

1 *Conference Proceedings Paper*

## 2 **The Role of the Minerals in Komsomolsk Tin-ore** 3 **District Slurry and Drainage Water's Formation, and** 4 **their Negative Impact on the Ecosphere**

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11 **Abstract:** The article describes slurry and drainage water's characteristics and shows the  
12 conditions of their formation in the technogenic system of the Komsomolsky Tin-ore District,  
13 Russian Far East. The investigation was conducted using environmental monitoring, and  
14 physico-chemical modeling method. In a wide ambient temperature range (from minus 25 to  
15 45 °C) the Eh-pH parameters of micropore solutions, which form technogenic (anthropogenic)  
16 waters at various host-rock – sulfide ratios (95:5, 50:50, 5:95), were determined. Depends on the  
17 primary ores and host rocks composition ionic and molecular composition of technogenic waters,  
18 as well as association of crystallized hypergene minerals were established.

19 The negative impact of slurry and drainage water on the hydrosphere and the health of the  
20 region's population is shown. Following to environmental monitoring, the content of dissolved  
21 metals exceeds background concentrations in slurry and drainage waters from hundredsto  
22 hundreds of thousand times. Modeling reveals, that from saturated technogenic waters, Fe, Cu,  
23 Zn, Pb, Al, Ca, Mg, K, and Na oxides and hydroxides, sulfates, carbonates, arsenates, phosphates,  
24 and silicates minerals are precipitate. The tendency of double growth for 24 types of digestive,  
25 respiratory, and nervous system diseases during 20-years period has been noted, moreover,  
26 children morbidity rate exceeds that of adults.

27 **Keywords:** physicochemical modeling; hypergenesis; technogenesis; hypergenic and technogenic  
28 minerals; association or paragenesis; enrichment tailings; technogenic waters (mine, sludge and  
29 drainage)

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### 31 **1. Introduction**

32 Komsomolsky Tin-ore District is located at the East of Khabarovsk krai, Russian Far East, left  
33 bank of the Amur River. The mining industry has been developing here for over 70 years and three  
34 types of ore mineralization have been revealed: tin, copper-copper and tin-polymetallic. As a result  
35 of mining operations, three tailing dumps were formed in the district: Solnechnoye concentration  
36 mill (SCM), Central concentration mill (CCM), and Third. The fine mass of grey tailings consists of  
37 (in %): vein quartz – 37.5, tourmaline – 12.1, corneal and sedimentary rocks – 45 and sulfides  
38 (chalcopyrite, pyrite, pyrrhotite, arsenopyrite, galena, sphalerite, chalcocite, covellite and bornite) –  
39 3.8.

40 Sulfides in the enrichment tailings are in the crushed state, it leads to increased access of  
41 weathering agents (water, oxygen, etc.) and activation of hypergenic processes. As a result of

42 hypergenesis, sludge and drainage waters are formed, and the content of both sulphide ore  
43 elements and the host rocks there are higher than the background characteristics of natural waters  
44 of the district [1–3].

45 Environmental monitoring have been showed that the content of the considered chemical  
46 elements exceeds natural background conditions (times): in slurry waters Zn – from 253 to 385000,  
47 Fe – 1.2–24253, Cu – 8–26230, Pb – 630–1703, Al – 2.1–915, Ca – 1830–44766, Mg – 1542–100285; in  
48 drainage waters Zn – 470–38200, Fe – 41–921, Cu – 416–768, Pb – 2–1470, Al – 3–253, Ca –  
49 17066–78133, Mg – 6442–60557. Therefore, if such waters get into hydrosphere, their dilution in  
50 thousands and hundreds of thousands of times is necessary, which is not always possible.

51 The purpose of this work was to study the conditions for the formation of sludge and drainage  
52 water at the tailings dumps of considerable district in a wide temperature range from –25 to 45 °C  
53 using the physico-chemical modeling software complex Selektor, as well as to show their negative  
54 impact on the hydrosphere and the health of people living in the area. To achieve this goal, we  
55 wanted to: (1) determine the Eh-pH parameters of formation for technogenic waters microporous  
56 solutions in a wide temperature range from –25 to 45 °C, (2) show the possibility of technogenic  
57 minerals crystallization from solutions and identify the association or paragenesis of these minerals,  
58 (3) determine the ionic and molecular composition of sulphide ore elements in mine waters,  
59 (4) determine the content of sulphide ore elements in the simulated solutions, (5) show the negative  
60 impact of hypergenic processes on the hydrosphere and health of people living in these areas.

