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Features of Soil Pollution in the Region of Storage of the Wastes from Pyrometallurgical Zinc Extraction at the Belovo Zinc Plant

O. L. GASKOVA¹, S. B. BORTNIKOVA², V. G. KABANNIK¹ and S. P. NOVIKOVA¹

¹*Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)*

E-mail: gaskova@igm.nsc.ru

²*Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Pr. Koptyuga 3, Novosibirsk 630090 (Russia)*

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Abstract

Total heavy metal content in the soil in the region of the storage of wastes from pyrometallurgical works (Belovo Zinc Plant) was investigated. It was established that the high level of zinc and copper pollution is conserved also after the plant stops its operation. The maximal pollution was detected in the direct vicinity of clinker mound; it exceeds the background values for zinc by a factor of 60. At a distance of 300 m pollution decreases (17-fold excess over the background value) but it can be followed even at a distance of 5 km from the Belovo Zinc Plant (5-fold level). The fraction of mobile forms of a number of elements extracted through stepwise leaching was determined. For the soil with the heaviest pollution (pH of water extract 5.58), the fraction of mobile zinc forms exceeds the MPC by a factor of 66, copper by a factor of 2, manganese is below the normal value, mobile forms of nickel were not detected. Thus obtained row depicts the geoecological condition of soil in the region of waste storage of the Belovo Zinc Plant.

Key words: pyrometallurgy, zinc, copper, soil pollution, step-by-step leaching, geoecology

INTRODUCTION

Average concentrations of heavy metals in soil has increased during the recent decades due to an increase in the contribution from industry, transport and agriculture. Being a note of ecological relations holding together the atmosphere, hydrosphere, lithosphere and living substance, soil is considered as a central link for the circulation of metals in the environment. Along with mineral fuel combustion, the most important route of technogenic aerial scattering of metals is their emission into the atmosphere from high-temperature technological processes, in particular from pyrometallurgical method of extraction and refinement of non-ferrous metals. Heavy metals are present in the

emissions of metallurgic works mainly in the form of poorly soluble compounds (silicate cakes, oxides and alloys) that are later transformed in organogenic and mineral soils. At the same time, at the territory of plants and the nearest residential areas inevitable suppliers of soil pollution are industrial wastes that are accumulated as dumps and drainage wastes.

Metals are transported in the atmosphere mainly in the form of aerosol (particle size varies from 1 nm to several tenths of a millimetre), while their dispersion is controlled by particle size (fractionation) during changes in the activity of atmospheric phenomena. In the case under consideration, either fine particles less than 1 µm in size carried through the gas phase are transported (gas particle conversion) or larg-

er particles (larger than 1 μm) coming directly from ash dust and removed from the surface of dumps. Removal of fine technogenic particles from the atmosphere and their subsequent sedimentation are especially efficiently promoted by the humid state of the atmosphere (rain, snow, mist). In particular, the propagation of heavy metals Pb, Cd, Cu, and Zn is connected with these processes [1].

The goal of the present study was to establish the effect of the industrial cycle and stored wastes on the composition of soil at the adjacent territories around the zinc plant in Belovo (Kemerovo Region). In agreement with the strategy of field testing (GOST P53123–2008), the stage of preliminary investigation was carried out; a conclusion concerning the possibility of pollution was drawn and assumptions on the nature, place and distribution of pollution were put forward.

OBJECTS AND METHODS OF STUDIES

Belovo city is situated in the Kuznetsk depression in the basin of the Inya River (a tributary of the Ob River). The major water artery is the Bachat River. The landscape of the region is plain, weakly undulating, which is characteristic of the Kuznetsk forest-steppe. The whole territory of the Kuznetsk depression is characterized by the same type of soil-forming rocks which are represented by carbonate, light-brown and brown-yellow loess-like muddy and dusty heavy clay loam or dusty-muddy light clay. The thickness of these loess-like deposits in different parts of the Kuznetsk depression varies from 15 to 20 m. According to the data of [2], the soil of Belovo is leached chernozem (about 70 %), common and podzolized (subtypes) medium-humus medium-thick kinds, loamy and heavy-loamy varieties on loess-like loamy sediments.

