The University of Tehran Press

Pollution

Print ISSN: 2383-451X
Online ISSN: 2383-4501

https://jpoll.ut.ac.ir/

Elements Migration from the Flotation Tailings of Copper Smelter Slags after Leaching to the Soil and Plant

Ekaterina Zolotova✉ | **Alla Kotelnikova**

A. N. Zavaritsky Institute of Geology and Geochemistry, Ural Branch of Russian Academy of Sciences, 620110, 15 Akad. Vonsovsky street, Yekaterinburg, Russia

Article Info

Article type:
Research Article

Article history:
Received: 31 May 2024
Revised: 18 August 2024
Accepted: 09 January 2025

Keywords:
Biogeochemistry
Environmental Safety
Metallic Pollution
Metallurgy Wastes
Russia

ABSTRACT

A field experiment was conducted to study migration of the toxic elements from the flotation tailings of copper smelter slags after sulphuric acid leaching into high-moor peat and lawn grasses. Leaching wastes were studied by X-ray fluorescence, spectral analysis, X-ray powder diffraction and scanning electron microscopy. It has been established that they contain diopside, gypsum, spinel group minerals, jarosite, barite, sphalerite and amorphous silica. 5% of wastes was introduced into lime-neutralized peat. A mixture of lawn grasses was grown on artificial soils in test plots (1 m2). Average samples of soils, shoots and roots were analyzed by inductively coupled plasma mass spectrometry. It was found that, the concentration of most elements is higher in the soil with leaching wastes than in the soil with the flotation tailings, the exceptions are Mn, Co, Ni, Cu, Zn, Cd. The greatest differences in concentration coefficients were noted for Sn (38 times) and S (5.1 times). V, Cr, Co, Ni, Se, Mn, Cu accumulated more strongly in roots on soil with leaching waste compared to both peat and soil with tailings. However, S, Mo, Cd, Sn, Sb, Ba, and Pb accumulate significantly less. The shoots grown on peat with leaching wastes have lower accumulation coefficients for most of the elements compared to both the peat and soil with flotation tailings. The research contributes to the study of the impact of copper smelter slag processing wastes on the environment and is of interest for the development of environmentally friendly and effective methods for their disposal.

Cite this article: Zolotova, E., & Kotelnikova, A. (2025). Elements Migration from the Flotation Tailings of Copper Smelter Slags after Leaching to the Soil and Plant. *Pollution*, 11(1), 161-174.
https://doi.org/10.22059/poll.2024.377322.2400

DOI: https://doi.org/10.22059/poll.2024.377322.2400

INTRODUCTION

Waste disposal is one of the most pressing problems of metallurgical industries around the world (Kasikov et al., 2023; Makhathini et al. 2023; Li et al., 2024). Non-ferrous metallurgical slags pose a danger to the environment due to their high content of heavy metals and metalloids (Men et al., 2023; Nadłonek et al., 2024). On the other hand, they can act as an additional source of mineral raw materials for production (Dzinomwa et al., 2023; Lim et al., 2024).

The recycling of metallurgical slag is a complex technological process, which saves natural resources and has a lower cost price than extracting valuable metals from ore (Tian et al., 2021; Phiri et al., 2022). Slag processing consists in crushing and subsequent extraction of metals, which occurs using pyrometallurgical, hydrometallurgical (flotation, chemical leaching or bioleaching) and combined pyrometallurgical approaches (Zhou et al., 2022; Kasikov et al., 2023).

Copper smelters mainly use flotation to process slag (Sibanda et al., 2022; Štirbanović et al.,

*Corresponding Author Email: *zolotova@igg.uran.ru*

2022; Zhai et al., 2023). Enrichment tailings accumulate as waste. They are finely dispersed, mechanically activated material, which is mostly transferred for burial. However, a sufficient number of valuable elements continues to remain in the flotation tailings, which allows them to be considered as a potential technogenic raw material (Gümüşsoy et al., 2023).

Currently, methods and technological solutions are being developed for the most efficient extraction of copper, zinc, cobalt, and iron from copper smelter slag flotation tailings. Hydrometallurgical methods, including sulfuric acid leaching, are of greatest interest (Muravyov et al., 2012; Urosevic et al., 2015; Seyrankaya, 2022). A new type of waste accumulates as a result of sulphuric acid processing flotation tailings of copper smelting slag requires comprehensive studies to ensure the goals of its rational use and safe disposal.

It is quite common to find studies on the selection of optimal conditions for sulphuric acid leaching of copper smelting slags (Shi et al., 2020; Mussapyrova et al., 2021) and less often on the products of their flotation processing (Muravyov et al., 2012; Urosevic et al., 2015; Seyrankaya, 2022). Of particular interest are studies using microorganisms (Fomchenko et al., 2014; Kaksonen et al., 2017). However, there are very few studies showing the material composition of the resulting leach wastes from copper smelter slags (Khalid et al., 2019), and there is none for flotation tailings.

Russia has accumulated a fairly large amount of waste slag from non-ferrous metallurgy (Zolotova, 2021; Kasikov et al., 2023). In 1995, the inventory of man-made objects recorded more than 700 thousand tons of waste slag from non-ferrous metallurgy only in the Sverdlovsk region. The shortage of copper ore raw materials stimulated the Sredneuralsky Copper Smelter and the Kirovograd Copper Smelter to begin processing these man-made wastes as a source of copper-zinc concentrate.