## 61 2. Materials and Methods

62 The computer physico-chemical modeling method in Selector software complex was used. The  
63 program is based on the convex programming mathematical approach, which allows an  
64 equilibrium to be established in heterogeneous systems by minimizing thermodynamic potentials  
65 (Gibbs energy) [4]. The formation of slurry and technogenic waters of tailings dumps was modeled  
66 as a result of sulfides ores and host rock oxidation with ratios 5:95, 50:50, 95:5. In total, 36 variants of  
67 physico-chemical models and 540 individual systems were analyzed.

68 Depending on the composition of primary ores and host rocks [5], the ionic and molecular  
69 composition of anthropogenic waters is determined, as well as the association of crystallizing  
70 hypergenic minerals.

## 71 3. Results and Discussion

72 Simulated microporous solutions that form slurry and drainage water have a wide range of  
73 Eh-pH parameters: from 0.76 to 1.15 V and 1.3–8.0. Modelling allowed us to reveal the hypergenic  
74 minerals that precipitated from saturated solutions in a wide ambient temperature range  
75 (Figures 1, 2). The following technogenic minerals are precipitate:

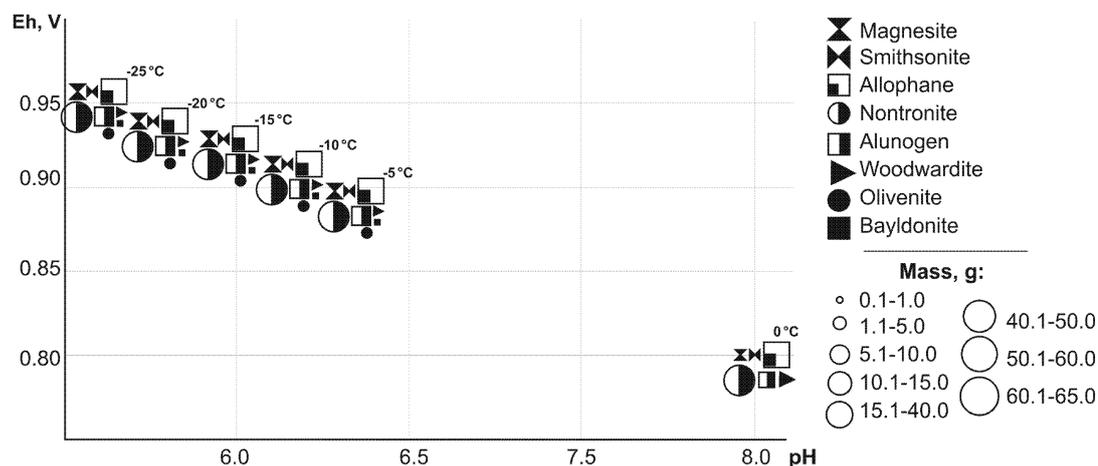
- 76 • oxides and hydroxides: Fe and Al – goethite, gibbsite;
- 77 • sulfates Cu – chalcantite, ktenacite, antlerite, Cu and Al – woodwardite, Pb – anglesite. Pb  
78 and Fe – plumbojarosite, Fe – fibroferrite, K and Fe – jarosite, Ca – gypsum, Mg – starkeyite,  
79 Al – alunogen;
- 80 • carbonates: Zn – smithsonite, Fe – siderite, Mg – magnesite;
- 81 • arsenates: Cu – Cu and Pb – bayldonite, clinoclase, Pb – mimetite, Cu and Pb – duftite,  
82 bayldonite, Fe – scorodite, pittitcrite;
- 83 • silicates: Na and Fe – nontronite, Al – allophane.

84 For all the considered minerals the temperature range of formation, as well as associations are  
85 estimated. The masses of minerals are varied from hundredths to 150 g.

86 The solutions obtained as a result of modeling contain all the elements of sulphide ores and  
87 host rocks: Cu, Zn, Pb, Fe, As, S, Al, Ca, Mg, K, and Na. Their concentration in the ion and  
88 molecular form reaches tens of grams, and under cryogenic conditions it is one order of magnitude  
89 and two orders of magnitude higher due to the reduction of solutions volume during ice  
90 crystallization.