The source of soil pollution is the Belovo Zinc Plant (BZP); it started production in 1931 and had been stably producing about 10 thousand t of zinc per year and up to 30 thousand t of sulphuric acid. In middle 1990s the plant was closed. The production at the BZP was aimed at pyrometallurgical processing of blende concentrate from the Salair lead and zinc concen-

trating mill. At present about 1 million t of wastes are stored at the territory of BZP as dumps of slag and ash; spontaneous combustion occurs there from time to time. At the east side the dump is limited by the drainage trench and the adjacent settling bog. According to the design documentation, water from the bog should enter the Bachat through additional drainage wells providing purification [3]. Assumed mechanism of soil pollution is transfer from the dump surface and propagation in the form of aerosol and larger particles under atmospheric phenomena (the contribution from the smoke stack of the plant is unclear). Moreover, slope to the river implies soil washout by contaminated water from the bog during spring flood and seasonal rising of ground water polluted with heavy metals (illuviation of solutions). Penetration of highly mineralized solutions into the horizon of ground water under the bog was established by us using the frequency induction and vertical electrical sounding [4].

Soil samples were taken at three areas with assumed non-uniform pollution at a distance of 5 km from the BZP (reference version, sample No. 1) due to the technogenic local emission of elements; at a distance of 20 m from the foot of the clinker dump at the leeward side near the residential houses and drinking well (sample No. 2), and at the area behind the settlement bog near the Bachat at a distance of about 300 m from the dump in the direction of prevailing south-western wind (sample No. 3). The samples typical for the given sampling sites were taken, corresponding to the upper horizon 8–10 cm thick. The united sample was composed by mixing five point samples collected at the same test ground. The mass of the united sample was not less than 1 kg. Visible parts of plants were preliminarily removed from the samples. Soil sampling time is unimportant because the technogenic emissions affected the soil during several decades.

It may be assumed on the basis of the general structure of chernozem soil that samples Nos. 1 and 2 relate to horizon A (humus horizon, uniform dark-gray colour), while sample No. 3 relates to horizon AB (humus transient horizon) where uniform dark-gray colour gets weaker, brownish or sandy colour occurs, and the structure is clearly cloddy.

The chemical composition of the concentrates and wastes of the BZP, their mineralogy and hydrochemistry of drainage wastes (in drainage solutions in the trench and settler) were described in detail in [3–5]. The clinker substance is represented mainly by silicate glass (15–25 % SiO_2) with inclusions of feldspar, olivine, spinel, different alloys with varied Fe–Cu–Zn–S ratios. The veins of native copper were found, along with a small amount of conserved copper sulphides, up to 20 % coke dust which was added into the technological process (subquality sulphuric acid was also poured into the dump); iron oxides, willemite Zn_2SiO_4 and zincite ZnO were also identified. Sulphates of Fe, Zn and Cu are present in the inner, weakly affected horizons of wastes [5]. The metals are non-uniformly distributed in the wastes; their concentrations vary within the ranges 0.3–8 % for copper, 0.7–15 % for zinc, 3–22 % for iron, and 4–6 % for CaO. Chemical weathering manifests itself as the abundance of secondary minerals on dump surface. Intense drainage explains the saturated blue colour of the solutions in the trench and white, blue, greenish colour of bottom sediments and bank deposits of the boggy neighbouring territory. Hydrogen secondary compounds are mainly represented by aquatic copper sulphates and hydroxyl sulphates. Copper concentration in the upper layer of the deposits reaches 27 %, which is 60 times higher than its content in the most concentrated drainage solutions, while the corresponding excess for zinc reaches only 9 times. Iron concentra-

tions in lower lying ochre-like sediments reaches 20 %; increased concentrations of Sb, As, Cr, Ni are observed. The settlement bog contains, along with sulphate compounds, also carbonates (malachite, azurite, rosasite). Among zinc minerals (with copper), only rosasite $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$ and shulenbergite $(\text{Cu,Zn})_7(\text{SO}_4)_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O}$ were identified.

