

## Potential Ecological Danger of Copper and Nickel Ore Concentrating Tailing Dumps Withdrawn from Operation

V. N. MAKAROV, T. N. VASILYEVA, D. V. MAKAROV, A. A. ALKATSEVA, E. R. FARVAZOVA,  
D. P. NESTEROV and V. V. LASHCHUK

*Institute of Chemistry and Technology for Rare-Earth Elements and Mineral Raw Materials,  
Kola Scientific Centre, Russian Academy of Sciences,  
Ul. Fersmana 26a, Apatity 184209 (Russia)*

*E-mail: makarovdv@chemy.kolasc.net.ru*

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### Abstract

Possible soil pollution, as a consequence of dusting of the tailings of copper and nickel ore dressing withdrawn from operation, is modeled. The results show that sulphide-containing final tailing products brought into soil cause rather intensive transformation of heavy metals into water-soluble forms. Thus formed organomineral complexes are stable and yield to no purification with the help of conventional reagents.

### INTRODUCTION

A large number of fine waste material is formed as a result of copper and nickel ore concentrating; the yield of waste material reaches 90 % of the initial ore and more. This waste material, containing not only ferric and magnesium silicates and hydrosilicates but also under-extracted sulphides of iron and nonferrous metals, is stored in tailing dumps. As a rule, the waste material is placed in natural shallow gullies, the valleys of brooks and temporary streams, gullies, depressions and cavities. In order to increase the capacity of tailing dumps, dams are built. Due to the recycling water supply, an artificial lake exists on the surface of the dumps during their exploitation; the tailings themselves are in water-saturated state. To avoid pollution of environment, *i.e.* surface and underground water, with reagents, and to decrease water loss, water-proofing is made at the dam and at the bottom of tailing dump.

During the period of dump operation, its state is monitored by special works; substantial financial and material expenses are made for maintenance of the dump due to the gain on

operation of the deposit. After the operation period is over, the financial source is exhausted, and maintenance of the safe state of the objects becomes problematical.

It is interesting to estimate the potential ecological danger of copper and nickel ore-concentrating tailing dumps withdrawn from operation. The following mechanisms of pollution of the environment (soil and water bodies) are principally possible:

- due to filtration of the pore water through the dam and bottom of water reservoir;
- due to dusting of the tailing dumps;
- as a result of failures of dams.

The probability of the latter events is determined by the engineering and geological status of the dumps; it is a subject of special investigation and goes out of the scope of the present work. Estimation of the role of dusting and filtration in the pollution of environment with heavy metals is of principal importance due to the following reasons. For filtration of solutions under the conditions of the Baltic shield with rather shallow occurrence of rocks, pollution can manifest itself lower along the local slope. In this case, the application of artificial geochemical barriers is efficient. For

