UDC 550.424.6

Migration of Heavy Metals (Cu, Pb, Zn, Fe, Cd) in the Aureole of Scattering at the Urskoye Tailing Dump (Kemerovo Region)

I. N. SHCHERBAKOVA, M. A. GUSTAITIS, E. V. LAZAREVA and A. A. BOGUSH

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

E-mail: sherbachok@ngs.ru

(Received August 4, 2009; revised March 29, 2010)

Abstract

Complete chemical composition of surface water, drainage solutions and the substance carried off in the aureole of scattering at the Urskoye tailing dump was investigated. The regularities of the migration of heavy metals were revealed in connection with the increasing distance from the pollution source. It was established that storing high-sulphide waste material in non-fixed piles resulted in dissemination of the material and therefore caused the formation of the aureole of scattering. It was discovered that the water of a natural brook draining the waste material get mineralized and acidified. In the lower part of the dump, the acid water of the brook contacts the peat material of a marsh-field. At the site where the brook flows into the Ur River (a tributary of the Inya River), the acidic Fe-Al sulphate water of the brook get mixed with the fresh Ca-Mg hydrocarbonate water of the river. As a consequence, the metal content of the river water increases sharply, while the recovery of water composition in the Ur River down to the background level occurs at a distance of 5 km from the mouth of the drainage brook. It was established that as a result of the gravitation differentiation the substance near the dump is enriched with larger and heavier fractions, while light-weighed finer particles are carried off along the ravine. The maximal Fe and Cu content in the carried-off waste material is confined with the sulphide material. Uliginous substance interstratified with organic residues and is characterized by increased Zn and Pb content. It was discovered that the element content of buried peat is comparable with their concentrations in the waste material overlapping the peat.

Key words: high-sulphide wastes, heavy metals, acid drainage

INTRODUCTION

Problems connected with heavy metal (HM) pollution of the territories of abandoned excavation sites became urgent with the start of mining industry development. Storage of the wastes from sulphide ore processing is accompanied by the formation of acid drainage solutions with high concentrations of Cu, Pb, Zn, Fe, Cd. The release and migration of these elements result in their wide spread and subsequent concentrating in different environmental objects [1–3]. The situation becomes even more urgent keeping in mind that during the 1930s and 1940s of the 20th century settlements were organized around mining sites, and at present the stored wastes of concentrating works are situated directly near the residential areas.

After piling sulphide-containing wastes from gold ore concentrating, the processes of oxidative leaching, dissolution and re-deposition start to develop in the storage. To study tailings, it is necessary to carry out fundamental research of the processes of modern oxidative leaching in technogenic systems. Researchers from Canada became pioneers in this area [4–7]. It is known that the solubility and oxidation degree of elements depend first of all on chemical processes and are governed by environmental parameters $E_{\rm h}$ – pH. Six main factors affecting the oxidation of sulphides were revealed: 1) pH of solutions in contact with sulphide minerals; 2) genesis, chemistry, surface area and morphology of mineral grains; 3) concentrations of oxygen and Fe^{3+} in solutions; 4) temperature; 5) galvanic interaction of sulphides with coexisting minerals; 6) bacterial action.

The indicated factors are characteristic of natural oxidation zones of sulphide deposits [9]. However, in the case of oxidation of tailings, one of essential factors is the composition of technological solutions. Wastes from cyanidation are prone to oxidative transformation processes to a higher extent than the wastes from floatation because of fine grinding of the material, and also due to active decomposition of sulphide minerals at the technological stage. Under alkaline conditions maintained during cyanidation (pH 11), the fields of stability of the majority of sulphide minerals (the most important of which is pyrite, the main acidproducing mineral) are limited by values $E_{\rm h} \leq 0.2$ V. Under neutral conditions (pH 7), pyrite is stable at $E_{\rm h} \leq 0.4$ V. After piling, the wastes start to interact with atmospheric precipitation, and with atmospheric oxygen. Oxidative processes proceed most actively in the zone of aeration into which completely technogenic bodies formed as piled mounds get. Oxygen concentration decreases sharply with depth; even in the subsurface layers (the first several ten centimetres) the mechanisms of oxidation of separate minerals are determined by the composition of pore solutions. Along with oxygen, Fe(III) acts as an oxidizer [6].