The data on the composition of drainage solutions in summer and in winter in 2005 and 2008 for several elements that were later determined in soils are listed in Table 1. The results of the analysis of water samples from the Bachat River (Table 2) in which the waste water from settler flows bringing contamination into soil and well water near sampling sites (samples Nos. 2 and 3, respectively) is of interest, too.

Drainage solutions in the trench and settler relate to technogenic type of moderately acidic sulphate water in which Zn and Cu, similarly to Ca, are macrocomponents. Previously, when clinker dumps were burning intensively from inside, the acidity of drainage solutions reached pH 2.5, while zinc concentration in it was comparable with the data for water samples taken from under ice in February 2008. Though settlers are built for additional purification of water through the deposition of a part of metals into the solid phase, the concentrations of dissolved Zn, Cd and Cu in them often exceed the concentrations of these metals in drainage trench around the dump or in priming tailing dump. This was demonstrated by us for also for other objects [6]. In the waste

TABLE 1

Composition of drainage solutions from the dump of clinkers of the BZP ((drainage) and settler

Elements	June 2005		February 2008	
	Drainage	Settler	Drainage	Settler
pH	5.8	4.81	3.30	3.4
SO_4^{2-}	1.7	3.7	20	23
Ca	0.25	0.51	0.28	0.39
Cu	0.15	0.46	3.0	2.5
Zn	0.15	0.37	1.7	1.6
Cd	0.0015	0.0042	0.0092	0.0094
Mn	0.0046	0.022	0.083	0.075
Fe	0.000018	0.0004	0.015	0.0088
Ni	0.0012	0.0045	0.021	0.018

TABLE 2

Composition of waste water flowing into the Bachat River and water in drinking wells near clinkers, mg/L

Elements	Water flowing into the Bachat		the Bachat		Water from wells		MPC*
	Surface	Drainage along pipe	30 m upstream of clinkers	300 m down stream of clinkers	100 m from the dump	150 m from the dump	
Cu	0.19	0.32	0.09	0.18	0.17	0.01	1
Zn	6.80	11.00	0.76	3.80	0.76	0.10	5
Fe	1.00	2.70	0.40	5.20	0.12	n. d.	0.3
Cd	0.230	0.430	0.005	0.091	0.030	0.003	0.001

Note. n. d. – not determined.

* According to the requirements of SanPiN 2.1.4.1074–01.

water flowing into the Bachat, the level of maximum permissible concentrations for drinking water was exceeded for zinc and its satellite element cadmium (incorporated into blende ZnS); on this ground, it was assumed that eroded clay soil near the river is contaminated with hydrogeneous flows. Only cadmium at a level exceeding the MPC (which is extremely low) was detected in drinking water from the well which is the closest to the dump (see Table 2).

Two approaches are used to choose components for determination in soil and in water: test sampling and complete sampling. Test sampling is characteristic of the stage of preliminary examination in the case when contaminating substances are known and the main goal of investigation is determination of soil pollution degree. The information on the total content of elements is necessary for establishment of technogenic anomalies and for evaluation of the capacity of geochemical barriers. At the same time, to estimate toxicity, it is necessary to know geochemical forms of element occurrence in solid phases because it is the mobile phases that determine the scale of the income of toxic elements from soil into plants and in drinking water. To estimate the amount of pollutants bound by the soil, and especially the strength of binding, we carried out stepwise leaching.

For the preliminary investigation of soil pollution around the BZP, we chose Zn and Cu as the major pollutants, Fe, Mn and Ca as major natural/technogenic cations (during stepwise leaching, correlations of the forms of heavy metal (HM) occurrence with the phases of the latter cations are revealed); we also followed

Ni, an accompanying heavy metal which only very rarely forms its own solid phases in the products of BZP clinker leaching, for example rammelsbergite NiAs₂. Manganese belongs to siderophiles, however, according to the data of [7], sufficient correlation between Fe and Mn content is absent from many soil objects. It appeared interesting to check whether this statement is correct. Moreover, according to GOST 17.4.1.02–83, the listed HM belong to different classes according to the degree of danger: Zn – highly dangerous, Ni and Cu – moderately dangerous, Mn and Fe – low-hazard.