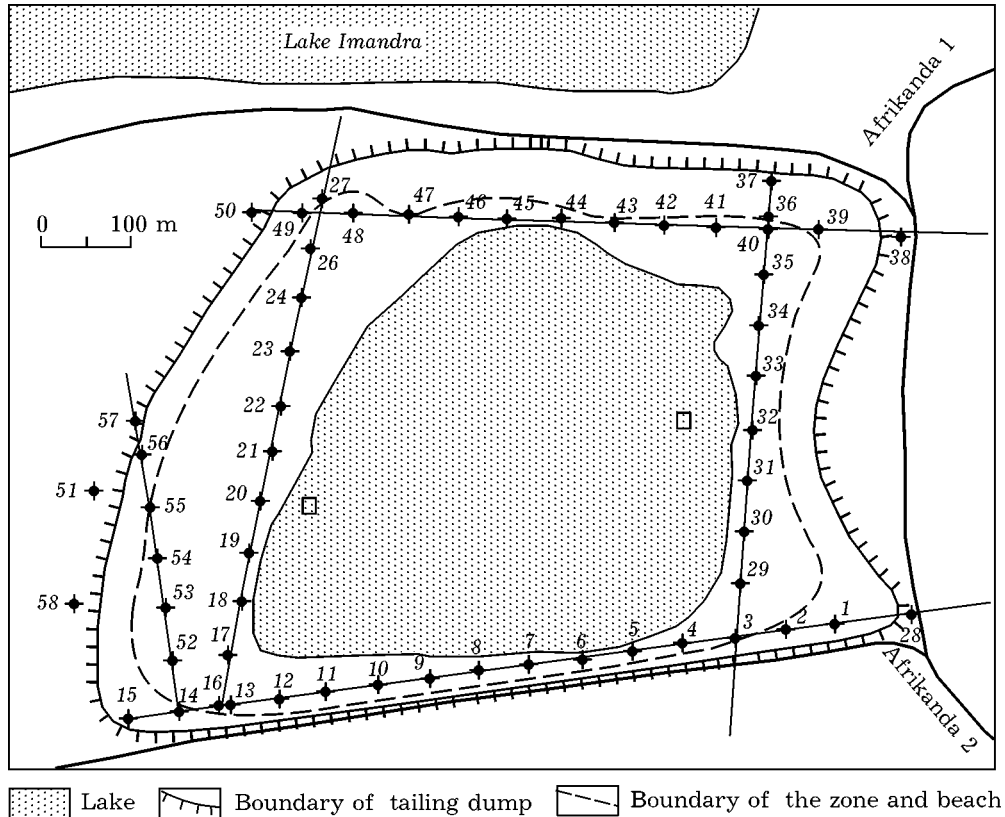


Fig. 1. Schematic of the tailing dump of the concentrating plant in Afrikanda settlement: 1–58 – sampling sites.

dusting of tailings, heavy metals can get into soil also upward the slope and occur over substantial territories.

In order to estimate the role of filtration and dusting of tailings in pollution of natural soil with heavy metals, we compared the concentrations of heavy metals in the tailings of a dump withdrawn from operation, in pore solutions of these tailings and in natural soil around the tailing dumps. We also took into account the fact that in the case of soil pollution with dusting tailings it is important to determine the possibility of transformation of sulphides present in the tailings into the water-soluble state. As it was shown previously, in the tailings themselves the formation of water-soluble sulphates of copper, nickel, cobalt and iron is connected with sulphide oxidation processes [1–3 and so on]. In natural soil, especially in the upper soil layer, under the conditions of tundra and forest-tundra, these processes are also possible due to the high concentration of organic matter. The interaction of sulphides with organic acids cannot be excluded, either.

The tailing dump of the experimental concentrating plant in the settlement of Afrikanda (Murmansk Region) was used as a model object. The plant had been built to process perovskite ore; however, in view of changes in the state of the market and due to the technological insignificance, processing ceased. After that, the copper-nickel ore from the Pechenga ore deposit was concentrated for several years at the plant. Later on, the plant was used as the experimental grounds of the Mekhanobr Research Institute (St. Petersburg) to master the technology of concentrating the ore from different deposits of the USSR. Since the amount of ore processed during those years was rather small, the major role in the composition of tailings is played by the waste products of copper and nickel ore concentrating process.

#### EXPERIMENTAL

In order to estimate the disposition of tailings to dusting, we collected the samples

of tailings with unbroken structure from the surface and from the depth of 0.5 m within the tailing over a net using a special sampling instrument. Since the central part of the tailings dump is covered with a lake, samples were taken only over the peripheral regions. Sampling sites are shown in Fig. 1.

The average density of sampled material in the natural and dry states, its true density and granulometric composition were determined using the standard procedures. Soil dampness, porosity, porosity coefficient, bulk density, degree of saturation with water. In addition, water-retaining capacity of the artificial ground was determined. Geochemical and hydrochemical characteristics of the tailings were determined by carrying out chemical analysis of the solid phase and pore fluid. Concentrations of nickel, copper, cobalt, iron and magnesium oxide were determined by means of atomic absorption, the sulphate sulphur was measured gravimetrically or with the help of spectrophotometer (depending on the concentration range). The samples of natural soil around the tailings were collected and analyzed similarly.

In order to estimate the effect of the organic matter on the transition of heavy metals into the water-soluble state, investigations were carried out with the laboratory models. High humidity and limited oxygen access are characteristic of the soil layer; these conditions are satisfactorily modeled in Soxhlet apparatus [4]. The material was placed in the lower part of the apparatus. Liquid droplet water conserving the film and capillary moisture was output. In the experiment we used the organic matter of the upper organogenic horizon of podzol soil (mass concentration 52.6 %). Acid water-soluble humus (pH 4.0) having the following composition, % of total carbon content: humic acids (HA), 22.4; fulvic acids (FA), 28.2; non-hydrolyzed residue, 49.4;  $C_{HA} : C_{FA} = 0.8$  promotes active weathering.