The sequences of relative stability of sulphide minerals in the oxidation zone proposed by different authors differ substantially from each other. Under different environments, at different concentrations and combinations of oxidizing agents, the positions of minerals in the sequence of relative stability vary. The author of [11] proposed a sequence (in the order of descending stability) obtained using the standard electrode potential for the conditions of aqueous solution corresponding to the initial stage of oxidation with oxygen (pH 6-8): sphalerite-galenite-pyrrhotite-tennantite-tetrahedrite-arsenopyrite-chalcopyrite-pyrite. In opinion of the authors, variations of pH cause changes of the electrode potential of minerals, which leads to the change of their relative stability. Using the data of observations and

experiments performed in different environments, the author of [12] proposed the following sequence of relative stability (in descending order): magnetite-bornite-chalcopyritepyrite (arsenopyrite)-galenite (sphalerite), pyrrhotite. Another sequence, the sequence of decreasing rates of sulphide interaction with Fe(III), was revealed as a result of experimental investigation at pH 2: pyrrhotite-galenite-arsenopyrite-pyrite-sphalerite-chalcopyrite [13]. Investigations performed with natural objects confirmed higher stability of chalcopyrite against oxidation due to Fe(III) [14, 15]. The rate of oxidation of pyrite, the major acidproducing mineral, is affected by the sample surface, initial concentration of oxidizing agent and (to a small extent) the initial pH value. Taking into account the sample surface, the position of minerals in the sequence appears as follows (in the order of decreasing stability): chalcopyrite- fine-grained pyrite-sphalerite-galenite-coarse-grained pyrite [16].

The secondary mineral phases formed during oxidative dissolution of sulphides and redeposition of the matter in the oxidation zone form the sequence: simple aqueous sulphates (vitriols)-basic sulphates-hydroxides [17]. The earliest secondary minerals are hydrated sulphates of divalent iron (melanterite, rosenite), zinc (goslarite), copper (chalcantite) and lead (anglesite). Anglesite is often present as a sole sulphate in tailings. Canadian researchers when studying the wastes with high sulphide content examined melanterite and gypsum that form lithified layers at a depth of 0.5 m, called hardpan [6]. Metals forming well soluble sulphates are actively carried out (Fe, Zn, Cu, Cd). A complete spectrum of simple sulphates is manifested in seasonal marks on the surface of technogenic bodies [12, 18]. Among basic sulphates, in the absence of carbonates the most widespread mineral is jarosite formed in the acidic environment (pH < 3) [19]. At the late stages of the formation of oxidation zone, jarosite is replaced by iron hydroxides.

The term «iron hydroxides» includes a large number of mineral phases. On the basis of investigation of the rate of Fe(II) oxidation in the presence of a number of inorganic complex forming agents, it was established that the products formed in the absence of ligands and at pH 6 is mainly goethite with small admixture of lepidocrocite. The amount of the latter increases in the presence of sulphate and carbonate. Silicate and phosphate promote the formation of non-crystalline oxides of Fe [20]. As a rule, iron hydroxides contain isomorphous admixtures of copper, zinc, lead, cadmium, antimony, arsenic *etc.* [9, 21] and thus they play important part in the processes of HM redistribution. The highest sorption capacity is exhibited by amorphous iron hydroxides.

Relying on the data reported in [5, 12] one may conclude that three major vertical zones are distinguished within the tailing dump:

1. The lowest part of wastes is weakly affected zone.

2. The next zone above the deep-lying one is the lithified horizon (hardpan). The bond base in the zones with not very high sulphide content was revealed to be hydroxides and sulphates of Fe^{3+} (jarosite, goethite), while in the regions with high sulphide content this role is played by aqueous sulphates of Fe^{2+} (FeSO₄ · $n\text{H}_2$ O). This layer is the region of active oxidation.

3. The upper zone may be followed to the depth of 0.5 m. It is characterized by almost complete substitution of initial sulphides by goethite, lepidocrocite etc. Jarosite is formed in this zone.

New technologies involving neutralization of acidic drainage solutions are introduced at present. The discovery of the fact that filtration of acidic source through boggy territories causes a decrease in the concentration of HM stimulated the construction of artificial boggy territories as a possible passive method of purification [22]. Various reagents are used to decrease the technogenic effect of wastes from ferrous and nonferrous metallurgy: carbonates, activated carbon, zeolites [23], iron hydroxides/ oxides [24], cellulose etc. The screens of different kinds are also used [25, 26]. During the recent years, methods of neutralization of acidic drainage flows are widely discussed in the world. For example, the reagents used as neutralizers include hydrated lime (Ca(OH)₂), calcium oxide (CaO), caustic soda (NaOH), soda ash (Na₂CO₃) [22, 27], ash from power plants [28, 29].