In the laboratory, soil samples were sieved through the mesh 2 mm [1, 8]. It is known that thorough attrition causes changes of the forms of metal occurrence because promotes the transition of metals into more mobile fractions and readsorption at the first stages of sequential leaching depending on the initial characteristics of soil. All determinations were carried out with air-dry samples. The concentration of organic carbon C_{org} was determined using the classical Tyurin's method, hygroscopic water and actual acidity (pH of water extract for the S/L = 20 g : 50 cm³) were determined according to ISO 11465 standards (Table 3). Chemical decomposition of samples was carried out to determine the total HM concentration in soil [8]: 50 cm³ of nitric acid (1 : 1) was added to the weighted portions of 10 and 5 g (the latter was used to provide control of the accuracy of results); boiling for 10 min was carried out, then 10 cm³ of concentrated hydrogen peroxide was added drop by drop to the sample. After cooling, the suspension was filtered; 10 cm³ of 1 M

TABLE 3

Hygroscopic water, organic carbon (C_{org}) content and actual acidity of soil samples under study

Parameters	Soil samples		
	No. 1	No. 2	No. 3
Hygroscopic water, mass %	5.87	5.38	3.19
C_{org} , mass %	5.81	5.77	1.66
pH of water extract	7.80	5.58	8.26
Soil structure (sieved)	Grained	Grained	Grained with clay fraction

HNO_3 solution was added to precipitate, and boiled for 30 min. Distilled water was added till the required volume (250 cm^3).

The forms of metal occurrence in soil were determined by means of selective extraction (stepwise leaching), which allows us to estimate the amounts of metals in different geochemical fractions [9]. According to the data reported in [9], metals in the water extract of soil (that is, water-related metals) are the most dangerous and aggressive fraction. In this connection, before selective extraction according to the procedure described in [9], we obtained the aqueous extract (fraction No. 1). Then, in order to extract exchange forms, 1 g of the sample was treated with 8 mL of 1 M $MgCl_2$ solution (pH 7.0) at room temperature for 1 h (fraction No. 2). Carbonate-bound forms were extracted during 5 h with 8 mL of 1 M CH_3COONa solution acidified with acetic acid to pH 5 (fraction No. 3). The forms bound with Fe and Mn oxides after the separation of carbonate forms were treated with 20 mL of 0.04 M $NH_2OH-HCl$ solution in 25 % (by volume) CH_3COOH at 96 °C for 6 h (fraction No. 4). Residual concentrations of metals were determined as the difference between the total content and the concentrations determined in four above-listed fractions (fraction No. 5). There is an opinion that if the major amount of a metal is present in the residual fraction, the situation is more satisfactory from the geocological viewpoint than it appears on the basis of total HM content.

According to the requirements of GOST P 50683-94 and 50686-94, ammonium acetate buffer with pH 4.8 is used to determine the mobile forms of HM (these values are standard-

ized by the Hygienic standards GN 2.1.7.2041-06). According to [10], the content of mobile forms corresponds to the sum of copper and zinc concentrations in the ion exchange and carbonate fractions of selective extraction. However, according to [1], only water-soluble and exchange forms relate to mobile ones. As a rule, extraction with acids is used to determine mobile HM forms in soils under technogenic pollution: mobile acid-soluble forms of Cu, Zn, Ni, Cd, and Pb are determined in extracts with 1 M HNO_3 or 1 M HCl [8]. In the present work, to calculate the total amount of HM in the mobile form (MF) we summed up fractions No. 1 (water-soluble part of humus, Na, Mg, Ca chlorides, Na sulphates etc.), Nos. 2 and 3 (see Tables 3 and 4). The necessity to extract fraction No. 4 (HM bound with Fe and Mn oxides) is due to the fact that adsorption properties of the oxides are essentially dependent on the changes of solution pH decreasing with an increase in acidity.