The material incorporating sulphide-containing mineral products and organic matter was placed in a special cylinder closed from the upper and lower ends with a silk cloth. This ensured free infiltration of solutions but prevented removal of solid particles. The mineral matter was placed inside the organic material in a special bag made of silk cloth. The

weighed portion of the material was 25 g, including 15 g of the mineral phase and 10 g of organics. The material was treated for 100 h; pH of solution was determined after each 8 h at 20 °C. After the experiment, the solid phase was dried, weighed and investigated with the microscope, then it was analyzed by means of roentgenometry and thermography. The solution was separated from the suspension and by filtering; chemical composition of the solution was determined. The suspension was analyzed by means of roentgenometry and with chemical methods.

The mineral phase was the massive sulphide ore of the composition, mass %: pyrrhotine 53.89, pentlandite 29.25, chalcopyrite 2.81, magnetite 5.7, and silicates, mainly talc and hydrochlorites (the rest); copper and nickel ore concentrating tailings consisting mainly of magnesium hydrosilicates but containing inclusions of sulphides (mainly pyrrhotine) were also used as the mineral phase. Total sulphide content was less than 3 mass %.

The treatment of the material in Soxhlet apparatus occurs at a temperature about 70 °C; water passes the vapour phase. These conditions are not favourable for the development of microorganisms which are indisputable participants of real processes in soil.

For preliminary estimation of the role of chemical and biochemical constituents for the transfer of heavy metals into water-soluble form, along with experiments in Soxhlet apparatus, we also carried out experiments in thermostat at 30 °C. Water extract of the organic matter of the upper organogenic horizon of the podzol soil was used as the reagent. The duration of experiments was 10 h.

## RESULTS AND DISCUSSION

The distribution of pollutants over the territory and their maximal concentrations in aerosol are due, on the one hand, to the combination of unfavourable meteorological factors, on the other hand, to the properties of natural or artificial ground. Meteorological factors include the local relief, the coefficient of temperature stratification, wind rose, amount and distribution of precipitation. The most

important characteristics of the ground determining its ability to form aerosol are granulometric composition, humidity, water-retaining capacity, and the occurrence of water-colloid bonds between the mineral particles.

It is known that, in agreement with Bernoulli effect, with an increase in the velocity of air flowing above an eminent particle, a lifting force starts to act upon the particle; at some critical wind velocity value, this lifting force can exceed the gravity force. In the air, the kinetic energy of such a particle increases substantially due to the acquisition of the horizontal constituent of velocity corresponding to the motion of wind.

The critical wind velocity  $V_{cr}$  depends on the size of particles and on their masses:

$$V_{cr} = a[(r_s/r_a)gd]^{0.5}$$

where  $a$  is an empirical coefficient depending on the distribution of particles over fractions, the degree of surface roughness, character of bonding between the particles, *etc.*;  $r_s$  and  $r_a$  are the densities of a dust particle and the air around the particle surface, respectively;  $g$  is

the acceleration of gravity;  $d$  is the diameter of a dust particle.

For natural ground, this dependence is true for the particles with diameter up to 0.1 mm [5]. For ground with smaller mean particle size, the role of clayish component becomes more important. Clayish particles are bound to each other by strong water-colloid bonds, so the critical velocity does not decrease with a decrease in the particle size; it even increases.

Fresh industry-related products are almost free from clayish particles and from organic matter promoting the formation of water-colloid bonds.

The analysis of granulometric composition and some other engineering geological characteristics of the stale tailings showed that they are substantially different from the tailings of the current mining activities. This is first of all due to a sharp increase in the role of fine particles and growth of the effect of water-colloid bonds in some kinds of particles. All the stale tailings can be divided into three groups according to their composition and properties:

1. Clay-like stale tailings with the finest particles in which the content of particles

TABLE 1

Statistical parameters of the distribution of granulometric composition of stale tailings and ground adjacent to the tailing dump

