







**Mini Review** 

Tailing dumps of the tyrnyauz tungsten-molybdenum mining and processing complex: Current state and outlooks

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#### **Abstract**

The Tyrnyauz W-Mo deposit was developed by opencast and underground mines until 2003. The assets of the Tyrnyauz Tungsten-Molybdenum Mining and Processing Complex (TTMC) include two tailing dumps: Tailing 2 (housed on the left-hand side of the Baksan River valley, 2 km south of the settlement of Bylym) and Supertailing 2 (a superdump housed in the valley of the Gizhgit River, a left-hand tributary of the Baksan River).

The height of the rock-filling dam of Supertailing 1 reaches 160 m. A pond on its top protects the ecosystems from the wind erosion of the dumped industrial wastes. The protecting pond is equipped with a tunnel drainage system, which is used to discharge excess water to the Baksan River, to a certain technological water level in the pond.

Shallow-focus earthquakes (with M = 5-7) and/or debris and mud flows are able to destroy the dam, and this will result in the transfer of toxic compounds to the Baksan River and water-bearing Quaternary alluvial rocks in the foredeep, where the river flows into the plain.

The following soil contamination sources were identified: (1) Winds continuously blowing along the Baksan valley erode fines where the recultivation layer of Tailing 2 is disturbed and in the beach parts of Supertailing 1; the extent of this contamination varies from hundreds of meters to a few kilometers; (2) Massive blasting operations at the opencast mines before 2003 resulted in atmospheric emissions of dust clouds with ore minerals; this pollutions extends for dozens of kilometers (along the valleys of the Baksan River and its tributaries).

The most ecologically hazardous emissions are those of quartz dust and dust with heavy-metal minerals, including sulfides. A method for utilizing TTMC wastes was engineered and patented. The results provide a basis for designing measures aimed at decreasing the adverse load on the ecosystems in the Elbrus area, which is highly attractive to tourists.

### Introduction

The Tyrnyauz W-Mo deposit was commissioned in 1940. When the risk emerged that the German Wehrmacht may occupy the Elbrus area in the Caucasus in 1942, the processing mill, the entrances to the adits, and some ropeway stations were blasted. After the reconstruction of the facilities in 1945, the annual production (which was then conducted only in underground workings) and processing of W and Mo ores was within 1 Mt.

Until 1992, the deposit was developed by both opencast and underground mines, and the maximum production and processing rate amounted to 8 Mt ore per a year. The enterprise then produced 55–60% W and 15% Mo of the total USSR production of the metals at that time. However, when the energy price jumped in 1992, the ore mining and processing cost (i.e., the primecost of the metal heads) became higher than the factory-gate prices of the manufactured concentrate. Because of this, operations at the Mukulansky opencast mine,

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which produced poor ores, were terminated, and the Molibden underground mine selectively extracted only the highest grade ores. All equipment at the Mukulansky mine and the "excess" equipment at the underground mine were sold off at dumping prices. The production and processing rate was scaled down in 2003 to 1 Mt per a year, and the flotation mill (which is located within the town of Tyrnyauz on the left-hand side of the Baksan River) was dismantled. The average W contents in the ores of the Tyrnyauz Tingsten-Molybdenum Deposit (TTMD) are six to eight time lower than at deposits in the Russian Far East and China, and hence, the deposit was written off the list of currently developed tungsten deposits in Russia.

Nowadays the reserves of the deposit are listed according to two conditions: provisional conditions as of 1996 (25 Mt of ore, with 111 119 tonnes of tungsten trioxide and 16 025 tonnes of molybdenum) and permanent ones, as of 1982 (352 100 000 tonnes of ore, including 528 832 tonnes of tungsten trioxide and 145 855 tonnes of molybdenum), i.e., the total (tungsten plus molybdenum) TTMD reserves are uniquely large. Moreover, the ores placed into the State Register contain low concentrations of gold, silver, copper, and bismuth, which even more increase the overall value of this deposit.

The registered assets of the Tyrnyauz Tungsten-Molybdenum Mining and Processing Complex (TTMC) list two tailing dumps: Tailing 2 (older tailing on the right-hand side of the valley the Baksan River, 2 km south of the settlement of Belym) and Tailing 1 (new supertailing in the valley of the Gizhgit River, a left-hand tributary of the Baksan River). The rock-fill dam of Tailing 1 is up to 160 m high. The pond on its top serves to protect the ecosystem against the dust erosion of the dumped industrial wastes. The protecting pond is equipped with a tunnel drainage system, through which 55 000 m<sup>3</sup> waste waters are daily poured off into the Baksan River. The dam of the supertailing is damaged by seven microdeformations. Shallow-focus earthquakes or debris flows are able to destroy this dam, and this shall then bring toxic compounds to the Baksan River, and newly formed mobile species of these compounds shall then occur in the Quaternary aquifers (the thicknesses of these sediments in the Baksan valley reach 250 m according to drilling data), and these compounds shall then be eventually accumulated where the river exits to the plain in the vicinities of the town of Baksan, i.e., where farmlands and agricultural facilities are situated (Figure 1).