Determination of metal content in solutions was carried out by means of atomic absorption spectrometry; three parallel samples were analyzed; the error of determination is $\leq 5\%$.

RESULTS AND DISCUSSION

One can see in the data shown in Table 3 that the soil sample No. 3 sharply differs from other samples in C_{org} content: the colour and structure of this sample also point to the low concentration of organic carbon. The amount of hygroscopic water absorbed by the dry ground from air depends on the mechanical composition of soil and relative humidity of the air. On the one hand, soil rich in organic

matter is able to retain larger amount of water (samples Nos. 1 and 2), on the other hand, soil depleted of organics (sample No. 3) but containing increased portion of the fine fraction (clay particles) also may possess this property, provided that the exchange capacity of the absorbing soil complex (ASS) is not occupied by the cations of technogenic metals.

Determining actual acidity, we discovered that the maximal acidity (pH 5.58) is characteristic of soil sample taken at a distance of 20 m from clinkers (sample No. 2); the reference sample (No. 1) has a neutral reaction, while sample No. 3 is weakly alkaline, which is maximally favourable for the accumulation of cations. It should be stressed that pH 8.26 (sample No. 3) corresponds to calcium stability under the atmospheric pressure of carbon dioxide which is equal to $10^{-3.5}$ atm. A noticeable contribution into acidification of soil sample No. 1 is made by the acid surface and drainage water from clinker dump.

The data on total HM content in soil under investigation are presented in Table 4, along with the clarkes in soil of the world according to Vinogradov, background total HM content

in the soil of the southern part of West Siberia, standardized MPC of the mobile forms of HM and the concentrations of HM in mobile forms. According to [11], soil kinds may be grouped with respect to HM content on the basis of their Clarke content. For example, one Clarke corresponds to the first (background) group in pollution level; 1–2 Clarkes – the second group, 2–4 – the third group *etc.* For sample No. 1 taken at a distance of 5 km from the BZP, a five-fold excess of the regional background zinc content was detected. The situation with other metals is satisfactory. The average total Zn content in loess-like loam soil in West Siberia (petrological background, that is, soil-forming rocks) is 9.2 mg/100 g [12], so technogenic soil pollution is assumed; its nature has not been revealed yet. According to [13], the background territory for pollution with gaseous emissions from the plants of nonferrous metallurgy starts at a distance of 20–50 km from the source, but the probability of changes of both the soil-forming rocks and the chemical composition of the soil is very high for such a long distance. For this reason, it is undesirable to use the territories situated at a long distance

TABLE 4

Total content of heavy metals and their concentrations in the mobile fraction in soil samples in comparison with the Clarke in world soil and MPC_{MF}

Sample No.	Weighted portion, g	Total content of metal, mg/100 g				
		Cu	Zn	Mn	Fe	Ni
1	10.06	4.87	39.76	62.62	2544.73	4.08
2	10.08	20.04	470.93	56.55	2145.83	3.67
3	10.10	15.15	134.75	40.59	1950.50	3.86
1	5.14	5.06	39.49	59.92	2607.00	5.25
2	5.22	21.84	463.98	61.49	2203.07	4.79
3	5.00	15.20	127.00	41.60	2088.00	5.40
1 (MF)	1.00	0.19	2.68	0.76	0.21	n/d
2 (MF)	1.00	0.53	153.0	3.24	0.50	n/d
3 (MF)	1.00	0.97	17.47	5.63	0.45	n/d
Clarke*	–	2	5	85	n/d	4
Background [12]	–	3	92	65	n/d	4
MPC_{MF}^{**}	–	0.3	23	14	n/d	0.4

Note. n/d – no data.

* According to Vinogradov.

