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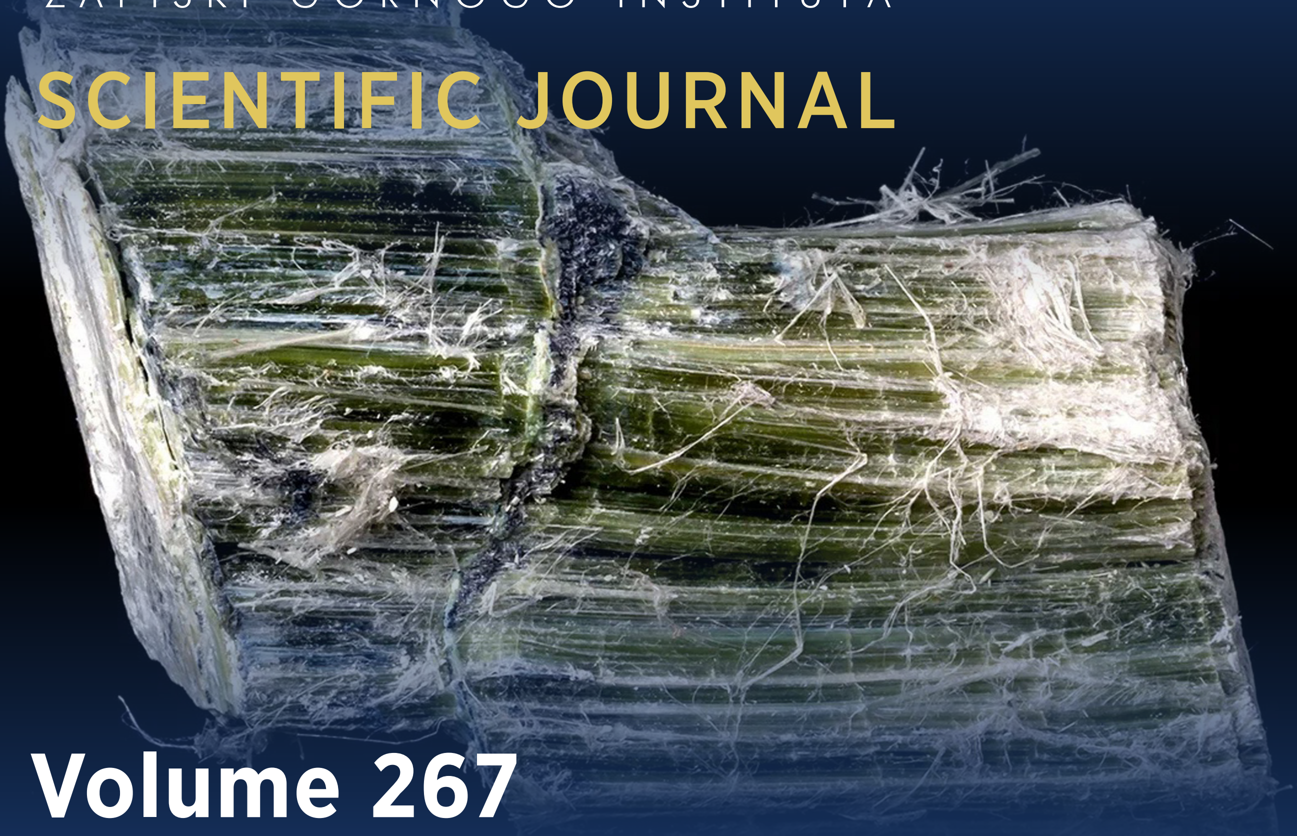

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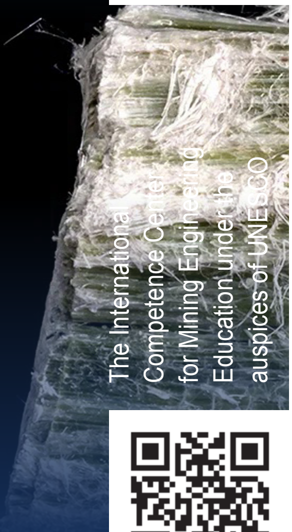

The International
Competence Center
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Education under the
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The scientific periodical “Journal of Mining Institute” is published since 1907 by Empress Catherine II Saint Petersburg Mining University – the first higher technical educational institution in Russia, founded in 1773 by the decree of Catherine II as the embodiment of the ideas of Peter I and M.V. Lomonosov on the training of engineers for the development of mining business.

The International Competence Center for Mining Engineering Education under the auspices of UNESCO operates on the basis of Empress Catherine II Saint Petersburg Mining University and contributes to active interaction of the Journal with the international scientific community.

The purpose of the Journal is to create an information space in which Russian and foreign scientists can present results of their theoretical and empirical research on the problems of the mining sector.

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The cover shows an exhibit of the Mining Museum – veins of a fine-fibered chrysotile-asbestos aggregate. The writings of the Jewish Levites mention “delicate stone fabrics” that cannot be destroyed by fire – chrysotile asbestos. The mineral is fire-resistant and alkali-resistant, and is a poor conductor of heat, electricity and sound.

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Editorial

ENVIRONMENTAL SAFETY AND SUSTAINABLE DEVELOPMENT: NEW APPROACHES TO WASTEWATER TREATMENT

In 2015, the UN member states adopted the 2030 Agenda for Sustainable Development. Despite significant progress, billions of people – one in three people – do not have access to safe, clean drinking water.

Modern wastewater treatment methods include a wide range of biological, chemical and physical processes, each having its own advantages and applications. This thematic volume considers the latest achievements in wastewater treatment technologies, wastewater purification and treatment as well as their potential applications at the local level.

The problem of surface water pollution is relevant for all regions of the world. One of the largest sources of pollutants is mining and processing industry. The first stage in the development of wastewater treatment technologies is monitoring of anthropogenically modified water bodies.

Long-term studies of the impact of the development of the Sibay deposit were carried out by scientists from Saint Petersburg State University under the *Anatolii Yu. Opekunov*'s supervision. An assessment of the effectiveness of geochemical barriers for water purification from Cu, Zn, Cd was carried on the Karagayly River, which was used for runoff of sub-dump and quarry water. The performed analysis of the efficiency of geochemical barriers in river water purification indicates the prospect of using nature-like *in situ* technologies in watercourses, canals and other water disposal systems.

Zoya A. Zhakovskaya and her colleagues' research presents the results of pollution by organotin compounds and heavy metals study in modern sediments of shelf areas of the Baltic Sea near Kaliningrad.

A new method of quantitative determination of various forms of sulfur in bottom sediments for express assessment of pollution of aquatic ecosystems was proposed in the paper of *Ivan P. Sverchkov* and *Vladimir G. Povarov*, which includes the analysis of X-ray emission spectra in the area of the S-Kβ line. The results are compared with the results of quantitative chemical classical methods analysis, as well as with the content of sulfur forms in certified standard samples.

Development of nature-like technologies for wastewater treatment for rational development and efficient use of natural resources is increasingly being used. One of such examples is the research of authors from the University of Continental (Peru) under supervision of *Pablo Espinoza Tumialán*. The method of neutralization of acid drainage water with a mixture of slaked lime and sodium bentonite (natural sorbent) was proposed. The sludge formed at treatment of acidic waters by mixture of neutralizing reagent with adsorbing material has better characteristics, reducing the degree of surface infiltration of water.

Scientists of the Institute of Mining Engineering (Ural Branch of the RAS) under the supervision of *Lyudmila S. Rybnikova* carried out research of the assessment effectiveness of acid mine water treatment by neutralization and sedimentation at flooded mines in the Middle Urals and identification of the main parameters that allow to achieve higher water quality indicators for discharge into water bodies.

The joint group of researchers of the Kyrgyz National University and Saint Petersburg Research Center for Ecological Safety of the RAS considered the possibility of using a sorbent based on coal from the Kara-Keche deposit for wastewater treatment from low molecular weight organic pollutants, the results of studies of the structure of the obtained sorbents and the effectiveness of their use were provided.

One of the goals of sustainable development is to significantly reduce the amount of waste by taking measures to prevent its generation, reduce it by recycling and reuse. The paper by *Natalya Yu. Antoninova* and her colleagues shows the results of research on determining the optimal conditions and parameters for afterpurification of underspoil water from metal ions using humic acid production wastes in order to develop effective measures for the ecological rehabilitation of ecosystems disturbed during the mining of copper pyrite deposits.

Researchers of Saint Petersburg Mining University and University of Leoben under the supervision of *Vera A. Matveeva* presented the results of experimental studies on obtaining coagulant from iron ore processing waste. The technical solution obtained in the work allows to solve the problem of environmental protection by creating new target products from wastes for wastewater treatment.

Conservation, restoration and sustainable use of terrestrial ecosystems can be also achieved by taking into account the use of wastes from sewage treatment. The study conducted by *Lyubov A. Ivanova* and her colleagues shows the results of evaluation of the effectiveness of re-cultivation measures using sewage sludge for accelerated formation of sustainable erosion control vegetation cover on low-productive techno-soil of a sand pit in the Kola North.

Marina V. Bykova and co-authors analyzed the existing approach to sewage sludge handling and experimentally substantiated the most promising technology of utilization, which allows to use maximally the resource potential of the considered waste.

The paper by *Olga M. Guman* and *Irina A. Antonova* provides a rationale for the composition and properties of material for reclamation of sludge reservoir from water treatment wastes placed in it.

The method of joint utilization of blast furnace slag with the filtrate of solid municipal waste landfills, the formation of which occurs when atmospheric precipitation passes through the deposited waste, was presented by a team led by *Mariya A. Pashkevich*. The proposed method is based on the transfer of filtrate from liquid phase to solid aggregate state by lithification with the use of blast furnace slag as a binding material.

Systems of complex treatment facilities are objects of critical infrastructure. *Evgeniya S. Novikova* and her colleagues proposed a methodology for identifying and subsequently assessing the risks of cyber sustainability of the wastewater treatment process, including an original method for generating training data sets and identifying anomalies based on deep learning methods.

Principle science editor of the volume Doctor of Engineering Sciences Mariya A. Pashkevich
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Research article

Analysis of the geochemical barriers effectiveness as the basis for the use of nature-like water purification technologies

Anatolii Yu. Opekunov✉, **Dariya V. Korshunova**, **Marina G. Opekunova**, **Vsevolod V. Somov**, **Daniil A. Akulov**
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Abstract. Nature-like technologies are being introduced into many human activities including mining wastewater treatment. This work is based on long-term studies of the Sibay copper-zinc-pyrite deposit development. It is dedicated to assessment of geochemical barriers effectiveness in Cu, Zn, Cd removal from water of the Karagayly River (receiving quarry and dump drainage water). The research is based on the elements' content and forms in water and bottom sediments, pH values etc. Four types of hydrogeochemical environment (formed due to changes in the water use over the past 20 years) were distinguished using discriminant analysis. The mechanisms of barriers formation and destruction were described. Statistical modeling of the metals' precipitation was performed by multivariate regression analysis. Cu is adsorbed by recently formed Fe hydroxides, and, to a lesser extent, precipitates with sulfates as water pH increases. Antagonism to Mn hydroxides has been demonstrated, due to different physicochemical conditions for their precipitation. Zn enters solid phase mainly with sulfates, this element also forms its own mineral phases. The second mechanism is adsorption by recently formed Mn hydroxides, which corresponds to the idea of similar conditions for the precipitation of metal hydroxides. Cd behavior reflects conditions intermediate between these of Cu and Zn. Contribution of both mechanisms (related to Fe hydroxides and aqueous sulfates) is equal. Antagonism to Mn is absent. According to the assessment results using of nature-like technologies *in situ* in watercourses, canals and other water drainage systems is promising. Developed statistical models can be used for needs of experimental studies and artificial geochemical barriers engineering.

***Keywords*:** bottom sediments; heavy metals; forms of metals; metal adsorption; statistical modeling; sub-dump and quarry waters; geochemical barriers

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Introduction. Currently scientists pay great attention to looking for the most effective methods of removing metals from mining wastewater. Modern approaches are focused on complex methods preventing formation of secondary hazardous substances [1]. A promising direction is development of nature-like technologies. Actively discussed "gray-green"/"green-gray" technologies (CGGT) [2] as well as passive and alternative ones [3] are particularly suitable for cases of solid mineral resources extraction, which often don't require use of chemicals for water purification. Therefore, nature-like approaches can be applied.

Non-ferrous metallurgy of the Southern Urals affects environment in a complex way [4]. Discharge of untreated wastewater and filtrate from dumps lead to small rivers degradation and the removal of heavy metals (Fe, Cu, Pb, Zn, Ni, Co, Cd, etc.) in the dissolved and suspended forms into higher-order rivers. Acidic mine, quarry and dump water decrease quality of water in rivers and lakes creating a potential threat to public health. Natural and artificial geochemical barriers reduce the migration ability of metals. Artificial barriers made of mining waste can also solve the problem of mineral resources rational using [5-7]. Geochemical barriers have several advantages such as feasibility of large-scale water purification projects *in situ*, no need for special equipment, relative inexpensiveness, implementing of several barrier types for different pollutants [8].

Artificial geochemical barriers are developed for wastewater treatment, they allow reducing of metal's migration by means of sorption (sorption barrier) or precipitation caused by changes of pH (acidic and alkaline barriers) and Eh (oxidative and reductive barriers) values. Such barriers are often constructed using natural materials. Following materials are proposed for artificial barriers: natural mineral substances (carbonates [9, 10], layered and framework silicates and aluminosilicates [11-13], hydroxides [14], oxides [15], etc.) and their mixtures [16, 17], including those obtained from mining waste [7, 18, 19]. Peat [20] and ferromanganese nodules [21] can also act as natural sorbents. There are also wastewater treatment methods based on biogeochemical barriers and using indigenous aquatic and coastal aquatic plant species [22-24], and other biological agents, such as fungi and bacteria [25-27].

Many of the listed mineral components are present in bottom sediments under natural conditions and contribute to blocking migration of dissolved metals. Geochemical barriers may appear during technogenic impact, which leads to the deposition of pollutants in the impact zone. Considering the wide range of natural reagents that are used in water purification, combination of such reagents for every case requires careful justification. The main factors of metals' phase transitions and deposition on barriers are the chemical composition of water, initial pH values, chemical properties of metals, their concentration and forms, hydrodynamic regime. These factors determine local hydrogeochemical conditions. Statistical modeling using mentioned data allows to recommend the most suitable reagents for water purification, taking into account local conditions. The modeling results can provide the basis for experimental and technological research required for *in situ* water purification systems engineering.

The purpose of the research is analysis of effectiveness of ore and related metals (Cu, Zn, Cd) removal from sub-dump filtrate and wastewater by the geochemical barriers in the Karagayly River (classified into several types); as well as statistical modeling of metal immobilization, which is the basis for development of nature-like technologies (not requiring specialized facilities) in mining industry.

Object and methods. Studied area is located near Sibay city (Republic of Bashkortostan) within the Krasnouralsk-Sibay-Gay copper ore zone. Devonian and Early Carboniferous volcanic and sedimentary rocks prevail [28]. Deposites of pyrite ore lies within contrasting volcanics of the Karamalytash complex (D_2kr) [29], which is overlapped by the Ulutau (D_{2-3}ul) and Kizil (C_{1-2}kz) complexes. The latter contain Khudolaz limestone deposit (south-east from Sibay). The Sibay copper-zinc-pyrite deposit was developed from 1939 to 2020. In 1956 development of the Sibay quarry began. It required redirection of the Karagayly River flow into the Kamyshly-Uzyak River (in 1957). The old river bed downstream from the quarry retained the former name and was used to drain dump and mining water (Fig.1).