Still another TTMC tailing dump, which was the first to be established and occurred within the boundaries of the town of Tyrnyauz, was destroyed by a catastrophic flooding in 2000, and all the industrial wastes flew down the Baksan River, contaminated the river and its bottom sediments, as well as those of the Malka and Terek rivers and, perhaps, those of the Caspian Sea near the Terek delta.

According to information from TTMC, Tailings 1 and 2 house, respectively, 80 and 26 million m<sup>3</sup> industrial wastes with the following average concentrations (wt %) of W ~ 0.03 and Mo ~ 0.0085 and with the following total reserves of metals (in thous. tonnes): W - 200, Mo - 60, Cu - 15, Bi - 4, and 1 to 5 tonnes Au and 4 to 20 tonnes Ag.

Over the past five decades, TTMC systematically increased its ore production and decreased the cutoff W and Mo concentrations of the ores. The recovery rates of tungsten and molybdenum reached 60-70%, those of the Cu-Bi concentrate was  $\sim 30\%$ , and that of Au was 3-4%.

In 2005, the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, launched a comprehensive mineralogical and geochemical study in the area of TTMC operations under the program "Geochemical Features of Industrial Wastes Dumped in Tailings and the Geochemical Safety of the Area" [1-7].

## Mineralogical and geochemical study of the dumped industrial wastes

In 2014, two boreholes were drilled throughout the whole thickness of Tailing 2, and two holes were penetrated to a depth of 20 m at Supertailing 1. The core material was sampled and examined. In addition, the surface material of the tailings was sampled to depths of 0.3-1.5 m along a series of transects, with the sampling sites spaced 25 m apart and the transects spaced 50 m apart. The beach part of the pond at Supertailing 1 was also sampled. All of the samples were analyzed by XRF, INAA, and ICP-MS. The average concentrations of ore elements were as follows (ppm): Mo - 111, W - 375, Pb - 22, Zn - 241, Cu - 37, and As - 73. The most widely spread minerals of the dumped rock material are quartz, calcite, pyroxene, garnet, feldspar, and fluorite. The rock material additionally contains minor amounts of wollastonite, vesuvianite, biotite, amphibole, kyanite, chlorite, molybdenite, scheelite, molybdoscheelite, chalcopyrite, bornite, pyrite, arsenopyrite, magnetite, zircon, and apatite.

#### Sources of soil contamination

The following sources of soil contamination were identified: (1) Wind, which usually blows along the Baksan valley, causes the wind erosion of fines at sites where the recultivating layer is disturbed at Tailing 2 and at the beach part of Supertailing 1. The eroded fines pollute farmland soils and natural grasslands of the settlement of Belym. The contamination extends to distances from a few hundred meters to a few kilometers. Some of the soil samples contain Mo, W, and Sn concentrations are tens of times higher than the standardized Maximum Permissible Concentrations (MPC), and the Cu and Zn concentrations are twice higher than the MPC. (2) Massive rock blasts in the opencast mines bring cloud of fine dust to elevations up to 1 km. The dust contains ore phases (W, Mo, Sb, etc.), which are transported up and downstream of the Baksan River and its tributaries, with larger ore particles settling at the tailing dumps and in the opencast mines. The dust thus produced contains relatively little fine material (aerosols), but the latter is the most active and mobile constituent of the dust. The most ecologically hazardous material is quartz dust and that of heavy metals, for example, sulfide minerals.