** MPC_{MF} is the MPC of the mobile form of the element extracted by the ammonium acetate buffer (pH 4.8) according to hygienic standards GN 2.1.7.2041(42)–06.

from pollution source as a background. In addition, there is a problem with establishing MOPC of HM in soil (not MPC of mobile forms, MPC_{MF}). To estimate the degree of soil pollution with these metals, an empirical dependence is used. According to this dependence, MPC exceeds background levels by a factor of 3–5 [14]. Thus obtained MPC values calculated as a product of the background level and the average factor (4) are then compared with the actual HM concentrations in polluted soil [14]. Thus calculated MPC values are somewhat exceeded in the reference sample No. 1. The concentrations of Zn and Cu in soil near the clinkers of the metallurgic plant (sample No. 2) are higher in comparison with the same data for the reference sample No. 1 by a factor of 12 and 4, respectively. The concentrations of both metals in soil near the Bachat River (sample No. 3) are only 3 times higher than those in the reference sample. The ratio Zn/Cu for three samples was 8, 22.4 and 8.6, respectively (background ones: 2.5). So, judging from the total metal content, soil is polluted mainly with zinc.

As we have mentioned above, it is the amount of the mobile HM forms that depicts their toxic action on the environment and is normalized by the MPC_{MF} level. According to [11], the solubility of HM from technogenic emissions is 1.5–2 times higher than the solubility of the compounds of these metals in soil itself, where these metals are present mainly as silicates. In addition, the solubility of Ni-, Mn- and Zn-containing compounds is much higher than the solubility of Cr-, Pb- and Cu-containing compounds. However, these properties vary strongly depending on the composition of the metallurgic raw material and the technology. According to the data shown in Table 4, Zn content in soil under technogenic pollution exceeds the standard MPC_{MF} substantially, especially in the case of sample No. 2 (pH 5.58) – by a factor of 66.5. For soil sample taken near the river (sample No. 2), zinc content is 7.5 times higher than the MPC, while no excess was detected in the reference sample. This is due exclusively to the distribution of the flow of surface and drainage water from clinker dumps. As a consequence, MPC of cadmium (admixture of Cd in ZnS) is observed in drinking water from the well which is the nearest to

the dump. High MPC is characteristic of zinc (5 mg/L), but according to many reference data its sulphates and chlorides are most toxic, while the presence of copper and nickel ions enhances this effect. There is little copper in the mobile fraction, which is connected with relative stability of its secondary compounds and high organophilic properties of copper in the upper soil horizons, which is determined by the large constants of formation of copper complexes with many organic ligands [15]. Unlike for the data reported in [11], the amounts of Mn and Ni in the region of waste storage of BZP are lower than standard MPC_{MF} .

A more detailed comparative analysis of the data on element content in five soil fractions is presented in Table 5. One can see that Ca, Mg^{2+} , H^+ , Al^{3+} , Na^+ are present in sufficient amounts almost in all the samples determining the physicochemical properties of soil. Judging from Ca content in water-soluble fraction of samples, technogenic soils are distinguished by the increased concentration of this element – up to 424 mg/100 g (clinker substance contains 4–6 % CaO). Usually about 90 % of the total amount of exchange-absorbed cations is accounted for by Ca^{2+} and Mg^{2+} ; a clear correlation between Ca content in soil and soil acidity is observed. Indeed, soil sample No. 2 with pH of water extract 5.81 contains 85.2 mg/100 g calcium in the exchangeable form, while sample No. 3 with pH 8.26 contains almost 12 times more (993.2 mg/100 g). This confirms the assumption concerning filling ASS in technogenesis zone. Nevertheless, the minimal amount of calcium is bound with carbonates in sample No. 3, which contradicts the above statement. However, if we take into account the fact that fraction No. 4 (metals bound with Fe and Mn hydroxides) of sample No. 3 calcium content is 18 times higher than that in the similar fraction of reference sample No. 1, it may be concluded that alkaline soil in which Ca is present mainly in the form of cations of the colloid complex sorbed on soil may be formed in the technogenesis zones under investigation.

