A Study of the Qualitative Chemical Composition of Technogenic Waters in the Tailing Dumps of the Russian Southern Far East in a Wide Temperature Range Using the Physicochemical Modeling Method

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Abstract. The article presents the results of technogenic waters composition physicochemical modeling for Kavalerovsky and Dalnegorsk ore districts closed tailing dams (Primorsky Krai, South of the Russian Far East). Thermodynamic modeling in “Selektor” software package in a wide temperature range from -10 to +30 °C allowed to establish the Eh-pH characteristics and to study quantitative and qualitative composition of slurry and drainage waters

1. Introduction
When exposed to the weather agents sulfide-bearing tailings oxidize and release acid sulfate and heavy metals to the environment. Discharge of these metal-rich technogenic waters is lead to contamination of receiving water bodies. The impacts of technogenic waters can be observed at a variety of scales ranging from small watercourses to entire watersheds, over several decades to many centuries [1, 2]. These processes occur all year round, including in the cold season, i.e. in cryogenic conditions [3-5]. Migration of technogenic waters from tailings dumps is result in hydrosphere contamination directly through surface runoff and drainage waters and indirectly from discharge of groundwater.

Over 100 years of mining at the south of Russian Far East in Kavalerovsky and Dalnegorsk districts, Primorsky kray, has resulted in accumulation of about one hundred million tons of tailings.

In Kavalerovsky district, in the Zerkalnaya river basin, fifteen tin-sulfide deposits were developed. Six mining and four concentrating mills were built here since 1941. Their tailings are stored in five tailing dumps. In 2001 the mining was completely closed and the tailing impoundments were abandoned without recultivation matters.

In Dalnegorsk district, in the Rudnaya river basin, the mining was started in 1907. Lead-polymetallic and silver-lead-zinc lead-zinc ores have been processed on two concentrating mills. Their tailings are stored in four tailing dumps, three of them were closed and only one was partly recultivated.
The Zerkalnaya and Rudnaya rivers receive both direct and indirect contamination from an active and abandoned tailings dumps severely affecting river water quality. Numerous studies have revealed the formation of technogenic (slurry and drainage) waters in the tailings; the concentrations of sulfide ores and host rock elements these waters reach several grams per liter.

In the places of technogenic waters release and downstream of the rivers, multiple exceedances of background concentrations for As, S, Al, Ca, Mg, Mn, Cu, Fe, Zn and Pb were established [6].

Ecological and chemical studies of technogenic waters by modern methods of atomic absorption spectroscopy, atomic emission and mass spectrometry allow reliably establish the quantitative characteristics of tailings slurry and drainage waters. Thus, the main objective of this article is to study the quantitative chemical composition of technogenic waters in the tailing dumps in a wide temperature range using the physicochemical modeling method.

To this end, we set ourselves the following tasks:
1. To develop the physicochemical models of slurry and drainage water formation for the closed tailing dumps of Kavalerovsky and Dalnegorsky districts in a temperature range from -10 to +30 °C.
2. To perform the physicochemical simulation, and to study quantitative and qualitative composition of the tailing dumps technogenic waters.
3. To verify the obtained results.

2. Research methods
The physicochemical modeling was performed using the “Selektor” software complex (authors I.K. Karpov and K.V. Chudenko). The program implements a convex programming approach to the calculation of equilibrium in heterogeneous systems by minimizing thermodynamic potentials. One of the key features of this product is the calculation of complex chemical equilibria in isobaric-isothermal, isochoric and adiabatic conditions in multisystems. An aqueous solution of electrolyte, gas mixture, liquid and solid hydrocarbons, minerals in the form of solid solutions and one-component phases, melts and plasma can exist at the same [7, 8].

The thermodynamic properties calculation for the components in the “Selektor” is made depending on the temperature, pressure and activity coefficients. In the calculation of thermodynamic functions isothermal changes are used the equations of volume change dependence of condensed phases on temperature and pressure and semi-empirical states of gases. Thermodynamic properties of the aqueous solution components in the temperature range until 1000 °C and pressure until 5000 bar are calculated by the modified HKF-model (Helgeson-Kircham-Flowers) [8, 9]. The water solution activity coefficients are calculated using the Helgeson modification of Debye-Huckel equation [8].

3. Experimental
The following common thermal and pressure conditions were used in all models: $T = 0$ to 45°C (step 5 °C) and $P = 1$ bar. The water-tailings ratio was set at 10:1. The models were open to atmosphere.