Statistical parameter	Fraction size, mm						Mean diameter of mineral grains, mm
	>0.5	0.5-0.25	0.25-0.1	0.1-0.05	0.05-0.025	<0.025	
<i>Clay-like stale tailings</i>							
$M(x)$	0.36	419	13.58	19.96	17.19	44.72	0.069
$Med(x)$	0.040	1.365	6.535	16.260	14.950	40.585	0.060
$S(x)$	0.730	6.122	13.270	13.798	10.856	27.791	0.047
<i>Non-cohesive stale tailings (analogues of dusty sand)</i>							
$M(x)$	2.75	27.20	47.73	15.72	4.63	1.97	0.212
$Med(x)$	1.950	26.340	47.880	12.560	3.680	1.240	0.210
$S(x)$	2.658	13.974	10.239	7.611	3.470	1.962	0.048
<i>Non-cohesive stale tailings with inclusions of clay-like layers</i>							
$M(x)$	3.1	15.54	37.22	24.33	12.98	6.88	0.159
$Med(x)$	1.270	16.12	35.310	18.350	6.045	6.665	0.165
$S(x)$	6.436	10.298	15.160	17.872	22.972	4.974	0.065
<i>Natural ground</i>							
$M(x)$	13.79	16.44	39.27	18.59	8.10	3.81	0.252
$Med(x)$	14.245	16.715	40.810	14.875	7.310	2.810	0.245
$S(x)$	16.572	6.515	17.074	8.096	4.405	2.166	0.109

*Note.*  $M(x)$  is a mean value of a parameter;  $Med(x)$  is the most frequent value of a parameter;  $S(x)$  is the square mean deviation.

smaller than 0.025 mm is, as a rule, more than 20 %. Such a ground has a stone-like constitution in the dry state. When humid, they possess plasticity; for the case of maximal humidity, they can pass into the fluid state. These artificial ground samples are characterized by low filtration coefficient (0.03–0.09 m/day) and high water-retaining capacity. In the sampling under analysis (108 samples), clay-like ground accounts for a little more than 40 %.

2. Non-cohesive stale tailings characterized by the maximal size of mineral particles and the content of particles smaller than 0.025 mm not more than 5–7 mass %, as a rule, and in many cases <1 %. The filtration coefficient for such a ground is much higher; as a consequence, the humidity is much lower than that of clay-like ground. Such a kind of ground accounts for a little more than 45 % in the analyzed sampling.

3. Non-cohesive stale tailings with inclusions of clay-like layers, seams and clusters. This group occupies an intermediate position in composition and properties.

The main statistical parameters of the distribution of granulometric composition of stale tailings and natural ground adjacent to the tailing dump are listed in Table 1. The cumulative curve of granulometric composition is shown in Fig. 2. One can see that for clay-like ground the mean content of particles smaller than 0.025 mm is nearly 45 %, while the particles with grain size more than 0.05 mm are almost absent. For non-cohesive ground, the fraction 0.25 to 0.1 mm is prevailing (nearly 48 %). The non-cohesive stale tailings are close in their granulometric composition to the natural ground near the tailing dump (Table 2, Fig. 2).

The authors of [6] presented calculations of the dust fluxes of the apatite nepheline ore concentrating tailings near the Khibiny station. Since the tailing dump is still in operation, it was assumed that 10 % of the total area of the tailing dump participates in dusting. For humidity 6–12 mass %, the mass flux of dust at a distance of several kilometers is 4–8 g/(m<sup>2</sup> day). The maximal dust flux is observed in the vicinity of the tailing dump.

Table 2 shows such parameters as humidity, water-retaining capacity, water saturation coefficient, filtration coefficient for the stale

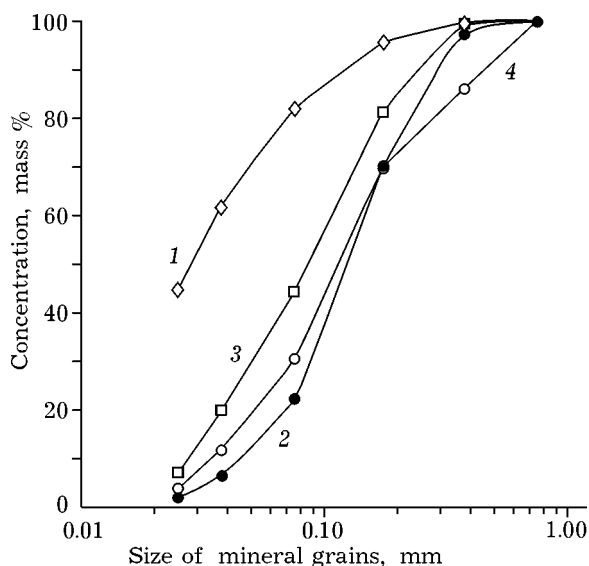


Fig. 2. Cumulative curves of granulometric composition of clay-like (1), non-cohesive (2), non-cohesive with inclusions of clay-like layers (3) stale tailings and natural ground in the vicinity of the tailing dump (4).

tailings. Taking into account the fact that the mean size of mineral grains of copper and nickel ore concentrating tailings is smaller than that of apatite nepheline ones, while the humidity of non-cohesive stale tailings and non-cohesive ones with clay-like layers is comparable with the humidity accepted for dusting simulation [6], it may be assumed that dusting of the tailings can affect substantial territory.