The flotation tailings of copper smelter slag from the Sredneuralsky smelter contain approximately 3.4% zinc, 0.4% copper, 0.4% lead, 35% iron. Analysis of the phase and mineral composition of wastes (Kotelnikova & Ryabinin, 2018) led to the conclusion that one of the rational methods of extracting copper and zinc is agitation leaching with aqueous solutions of mineral acids. The Sredneuralsky smelter produces sulphuric acid, so it is preferable to use sulphuric acid leaching. The dependence of zinc and copper extraction on the concentration of sulphuric acid, temperature and duration of the process has been established (Reutov & Khalezov, 2015). Sulphuric acid leaching of flotation tailings is cost-effective, despite the relatively low content of zinc and copper in the waste. Because this process not only extracts additional amounts of copper and zinc, but also makes it possible to obtain other useful products, for example, for the construction industry, as well as solving a number of environmental problems. In particular, lead and barium are converted to an inert form, and the storage areas of flotation tailings are reduced.

The purpose of our research was to study the migration of toxic elements from sulphuric acid leaching wastes from the flotation tailings of the Sredneuralsky copper smelter into the soil and plants. The following tasks were set: to study the material composition of wastes; to analyze the content of toxic elements in artificial soil based on high-moor peat and leaching wastes, as well as in lawn grasses grown on this artificial soil; conduct an environmental assessment of the artificial soils and plants. Researches of the interaction of this type of wastes with environmental objects have not been studied before.

MATERIALS & METHODS

The chemical and mineralogical composition of flotation tailings of dump cast copper smelter slags of the Sredneuralsky Smelter (Revda city, Sverdlovsk region, Russia) was studied previously (Kotelnikova & Ryabinin, 2018). The flotation tailings were leached using an aqueous solution of sulphuric acid with a concentration of 300 g/dm^3, a solution to waste ratio of 1:4, a temperature of 90 °C, and a process duration of at least 15 hours. With these parameters, it was possible to extract 73% copper and 82% zinc from the tailings (Reutov & Khalezov, 2015). The experiment was carried out at the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences.

Leaching waste was analyzed at the "Geoanalitik" Collective Use Center of the Zavaritsky Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences. The material composition was determined using an X-ray fluorescence energy dispersion spectrometer EDX-8000 and an X-ray spectral microanalyzer CPM-35. The phase composition of the sample was determined by X-ray powder diffraction on DRON-3 diffractometer. The composition of the waste was also studied using a TESCAN MIRA LMS (S6123) scanning electron microscope equipped with an INCA Energy 450 X-MaxEDS spectrometer and AZtecOne software with an acceleration voltage of 20 kV and an exposure time of 5 ms per. The samples were studied in bulk preparations, carbon deposition.

The field experiment was carried out on the territory of the Institute of Geology and Geochemistry Ural Branch of the Russian Academy of Sciences (south-western part of the Yekaterinburg city, Sverdlovsk region, Middle Urals, Russia) (Fig. 1). The climate is classified as according to the Köppen-Geiger climate classification (Beck et al., 2018). The average long-term temperature in the coldest month (January) is -18°C, in the warmest month (July) is +24°C, the average annual precipitation is 491 millimetres, and the height above sea level is 250 meters. The prevailing winds are westerly and south-westerly. The growing season averages 110 days.

In this experiment, high-moor peat (Histosols Fibric (Basayigit et al. 2017)) was used as a soil matrix with known characteristics, high content of humic and fulvic acids and relatively