About 10 billion dollars is spent every year in the world to solve the problems connected with acidic drainage [30]. The first step to propose various purification methods may become investigation of real situations around the wastes of concentrating works. Investigation of the distribution of HM and the processes of their migration in the scattering aureoles allows one to predict the state of the environment around ore mining and processing plants and tailing dumps.

The goal of the present work is investigation of the redistribution of HM among the components of a natural and technogenic system through surface water, pore solutions, waste material and peat (buried under high-sulphide wastes) in the scattering aureole of the tailing dump storing the wastes from cyanidation of pyrite ore from the Urskoye deposit.

OBJECTS AND METHODS OF INVESTIGATION

The territory of the region under study is a low-mountain surface sharply lifted above the Kuznetsk depression and gently sloping toward the West Siberian Lowland [31]; the territory is related to the Salair Ridge. Numerous ore sites containing polymetallic, sulphur-pyrite ores are genetically bound with the intrusion of keratophyres which occur among the carbonate deposits related to middle and upper Cambrian time. Underlying rocks are composed of Quaternary alluvial and alluvial-dealluvial deposits.

The Urskoye tailing dump (Ursk settlement, Kemerovo Region, Russia) was formed more than 50 years ago and contains the wastes from cyanidation of primary polymetallic Cu-Zn sulphur pyrite and ore of the oxidation zone of the Urskoye deposit. The wastes of primary ores are composed of pyrite by 50-90 %. Worked out primary ores and the ores of oxidation zone are stored in the form of two piles 10–12 m high. A natural brook flows over the ravine where the tailing dump is situated. The water of the brook drains the waste material and gets acidified. Under the effect of acidic solutions, the boggy territory situated downward the tailing dump is scorched, and vegetation is destroyed. The waste material is not fixed, so during the time of existence of the tailing dump it was washed out by rainwater and flood water. The boggy territory of the ravine below the dump down to the Ur River (a tributary of the Inya River) is covered with

the waste material carried downward (Fig. 1). The open pit situated at the territory of the store is filled with water and used as a bathing pond by local people.

During the field operations (2007) we sampled the solid material and aqueous solutions. Surface water was tested at different distances from tailing dump and the site where the drainage water flows into the Ur River. Water samples were also taken from the local water reservoir situated near the dam on the Ur River upstream of the inflow of the drainage brook not far from the Kopna mountain (see Fig. 1, point 1). The samples of non-filtered aqueous solutions were taken into plastic vessels 0.5 L in volume. A part of water was filtered with the help of a Kuprin's apparatus. Separate samples were taken to examine the basic ion composition. Using the Anion 4100 instrument we measured pH and $E_{\rm h}$ in non-filtered solutions. The glass electrode and the reference electrode were calibrated using three buffer solutions: potassium biphthalate (pH 4.01), solution of phosphate salts (pH 6.86), and sodium tetraborate (pH 9.18). The error of pH measurement was ± 0.1 . Then the solutions were acidified with concentrated HNO₃ to carry out subsequent analysis of metal content. Determination of the basic anions was carried out by means of capillary electrophoresis using a standard procedure with the analysis error of 10-15 % (Capel 103R, Lumex, Novosibrsk). Metal content of solid samples and solutions was determined using a SP-9 Pye Unicam and Perkin-Elmer 3030Z AAS. The standard error of analysis was 5-20 % depending on the concentration level.

The material in the carry-out zone was tested in trenches at different distances (60, 130 and 600 m) from the dumps (see Fig. 1). The solid



Fig. 1. Scheme of the Urskoye tailing dump, adjacent territory and sampling sites for surface water and solid matter: 1 - residential areas of Ursk settlement; 2 - tillage; 3 - forest; 4 - rock debris; 5 - zone of carried waste material; 6 - tailing dump; 7 - surface water sampling sites; 8 - trenches; 9 - automobile roads; 10 - dam near the dredge; 11 - Ur River.

substance was tested over the vertical taking into account the macroscopic nonhomogeneity of horizons. The number of samples collected for examination was 15. The pore solution was pressed out of the solid matter with the help of the hand-operated hydraulic press under the pressure of 150 g/cm³. In the resulting solutions we measured pH and $E_{\rm h}$, and then the samples were acidified with the solution of concentrated HNO₃ for subsequent analysis for metal content. The pressed solid matter was dried to the air-dry state and packed into polyethylene bags. The determination of granulometric composition was carried out using the method proposed by N. A. Kachinsky [32]. Under laboratory conditions, the solid substance was ground for subsequent analysis for metal content. Then it was described on the basis of visual characteristics, and its mineral composition was studied with a JSM-6380 LA scanning electron microscope.