During the development of the Novo-Sibay deposit sub-dump drainage and mining water formed the Karagayly River flow. Sub-dump sulfate-magnesium water (mineralization 2.5-9.0 g/l) is a pro-duct of mixing of infiltrated rainwater and groundwater discharged in the same place. In summer the average flow here over the past eight years is about 25 l/s (from 7 to 48 l/s depending on the rainfall). The mining water (quarry water) was discharged 1000 m downstream. The average wastewater flow reached 50-70 l/s. The Karagayly River flows east along the southern outskirts of Sibay and around 10 km downstream flows into the Khudolaz River. In the lower reaches of the river several tailing storage facilities (TSF's) are located (Fig.1). Two new sections, including the one in use, are lined with geotextiles, which prevents water infiltration and its entry into the

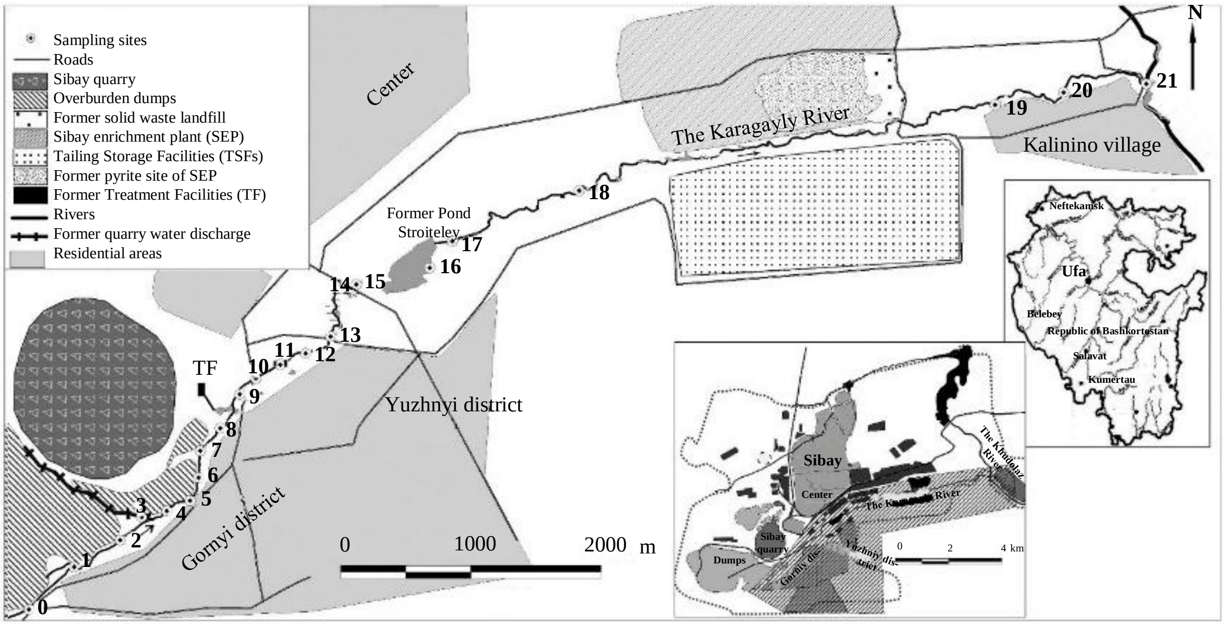

Fig.1. Scheme of water and bottom sediment sampling sites on the Karagayly River (according to [30] with additions)

Karagayly River. Despite the lack of modern isolation materials in old sections of TSF's, no water infiltration and no effect on pH and composition of river water were found. Small amount of acidic drainage water leaves tailing dam (pH of 4.1-4.4), but it does not reach the Karagayly due to relief peculiarities. pH values of the pulp discharged into the tailing dumps is 11.2-11.5. Described water regime existed for more than half a century. However, in the last 15 years, changes of water use led to the transformation of the existing geochemical barriers and pollutants flows.

In 2011, a quarry water treatment facilities were launched below the dicharge. Purified alkaline water was discharged into the river for several years. In 2015-2016 dredging work was carried out in mid- and lower reaches (from the treatment facilities downstream to the Kalinino village near the Karagayly mouth). They disturbed a layer of anoxic sediments accumulated since 1956. In winter of 2018-2019, a pyrite deposit ignited in the Sibay quarry. Under unfavorable weather conditions air was polluted with sulfur dioxide. The quarry was flooded to stop the fire. Therefore, in 2019, the discharge of quarry water into the Karagayly River was ceased and treatment facilities were stopped.

Research of the Karagayly River including sampling of water and bottom sediments has been carried out since 2004, on the basis of sampling sites network (Fig.1). Metal content in water and sediments initially was measured by atomic absorption spectroscopy (AAS) at VNIIOkeangeologia. Since 2014, samples of bottom sediments and water have been analyzed by mass spectrometry with inductively coupled plasma (ICP-MS) at Karpinsky Institute (VSEGEI). In both laboratories, complete acid decomposition of bottom sediment samples was carried out. Content of many metals and metalloids was measured, but in this research we focus on Cu, Zn, Cd, Fe, Mn, Co, Ni, Pb and Cr, monitored during the entire study period.

Mobile forms of metals were extracted with an ammonium acetate buffer solution (pH 4.8). Elements' forms were studied using sequential extraction [30]. Six fractions were identified (residual does not count): exchangeable, carbonate and easily degradable organic matter, oxidizable, reducible and fraction of crystalline Fe hydroxides. The extracts were analyzed at the Resource Center of Saint Petersburg State University "Chemical Analysis and Materials Research Center" (analyst V.N.Grigoryan).

In the geoecological monitoring laboratory of Saint Petersburg State University, organic carbon (C_{org}) content in bottom sediments was measured using I.V.Tyurin's method. Granulometric analysis of sediments was carried out using sieve and pipette methods. Biotesting of bottom sediments was accomplished using *Daphnia magna* Straus. (PND F T 14.1:2:3:4.120-06 T 16.1:2:2.3:3.9-06) and *Chlorella vulgaris* Beijer. (PND F T 14.1:2:3:4.10-04 T 16.1:2:2.3:3.7-04). Exposure time (acute toxicity) for *Daphnia magna* was 48 h, for *Chlorella vulgaris* – 22 h.

Scanning electron microscopy was carried out in the Resource Center for Microscopy and Microanalysis of the Scientific Park of Saint Petersburg State University (desktop scanning electron microscope TM 3000 (Hitachi, Japan) with energy dispersive microanalysis attachment OXFORD) in reflected electron mode.

Statistical processing of geochemical data (descriptive statistics, discriminant and variance analyses, as well as multivariate regression analysis) was performed in the Statistica 28.0 software package (StatSoft). Logarithms of metal content were used in multivariate statistical analysis, considering that the analyzed samples do not correspond to the normal distribution law. The criteria for normal distribution in the sample were the values of asymmetry (less than 1) and kurtosis (less than 5) [31].

Distribution of metals in bottom sediments and water of the Karagayly River was assessed using the multiplicative index (MC), which was calculated as the product of the content (bottom sediments in %, water in mg/l) of Cu, Zn and Cd, multiplied by 1000 to reduce the digit value.

Results and discussion. The system of geochemical barriers that formed on the river before 2011 mainly consisted of acidic-alkaline barriers. Besides that, in wide and shallow river sections, covered with reeds and sedges, complex barriers of mechanical and biogeochemical types were formed, but they were not effective at metals immobilization. The first alkaline barrier was formed by mixing of acidic sub-dump drainage water (pH 1-3 [32]) and slightly alkaline groundwater. Today it still works, since water use changes of recent years have not affected this section of the river. The mixing of two water flows leads to the neutralization of acidic sub-dump filtrate and intensive precipitation of whitish powder, consisting of gypsum, clay minerals and sulfates of heavy metals (here and further referred as "aqueous sulfates"). Precipitate is rich in the studied metals. According to the results obtained in different years, Zn content in aqueous sulfates reaches 1.57-1.78 %, Cu – 0.91-1.24 %, Cd – 11.5-13.3 mg/kg; values of the multiplicative indicator are also very high (Fig.2). The pH value of mixed water varies widely – from 4.98 to 7.52. The pH value depends on

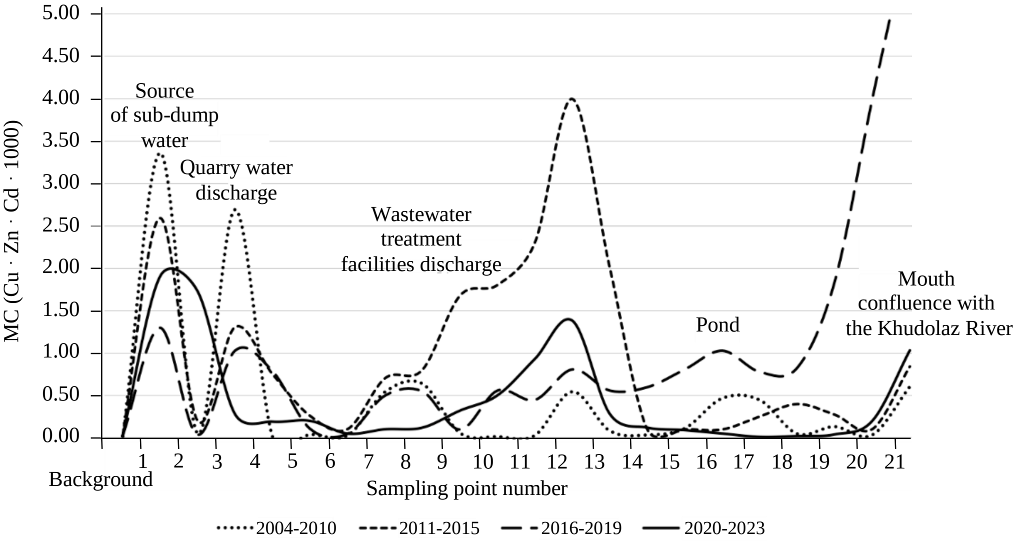

Fig.2. Values of the multiplicative indicator for Karagayly River bottom sediments at different hydrogeochemical stages of the watercourse evolution

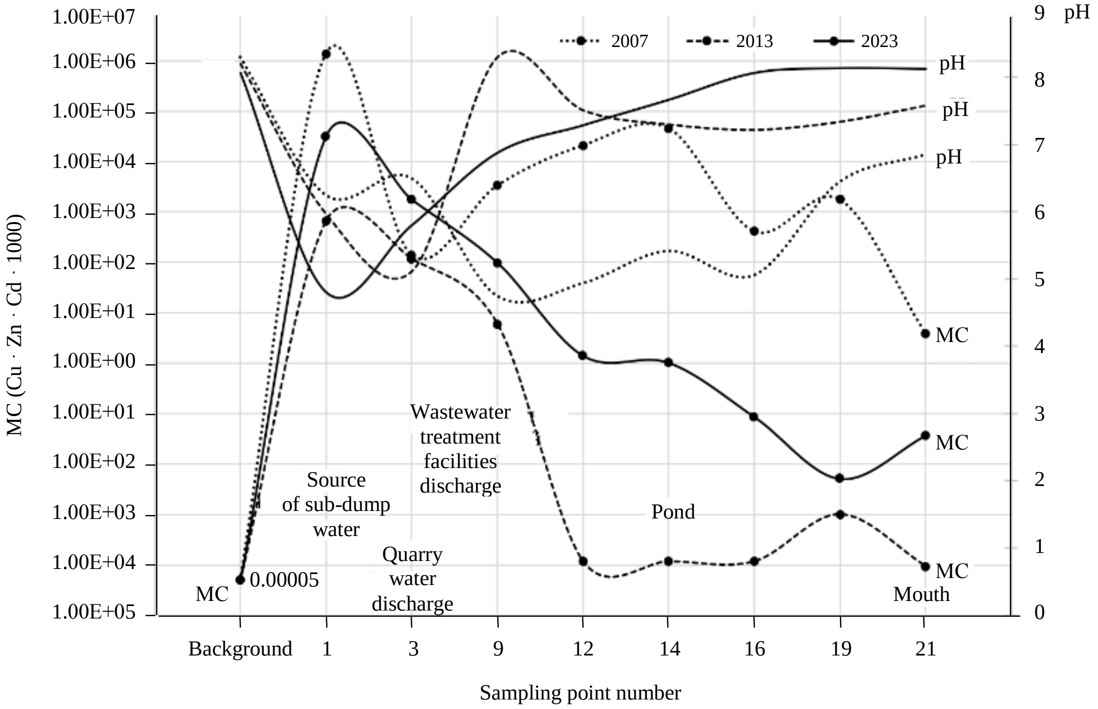

Fig.3. Values of the multiplicative indicator in the Karagayly River water at different hydrogeochemical stages of the watercourse evolution

the rainfall before sampling and the ratio of drainage and groundwater. Besides that, a weak relationship between values of pH and water flow from the dumps was found. Intensive rains and high values of water flow are combined with low pH and vice versa. Despite massive sulfates precipitation, concentration of ore metals in the sub-dump water remains extremely high. During the research period, content of elements in water reached 24.1-111 mg/l (Zn), 0.58-21 (Cu), 0.048-0.39 mg/l (Zn). High concentrations determine maximal values of the multiplicative indicator throughout the entire observation period (Fig.3).

Quantitative assessment of metal deposition efficiency for the alkaline barrier is difficult, since sampling of sub-dump water before mixing with groundwater is impossible. However, characteristics of drainage water leaving dumps are available [32]: Zn concentration reaches 100 g/l, Cd – 0,38 g/l. These values suggest a decrease of metals concentration by three orders of magnitude. Such change probably occurs due to dilution, but one should not underestimate the role of the alkaline barrier in the sub-dump “lake”, where melanterites and, possibly, chalcanthite and goslarite are formed [32]. The last two minerals crystallize due to the supersaturation of solution with Cu and Zn. In the current hydrogeochemical situation, acidic drainage is diluted and an alkaline barrier works, reducing the flow of metals into superaquatic and subaquatic sites. The concentration of metals in water leaving the dumps is far from saturation. It is indicated by the absence of detectable own mineral phases of Zn, Cu and Cd in aqueous sulfates [33]. However, a ratio of mobile (sorption-carbonate) species of Zn, Cu, Cd in the precipitate is high – 33, 26 and 22 % of the total content, respectively. Thus, the effectiveness of described acidic-alcaline barrier is relatively high, but it does not provide the required level of water purification (to background levels). Some metals are transported downstream as free cations and in suspended forms.

Until 2019, quarry water was discharged downstream of the Karagayly River. At that point flow of quarry water exceeded the river flow. pH of wastewater was low and stable (3.32-4.95), which ensured high metals concentration in water and prevented precipitation of aqueous sulfates. Metals concentration in wastewater reached 36.6-49 (Zn), 5.4-8.1 (Cu), 0.13-0.15 mg/l (Cd). High flow values of wastewater led to the acidification of neutral and slightly alkaline river waters (pH decreased to 4.60-5.30). So, one more acidic-alkaline barrier was formed, but effectiveness of metals immobilization was low. In alkalized environment metals from the wastewater were partly adsorbed by clay minerals. Some elements' content in bottom sediments exceeded their content upstream and downstream 4.2 times (Zn, Cd) and 5 times (Cu). However, peaks of the multiplicative indicator at this barrier were consistently lower than in the upper reaches of the river (see Fig.2). River water acidification led to the aqueous sulfates dissolution and further migration of metals in solution. This is reflected by the shape of the multiplicative indicator graph (for water): clear increase (2007) and slow decrease downstream to the point of the river Karagayly mouth (see Fig.3). In turn, a gradual pH increase provoked the repeated formation of aqueous sulfates, visually recognised in the middle and lower reaches of the river (to the Kalinino village). According to the results of metals' sequential extraction from bottom sediments samples, the percentage of the sulfate forms in the upper reaches and near the river mouth was 78 % and 15 % of total content (Cu), 29 and 9 % (Zn), 43 and 7 % (Cd) respectively [30]. The existed system of barriers in the considered hydrogeochemical environment did not ensure decrease of metals' concentrations to background levels at the confluence of the Karagayly and the Khudolaz Rivers (Fig.3).

The treatment facilities, launched in 2011, were focused on removal of chalcophilic elements from the quarry and mine water coming from the Kamagan quarry. Liming followed by flocculation were used; no preliminary Fe removal was carried out. So, alkaline water (pH > 10), purified from chalcophilic metals, but rich in Fe^{2+}, was being discharged into the river. As a result, an artificial acidic-alkaline and sorption (hydroxide) barrier appeared. After the treatment facilities launch, the river water pH at the discharge site increased from 4.5-4.8 to 7.5-9.1. This led to decrease of metals' stability in the solution. Precipitation of aqueous sulfates intensified. Even more significant was the iron bicarbonate formation $FeSO_4 + Ca(HCO_3)_2 \rightarrow CaSO_4 + Fe(HCO_3)_2$ with its transition to hydroxide: $2Fe(HCO_3)_3 \rightarrow 2Fe(OH)_3\downarrow + 6CO_2$ [30], accompanied by adsorption and almost total precipitation of Zn, Cu and Cd. It provided a decrease of metals concentration in river water to background levels (Fig.3).

The results of bottom sediments' column study confirmed the sedimentation acceleration (the upper layer was formed after the treatment facilities launch). This part of the river is wide, shallow and calm. Under these conditions, sedimentation rate increased to several centimeters per year (approximately). The metals' content in the upper layer of sediments was significantly higher than in the lower one: 10 times (Zn – 19200 and 1580 mg/kg in the upper and lower layers respectively), 1.3 times (Cu, 8260 and 6380 mg/kg), 20 times (Cd, 48.2 and 2.4 mg/kg). This feature is reflected by the multiplicative indicators graph (Fig.2). Even more significant changes were found for river water. The comparison series is based on data from 2007 and 2013. Below the point of wastewater discharge, Zn content decreased from 21 to 0.098 mg/l, Cu – from 1.6 to 0.042 mg/l and Cd – from 0.1 to 0.001 mg/l. Thus, it can be stated that the purification level of river water at the formed complex barrier was around 97 % for Cu, and more than 99 % for Zn and Cd. Before and after treatment facilities' operating period, this part of the river lacked a geochemical barrier and was a transition one, not affecting elements' migration (Fig.3).