The most important supergene processes in stale copper and nickel ore concentrating tailings were considered by us in [7]. These include, first of all, substantial oxidation of sulphide minerals and their substitution by hydroxides of iron. The same processes can be referred to to explain a higher role of chlorites and hydrochlorites in the stale tailings. The presence of gypsum was detected in some samples. Comparison of the results of analyses of the samples of stale tailings and the tailings of current concentrating process showed that substantial differences are observed in the content of ore-forming elements: nickel, copper, cobalt and sulphur, as well as iron and magnesium oxide. During the storage of tailings, not only mean content of ore-forming elements changes but also their forms (the ratio of sulphide and oxygen-containing phases). The correlation between nickel and copper concentrations weakens, while similar

TABLE 2

Some hydrological characteristics of stale tailings

Statistical parameter	Humidity, %	Water-retaining capacity of ground, %	Water saturation coefficient	Filtration coefficient, m/day
<i>Clay-like stale tailings</i>				
$M(x)$	24.829	37.223	0.476	0.208
$Med(x)$	23.46	35.39	0.47	0.30
$S(x)$	7.691	9.692	0.132	0.116
<i>Non-cohesive stale tailings (analogues of dusty sand)</i>				
$M(x)$	10.08	24.83	0.211	25.26
$Med(x)$	8.7	23.31	0.185	18.8
$S(x)$	5.074	8.104	0.098	19.91
<i>Non-cohesive stale tailings with inclusions of clay-like layers</i>				
$M(x)$	13.766	32.628	0.276	0.806
$Med(x)$	11.110	33.265	0.225	–
$S(x)$	7.281	7.602	0.141	–

correlations between nickel, on the one hand, and cobalt, iron and magnesium, on the other hand, strengthen. The correlation between the content of ore-forming elements and particle size is distorted, too [7].

A comparison between the statistical parameters of the distribution of nickel,

copper, cobalt, iron and magnesium oxide for the stale tailings and the ground adjacent to the tailing dump shows that the latter ground is most close in the mean content to the non-cohesive tailings with inclusions of clay-like layers (Table 3). At the same time, these samplings have significant differences in Fisher's criterion, which is quite natural because pollution of natural ground occurs extremely non-homogenously over different directions and at different distances. Even more close similarity is revealed in these two samplings with respect to nickel to copper, nickel to cobalt, nickel to iron, nickel to magnesium ratios (Fig. 3). It should be assumed that non-cohesive tailings with inclusions of clay-like layers were the main source of dust. Unlike clay-like stale tailings, they contain a small amount of fine particles forming water-colloid bonds, but at the same time they are richer in dusty fractions than non-cohesive tailings.

So, dusting tailings act as an essential source of pollution of environment with heavy metals. Precipitation of dust at a level of 4–8 g/(m<sup>2</sup> day) is equivalent to the arrival of 6–12 mg/(m<sup>2</sup> day) of nickel into the soil. If the snow-free period in Kolsky polar region is accepted to be not less than 100 days, while fair weather occurs about one third of a year, it may be considered that 200–400 mg of this metal can get precipitated onto each square meter of soil during a year. If nickel was present completely in water-soluble

TABLE 3

Statistical parameters of the distribution of several components in stale tailings and in the ground adjacent to the tailing dump