RESULTS AND DISCUSSION

The effect of atmospheric factors causes oxidation of the sulphide material in wastes (first of all pyrite, the major acid-producing mineral), its dissolution and, as a consequence, to the formation of water-soluble sulphates [3, 33]:

 $\begin{aligned} \mathrm{FeS}_2 + 7/2\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} &= \mathrm{Fe}^{2^+} + 2\mathrm{SO}_4^{2^-} + 2\mathrm{H}^+ \ (1) \\ 2\mathrm{FeSO}_4 + 1/2\mathrm{O}_2 + \mathrm{H}_2\,\mathrm{SO}_4 &= \mathrm{Fe}_2(\mathrm{SO}_4)_3 + \mathrm{H}_2\mathrm{O} \ (2) \end{aligned}$

The natural water source draining through the dump becomes acidic (pH 2.2–2.7) drainage brook. According to A. A. Alekin's classification [34], the composition of initial water in the brook, as well as the composition of water in the Ur River into which the brook flows later on, corresponds to the boundary between weakly alkaline and strongly alkaline kinds of water. This is calcium-magnesium hydrocarbonate fresh water unsaturated with compounds (pH 7.5–8). Figure 2 shows the data on the concentrations of Cd, Zn, Pb, Cu and Fe in this water, along with the MPC for water objects of domestic, drinking, cultural and welfare facilities (GN 2.1.5.1315–03) [35].

Water in the drainage brook can be related to salty acidic water (M = 4.8 g/L, pH 2) of Fe-Al sulphate type; metal concentrations are

2-3 orders of magnitude higher than those in the water of natural brook (see Figs. 2, 3). As the distance from the tailing dump increases, we observe a slight increase in the pH value for brook water due to insignificant dilution (see Fig. 2, points 4-6, and Fig. 3), and an increase in the redox potential due to an increase in the fraction of Fe(III). A significant decrease in the concentrations of Fe, Cu, and Zn by a factor of 5 as an average is detected, while the concentrations of Cd and Pb decrease only not more than by a factor of 2. This fact is due either to partial dilution or to the removal of elements from solution as a result of the deposition of secondary minerals of iron (III). In the bottom sediment of the drainage brook, iron gets precipitated most probably in the form of jarosite group minerals ((K, Na, H_3O)(Fe, Al)₃(SO₄)₂(OH)₆), schwertmanite ((Fe₈O₈(OH)_{8 - 2x}(SO₄)_x · nH₂O) [14, 19]: $3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H^2O = KFe_3(SO_4)_2(OH)_6$ $+ 6 H^{+}$ (3)

It is known that the minerals of alunitejarosite group and related groups are characterized by the common formula $AB_3[(XO_4)_2(OH)_6]$ and trigonal symmetry, with some exceptions. According to the character of the anion component in position (XO_4) , three final groups are distinguished, depicting predominance of SO_4^{2-} , PO_4^{3-} , AsO_4^{3-} . The minerals of alunite-jarosite group include the compounds with the general formula $AB_3(SO_4)_2(OH)_6$ in which position B is occupied by cations Al^{3+} and Fe^{3+} , position A is occupied by ions K^+ , $Na^+ H_3O^+$, more rarely Ag^+ , NH_4^+ or Pb^{2+} . It is known that inside all the structural positions between the final terms the series of solid solutions are formed [36]. Copper and zinc are usual admixtures in lead-containing minerals, which is due to the presence of Pb(Cu, Fe, Al)₃(SO₄)₂(OH)₆) and/or $(PbCuAl_{2}(SO_{4})_{2}(OH)_{6})$ [37]. Experimental studies also indicate the deposition of copper and zinc as admixtures not only in jarosite but also in schwertmanite [14, 15].

As a result of settling the acid solutions, a technogenic bog was formed near the mouth of the brook; it has a reddish-brown deposit at the bottom (see Fig. 1, point 7), which serves as a favourable medium for the formation of secondary Fe(III) minerals, and its bottom is covered with an ochre deposit. The concentrations of the metals under investigation decrease in solution (see Fig. 2) with respect to the brook water.