Dredging works without the necessary scientific justification led to removal and disturbance of sediments, accumulated during the development of the ore deposit. The ditch-like shape of the channel increased water flow rate and banks erosion. Fe^{2+}, once deposited in the sediments, began to move with water flow, oxidize and precipitate not only in Karagayly, but also in the Khudolaz River at a distance of more than 25 km downstream [33]. In 2016-2019 sediments accumulated at the bottom of the river contained 20-25 % Fe. During dredging and straightening of the riverbed, all geochemical barriers in the middle and lower reaches of the Karagayly River were destroyed. An increase of the water flow energy led to the metals' transit and accumulation at the river mouth (Fig.3). At the same time, emerging of additional pollution source (erosion of technogenic sediments) caused a slight increase of the multiplicative indicator values (in comparison with other periods of the river's evolution; see Fig.2). In the river mouth one more alkaline barrier appeared, causing massive precipitation of Fe oxyhydroxides and metals sorbed by them.

The current stage of water use is characterized by cease of quarry water discharge, stop of water acidification, and the decrease in the metals supply in the upper reaches of the Karagayly. As a result, river water pH rapidly returned to background values (from 4.8 to 8.13), metals concentrations began to follow a pattern of steady decrease along the river (towards the mouth) and almost reached background values (Zn – 0.50, Cu – 0.073, Cd – 0.001 mg/l; Fig. 3). The values of multiplicative indicator in bottom sediments are low in the middle and lower reaches of the river (see Fig.2). Described features of the Zn, Cu and Cd distribution in water and bottom sediments are caused by significant decrease in the metal's influx (after cease of the quarry water discharge). However, erosion of sediments, oxidation and migration of elements, previously deposited in sediments are possible.

Analysis of nature-like technologies effectiveness for treating polluted waters is based on study of the bottom sediments' composition (they can be considered as sewage sludge – SS). The reason is that the assessment of sediments' toxicity and the aquatic environment's secondary pollution risk during SS's removal and neutralization are necessary. Bottom sediments of a watercourse formed on different types of geochemical barriers can be taken as model objects. Not only total content of metals, but also mobile forms' content and elements' forms (using sequential extraction method) were studied (2007, 2022). Considering that in the lower reaches of the river limestone is present, the mobile forms extracted by the ammonium acetate buffer solution should be considered as the sum of exchangeable, adsorbed on clay minerals and contained in carbonates species. In the context of the Karagayly River hydrogeochemical conditions changing (with significant variability in the incoming volumes of technogenic material and contrasting acidic-alkaline conditions), an assessment of the metals' total content and their mobile forms were carried out for each stage of the river transformation (Table 1). However, only data for the middle and lower reaches of the river were used for calculations, because in the upper reaches the hydrogeochemical situation did not change until 2019.

Table 1

Total content (mg/kg) and ratio of mobile forms (%) of metals in bottom sediments of the Karagayly River (middle and lower reaches)

Stages, years, number of samples	Cu	Zn	Cd	Fe	Mn
2004-2010, *n* = 24	4786±751* 15	5200±888 36	9.3±1.8 38	122800±16500 0.4	824±88 9.3
2011-2015, *n* = 10	7186±1314 31	8928±1465 49	16.3±4.1 47	101200±16500 4.5	1410±324 18
2016-2019, *n* = 12	8522±1839 9	11207±4257 34	22.4±8.5 20	214000±18600 0.5	943±223 7.3
2020-2023, *n* = 12	4013±2582 27	5752±1638 45	11.3±3.0 75	97100±11600 2.3	1090±91 49

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* In the numerator – mean ± standard error of the mean ($p = 0.05$), in the denominator – percentage of mobile forms.

One-factor analysis of variance of the metal content in bottom sediments allowed to identify the following features (caused by changes in the water use system). Sediments accumulated in 2011-2015 and 2016-2019 (during the operating period of the treatment facilities) stand out for significantly higher metals content in comparison to ones formed before 2011 and after 2019. It is caused by the influence of the alkaline Fe-rich water discharge on the immobilization of chalcophiles. Until 2011, the transit regime with the removal of metals into the Khudolaz River prevailed. Moreover, in 2016, as a result of dredging work, masses of metals from the exposed sediments were involved in the migration. After the cease of the quarry water discharge and the treatment facilities closure, the transit regime was restored, but masses of elements involved were significantly reduced.

At the same time, the ratio of metals main species was changed. The maximal ratio of mobile forms is typical for periods with consistently high pH values (2011-2015 and 2020-2023), which provide favorable conditions for the accumulation of metals, including in the adsorbed state. The transit regime (2004-2010) determined lower content and ratio of mobile forms in bottom sediments. It contributed to the removal of metals to higher-order rivers. During dredging and mobilization of large masses of ferrous iron, the ratio of exchangeable forms decreased due to the increased accumulation by Fe hydroxides. At the same time, Mn activity did not increase due to its low content in sediments. The contrast in the Fe and Mn content is caused by different pH values of these elements' hydroxides precipitation.

The geochemical specialization of the forming bottom sediments at each of the four identified hydrogeochemical stages (determined by the water use system) is confirmed by the results of discriminant analysis of the metal content in sediments, performed by stepwise selection using the Wilks method. As in the previous calculation of average values, only samples taken in the middle and lower reaches of the river were taken into account (starting from the area affected by wastewater treatment facilities). The dependent variable in the analysis was the four distinguishable stages. The discriminating variables were Cd, Fe, Mn, Pb, Ni, Co content, as well as the pH value. According to the results, 89.1 % of the grouped observations from the original 55 were classified correctly, which highlights the reliability of the geochemical specialization of the hydrogeochemical environment types. The greatest contribution to the classification of groups was made by the pH level and the content of Fe and Co in bottom sediments.

During the treatment facilities's operating period (2011-2019) and after the cease of quarry water discharge, the ratio of mobile forms decreased. It is related to the formation of a hydroxide sorption barrier and the adsorption of metals on newly formed Fe and Mn hydroxides. This is confirmed by the results of sequential extraction performed in 2007 [30] and 2022. At the first stage the share of hydroxide (reducible) forms was 1-7 %, then in 2022 it increased to 6-15 %, with Zn having the maximum affinity for the reducible form. The importance of hydroxide-sorption accumulation of metals is proven by the results of microscopic analysis: despite the absence of their own secondary mineral phases in sediments, Cu, Zn, Cd are found in the formations of microcrystalline aggregates with Fe compounds and clay minerals, acting as adsorbents (Fig.4, *a*). Mn-Zn aggregates were discovered (Fig.4, *b*) together with apatite and Fe oxides [33].

High content and mobility of metals in sediments caused their significant toxicity, which all chalcophilic elements (including Pb, As, Hg, Sb, etc.) contribute to. It was proven by the biotesting of bottom sediments (seven samples) using *Daphnia magna Straus* and the *Chlorella vulgaris Beijer*. A 100 % death of *Daphnia* in almost all samples was observed, with the exception of the river mouth zone, where it decreased to 80 %. The deviation of optical density from the *Chlorella* culture control for three samples was 50-80 %, for the remaining four samples it was more than 80 %. The results confirm contemporary ideas about emergent pollutants (such as As, Mn, xanthates) entering the environment during the development of sulfide ore deposits and their high toxicity in highly mineralized, sulfate-rich water [34].

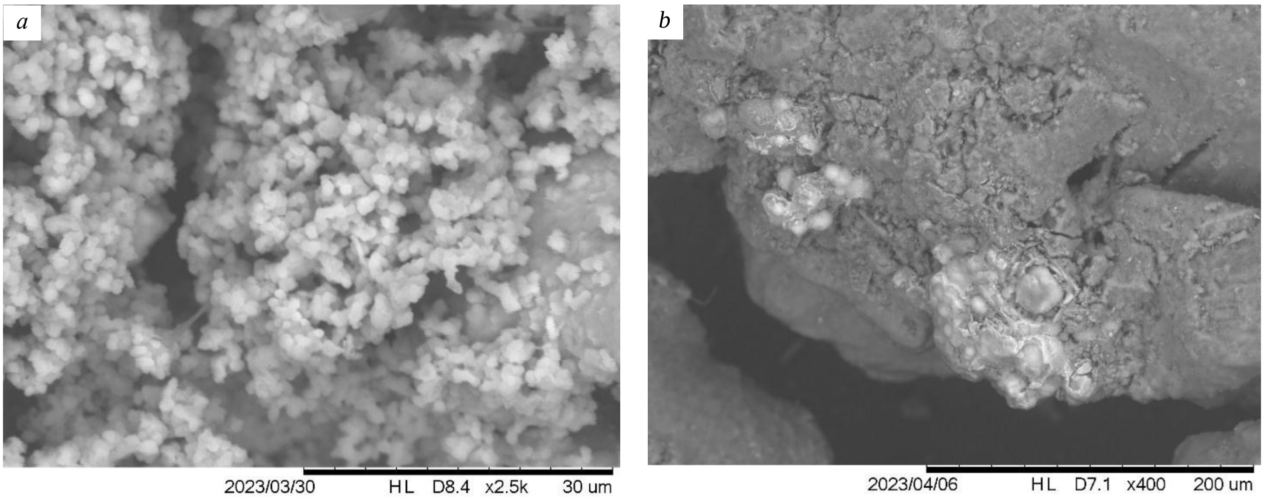

Fig.4. Mineral phases of iron in bottom sediments of the Karagayly River near the dumps of the Sibay quarry:
a – iron hydroxides (in the area of acid quarry water discharge); *b* – ferromanganese formations (light shade)
with Zn, Cu and Co against the background of a clay matrix (dark shade)

Statistical modeling of the metal deposition mechanisms at different hydrogeochemical stages of watercourse evolution was carried out using multiple regression analysis (MRA). The hypothesis is the possibility of phase transitions and precipitation of metals in an acidic environment (low pH of river water) via adsorption by newly formed Fe and Mn hydroxides, clay minerals and organic matter. Hydroxides, clay minerals and C_{org} can act as metal carrier phases. Thus, when conducting MRA, Cu, Zn and Cd content in bottom sediments successively acted as dependent variables. The content of Fe, Mn, C_{org}, pelitic (clay minerals), silt (secondary mineral phases) fractions and water pH were considered as predictors.

Regression equations were obtained ($p = 0.05$). Main mechanisms and factors of metal deposition at the artificial barriers of the Karagayly River were revealed (Table 2). Phase transitions and accumulation of Cu are caused by adsorption on Fe hydroxides, an increase in pH, and the Mn content in sediments (in descending order of correlation significance). The coefficient of determination is 0.385, which explains 38.5 % of the variance of Cu content in sediments. In this case, Fe plays a decisive role, according to the value $\beta = 0.472$ (Table 2). Mn has a negative coefficient value in the regression equation and a negative correlation with the dependent variable. It can be considered as a factor counteracting Cu accumulation. To explain this phenomenon, one should take into account alkalization of the Karagayly water downstream, (the pH of Mn hydroxides precipitation is significantly higher than that of Fe and Cu hydroxides). Mn accumulation occurs in the upper and lower reaches, and Cu accumulation in the middle reaches, which corresponds to the precipitation regime of Fe hydroxides (Table 3).

Table 2

The role of carrying phases and physicochemical conditions in the deposition of Zn, Cu, Cd into bottom sediments of the Karagayly River according to the results of multiple regression analysis

Dependent variable	Model (*n* = 57)	Determination coefficient	Standardized coefficient β	Regression equation
Cu	Fe	0.385	0.472	Cu = 0.044 + 0.59 Fe + 2.264 pH – 0.392 Mn
	pH		0.383	
	Mn		–0.250	
Zn	pH	0.330	0.406	Zn = 1.434 + 1.882 pH + 0.271 Mn
	Mn		0.245	
Cd	pH	0.352	0.476	Cd = –4.718 + 3.081 pH + 0.614 Fe
	Fe		0.400	

Table 3

Total content (mg/kg) of metals in bottom sediments of the upper, middle and lower reaches of the Karagayly River

Reach of the river, number of samples	Cu	Zn	Cd	Fe	Mn
Upper, $n = 24$	6649 ± 1778*	10053 ± 2203	9.92 ± 1.53	59100* ± 18400	1400 ± 250
Middle, $n = 10$	6420 ± 468	5780* ± 563	9.54 ± 1.18	142600 ± 10200	940 ± 93
Lower, $n = 12$	4326* ± 713	7970 ± 1150	16.2 ± 2.47	115300 ± 16600	1280 ± 128

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* Mean ± standard error of the mean ($p = 0.05$) – significantly low content (according to the results of analysis of variance).

The activity of the Zn transition into the solid phase is determined by the pH value and Mn content (in order of their significance). Dependence on these predictors explains 33 % of the variance. Thus, there are two main mechanisms of Zn accumulation: precipitation in sulfates (in case of pH increase) and adsorption on newly formed Mn hydroxides. The former ($\beta = 0.41$) dominates over the latter ($\beta = 0.245$). Similar pH values of Mn and Zn hydroxides precipitation and the coinciding peak of concentrations in the lower reaches of the river support the hypothesis of adsorption on newly formed Mn hydroxides as opposed to interaction with Fe hydroxides (Table 3).

Cd accumulation is caused by the precipitation with sulfates along with water alkalization and adsorption by Fe hydroxides. These mechanisms accounted for 35.2 % of the variance. The values of the pH and Fe standardized coefficients are close (see Table 2). The peak concentration, like that of Zn, is observed in the lower reaches, which is explained by the high pH of the Cd hydroxide precipitation, Cd stability in solution, and a single source of influx (oxidation of sphalerite).

Intensity of ore elements water migration in secondary dispersion halos of pyrite copper-zinc ores: Cd (1.3) – Zn (1.0) – Cu (0.7) – Fe (0.04) confirms the revealed patterns of metals and their potential carrying phases migration and accumulation [32].

Preliminary analysis of the C_{org} adsorption and complexing activity (based on MRA) establishes its inclusion as a predictor in the regression equation for Zn content. It confirms that research of organic matter as precipitating agent at copper-zinc-pyrite ore development sites is promising. However, decisive conclusions require higher number of objects (in this research 19 samples were studied).

When determining the main mechanisms of metal precipitation, the role of carbonates was not taken into account, due to absence of quantitative data. However, in the bottom sediments of the Karagayly River lower reaches, an increase in the number of carbonate phases is noted. It is caused by the bedrock: Karamalytash complex (D_2kr) mafic igneous rocks is replaced with the Kizil complex ($C_{1-2}kz$) sedimentary rocks. The latter has predominantly carbonate composition. It is reflected by increase of carbonate forms according to sequential extraction in 2007 (in the first hydrogeochemical stage of the evolution of a watercourse with low pH values and a high content of metals in water). The ratio of carbonate species of metals increased from the source to the mouth of the river: Cu – 9.2-51, Zn – 24.5-36.7, Cd – 8.1-31.7 %. In 2022 (the fourth stage of evolution) the ratio of carbonate forms of metals noticeably decreased, which could be caused by a decrease of elements' concentrations in river water.

A high ratio of oxidizable (sulfate) forms (Cu up to 86, Zn up to 29, Cd up to 60 % of total content) in sediments in 2007 should be mentioned, as well as an increase in ratio of the reducible (connected with Fe-hydroxides) form in 2022: Cu – up to 43, Zn – up to 31 and Cd – up to 24 %. The obtained results are fully consistent with the model of sedimentation and its transformation during the change in hydrogeochemical conditions from the acidic-alkaline type to the hydroxide-sorption type.

Conclusion. Long-term studies of metals migration and accumulation conditions (during the development of the Sibay copper-zinc-pyrite deposit) provide arguments of effective immobilization and sedimentation of pollutants by geochemical barriers (natural, technogenic and artificial). Changes in the management of quarry and dump drainage water of the deposit along the Karagayly River caused formation of different hydrogeochemical conditions. Each stage of water use has specific geochemical features of water and bottom sediments composition, as well as ore metals' migration and accumulation, which was confirmed using multivariate statistics. Over a long period, acidic-alkaline technogenic barriers were the main factors of river water purification and pollutants' precipitation. Their effectiveness in regard to specific metals is controlled by pH values. Precipitation occurs in sulfate form when water is alkalized. Complex alkaline-hydroxide-sorption barrier was formed unintentionally after the launch of wastewater treatment facilities which dumped into the Karagayly River highly alkaline Fe-rich water. This barrier turned out to be more effective, removing 97 % of Cu and more than 99 % of Zn and Cd.

Statistical modeling revealed the behavior of the studied metals in different hydrogeochemical environments, as well as factors and mechanisms of their accumulation. Different metals have distinct characteristics of phase transitions. Cu precipitation occurs due to adsorption by newly formed Fe hydroxides, and, to a lesser extent, with sulfates depositing as water pH increasing. Revealed antagonism with Mn hydroxides is probably caused by different physicochemical conditions of precipitation.

