Forms of Occurrence and Redistribution of Silver in the Tailings Dam System of Dalnegorsk District (Primorye Region, Russia)

E V Ovodova

1Candidate of Geological and Mineralogical Sciences, Far Eastern Federal University, Vladivostok

E-mail: ovodova.2011@mail.ru

Abstract. The forms of occurrence and redistribution of silver between the sulfide ore tailings and surface waters of the Krasnorechensk tailingsdam of Dalnegorsk District have been studied. Using the Selector-S software complex, physicochemical simulation of oxidation of tetrahedrite-freibergite and silver-containing pyrite was performed, and the mass of annual silver removal by surface runoff from the tailings site was calculated.

1. Introduction

Krasnorechensk(old) tailingsdam, one of the largest tailing dams in the DalnegorskDistrict, containing 2.9 mln tons of tailings, was formed as a result of the concentration of tin-polymetallic and silver-lead-zinc ores from the Smirnovsky and Yuzhnoye deposits located within the Upper-Ussursk ore territory of PrimoryeRegion.

Man-made mineral formations were accumulated from 1956 to 1972, and according to [6] they are a mechanical mixture of various mineral components.

After concentration about 10% of silver, 2–8% of galena, 1–5% of sphalerite, 56.3–93.8% of iron (in the form of magnetite, pyrrhotine, pyrite, marcasite), 66–98% of arsenic, 10–15% of antimony, 38–46% of silica (in the form of quartz and hedenbergite), as well as Se, Te, In, Ge, Tl, Ga, F, and other elements were dumped in the tailings

Waste dump sands are located in close proximity to Rudnaya river. Drainage waters of man-made mineral formation carry a significant amount of toxic metals and their compounds [3], including silver, causing significant damage to Rudnaya river ecosystem.

Silver has long been regarded as a microelement necessary for normal functioning of internal organs and body systems, as well as a powerful means of improving immunity. However, recent studies indicate high toxicity of silver nanoparticles compared to their macroscopic counterparts, since they have an increased reactivity and catalytic ability, solubility, adsorption and the ability to penetrate the body's biological barriers [1]. Silver ions have a high degree of health hazard, they are able to accumulate in the body and even in small doses can cause severe poisoning and argyrosis [2]. According to Russian health and hygiene rules and standards (SanPiN 2.1.4.559-96) silver has been assigned hazard class 2 and is characterized as a highly hazardous substance [5].

This paper describes a research work aimed at studying the forms of stay and redistribution of silver in the system of the old tailingsdam of the Krasnorechenskaya concentrating mill (KCM).
2. Research materials and methods

In June 2014, hydrogeochemical sampling of surface and drainage waters, and bottom sediments was performed, and samples of old tailings and solid mineral formations were collected in the old tailingsdam system of the Krasnorechenskaya concentrating mill.

Analytical studies of the chemical composition of water and solid mineral formations were carried out in the analytical center of the Far Eastern Geological Institute of the Far East Branch of the Russian Academy of Sciences (FEGI FEB RAS) in Vladivostok (accreditation certificate No. ROSS RU.0001.518996) in the laboratory of analytical chemistry and the laboratory of micro- and nano-research. The instruments and methods for analysis of the chemical composition of water are presented in Table 1, and the solid mineral formations – in Table 2.

Table 1. Laboratory methods for analysis of the chemical composition of water.

| Components | Analysis method | Instrument |
|------------|----------------|------------|
| pH         | Potentiometer method | Hanna pH meter model HI 9025C |
| HCO₃⁻      | Titration method | Anion-7051 (Russia) |
| SO₄²⁻, Cl⁻ | Capillary electrophoresis | Kapel-103PT (Russia) |
| Ca²⁺, Mg²⁺, Na⁺, K⁺, B, Si, Mn, Al, Cr, Sr, Ba, Ag, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Ga, As, Rb, Se, Sr, Y, Cd, Cs, Ba, Ti, Th, U, REE | Inductively coupled plasma atomicemissionspectrometry | ICAP 6500Duo Spectrometer (Thermo Scientific Corporation, USA) |

