

# Mobilization Of Environmentally Hazardous Elements Dressing Tailings Of Loparite Ores Under Atmospheric Precipitation

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## Abstract

The paper investigates the mobilization of environmentally hazardous elements from loparite ore concentration tailings when exposed to atmospheric precipitation. A sulfuric acid solution simulating acid rain and distilled water were used as model solutions. When exposed to a weak sulfuric acid solution, a manifold increase in the decomposition rate of the tailings was observed. The concentrations of non-ferrous metals in the resulting solutions, when the test material was moistened with an acid solution, many times exceeded the maximum permissible concentrations for fishery water bodies. An intense transfer to the solution of rare earth elements was observed.

**Keywords:** Loparite Ores, Acid Rain, Environmental Hazard, Pollutants, Rare Earths

## Introduction

The operation of mineral deposits involves the formation of a large amount of waste – overburden and tunneling rock, tailings, etc. In Russia’s Murmansk Region, where a number of major mining projects are located, over 200 million tons of mining waste is generated and stockpiled annually (2019 Report). Russia’s only loparite mine is located on the Kola Peninsula in Murmansk Region. Over many years of operation, its tailing storage facilities (TSF) have accumulated a huge amount of waste that remains when loparite is recovered — approx. 6.5 million tons held in the decommissioned TSF section and over 11 million tons in the operating TSF (Goryachev 2020, Ratkin 2008). The annual increment in the tailings quantity is 440 000 t tons.

Outdoor storage of finely ground rare-metal ore concentration tailings involves the risk of interaction with atmospheric oxygen, precipitation, and soil water. Air pollution with acid anhydrides (SO<sub>2</sub>, SO<sub>3</sub>, NO, NO<sub>2</sub>) due to anthropogenic emissions results in acid precipitation (Mesyats 2013).

Further, the effects of acid rain are felt both in the areas adjacent to non-ferrous smelters and at a considerable distance from those. Major sources of atmospheric pollution with sulfur dioxide, nickel, and copper include the Severonickel and Pechenganickel smelters (Kryuchkov 1989). In Ratkin (2008) it was shown that the average long-term local sulfate pollution zone of both snow cover and liquid precipitation is located at a distance of up to 70 km from the center point of the industrial site in Monchegorsk.

In a number of papers examining the interaction of mining waste with acid rain, dissolved organic matter, etc., it was shown that the introduction of an aggressive agent leads to an intensification of the conversion of environmentally hazardous elements into mobile forms (Lugovskaya 2003, Smolyakov 1996, Dehaye 1988, Nazreen 2017). Studies also exist on the interaction of a number of minerals and rocks with dilute solutions of sulfuric acid and acidified river water (Sokolova 2013, Savenko 2018). Modeling of chemical weathering and hypergene transformation processes of apatite-nepheline and

copper-nickel ores is thoroughly discussed in (Masloboev 2014, Maksimova 2013).

The study goal was to examine environmentally hazardous elements migration from the concentration tailings of loparite ores when exposed to acid atmospheric precipitation under model conditions.

## Methods

Fresh concentration tailings from a loparite ore mine were studied. Since the differentiation of the tailings material in terms of grain size and material composition was noted as early as at the storage stage (Goryachev 2020), tailings collected in February 2020 from a sump at the concentrator plant, before these were sent to the TSF, were studied.

The concentration tailings are fine-grained sand with the mineral particles sized 0.01–0.5 mm.

Chemical composition of the fresh concentration tailings of loparite ore, wt. %: SiO<sub>2</sub> – 48.53, TiO<sub>2</sub> – 1.35, Al<sub>2</sub>O<sub>3</sub> – 22.40, Fe<sub>2</sub>O<sub>3</sub> – 5.12, FeO – 0.66, MnO – 0.25, CaO – 1.42, MgO – 0.38, K<sub>2</sub>O – 4.24, Na<sub>2</sub>O – 13.43, P<sub>2</sub>O<sub>5</sub> – 0.68, SrO – 0.35, F – 0.08, SO<sub>3</sub> – 0.11.

Mineral composition analysis was conducted by PJSC Kola Geological Information Analytical Center. The mineral composition of the fresh loparite ore concentration tailings is dominated by nepheline (62.22%), aegirine (18.71%), feldspar (16.51%). Impurities of apatite, sodalite, loparite were found.

Samples of the loparite ore concentration tailings underwent open acid unlocking and subsequent analysis for trace element content by inductively coupled plasma mass spectrometry at the Shared Use Center, Institute of North Industrial Ecology Pro-

blems – Subdivision of the Federal Research Centre "Kola Research Center of the Russian Academy of Sciences" (INEP KSC RAS) (using ELAN 9000 DRC-e mass spectrometer by Perkin Elmer, USA). Chemical analysis results are shown in Table 1.