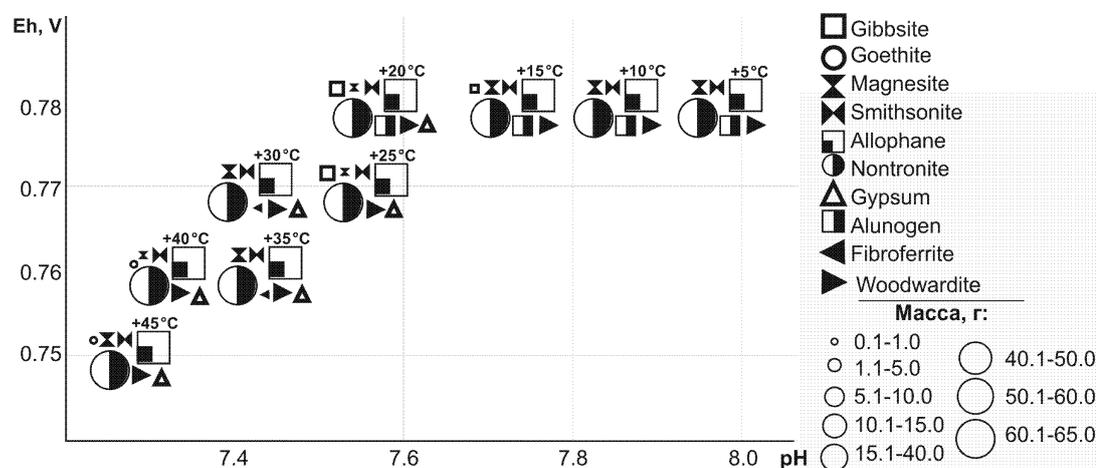
91 The total composition of ions and molecules in the simulated solutions is presented by:

- 92 • sulphide ore elements:  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{CuO}$ ,  $\text{CuOH}^+$ ,  $\text{CuHCO}_3^+$ ,  $\text{CuCO}_3$ ,  $\text{Cu}(\text{CO}_3)_2^{2-}$ ,  $\text{CuSO}_4$ ,  $\text{HCuO}_2^-$ ,
- 93  $\text{Pb}^{2+}$ ,  $\text{PbO}$ ,  $\text{PbOH}^+$ ,  $\text{PbCO}_3$ ,  $\text{Pb}(\text{CO}_3)_2^{2-}$ ,  $\text{PbHCO}_3^+$ ,  $\text{PbSO}_4$ ,  $\text{Pb}(\text{SO}_4)_2^-$ ,  $\text{HPbO}_2^-$ ,  $\text{Zn}^{2+}$ ,  $\text{ZnO}$ ,  $\text{ZnO}_2^{2-}$ ,
- 94  $\text{ZnOH}^+$ ,  $\text{ZnCO}_3$ ,  $\text{Zn}(\text{CO}_3)_2^{2-}$ ,  $\text{ZnHCO}_3^+$ ,  $\text{ZnSO}_4$ ,  $\text{Zn}(\text{SO}_4)_2^{2-}$ ,  $\text{HZnO}_2^-$ ,  $\text{HFeO}_2^-$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ ,  $\text{AsO}_4^{3-}$ ,
- 95  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ;
- 96 • host rocks elements:  $\text{Al}^{3+}$ ,  $\text{AlO}^+$ ,  $\text{AlO}_2^-$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{HAlO}_2^-$ ,  $\text{Ca}^{2+}$ ,  $\text{CaOH}^+$ ,  $\text{Ca}(\text{HCO}_3)^+$ ,  $\text{CaCO}_3$ ,
- 97  $\text{CaSO}_4$ ,  $\text{CaHSiO}_3^+$ ,  $\text{K}^+$ ,  $\text{KOH}$ ,  $\text{KSO}_4^-$ ,  $\text{KHSO}_4^-$ ,  $\text{Na}^+$ ,  $\text{NaOH}$ ,  $\text{NaAsO}_4^{2-}$ ,  $\text{NaHSiO}_3^-$ ,  $\text{NaSO}_4^-$ ,  $\text{Mg}^{2+}$ ,
- 98  $\text{Mg}(\text{HCO}_3)^+$ ,  $\text{MgCO}_3$ ,  $\text{MgHSiO}_3^+$ ,  $\text{HSiO}_3^-$ ,  $\text{SiO}_2$ .
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Figure 4. Dependence of mineral masses on Eh-pH parameters ( $T = -25$  to  $0$  °C).