Statistical parameter	Concentrations of components, mass %				
	Ni	Cu	Co	Fe	MgO
<i>Clay-like stale tailings</i>					
$M(x)$	0.166	0.043	0.006	10.811	16.931
$Med(x)$	0.168	0.043	0.006	10.690	17.150
$S(x)$	0.032	0.011	0.001	1.147	1.294
<i>Non-cohesive stale tailings (analogues of dusty sand)</i>					
$M(x)$	0.169	0.061	0.008	11.558	16.623
$Med(x)$	0.167	0.063	0.007	11.365	16.850
$S(x)$	0.033	0.014	0.001	1.068	1.977
<i>Non-cohesive stale tailings with inclusions of clay-like layers</i>					
$M(x)$	0.147	0.048	0.006	10.311	15.700
$Med(x)$	0.160	0.051	0.007	10.930	16.750
$S(x)$	0.049	0.018	0.002	2.418	4.018
<i>Natural ground</i>					
$M(x)$	0.106	0.039	0.005	8.161	11.236
$Med(x)$	0.089	0.037	0.005	9.900	12.300
$S(x)$	0.093	0.029	0.004	4.346	9.266

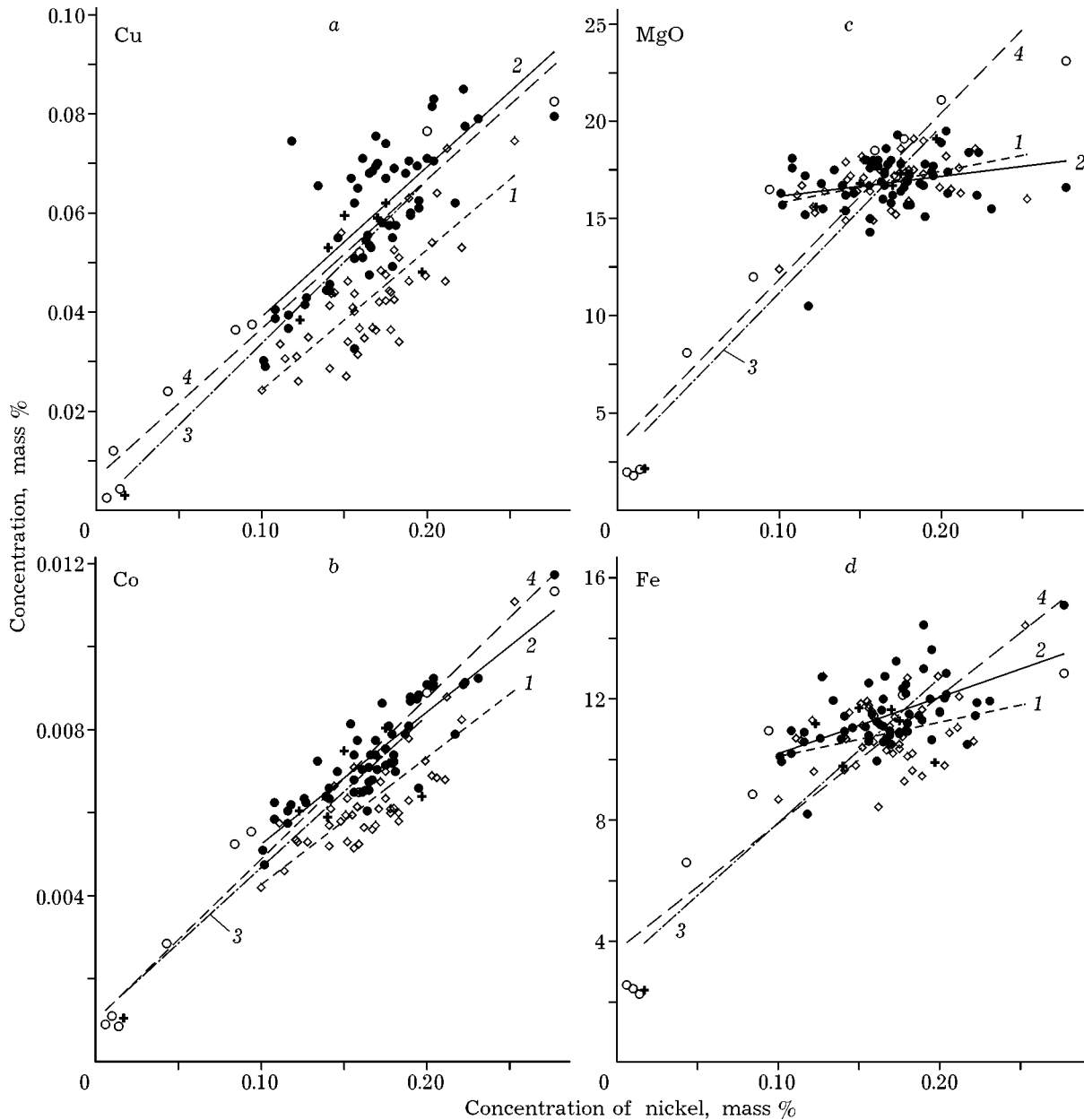


Fig. 3. The ratios of contents of ore-forming elements in the samples of clay-like (1), non-cohesive (2), non-cohesive with inclusions of clay-like layers (3) stale tailings and natural ground in the vicinity of the tailing dump (4): a - nickel and copper, b - nickel and cobalt, c - nickel and magnesium oxide, d - nickel and iron.

form, then, we would have 0.4–0.8 mg of nickel per each litre of atmospheric precipitation, which is 40–80 times as high as the maximum permissible level for fishery water bodies.