Chemical composition of the atmosphere was calculated based on the work of R. Horn [10]. In each case models included independent components: the most probable gases, dissolved particles, as well as hypogene and supergene minerals.

The standard “Selektor” package thermodynamic data (Gibbs energy, enthalpy, entropy, coefficients for the heat capacity equation) as well as information from relevant literature were used [11-14].

The simple model was formed for slurry waters modeling. Oxidation of the surface tailings layer with the weathering agents was considered. The model consisted of a chemical composition obtained by x-ray fluorescence method (%): O – 50, Si – 32, S – 7, Fe – 6, K – 2, Mg – 1, Al – 1, Ca – 0.3, H – 0.2, Sn – 0.2, Na – 0.2, As – 0.05, Zn – 0.04, Pb – 0.02, Cu – 0.01.

The two-reservoir model was formed for drainage waters modeling. The model consisted of a chemical composition obtained by ICP-AES (on the iCAP 6500duo) and ICP-MS (on the Agilent 7700) methods [15]. The slurry waters formation were simulated at first reservoir, then slurry waters
were moved to the second reservoir and interact with the compound of tailings from the -20 cm horizon and formed the drainage waters.

Table 1. Tailings chemical composition, %.

| Component | Reservoir | № 1 | № 2 |
|-----------|-----------|-----|-----|
| SiO₂      |           | 45.66 | 52.91 |
| Al₂O₃     |           | 5.68  | 5.85 |
| Fe₂O₃     |           | 11.89 | 11.14 |
| MnO       |           | 1.63  | 1.61 |
| MgO       |           | 1.01  | 0.83 |
| CaO       |           | 19.95 | 15.89 |
| Na₂O      |           | 0.43  | 0.25 |
| K₂O       |           | 1.32  | 1.73 |
| P₂O₅      |           | 0.07  | 0.06 |
| H₂O       |           | 0.25  | 0.24 |
| Cu        |           | 0.014 | 0.043 |
| Zn        |           | 0.240 | 0.460 |
| Pb        |           | 0.070 | 0.134 |
| S         |           | 11.784 | 8.810 |
| As        |           | 0.005 | 0.039 |
| Ag        |           | 0.0006 | 0.0005 |
| Sb        |           | 0.00009 | 0.00007 |

4. Results and discussions
The pH and Eh technogenic waters characteristics, obtained by physicochemical modeling, are shown on figures 1-3.

Figure 1. Slurry waters characteristics, Kavalerovsky district.
The pH of obtained technogenic waters varies from 2.98 to 8.01. In negative temperature range it is 2.98-5.96 and 5.87-8.01 in positive range. The Eh varies from 0.79 to 0.86 V. In negative temperature range it is 0.92-1.06 V and 0.79-0.86 V in positive range.

As a result of cryogenic concentration (crystallization of ice from technogenic solutions) in temperature range from -5 to -10 °C, there is a decrease in pH and increase in Eh. With increasing of temperature in the range from 0 to +30 °C, there is an increase in Eh and a decrease in pH.
Due to different chemical composition of the tailings, the characteristics of Kavalerovskiy (figure 1) and Dalnegorsk district technogenic waters (figure 2 and 3) are vary.

Kavalerovskiy district slurry waters have pH from 5.43 to 8.01 and Eh from 0.79 to 0.94 V. In negative temperatures they are slightly acidic (5.43-5.68) and are near-neutral (6.28-8.01) in positive temperature range.

The pH of the Dalnegorsk district slurry waters vary from 2.98 to 6.62, and the Eh value – 0.86-1.07 V. In negative temperatures they are acidic (2.98-3.18) and are near-neutral and slightly alkaline (6.62-5.87).

As a result of Dalnegorsk district slurry waters and the lower tailings horizon interaction, drainage waters are formed. In negative temperatures drainage waters is slightly acid (5.63-5.96) and are near-neutral (7.10-8.00) in positive temperature range.

The high concentrations of sulfide ores and host rock elements are considered in all the temperature range. Their particular concentrations depends crystallization of secondary (supergene and technogenic) minerals from saturated solutions. The Na, Al, Fe, Mg, Cu, Zn, and Pb minerals of the following classes are crystallized in modeling systems: oxides and hydroxides (goethite), sulfates (fibroferrite, alunogen, woodwardite and gypsum), arsenate (duftite, bayldonite), carbonates (calcite, magnesite, and smithsonite) and silicates (allophane and nontronite).