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Figure 5. Dependence of mineral masses on Eh-pH parameters ( $T = 5$  to  $45$  °C).

105 The comparison of modelling results (case of the Third tailings dump oxidation at 25°C based  
 106 on tailings drilling composition) was verified by the hydrochemical analyses results of the  
 107 considered tailings slurry waters sampled at this temperature. Thus, we can compare the contents  
 108 of Cu, Fe, Pb and Zn in modelling solutions of this tailings dump both with their natural  
 109 background concentrations in rivers and maximum permissible concentrations for fishery needs,  
 110 and for drinking consumption. It shows the excess of background and maximum permissible  
 111 concentrations (in times): As, fishery needs– 18, drinking consumption– 89, background – 1481; Cu,  
 112 fishery needs–6470, drinking consumption– 6,5, background – 12940, Fe, fishery needs– 118,  
 113 drinking consumption–39, background – 787; Pb, fishery needs–31, drinking consumption– 19,  
 114 background – 1850; Zn, fishery needs–528, drinking consumption– 5, background – 17600.

115 The obtained data show that solutions of the Third tailing dump must be diluted tens,  
116 hundreds and even thousands of times to reach background and maximum permissible  
117 concentrations. It should also be noted that sludge and drainage waters of this tailings dump are  
118 discharged into the Levaya Silinka River (drinking water intake of the Gorny settlement), then it  
119 flows into the Amur River, and enters the Sea of Okhotsk.

120 It is well known that both lack and excess of vital elements leads to numerous diseases of  
121 people living in mining areas [6, 7]. Toxic effect of the elements on humans depends on their  
122 chemical nature, concentrations and composition of ions and compounds, as well as individual  
123 features of the organism [8], so it was important to establish forms of migration for elements.

124 An analysis of morbidity in the population carried out by the author in Komsomolsky district  
125 from 1991 to 2001 showed the following results. The most common diseases include digestive  
126 organs, which in that period were sick up to 20 % of children and adults; respiratory organs – up to  
127 70 % of children, and 20 % of adults; and nervous system – up to 17 % of children, and 10 % of  
128 adults. During the period under review, there was a trend of doubling of almost all types of  
129 diseases, both in adults and children, and the morbidity of the child population for almost all 24  
130 analyzed diseases is much higher than for adults. It should be noted that during this period, ore  
131 extraction and processing decreased significantly, and the population of the district decreased by  
132 18 % [9, 10].

#### 133 4. Conclusions

134 We have found that minerals play a major role in mobility and spreading of inorganic  
135 contaminants into the environment, including surface and ground water, as they participate in the  
136 processes associated with the change of primary phases (hypogenic) and in the formation of  
137 secondary phases (hypergenic and technogenic minerals).

138 The relationship between minerals and pollutants in the form of ions and molecules from  
139 sludge and drainage waters is an important issue of ecological mineralogy and geochemistry of  
140 natural waters. The main objective of such type studies is the development of models capable to  
141 link the obtained data with macroscopic observations at tailings dumps, but the latter are not  
142 always possible due to the fine dispersion of the tailings and the laborious selection of  
143 anthropogenic minerals.

144 Highly concentrated solutions, which get into the surface and ground waters before and after  
145 mineral deposition 24 hours a day and all the year round for decades, are contaminate them. Over  
146 time, this may lead to a worsening of the background water characteristics of Komsomolsk Tin Ore  
147 District. To understand these processes, the results of the analysis of hydrochemical samples of  
148 slurry and drainage water were demonstrated, as well as their characteristics were revealed using  
149 physico-chemical modelling. The conducted researches help to show the negative impact of  
150 hypergenic and technogenic processes, as well as of discharging technogenic waters on the river  
151 network. The consumption of such water by the population, as it was noted, leads to high  
152 morbidity in the mining areas of the Russian Far East.

153 Using modern methods of analysis and mathematical modeling it is possible to estimate the  
154 elemental composition of waters, to trace their chemical forms and to consider the transformation of  
155 elements depending on natural environmental physical conditions of this processes (such as  
156 temperature). Therefore, the application of modeling makes it possible to assess the temporal  
157 evolution of the water system. The obtained results can be useful for monitoring measures and  
158 reclamation activities.

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