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Waste storage for Cu-Co-Ni arsenide ores of the Khovu-Aksy deposit (trench) as a source of metals and arsenic in drainage and vapor-gas flows

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Abstract

The article presents the results of a comprehensive survey of the trench at the Tuvakobalt plant, which contains waste from the hydrometallurgical processing of Cu-Co-Ni arsenide ores from the Khovu-Aksy deposit. Using electrical resistivity tomography, geoelectric maps and cross-sections were obtained, and a 3D model of the storage was constructed. A highly conductive (low-resistance) zone has been delineated in the central part of the trench – a substance with relatively higher moisture content than the surrounding side parts. The groundwater uncovered in the pit faces consists of mineralized solutions with a high arsenic content (up to 15 mg/l), which indicates active processes of interaction between seasonal waters and the trench material, as well as the accumulation of dissolved forms of metals and metalloids in the liquid phase of the highly conductive zone. This zone, which is narrow at the surface, widens towards the bottom of the trench and extends deeper than 40 m, which indicates the possibility of high-mineralized solutions entering the underground aquifers. Another pathway for the migration of pollutants is through emanations from the surface of the storage. A high concentration of chemical elements, including potentially toxic ones, enters the surface layer of the atmosphere with vapor-gas flows, as established by collecting and analyzing condensates. The forms of element migration in these flows were determined through laboratory experiments involving the capture and deposition of substances carried by the flows. The composition of the flows is primarily made up of amorphous organic compounds, with a small proportion of chlorides and sulfates; metals and arsenic are transported in the true gas flows in combination with organic ligands. The results of field and laboratory studies of the storage state indicate the presence of channels for water migration into underlying horizons, and under favorable conditions, a vapor-gas mixture rises from the surface, carrying metals and arsenic in a volatile, bioavailable form.

Keywords

arsenic; mining and ore waste dumps; electrical resistivity tomography; atmospheric pollution; migration of toxicants; oxidative processes

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Introduction

The storage of ore processing waste on the open surface has entailed the occurrence of large-scale storage facilities, in which the aluminosilicate matrix is to varying degrees enriched with sulfide under-extracted minerals. Tailings storage facilities represent new technogenic ore bodies, in which the processes of substance transformation occur at a rate that is not comparable to geological time. The result of these processes is the formation of water, air, and dust flows that carry many chemical elements beyond the storage areas. The need to monitor and assess the impact of tailings storage facilities on the surrounding environment areas, the biota, and the population is dictated by the high degree of danger that metals and metalloids pose to living organisms.

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An adequate description of technogenic bodies, their composition, structure, zonality, forms of occurrence of potentially toxic elements, and their impact on surrounding areas requires their comprehensive examination of the technogenic bodies characteristics, water and air flows, and an assessment of their impact on natural components and the human body.

One of the effective methods for determining the internal structure of tailings storage facilities, delineating water-saturated horizons and lenses, and identifying migration pathways of drainage flows is electrical exploration, which, when combined with geochemical and hydrochemical methods, significantly increases the efficiency of the research [1]. The possibility of studying the geological environment using electrical exploration methods is based on the dependence of the electromagnetic properties of a substance on its moisture content, temperature, lithological and mineral composition, and the mineralization of pore water [2].

Resistance methods are often used to determine the volumes of old/abandoned tailings dumps [3-5], as well as to represent their internal structure and heterogeneity [6, 7]. Coarse-grained, relatively dry areas and interlayers are characterized by higher resistance than fine- and medium-grained layers that retain moisture [8, 9], which makes it possible to visualize the hydrogeochemical zoning of tailings storage facilities on geoelectric sections [10]. The material in the tailings storage facility typically has higher electrical conductivity than the surrounding environment, which allows to map the boundary between the bedrock and the dams containing stored waste [11, 12].

The authors used the electrical tomography (ET) method, which has proven effective in examining storage facilities and waste dumps in Siberia. When describing the structure of the old trench at the Tuvakobalt plant, electrical resistivity tomography was used, firstly, to identify possible areas where highly mineralized inter-pore solutions could enter the underground horizons, and secondly, to select suitable areas for collecting condensates (the most conductive low-resistance zones).

The geochemistry of oxidative processes in mining and ore industry waste, as well as the migration of toxic elements via drainage flows and dust, is widely discussed in foreign [13, 14] and Russian [15-17] scientific literature. Researchers pay significantly less attention to gas anomalies in adjacent areas and to the transfer of chemical elements in vapor-gas flows from technogenic structures. Recent studies by the scientists of the Trofimuk Institute of Petroleum Geology and Geophysics SB RAS have established that tailings dumps and waste heaps are sources of sulfur-, nitrogen-, and selenium-containing gases that enter the atmosphere [18], in addition, a high concentration of elements in volatile, bioavailable forms is released beyond the boundaries of the tailings dumps [18]. In Barun-Naryn and Zun-Naryn tailings, where waste from the Dzhida tungsten-molybdenum plant is stored, the composition of condensates has been determined, and it has been established that contamination forms above their surfaces, consisting of aerosols of sulfuric acid, aluminum, iron, manganese, zinc, and phosphorus [19]. Condensation moisture collected from the mining waste of the Ozernoe deposit contained high concentrations of many elements (Pb, Zn, Mn, Al, P, Fe, Cu) [20]. Laboratory experiments have proven that elements can be transported in a true gas flow without forming solid aerosol particles. The scale of these processes indicates the need to study them, to determine at least the basic patterns of volatile form formation, and to assess the role of inorganic and biotic interactions in gas generation processes.