In the water of the Ur River, after the drainage brook flows into it, mixing of alkaline Ca–Mg hydrocarbonate water and acid Fe– Al sulphate solutions occurs, followed by neutralization and profuse formation of amorphous iron compounds represented mainly hydroxides [19]:

 $2Fe^{2+} + 3H_2O + 1/2O_2 = 2Fe(OH)_3$ (4)

Metals precipitate together with iron hydroxide. At the same time, metal concentrations in solution near the inflow of the drainage brook are an order of magnitude higher than those for surrounding water reservoirs. With an increase in the distance from the inflow of the sulphate brook into the river (see Fig. 2, points 8-10), metal concentrations decrease to the background level at a distance of 4-5 km. Metal concentrations in water decrease downstream, while pH increases. Substantial amounts of metals are deposited at this distance into bottom sediment which can be easily brought up later on by flood water and carried in the form of suspension over long distance. The concentrations of HM in the water of the Ur River were compared with MPC of



Fig. 2. Concentrations of heavy metals and pH in surface water (over the vertical axis: concentrations, over the horizontal axis: surface water sampling sites): 1 - the Ur River, dam upstream of the inflow of acid drainage brook; 2 - the same, upstream of the inflow of the Maslikha River; 3 - cutest; 4 - drainage dump directly beneath the tailing; 5 - the same, in the middle of the ravine; 6 - the same, before inflow into the Ur River; 7 - reddish-brown bog; 8 - the Ur River after the inflow of the drainage brook; 9 - the same, at a distance of 200 m after the inflow of the drainage brook; 10 - the same, dam near the dredge; 11 - the same, Ursk settlement; to depict the migration of elements, the average concentration values were calculated over 2-4 samples.

chemical substances in water objects of domestic, drinking, cultural and welfare facilities (hygienic standards GN 2.1.5.1315-03) [35]. In drainage solutions (see Fig. 2, points 4-7), the concentrations of metals exceed the MPC by 1-3 orders of magnitude but in the water of the Ur River after the inflow of the drainage brook the concentrations of Cd, Zn, Pb and Cu are not higher than the MPC level. In the upper reach of the Ur river (see Fig. 2, points 1, 3) and at a distance longer than 5 km (see Fig. 2, point 10) from the inflow of the acid drainage brook the concentration of Fe does not exceed 0.3 mg/L, which corresponds to the MPC [35]. Directly after the inflow of the drainage brook (see Fig. 2, points 8-10), the concentration of Fe exceeds the MPC by an order of magnitude.

The changes in the basic ion composition of water in the Ur River after the inflow of the drainage brook are clearly seen in Durov's diagram (see Fig. 3). While the concentrations of $SO_4^{2^-}$ ions, Fe and Al decrease, the concentrations of ions HCO_3^- , Ca, Mg, Na increases; pH of solutions increases. Total salt content in water at a distance of 5 km from the inflow point corresponds to the salt content of surrounding water reservoirs upstream from the point of mixing with the drainage brook.

The thickness of the layer of waste material carried off downstream from the tailing dump does not exceed 0.5 m. As a result of gravitational differentiation, the lateral zoning was formed in the carried material, which is characteristic of the filler tailings [38]. On the basis of the data of granulometric analysis of the carried material, three zones were revealed relying on the prevailing fraction: sandy, sandyoozy, and oozy. At a distance of 60 m from the tailing, in the nearest zone, fine sand dominates (Fig. 4, samples 1-2 and 1-3); at a distance of 130 m (the medium zone) from the tailing, the fractions of sandy and oozy frac-



Fig. 3. Changes of the composition (basic ions, salt content, pH) of surface water in the zone affected by the acid drainage brook from the Urskoye deposit and the adjacent territory. For design., see Fig. 2.

tions are almost identical (samples 2-1 and 2-3), while at the largest distance from the tailing (600 m) the oozy fraction dominates (samples 3-1 and 3-2).

In the vertical section, the waste material downstream of the tailing is non-homogeneous due to non-uniform carrying off the tailings. Lower lying horizons are composed of finer fractions (see Fig. 4, samples 1-4 and 3-2). At the largest distance from tailing dumps (600 m), in the lowest horizons we observe the maximal amount of fine fractions (see Fig. 4, sample 3-2). In separate parts of the section, the waste material is interstratified with detrital material. The largest amount of organic residues is present in oozy matter. Buried peat matter is distinguished separately.

