Study of organic matter influence on environmentally hazardous elements transition from the fine fraction of tailings

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Abstract. The interaction of tailings fine fraction (-0.071 mm) of loparite, complex and apatite-nepheline ores with solutions simulating soil waters was experimented in laboratory conditions. Applying the phytotesting method, the toxic effect of an aqueous extract of a loparite and complex ores tailings fine fraction on the growth and development of higher plants was determined. It was found that introduction of dissolved organic matter intensifies the process of rare and non-ferrous metals transition into soluble forms. At the same time, concentrations of pollutants in solutions after five hours of interaction by several times exceed the maximum permissible figures for fishery farms. The research results indicate the environmental hazard of tailings fine fraction as a result of the ingress of mineral particles into the soil and their interaction with soil waters.

1. Introduction

The Arctic zone belongs to the regions with the highest sensitivity to environmental pollution. The Murmansk Region is one of the most industrially developed and urbanized regions of the Russian Arctic. The mining industry, which includes extraction and processing of mineral raw materials, forms the basis of the economic activity of the region.

Currently, the mining industry in all Arctic regions is faced with the task of maintaining sustainable development in the context of climate change and minimizing both the volume of waste disposal and their impact on the environment [1].

The environmental hazard of mining waste depends on many factors, for example, on the material composition of waste, temperature requirements and climatic features of the region, material dispersion, etc. Environmental damage is caused not only during the active filling of waste storage facilities, but also after the completion of deposit development.

In tailing dumps, a whole complex of physical and chemical interactions of tailings matter with atmospheric and circulating waters and pollutants dispersion into environment inevitably occur. An important component of the negative impact of finely dispersed refuse ore on the air and water basins is dusting of tailing dumps [2].

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As it is known, the aeolian transfer of matter from tailing dumps is one of the main mechanisms of polluting elements exposure into the environment. When fine dust appears on the soil surface, or when the surface of tailing dumps is overgrown, it interacts with soil solutions. Soil organic substances affect minerals, contributing to the modification of their surface, and are involved in both aggregation and weathering of minerals. Humic substances, which are a multi-component system, enter into chemical reactions with metal ions, including chelation, and are able to both increase and decrease the adsorption of heavy metals, depending on the stability of the complexes formed and soil-ecological conditions [3].

The obtained results of studies on the interaction of loparite ore tailings of “Lovozersky MPP” JSC, apatite-nepheline ores of “Apatit” JSC and complex ores of “Kovdorskoy MPP” JSC with soil waters will make it possible to assess the influence of biogenic factors on the processes of minerals of tailings of concentration transformation and transition of ecologically hazardous elements into mobile forms.

2. Objects and methods of research
The objects of study were the tailings of apatite-nepheline ores (apatite-nepheline concentrating plant (ANOF-2) of “Apatit” JSC), complex ores (“Kovdorskoy MPP” JSC) and loparite ores (“Lovozersky MPP” Ltd.) (figure 1).

![Figure 1. Schematic map of the study area.](image)

Lovozersky Mining and Processing Plant Ltd. is located in the center of the Kola Peninsula and is the backbone enterprise for the village of Revda. The enterprise develops a deposit of niobium, tantalum and rare earth elements of the cerium group, with the main marketable product loparite concentrate. The commercial product obtained at the enterprise (loparite concentrate) is a complex raw material for further production: tantalum, niobium, cerium group of rare earths and titanium [4].

“Kovdorskoy Mining and Processing Plant” JSC is one of the leading enterprises in the North-West part of Russia, it carries out complex processing of mineral raw materials applying low-waste technologies and produces three commercial concentrates: iron ore, apatite and gadolinite.

The Kirov branch of “Apatit” JSC is European largest producer of phosphate raw materials for the production of mineral fertilizers, the only producer of nepheline concentrate in Russia. The enterprise develops Khibin deposits of apatite-nepheline ores, produces and concentrates them. Apatite concentrate is the main product of the enterprise.

The mineral composition of the studied tailings is shown in table 1.
The results of the tailings sieve analysis show a sufficiently high content of the fine fraction, which contributes to tailings dusting (table 1).

In the process of wind erosion, dust particles of tailings interact with atmospheric precipitation and with soil organic solutions. This occurs due to geo-migration processes during penetration into deeper soil horizons and in the process of dumps and tailings overgrowing (primary successions).