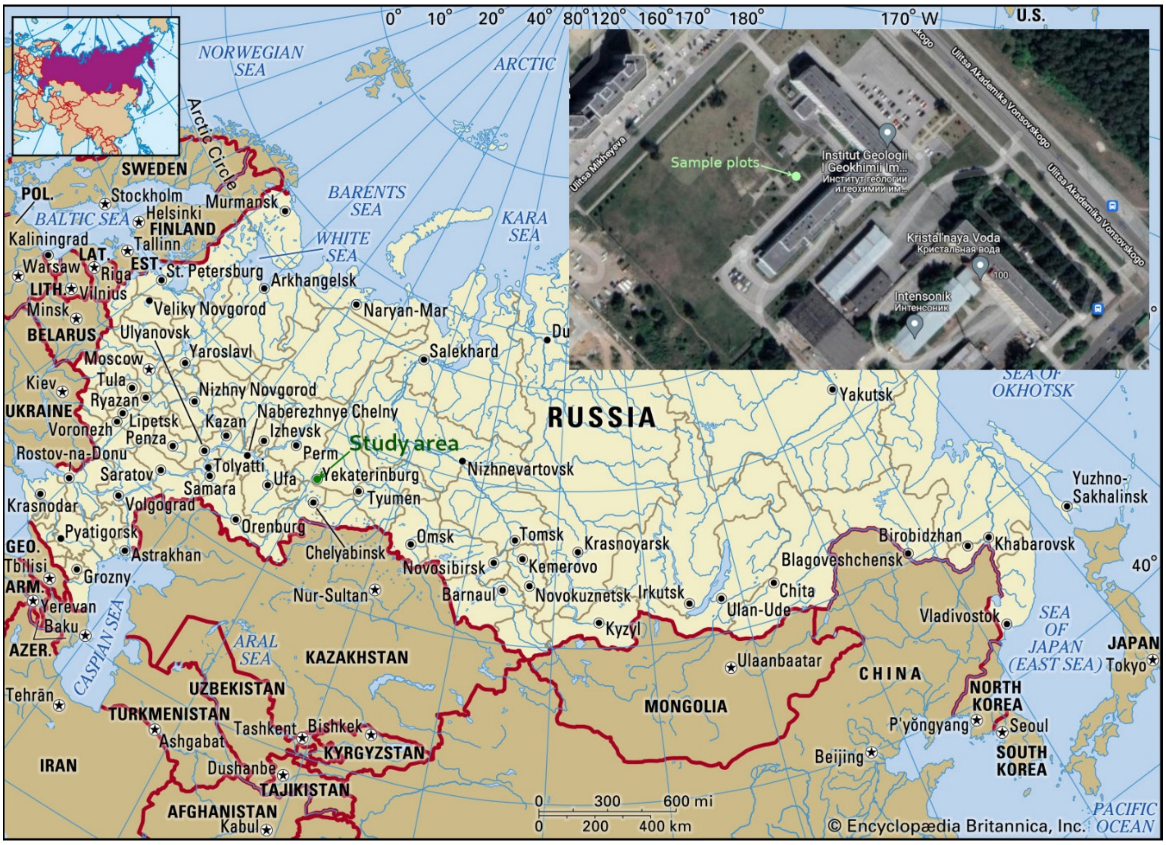

Fig. 1. Study area on the map of Russia and test plots on the territory of the Institute of Geology and Geochemistry Ural Branch of RAS (south-western part of the Yekaterinburg city, Sverdlovsk region, Middle Urals)

sterile. Artificial soils were prepared from peat, previously neutralized with lime to pH=6.0, and 5% waste (9.5 kg of peat per 0.5 kg of waste). The artificial soils were mixed and placed on 1 m^2 test plots. Granite screenings were used as a substrate. 3 test plots were laid: original peat, peat with 5% flotation tailings and peat with 5% leaching wastes. The thickness of the soil profile was 15-18 cm, volume of the soil – approximately 0.06 m^3. The active acidity pH of soils was determined in the soil extract with distilled water, and the exchangeable acidity pH_{KCL} in the KCl extract (1 M) was determined by the potentiometric method (Sokolova et al., 2012).

Lawn grasses were sown in sample plots in early May. The following mixture of lawn grasses was used in the experiment: *Festuca pratensis* Huds. – 30%, *Phleum pratense* L. – 30%, *Lolium perenne* L. – 30%, *Loliym multiflorum* Lam. – 10%.

We sampled the soils, shoots and roots of lawn grasses after the growing season (at the end of August). The sampling was carried out at five points, evenly distributed over the area of each test plot (GOST 17.4.4.02-84). The samples were dried at room temperature to constant weight and crushed. An average soil sample, plant stems and roots were collected for chemical analysis. Plants were not divided by species. Roots were extracted from a peat at the stage of sifting with a 1 mm sieve, washed in distilled water, dried, crushed and submitted for analysis. Sample preparation for microelement analysis was carried out by acid digestion: the weighed portions (50 mg) were dissolved in 3 ml of 14M HNO_3 with the addition of 1 ml of 42M H_2O_2 at 150°C in an open vessel.

The chemical composition of the samples according to the experiment was determined at the "Geoanalitik" Collective Use Center of the Zavaritsky Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences using inductively coupled plasma mass spectrometry (ICP-MS) on a NexION-300S quadrupole mass spectrometer. Several state standard samples for soils (GSO, Russia) were used to verify the results of the analysis: State register No. - 2499-83, 2509-83. The accuracy of the element determination was additionally controlled in plants using the international certified sample of beech leaves BCR-100. The obtained element concentrations agree with available reference values to a tolerance of about 15%.

The concentration coefficient (Kc) was used in our study. This is the ratio of the content of the i-th element in any two compared objects (Avessalomova, 1987). The following formula was used to evaluate the artificial soil:

$$K_c = \frac{C_i}{C_0}$$

where C_i – concentration of element in the soil with wastes, C_0 – concentration of element in the original peat.

The assessment of the efficiency of the absorption of trace elements by plants from the abiotic environment and to determine the direction of the biological cycle was carried out using the accumulation coefficient (Kn). The accumulation coefficient is the ratio of the concentration of an element in an environment or living organism to the concentration of the same substance in a neighboring environment or in food in an equilibrium state. This indicator is quite often used in environmental studies to assess pollution (Li et al., 2007; Lovynska et al., 2024). We used the following formula to calculate:

$$K_n = \frac{C_1}{C_2}$$

where C_1 – concentration of element in the aboveground or underground parts of plants, C_2 – concentration of element in the root layer of the soil.

The ecological assessment of soils was carried out in accordance with the regulated concentrations of toxic elements in Russia (SanPiN 1.2.3685-21), as well as in accordance with the Soil Quality Guidelines (SQG) developed in Canada (CCME), whose natural conditions are close to our experimental test plots. The content of toxic elements in lawn grasses was compared with recommendations on maximum permissible levels of toxic elements (MRL) have been developed for agricultural plants (VetPin 13.7.1-00).