To evaluate the degree of soil contamination at the natural grasslands and farmlands in the vicinities of TTMC tailings, we have collected a background soil sample (BS) north of the

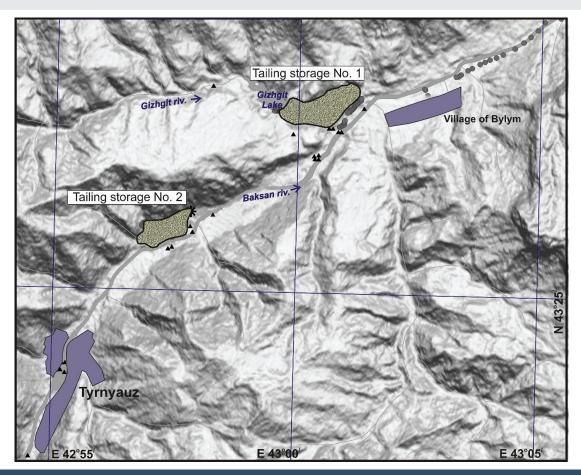


Figure 1: Schematic location map of tailing dumps of the Tyrnyauz Tungsten-Molybdenum Complex, the contours of the tailing dumps, and the pond protecting against wind erosion (so-called Gizhgit Lake)

Skalistyi Range, which is not crossed by the dust clouds. The sample taken in front of the Skalistyi Range contained higher than in BS concentrations of S, V, Ni, Ba, W (1.5 times higher), Pb (~2 times higher), and Cu and Zn (2.5 times higher).

The soil sample from a natural grassland on the left-hand flank of the Baksan valley (180 m northeast of Supertailing 1) contained higher (than in BS) concentrations of Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>2</sub>, Cu, Ba, Pb, Rb, Cr, V, Co, Pb, Sc, and Cs (1.5-2 times higher), MnO (2 times higher), As (3 times higher), Zn (4 times higher), Sn (7 times higher), Sb and Mo (~9.5 times higher), and W (50 times higher).

Modern soils at the grasslands and farmlands of the settlement of Belym near TTMC tailings were thus proved to be contaminated with ecologically hazardous metals.

#### Contamination sources of the baksan water

Surface waters in the TTMC area and adjacent territories were sampled in 2014-2016 and analyzed by iCAP 6500 Duo, and ICP-MS. Elevated concentrations (dozens of times higher than MPC) were detected for Mo (up to 11 mg/L), W (4.4 mg/L), As (1.5 mg/L), Mn (8.4 mg/L), and Tl (up to 3.3 mg/L) in the water of Bolshoy Mukulan Stream, which flows across opencast ore mines and waste-rock dumps, in which fine ore material settled from the dust clouds (produced by intense blasting operations at TTMC opencast mines) and was accumulated. The dominant contamination source of the Baksan water was proved to be Bolshoy Mukulan Stream but not the tailings.

Analysis of concentrations of major and trace elements in surface waters in the basin of the Baksan River led us to the following conclusions: (1) The water of the Baksan River where the river flows into the piedmont plain contains Al, Fe, Mn, Be, Si, Ti, Tl, and Hg concentrations that are notably higher than MPC in summertime and Si, Ti, Hg, and Tl concentrations that are lower than MPC in spring. (2) Bolshoy Mukulan Stream has the highest flow rate among other streams flowing through the opencast mines and bear the highest concentrations of Al, Si, Fe, Mn, Ti, V, Ni, As, Li, Be, Mo, Cd, and Tl concentrations, which are one to two orders of magnitude higher than the MPC in summer. (3) Elevated concentrations of the same elements, as well as B, Hg, Sb, and W, are typical of the water of Maloe protecting pond (which is not running), whereas the water of Bolshoy pond (which is running) of Supertiling 1 contains elevated (higher than MPC) concentration only of As and W.

# **Utilization of dumped TTMC wastes**

To minimize the material damage from natural and anthropogenic processes and decrease the adverse load on the ecosystems and human health, it is obviously necessary to completely utilize the industrial wastes stored in TTMC tailings and recover all economically valuable and ecologically hazardous metals from these tailings.

The application of acid leaching techniques is a complicated academic and applied problem, which implies that the following two major tasks shall be fulfilled. First, it is necessary to principally decrease the concentrations of the major complex of elements and thus produce ecologically safe solid materials suitable for further usage as starting products for manufactuting construction materials. Second, the above complex of elements shall be concentrated and subsequently subdivided into ecologically hazardous (As, Tl, and others), which require specialized dumping technique and methods, and economically valuable (W, Mo, Cu, Re, etc.) elements. The selective extraction of the latter will, perhaps, be able to compensate the operation costs, provided that the extraction and isolation of ecologically hazardous elements is a top-priority task. This problem can be solved using physical separation techniques (such as gravitational, magnetic, etc.), which were suggested over the past 25 years to produce W and Mo concentrates from the wastes, because ore minerals in the wastes occur as finely divided phases in aggregates with the aluminosilicate groundmass. In view of this, a method of acid leaching of the wastes was suggested, with the subsequent adsorption of a geochemically diverse complex of elements from the working solution, with the use of sorbents of various type for the separation and concentration of the elements.