One of the most pressing, yet completely misunderstood, issues is determining the forms of element transport in these flows. To clarify this, the authors engaged the experience of volcanological studies, in which conclusions about the predominant forms of element transport are drawn based on the composition of inclusions in quartz tubes placed in fumaroles and gas jets, as well as on sublimates [21, 22]. When capturing gases from fumaroles, researchers are dealing with high-temperature processes that release a large number of various compounds [23, 24]. In this case, the conditions are low-temperature; during the transport of the vapor-gas mixture, significantly smaller volumes of substance are carried away, and detecting deposited metal-containing phases is a challenging task.

The objectives of the work were to determine the internal structure of the technogenic body – the old trench of the Tuvakobalt plant by identifying highly conductive zones and areas through which drainage flows could migrate beyond the storage facility; and to establish the possible forms of transport and deposition of metals and metalloids in a process that has been extremely poorly studied – low-temperature vapour-gas flows originating from technogenic substances.

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Object and methods

Deposit and waste storage facilities. The Khovu-Aksy deposit is located on the left bank of the Elegest River (a left tributary of the Yenisei River), 70 km from its mouth. At the As-mineralization deposit, there are two stages. The first is related to the imposition of arsenide mineralization on carbonate veins along cracks in the form of interspersed, breccia-like and rhythmically-zonal structures. Two main paragenetic groups are distinguished – the schmaltite-safflorite association and the schmaltite-nickeline-rammelsbergite association. The second stage is the sulfide-sulfosalt stage, where the main components are chalcopyrite, pyrite, and tennantite [25, 26]. The deposit has an advanced oxidation zone that reaches a depth of 35-65 m [27]. In hypergene ores, arsenates, hydroxides, and individual minerals of trivalent arsenic (arsenolite, arsenites) have been observed. Arsenide minerals form massive and vein ores. Oxidized minerals occur only in the form of vein-like inclusions. The host rocks have a quartz-carbonate composition, including calcium and magnesium carbonates, silicon oxide, alumina, and skarn minerals (garnet, pyroxenes).

The ore processing technology and the design of the main production facilities of the Tuvakobalt plant were carried out by the Gipronikel Institute. The technological scheme is based on an ammonia-autoclave method for processing arsenic ores, with the final product being a collective Co-Ni-Cu concentrate [28-30]. According to the technological scheme, the pulp was subjected to separation into tailings and a solution of ammonium salts of non-ferrous metals and arsenic. Arsenic was precipitated in the form of an arsenate-magnesium precipitate (cake) – low-soluble compounds $Mg(AsO_4)_2 \cdot nH_2O$, $Mg(NH_4)AsO_4 \cdot nH_2O$.

In the early years of the plant's operation (1970-1975), ore processing waste was transported to a remote, isolated site located 2 km from the plant and stored in trenches (Fig. 1). Later, five pond-type tailings storage facilities (tailings ponds) were set up in close proximity to the process site; waste was pumped into them via pipelines. Unlike the tailings ponds, the trenches do not have an anti-seepage layer and were not planned for reclamation. The work was carried out at trench tailings pond N 3, which is a rectangular area measuring 150×450 m.

Field work. The study of processes at waste storage facilities was carried out using a combination of electrical exploration methods (electrical resistivity tomography), geochemical methods (sampling along the vertical extent of excavated pits), field and laboratory experiments (collecting condensates *in situ*, capturing deposits and films during the condensation of vapor-gas flows), and analytical determinations of the samples.

Electrical resistivity tomography. In 2022, during dry, warm weather, more than 30 electrical resistivity tomography profiles (Fig.2) were carried out on the old trench of the Tuvakobalt plant using Schlumberger and dipole – dipole configurations. Under these conditions, the Schlumberger configuration provided greater depth and a stable signal during sounding. The soundings were carried out using a single coaxial cable with 24 electrodes, an inter-electrode distance of 5 m, and a distance of 15 m between profiles.

Geochemical sampling. To determine the composition of the stored tailings, three prospecting pits (P) with a depth of 0.8-1 m were dug, and visually distinct layers were sampled. The depth of the pits was determined by the level of groundwater that appeared in the faces. Groundwater samples were taken from each pit for analysis. On-site, water samples were filtered through a 0.45 μm filter and acidified with distilled nitric acid to pH ~2.

Condensates of the vapor-gas mixture (CP) were collected at three sections of the trench (Fig.2) in the area of the most conductive zone delineated by electrical resistivity tomography, as well as in a larch forest, 500-1000 m to the southwest of the stored waste. Condensate collection was carried out using a scheme with a Peltier cooler, a detailed description of which is provided in the paper [30]. Condensate samples were collected from the tailings ponds in 2020, and the results are presented in detail in [30]. Following the remediation carried out in 2021 (sealing the tailings ponds surfaces with a geomembrane, a clay layer, and soil, followed by sowing with weedy grasses), condensate was also collected from the surface of the remediated areas in 2022 for comparison.