RESULTS & DISCUSSION

Sulphuric acid leaching wastes from flotation tailings of the Sredneuralsky copper smelter mainly consist of SiO_2 – 32.5% and Fe_2O_3 – 18% (Fig. 2). They contain less zinc, copper, manganese, arsenic and lead compared to the original flotation tailings. The sulphur content increased significantly (13.9%), which is mainly in the form of sulfates.

The phase composition of copper smelter slag flotation tailings changes significantly after sulfuric acid leaching (Table 1). X-ray phase analysis made it possible to establish that the wastes contain diopside, gypsum, spinel group minerals, jarosite, barite, sphalerite and amorphous silica. Siderophile and chalcophile elements, present in a glass and fayalite of flotation tailings as impurities, are concentrated together with iron and sulphur in newly formed sulphates of leaching wastes.

The leaching wastes were analyzed by scanning electron microscopy and found an association of silica, crystalline sulphur, iron compounds, lead, zinc, copper and their sulphides. Characteristic structures of leaching of the glass phase, filled with silica, with cavities apparently

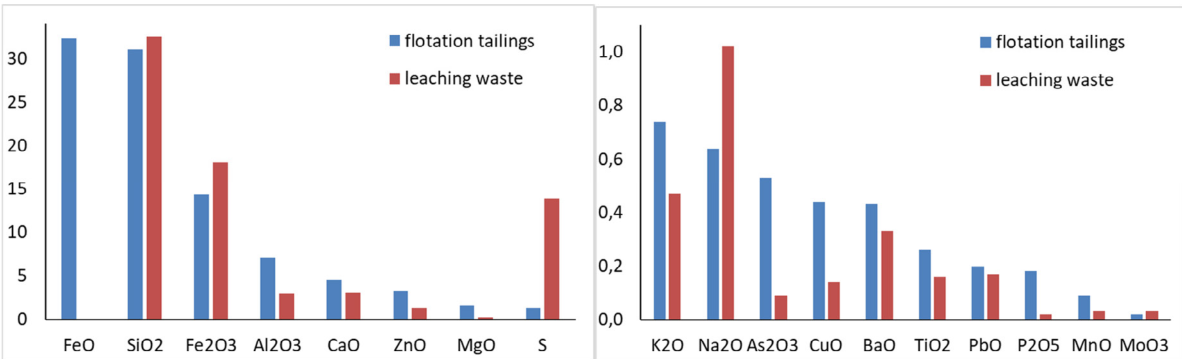

Fig. 2. Basic chemical composition of sulphuric acid leaching wastes from flotation tailings of the Sredneuralsky copper smelter, wt. %

Table 1. The phase composition of leaching wastes of copper smelter slag flotation tailings, wt. %

Copper smelter slag flotation tailings		Sulphuric acid leaching wastes	
Mineral	wt. %	Mineral	wt. %
Fayalite Fe_2SiO_4	45.0	Diopside $CaZn(Si_2O_6)$	32.0
Fayalite glass	30.0	Gypsum $CaSO_4 \cdot 2H_2O$	25.0
Willemite Zn_2SiO_4	8.0	Minerals of the spinel group	17.0
Diopside $CaZn(Si_2O_6)$	8.0	Jarosite $KFe_3(SO_4)_2(OH)_6$	12.0
Magnetite Fe_3O_4	3.5	Barite $BaSO_4$	8
Pyrite FeS_2	1.0	Sphalerite ZnS	3.0
Pyrrhotite Fe_nS_{n+1}	1.0	SiO_2 (amorphous)	3.0
Quartz SiO_2	1.0		
Bornite Cu_5FeS_4	0.5		
Covelline CuS	0.5		
Cuprite CuO	0.5		

remaining after leaching of magnetite and sulfide grains and filled with iron sulphate and oxide, as well as fragments that retain the original spinifex structure were identified.

The presence of mineral phases of spinel, gypsum and barite was confirmed. The detected barite can be either original or newly formed. Gypsum is a product of calcium-containing silicate leaching.

The use of mineral wastes from non-ferrous metallurgy as a microelement additive in the creation of artificial soils is possible provided that they are environmentally safe and also that they contain a sufficient number of elements that the soil needs. Previously, we investigated the migration of elements from copper smelter slag flotation tailings into soils and plants (Kotelnikova et al., 2023; Zolotova et al., 2023). It is established that the cation exchange mechanisms with the participation of organometallic complexes of metals, as well as metal hydroxides and sulphides, are activated in the system of high-moor peat - flotation tailings of copper smelter slag. Metal hydroxides and sulphides, which were formed during the leaching of flotation tailings minerals, acted as regulators of the migration flows of heavy metals and other elements with variable valence (Kotelnikova et al., 2023).

The interaction of sulphuric acid with flotation tailings of copper smelter slag leads to the formation of more bioavailable secondary minerals, which in the presence of organic compounds, products of biota activity, can dissolve with the release of many elements, including heavy metals, into soil solutions (Kostina et al., 2014; Kuznetsova, 2021).