Zn accumulation mechanisms are different. They are mainly related to phase transition in sulfates (as pH increases) and include formation of zinc's own mineral phases like goslarite. The second mechanism is adsorption by newly formed Mn hydroxides, which corresponds to the idea of similar conditions for the precipitation of metal hydroxides. Cd behavior reflects conditions intermediate between these of Cu and Zn. Contribution of both mechanisms (related to Fe hydroxides and aqueous sulfates) is equal. Antagonism to Mn is absent (unlike the case of Cu). Organizing purification systems, one must take into account distinct behavior of Fe and Mn in contrasting physicochemical conditions arising during sulfide ores development. It is caused by significantly different pH values of these metals' hydroxides precipitation.

Study of metals' forms in bottom sediments and preliminary calculations indicate potential role of organic matter (Zn) and carbonates (Cu, Zn) in metals' accumulation. However, confirmation requires additional research using representative sampling. Analysis of clay minerals participation in precipitation processes did not give a positive result.

Assessment of geochemical barriers effectiveness in wastewater purification allows to conclude that using of nature-like technologies *in situ* (in watercourses, canals and other water drainage systems of developed pyrite deposits) without complex treatment facilities is promising. Developed statistical models are preliminary but still can be used for needs of experimental studies and engineering.

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Research article

Organotin pollutants in emerging coastal-marine sediments of the Kaliningrad shelf, Baltic Sea

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Abstract. Based on two years of monitoring of modern bottom sediments of two sections of the Kaliningrad shelf of the Baltic Sea – “Curonian Spit” and “Northern Sambian” – an assessment of the sources of pollution with organotin compounds (OTs) and heavy metals was carried out. The content of individual organotin compounds and OTCs spectra obtained by gas chromatography with mass spectrometry of relatively coarse-grained bottom sediments indicate the presence of organotins in significant quantities – the total OTs content (∑OTs) is from 0.6 to 8.3 ng/g. However, the content of tributyltin (TBT), the main component of anti-fouling systems for marine vessels and the most dangerous endocrine-disrupting compound among the hazardous substances for marine ecosystems, is at a low level (0-2.3 ng/g) in all studied samples and has not increased over the two-year observation period (biodegradation index 1.7-12.4). At the same time, the presence of abnormally high concentrations of mono-, triphenyl- and tricyclohexyltin in the sediments of the ”Northern Sambian” site (up to 30, 7 and 6.4 ng/g, respectively) indicates an additional source of pollution of coastal waters and shelf sediments (for example, plastic litter and agricultural runoff). The absence of significant shipping in the study areas ensures a consistently low level of pollution with tributyltin and its derivatives (less than 0.3 and 2.3 ng/g of TBT in 2017 and less than 0.1 and 1.3 ng/g in 2018 for the sites “Curonian Spit” and “Northern Sambian”, respectively), which indicates the activity of the processes of TBT transformation and self-cleaning of sandy sediments. However, the identified trends and their predictive accuracy require long-term observation and monitoring of the sediment environment using data on the deep-water part of the shelf, enriched in clay and humus components.

***Keywords*:** organotin compounds; tributyltin; bottom sediments; Curonian Spit; Baltic Sea

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Introduction. Organotin compounds (OTs) are substances highly in demand by modern industry and are used throughout the world as stabilizers for PVC and in the production of polyurethanes, silicones, paints and pesticides [1-3]. Until recently, tributyltin compounds (TBT) were widely used as biocide components of anti-fouling systems in shipbuilding [4]. However, since the 70s of the last century, the harmful effects of these components, which are endocrine-disrupting compounds [5], on non-target marine biota have become obvious: the appearance of male sexual characteristics in female marine snails and mollusks, gastropods and bivalves; disorders of reproduction and growth in mussels; abnormalities of calcification of oyster and crustacean shells; immunological dysfunctions in fish [6]. At the same time, TBT has high toxicity (chronic) even in extremely low concentrations (1 ng/l), and its presence in the marine ecosystem has a serious impact at all levels of the food chain – from phytoplankton [7] to marine mammals [8], as well as potentially dangerous for humans – natural steroid/receptor binding and steroid signaling are disrupted, leading to excess obesity [5].

Currently, the problem of pollution of marine and freshwater areas with organotin compounds is relevant for the whole world – from Europe [3, 9, 10], Asia [8, 11], Africa, North and South America [5, 12] to the Arctic and Antarctic [13]. Some countries have introduced strict standards regarding the content of TBT in water, sediments and biota. In 2012, the Russian Federation acceded to the International Convention for the Control of Noxious Anti-fouling Systems on Ships (AFS Convention), which prohibits or restricts the use of any anti-fouling systems[1]. Earlier, in 1998, the Russian Federation, having become a member of the Helsinki Commission (HELCOM), ratified the Convention for the Protection of the Marine Environment of the Baltic Sea Area. The Convention established a list of priority hazardous marine pollutants, which included TBT and its derivatives[2]. However, despite the introduction of international restrictions on use, the level of OTs content in modern sediments remains high over the past decades, including in the Baltic Sea region [14, 15]. Recent studies have confirmed the high content of TBT in bottom sediments along the fairway and port areas of the Gulf of Finland [16].

The accumulation of OTs in bottom sediments is an acute problem for the marine environment and is determined by the influx of technogenic pollution, its stability and the rate of degradation in bottom sediments. If in the aquatic environment the half-life of OTs is several days, then in bottom sediments this process can last several years [14, 17]. Understanding which environmental factors and how they influence the distribution and accumulation of organotin compounds in marine sediments is necessary to predict the situation with these types of pollutants in specific regions.

Previously, the contamination of bottom sediments with organotins and heavy metals in the area of the islands of Gogland and Moshchny in the eastern part of the Gulf of Finland was studied, and the influence of environmental conditions was assessed – the nature of sediments, particle size distribution, the presence of certain chemical elements and inorganic compounds, gas saturation, the presence of anoxic zones – on the distribution and mobility of OTs in the sediments of this region [18].

An increase in the OTs content in gas-saturated zones of sediments and a decrease in their content with increasing alkalinity of sediments were discovered. At the same time, in the anoxia zone, a twofold increase in the content of OTs was recorded, and a tenfold increase in tetrabutyltin compared to the aerobic zone. This indicates the stimulating role of oxygen in the biotic degradation of OTs and the negative impact of the constantly expanding anoxic zones of the Baltic Sea on the processes of degradation of accumulated organotins.

A direct correlation has been established between the content of OTs and heavy metals and metalloids in fine-grained sediments. Analysis of the profiles of organotin compounds in samples taken over a two-year period in the eastern part of the Gulf of Finland showed the greatest contribution of tributyltin, the high level of which and low values of the degradation coefficient indicate the presence of a permanent source of pollution [18].

The purpose of the work is to study the state of contamination with organotins and heavy metals in modern sediments of the shelf areas of the Baltic Sea in the Kaliningrad region under anthropogenic loads that differ significantly from the Gulf of Finland region. Particular attention is paid to studying the influence of the granulometric characteristics of the sediment on the accumulation of OTs, the processes of sorption and binding of pollutants in the sediment, as well as the degradation of TBT and the possible self-purification of the sediment over time.

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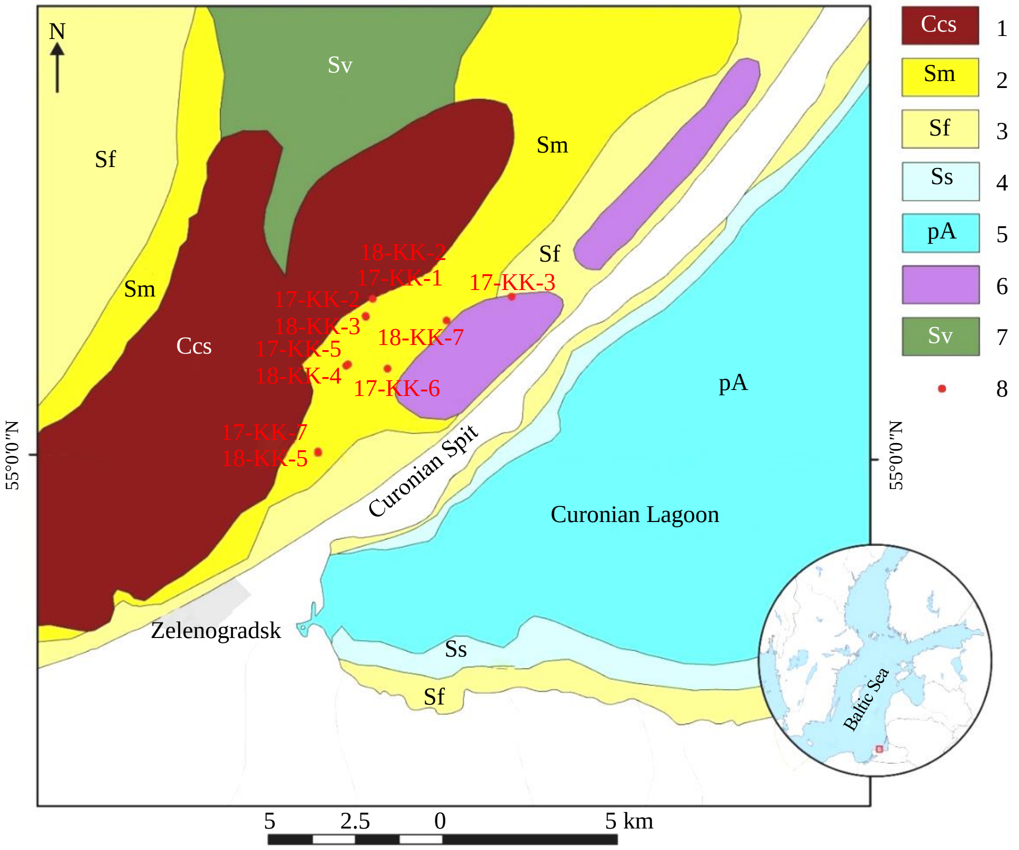

Fig.1. Sampling points on the lithological map (according to [19]) of the Curonian Spit region

1 – coarse clastic sediments; 2 – medium-grained sand; 3 – fine-grained sand;
4 – silty sand; 5 – pelitic alevrite; 6 – outcrops of Quaternary sediments; 7 – sand of various granulometric compositions; 8 – sampling point and number

Methods. The samples were taken by specialists from the A.P.Karpinsky Russian Geological Institute during the 2017-2018 field seasons on the "Nord-3" vessel using a box corer within the Kaliningrad shelf in areas north of the Curonian Spit and near the northern coast of the Sambian Peninsula. All samples taken (depth 0-5 cm) are sands of various granulometric compositions from coarse-grained to fine-grained. On lithological maps, sampling points fall within the sand development fields (Fig.1 and 2). A total of 23 samples were selected for analysis.

Geological settings. The Kaliningrad shelf belongs to the region of the platform cover, represented by sedimentary rocks of the East European Platform (carbonate and clastic), the age of the rocks is from Devonian to Paleogene. The bedrock is overlain by Quaternary sediments (clays, sands, boulders) no more than 30 m thick [19]. The studied areas (Curonian Spit and the northern coast of the Sambian Peninsula) are located in shallow coastal waters with alternating denudation and accumulation surfaces – in places of wave erosion moraine deposits are exposed (boulder loams, sands with gravel and pebbles, bedrock outcrops), in places of wave accumulation – sands are predominantly widespread. Most of the studied samples were taken in places of wave accumulation, which is visually confirmed by the presence of a typical wave relief on the surface of sediments.

Quantitative assessment of the content of cation-organic tin compounds in bottom sediments – monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), tetrabutyltin (TTBT), triphenyltin (TPhT) and tricyclohexyltin (TCyT) – was carried out using gas chromatography/mass-spectrometry (GC/MS) in accordance with the analytical procedure developed by the authors [20] based on the ISO 23161:2018[3] standard. Samples of bottom sediments with

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[3] ISO 23161:2018. Soil Quality – Soil quality – Determination of selected organotin compounds – Gas-chromatographic method. URL: https://www.iso.org/standard/73990.html (accessed 30.05.2024).

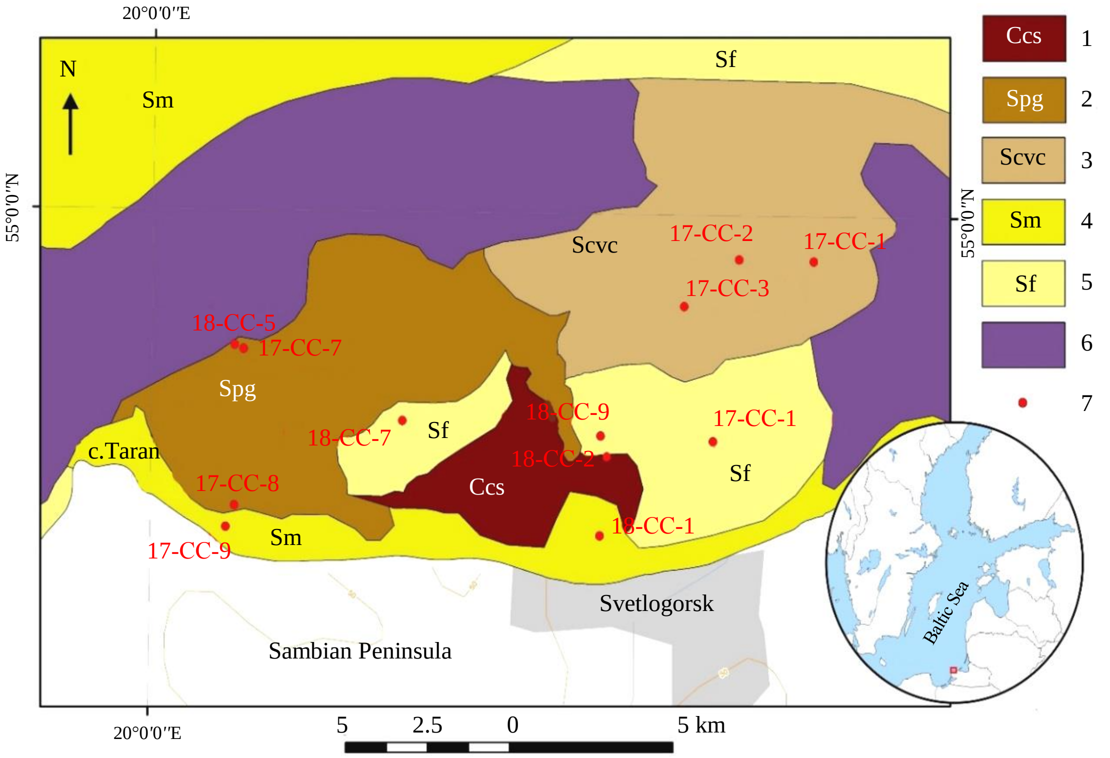

Fig.2. Sampling points on the lithologic map (by [19]) of the northern coast of the Sambian Peninsula

1 – coarse clastic sediments; 2 – pebble-gravel sand; 3 – coarse – to very coarse-grained sand;
4 – medium-grained sand; 5 – fine-grained sand; 6 –outcrops of Quaternarysediments;
7 – sampling point and its number

natural moisture were thoroughly mixed, homogenized, after which a sample weighing 1-3 g was taken, depending on the type of sediment. A 1:1 mixture of methanol and glacial acetic acid was then added to the sample, along with 50 ng of internal standard (tripropyltin) and ultrasonically extracted for 60 min. After centrifugation, acetate buffer (pH 4.5) was used and a derivatizing agent (sodium tetraethylborate) and hexane were added to the extract. The resulting mixture was stirred with a magnetic stirrer for 30 min. The hexane layer was then separated, dried over anhydrous sodium sulfate, and concentrated under a stream of nitrogen to a volume of 50 μL.

The analysis of the main derivatives was carried out in SIM (Selection ion monitoring) mode on a QP 2010 gas chromato-mass-spectrometer (Shimadzu, Japan). Parameters for recording spectra using the GC/MS method: ion source temperature – 200 °C, interface – 300 °C, injector– 300 °C; mode with constant gas carrier flow (helium) 1 ml/min; ionization energy 70 eV. The analysis was carried out on a capillary column of medium polarity TR-5 MS (60 mm × 0.25 mm × 0.25 μm, Thermo Electron, USA) according to the following temperature program: from 60 °C (2 min); heating 20 °C/min – up to 130 °C; 10 °C/min – up to 210 °C; 5 °C/min – up to 260 °C; 7 °C/min – up to 300 °C (holding time 10 min). The volume of the injected sample was 1 μl, the total analysis time was about 40 min.