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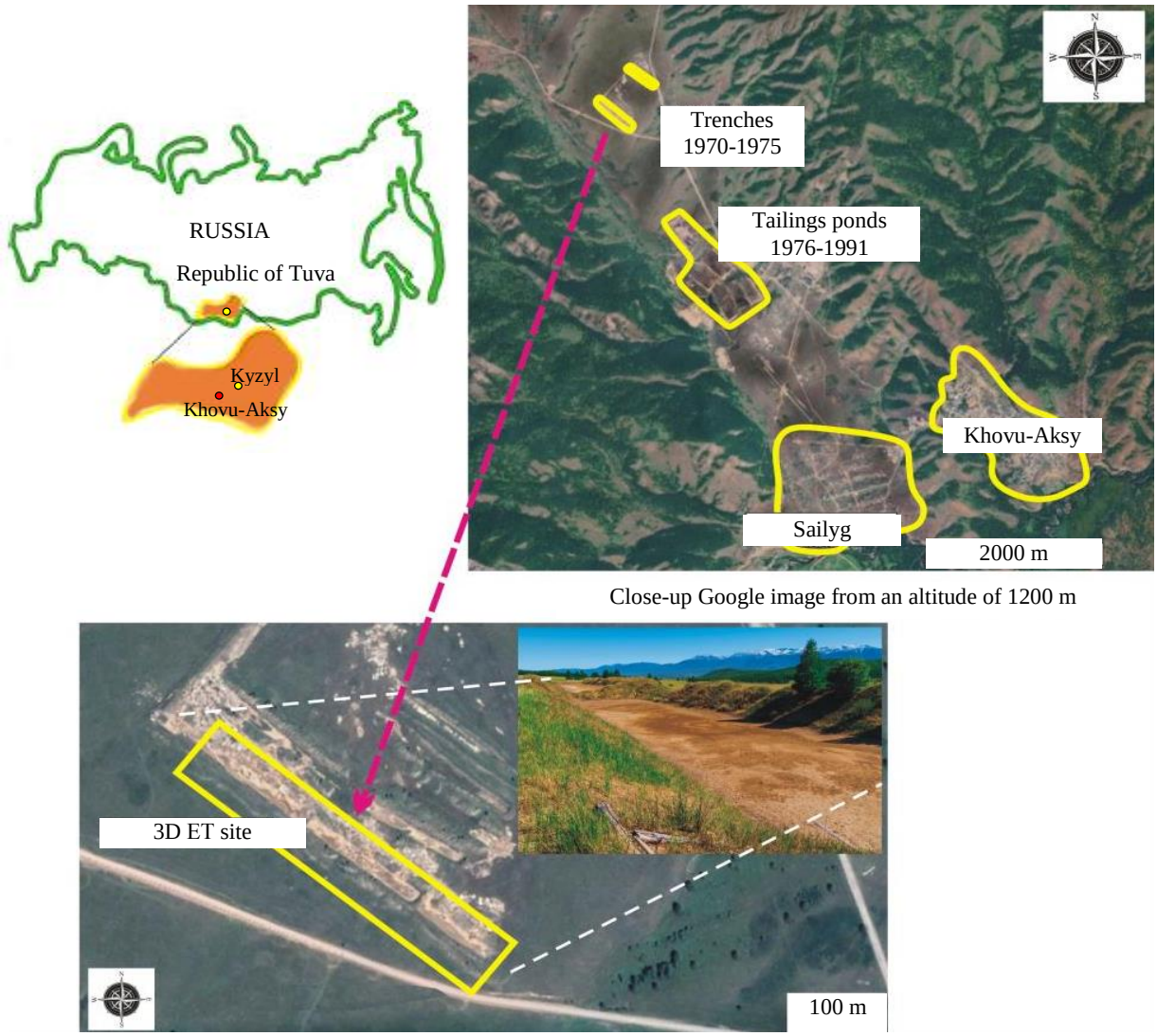


Fig.1. The geographical location of the object under study and the trench

Laboratory analyses and experiments. *Processing of geophysical data.* In 2025, a detailed processing of the obtained electrical tomography data was carried out. All 30 profiles were combined into a single data array using the Res2DInv software, inversion was performed (Res3DInv), and visualization of the array was created (Voxler). As a result, geoelectric maps and sections were obtained, and a 3D model of the trench was built, demonstrating the change in geoelectric zonation.

Substance analyses. Under laboratory conditions, the samples are homogenized and divided into two parts using the quarting method. From the first part, pastes are prepared (the ratio of solid substance to water is 2:1) to determine the acid-base balance of the substance [31], the pH values were measured using a pH thermometer HI 9025 C (HANNA Instruments, USA). The specific electrical conductivity (SEC) in the pastes and solutions was determined using the direct conductometric method with the Cond315i instrument (Wissenschaftlich-Technische Werkstätten GmbH, Germany). It was carried out in the range of 0-500 mS/cm with a relative error of ±0.5 %. The second part of the sample was ground for analysis.

In samples of solid matter, the content of silicate group oxides was determined using X-ray fluorescence analysis (XRF) (Analytical Center of the V.S.Sobolev Institute of Geology and Mineralogy SB RAS) on an ARL-9900XP spectrometer (Thermo Fisher Scientific Ltd, USA) at the Center for Multielemental and Isotope Research SB RAS (analyst N.G.Karmanova).

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Fig.2. Profiling and sampling map of the Tuvakobalt plant old trench
1 – electrical resistivity tomography profile; 2 – pits; 3 – profile number; 4 – location of the "barrel" for collecting condensate; 5 – roll-along electrical resistivity tomography profile

The elemental composition of the tailings was determined by energy dispersive X-ray using synchrotron radiation at the Siberian Center for Synchrotron and Terahertz Radiation at the Institute of Nuclear Physics SB RAS (Novosibirsk) at the station for local and scanning X-ray fluorescence elemental analysis "Complex VEPP-4 – VEPP-2000" (analyst Yu.P.Kolmogorov).

The composition of water samples (condensates, groundwater) was determined using inductively coupled plasma mass spectrometry on a NexION 300D mass spectrometer (PerkinElmer, USA) with a UCT background elimination cell (Problem-Based Research Laboratory of Hydrogeochemistry "Water" of the School of Natural Resources Engineering, Tomsk Polytechnic University). All measurements were taken in three parallel measurements for each element. The standard deviation did not exceed 13 %.

Experiments to determine the forms of element transfer in vapor-gas flows. The experiments used a proven scheme for capturing substances that migrate with vapor-gas flows under low-temperature conditions [32]. For the experiment, samples were taken from different layers of the pits in the trench. The selection was made based on the chemical composition (samples with a relatively high content of arsenic and metals were taken) and the values of the electrical conductivity of the pastes (the difference in the electrical conductivity of the liquid phase indicates a difference in the amount of secondary soluble forms). Approximately 100 g of the sample material was placed in six heat-resistant test tubes. The test tubes were secured in a heat-resistant test tube filled with sand and covered with glass slide covers. The test tube was placed on a stove and heated for 3 days at a temperature of 60 °C. The temperature in the sand and the substance in the test tubes did not exceed 40 °C. A barely visible coating gradually appeared on the glass surfaces. After three days, the glass surfaces were removed and dried in Petri dishes.