Table 2. Laboratory methods for determining the content of elements in solid mineral formations.

| Components | Analysis method | Instrument |
|------------|----------------|------------|
| Ag, Li, Be, Fe, Mn, Sc, V, Cr, Co, Ni, Cu, Zn, Pb, Y, Zr, Nb, Mo, Cd, Sn, Cs, Ba, Hf, Ta, W, Th, U, REE | Inductively coupled plasma mass spectrometry | Agilent 7700 spectrometer (Agilent Technologies, USA) |
| H₂O, SiO₂ | Gravimetric analysis | Precisionbalance |
| TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅ | Inductively coupled plasma atomicemissionspectrometry | ICAP 6500Duo Spectrometer (USA) |

The study of chemical composition of minerals, morphology of crystals and the analysis of microinclusions were carried out on a JXA 8100 electron probe microanalyzer (JeolSuperprobe) with an INCA-sight energy dispersive spectrometer (Oxford Instruments, United Kingdom). X-ray analysis was performed using a DRON-3 diffractometer with monochromatic radiation and a D8-Discover microdiffractometer in the X-ray research laboratory of FEGI FEB RAS.

3. Results and discussion

Chemical composition research of tailing sands showed that silver content in the samples varied from 8.11 to 19.41 g/t.

In man-made waste silver was found in two forms, as an impurity in pyrite (up to 0.8 wt%), forming its own mineral from grey ore group – tetradrite-freibergite.

Freibergite is found in close association with sulfides, mainly with pyrite and galena (Figure 1). It forms irregular-shaped impregnationsin pyrite, 0.1–15 μm in size, and in intergrowth with galena it makes interstices between grains. For the X-ray study of freibergite three samples were selected with

2. Research materials and methods
In June 2014, hydrogeochemical sampling of surface and drainage waters, and bottom sediments was performed, and samples of old tailings and solid mineral formations were collected in the old tailingsdam system of the Krasnorechenskaya concentrating mill.

Analytical studies of the chemical composition of water and solid mineral formations were carried out in the analytical center of the Far Eastern Geological Institute of the Far East Branch of the Russian Academy of Sciences (FEGI FEB RAS) in Vladivostok (accreditation certificate No. ROSS RU.0001.518996) in the laboratory of analytical chemistry and the laboratory of micro- and nano-research. The instruments and methods for analysis of the chemical composition of water are presented in Table 1, and the solid mineral formations – in Table 2.

Table 1. Laboratory methods for analysis of the chemical composition of water.

| Components | Analysis method | Instrument |
|------------|----------------|------------|
| pH         | Potentiometer method | Hanna pH meter model HI 9025C |
| HCO₃⁻      | Titration method | Anion-7051 (Russia) |
| SO₄²⁻, Cl⁻ | Capillary electrophoresis | Kapel-103PT (Russia) |
| Ca²⁺, Mg²⁺, Na⁺, K⁺, B, Si, Mn, Al, Cr, Sr, Ba, Ag, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Ga, As, Rb, Se, Sr, Y, Cd, Cs, Ba, Ti, Th, U, REE | Inductively coupled plasma atomicemissionspectrometry | ICAP 6500Duo Spectrometer (Thermo Scientific Corporation, USA) |

Table 2. Laboratory methods for determining the content of elements in solid mineral formations.

| Components | Analysis method | Instrument |
|------------|----------------|------------|
| Ag, Li, Be, Fe, Mn, Sc, V, Cr, Co, Ni, Cu, Zn, Pb, Y, Zr, Nb, Mo, Cd, Sn, Cs, Ba, Hf, Ta, W, Th, U, REE | Inductively coupled plasma mass spectrometry | Agilent 7700 spectrometer (Agilent Technologies, USA) |
| H₂O, SiO₂ | Gravimetric analysis | Precisionbalance |
| TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅ | Inductively coupled plasma atomicemissionspectrometry | ICAP 6500Duo Spectrometer (USA) |

The study of chemical composition of minerals, morphology of crystals and the analysis of microinclusions were carried out on a JXA 8100 electron probe microanalyzer (JeolSuperprobe) with an INCA-sight energy dispersive spectrometer (Oxford Instruments, United Kingdom). X-ray analysis was performed using a DRON-3 diffractometer with monochromatic radiation and a D8-Discover microdiffractometer in the X-ray research laboratory of FEGI FEB RAS.