For the integral assessment of the studied tailings toxicity, the phyto-testing method was applied. The "Phyto-test" methodology is taken as a basis, which allows to experimentally determine the hazard class of production waste. We studied the effect of an aqueous extract of an average sample and a fine fraction of concentrated tailings on the growth and development of higher plants. As a test culture, we used oat seeds of Avéna sativa. Sheets of filter paper moistened with aqueous extracts of the studied tailings were placed in Petri dishes; distilled water acted as a control. The exposure time was 7 days. The toxic effect of waste is considered proven if the test function - the length of the roots of seedlings in relation to the control - inhibition of root growth exceeds 20% [8].

To determine the effect of organic matter on the rate of elements transition into solution, a series of laboratory experiments were carried out. The source of water-soluble organic matter was milled high-moor peat (GOST R 52067-2003), from which a water extract was prepared at S: L ratio of 1: 1.5 and 1: 3 for 24 hours; the resulting solution was filtered through a double paper filter "blue ribbon". The organic carbon content in the extracts was about 100 mg / l and 50 mg / l, respectively. Weighed portions of the investigated waste (fr. -0.071 mm) were introduced into the resulting solutions in the ratio S: L 1:10. To assess the migration of elements in the absence of organic matter, a similar series of experiments with distilled water was carried out. The interaction time was from one to five hours with continuous stirring. The resulting solutions were filtered through a membrane filter ("Vladipor" type MFAS-OS-2) and sent for quantitative chemical analysis.

### Table 1. Mineral composition of the studied tailings and the average content of -0.1 mm fraction.

| Mineral Composition                        | Lovozersky MPP [5] | Kovdorsky MPP [6] | ANOF-2 [7] |
|-------------------------------------------|---------------------|-------------------|------------|
| Nephelin (Na,K)AlSiO₄                    | 67.01               | -                 | 61.42      |
| Feldspars (Na,K)AlSi₃O₈                  | 18.49               | -                 | 7.41       |
| Aegirite (NaFe³⁺)(Si₃O₇)                  | 11.91               | -                 | 12.94      |
| Eudialyte                                 | -                   | -                 | -          |
| Na₄(CaCeFeMn)₂ZrSi₆O₁₇(OHCl)₂               | 0.63                | -                 | -          |
| Apatite Ca₁₀(PO₄)₆(OH,F,Cl)₂               | 0.36                | 12                | 5.43       |
| Loparite (Na₄Ce₃Ca₃Sr₃Th(Ti,Nb,Fe)O₁₃)    | 0.27                | -                 | -          |
| Boltonite Mg₂[SiO₄]                       | -                   | 30                | -          |
| Carbonates                                | -                   | 25                | -          |
| Phlogopite KMg₃[Si₃AlO₁₀]·[F,OH]           | -                   | 14                | -          |
| Black iron ore FeO₆Fe₂O₃                  | -                   | 12                | -          |
| Sphen CaTi[SiO₃]O                         | -                   | -                 | 3.19       |
| Fr. -0.1 mm, %                           | 15.3                | 21.2              | 50.2       |

*- analyzed for -0.25 mm fractions

### 3. Results and discussion

The results of phyto-testing of the average sample water extracts and the tailings fine fraction are presented in table 2. Phyto-testing of the averaged tailings sample did not reveal inhibition effect, which experimentally confirms the V hazard class of these wastes. In case of finely dispersed waste, the results were somewhat different. As you can see, the native extract of the tailings fine fractions of loparite (Lovozersky MPP Ltd.) and complex ores (Kovdorsky MPP JSC) has a toxic effect (inhibitory effect). In terms of the integral level of negative impact on the growth and development of higher plants, in general, the average sample and the fine fraction of considered tails show the same tendency and can be arranged in the following sequence: apatite-nepheline (ANOF-2) <complex ("Kovdorsky MPP JSC ") <loparite (Lovozersky MPP Ltd.).
Table 2. Characteristics of the average sample water extracts and fine fraction of concentrated tailings impact on oat seeds.

| Water extract          | Average oats root length (Lav), % to contr. | Phyto effect, % | Test reaction |
|------------------------|--------------------------------------------|-----------------|--------------|
| Control                | 100                                        | 0               | Standard     |
| LMPP, average sample   | 84.62                                      | 15.38           | Standard     |
| LMPP, fine fraction    | 72.37                                      | 27.63           | Inhibitory effect |
| KMPP, average sample   | 88.21                                      | 11.79           | Standard     |
| KMPP, fine fraction    | 79.71                                      | 20.29           | Inhibitory effect |
| ANOF-2, average sample | 96.12                                      | 3.88            | Standard     |
| ANOF-2, fine fraction  | 93.74                                      | 6.26            | Standard     |

Based on the data of quantitative chemical analysis, diagrams were constructed illustrating the effect of the given amount of the introduced dissolved organic matter (0, 50, and 100 mg Corg / L) on the content of chemical elements in the resulting solutions.