The substance formed on the glass surfaces covering the test tubes was studied using a scanning electron microscope (SEM) MIRA 3LMU (Tescan Ltd, Czech Republic) equipped with an INCA Energy 450+ X-Max 80 microanalysis system (Oxford Instruments Ltd). The accelerating voltage was 20 kV, the probe current was 1.6 nA, and the time required to acquire spectra on the samples was 20 s. The main focus was on identifying phases that concentrate metals and arsenic.

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Discussion of results

Composition of the trench substance. The tailings material stored in the trench corresponds in its main composition (silicate group oxides) to the material found in the tailings ponds [30]. The arsenic content in the trench material is approximately the same – 1.5-3.5 wt.%, but the concentrations of metals (Co, Ni, Cu, Zn) are noticeably higher, possibly due to the fact that in the early years of the plant's operation, the technology was not fully optimized and a larger amount of useful components was lost as waste. Here, only the composition of the samples used for the experiment and those in which deposits were found on the glass is presented; however, the material from all three pits is characterized by a fairly stable content of elements (Table 1).

Table 1

Composition of the samples from the trench pits selected for the experiments

Parameter	P-1		P-2		P-3
	10 cm	40 cm	20 cm	40 cm	40 cm
pH of the paste	7.15	7.93	7.86	8.67	8.31
SEC of the paste, μS/cm	6570	4440	4450	244	360
SiO_2, %	34.45	30.54	30.33	37.37	35.23
TiO_2, %	0.37	0.33	0.33	0.41	0.31
Al_2O_3, %	7.22	7.61	7.58	8.25	8.12
Fe_2O_3, %	7.56	7.21	7.42	6.15	6.76
MnO, %	< 0.01	0.27	0.20	0.24	0.23
MgO, %	4.63	5.12	5.28	3.01	3.74
CaO, %	16.53	16.01	15.43	20.60	20.31
Na_2O, %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
K_2O, %	1.65	1.33	1.30	1.73	1.65
P_2O_5, %	0.24	0.15	0.16	0.30	0.30
BaO, %	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_3, %	1.63	1.60	1.56	1.47	1.88
As, %	1.44	3.07	2.68	3.16	2.64
LOI, %	23.86	26.22	26.54	16.42	17.64
Ni, g/t	830	1300	1700	2200	1200
Co, g/t	1100	1200	1500	2300	3500
Cu, g/t	990	1230	1700	1800	1250
Zn, g/t	300	430	560	800	680
V, g/t	35	43	21	44	79
Cr, g/t	60	46	26	34	47
Mo, g/t	< 0.01	1.8	< 0.01	< 0.01	< 0.01
Rb, g/t	9.7	< 0.01	< 0.01	< 0.01	< 0.01
Sr, g/t	190	100	100	120	110

The pH values of the pastes are in the neutral to slightly alkaline range; the electrical conductivity level in three samples (P-1, 10 cm; P-1, 40 cm; P-2, 20 cm) indicates the presence of secondary compounds, which, upon interaction with water, dissolve and form a highly mineralized liquid phase. The newly formed phases in the trench material have been previously identified and described in sufficient detail [33]. In two samples (P-2, 20 cm and P-3, 40 cm), the SEC is an order of magnitude lower.

Geoelectric zoning. Three-dimensional models of the tailings are based on 30 electrical resistivity tomography profiles, the first of which was laid in the reference zone before the start of the trench (Fig.2). This makes it possible to visualize the contrast between the host rocks and the stored tailings. The maps of the electrical resistivity distribution (ERD) are shown down to a depth of 40 m with a step of 10 m (Fig.3, *a*). It is clear that the reference zone has a higher resistance both at the surface and at depth (from 180 to 300 Ohm·m), while the resistivity of the trench itself at the surface does not exceed 250 Ohm·m; at depth, the low-resistance zone (no more than 250 Ohm·m) extends over the entire area. The volume of a substance with a specific electrical resistance < 100 Ohm·m is 1,200,000 m^3, and its mass is about 1.8 million tons, which indicates the scale of potential generation of highly mineralized pore solutions.