Analytes were identified by two characteristic ions taking into account precise retention times. The mass fraction of each compound was calculated using the internal standard method using the organic tin cation conversion factors given in the ISO 23161:2018 method. The quantitative detection limit at the specified GC/MS parameters was 0.5 ng/g (recalculate to the dry weight). The suitability of the applied analytical technique was assessed before each series of analyses by adding control samples. Solvent control was carried out under the same concentration and chromatography conditions as for the samples under study.

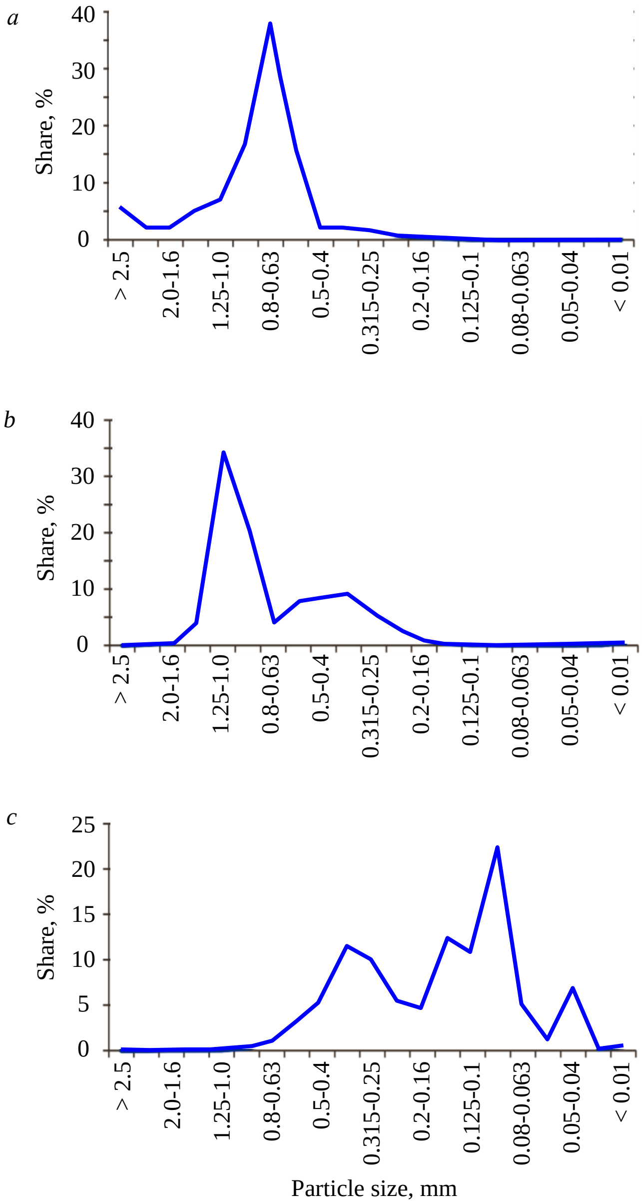

Fig.3. Particle distribution profiles by size class (granulometry) for sandy sediments of the studied samples:
a – typical unimodal distribution (sample 17-KK-2), characteristic of most samples from the "Curonian Spit" site (2017, 2018);
b – typical bimodal distribution of particles (sample 17-CC-2), characteristic of the studied sediment samples from the "Northern Sambian" site (2017, 2018); *c* – polymodal distribution (anomalous) for sample 18-CC-1 ("Northern Sambian", 2018)

In the Central Laboratory of the A.P.Karpinsky Russian Geological Institute the researchers measured the concentrations of Sr, Pb, As, Zn, Cu, Ni, Co, V, Cr, MnO, Fe_2O_3, TiO_2 in 12 samples from the 2017 collection using the ICP-MS method (Agilent-7700 and Elan-DR-e) with preliminary acid decomposition of the sample (Co, Ni, Cu, Zn, Pb in a mixture of $HNO_3 + HF + HClO_4$ or $HNO_3 + HCl$ for As) or fusion with lithium metaborate (MnO, Fe_2O_3, TiO_2, Sr, V, Cr), according to the approved method N10/2010 "Determination of macro- and microelements by mass spectrometry with inductively coupled plasma in rocks, ores, soils and soft sediments".

The assessment of the granulometric characteristics of the sediment was carried out using a laser particle analyzer "Microsizer 201A" (VA Instal, Saint Petersburg, Russian Federation, range 1-300 μm). Granulometric analysis of samples was carried out in an aqueous suspension according to the standard method for a sample of 100 g, after stirring up of which weight measurements were carried out according to 21 size classes with registration of particles in the range of > 2.5 mm till < 0.01 mm in diameter. The results, presented by the characteristic particle size distribution curves for each sample (Fig.3), allow us to classify them according to sediment types – from very-coarse-grained (Svc) to very-fine-to-fine-grained (Svff) sands.

The significance of the relationship between all studied parameters (OTs, granulometry and elemental composition) of the samples was assessed based on correlation analysis using the Spearman method (calculation and construction of a matrix of paired correlations, $p < 0.05$ (probability > 95 %) was set to identify a significant relationship) using the library Scipy, implemented in Python.

To assess the ecological state of the environment of the emerging coastal sandy sediment of the Kaliningrad shelf, several complex indicators were used. The butyltin degradation index (BDI) is often used to assess the novelty of TBT pollution sources [2, 12, 15]. The calculation is based on the ratio of the concentrations of the two main decomposition products (DBT and MBT) and the parent compound (TBT): BDI = (DBT + MBT)/TBT. BDI values below 1 indicate recent input of organotins into the accumulation area or low levels of biodegradation in the body [3, 17]. BDI values greater than one suggest progressive degradation of TBT deposited in the past. However, in coastal regions adjacent to river mouths and estuaries, BDI should be used with caution because DBT and MBT may come directly from other sources (e.g., domestic and industrial wastewater discharges) [17].

To assess natural or anthropogenic sources of heavy metals in sediments, various enrichment factors (EF) are often used, which are calculated relative to conservative elements such as Al, Fe, Sc, and Ti as reference elements, as well as a geoaccumulation index which allows assessing the accumulation of metals in bottom sediments by comparing current and pre-industrial concentrations,

$$I_{geo} = \log_2(C_x^i / 1{,}5C_b^i),$$

where C_x – are the measured concentrations of metals in the sediment fraction; C_b – geochemical background (concentration) of metals in global shale.

A coefficient of 1.5 is introduced to take into account possible changes in the background value due to natural fluctuations (effect of lithology). In this case, an estimated classification of the geoaccumulation index is used according to the level of potential environmental pollution: $I_{geo} \leq 0$ – absence of pollution; $0 < I_{geo} \leq 1$ – minor to moderate contamination; $1 < I_{geo} \leq 2$ – moderate pollution; $2 < I_{geo} \leq 3$ – from moderate to heavy pollution; $3 < I_{geo} \leq 4$ – heavy pollution; $4 < I_{geo} \leq 5$ – from strong (heavy) to extreme and $I_{geo} > 5$ – extreme pollution.

Results. *Granulometry of sediments*. All studied samples (23 samples) are represented by medium-to-coarse-grained sands with a minimal proportion of clay component (less than 1%), which are characterized by a predominantly unimodal distribution of particle grain size – from 0.05 to 1.65 mm (Tables 1 and 2). There are samples with bimodal and more complex distributions (Fig.3). Obviously, this distribution pattern depends on the conditions of sediment formation at the sampling point, the presence of certain complicating relief forms, as well as local along-shore currents, which can be an additional source of sandy material. However, the main process that forms the sediment is wave surf, as well as tidal currents, which lead to the formation of fairly well washed and sorted sandy sediments.

Since the area and depth varied slightly, the particle size distribution of the 2017 and 2018 samples from each site is similar. Thus, for the “Curonian Spit” site in 2017, out of six studied samples, five were represented by fine-medium-grained sands with grain sizes of 0.25-0.125 mm, and one was coarse-grained sand with grains of 0.8-0.63 mm, and in 2018, out of five samples, four are represented by the same fine-medium-grained sand (0.25-0.125 mm), and one is very-coarse to coarse-grained sand with a particle size of 1.0-0.8 mm (Fig. 3, *a*).

At the “Northern Sambian” sampling site, samples in 2017 are represented by very-coarse to coarse-grained sands (four samples, 1.6-0.8 mm) and fine-medium-grained sands (three samples, 0.4-0.1 mm), and in 2018 – out of five samples, two are represented by very-coarse to coarse-grained sands (1.6-0.4 mm) and two fine-medium-grained sands (0.4-0.1 mm) (Fig. 3, *b*).

Another sample (Fig.3, *c*) has an anomalous particle size distribution with a wide range of 0.6-0.04 mm. It is obvious that the sampled deposits of the “Northern Sambian” site are distinguished by a larger proportion (representativeness) of coarse-grained sands compared to samples from the “Curonian Spit” site.

Samples from the “Northern Sambian” site are characterized by the presence of more complex types of particle grain-size distribution (bimodal, anomalous) compared to the sands of the site “Curonian Spit”, which are characterized by different, but exclusively unimodal distributions. This difference may be due not only to different conditions of sediment formation, but also, in part, to the low representativeness of the samples. However, the sampling sites are characterized by a comparable number of samples (11 and 12), and the granulometric characteristics of the sediments are consistently reproduced for the samples of 2017 and 2018, which may indicate the real differences between the sandy sediments of the two studied sites.

Organotin compounds. The results of a study of bottom sediments of the Kaliningrad shelf (11 samples from the “Curonian Spit” site and 12 samples from the “Northern Sambian” site) demonstrated the presence of detectable amounts of organotin compounds in all but one samples, 18-KK-5, from 0.6 to 32 ng/g (dry weight – d.w.).

Table 1

Granulometric characteristics (distribution by size class, mm) of bottom sediments of the 2017 sampling sites (in % per 100 g of the initial sample weight)

Sample	Water depth, m	Sediment type	>2.5	2.5-2.0	2.0-1.6	1.6-1.25	1.25-1.0	1.0-0.8	0.8-0.63	0.63-0.5	0.5-0.4	0.4-0.315	0.315-0.25	0.25-0.2	0.2-0.16	0.16-0.125	0.125-0.1	0.1-0.08	0.08-0.063	0.063-0.05	0.05-0.04	0.04-0.01	<0.01
17-KK-1	19.5	Sf	0	0	0	0	0.02	0.14	0.30	0.12	0.14	0.64	2.98	6.02	11.71	26.84	27.35	18.7	2.74	0.58	0.08	0.14	0
17-KK-2	19.9	Sc	5.6	1.98	2.14	5.10	7.07	16.9	37.6	16.2	2.18	2.00	1.61	0.79	0.42	0.22	0.02	0	0	0	0	0	0
17-KK-3	13.7	Sf	0	0	0	0.02	0.14	0.66	1.03	2.91	1.89	4.32	11.0	21.6	23.6	18.6	8.60	3.78	1.07	0.22	0.08	0.06	0.44
17-KK-5	17.2	Sf	0	0	0	0	0.04	0.10	0.24	0.52	1.22	5.73	19.8	32.1	23.0	12.0	2.77	1.30	0.36	0.08	0.02	0.02	0.68
17-KK-6	16.2	Smf	0	4.53	0.71	0.73	0.79	0.77	0.63	1.29	1.98	5.78	10.6	13.3	13.1	19.6	14.2	7.66	1.90	0.59	0.06	0.36	1.46
17-KK-7	14.5	Smf	0	0.06	0.02	0.02	0.06	0.18	0.36	1.19	2.59	7.31	11.7	17.6	21.2	18.2	8.97	6.87	2.24	0.46	0.02	0.14	0.8
17-CC-1	25.6	Scvc	0	1.62	3.55	22.6	39.0	10.6	1.72	1.68	2.12	5.09	6.34	3.78	1.07	0.24	0.08	0.12	0.04	0.02	0.02	0.02	0.28
17-CC-2	25.4	Scvc	0	0.16	0.36	3.88	34.2	22.0	4.06	7.79	8.57	8.87	5.47	2.78	0.89	0.26	0.08	0.02	0.04	0.02	0.02	0.06	0.44
17-CC-3	25.0	Scvc	0	0.58	2.47	5.95	38.9	22.2	4.10	7.24	4.73	5.55	4.81	2.31	0.58	0.04	0.02	0.02	0	0	0	0	0.52
17-CC-5	19.0	Svcc	0	0.79	0.44	2.05	35.3	46.7	4.89	2.92	1.81	1.93	0.50	0.50	0.50	0.50	0.04	0.02	0	0	0	0	1.12
17-CC-7	21.4	Svff	0	0.64	0.48	0.74	2.23	1.89	0.92	1.29	1.81	2.75	5.66	9.10	7.49	7.85	7.35	24.1	12.2	4.96	0.80	3.48	4.18
17-CC-9	6.4	Sm	0	0.04	0.10	0.12	0.28	0.74	1.67	9.70	33.1	45.3	6.92	0.87	0.18	0.12	0.24	0.26	0.14	0.02	0.02	0.02	0.18
17-CC-10	17.9	Smc	0	0.16	0.24	0.50	1.75	12.7	19.9	22.0	13.6	13.6	9.72	3.81	1.15	0.24	0.16	0.02	0.02	0.02	0.02	0	0.22

Note. KK – Curonian Spit; CC – Northen coast of Sambian Peninsula. Sediment types: Suf – unsorted, mostly fine-grained sand; Svc – very coarse-grained sand; Scvc – coarse to very coarse-grained sand; Svcc – sand very coarse to coarse-grained sand; Sc – coarse-grained sand; Smc – medium to coarse-grained sand; Scm – coarse to medium-grained sand; Sm – medium-grained sand; Sfm – fine to medium-grained sand; Smf – medium to fine-grained sand; Sf – fine-grained sand; Svff – very fine to fine-grained sand.

Table 2

Granulometric characteristics (distribution by size class, mm) of bottom sediments of the 2018 sampling sites (in % per 100 g of the initial sample weight)

Sample	Water depth, m	Sediment type	>2.5	2.5-2.0	2.0-1.6	1.6-1.25	1.25-1.0	1.0-0.8	0.8-0.63	0.63-0.5	0.5-0.4	0.4-0.315	0.315-0.25	0.25-0.2	0.2-0.16	0.16-0.125	0.125-0.1	0.1-0.08	0.08-0.063	0.063-0.05	0.05-0.04	0.04-0.01	<0.01
18-KK-2	17.3	Smf	0	0	0	0	0.02	0.1	0.44	3.42	3.64	8.4	18.1	24.3	18.92	14.38	5.18	1.86	0.54	0.24	0.1	0.04	0.28
18-KK-3	19.5	Svff	0.02	0	0	0.04	0.02	0.3	0.74	0.38	0.44	1.72	5.17	8.74	13.7	29.0	22.4	12.1	3.09	0.96	0.28	0.14	0
18-KK-4	20.0	Sc	0.02	0.02	0.04	0.30	3.24	35.8	29.2	4.62	0.58	1.16	2.24	1.82	1.50	3.54	6.91	6.59	1.36	0.44	0.14	0.08	0.38
18-KK-5	13.9	Sf	0	0.02	0	0.02	0.02	0.14	0.26	0.66	1.28	4.60	11.5	18.5	23.4	19.0	8.20	7.24	3.30	1.02	0.32	0.16	0.36
18-KK-7	15.4	Sf	0	0.04	0.04	0.04	0.14	0.3	0.42	0.94	1.16	3.42	10.7	24.1	25.9	20.8	6.87	3.20	1.22	0.42	0.14	0.01	0.08
18-CC-1	8.5	Suf	0	0	0.02	0.02	0.04	0.25	0.99	3.09	5.55	11.5	9.93	5.49	4.59	12.2	10.75	22.3	4.95	1.13	6.59	0.17	0.44
18-CC-2	17.5	Sfm	0	0	0.02	0.10	0.42	2.26	3.48	5.22	9.49	25.2	28.1	15.4	5.20	1.62	0.72	1.20	0.78	0.44	0.14	0.06	0.16
18-CC-7	19.2	Scvc	0.98	0.62	0.96	10.6	35.6	15.2	6.87	8.29	7.03	7.35	3.34	1.42	0.50	0.18	0.10	0.24	0.24	0.2	0.1	0.1	0.06
18-CC-9	24.2	Scvc	0.98	0.62	0.96	10.6	35.6	15.2	6.87	8.29	7.03	7.35	3.34	1.42	0.50	0.18	0.10	0.24	0.24	0.2	0.1	0.1	0.06

The total content of six OTs (ΣOTs = MBT + DBT + TBT + TTBT + TPhT + TCyT) varies over a wide range of values both for samples from one sampling site and between sites (Tables 3, 4). Thus, for samples taken in 2017 at the "Curonian Spit" site, ΣOTs varies from 0.6 to 5.0 ng/g d.w. with an average value of 1.83±1.71 (1σ). In this case, the main contribution is made by MBT (av. 0.93±0.59 ng/g d.w.), TPhT (av. 0.61±1.27 ng/g d.w.) and TTBT (av. 0.23±0.38 ng/g d.w.), while the TCyT in all samples from the site is not higher than the detection limit.