It was essential to determine how rapidly and completely the nickel arriving with dust can pass into water-soluble form. Table 4 shows the results of analysis of the solutions and solid organic phase after processing the massive sulphide ore and copper and nickel concentrating tailings in Soxhlet apparatus, and

also the results of analysis of the solution after treating the ore with water in thermostat. In all the experiments, the final pH of solution remained acidic. The largest pH (up to 5.3) is characteristic in the experiments with tailings, the lowest (<3.8) in the experiments with massive sulphide ore (fraction with particle size smaller than 0.071 mm). As one could expect, the degree of metal extraction from solutions is substantially affected by particle size (exp. 1 and 2), as well as by sulphide content of the

TABLE 4

Composition of solutions and the solid organic phase after the interaction with sulphide-containing products

Exp. No	Product	Concentration in solution, mg/l,				Extraction degree, %			
		and concentration in the solid phase,							
		mass %							
		Ni	Cu	Fe	Co	Ni	Cu	Fe	Co
1	Solution	92	025	354	H. o.	5.52	0.15	4.85	–
	Solid phase	0.081	0.016	2.28	H. o.	0.28	0.558	2.20	–
	<i>Total</i>					5.80	0.71	7.05	–
2	Solution	5.22	0.239	4.20	0.071	0.031	0.144	0.058	0.005
	Solid phase	0.154	0.037	2.74	H. o.	0.86	0.517	3.51	–
	<i>Total</i>					0.89	0.66	3.57	–
3	Solution	0.12	0.395	0.174	0.067	0.53	3.29	0.006	2.98
	Solid phase	0.013	0.023	2.28	H. o.	5.74	19.03	6.69	–
	<i>Total</i>					6.27	22.32	6.70	–
4	Solution	192	117	258	1.18	11.96	0.73	3.67	0.70

*Note.* Experiments 1–3 were carried out in Soxhlet apparatus: 1 – massive sulphide ore, fraction <0.071 mm, 2 – the same, fraction 0.1–0.071 mm, 3 – copper and nickel ore concentrating tailings, 4 – experiment in thermostat, massive sulphide ore, fraction <0.071 mm.

initial product (exp. 2 and 3). However, even in the case of low sulphide content in the initial solid phase, the concentration of heavy metals in solution is many times higher than the maximum permissible concentration for fishery water bodies: cobalt, 7 times; nickel, 12 times; copper, 395 times. Unlike the case with sulphide dissolution according to the electrochemical mechanism, organogenic decomposition of sulphides does not lead to precipitation of ferrous and ferric hydroxides (microscopic analysis revealed no indices of these compounds). The major amount of heavy metals is present in solution in organomineral complexes and cannot be precipitated with the help of conventional reagents. A notable amount of heavy metals is accumulated in the solid organic residue and in the organic suspension.

Even more intensive extraction of heavy metals into solution occurs during the treatment of sulphides with the aqueous extract in thermostat. Though temperature was lower in this experiment by 35–40 °C than that in the previous experiments, and the rates of chemical reactions decrease 2–4 times with a 10 °C decrease in temperature, extraction of nickel into solution increased more than by a factor of 2, while that for copper remained at the same level. At the same time, extraction of iron

decreased almost by a factor of 2. It may be assumed that the acid medium and temperature were optimal for the development of microorganisms activating the oxidation processes [8].

## CONCLUSIONS

So, simulation results confirm that the arrival of sulphide-containing products into soil causes rather intensive transformation of heavy metals into water-soluble form. Organomineral complexes formed in this process are stable and are not amenable to purification (removal) with the help of conventional reagents.

The interaction of organic matter with sulphides involves both chemical exchange reactions and biochemical processes. Further research is necessary to estimate the role of each of these constituents.

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