Enormous number of published works of soil scientists deals with geochemistry of natural soil that inherited the major fraction of microelements from mother rock. However, another situation is observed in the regions of

TABLE 5

Forms of occurrence of heavy metals and calcium in soil, % of total content (averaged data, $n = 3$)

Fraction No.	Fraction	Sample No.	Cu	Zn	Mn	Fe	Ni	Ca*
1	Water-soluble	1	2.42	0.30	<	<	<	15.00
		2	0.48	1.16	<	<	<	42.40
		3	0.79	<	<	<	<	36.20
2	Exchangeable	1	<	1.62	0.20	0.01	<	136.40
		2	<	20.58	0.47	0.02	<	85.20
		3	<	0.18	0.27	0.02	<	993.20
3	Carbonate-bound	1	1.41	4.85	1.04	<	<	492.00
		2	2.05	11.00	5.02	<	<	238.00
		3	5.60	13.17	13.43	<	<	181.20
4	Bound with amorphous Fe and Mn hydroxides	1	<	24.53	38.91	0.77	<	90.20
		2	5.59	23.50	36.26	1.35	<	58.80
		3	15.49	70.14	48.08	2.69	47.51	1610.80
5	Bound with organics and crystal phases	1	96.17	68.71	59.85	99.22	100	n/d
		2	91.88	43.77	58.25	98.63	100	n/d
		3	78.12	16.51	38.22	97.28	52.49	n/d

Notes. 1. < – below detection limit of atomic absorption spectroscopy. 2. n. d. – not determined.

** in mg/200 g.

technogenic geochemical anomalies: due to the aerial emissions or hydrogen flows, soil is enriched with HM that are characteristic of the object of their emission; as a result, non-uniformities of soil substrate are levelled. As we have stressed above, copper is concentrated in the residual low-mobile fraction (92–96 %). Excess over MPC_{MF} in soil sample No. 3 is due to the presence of Cu in the form of typical carbonates (5.6 %) soluble in sodium acetate with pH 5. A more close connection between copper and amorphous hydroxides of Fe and Mn at pH 8.26 (up to 15.5 %) was established in sample No. 3.

The distribution of zinc over geochemical forms of its occurrence in polluted soils varies (see Table 5). First of all, in acidic soil (sample No. 2) with total zinc content 470 mg/100 g more than 20 % of this element is present in the easily mobile ion-exchange form, which is 100 times more in comparison with weakly alkaline soil (sample No. 30). A positive correlation of zinc and ion-exchange fraction with a decrease in pH of water suspension of the samples (actual acidity) is due not to the own acidity of soil solutions but to the increased concentration

(activity) of zinc in them. In clay soil (pH 8.26, C_{org} 1.66 %), 70 % of zinc is bound with amorphous hydroxides of Fe and Mn, while only 23.5 % of zinc is bound with them in the soil with actual acidity pH 5.53 (C_{org} 5.77 %) (see Table 5, fraction No. 4). It is known that manganese oxides tightly fixes in its lattice heavy metals Co, Ni and Zn [16]. So, soil sample No. 3 is a type of geochemical barrier connected with sorption on (hydr)oxides.

The clarke amounts of nickel in soil point to the absence of technogenic pollution. Only in sample No. 3 the distribution of this element between the organomineral residue and Fe and Mn hydroxides is outlined (47.5 %), while this element is not present in the mobile fraction. According to the data published in [17], it is the clay soil in which Ni content is increased over the average values. The next element which is maximally accumulated in insoluble residue and thus related to the composition of the primary minerals is Fe (97–99 % in fraction No. 5). In general, total iron content is almost 40 times higher than the total content of manganese. However, the latter element is bound in ion-exchange form both with

carbonates and with amorphous hydroxides (it is absent only in water-soluble fraction). As a result, its content in fraction No. 5 its content is only 40–60 %, unlike for iron.