For samples from the "Northern Sambian" site from the 2017 collection, the level of ΣOTCs is significantly higher and varies from 1.3 to 32.4 ng/g d.w. with an average of 4.25±2.7 ng/g d.w., with the dominant components of TBT (av. 1.04 ± 0.84 ng/g d.w.), TCyT (av. 1.06±1.4 ng/g d.w.), MBT (av. 0.85±0.41 ng/g d.w.) and subordinate but significant TTBT (av. 0.67±0.37 ng/g d.w.) and DBT (av. 0.53±0.52 ng/g d.w.). Sample 17-CC-8 is anomalous both in terms of the total OTs content (32.4 ng/g d.w.) and the OTs spectrum: MBT – 30.0, DBT – 0.4, TBT – 1.8 ng/g d.w.

Table 3

Organotin compounds (ng/g d.w.) in the sands of the sampling sites in 2017

Sample	MBT	DBT	TBT	TTBT	TPhT	TCyT	∑OTs
17-KK-1	0.60	<0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.60
17-KK-2	0.40	0.10	0.30	< 0.1	0.20	< 0.1	1.00
17-KK-3	0.40	0.10	< 0.1	0.20	< 0.1	< 0.1	0.70
17-KK-5	0.90	0.20	< 0.1	< 0.1	< 0.1	< 0.1	1.10
17-KK-6	1.50	< 0.1	< 0.1	1.00	0.10	< 0.1	2.60
17-KK-7	1.80	< 0.1	< 0.1	< 0.1	3.20	< 0.1	5.00
17-CC-1	0.60	0.10	< 0.1	0.90	< 0.1	< 0.1	1.60
17-CC-2	0.30	< 0.1	< 0.1	1.00	< 0.1	< 0.1	1.30
17-CC-3	1.50	0.20	1.30	0.30	0.10	0.60	4.00
17-CC-7	1.10	1.50	2.30	0.60	< 0.1	3.00	8.50
17-CC-8	30.00	0.40	1.80	0.20	< 0.1	< 0.1	32.4
17-CC-9	0.80	0.20	0.90	0.50	0.30	3.20	5.90
17-CC-10	0.80	0.80	0.90	1.20	< 0.1	0.50	4.20

Table 4

Organotin compounds (ng/g d.w.) in the sands of the sampling sites in 2018

Sample	MBT	DBT	TBT	TTBT	TPhT	TCyT	∑OTs
18-KK-2	1.30	< 0.1	< 0.1	0.20	< 0.1	< 0.1	1.50
18-KK-3	1.30	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.30
18-KK-4	2.00	0.40	< 0.1	< 0.1	< 0.1	< 0.1	2.40
18-KK-5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
18-KK-7	2.90	0.90	< 0.1	< 0.1	0.10	< 0.1	3.80
18-CC-1	2.80	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2.80
18-CC-2	4.90	0.70	< 0.1	< 0.1	< 0.1	< 0.1	5.60
18-CC-5	3.60	2.30	0.70	< 0.1	< 0.1	< 0.1	6.60
18-CC-7	4.90	3.40	< 0.1	< 0.1	< 0.1	< 0.1	8.30
18-CC-9	1.70	0.50	1.30	1.30	7.00	6.40	18.2

The composition and content of organotin compounds of the 2018 samples is significantly different. For the "Curonian Spit" site the level of ΣOTs is higher than in the samples of 2017 (1.3-8.3 ng/g d.w.), but the average value does not change (1.81±1.4 ng/g d.w.). The spectrum of compounds is limited to only two components – with the largest contribution of MBT (av. 1.51±1.0 ng/g d.w.) and a detectable amount of DBT (av. 0.29±0.37 ng/g d.w.), the other four components (TBT, TTBT, TPhT, TCyT) turned out to be below the sensitivity threshold of the analysis.

For the "Northern Sambian" sampling site, the total OTs content of the 2018 samples ranged from 2.8 to 18.2 ng/g dry weight (av. 5.83±2.3 ng/g d.w.) with the highest contribution from MBT (av. 3.58±1.38 ng/g d.w.), DBT (av. 1.39±1.4 ng/g d.w.) and TBT (av. 0.43±0.56 ng/g d.w.). The

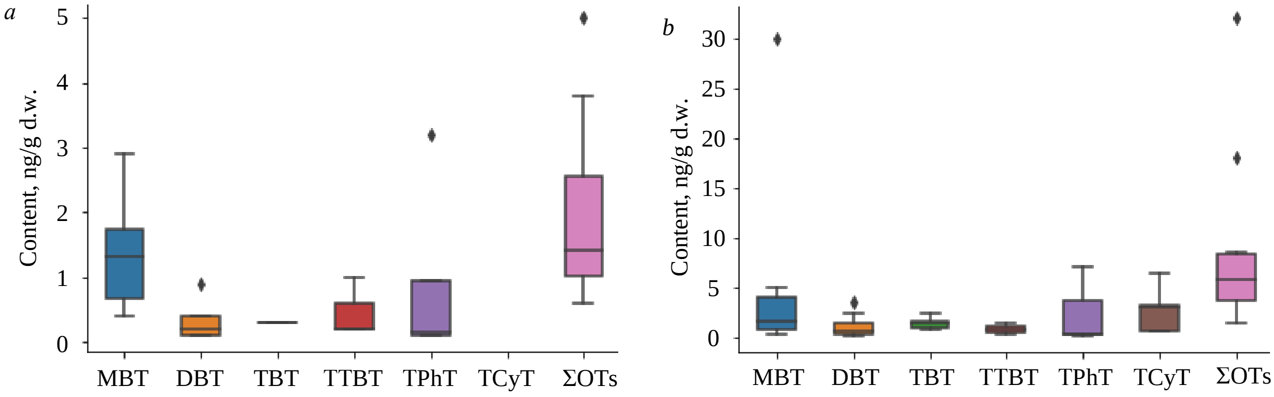

Fig.4. Distribution of the content of organotin compounds in sediments of the “Curonian Spit” (*a*) and “Northern Sambian” (*b*) sampling sites: monobutyltin, dibutyltin, tributyltin, tetrabutyltin, triphenyltin, tricyclohexyltin, and total

other components of OTs (TCyT, TPhT, TTBT) are below the detection limit. However, in the composition of the OTs of sample 18-CC-9 these components were in the highest concentration: TCyT – 6.4 ng/g d.w., TPhT – 7.0 ng/g d.w., and TTBT up to 1.3 ng/g d.w., and the total OTCs content was maximum – 18.2 ng/g d.w. (with TBT – 1.3, DBT – 0.5, MBT – 1.7 ng/g d.w.).

The range diagrams (Fig.4) show the distribution of OTCs contents in sediments. It is obvious that the content of ΣOTs in samples from the “Northern Sambian” site is statistically higher than in samples from the “Curonian Spit” site.

Analysis of the values of international regulations[4] shows that the permissible level of TBT content in bottom sediments ranges from 0.01 to < 10 ng/g d.w. [11, 15], so none of the studied samples exceeded the recommended maximum value (10 ng/g d.w.). TPhT, TTBT and TCyT were detected in significant amounts only in the bottom sediments of the “Northern Sambian” site: 0.2-1.3, 0.1-7.0, and 0.1-6.4 ng/g d.w., respectively. The most probable source of their input into the aquatic ecosystems is water carriage, while MBT and DBT are formed to a large extent as a result of degradation of initial compounds – TBT and TTBT.

To assess the degree of TBT transformation in bottom sediments, the BDI coefficient is used – the ratio [MBT + DBT]/[TBT] [17]. If the value is greater than one, this indicates active processes of TBT transformation and self-purification of the aquatic ecosystem. For all the studied samples, the value of this coefficient was greater than one, indicating the efficiency of the deposit purification due to the TBT destruction. The change of this characteristic over the two-year observation period is also remarkable: BDI in the samples of the site “Curonian Spit” 2017 is characterized by the value of 1.7, while for the samples of 2018 this indicator reaches already 14-38, and in the samples of the site “Northern Sambian” it changes from 1.3 in 2017 to 12.4 in 2018. However, for the anomalous sample 18-CC-9, this index (BDI = 1.7) does not differ from the average for 2017 (av. 1.33), which, together with the anomalous structure of the OTs distribution for this sample, may indicate the input of organotins from an additional source, such as urban (Svetlogorsk) and/or agricultural runoff enriched with plastic waste and pesticide derivatives.

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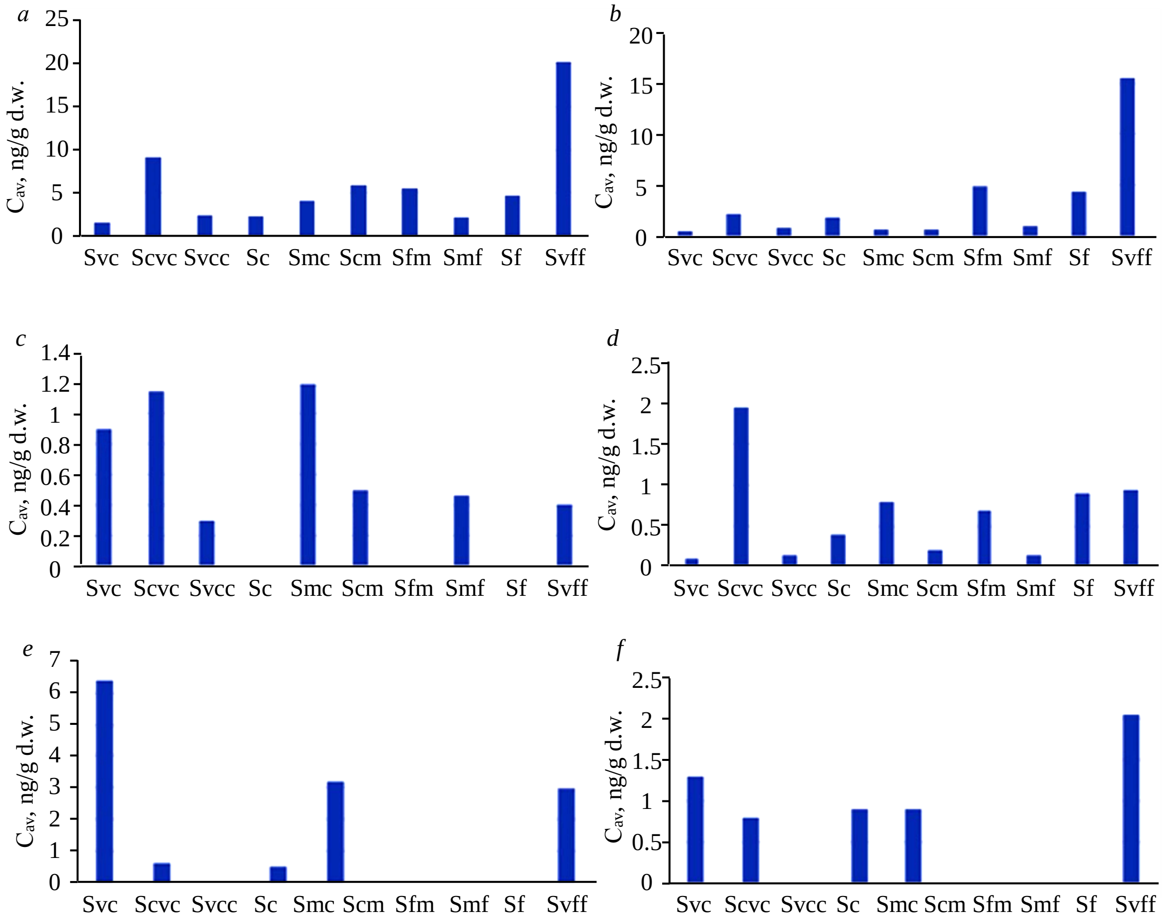
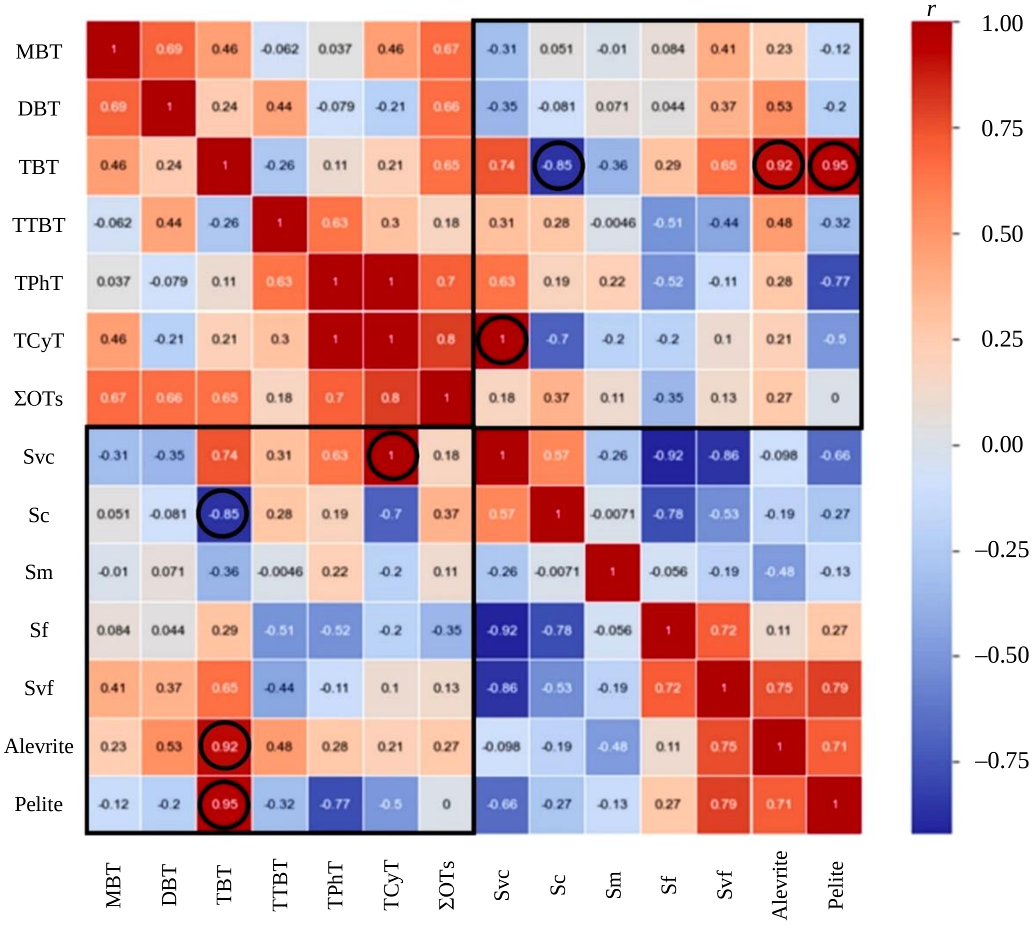


Fig.5. Average content of organotin compounds (C_{av}) depending on the granulometric type of sediment: total content of ΣOTs (*a*); MBT (*b*); TTBT (*c*); DBT (*d*); TCyT (*e*); TBT (*f*)

The total OTs content is the highest in the sands of the smallest grain size – very-fine to fine-grained (Fig.5, *a*). The greatest contribution to this result was the anomalously high content of MBT in the very-fine to fine-grained sand sampled at point 17-CC-8. Also in very-fine to fine-grained sands the increased content of TBT was recorded. At the same time, the maximum content of TCyT, TPhT and DBT is observed in very-coarse-grained and coarse- to very-coarse-grained sands, while the distribution of TTBT is more complex, but coarse-grained sands are characterized by relative enrichment with this component (Fig.5, *b*-*f*).

In order to reveal the relationship between the OTs content and sediment granulometry, Spearman's pair correlation coefficients were calculated, since the samples are small (10-12 samples, see Tables 1, 2) and the normal law of distribution of values cannot be expected. The analysis of the calculated relationships was performed using the Scipy library, implemented in Python. The level of significant correlation was set at $p < 0.05$.

Visualization of the matrix of pair correlation coefficients is presented in Fig. 6 in the form of a heat map [21, 22]. High positive correlation characterizes the relationship of TBT with alevrite ($r = 0.92$) and pelitic fractions ($r = 0.95$). For TCyT and very coarse-grained sand $r = 1$, but only three pairs of values were used for the calculation, i.e. the result is unreliable. A high negative correlation was established for TBT and coarse-grained sand ($r = –0.85$). The results of the correlation analysis show that the concentration of TBT in sediments increases with increasing proportion of the fine-grained fraction (pelites and silts) and decreases with increasing proportion of coarse-grained sand. The positive relationship between TCyT content and the proportion of the very coarse-grained sand in the samples requires further investigation with an increase in the number of analyses and sample representativeness.