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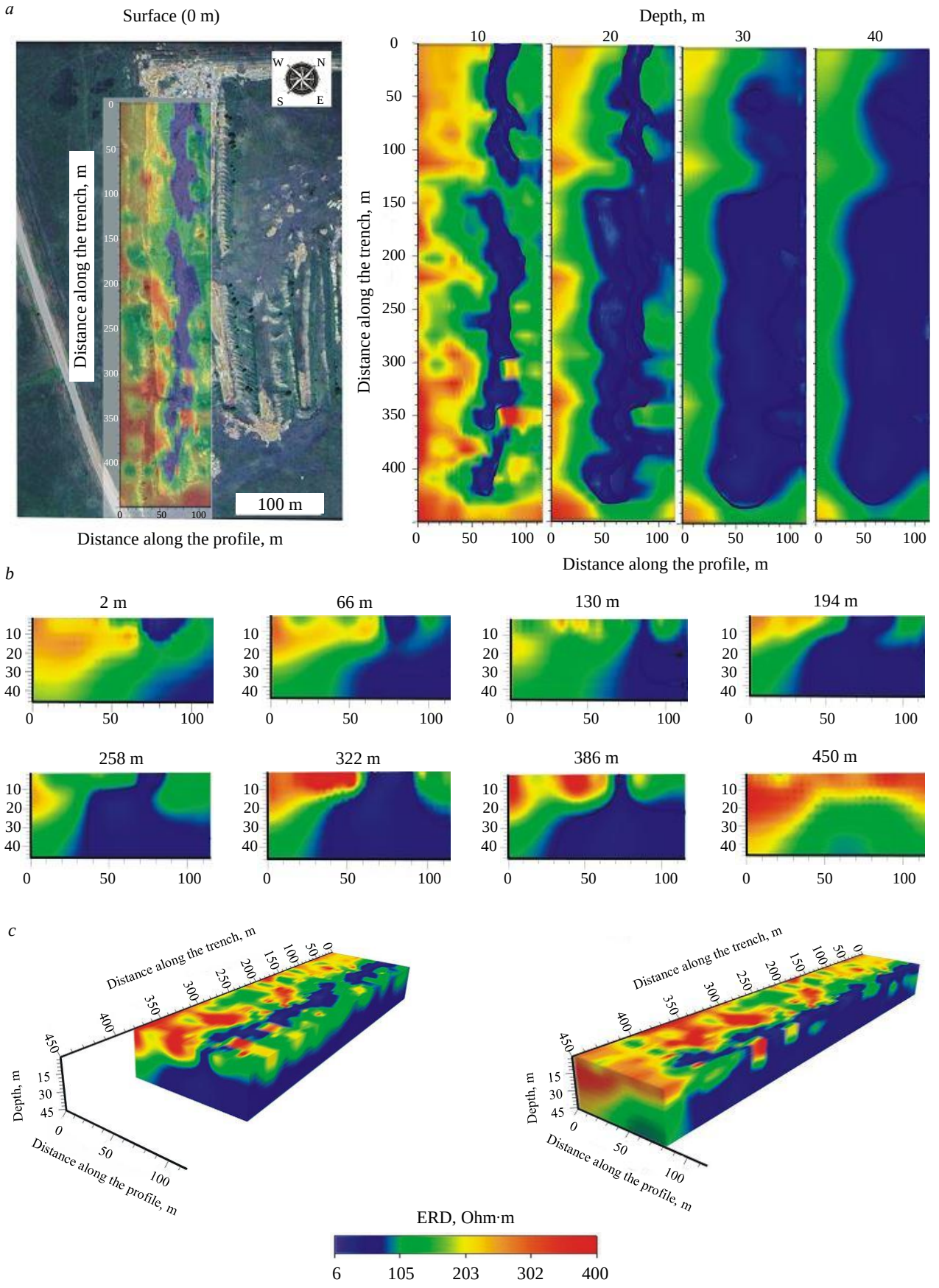


Fig.3. Distribution map of resistivity at different depths (*a*), geoelectric cross-sections at distances along the *Y*-axis (*b*) and 3D models (*c*) of the old trench at the Tuvakobalt plant

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This geoelectric zonality, extending to the maximum sounding depth (48 m), indicates that the highly conductive, moist tailings material continues to exert its influence downward, apparently lacking a physical barrier between the host rocks and the stored tailings. This creates the possibility of solutions penetrating from the trench into the underground horizons.

The geoelectric sections also revealed contrasting zonality (Fig.3, *b*). The three-dimensional data array is divided into sections along the *Y*-axis, running along the body of the trench. Conductive areas (up to 80 Ohm·m) are embedded in the overall tailings layer (150-400 Ohm·m); moreover, in all sections, this zone, which is relatively narrow at the surface, widens towards the bottom of the trench and extends deeper into the ground. Based on the experience of studying tailings storage facilities using electrophysical methods [9-11], low-resistance lenses in areas where the inter-pore space is filled highly mineralized solutions, from which aggressive drainage flows subsequently form.

Regarding this storage facility, it can be stated that in the central part of the trench, which is visually somewhat recessed relative to the sides, the flowing streams stagnate, thereby allowing their composition to develop over a long period. This entails the emergence of the most conductive zones, which is clearly evident in the three-dimensional models (Fig. 3, *c*). Indeed, in the groundwater of the trench exposed in the bottoms of the pits, arsenic concentrations reach high values – 15 mg/l (Table 2), while the content of metals is at a low level due to their binding into secondary phases and deposits from solutions.

Table 2

Content of certain elements in the groundwater of the trench

Element	P-1	P-2	P-3	Element	P-1	P-2	P-3
pH	8.16	7.52	7.9	Mn, μg/l	7.8	15	12
Eh, mV	424	418	396	Al, μg/l	26	22	32
Ca, mg/l	40	170	120	Cu, μg/l	22	36	18
Mg, mg/l	420	250	340	Zn, μg/l	<4	12	10
Na, mg/l	52	38	73	Ni, μg/l	36	48	42
K, mg/l	18	24	22	Co, μg/l	49	32	36
As, mg/l	12	8.5	15	Cr, μg/l	3.7	10	8.6
Fe, μg/l	65	110	86	Sb, μg/l	20	12	5.8

The oxidation of the substance and the redistribution of elements cause their concentration in certain areas with suitable conditions. On the residual grains, secondary phases – readily soluble aqueous arsenates and arsenites are redeposited, as a result of which ~30-40 % of the total arsenic content is in a bioavailable form [33]. Using electrotomography methods, the areas of the storage facilities most susceptible to substance transformation and the accumulation of mobile forms of metals and metalloids are reliably identified. Based on data about the geoelectric structure of the trench, locations for setting a condensate collection system have been selected – on the most moist, highly conductive areas.