The matter in the zone which is the closest to the tailing dump is represented by highsulphide fine-grained sandy material of gray colour (Fig. 5, trench No. 1). Predominant minerals in its composition are pyrite, barite and quartz. Pyrite occurs as isometric grains and crystals having the cubic shape, barite occurs as flattened fine-tabled crystals. Secondary minerals are formed between sulphide grains. These minerals are represented mainly by the aggregates of jarosite (rhombohedrons, pseudocubes etc.) (Fig. 6, a, b). The sandy-oozy substance contains the grains of barite, quartz, jarosite, muscovite (see Fig. 6, c, d). The organic matter printed in the sandy oozy material near the tailing is often coated with zonal concentric encrustations composed of iron (III) hydroxides



Fig. 4. Gravitational differentiation of the matter in waste material with an increase in the distance from the tailing. Vertical axis: percentage of fractions in the matter; horizontal axis: size of fractions, mm: 1-0.25 mm, medium sand; 0.25-0.05, fine sand; 0.05-0.01, coarse dust; 0.01-0.005, medium dust; 0.005-0.001, fine dust; <0.001, coarse and fine mud.







Fig. 6. Composition of water material: a – initial; b – secondary aggregates of jarosite; c, d – sandy-oozy carried waste material with organic residues under different magnification; e – zonal concentric encrustations with Fe hydroxides on the organic residue; f – peat hillock.

(see Fig. 6, *e*). Most probably, the formation of iron hydroxides is connected with the formation of a local geochemical barrier during the interaction of pore solutions with the organic matter, because jarosite must be formed under acid conditions (pH < 3) [19]. Peat matter is represented by decomposed plant residues (see Fig. 6, *f*). Secondary minerals are almost completely absent.

The pore solutions of carried waste matter are similar in ionic composition and salt content with the solutions in the drainage brook: they are salty Fe-Al sulphate. However, their salt content is higher (6–18 g/L), pH 1–4, $E_{\rm h}$ 380– 840 mV. The heist concentrations of elements are observed in the subsurface layers (see Fig. 5, samples 1-3, 2-1 and 3-1), where salt content in pore solutions is 4-5 times higher than that in lower-lying horizons independently of the characteristics of the matter (Fe 2700-7500, Pb 0.36-5.2, Zn 9-57, Cu 7-12, Cd 0.07-0.08 mg/L). Evaporation of pore solutions is likely to cause their concentrating. Sampling was carried out during a dry period, and sulphate stain was observed on the surface.

With an increase in the distance from the tailings, while the oozy fraction in sandy

material increases, metal content in pore solutions increases. Metal concentrations in the pore solutions of the sandy sulphide material is lower than that in the pore solutions of sandy oozy material at a distance of 130–600 m from tailings (see Fig. 5, samples 1-2, 2-3 and 3-1). The permeability of the oozy material is an order of magnitude lower than the permeability of sandy material [38], which leads to the accumulation of HM in pore solution. As a consequence, high concentrations of metals are observed in it (see Fig. 5, samples 1-4, 2-1, 3-2 and 3-5). The maximal concentrations of Fe, Pb, Zn, Cu, Cd were detected in solutions pressed out of the oozy material sampled in the most remote part. The highest concentrations of Fe, Cu and Zn in pore solutions are confined to the ochred sandy matter, while the highest Pb content is observed in the pore solution of oozy material (Fig. 7).

The concentrations of HM in the pore solution of buried peat are the lowest (Fe 50, Pb 0.25, Zn 4.5, Cu 0.1, Cd 0.001 mg/L, see Fig. 5, samples 1-5 and 2-5). This is connected mainly with the sorption ability of the peat material, as well as with its increased porosity, due to which the metals present in pore solutions are efficiently deposited.



Fig. 7. Concentrations of heavy metals in the solid matter (histograms) and in pore solutions (diagrams) over the classes of the carried waste material. Vertical axis: concentration, horizontal axis: classes of compounds; 1 - sulphide-containing material; 2 - oxidized sandy material; 3 - oozy material with bands of organic matter; 4 - buried peat; 5 - peat of bog hillocks; to depict the variations of metal concentrations, average values over 2-4 samples were taken.

The metal concentrations in sandy oozy material (Table 1) differ from those in the sandy substance but no regularities can be followed in this situation. For fine-grained material, rather high metal concentrations are detected (see Fig. 5, sample 3-5). The maximal concentrations of Fe (14 %) and Cu (350 g/t) were detected in the material enriched with sulphides (see Fig. 5, sample 1-2). The highest concentrations of Pb (up to 4500 g/t) are observed in the sandy oozy material. The oozy matter, which is in the major part layered with the organic residues, is distinguished by increased concentrations of Zn (410 g/t). The concentrations of HM in buried peat only slightly differ from their concentrations in the overlying waste material and are 4-6 times higher than HM concentrations in surrounding soil (as an average, 30, 72 and 32 g/t for Pb, Zn and Cu, respectively). Buried peat gets enriched due to the percolation of pore solution and sorption of HM on the organic matter.