The utilization technology of TTMC wastes was developed with regard for the following three issues: (1) Neither theoretical considerations nor experimental data are currently available on the behavior of geochemically diverse complex of elements at various acid leaching techniques of wastes. To select the optimum parameters for the leaching of the main complex of elements from the wastes, numerous experiments were conducted with the application of various acids, addition of oxidizing ligands, at various temperatures, and various time and other processing regimes. (2) No data are available on the character, adsorption capacities, and adsorption sequences of various metals and metalloids from a multielemental solution on various cation and anion exchangers. Experiments were conducted to determine the sequences and degrees of separation of geochemically different elements on various sorbents, first of all, to evaluate the succession of their application and their efficiency. (3) Wastes dumped in the tailings broadly vary in trace-element composition. The wastes of Tailing 2 (28 Mt), which were stored in it in the 1950s and 1960s, contain relatively little carbonates (6-8 relative %), whereas the wastes of Supertailing 1 (80 Mt), which were dumped later, contain much more carbonates (~15 wt %). At IGEM RAS, seventeen sets of laboratory experiments were conducted to study the leaching of the tailing wastes at various pH and Eh and at different processing regimes. The experiments were carried out under conditions favorable for the leaching of the main complex of elements and involved treatment of samples (~10 g) with 1N H<sub>2</sub>SO, or 1N HCl solutions at solid/liquid ratios of 1:5-10. Concentrations of the main complex of elements (W, Mo, Cu, As, Zn, and Pb) were determined in the original sample and in the dry solid residue after leaching. The analyses were made by XRF, and the relative yields of the elements to the solutions were calculated as the differences between their concentrations, with regard for the mass of the dry product.

The experiments were conducted at 100°C and yielded the best results when conducted with HCl and H<sub>2</sub>SO<sub>2</sub>, with the addition of H<sub>2</sub>O<sub>2</sub> as an oxidizer, at temperatures of 60-80°C for 2 h. The recovery of the metals (in relative %) was as follows: Mo 70-75, Cu 40-60, W and as 40-50, and Pb 20-60. This allowed us to identify the conditions of the sufficient levels of acid treatment. These data can be utilized to develop a low-cost technique for leaching dumped wastes with regard to (a) the production of an ecologically safe solid phase (precipitate) that can be later used in construction operations, and (b) obtaining working solution with relatively high concentrations of valuable (Mo, W, and Cu) and ecologically hazardous (Hg etc.) elements. These concentrations shall be high enough to enable adsorption concentrating of the metals and their subsequent separation. Comparable results were obtained with a sample 10 kg in mass (i.e., the mass of the wastes was 1000 times higher).

Our still-scarce experiments on the deactivation of the wastes of Supertailing dump 1 have demonstrated the efficiency of soda leaching. The developed utilization technique of TTMC wastes was patented [8].

It has been determined that contamination impacts not only soils at the farmlands and grasslands in the surroundings of the town of Tyrnyauz but also streams in the basin of the Baksan River. The contaminants contain toxic elements from industrial wastes dumped in the tailings. These elements are transferred to the waters of streams flowing across TTMC opencast mines and out of the underground mining workings. The data thus acquired can be used as a basis for engineering measures and operations aimed at diminishing the adverse load on the ecosystems of the Elbrus area and on the health of the local human population.

### **Conclusions**

# Thus, the data obtained allow us to make the following conclusions

- The dumped industrial wastes of the Tyrnyauz Tungsten-Molybdenum Complex (TTMC) are multicomponent anthropogenic deposit of metallic and nonmetallic minerals. TTMC had operated for decades before 2003. The ore was developed by opencast and underground mines and was processed using flotation and chemical technologies. The industrial wastes are dumped in two tailings and partly recultivated.
- 2. An artificial pond on the top of the dam of Supertailing 1 is intended to protect against wind erosion. This pond (lake) was named Ullu Gizhgit; it gradually self-purifies because of the inflow of fresh water portions from the Gizhgit River and the addition of rain and spring-flood (melt) waters. The pond is equipped with a tunnel system for discharging excess waters into the Baksan River.
- Based on numerous laboratory experiments, economically rational technological approaches were designed targeted at the complete utilization of the industrial wastes of TTMC, with the extraction of

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- valuable and ecologically hazardous elements from these wastes.
- 4. TTMC tailing dumps are situated in an earthquake zone, where debris and mud flows are possible. Continuous geochemical and geophysical monitoring enables precluding ecological catastrophes in this area in the Northern Caucasus attractive to tourists.

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