Geochemistry and mineralogy of old concentration tailings (Dal’negorsky ore district, Primorsky Krai, Russia)

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Abstract. The paper gives the granulometric characteristics of the old tailings of the Krasnorechenskaya concentration mill (Primorsky Krai, Russia) and discusses their mineralogical-geochemical features. The original ore and newly formed mineral associations belonging to certain subzones are characterized by the concrete formation conditions and occupy a definite position in space thus forming a mineral zoning. The resources of main elements concentrated in the tailing dumps have been calculated. The KCM tailing dumps are shown to be the promising objects for the repeated extraction of mineral raw material and, at the same time, the sources of environment pollution with toxic elements.

1. Introduction
The commercial operation of ore deposits was responsible for a significant increase of the technogenic load on the ecological situation of the territories, including the location of a great volume of the concentration products. All over the world the interest is heightened to the concentration wastes, which often contain considerable reserves of both valuable and toxic elements [1–13]. The investigations of the geochemistry and mineralogy of the old concentration tailings are directed to the improvement of the risk evaluation, the understanding of the physicochemical processes taking place in the mass of technogenic formations, and optimization of the works on the minimization of the ecological action of tailing dumps on the natural environment.

The paper presents the results of the mineralogical-geochemical study of the old concentration tailings of the Krasnorechenskaya concentration mill (KCM) in Dal’negorsk district, Primorsky Krai, Russia (Fig. 1). In the operation period, the mill concentrated the complex tin-polymetallic and silver-lead-zinc ores of Smirnovskoe and Yuzhnoe deposits of the Krasnorechensky ore node. The technology of ore processing was not perfect. Extraction of the main metals into lead and zinc concentrates was as follows: 92–98% of galena and sphalerite, 80–85% of silver and the remainder together with sulphides of other metals were discharged into the pulp composed of about 87% of nonmetallic minerals. The bowls of the tailing dumps have been filled with the pulp for 40 years (from 1956 to 1995), and now they contain more than 6.8 million tonnes of wastes with tremendous amounts of sulphides, which are of great interest for the secondary concentration, and toxic elements that attract a great attention to the old tailings as the source of potential raw material and environment pollution.

In this connection, the tasks of our investigation were the following: to give the granulometric characteristics of the KCM’s tailings; to consider the mineralogical-geochemical features of the old
concentration tailings; to study the original ore and newly formed mineral associations; to evaluate the resources of the main elements concentrated in the tailing dumps; to distinguish the elements of industrial interest for their extraction and the prior contaminators of the environment capable to create serious ecological problems.

![Figure 1. Geographic area of the district under study](image)

2. Methods of investigation
The investigations included geochemical, mineralogical and hydrochemical sampling of the old concentration tailings and waters formed in the tailing dumps. To obtain a reliable mineralogical–geochemical information the samples were taken from the surface of the old tailing dumps and trough sinking the pits 2–2.5 m deep. In addition, the geochemical sampling of five holes passed on the optimally predetermined net by the convert method to a depth of 10–15 m was taken. The distance between the holes was 100 and 150 m.

The geochemical samples were taken by the furrowing way vertically on each visually distinguished layer of the most variability of the composition and structure of the old tailings. The mineralogical samples were taken by the dotted method into the hermetic glassy weighing bottles. The hydrochemical samples for the analysis of cations and sulphides were filtrated through the cellulose filter (0.45 mkm) in situ to remove suspensions and were acidified with nitric acid. For the analysis of ions the samples were also filtered and gathered into polyethylene vessels without acidifying. The unstable parameters were measured at the place of the water sampling.

The analytical works were done at the Analytical Center of the Far East Geological Institute, FEB of RAS. The element contents in samples were determined by the methods of mass spectrometry (Agilent 7700 c, USA) and atomic-emission spectrometry (iCAP 6500Duo, USA) with the plasma coupled by induction.

The mineralogical investigations were carried out with the methods of X-rayspectral (INCA-sight, Great Britain) and roentgenographic analysis (DRON-3; D8-Discover). The micromorphology and composition of mineral phases were studied using the scanning electron microscopes JSM-6490LV and ZEISS EVO 50XVP, equipped with the roentgen energy-dispersive spectrometers INCA Energy and light microscope Nikon Eclipse LV100 Pol.
3. Results of investigations and discussion

The study of the physicomechanical properties of the old concentration tailings showed that they are represented by the mixture of mineral particles of different size from a micron fraction to 3 mm. With regard to the granulometric composition, the grounds of the studied tailing dumps are characterized by the presence of coarse-grained sandy varieties (+0.4 mm) in amounts of 2%, medium-sized grounds (–0.4 to +0.2 mm) – 10%, fine (–0.2 to +0.071 mm) – 36% and dust-like (–0.07 mm) – 52%.