The addition of 5% sulphuric acid leaching wastes of copper smelter slag flotation tailings to peat reduces pH from 6.0 to 3.1, pH_{KCl} from 5.7 to 4.2. The content of potassium, one of the main macroelements for plant nutrition, increases in 1.5 times: peat – 29.1 mg/kg, peat with leaching wastes – 154 mg/kg. However, the accumulation coefficients showed that there is a significant increase in the content of such toxic elements as Sn (85 times compared to peat), Sb (31 times, 34.8 mg/kg) and Pb (31 times), Cu (19.5 times), Zn (in 18.7 times), Mo (16.3 times), As (8.9 times), S (3 times) (Figure 3). This is due to the fact that the soil acidity significantly affects the biogeochemical cycles, the accumulation of toxic elements (Meng et al. 2019; Gondal et al. 2021). A decrease in the pH of the soil solution increases the solubility of many heavy metals (metalloids), for example, copper, zinc, lead, cadmium, mercury, arsenic (Sarapulova, 2018; Plekhanova et al., 2019).

A comparison of soils with different types of wastes showed that the concentration of most toxic elements is higher in soil with leaching wastes than in soil with the flotation tailings. Exceptions are Mn, Co, Ni, Cu, Zn, Cd (Table 2). Figure 3 clearly shows the difference in the concentration coefficients of toxic elements in soils with different types of copper smelter slag processing wastes. The maximum differences were noted for Sn; its concentration coefficient is 38 times higher on the soil with leaching wastes than on the soil with the flotation tailings. For

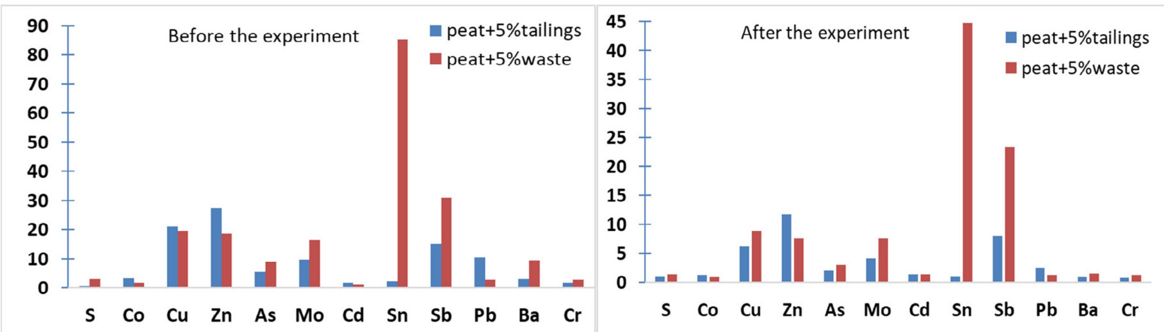

Fig. 3. Concentration coefficient of toxic elements in peat with different types of copper smelter slag recycling wastes: slag flotation tailings and wastes from their sulfuric acid leaching

Table 2. The content of toxic elements in high-moor peat with flotation tailings of copper smelter slags and wastes from their leaching, mg/kg

	MPC (Russia)	SQG (Canada)	Peat with different wastes from processing copper smelting slags					
			before the experiment			after the experiment		
			peat	5% tailings	5% wastes	peat	5% tailings	5% wastes
S	160	-	65.4	38.8	197	15.7	17.1	21.8
Mn	1500	-	207	186	124	257	221	158
Co	-	40	3.1	10.01	5.58	4.46	5.66	4.12
Ni	40	45	15.8	10.8	9.09	17.1	14.5	12.2
Cu	66	63	15.5	327	302	16.6	104	149
Zn	110	250	74.7	2049	1398	55	647	420
As	5	12	6.81	37.6	60.5	6.16	12.7	19.0
Se	-	1.0	1.03	0.76	1.01	0.81	0.7	0.74
Mo	-	5	1.47	14.4	24.0	1.02	4.24	7.85
Cd	1.0	1.4	0.73	1.27	0.74	0.61	0.85	0.83
Sn	-	5	1.86	4.18	158	1.67	1.69	74.7
Sb	4.5	20	1.12	17.1	34.8	0.48	3.85	11.2
Pb	65	70	15.3	161	476	15.6	39.7	215
Ba	-	750	42.3	131	404	99.1	95.6	157
Cr	-	64	9.18	16.2	25.9	14	11.7	18.1
V	150.0	130	5.04	6.18	6.56	15.3	10.18	9.73
Tl	-	1.0	0.09	0.09	0.14	0.13	0.1	0.12

Note: MPC - the maximum permissible concentrations for gross forms of elements are given for acidic soils (SanPiN 1.2.3685-21); SQG - soil quality guidelines (CCME); "-" - not regulated. Mercury was not considered, since it is not contained in the wastes

S and Ba, the difference in coefficients is not so significant: 5.1 and 3.1 times. An opposite trend was revealed for Pb; its concentration coefficient is 3.7 times higher on the soil with flotation tailings.