3. Results and discussion

Chemical composition research of tailing sands showed that silver content in the samples varied from 8.11 to 19.41 g/t.

In man-made waste silver was found in two forms, as an impurity in pyrite (up to 0.8 wt%), forming its own mineral from grey ore group – tetradrite-freibergite.

Freibergite is found in close association with sulfides, mainly with pyrite and galena (Figure 1). It forms irregular-shaped impregnations in pyrite, 0.1–15 μm in size, and in intergrowth with galena it makes interstices between grains. For the X-ray study of freibergite three samples were selected with
silver content of up to 4.85 atoms in the formula. The results of microprobe analysis are presented in Table 3.

![Figure 1](image_url)

**Figure 1.** Mineral forms in old concentration tailings of the Krasnorechenskaya concentrating mill: py - pyrite, gn - galena, frb - freibergite, bt - biotite, q - quartz, FeSO₄ - iron sulfates, as – arsenic.

The calculation of crystal chemical formulas was carried out according to the generally accepted method based on 29 atoms.

**Table 3.** Chemical composition of samples of tetrahedrite-freibergite series according to microprobe research, wt%.

| No. | Components | Cu   | Ag   | Zn   | Fe   | Sb   | S    | Sum  |
|-----|------------|------|------|------|------|------|------|------|
| 1   |            | 14.58| 29.19| 0.74 | 9.56 | 24.41| 23.43| 101.9|
| 2   |            | 18.57| 26.31| 0.59 | 7.1  | 26.99| 22.47| 102.03|
| 3   |            | 18.72| 25.32| 0.77 | 6.41 | 26.51| 22.09| 99.82|

Crystal-chemical formulas:

1. Cu₄₄Ag₄₂Sb₂₄Fe₂₂S₄₁₃₁₃
2. Cu₅₃Ag₄₁Sb₂₄Fe₂₈S₄₂₇₄
3. Cu₆₆Ag₃₁Sb₂₄Fe₃₂S₄₂₇₈

All studied samples in their chemical composition are characterized by a fairly stable content of silver and zinc and a slightly varying number of atoms of copper, antimony and iron.

The interaction of finesulphide-containing wastes with precipitation leads to oxidation, leaching and migration of mineral-forming chemical elements with man-made solutions to natural surface water courses. For this reason, the next objects of study were the water pond zone, formed at the upper level of the tailings in the process of ascending circulation of detached water, as well as the water of drainage stream and water of Rudnayariver (Figure 2).
Figure 2. The scheme of water sampling in Dalnegorsk District.

Legend: 1 – contours of: I - KCM old tailings dam; II - KCM new tailings dam; III - new tailings of the Central concentrating mill; 2 - lake (pond); 3 - water sampling points.

Studies showed that silver was detected in more than 80% of samples taken from water bodies and leakage fluxes. The content of the element varied from 0.0 to 10.0 µg/dm³, the highest content was observed in the pond waters of KCM tailings dam (Table 4).

Silver content in bottom sediments varied from 1.49 to 2.56 g/t [3].

It is known that pyrite and freibergite are highly unstable minerals in the oxidized leach cap. The simulation of hypergenetransformation processes of 10 g of freibergite (Cu₄.₁₂Ag₄.₈₅Zn₅.₂₀Fe₃.₆₃Sb₃.₆₂S₁₃.₁₃), dissolved in 10 kg of water, balanced with the atmosphere, showed that this mineral completely dissolves with the formation of secondary mineral phases of bianchite (Zn[S₄O₆]·6H₂O), fibroferrite (Fe[S₄O₆](OH)·5H₂O) and wroeolfeite (Cu₄(OH)₆[S₄O₆]₂H₂O), and part of it enters the solution in the form of Ag⁺², AgOH, AgCO₃⁻ ions. Pyrite oxidation (Fe₀.₉₆Ag₀.₀₄S₂.₀₀) is accompanied by the formation of fibroferrite mineral phase and the release of Ag⁺² ions into the solution [3].