It follows from the data presented in Table 1 that Mn cations are more mobile in the formation of the composition of drainage water, and these ions are accumulated in solutions, while Fe is intensively deposited in the lower layers of bottom sediments. According to the data of [18], the conditions of the formation of separate (hydr)oxides of Mn are not quite clear; usually mixtures containing ransieite, chalcophanite, todorokite are formed. Ransieite ((Ca,Mn⁺²)Mn⁺⁴O₉ · 3H₂O) was discovered by us in the blue-coloured sediments in the drainage trench around clinkers of BZP. Manganese hydroxides are formed practically from colloid systems, so the fraction of manganese in fraction No. 4 is substantial (39–48 %). The high mobility of manganese in oxidative chemical weathering of sulphide-containing sediments is well known. For example, the authors of [19] discuss in detail the reasons of its increased leaching in comparison with a number of elements (Ni, Cu, Cr, Fe, Al). The regularities of Mn accumulation in soil of technogenesis zone observed by us are also of definite interest. However, it is untimely to make conclusions about the character of correlations, for example with humus content. The questions concerning the behaviour of HM and metalloids in the soils of anomalously polluted zones affected by the BZP will be solved in future using detailed testing and mineralogical analysis of the matter.

So, in the region of long-term storage of clinker of BZP even after the cessation of industrial activities of the plant, zinc-copper pollution of soil is prevailing. As stressed above, Zn belongs to the first class of danger. According to the data of [20], large amounts of zinc are accumulated in tailings of mining plants; it easily gets leached and pollutes water and soil. For example, in England the soil in the regions of this kind contains Zn 31–135 mg/100 g; its high concentration (80–450 mg/100 g) was detected in technogenic soil of old tailings of pyrite deposits in the Urals. Large territories are polluted with zinc as a result of the work of smelting plants with out-of-date

pyrometallurgical technology when large amounts of smoke and dust enriched with HM were emitted into the atmosphere. This can be attributed also to the region of one of the first metallurgical plants of the USSR – the BZP. Zinc is a mineralogenic element, 143 minerals are known for it. This is the reason of difficulties caused by Zn phase identification in soil. A detailed review over different regions was made in [20]. On this basis, we are preparing the publication on the mineral forms of zinc occurrence in polluted soils of BZP and the forms of its migration in the form of aerosols.

The duration of pollutant presence in soil is much longer that in other parts of the biosphere, and the pollution of soil with HM seems to be practically eternal [21]. The first period of semi-removal varies strongly for different HM: it is 70–510 years for zinc, 310–1500 years for copper, 740–5900 years for lead. Therefore, polluted territories may be used only as industrial objects for a long time, even after the cessation of production process and recultivation of tailings. An estimate of the complex index of total pollution of BZP soil taking into account the toxicity coefficients of HM and metalloids is given.

CONCLUSIONS

1. Total HM content in soil in the region of the dumps of pyrometallurgical plant provides evidence of the high level of mainly Zn pollution conserved long after the plant stopped its work. The assumed mechanisms of its propagation include the transport of aerosol and larger particles from the dump surface, washing of soil polluted with water from clinker dump and from settler, seasonal rise of ground water polluted with heavy metals (illuviation of solutions).
2. Technogenic pollution of soil is maximal in the direct vicinity of clinkers (60 times excess of the regional background for Zn), weakens at a distance of 300 m (17 times excess) and is conserved even at a distance of 5 km (5 times excess) in the reference samples.
3. The samples of polluted soil differ from the reference sample by lower amounts of metals in the residual fraction, that is, metals bound with organics and crystal phases. In this situa-

tion, the maximal portion of these fractions is conserved for Cu and Fe (up to 92 and 99 %, respectively), smaller portion – for Mn (38–58 %) and the minimal portion for Zn (16–44 %) in samples Nos. 2 and 3.

4. The portion of mobile forms of elements revealed on the basis of stepwise leaching in the most heavily polluted soil with pH of water extract 5.58 exceeds the MPC_{MF} by a factor of 66 for Zn, almost by a factor of 2 for copper, below the MPC_{MF} for manganese, and was not detected for nickel. This row depicts the geoecological state of soil in the region where the wastes from the BZP are stored.

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