Condensate composition. Special attention is paid to the formation of volatile forms of elements, which are determined based on the compositions of condensates. The condensates collected in the trench are compared with the condensates sampled from the tailings ponds before and after reclamation, and with the condensates collected in the forest, 500-1000 m from the tailings ponds (Table 3, Fig.4). Almost all elements in the trench condensates are present in lower concentrations than in the condensates from the reclaimed tailings ponds. The exception is arsenic, the concentrations of which in condensates are stable (21-37 μg/l in tailings ponds and an average of 29 μg/l in the trench). The concentrations of antimony, barium, and rubidium are noticeably higher in the trench condensates. The possibility of element transport by vapor-gas flows under environmental conditions means a high risk of pollution of the ground-level air and the atmosphere. A quantitative assessment of the removal of elements from the surface of tailings ponds has previously been made [30], in accordance with which, during the summer months, approximately 20 kg of As (plus approximately the same amount of Mn, Cu, Ni, Ba, and an order of magnitude more Zn) can be released into the atmosphere in volatile form.

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Table 3

Concentrations of cations and trace elements in condensates collected from the waste storage area of the Tuvakobalt plant

Element	Trench			Ponds*	Reclaimed ponds				Background sites		
	CP-1	CP-2	CP-3	Average	K-2	K-3	K-4	K-5	B-1	B-2	B-3
Ca, mg/l	1.3	1.4	0.91	1.4	0.65	0.5	0.65	0.71	1.3	0.6	0.78
Mg, mg/l	0.034	0.062	0.041	0.24	0.15	0.035	0.088	0.048	0.43	0.33	0.2
Na, mg/l	0.051	0.056	0.1	0.63	0.65	0.15	0.42	0.12	0.67	0.66	0.49
K, mg/l	0.14	0.16	0.27	0.30	0.48	0.27	0.22	0.17	0.16	0.31	0.12
Al, μg/l	5.4	1.1	1.8	7.0	1.3	0.6	1.5	13.6	1.1	1.4	1.2
Mn, μg/l	5.6	13.9	7.0	26	29.2	6.5	6.8	12.2	1.1	4.8	5.8
Cu, μg/l	2.4	5.4	2.4	33	26	12	8.9	14	1.9	12.1	2.1
Zn, μg/l	11	81	32	490	260	150	62	121	94	49	76
Pb, μg/l	n.d.**	n.d.	0.21	0.21	0.43	2.1	0.61	4.8	n.d.	0.46	0.11
Cd, μg/l	3.4	5.1	3.9	1.5	6.3	4.2	3.2	4.4	5.8	1.9	5.6
Co, μg/l	0.5	3.6	0.9	3.2	16.3	1.1	0.9	2.2	0.7	1.6	1.3
Ni, μg/l	3.0	16	5.3	15	17	20	4.2	31	16	8.2	4.7
As, μg/l	20	40	27	36	19	16	17	34	39	21	27
Sb, μg/l	1.2	1.2	1.5	0.41	0.61	1.5	0.54	1.2	0.72	0.70	0.49
Mo, μg/l	0.22	0.15	0.24	0.82	0.002	0.06	0.12	0.16	0.6	0.37	0.3
Ba, μg/l	93	168	180	42	49	235	84	135	70	45	57
Rb, μg/l	0.70	0.76	0.72	0.44	0.59	0.34	0.18	0.20	0.05	0.20	0.044
Sr, μg/l	3.5	5.2	4.3	5.2	4.1	3.0	2.2	3.28	18	11	7.9
Ti, μg/l	0.79	0.74	0.62	0.8	0.47	0.39	0.37	0.53	0.81	0.59	0.56
P, μg/l	6.94	11.38	26.27	56	9.96	9.51	7.13	8.79	10.47	22.88	4.44
Sn, μg/l	n.d.	n.d.	0.04	0.19	n.d.	0.30	n.d.	n.d.	n.d.	n.d.	n.d.

* The average composition of condensates (n = 7) collected from unreclaimed disposal ponds, data from [30].
** n.d. – not determined.

It should be noted that some elements (Zn, Cu, Ni, Cd, Pb, Mo, Sr) in the trench condensates are present in even lower concentrations than in condensates collected in the forest, in a nominally background area. We attribute the increase in the amount of volatile forms of elements in visually "natural" areas to the high activity of bacteria, which play a significant role in the formation of mobile forms of elements and their transport in vapor-gas flows. Conversely, microbial activity is suppressed in the aggressive trench material, and as a result, the formation of volatile forms of many elements occurs with much lower intensity than in soils containing significantly less metals and arsenic, but rich in biota.

When a wide range of elements is detected in the condensate composition, and therefore in the vapour-gas flows, the question arises as to the forms in which metals and metalloids are transported, since many of them are considered inert in geochemical processes.

Forms of transport and deposition. To make well-founded assumptions about the mechanisms and forms of migration of metals and metalloids in the composition of emanations, a series of experiments was conducted to collect deposits from vapor-gas flows originating from technogenic substances onto glass slides.

Examination of the obtained specimens using SEM showed that, as a result of the experiments, shapeless deposits and films formed on the microscope

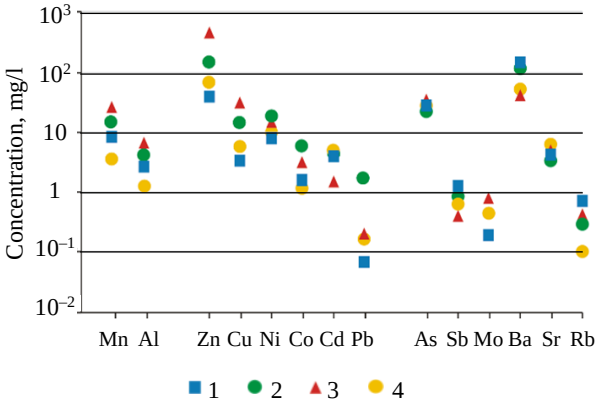


Fig.4. Comparison of element concentrations in condensates collected from different areas of the technogenic-natural system of waste storage facilities

1 – trench; 2 – reclaimed tailings ponds; 3 – tailings ponds before reclamation; 4 – background

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slides (Fig.5, *a-f*), in rare cases, needle-like intergrowths (Fig.5, *g*, *h*), tabular formations (Fig.5, *i*). The sizes of these new formations are usually extremely small, therefore, when determining the composition of the material, the possibility of their "burning" through with the capture of the substrate, i.e. glass slide, was taken into account. In this case, new formations were captured on a sodium-calcium silicate glass slide, which contained, wt.%: Si 33.4; Al 0.6; Mg 2.4; Ca 5.9; Na 9.0; K 0.4. When assessing the qualitative composition of newly formed compounds, the presence of elements characteristic of glass was not taken into account, although in some cases there were quite "thick" films, the analysis of which visually showed their own composition (Fig.5, *d*, *e*). In this study, we will examine elements that were not present in the glass composition or were present in significantly lower concentrations than in the samples.

