation is as follows: $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, at the precipitation conditions of: $E_h = 0.5\text{--}1.2$ V, pH 0.9–13.9 and $E_h = 0.57\text{--}1.16$ V, pH 1.1–11.6.

Calcite can crystallize by the following reactions:



or



It was identified only in the tailings of TSFs of the Dalnegorsk district, where at the CPP it was present in association with goethite, gypsum, broshantite, adamine, montmorillonite, and, at the KPP, with valentinite, goethite, hydrogoetite, gypsum, fibroferite, cerussite. Parameters of the solutions for its formation were as follows: $E_h = 0.56\text{--}0.77$ V, pH 8.3–13.7 and $E_h = 0.66\text{--}0.76$ V, pH 7.1–9.6.

Conclusion

The use of the “Selector” software package allowed to analyze the processes of present-day mineral formation in the processing tailings (in tailings storage facilities) and to present the reactions of their crystal-

lization from solutions, as well as to estimate the physico-chemical conditions of the minerals formation: E_h -pH parameters and temperature intervals, and establish their parageneses and ionic composition of the solutions.

Among the main ions of sulfide ore components, the following ones were established in the composition of the slime and drainage water solutions: Cu^+ , Cu^{2+} , CuOH^+ , Pb^{2+} , PbOH^+ , $\text{Pb}(\text{SO}_4)_2^{2-}$, Zn^{2+} , ZnO_2^{2-} , ZnOH^+ , $\text{Zn}(\text{SO}_4)_2^{2-}$, As^{5+} , AsO_4^{3-} , $\text{Sb}(\text{OH})_2^+$, SbO_2^- , SO_4^{2-} , HSO_4^- , many of which were toxic [27, 28]. The main ions of the components of the host rocks were as follows: Ca^{2+} , CaOH^+ , K^+ , Mg^{2+} , Al^{3+} , $\text{Al}(\text{OH})_2^+$, AlO_2^- , AlO^+ , $[\text{Si}(\text{OH})_2]^{2+}$.

The possibility of precipitation of 37 secondary minerals of Fe, Cu, Pb, Zn, Sb, K, Ca, Mg and Al from the classes of oxides and hydroxides, sulfates, carbonates, arsenates and silicates from the technogenic solutions of tailings storage facilities was demonstrated. Oxidation of sulfide components of processing tailings leads to crystallization of secondary Fe minerals: goethite, hydrogoetite, fibroferite, jarosite, pitticite, siderite and scorodite. Among the Cu minerals, tenorite, chalcantite, poznyakite, wroewolfeite, antlerite, broshantite, olivenite, and clinoclase were established, and together with Zn, ktenasite, with Al, vudvardite, and with Pb, duftite and bayidonite. The secondary Pb minerals included anglesite and cerussite; in the presence of Fe, plumbojarosite was formed. Among the hypogene minerals of Zn, adamine and smithsonite were identified. The only Sb mineral was valentinite. Action of sulfate solutions (originated due to oxidation of sulfides) on the host rocks in the tailings leads to precipitation of the following secondary minerals from the technogenic water solutions: For Mg, starkeyite, epsomite and magnesite; for Al, gibbsite, rostitite, alunogen, allophane and kaolinite; for Ca, gypsum and calcite. The presence of Fe or Fe together with Al and Mg in the highly concentrated technogenic water solutions leads to the formation of silicates: nontronite or montmorillonite.

It was found that secondary minerals: jarosite, pitticite, siderite, tenorite, poznyakite, antlerite and ktenasite crystallize in the interval of positive temperatures, while scorodite, chalcantite, broshantite, cerussite, starkeyite, epsomite and rostitite originate in cryogenic conditions (below 0 °C). All other minerals, the possibility of precipitation of which was shown in the paper, crystallize in the whole considered temperature interval, from -25 to $+45$ °C.

The obtained data can be an important contribution to the mineralogy of hypogene and technogenic processes and assessment of environmental conditions in the Far Eastern Region. pH of the slime and drainage water ranges from strongly acidic to



strongly alkaline. After precipitation of technogenic minerals, the total mass of which reaches 230 g, the concentration of ore elements in the solution can be up to 340 g/L.

Field studies [1, 2] and modeling data on formation of technogenic waters (solutions) and crystallization of the secondary minerals on the surface of and inside tailings at the tailings storage facilities of the Far Eastern Region allowed demonstrating high intensity of the technogenic processes. It was found that the excess of the baseline concentrations of both elements of sulfide ores and their host rocks in the TSF's slime and drainage waters reaches tens of thousands times. Consequently, the tailings storage

facilities polluted the environment and the hydrosphere for a century² [29–31], but since they were not reclaimed, this process would continue for many decades to come.

² Ulanova D.I. Silica brought sands with dangerous salts. Pacific Star Newspaper. August 30, 2011. URL: https://toz.su/newspaper/chp/silinka_prinesla_opasnye_soli/

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