The laboratory study of the chemical weathering of minerals when exposed to atmospheric precipitation was carried out as described in (Maksimova 2013). Considering the time span of the natural hypergene processes in minerals, the experiment was carried out in accelerated conditions. Tailings samples weighing 70 g were placed in temperature-controlled cells at 50 °C; the samples were periodically moistened with 0.002 N sulfuric acid solution or distilled water (control samples) at 25 ml/day for 20, 40, and 60 days. After 60 days, the samples treated with distilled water at a S:L ratio of 1:10, the resulting solutions were filtered through an MFAS OS-2 membrane filter (pore size 0.47 µm). Filtrate pH was measured and the filtrates were sent for quantitative chemical analysis (ICP-MS, ion exchange chromatography, direct potentiometry, atomic adsorption spectrometry).

## Results and discussion

The initial pH values and element concentrations were measured in a solution obtained after treating the loparite ore concentration tailings with distilled water at the same S:L ratio and exposure time (t = 1 day).

When interacting with water, the pH value slightly increases from 8.2 to 8.8 in the time interval from 20 to 40 days, and then returns to close to the initial value. After the interaction of the tailings with a 0.002 N

*Table 1 Element composition of the fresh loparite ore concentration tailings.*

Element	Contain, mg/kg	Element	Contain, mg/kg	Element	Contain, mg/kg
Ni	7.51	Ce	1031	U	17.4
Cu	6.44	Pr	38.8	Ta	123
Cr	2.3	Nd	121	Nb	1459
Sr	1289	Sm	14.7	Mn	1580
Zn	240	Ba	179	Al	75800
Pb	16	V	34.9	Fe	26300
La	202	Th	26.3	Zr	2630

**Table 2** Concentrations of aluminum, silicon, sodium, and potassium in the resulting solutions when interacting with water and sulfuric acid.

Contain, µg/L	Distilled water				0.002 N H <sub>2</sub> SO <sub>4</sub>			
	1 day	20 days	40 days	60 days	1 days	20 days	40 days	60 days
Al	0.95	0.54	0.45	0.50	0.95	4.00	8.60	14.30
Si	5.3	5.12	6.29	5.22	5.3	4.11	7.63	10.04
K	1.57	1.63	1.93	2.10	1.57	24	56.4	103
Na	48.4	54.0	47.40	83.20	48.4	336	617	900



**Figure 1** Appearance of the loparite ore concentration tailings at the end of the experiment. From left to right: moisturizing agent – distilled water, sulfuric acid solution.

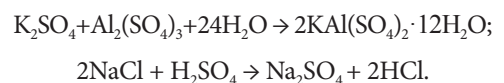
solution of sulfuric acid, the pH of the leach solution decreases with increasing time of the experiment and reaches 4.68 by the end of the experiment. The largest decrease in the pH value — from 8.2 to 5.1 — was observed in the first twenty days.

The dissolution of the mineral matrix under the action of leaching agents was assessed by the results of filtrate analysis for potassium, sodium, aluminum, and silicon, which are some of the elements found in the main minerals of the tailings material (Table 2). Compared to the control series of experiments, where the leaching agent was distilled water, after the interaction of the tailings particles with sulfuric acid, the concentration of basic cations in the resulting solutions increased by a factor of 2 to 10. At the same time, uneven transfer of elements into solution was observed. In particular, the release of sodium

ions: its concentration exceeded that of potassium by a factor of almost 20 at the end of the experiment, which indicates incongruent dissolution of nepheline.

Figure 1 shows the tailings at the end of the experiment (after 60 days). X-ray phase analysis identified the composition of the salt bloom formed on the surface of the tailings material – a mixture of thenardite and 12-hydrate aluminum-potassium sulfate.

Possible reaction equations for the formation of the newly identified phases are as follows:



The change in the concentrations of Zn, Sr, and Mn is shown in Figure 2. As one

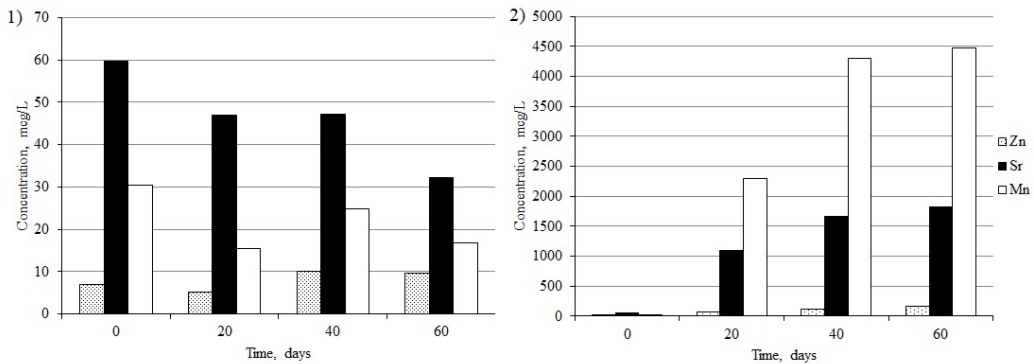


Figure 2 Concentrations of non-ferrous metals in the resulting solutions when interacting with water (1) and sulfuric acid (2).

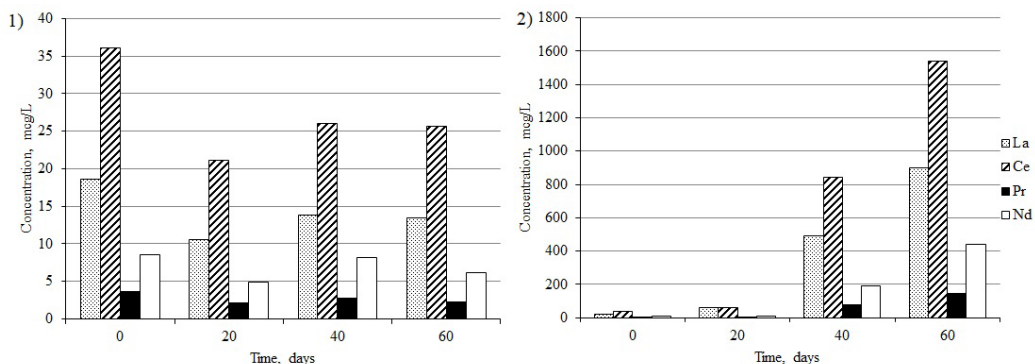


Figure 3 Concentrations of REEs in the resulting solutions when interacting with water (1) and sulfuric acid (2).

can see, after the interaction of the tailings material with distilled water, a slight excess of the MPC is observed already on the first day for Mn (10 µg/L) (Fig. 2.1) (Order 2016).

After the interaction of the tailings particles with a sulfuric acid solution, the transfer rate of Zn, Sr, and Mn into the solution increased sharply (Fig. 2.2). At the end of the experiment, the MPC was exceeded as follows: by a factor of 5, 17, and 448 for Sr, Zn, and Mn, respectively.

The change in the concentrations of rare earth elements (REEs) contained in the loparite ore tailings, in the leaching solutions after the interaction of the tailings with water and dilute sulfuric acid depending on the duration of the experiment is shown in Figure 3. Note that neither MPCs nor maximum and approximate permissible concentrations of REEs in soils are established.

Once in the soil, REEs, due to the different stability of the bond with humic substances, can both be adsorbed and desorbed when exposed to the dissolved organic matter (Xiangke 2000, Savenko 2019). In general, the behavior of REEs in soils is similar to that of non-ferrous metals; however, their phytotoxicity has not yet been sufficiently studied (Thomas 2013). It is known that the concentration of light REEs in the roots of vascular plants is usually higher than in other plant organs, including shoots (Carpenter 2015, Grosjean 2019, Mikołajczak 2017, Nazreen 2017, Thomas 2013). However, the accumulation of these in leaves and stems, being the main organs of photosynthesis, can have major consequences for plant development (Thomas 2013).

The transition of REEs into solution is also intensified when dilute sulfuric acid is

added as a leaching agent instead of distilled water. Compared to the control series of experiments, the concentration of La and Ce in the solution increased by a factor of 45 and 60, respectively.

It can be concluded that the interaction of the tailings material with sulfuric acid solution intensifies the process of metal transition, in particular, Zn, Mn, Sr, La, Ce, Pr, Nd, into a soluble, i.e. more bioavailable, form.

## Conclusions

Mobilization of environmentally hazardous elements from fresh loparite ore concentration tailings when exposed to atmospheric precipitation was studied in laboratory conditions.

A significant acceleration of chemical weathering is noted under model conditions that simulate the effects of acid rain.

The concentrations of Zn, Mn, Sr in the resulting solutions at the end of the experiment, when the tailings material was moistened with a dilute solution of sulfuric acid, were many times above the applicable MPCs. Intense transition of light REEs, in particular, La, Ce, Pr, Nd, into a dissolved, more bioavailable form was observed.

The probability and intensity of acid precipitation should be taken into account in the geoenvironmental assessment of the risk of the negative environmental impact of loparite ore concentration tailings.

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