The technogenic formations of tailing dumps are lithified to a different degree, and it is quite rightful to assign them to the group of technogenic sandstones.

One can observe in them the coexistence of the contact and pore types of cement represented by the following mineral varieties: hydroxide iron, clay limonite, and sulphate microcrystalline one. In the cement composition there are aggregate accumulations of hydromica of phlogopite type.

The sum of sulphide in the technogenic formations varies from 5 to 35%. Pyrite and marcasite account for 80% of them, sphalerite and galena – 15%, and pyrrhotinite, stannite, and arsenopyrite – 4–5%. Sphalerite and pyrrhotinite occur as thin mutual intergrowths and as impregnations in the pyrite metacrystals. Galena is present in the pyrite and pyrrhotinite metacrystals in the form of isometric grains (Fig. 2(A)). In the case when the galena fills the microfractures in pyrite, the latter is almost in full replaced by marcasite (Fig. 2(B)). Chalcopyrite grains were also noted (Fig. 2(A)). The size of the chalcopyrite, galena, marcasite and pyrrhotinite grains is less than 0.05 mm (Fig. 2(A–D)). Isolated grains of pyrite, arsenopyrite and sphalerite 0.3 mm in size are found, in which the emulsion impregnation of chalcopyrite and galena was found (Fig. 2(A), (C)). The silver mineral grains, having $R_{Ag} = 25–32\%$, rather close to $R_{PbS}$, $T_{Ag} < T_{PbS}$, and distinct anisotropy are represented by argentite, hessite, and sulfosalts of the row of pearceite-polybasite in galena (Fig. 2(E)) or in jamesonite. The old tailings are characterized by the presence of oxidized ores, which show a very diverse mineral composition. The phase analysis of Pb, Zn and S showed that lead is represented by four forms: sulphide, carbonate, sulphate and plumbojarosite.

This suggests that the hypogene galena in the process of physicochemical transformations, taking place in the tailing dumps, is changed and turns into anglesite, cerrusite and plumbojarosite that was diagnosed by mineralogical investigations (Fig. 2(F)).

Zinc is represented by the sulphide and oxide-carbonate-sulphate phase groups. The inverse relationship is established between zinc sulphide and oxidized phases. The oxidized phase is most likely represented by smithsonite and goslarite. The quantitative comparison of the phase composition of sulphur, lead and zinc and a significant prevalence of sulphate sulphur over the total amount of sulphate phases of lead and zinc testify to the presence of sulphates of other metals. The analytical methods in the studied tailing dumps defined the presence of melanterite, ferrohexahydrite, roséinite, fibroferrite, copiapite, hydroalumogoethite, basaluminite, gypsum and other sulphates [13–16], which in chemical composition are rather similar to the findings in other districts and, at the same time, differ from them in content of some elements [17–25]. For example, melanterites and roséinites of the studied tailing dumps differ from the findings in other districts in higher contents of zinc (1.65–7.19 mass %) and calcium (0.08–0.62 mass %) and low concentrations of copper. The hydroalumogoethite studied is most similar in chemical composition to goethite of the Epleni bauxite deposit and is characterized by higher concentrations of Al (0.05 mass %), Mg (0.1 mass %), Mn (0.03mass %) and Au (0.0005 mass %).

The mineralogical investigations established that the oxidation zone of tailing dumps is the area with equal conditions in all its parts. Its different horizons are characterized by typomorphic epiminal associations assigned to certain subzones with the concrete formation conditions and occupy a definite position in space thus forming the mineral zoning. The study of the epiminal associations revealed the stages of development of the hypergenesis zone of the tailing dumps of KCM.

The use of the methods of mathematical statistics (cluster analysis) allowed us to establish the natural geochemical delamination of the spatial–qualitative structure of technogenic formations not stratified visually and to determine the unique characteristic of element correlations of each
distinguished geochemical layer. It was found out that there is the layer-by-layer manifestation of the processes of hypergene transformations in the technogenic deposits. It was revealed that the contents of Pb, Sn, As, Zn and Cu increase with depth.