As a result of cryogenic concentration, the highest content of elements in technogenic waters is observed at negative temperatures. Aqueous solutions consist of bound, free and vaporous water, osmotically absorbed, and capillary moisture.

| Table 2. Technogenic waters qualitative composition, mg/L. |
|-----------------|-----------------|-----------------|-----------------|
| Element         | Kavalerovskiy district | Dalnegorsk district |                 |
|                 | Slurry waters     | Drainage waters  |                 |
| Na              | 202.64-6810.10    | < 0.001          | < 0.001         |
| Mg              | 0.05-1013.20      | 0.49-426.32      | 0.03-832.39     |
| Al              | < 0.001           | 0.001-4.31       | < 0.001         |
| Si              | 0.02-3.26         | 0.03-3.43        | 0.03-3.40       |
| K               | 242.74-3474.35    | 0.01-22.88       | 0.04-266.52     |
| Ca              | 21.00-253.34      | 23.95-256.69     | 21.94-230.76    |
| Cu              | 0.001-27.12       | 3.17-1039.60     | 0.08-2047.10    |
| Zn              | 40.53-1362.00     | 235.53-17175.00  | 643.73-22382.00 |
| Pb              | 20.26-680.99      | 0.001-71.28      | 0.001-210.72    |
| S               | 1729.90-33418.00  | 1519.00-62100.00 | 2881.60-60420.00 |
| As              | 50.66-1517.80     | 0.001-5.09       | 0.001-45.45     |

Their volume increases with the increasing of temperature. Thus, the volume of Kavalerovskiy district slurry waters nonfreezing solutions is 20.17-34.67 mL and volume of Dalnegorsk district slurry and drainage waters nonfreezing solutions is 22.81-36.66 and 11.24-17.71 mL, respectively.

In negative temperature range the concentration of sulfide ores and host rock elements in Kavalerovskiy slurry waters reaches hundreds and thousands mg/L: S – 33418.00, Na – 6810.00, K – 3474.35, As – 1817.80, Zn – 1362.00, Mg – 1013.20, Pb – 680.99, and Ca – 253.34. Similarly, at -5 and -10 °C the Dalnegorsk slurry waters have maximum concentration of sulphide ores elements (mg/L): S – up to 60420.00, Zn – 22382.00, and Cu – 2047.10.

In positive temperature range the elements concentration decrease. The concentration of elements in Kavalerovskiy slurry waters reaches (mg/L): S – 2496.30, K – 2030.4, Mg – 1013.20, Ca – 253.34,
Na – 203.04, As – 50.76, and Pb – 20.30. The Dalnegorsk slurry waters contain (mg/L): S – 1565.10, Mg – 426.32, Ca – 256.69, Zn – 244.37, and Pb – 71.28.

At the same time, the concentration of sulfide ores and host rock elements in Dalnegorsk drainage waters are higher and contain (mg/L): S – up to 2924.80, Mg – 832.39, Zn – 723.07, K – 266.52, Ca – 230.76, Pb – 210.72, and As – 45.45.

Thus, the concentration of sulfide ores and host rock elements in the simulated technogenic waters reaches hundreds and thousands mg/L. In the Kavalerovsky district slurry water noted the highest content of Na, K, As, Mg and Pb. In the Dalnegorsk district, the maximum content of S and Al is observed in slurry, and Zn and Cu – in drainage waters.

The quantitative composition of technogenic waters is shown in table 3; it consist of dissolved particles with a concentration more than 1 mg/L.

| Particle                  | Kavalerovsky district slurry waters | Dalnegorsk district slurry waters |
|---------------------------|------------------------------------|----------------------------------|
| Na+                       | 176.28-184.53                      | < 1                              |
| Mg2+                      | 453.76-1013.10                     | 416.18-426.23                    |
| K+                        | 1656.60-1757.40                    | 3.20-19.92                       |
| Ca2+                      | 88.20-114.78                      | 80.09-104.52                     |
| Cu2+                      | < 1                                | 1.07-2.34                        |
| Mg(HCO3)2+                | 2.78-5.37                         | < 1                              |
| ZnHCO3+                   | 78.35-78.50                       | 455.31-472.40                    |
| PbHCO3+                   | 26.23-26.28                       | 92.26-92.27                      |
| SO42-                     | 4112.50-6099.30                    | 3210.50-3263.10                  |
| NaSO42-                   | 95.77-136.52                      | 7.00-7.33                        |
| KSO42-                    | 943.72-1278.40                    | 1.61-10.23                      |
| CaSO42-                   | 403.65-510.38                     | 406.29-516.91                   |
| CuSO42-                   | < 1                                | 5.69-14.06                      |
| Zn(SO4)23-                | < 1                                | < 1                              |
| HAsO42-                   | 35.01-90.86                       | 1.57-3.70                       |
| H2AsO42-                  | 3.95-60.03                        | 5.64-8.00                       |