	MBT	DBT	TBT	TTBT	TPhT	TCyT	ΣOTs	Svc	Sc	Sm	Sf	Svf	Alevrite	Pelite
MBT	1	0.69	0.46	-0.062	0.037	0.46	0.67	-0.31	0.051	-0.01	0.084	0.41	0.23	-0.12
DBT	0.69	1	0.24	0.44	-0.079	-0.21	0.66	-0.35	-0.081	0.071	0.044	0.37	0.53	-0.2
TBT	0.46	0.24	1	-0.26	0.11	0.21	0.65	0.74	-0.85	-0.36	0.29	0.65	0.92	0.95
TTBT	-0.062	0.44	-0.26	1	0.63	0.3	0.18	0.31	0.28	-0.0046	-0.51	-0.44	0.48	-0.32
TPhT	0.037	-0.079	0.11	0.63	1	1	0.7	0.63	0.19	0.22	-0.52	-0.11	0.28	-0.77
TCyT	0.46	-0.21	0.21	0.3	1	1	0.8	1	-0.7	-0.2	-0.2	0.1	0.21	-0.5
ΣOTs	0.67	0.66	0.65	0.18	0.7	0.8	1	0.18	0.37	0.11	-0.35	0.13	0.27	0
Svc	-0.31	-0.35	0.74	0.31	0.63	1	0.18	1	0.57	-0.26	-0.92	-0.86	-0.098	-0.66
Sc	0.051	-0.081	-0.85	0.28	0.19	-0.7	0.37	0.57	1	-0.0071	-0.78	-0.53	-0.19	-0.27
Sm	-0.01	0.071	-0.36	-0.0046	0.22	-0.2	0.11	-0.26	-0.0071	1	-0.056	-0.19	-0.48	-0.13
Sf	0.084	0.044	0.29	-0.51	-0.52	-0.2	-0.35	-0.92	-0.78	-0.056	1	0.72	0.11	0.27
Svf	0.41	0.37	0.65	-0.44	-0.11	0.1	0.13	-0.86	-0.53	-0.19	0.72	1	0.75	0.79
Alevrite	0.23	0.53	0.92	0.48	0.28	0.21	0.27	-0.098	-0.19	-0.48	0.11	0.75	1	0.71
Pelite	-0.12	-0.2	0.95	-0.32	-0.77	-0.5	0	-0.66	-0.27	-0.13	0.27	0.79	0.71	1

Fig.6. Spearman's correlation coefficient r. Circles indicate significant (strong) correlation values, probability level $p \leq 0.05$.

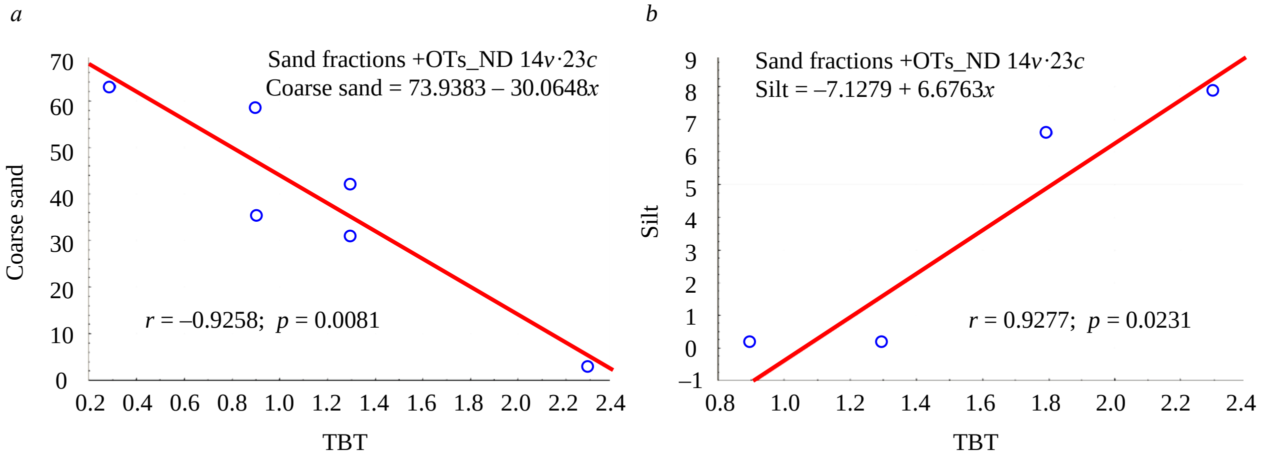


Fig.7. Scatter diagrams: content of TBT and coarse sand fraction (*a*), content of TBT and silt fraction (*b*). The red line shows the calculated regression line

Scatter plots of the most significant correlations between TBT and the proportion of coarse-grained sand and alevrite component are presented in Fig.7; there is a significant correlation (negative $r = –0.926$ (Fig.7, *a*) and positive $r = 0.928$ (Fig.7, *b*)). However, the correlation covers only a limited number of samples: six and four out of eight samples with TBT content above the detection limit. The results obtained are consistent with literature data indicating that sediments with a higher proportion of fine fractions adsorb TBT better [3, 10].

Element composition. The results of the analysis of the content of metals and oxides of 12 bottom samples from the 2017 collection are presented in Table 5. Samples from the “Curonian Spit” (KK) site are characterized by an increased metal contents compared to samples from the “Northern Sambian” site (CC): Ni – 2.56±0.4 µg/g (CC – 1.99±0.4), Cu – 1.91±0.4 (CC – 1.16±0.2), Zn – 25.1±6.4 (CC – 13.6±7.3), Pb – 7.34±1.1 (CC – 47±1.3), V – 24.8±4.1 (CC – 10.9±2.2), Sr – 58.3±8.6 (CC – 33.6±10.1). This can be compared with a larger share of fine-grained fraction in the sand deposits and a higher content of oxides: Fe_2O_3 – 1.78±0.3% (CC – 1.2±0.2 %) and TiO_2 – 0.76±0.1 % (CC – 0.2±0.1 %). At the same time, the increased As – 6.65±5.3 µg/g (KK – 2.18±0.46 µg/g) correlates not only with the relative coarse-grained of the sediment, but also with an increased content of ΣOTs in samples from the “Northern Sambian” site. A similar pattern was previously noted when studying bottom sediments of the Gulf of Finland [18].

Table 5

**Microelement and oxide contents in the sands of the sampling sites in 2017:
“Curonian Spit” and “Northern Sambian”**

Sample	Co, µg/g	Ni, µg/g	Cu, µg/g	Zn, µg/g	Pb, µg/g	TiO_2, %	V, µg/g	Cr, µg/g	MnO, %	Fe_2O_{3tot}, %	Sr, µg/g	As, µg/g
17-KK-1	2.00	2.98	1.77	25.0	9.03	0.98	31.2	61.0	0.03	2.22	70.60	2.99
17-KK-2	1.15	1.68	1.65	19.3	4.52	0.14	5.95	7.24	0.02	0.53	60.20	2.42
17-KK-3	1.55	2.25	1.39	16.7	6.45	0.70	22.0	60.9	0.03	1.55	53.70	1.85
17-KK-5	1.52	2.03	2.21	26.9	6.29	0.62	21.2	46.1	0.02	1.47	44.80	2.12
17-KK-6	1.85	3.02	2.50	34.4	7.52	0.82	26.5	66.7	0.03	1.92	61.10	1.90
17-KK-7	1.71	2.50	1.94	28.4	7.41	0.68	23.0	66.7	0.03	1.76	59.30	1.79
17-CC-2	2.17	2.22	1.09	22.2	5.37	0.16	11.2	11.5	0.04	1.73	36.70	10.70
17-CC-3	2.31	2.64	1.39	20.4	6.74	0.13	11.8	10.7	0.04	1.81	33.40	13.50
17-CC-5	1.30	1.83	1.01	10.3	3.90	0.11	8.63	9.37	0.02	0.80	29.50	5.24
17-CC-7	2.62	6.13	4.32	31.6	11.7	0.73	39.3	69.8	0.03	2.57	78.00	2.78
17-CC-9	1.22	1.76	<1	5.60	3.93	0.16	8.80	11.6	0.01	0.77	48.00	1.49
17-CC-10	1.07	1.50	<1	9.51	3.52	0.42	13.8	19.4	0.02	0.75	20.50	2.30
Detection limit	0.5	1	1	1	1	0.001	2.5	1	0.0002	0.01	1	0.50

Discussion of the results. *Environmental factors affecting the distribution and accumulation of organotin compounds in bottom sediments.* The ability of bottom sediments to accumulate substances depends on the physicochemical characteristics of both the compounds themselves and the sediments (composition, particle size, organic matter). Nature and model studies have shown that the granulometric characteristics of sediments play a significant role in the sorption of OTs [10, 12, 22]. As the size of sediment granules decreases, their surface area increases, that leads to increased efficiency of adsorption of chemical compounds, including organotin compounds [23-25]. Fine-grained fractions of sediments adsorb more organic (humic) matter, which, in turn, accumulate OTs [24, 25]. The contribution of organic substances to the overall process of OTs sorption by bottom sediments can range from 55 to 85 % [24].

OTs belong to the group of organometallic compounds and therefore are characterized by many behavior features common to heavy metals in bottom sediments; they exhibit high sorption abilities for both the mineral and organic components of sediments. In this case, it is assumed that there is a competitive relationship for negatively charged sorption points (sites) on the surface of minerals between the TBT cation and divalent cations (Ba^{2+}, Ca^{2+} and Mg^{2+}). In addition, the competing influence of cations depends on their radii: larger cations (for example, Cs^+) significantly reduce the sorption of TBT than smaller ones, for example Na^+ [24]. The determining factors are the complexation of the corresponding cations with negatively charged ligands (with carboxyl and phenolic groups) and hydrophobic interactions [26, 27].

Positive or negative correlations between OTs and metal contents are determined by synergetic or competitive relationships in the process of sorption by bottom sediments; the toxic effect of metals on microorganisms involved in the biotic degradation of OTs; possible catalytic activity of metals in reactions of abiotic degradation of the OTs.

A factor regulating many processes occurring in water basins is also the pH value of the environment, which determines the form of the state of OTs, the rate of degradation, bioavailability, and sorption. Depending on the pH of the aquatic environment, OTs can be in different forms: ion – in the form of cations (if $pH < pK_a$, constant of the acid dissociation) or neutral – in the form of hydroxyl complexes like TBTOH (if $pH > pK_a$). Moreover, the value for TBT is $pK_a = 6.3$ [28], and for TPhT $pK_a = 5.2$ [26]. At a pH of 8, zooplankton concentrates OTs to the maximum, since 98 % of TBT and TPhT in this case are represented by neutral complexes (TBTOH and TPhTOH), which is preferable to the cationic form for penetration into living tissues [29]. The pH of the aquatic environment has a significant influence on the state of the sorbent surface. According to studies of the OTs sorption by various sorbents (mineral, organic, natural bottom sediments, etc.), the adsorption of TBT and DBT increases with increasing pH from 4 to 7 and decreases with a further increase in pH to alkaline conditions. While, the sorption of DBT on iron hydroxide decreases in the pH range from 6 to 8, and does not change on charcoal at pH 4-7. In contrast to TBT and DBT, the MBT sorption in bottom sediments onto iron hydroxide decreases when the pH changes from 6 to 8 [24].

The main OTs transformation occurs biotically [24, 26, 30] with the participation of various organisms, including bacteria [31], fungi [32] and algae [33]. It is known that biotic degradation occurs much faster under aerobic conditions than under anaerobic [31, 32, 34]. At the same time, the processes of OTs transformation occur predominantly in the pore water of bottom sediments, and the level of degradation of OTs in marine sediments is limited by desorption into pore waters, where their degradation occurs quite quickly – for TBT in aerobic conditions the half-life is 9.2 days, and for DBT in aerobic and anaerobic conditions – 2.9 and 9.1 days, respectively [24, 35].

Features of the accumulation of organotin compounds in bottom sediments of the Kaliningrad shelf. The main feature of the bottom sediments of the Kaliningrad shelf in the “Northern Sambian” and “Curonian Spit” areas is their relative coarse grain size (particle diameter 0.4-0.16 mm) with the presence of a small share of pelite-silty (less than 15%) and humus components, which explained by the formation conditions – coastal-marine deposits of the zone of surf-wave accumulation (depth 10-20 m below the sea surface). The constant wave action on the sand sediment ensures the formation of a monotonous sand fraction and prevents the sorption of both chemogenic and biogenic adsorbents on the surface of solid particles.

Despite the fact that the sampled sedimentary layer is in the aerobic zone, the conditions of its formation are not favorable for the accumulation of pollutants such as organotins and heavy metals. However, in all but one samples organotin compounds were found in significant quantities, the total content of which varied from 0.6 to 8.5 ng/g d.w., with maximum values for samples from the “Northern Sambian” site (32.4 and 18.2 ng/g d.w.). Moreover, the well-known [9] positive correlation between the content of TBT and the proportion of the silt-pelite fraction of the sand matrix ($r = 0.95$) is also well demonstrated. At the same time, for both sampling sites over a two-year observation period, the positive dynamics of tributyltin degradation is obvious: the BDI coefficient increases from 1.7 to 14-38 for the “Curonian Spit” and from 1.3 to 12.4 for the “Northern Sambian" sites. In addition, the content of TBT for the majority of the studied samples (15 out of 23) is below the detection limit and significantly lower than in adjacent areas of the Baltic Sea coast, as in the west (cf. for the Northern Sambian site 0.1-2.3 ng/g d.w., and for the area of the Szczecin Lagoon – from 2 to 3200 ng/g d.w., in the area of the National Nature Reserve of the Wřozovsky Bay, Oder River estuary – up to 80 ng/g d.w., 2017-2018 [21]), and in the east (Klaipeda port area: 0.5-333 ng/g d.w., Curonian Lagoon: 1-5 ng/g d.w., in the Baltic Sea, at a distance of 10 km from the coast – up to 20 ng/g d.w., 2019-2020 [22]). This indicates the efficiency of sediment self-purification in the studied areas and the absence of a significant tributyltin input as a component of anti-fouling paints.

Since the sampling sites are not an area of transit shipping, ship repair and construction, offshore sand mining and other industrial activities, this observation is expected and reflects a general decrease in organotin pollution of the Baltic Sea coastal waters with the introduction of a complete ban on the use of anti-fouling paints based on organotin complexes [4, 14, 15]. However, the presence of single sediment samples with anomalously high levels of organotin derivatives (MBT, TPhT, TCyT) at the "Northern Sambian" site, as well as a constant level of total OTs content over the two-year observation period for both sampling sites (mean ΣOTs content of 1.82±1.5 for KK, and 4.88±2.5 ng/g d.w. for CC) indicates an additional source of input of these contaminants into the coastal environment. The most likely source may be industrial wastewater enriched with plastic debris or pesticides. At the same time, it is obvious that at the "Northern Sambian" site, which is close to the Svetlogorsk urban runoff, the intake and levels of OTs pollution are higher than at the "Curonian Spit" site, the coast of which is a nature reserve.

Heavy metal contamination, which is often correlated with elevated levels of organotins (such as zinc, lead and copper from antifouling paints), was found to be below international limits [36-38] at the sampling sites and significantly lower than that recorded in bottom sediments of other regions of the Baltic Sea [39, 40]. Moreover, the content of metals and oxides in these sediments turned out to be lower than the average crustal values [41], and the I_{geo} factor for all studied samples (sampling in 2017) turned out to be negative, indicating the absence of any significant anthropogenic factor in the accumulation of these elements [39].

Differences in the level of content of the studied components for sandy sediments of two sites (relative enrichment of 2-3 times in KK samples compared to CC samples) are due to both the granulometric parameters of the sediments themselves (sandy sediments in the KK site are finer-grained and with a higher share of silt-pelite component) , as well as local features of the eroded rocks and the mineral composition of the sediment (for example, the sediment of the KK site is on average five times enriched in chromium compared to the sediment of the CC site). At the same time, it is necessary to note the relative enrichment in arsenic (As) of coarser-grained sandy sediments of the "Northern Sambian" site, which is associated with increased contents of organotin compounds in a number of samples, which requires increased attention and annual monitoring, since it may be associated with uncontrolled urban runoff in the Svetlogorsk area [37].

Conclusion. Analysis of bottom sediment samples collected in 2017-2018 on the Kaliningrad shelf of the Baltic Sea, showed the presence of detectable amounts of organotin compounds, although at least 10 years have passed since the complete ban on the use of anti-fouling paints for marine vessels based on TBT. However, the low contents of tributyltin in the studied samples (maximum 2.3 ng/g d.w.) and the high level of its degradation (BDI from 1.3-12.4 to 14-38) indicate the high efficiency of tributyltin transformation processes and self-purification of sandy sediments of two tested areas.