Figure 2. Predominant mineral forms in the old concentration tailings (A–F): galena is present in the pyrite metacrystals in the form of isometric grains and the emulsion impregnation of chalcopyrite in sphalerite (A); relics of pyrite and the resulting sulphate of iron (B); emulsion impregnation of galena in arsenopyrite (C); emulsion impregnation of galena in pyrite and the resulting sulphate of iron (D); the silver sulphosalts of the row of pearceite-polybasite in galena (E); plumbojarosite (F). Apy – arsenopyrite, Bt – biotite, Chl – chlorite, Cpr – chalcopyrite, Cst – cassiterite, Gn – galena, Pb-jrs –
plumbojarosite, Pbz – polybasite, Py – pyrite, Qz – quartz, Sp – sphalerite, FeSO4 · xH2O – in the form of cementing phases

The potential resources of the main elements, contained in the tailing dumps, have been determined. It is shown that in the studied tailing dumps, the promising kinds of raw mineral materials are Pb, Sn, Zn and Ag. Lead enters the composition of galena (51.63% of the whole lead volume) and cerussite (35.3%), and its insignificant amounts are found in plumbojarosite (11.11%) and anglesite (1.96%).

Tin is a constituent of cassiterite (93.6% of whole Sn volume) and stannite (4.3%), and it is present in the easily destroyed colloidal forms (2.1). Zinc is contained for the most part in marmatite (49.54%). Cadmium (0.12%), indium (0.06%) and copper (0.08%) are also concentrated in marmatite. Silver forms the independent mineral phases (argentite, hessite and polybasite), which occur as the emulsion impregnation in galena, jamesonite and more rarely pyrrhotite and sphalerite.

Thus, the elements accumulated in the tailing dumps may be of economical interest (Pb, Sn, Zn and Ag), and at the same time they are the prior contaminators of the environment (As, Pb, Zn, Cd, Cu, Ni and Co) as the source of ecological problems.

And only thanks to the fact that the colloid-dispersive minerals (including sulphates) in the form of cementing phases and surface (films and sinters) formations control both the resistance of the technogenic systems to mechanical stresses and migration abilities of elements, the process of intoxication of the ecosystem with the derivates of tailing dumps is restrained in part.

4. Conclusion

The study of the mineralogical–geochemical features of the old tailings of KCM has established the following facts:

1. In granulometric composition, the technogenic deposits are represented by fine (+0.1–0.25 mm) and dust (–0.1 mm) materials.
2. The sum of sulphides in the technogenic formations varies from 5 to 35%; 80% of them are shared by pyrite and marcasite, 15% by sphalerite and galena, and approximately 4–5% by pyrrhotite, stannite and arsenopyrite. Grains of chalcopyrite, argentite, hessite and sulfosalts of the pearceite-polybasite row are noted in galena or jamesonite.
3. In the technogenic formations, one can observe the simultaneous existence of the contact and pore types of cement, represented by hydroxide iron, clay limonite, and sulphate monocrystalline mineral varieties.
4. The hypogene minerals and rocks, present in the old tailings under the action of the hypergene transformations, experience the alterations resulted in the formation of sulphates, carbonates and hydroxides. They restrain in part the process of intoxication of the ecosystem with derivates of the tailing dumps and control both the resistance of the technogenic systems to the mechanical stresses and the migration abilities of the elements.
5. The hypergenesis zone of the old tailing dump shows a middle stage of development characterized by the predominance of hypergene material over hypogene one and by the development of carbonates and hydroxides together with sulphates, and the hypergenesis zone of the new tailing dump belongs to the initial stage of development with insignificant alteration of hypogene minerals and little distribution of newly formed minerals.
6. The natural geochemical delaminations of the spatial–qualitative structure of the old tailings not stratified visually are characterized by the definite correlations unique to each distinguished layer.
7. The contents of Pb, Sn, As, Zn and Cu increase with depth.
8. In the KCM old concentration tailings some elements (Pb, Sn, Zn and Ag) are concentrated in amounts interesting for their extraction, as well as the prior contaminators of the environment (As, Pb, Zn, Cd, Cu, Ni and Co) capable to create serious ecological problems. In this connection, it is necessary to take measures directed to the utilization of the old tailing of ore concentration or to the suppression of harmful element activity with the method of laying up of the tailing dumps.
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