Table 4. The content of silver in pond waters and leakage fluxes.

| Sample No. | Studied water                          | Ionic composition of mineralization, g/dm³ | pH      | Silver content, µg/dm³ |
|------------|----------------------------------------|------------------------------------------|---------|------------------------|
| 1          | Rudnaya river                          | SO₄⁵¹HCO₃⁵¹Ca₆₅Na¹⁹Mg¹⁶                  | 6.93    | 0.001                  |
| 2          | Rudnaya river                          | SO₄⁷¹HCO₃²₈Ca⁶¹Mg³¹                      | 6.9     | 0.00                   |
| 3          | Lake                                   | SO₄⁷⁹HCO₃²¹Ca⁵¹Mg⁴₅                      | 7.76    | 0.06                   |
| 4          | Water in pond 1 of the KCM old tailings dam | SO₄¹⁰₀Ca⁶₆Mg³₄                     | 2.48    | 10.00                  |
The data obtained as a result of physico-chemical modeling made it possible to calculate the annual removal of silver by surface runoff from the territory of the tailings dam into Rudnaya river. The mass of removed substance was calculated according to the formula:

\[ M_i = S \cdot (W_r \cdot m_{ir} + W_m \cdot m_{im}) \cdot 10^{-6}, \]

where: \( S \) – tailings dam area, ha; \( W_r \) – the volume of rainwater runoff, \( m^3/ha \); \( W_m \) – the volume of melt water runoff, \( m^3/ha \); \( m_{ir}, m_{im} \) – the concentration of \( i \)-th pollutant in the runoff of rain and melt water, mg/l.

Estimates suggest that if only 10 g of freibergite are dissolved per year, 10.77204 kg/year of \( \text{Ag}^{+} \) can be removed into the river network; and if 10 g of pyrite are oxidized – 0.245512 kg/year.

**4. Conclusion**

Based on the ecological and hydrogeochemical research, it was established that the main source of silver ions (\( \text{Ag}^{2+}, \text{AgOH}, \text{AgCO}_3^- \)) in the waters of Rudnaya river is migration metal-bearing streams produced by the objects of mining technogenesis. In tailing sand silver was found as an impurity in pyrite and tetrahedrite-freibergite mineral. The analysis of the results obtained during the simulation of hypergene transformation of minerals suggests that sulfide ore concentration wastes accumulated in the tailings dam are a powerful and long-lasting source of toxic metals, including silver, in water bodies of Dalnegorsk District.

**5. References**

[1] Andrusishina I N, Golub I A, Didikin G G, Litvin S E, Gromovoy T Yu, Gorchev V F, Movchan V A 2011 Structure, properties and toxicity of nanoparticles of silver and copper oxides Biotechnology vol 4 6 51-59

[2] Ignatov I, Mosin O V 2014 Methods for obtaining finely dispersed colloidal silver nanoparticles Online journal “Naukovedenie” 3 http://naukovedenie.ru/PDF/85TVN314.pdf

[3] Ovodova E V 2017 Transformation of natural waters under the influence of mineralogical and geochemical transformation processes in natural and man-made systems (the case of Kavalerovsk and Dalnegorsk districts of the Primorye Region) Dissertation of candidate of
[4] Ovodova E V, Zinkov A V, Salnikova L A 2015 Hydrogeochemical features of natural and industrial waters of Dalnegorsk ore region (Primorye) *Geological evolution of the interaction of water with rocks: proceedings of the Second All-Russian Conference with international participation* (Vladivostok, September 06–11, 2015) 298 -301

[5] 2002 Health and hygiene rules and standards SanPin 2.1.4.1074-01 Ministry of Health of Russia (Moscow) 62

[6] Tarasenko I A, Zinkov A V 2001 Ecological consequences of mineralogical and geochemical transformations of Sn-Ag-Pb-Zn mill tailings (Primorye, Dalnegorsk district) (Vladivostok: Dal'nauka) 194