The newly formed precipitates contain a range of chemical elements, such as Ti, Cr, Mn, Ba, Co, Ni, Cu, Zn, Sn, Mo, As, P, S, Cl, and F. Their concentrations are significant, ranging from fractions to tens of wt.% (Fig.5), which eliminates the possibility of error in the determination. The chemical composition of the new formations clearly indicates the following, wt.%: Mn 0.2-1.5; Zn 0.4-7.7;

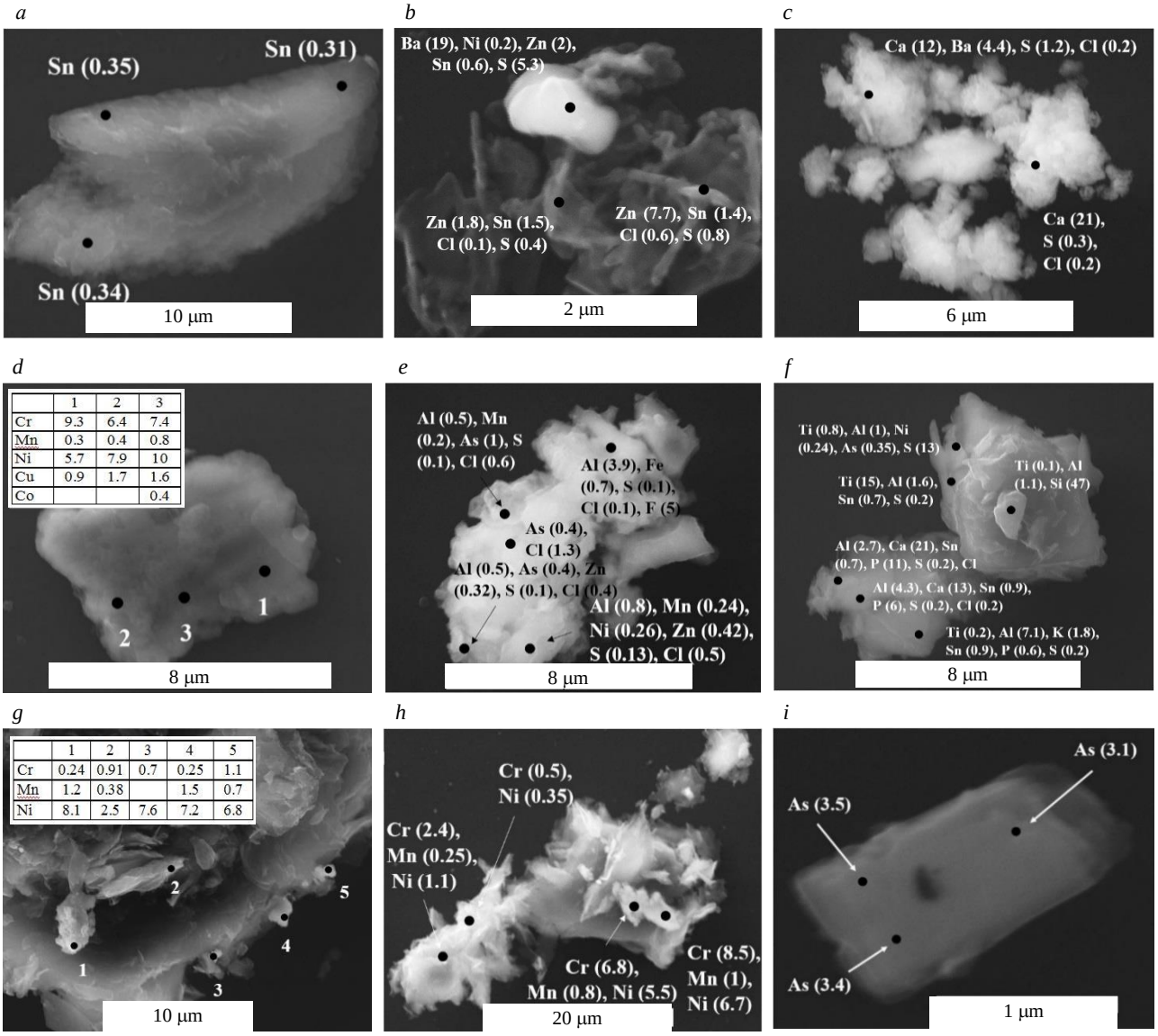


Fig.5. Aggregates and phases deposited on the glass slide in the experiment: *a* – feathery formation (only the Sn content was reliably determined, the content of the remaining components was significantly lower than in the glass); *b* – an aggregate of lamellar secretions with a concentrator of Ba and metals (Ni, Zn); *c* – an aggregate of shapeless secretions Ca-, Ba-containing compounds; *d* – relatively homogeneous separation-metal concentrator (Mn, Ni, Cr, Cu); *e-h* – aggregates of cloudy and tabular formations of complex composition; *i* – tabular As-containing formation.
The content of elements in weight percentages is provided in parentheses and tables

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Cu 1.6-1.7; Co 0.4; Ni 0.2-10.1; As 0.4-3.5; Ba 4.4-18.9; P 0.6-10.6. These are elements whose concentrations in condensates from different areas of the storage facilities may exceed 10 μg/l (Table 3, see Fig.4). In addition, the following compositions were determined, wt.%: Ti 0.2-15.0; Cr 0.2-8.5; Mo 0.5-0.9; Sn 0.3-10.4; S 0.4-1.34; Cl 0.1-1.33; F 5.0. In some cases, the concentrations of Al, Ca, and K in the neoplasms are several times higher than those in the glass slide, which indicates their involvement in the composition of these secretions (Fig.5, *c*, *e*, *f*).