Figure 2 shows the change in heavy metals concentration in test solutions after five hours of interaction with tailings. For complex ores (“Kovdorsky MPP” JSC) there is a significant excess of the maximum permissible for fishery farms concentrations for a number of elements: copper - 131 times, nickel - 4.7 times, zinc - 6.7 times and cobalt - 1.5 times. A similar situation is observed for two other tails: loparite - the excess in zinc - 3.3 times, copper - 29 times, apatite-nepheline - in copper - 46 times, nickel - 1.5 times, zinc - 2.5 times.

Heavy metals are transition metals and are characterized by the formation of complex compounds with a coordination bond HA (FA) - metal. Presence of organic complexes with humic substances, along with the level of acidity and ionic strength of the solution, is one of the most significant factors affecting the migration ability and bioavailability of heavy metals in soils and aqueous solutions. The effect of humic substances is determined by the ratio of competing processes in the solution - an
increase in the migration ability during the formation of highly soluble metal fulvates, and the sorption concentration of elements on humic acids with the formation of insoluble complexes [3].

The effect of water-soluble organic matter on the transition of rare-earth (REM) metals from the tailings of concentration of loparite and apatite-nepheline ores into the solution is shown in Figure 3. The introduction of organic matter leads to a sharp acceleration of the transition process of REM into solution, presumably due to the fulvic acids. The total increase in the mass of dissolved REM is proportional to the increase in the introduced organic matter, while with an increase in the proportion of organic matter, the peak concentration is shifted from 3 hours of interaction to 5 hours. The process is more intense for lanthanum, cerium, neodymium for Lovozersky MPP. Then, most of the elements under consideration are characterized by a decrease in concentrations due to the formation of complex compounds with humic substances, which correlates with the research data [9, 10].

![Figure 3](image)

**Figure 3.** Change in the concentrations of rare earth elements in the test solutions after five hours of interaction with the tailings of concentration of loparite (1) and apatite-nepheline (2) ores, μg / L.

Substances passing into the aqueous extract represent the most mobile part of organic matter. Organic acids cause decomposition of primary minerals, especially during the weathering of rocks, rich in mineralogical composition and participate in the migration of mineral destruction products along the soil profile [11].

### 4. Conclusions

In the present work, the laboratory study of finely dispersed concentrated tailings interaction with model solutions that simulate the composition of soil waters was carried out.

Applying the phyto-testing it was found that an aqueous extract of the tailings fine fraction of complex and loparite ores has a toxic effect on the growth and development of higher plants. At the same time, this effect was not revealed for the average sample. According to the integral level of negative impact, the considered wastes can be arranged in the following sequence: apatite-nepheline (ANOF-2) <complex (Kovdorsky MPP JSC) <loparite (Lovozersky MPP Ltd.).

Thus, the results of experiments carried out under static conditions indicate the potential environmental hazard of tailings due to the ingress of mineral particles into the soil, their interaction with soil waters and transition of environmentally hazardous elements into mobile forms. It should be noted that the concentrations of these elements in solutions after five hours of interaction are many times higher than the maximum permissible for fishery reservoirs: for all objects, an excess of LOC<sub>fishery</sub> for copper and zinc was revealed, from 29 to 131 and from 2.5 to 6.7 times, respectively. The excess for nickel was found in two objects, 1.5 times for ANOF-2 and 4.7 times for Kovdorsky MPP.

It was found that the nature of ions behavior in the solution with organic matter added, depends on several simultaneous processes: extraction from minerals into the solution under the influence of a
spectrum of organic acids; fulvic acids, in particular, with the formation of soluble fulvates; and binding of ions with humic acids followed by respective formation of insoluble humates. Rare earth elements are characterized by a slowdown while reaching the peak concentration commensurate with the amount of introduced organic matter, while the value of the peak concentration increases significantly. A decrease in concentration due to the formation of insoluble compounds of metal ions with residues of organic acids is typical for iron, aluminum, strontium, manganese, which are part of the tailings minerals. Thus, depending on the distribution of the existing forms of elements, the introduced organic matter can both reduce the environmental hazard of the tailings, and vice versa, increase the concentration of the pollutant in the liquid phase, increasing the migration ability.

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