The concentration of most of the elements in soils with wastes decreases by the autumn. However, an increase in the content of V, Mn, Ni is observed (Table 2). The analysis of the peat with 5% leaching wastes showed that the concentration decreases most strongly at the end of the vegetation period for the following elements: S (9 times), Zn (3.3 times), As (3.2 times), Mo and Sb (3.1 times), Ba (2.6 times), Pb (2.2 times), Sn (2.1 times), Cu (2 times). Slightly different trends were found on soil with 5% flotation tailings. For them, the content of elements decreases most strongly for Sb (4.4 times), Pb (4.1 times), Mo (3.4 times), Zn (3.2 times), Cu (3.1 times), As (3 times), Sn (2.5 times), S (2.3 times), Co (1.8 times), Cd (1.5 times). Concentration coefficients for soils with different types of wastes decrease almost twice after the vegetation period (Figure 3). The maximum differences were noted for Sn and Sb; their concentration coefficients are 44 times higher and 2.9 times higher on soil with leaching wastes than on peat with flotation tailings. For Pb, the previously identified trend persists; its concentration coefficient is 2 times higher on the soil with flotation tailings. The copper concentration coefficient after the experiment becomes higher on the soil with leaching wastes than on the soil with the flotation tailings, although the opposite trend was before the experiment.

Stronger excesses of maximum permissible concentrations (MPC) regulated in Russia (SanPiN 1.2.3685-21) were revealed for copper, zinc, arsenic, antimony, lead, sulphur for soil with leaching wastes, compared to the soil with flotation tailings of copper smelter slags (Figure 4). Regulated values for acidic soils were used for the assessment. The concentration of toxic elements decreases during the vegetation period, but excesses continue to be recorded, except for sulphur and cadmium.

The values for cobalt, selenium, molybdenum, tin, barium, chromium, and thallium are given in the Soil Quality Guidelines (SQG) (Table 2). Their exceedances for modified peat with leaching wastes were revealed for molybdenum (4.8 times; for peat with flotation tailings – 2.9

times) and tin (32 times). The selenium concentration is at the level of regulated values. At the end of vegetation period, the excess concentrations of molybdenum and tin are 1.6 times and 15 times, respectively.

A chemical analysis was carried out of the plant shoots and roots to assess the migration of elements from the soil with leaching wastes into the plants (Table 3). The shoots of the lawn grasses have a lower concentration of the considered elements compared to the roots, where most of the heavy metals are retained. The largest difference was found for Sn (112 times more in roots than in shoots), Pb (57 times), Sb (34 times), Co (26 times), Cu (24 times). For lawn grasses grown on soil with flotation tailings, the maximum difference in element content between roots and shoots was for Co (16 times), Cd (10 times), Sb (7.4 times), Pb (7.1 times) (Table 3). No exceedances of the regulated values for plant shoots (VetPin 13.7.1-00) were found.

The accumulation coefficients of elements (Table 4) were calculated based on data from

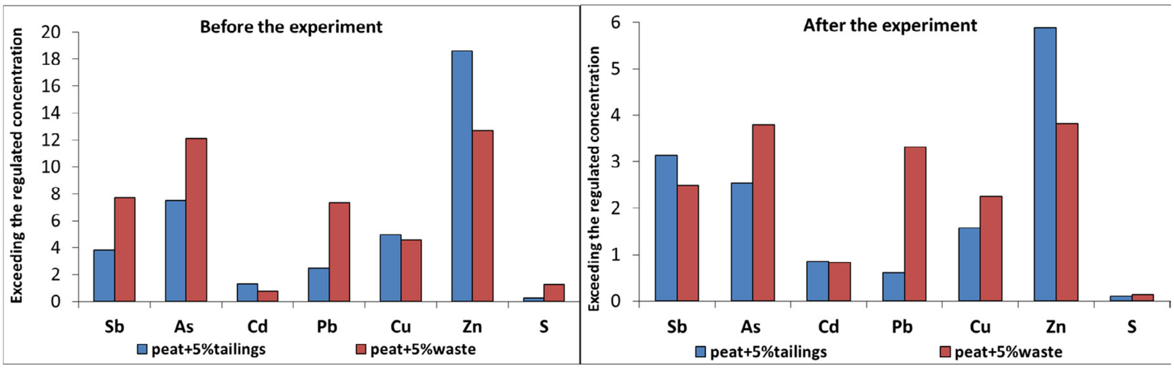

Fig. 4. Environmental assessment of peat with flotation tailings of copper smelter slags and wastes from their sulphuric acid leaching

Table 3. The content of toxic elements in the shoots and roots of lawn grasses grown on high-moor peat with flotation tailings of copper smelter slags and wastes from their leaching, mg/kg

Element	MRL	Peat with different waste from copper smelting slag recycling wastes					
		0%		5% tailings		5% leaching wastes	
		root	shoot	root	shoot	root	shoot
S	-	9.13	3.03	6.67	1.41	4.55	0
Mn	-	146	137	93.8	64.3	95.9	30.1
Co	1.0	2.39	0.26	2.15	0.14	2.86	0.11
Ni	3.0	6.5	2.16	5.59	1.16	9.2	1.61
Cu	30	8.66	5.59	22.6	4.27	91.2	3.77
Zn	50	37.4	22.5	121	27	172	3.77
As	0.5	1.88	0.6	2.77	0.58	5.62	0.48
Se	-	0.35	0.19	0.2	0.1	1.67	0.1
Mo	1.0	1.22	1.72	1.5	1.76	1.84	0.88
Cd	0.3	0.87	0.2	1.06	0.1	0.68	0.04
Sn	-	0.53	0.16	0.4	0.06	10.5	0.09
Sb	0.5	0.24	0.1	0.8	0.11	1.87	0.06
Pb	5.0	4.11	1.55	7.3	1.03	33.9	0.6
Ba	-	28.1	44.8	26	40.8	27.1	15.7
Cr	0.5	2.1	2.3	1.51	0.94	4.9	2.02
V	-	1.9	1.11	1.12	0.38	2.85	0.68
Tl	-	0.19	0.09	0.24	0.07	0.23	0.03

Note: MRL - the maximum permissible levels of toxic elements for agricultural plants (rough and succulent animal feed) (VetPin 13.7.1-00); "-" - not regulated.