The ionic composition of the detected deposits is difficult to determine due to their small size. It is assumed that the detected deposits and films consist of organic components in which metals and metalloids are deposited, most likely in the form of compounds with organic anions – formates, acetates, and oxalates. These anions are quite often found in condensates, and thermodynamic modeling has shown the possibility of migration of chemical elements in organic complexes. The presence of chlorine and sulfur in the composition of the secretions indicates the possible involvement of chlorides and sulfates.

The above is supported by the fact that in some cases, when analyzing micron-scale formations that are "burned through" with the substrate being captured, only the elements of the glass slides are detected, along with a small amount of elements that are not typical for glass, for example, Sn (Fig.5, *a*); Zn, Sn, S, Cl (Fig.5, *b*); Ba, S, Cl (Fig.5, *c*); As (Fig.5, *i*). In two cases, fairly large formations were encountered in which the presence of virtually no elements was detected; possibly, these are hydrocarbon compounds (Fig.5, *g*, *h*). By comparing the composition of condensates collected *in situ* in the trench with the composition of the deposited films, we can draw a well-founded conclusion that the vapor-gas flows from the anthropogenic substance consist, in addition to water vapor, of various organic compounds formed as a result of biogenic transformations of the substance. These flows are capable of carrying many chemical elements into the atmosphere in a bioavailable form (in compounds with organic ligands).

The results of studying the deposits from the trench substance on the microscope glass slides correlate well with the results of previous experiments with erythrite [33], in which shapeless amorphous aggregates containing inclusions of metals and arsenic in the form of compounds of unknown composition were also obtained.

A comprehensive survey of the trench revealed the existence of two pathways through which technogenic substances enter the environment: the seepage of highly mineralized water into underground horizons, which was established based on the geoelectric structure and the extension of a highly conductive zone significantly below 40 m; and the removal of many chemical elements by vapor-gas flows in the form of mobile complexes capable of migrating in the volatile phase.

It should be emphasized that the presence of vapor-gas flows from sulfide tailings containing many metals and metalloids raises the problem of their impact on living organisms, especially humans, since the elements found in their composition are in an ionic, bioavailable form, as demonstrated by the study of sediments and deposits. The interaction of biological objects with metals and metalloids entails a dual effect on living organisms: some act as trace elements, fulfilling a physiological role (Cu, Zn, Se), while others are xenobiotics (Hg, Ag, As).

Unlike dust fractions of varying particle size, vapors can penetrate the respiratory regions of the lungs, damaging the epithelium responsible for gas exchange, and are absorbed into the bloodstream at a rate comparable to direct parenteral administration. The combination of these factors significantly increases the biological availability and toxic effects, which are difficult to predict when the substances contained in the condensate act together.

It is obvious that the toxic effects of the combined action of mixtures of heavy metals in biological systems are more diverse, and some of them are not yet known; however, all of them entail the disruption of cellular respiration and then to necrosis or apoptosis, depending on the duration of exposure. The development of adequate models that allow assessing the level of impact of a mixture of toxins on biological objects and understanding the mechanism of their combined effects is the next step in studying the flow of substances from sulfide dumps and other technogenic facilities.

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Conclusion

Using electrical resistivity tomography, maps, cross-sections and 3D geoelectric models of the trench containing the waste from the Tuvakobalt plant were made. It was shown that the central part of the trench is composed of a highly conductive substance, the inter-pore waters of which are highly mineralized solutions with an arsenic content of up to 15 mg/l. The low-resistance (highly conductive) zone, relatively narrow at the surface (~20-30 m), gradually widens towards the bottom (at a depth of 40 m, its width is more than 100 m) and continues beyond the boundaries of the constructed model. The zone extends deeper than 48 m, which indicates the penetration of inter-pore solutions into the groundwater horizons.

The composition of the condensates of the vapor-gas mixture collected from highly conductive sections of the trench indicates the possibility of migration of a wide range of elements with vapor-gas flows under environmental conditions and their release into the atmosphere. These results indicate the existence of a powerful "breathing" process of tailings storage facilities and dumps, which has been extremely poorly studied but exerts a strong influence on the composition of the atmosphere and surface air, and therefore on the health of the population living nearby. At the same time, the concentrations of elements in condensates collected from the trench are in some cases lower than in condensates collected nearby in a larch forest and on reclaimed disposal sites. We attribute the observed facts to the low activity of the bacterial community in the aggressive environment of the trench, which is the main factor in the formation of volatile forms of metals and metalloids.

The deposits and films on the glass, formed during the deposition of vapor-gas flows in the experiment, consist mainly of amorphous matter consisting of organic compounds. Areas enriched with typomorphic metals and arsenic have been detected, with no visible boundaries or isolated grains. The obtained results indicate that chemical elements are transferred not in the form of separate particles, but in a true gas flow in combination with organic anions (in rare cases, with chlorides and sulfates), which determines their bioavailability and danger to living organisms.

Through a comprehensive survey of the waste storage facility at the Tuvakobalt plant, the pathways for the migration of technogenic substances via water flows (penetration of highly mineralized solutions into underground horizons) and vapor-gas flows (entry of elements in volatile form into the surface layer of the atmosphere) were identified. Laboratory experiments determined the most likely forms of transfer of metals and metalloids in the gaseous phase.

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