CONCLUSIONS

1. The scattering aureole of the Urskoye tailing was formed both due to carrying the wastes from the tailing with flood water and redeposi-

TABLE 1

Concentrations of heavy metals in the solid matter, g/t

Substances	Pb	Fe*	Cu	Zn
Sandy material	300-600	0.3 - 14	300-410	45-310
Sandy-oozy material	1970 - 4500	0.3 - 0.6	63 - 145	140 - 260
Oozy material	155-1830	0.5 - 10	95-190	180-410
Buried peat	250	1	100	350

*Iron content is given in per cent.

tion over the adjacent territories and due to the transfer of elements in dissolved state and redeposition in bottom sediments, peat material. Gravitational differentiation of waste material is observed in the scattering aureole.

2. Migration of elements in dissolved state is promoted by the natural source draining through the tailing dump of the store. Secondary compounds of Fe(III) get deposited at the bottom of the acid Fe–Al sulphate brook, which causes a decrease in zinc and copper concentrations with an increase in the distance from the tailings. The concentrations of metals sharply decrease during settling in the technogenic bog.

3. During mixing acidic Fe-Al sulphate water of the drainage brook with fresh Ca, Mg hydrocarbonate water in the Ur River, affluent precipitation of the secondary compounds of Fe(III) occurs as a result of neutralization. As a result, metal concentrations in river water increase insignificantly. The recovery of water composition in the Ur River and a decrease in metal content to the values typical for neighbouring water reservoirs upstream of the inflow of the acid brook occurs at a distance of 5 km from the mouth of the brook. However, repeated mobilization of the metals in suspended state is possible during flood.

4. Evaporation processes taking place during dry periods cause concentrating of pore solutions near the surface; as a consequence, maximal mineralization of pore solutions is observed, independently of the characteristics of the matter.

5. In the solid matter, the maximal Fe and Cu concentrations are confined with the sandy sulphide material. The oozy matter contains increased concentrations of Pb and Zn. The concentrations of heavy metals in buried peat in the region of technogenic action are 4-6 times higher than those in nearby soil. Metal content in the upper horizons of waste material overlying buried peat only slightly differs from metal content of buried peat itself. This regularity is explained by infiltration of pore solutions and metal sorption on buried peat.

REFERENCES

1 Alpers C. N., Blowes D. W., Nordstrom D. K., and Jambor J. L., Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, in Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, 1994, vol. 2, p. 247.