All the simulated technogenic waters contain the ions of metals – Mg2+, K+ and Ca2+, Zn and Pb hydrocarbontes, sulfate ion, K and Ca sulfates, and arsenates HAsO42- and H2AsO42-.

The SO42- concentrations in obtained technogenic waters are high (mg/L): 6099.30, 3263.10 and 5763.00 in Kavalerovsky district slurry waters, Dalnegorsk district slurry and drainage waters respectively.

The highest Mg2+ (up to 1013.10 mg/L), K+ (1757.40 mg/L), Ca2+ (114.78 mg/L), NaSO42- (163.52 mg/L), KSO42- (1278.40 mg/L), HAsO42- (90.86 mg/L), and H2AsO42- (60.03 mg/L) concentration are seen in Kavalerovsky district slurry waters. Na+ (up to 184.53 mg/L) and Mg(HCO3)2+ (5.37 mg/L) particles are present only in Kavalerovsky district slurry waters.

The Cu2+ (up to 2.34 mg/L) and CuSO42- (up to 5141.50 mg/L) particles contain all the Dalnegorsk district technogenic waters.

The Dalnegorsk district slurry waters have the maximum concentrations of ZnHCO3+ (29902.00 mg/L) and PbHCO3+ (272.78 mg/L). It should be noted that Zn(SO4)22- with a concentration 27230.00 mg/L are present only in Dalnegorsk district drainage waters.
Thus, all the considered technogenic waters have high SO$_4^{2-}$ concentrations. The highest concentrations of Mg$^{2+}$, K$^+$, and Ca$^{2+}$, Mg(HCO$_3$)$_2$, NaSO$_4$, KSO$_4$, HAsO$_4^{2-}$, and H$_2$AsO$_4$ particles are typical for the Kavalerovsky district slurry waters. In Dalnegorsk district slurry waters the maximum concentration of Cu$^{2+}$, SiO$_2$, CaSO$_4$ particles are observed. And the the Dalnegorsk district drainage waters have the highest concentrations of ZnHCO$_3^-$, PbHCO$_3^-$, CuSO$_4$, and Zn(SO$_4$)$_2^{2-}$ particles.

The validity of the obtained results was confirmed by verification of the mineral compositions [6] and by comparison of the elements concentrations in solution with those in slime and drainage waters [16, 17].

5. Conclusions

The physicochemical modeling of the slurry and drainage waters composition for the closed tailing dumps of Kavalerovsky and Dalnegorsk districts (Primorsky Krai, South of the Russian Far East) was performed at this work. For a temperature range from -10 to +30°C the the Eh-pH characteristics were established, as well as quantitative and qualitative composition of slurry and drainage waters was considered.

The concentration of sulfide ores and host rock elements in the simulated technogenic waters reaches hundreds and thousands mg/L. In the Kavalerovsky district slurry water noted the highest content of Na, K, As, Mg and Pb. In the Dalnegorsk district, the maximum content of S and Al is observed in slurry, and Zn and Cu – in drainage waters. All the considered technogenic waters have high SO$_4^{2-}$ concentrations. The highest concentrations of Mg$^{2+}$, K$^+$, and Ca$^{2+}$, Mg(HCO$_3$)$_2$, NaSO$_4$, KSO$_4$, HAsO$_4^{2-}$, and H$_2$AsO$_4$ particles are typical for the Kavalerovsky district slurry waters. In Dalnegorsk district slurry waters the maximum concentration of Cu$^{2+}$, SiO$_2$, CaSO$_4$ particles are observed. And the the Dalnegorsk district drainage waters have the highest concentrations of ZnHCO$_3^-$, PbHCO$_3^-$, CuSO$_4$, and Zn(SO$_4$)$_2^{2-}$ particles.

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