Table 4. The accumulation coefficients of toxic elements for plants grown on high-moor peat with flotation tailings of copper smelter slags and wastes from their leaching

Element	The roots on peat with different wastes of the processing copper smelter slags			The shoots on peat with different wastes of the processing copper smelter slags		
	peat	5% tailings	5% leaching wastes	peat	5% tailings	5% leaching wastes
S	0.58	0.39	0.21	0.19	0.08	0
Mn	0.57	0.42	0.61	0.53	0.29	0.19
Co	0.54	0.38	0.69	0.06	0.02	0.03
Ni	0.38	0.39	0.75	0.13	0.08	0.13
Cu	0.52	0.22	0.61	0.34	0.04	0.03
Zn	0.68	0.19	0.41	0.41	0.04	0.05
As	0.31	0.22	0.3	0.1	0.05	0.03
Se	0.44	0.28	2.25	0.23	0.14	0.13
Mo	1.19	0.35	0.23	1.68	0.41	0.11
Cd	1.43	1.25	0.83	0.33	0.12	0.05
Sn	0.32	0.23	0.14	0.09	0.04	0.001
Sb	0.51	0.21	0.17	0.1	0.03	0.005
Pb	0.26	0.18	0.16	0.2	0.03	0.003
Ba	0.28	0.27	0.17	0.43	0.43	0.1
Cr	0.15	0.13	0.27	0.16	0.08	0.11
V	0.12	0.11	0.29	0.07	0.04	0.07
Tl	1.47	2.31	1.91	0.66	0.65	0.28

chemical analysis of soils (Table 2) and plants (Table 3). More of the elements accumulate in the roots of lawn grasses than in the shoots.

It was established that when 5% leaching wastes from the flotation tailings of copper smelter slag are added to peat, the accumulation coefficients of elements for the roots of lawn grasses change

more significantly for such elements as S, Ni, Se, Mo, Cd, Sb, Tl (Table 4).

Plant roots on soil with leaching wastes accumulate V, Cr, Co, Ni, Se, Mn, Cu more strongly compared to both peat and soil with flotation tailings. However, S, Mo, Cd, Sn, Sb, Ba and Pb accumulate significantly less. The concentration coefficient of Zn in roots on soil with leaching wastes is lower than for peat, but higher than for soil with flotation tailings. The roots of lawn grasses accumulate arsenic equally on both the original peat and on the soil with leaching wastes, but less on the soil with flotation tailings.

Concentration coefficients greater than one indicate that plants are accumulators of these elements. The roots of lawn grasses are accumulators for the following elements: Mo, Cd and Tl - on neutralized high peat; Cd, Tl - on the soil with copper smelter slag flotation tailings; Tl, Se - on the soil with leaching wastes.

The shoots of lawn grasses grown on soil with leaching wastes have a lower concentration of toxic elements compared to the roots. This is explained by the fact that roots retain most heavy metals (Soriano-Disla et al., 2014; Jalali et al., 2023).

It has been established that the ability to absorb trace elements changed more significantly for the shoots of lawn grasses than for the roots when copper smelter slag processing wastes were added to the peat. However, accumulation trends, as well as the order of some accumulation coefficients, differ for shoots on soil with flotation tailings and on soil with leaching wastes (Table 4). The accumulation coefficients of most elements decrease for shoots in the series: peat – soil with flotation tailings of copper smelter slag – soil with leaching wastes of flotation tailings. Moreover, the coefficient values for some elements differ significantly on soil with leaching wastes, for example, for Sn, Pb, Sb. However, slight increases in accumulation coefficients for Co, Zn, V, Cr, Ni were revealed for shoots grown on soil with leaching wastes compared to soil with flotation tailings.

The shoots of lawn grasses are accumulators (their concentration coefficients are greater than one) for Mo on neutralized high-moor peat. The shoots grown on artificial soils with wastes were not accumulators of the considered toxic elements.

The accumulation series of elements are constructed on the basis of Table 4. The elements are arranged in order of increasing accumulation coefficient (from left to right) and look as follows:

a) The roots on artificial soils with different wastes of the processing copper smelter slags.

Peat: V < Cr < Pb < Ba < As < Sn < Ni < Se < Sb < Cu < Co < Mn < S < Zn < Mo < Cd < Tl.

Peat with flotation tailings: V < Cr < Pb < Zn < Sb < Cu < As < Sn < Ba < Se < Bi < Mo < Co < Ni < S < Mn < Cd < Tl.

Peat with leaching wastes: Sn < Pb < Sb < S < Mo < Cr < V < Bi < As < Zn < Cu < Mn < Co < Ni < Cd < Tl < Se.

b) The shoots on peat with different wastes of the processing copper smelter slags

Peat: Co < V < Sn < As < Pb < Ni < Cr < S < Sb < Se < Cd < Cu < Zn < Ba < Mn < Tl < Mo.