- 2 Borman R. S., Watson D. M., Can. Inst. Min. Metal., 69 (1976) 86.
- 3 Seal R. R., Hammarstrom J. M., Environmental Aspects of Mine-Wastes: Mineralogical Association of Canada Short Course Series, in Jambor J. L., Blowes D. W., Ritchie A. I. M. (Eds.), Vancouver, British Columbia, 2003, vol. 31, p. 11.
- 4 Al T. A., Blowes D. W., Martin C. J., Cabri L. J., Jambor J. L., Geochem. Cosmochem. Acta, 61 (1997) 2353.
- 5 Blowes D. W., Jambor J. L., Appl. Geochem., 5 (1990) 327.
- 6 Blowes D. W., Cherry J. A., Reardon E. J. and Jambor J. L., *Geochim. Cosmochim. Acta*, 55 (1991) 965.
- 7 Blowes D. W., Al T. A., Lortie L., Gould W. D. and Jambor J. L., *Geomicrobiol. J.*, 13 (1995) 13.
- 8 Shaw S. C., Groat L. A., Jambor J. I., Blowes D. W., Hanton-Fong C. J., Stuparyk R. A., *Environ. Geol.*, 33 (1998) 209.
- 9 Yakhontova L. K., Grudev A. P., Mineralogiya Okislennykh Rud, Nedra, Moscow, 1987.
- 10 Sato M., Geochim. Cosmochim. Acta, 56 (1992) 3133.
- 11 Sveshnikov G. B., Elektrokhimicheskiye Protsessy na Sulfidnykh Mestorozhdeniyakh, Izd-vo LGU, Leningrad, 1967.
- 12 Jambor J. L. Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, in Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, 1994, vol. 22, p. 59.
- 13 Rimstidt J. D., Chermak J. A. and Gagen P. M., Environmental Geochemistry of Sulfide Oxidation, in Alpers C. N. and Blowes D. W. (Eds.), Washington, DC, 1994, vol. 550, p. 2. (Amer. Chem. Soc. Symp. Ser., No. 550).
- 14 Sidenko N. V. Lazareva E. V. Bortnikova S. V. Kireev A. D., Canad. Mineralogist, 43, 4 (2005) 1141.
- 15 Sidenko N. V., Sherriff B. L., Appl. Geochem., 20, 6 (2005) 1180.
- 16 Bierens de Haan S., Earth-Sci. Rev., 31, 1 (1991) 1.
- 17 Yakhontova L. K., Zuev V. V., Grudev A. P., IX Syezd Mineralogicheskogo Obshchestva pri RAN, May 17–21, 1999 (Thesises), St. Petersburg, 1999, pp. 272–273.
- 18 Usmanov M. L., Gipergennye Preobrazovaniya Otkhodov Obogashcheniya Sulfidnykh Rud, in: Uralskiy Mineralogicheskiy Sbornik, Izd-vo UrO RAN, Miass, No. 5, pp. 138–142.
- 19 Bigham J. M. // Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Waters. In Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, 1994, vol. 22, p. 103.
- 20 Krishnamurti G. S. R. and Huang P. M., Talanta, 37 (1990) 745.
- 21 Bowell R. J., Bruce I., Appl. Geochem., 10, 2 (1995) 237.
- 22 Reinhardt C. H., Acid Mine Drainage in Pennsylvania Streams. [Electronic resource]: Ironing Out the Problem, 1999. URL: http://horticulture.cfans.umn.edu/vd/h5015/ 99fpapers/reinhardt.htm
- 23 Motsi T., Rowson N. A., Simmons M. J. H., Int. J. Miner. Process, 92 (2009) 42.
- 24 Herrera P., Uchiyama H., Igarashi T., Asakura K., Ochi Y., Iyatomi N., Nagae S., *Minerals Eng.*, 20, 13 (2007) 1255.
- 25 Blowes D. W., Ptacek C. J., Jambor J. L., Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, in Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, vol. 22, 1994, p. 365.

- 26 Evvie Chockalingam, Studies on Acid Production Potential of Some Sulphide Minerals and Bioremediation of Acid Mine Drainage (Doctoral Dissertation in Philosophy), Indian Institute of Science, Bangalore, 2007. URL: http://etd.ncsi.iisc.ernet.in/handle/2005/597
- 27 McGinness S., Res. Paper. Sci. Environ. Sect. House Commons Library, 10 (1999) 1.
- 28 RHos C. A., Williams C. D., Roberts C. L., J. Hazard. Mater., 156, 1–3 (2008) 23.
- 29 Xenidis A., Mylona E., Paspaliaris I., Waste Management, 22, 6 (2000) 631.
- 30 Weatherell C. J., Feasby D. G., Trembly G., PMU 97 28th Ann. Sem. and Symp. (Proceedings), Chicago, 1997.
- 31 Bessonenko V. V., Vinkim M. K., Kuznetsov A. M., Geologicheskaya Karta SSSR, Masshtab 1:200000, Ser. Kuzbasskaya, list N-45-XIV, Moscow, 1970.
- 32 Arinushkina E. V., Rukovodstvo po Khimicheskomu Analizu Pochv, 2nd Ed., Izd-vo MGU, Moscow, 1970.

- 33 Ritchie A. I. M., Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, in Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, 1994, vol. 22, p. 201.
- 34 Reznikov A. A., Mulikova E. V., Sokolov I. Yu., Metody Analiza Prirodnykh Vod, 3rd Ed., Nedra, Moscow, 1970.
- 35 PDK Khimicheskikh Veshchestv v Vode Vodnykh Ob'ektov Khozyaystvenno-Pityevogo i Kulturno-Bytovogo Vodopolzovaniya. Gigiyenicheskiye Normativy GN 2.1.5.1315-03". URL: http://www.tehdoc.ru/ files.1699.html
- 36 Novak F, Jansa J., Prachar I., Věst. Čes. Geol. Úst., 69, 2 (1994) 51.
- 37 Alpers C. N., Nordstrom D. K., Ball J. W., Sci. Geol. Bull., 42, 4 (1989) 281.
- 38 Robertson W. D. Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, in Jambor J. L. and Blowes D. W. (Eds.), Mineralogical Association of Canada, Nepean, 1994, vol. 22, p. 2.