Peat with flotation tailings: Co < Pb < Sb < Sn < V < Cu < Zn < As < Ni < Cr < S < Cd < Se< Mn < Mo < Ba < Tl.

Peat with leaching wastes: Sn < Pb < Sb < As < Cu < Co < Zn < Cd < V < Ba < Mo < Cr < Ni< Se < Mn < Tl.

The data on the element's accumulation coefficients for lawn grasses growing on peat with different types of copper smelter slag recycling wastes were summarized, and the following patterns were identified:

1. The roots of lawn grasses have higher accumulation coefficients for a number of elements in soil with leaching wastes from copper smelter slag flotation tailings compared to both the peat and the soil with flotation tailings. The accumulation coefficients of most elements for plant roots increase in the order: soil with flotation tailings of copper smelter slag – peat – soil with leaching wastes of flotation tailings.

2. The trends of the element accumulation in the shoots of lawn grasses are different from those observed for the roots. The shoots grown on soil with leaching wastes have lower accumulation coefficients for most of the elements compared to both the original peat and the soil with flotation tailings. The values of the coefficients decrease in the series peat – soil with flotation tailings of copper smelter slag – soil with leaching wastes of flotation tailings.

Perhaps the observed pattern is explained by the fact that a lack of nutrients in the soil quite often lead to excessive accumulation of heavy metals in plants (Yaashikaa et al., 2022). Therefore, we observe a higher accumulation coefficient for Zn, Cu, Cr, Mn, Co, As, Mo, Cd, Sn, Sb, Pb in the shoots of lawn grasses grown on peat than on soils with copper smelter slag processing wastes. Although, of course, there are complex interactions between the absorption of nutrients by the plant and the intake of heavy metals from the soil (Uchimiya et al., 2020). It is known that there is a positive correlation between the accumulation of heavy metals and the absorption of potassium and phosphorus, and the relationship with nitrogen absorption has not been revealed (Matveev et al., 1997; Xu et al., 2022). The presence of humic substances reduces the content of metals in plant phytomass (Terekhova et al., 2021). The effects of silicon on the heavy metal uptake by plants is also considered separately (Khan et al., 2021).

3. The roots of lawn grasses, growing on soil with leaching wastes, are accumulators for Tl, Se. The shoots grown on this artificial soil are not accumulators of the considered toxic elements.

CONCLUSION

Our studies have revealed changes in the chemical and phase composition of flotation tailings of copper smelter slags after sulphuric acid leaching. Leaching wastes include diopside, gypsum, spinel group minerals, jarosite, barite, sphalerite and amorphous silica. The chemical composition of the wastes is mainly SiO_2 – 32.5% and Fe_2O_3 – 18%. According to scanning electron microscopy, the phase composition of the leaching wastes is represented by an association of silica, crystalline sulfur, compounds of iron, lead, zinc, copper and their sulfides.

Our field experiment showed that the addition of 5% of sulphuric acid leaching wastes to neutralized ombrotrophic peat leads to soil contamination with heavy metals (metalloids). Exceedances of regulated concentrations of toxic elements have been established. A comparative analysis of the mobility of toxic elements in artificial soils with different types of copper smelter slag recycling wastes was carried out, and concentration coefficients were calculated. The concentration of most elements is higher in the soil with leaching wastes than in the soil with the flotation tailings, with the exceptions of Mn, Co, Ni, Cu, Zn, Cd. The greatest differences in concentration coefficients were noted for Sn and S. During the vegetation period, the concentration of most toxic elements decreases in soils with wastes, and the concentration coefficients decrease by almost half.

We showed the distribution of elements in the roots and shoots of lawn grasses grown on soil with leaching wastes from copper smelter slag flotation tailings, compared them with plants on soil with the original flotation tailings, and calculated accumulation coefficients. The shoots of the lawn grasses had a lower concentration of the elements compared to the roots. V, Cr, Co, Ni, Se, Mn, Cu accumulated more strongly in plant roots on soil with leaching wastes compared to both peat and soil with flotation tailings. However, S, Mo, Cd, Sn, Sb, Ba and Pb had the opposite tendency, they accumulate in the roots of plants on soil with leaching wastes much less than on other soils. According to the concentration coefficients, the roots of the lawn grasses on soil with leaching wastes are accumulators for Tl, Se. No exceedances of the regulated values for plant shoots were found.

An experiment on the migration of elements from leaching wastes of copper smelter slag flotation tailings showed that they may pose a greater risk to the environment than the initial enrichment tailings. It is therefore important to continue research into the environmental consequences of the impact of sulphuric acid leaching wastes from copper smelter slag flotation tailings on the environment in order to develop environmentally friendly and effective methods for their integrated use, recycling and disposal.

ACKNOWLEDGMENTS

The authors are deeply grateful to V.F. Ryabinin, initiator of geoecological research at the A.N. Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences, for participation in conducting field experiments, D.V. Kiseleva for determining the elemental composition, T.Ya. Gulyaeva and L.V. Leonova for help in determining the phase composition of the samples.

GRANT SUPPORT DETAILS

The studies are carried out as a part of the IGG UB RAS State assignment (state registration No. 123011800011-2).

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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