Differences in the local conditions of sediment formation in the studied sites of the "Curonian Spit" and "Northern Sambian" are manifested not only in granulometric features, but also in the OTs spectra and the content of heavy metals. Well-sorted sediment with a minor amount of pelite-silty material due to wave impact and the absence of significant anthropogenic impact, including sea traffic, in areas adjacent to the coast, determine the minimum level of contamination of the studied marine sediments. But the presence of single anomalous samples in terms of content and spectrum of OTs in a limited number of samples from the "Northern Sambian" site indicates additional sources of pollution, the control of which must be ensured by annual environmental monitoring of the state of bottom sediments, since the negative impact of such pollutants can lead to an irreversible change in the environmental situation for the Baltic region.

The content of organotin compounds and heavy metals must also be taken into account when assessing the environmental risks of engineering work on the seabed due to the identified correlation of harmful substances and fine-grained fractions.

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Research article

Quantitative determination of sulfur forms in bottom sediments for rapid assessment of the industrial facilities impact on aquatic ecosystems

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Abstract. The article describes an X-ray fluorescence method for quantitative analysis of sulfate and total sulfur in bottom sediments of watercourses and reservoirs located in the area of industrial enterprises impact. The quantitative determination of sulfur forms was carried out by analyzing the characteristic curves $SK\alpha_{1,2}$ and $SK\beta_{1,3}$, as well as the satellite line $SK\beta'$ on X-ray emission spectra measured by an X-ray fluorescence spectrometer with wavelength dispersion. The study shows that these characteristic curves allow not only to determine the predominant form of sulfur, but also to separately conduct quantitative analyses of sulfates and total sulfur after fitting peaks and to separately analyze overlapping spectral lines. The results of quantitative analysis of the chemical state of sulfur by the proposed X-ray fluorescence method were compared with the results of inductively coupled plasma atomic emission spectroscopy and elemental analysis, as well as certified standard samples of soils and sediments. The results are in good agreement with each other.

Keywords: bottom sediments; sulfur; sulfates; X-ray fluorescence analysis; fitting peaks; satellite lines; quantitative analysis

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Introduction. Sulfur is one of the most important elements of various components of the natural environment. It is also a necessary element for soils and plants, since it is a component of amino acids and enzymes that are vital for the livelihood of organisms and for metabolism in soils. However, an excess of sulfur in the soil can contribute to its acidification, inflict damage on plants and slow down their growth [1-3]. Also, sulfur can serve as one of the indicators of environmental pollution resulting from discharges and emissions of industrial enterprises. Analysis of the content and forms of sulfur in sediments and soils allows us not only to assess the ecological state, but also to develop measures to reduce pollution [4-6]. At the sediment-water interface, sulfur in bottom sediments undergoes a complex geochemical process before it finally forms a stable compound. The study of the content and forms of sulfur in the bottom sediments of water bodies is of great ecological importance for the early diagnosis of their contamination with heavy metals and control of the chemical composition of water [7-9].

Data on the chemical state of sulfur is also necessary for geochemical studies in the analysis of ores. Information about the content of sulfides and sulfates is important in assessing the genesis of the deposit and determining its industrial value. The method that is usually used to determine the forms of sulfur is the laborious gravimetric method with the sequential dissolution of sulfur-containing compounds and further precipitation of sulfates in the form of $BaSO_4$ [10-12].

XRF is one of the most universal analytical methods for studying the elemental composition of objects of different composition. The method does not require time-consuming and expensive stages of sample preparation [13-15]. As noted in the studies [16-18], the position and shape of the SKα и SKβ lines for sulfur can vary greatly depending on the degree of oxidation of this element. The presence of various types of satellite lines on the spectra is explained by various processes and effects: multiple ionization, exchange interaction, plasmon excitation, radioactive Auger effect and molecular orbitals [19]. Also, the structure of the characteristic X-ray spectrum is affected by the valence and the compound the atom is in. For sulfur, this effect is more significant in the area of the SKβ line than in the area of the SKα, since the SKβ lines arise as a result of transitions that involve 3p-orbital, which is more external than the 2p-orbital associated with the SKα line. The intensities and widths of the forbidden and satellite SKβ lines depend on the concentration and degree of oxidation of sulfur atoms. These spectra differences can be used for qualitative and quantitative analysis of sulfur forms, which can significantly reduce the analysis time [20].

Methods. *Chemical reagents*. To study the spectra of pure sulfur compounds having different degrees of oxidation, we used high purity elemental sulfur (AO REAChem, Moscow, Russia), chemically pure anhydrous sodium sulfate (AO LenReactiv, Saint Petersburg, Russia) and 99.9 % iron disulfide (Sigma-Aldrich Co. LLC, Saint Louis, USA).

When studying the effect of the cation on the intensity of peaks SK$\beta_{1,3}$ и SKβ′ samples of sulfates of various metals with a mass sulfur content of 2 % were prepared from chemically pure reagents: $CaSO_4$, $CuSO_4$, $FeSO_4 \cdot 7H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, $MgSO_4$, Na_2SO_4 (AO LenReactiv).

Sample preparation. To calibrate the wavelength dispersive X-ray fluorescence spectrometer, a set of 9 samples of artificial mixtures obtained by mixing sulfur-free rock and pure anhydrous calcium sulfate was prepared. The composition of the sulfur-free rock, on the basis of which artificial reference samples were made, wt.%: SiO_2 – 58.9; Al_2O_3 – 16.8; K_2O – 5.59; Fe_2O_3 – 5.05; Na_2O – 4.49; CaO – 3.58; MgO – 3.23; TiO_2 – 0.95; P_2O_5 – 0.25; MnO – 0.06; LOI < 0.01.

The samples of soil and calcium sulfate previously dried in a drying cabinet (ED 23, Binder, Tuttlingen, Germany) were weighed on electronic scales (MSE124S-1CE-DU, Sartorius, Göttingen, Germany) and thoroughly homogenized using a mixing device (Ultra Turrax, IKA, Staufen, Germany). The samples were prepared by pressing the samples with a binder into reusable steel rings with a diameter of 32 mm using an automatic press (PP 40, Retsch, Haan, Germany) with a maximum pressing force of 25 tons.

To check the calibration dependencies, 8 samples were taken, a standard sample of bottom sediments with a certified total sulfur value (SGHM-4, Vinogradov Institute of Geochemistry SB RAS, Irkutsk, Russia), a standard rock sample with an approximate sulfur content (SP89, Rocklabs, Dunedin, New Zealand), 4 samples of bottom sediments and 2 samples of copper ore enrichment waste. Sample preparation was carried out in the same way as for artificial mixtures.

Determination of sulfur spectra. A scanning wavelength dispersive X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Kyoto, Japan) with a power up to 4 kW equipped with an X-ray tube with Rh anode was used to obtain the spectra of the prepared samples. The parameters of the spectrometer operation for the studies carried out in the work: X-ray fluorescence spectrometer – XRF-1800 (Shimadzu); material of the X-ray tube anode – rhodium (Rh); Voltage/current of the X-ray tube – 25 kV/100 mA; crystal analyzer – Ge (2d-6.532 Å); scanning range – 98.5-112.5 degree (2.283-2.505 keV); scan step – 0.05 degree; total scan time – 840 s; detector – FPC; collimator diameter – 30 mm; atmosphere – vacuum.

Determination of total sulfur and sulfates. The total sulfur concentrations in all samples were determined using an elemental analyzer (628S, LECO, Michigan, USA) by analyzing the composition of gases formed after complete combustion of the sample at a temperature of 1450 °C. The measurements were carried out in accordance with ISO 15178:2000. Soil quality – Determination of total sulfur by dry combustion. To determine the content of sulfates, the samples were boiled in a 15 % hydrochloric acid solution. Then the solution was filtered, the filter and the precipitate were repeatedly washed with hydrochloric acid. The resulting solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICPE-9000, Shimadzu).

Results and discussion. *Investigation of spectral lines of various types of sulfur*. Sulfur has different degrees of oxidation, S^{-2}, S^{-1}, S^{0}, S^{+1}, S^{+2}, S^{+4} и S^{+6}. However, native (S^0), sulfide (S^{-2}) and sulfate (S^{+6}) forms are most often found in nature [21, 22]. With the help of WDXRF, spectral lines of sulfur with different valence can be observed. As can be seen in Fig.1, the lines $SK\alpha_{1,2}$ и $SK\beta_{1,3}$ are observed for all types of sulfur, and the satellite line $SK\beta'$ is characteristic of sulfates. Along with the additional spectral line $SK\beta'$, a shift of the main peak $SK\alpha_{1,2}$ by about 2 eV, towards lower energies is also observed for sulfates [23]. Such a slight shift of the analytical line is difficult to interpret for determination of the type of sulfur.

Determination of total sulfur by analyzing the intensity of the $SK\alpha_{1,2}$ line is a routine operation [14, 15, 24], therefore, further attention will be paid to the quantitative determination of sulfates in samples containing various types of sulfur and will focus on the analysis of the characteristic lines $SK\beta_{1,3}$ and $SK\beta'$. As can be seen from Fig.1, the peak of the $SK\beta$ sulfate ion has two main components, $SK\beta_{1,3}$ и $SK\beta'$, in contrast to elemental and sulfide sulfur. This is due to the fact that the $SK\beta$ region of the sulfur line significantly depends on the degree of oxidation. For pure sulfur, the main transition of $SK\beta_{1,3}$ corresponds to a peak formed by two lines caused by molecular orbitals that bind different levels of the S_8 molecule [25], and in oxides it is associated with the transition of electrons from the molecular orbital consisting of the atomic orbitals 3p of sulfur and 2p of oxygen to the 1s orbital of sulfur. Thus, the difference between the transitions $SK\beta_{1,3}$ и $SK\beta'$ is determined by the atomic orbital of the ligand involved. Therefore, the energy difference is approximately determined by the energy difference of the 2s and 2p orbitals of the ligand, which for oxygen is approximately 15 eV [18, 19, 26].

Along with the $SK\beta_{1,3}$ and $SK\beta'$, lines, the spectra in the region selected for analysis may contain the $SK\beta_x$ and $SK\beta''$ lines. However, $SK\beta''$ is not characteristic of sulfates, and $SK\beta_x$ is not observed on the spectra obtained using WDXRF due to insufficient resolution [27, 28]. For these reasons, the analysis of these characteristic lines was not carried out.

Fitting peaks. Overlapping peaks of $SK\beta_{1,3}$ and $SK\beta'$ are difficult to analyze without preprocessing (Fig.1). This is especially difficult for cases when the sample includes a mixture of various compounds containing sulfur, in which case the main peak of $SK\beta_{1,3}$ can raise several times higher relative to $SK\beta'$ and cover the satellite line even more. For this reason, peak fitting was further used for all spectral lines (OriginPro, OriginLab Corporation, Northampton, USA). An example of a decoded peak after the fitting is shown in Fig.2. The position of the spectral lines $SK\beta_{1,3}$ and $SK\beta'$ at 2,464 and 2,452 keV respectively, agrees well with the values obtained in other studies where devices with better resolution were used [18, 29, 30].

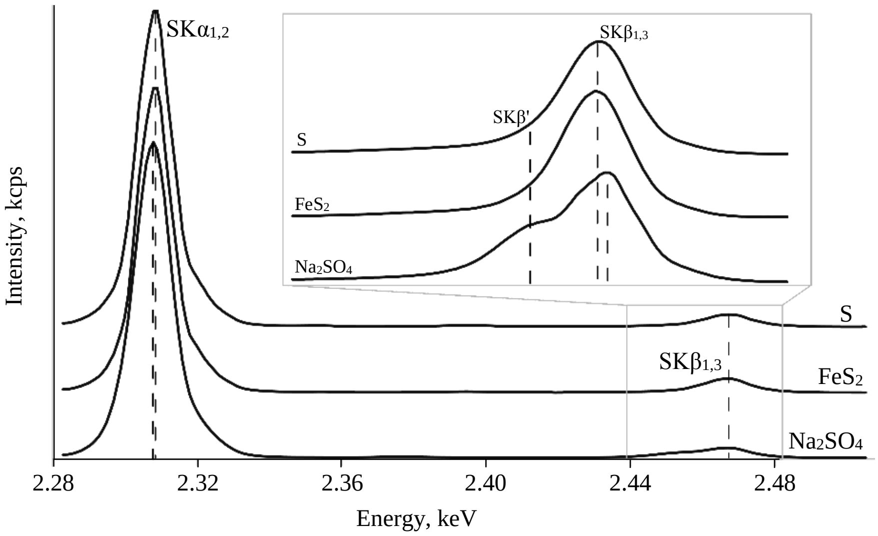

Fig.1. X-ray spectra of various sulfur compounds

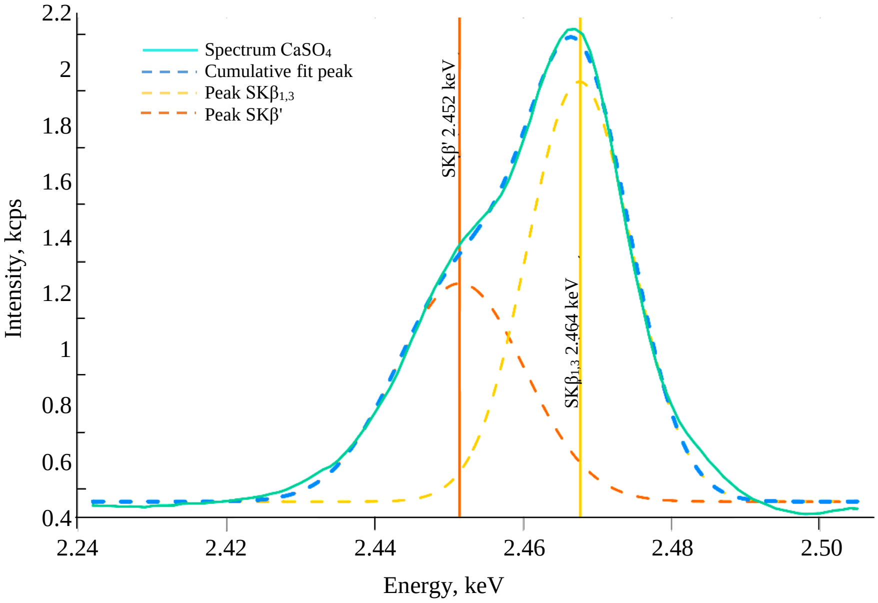

Fig.2. X-ray spectrum after fitting for a sample with a sulfur sulfate content of 1 wt.%

Gaussian function was used to fit the peaks. The function has the following equation

$$y = y_0 + \frac{A \cdot e^{\frac{-4\ln(2)(x-x_c)^2}{w^2}}}{w\sqrt{\frac{\pi}{4\ln(2)}}},$$

where y_0 – the height of the baseline; x_c is the position of the peak center; A – the area under the peak; w is the width of the peak at half of its height [31, 32].

Using the Gaussian function to fit the peaks provided a correlation between the initial and the total spectrum. The total spectrum was obtained after adding the peaks SKβ$_{1,3}$ and SKβ′, more than 0.995 for each of the experiments.

Effect of the cation in sulfates on the intensity ratio of SKβ′/SKβ$_{1,3}$. The ratio of the intensity of the lines and the areas under the peaks SKβ′ and SKβ$_{1,3}$ carries information about the form in which sulfur is contained in the sample only in the form of sulfates or other compounds. As shown in the conducted studies [26, 33], the ratio of the intensities of the SKβ′ satellite line to the main SKβ$_{1,3}$ line in the sample correlates with the concentration of sulfates in the sample.

To confirm that the cation does not significantly affect the intensity ratios of the lines (areas under the peaks) SKβ′ и SKβ$_{1,3}$, samples were prepared (sulfates of various metals with a mass sulfur content of 2 %), and the intensity ratios (excluding background) and peak areas (excluding background) of the selected analytical lines were determined, SKβ′/SKβ$_{1,3}$ (Table 1). The ratios of intensities and peak areas of SKβ′/SKβ$_{1,3}$ for sulfates having different cations remain the same. The largest deviation from the average value for the intensity ratio was 2.83 % and for the areas ratio it was 1.75 %, which means that the influence of the cation on the sulfur spectrum is insignificant. This is due to the fact that in the ions of polyatomic compounds, individual ionic groups, for example SO_4^{2-}, are isolated anions and they are not significantly affected by cations [30, 34]. Thus, the influence of the cation on the intensity of the characteristic sulfur lines in the SKβ region will be insignificant and will have no recognizable effect on the quantitative determination of sulfates in real samples.

Table 1

Intensity ratio of SKβ′/SKβ$_{1,3}$

Salt	Intensity	Area
$CaSO_4$	0.526	0.627
$CuSO_4$	0.515	0.632
$FeSO_4 \cdot 7H_2O$	0.500	0.616
$KAl(SO_4)_2 \cdot 12H_2O$	0.507	0.623
$MgSO_4$	0.511	0.636
Na_2SO_4	0.510	0.628

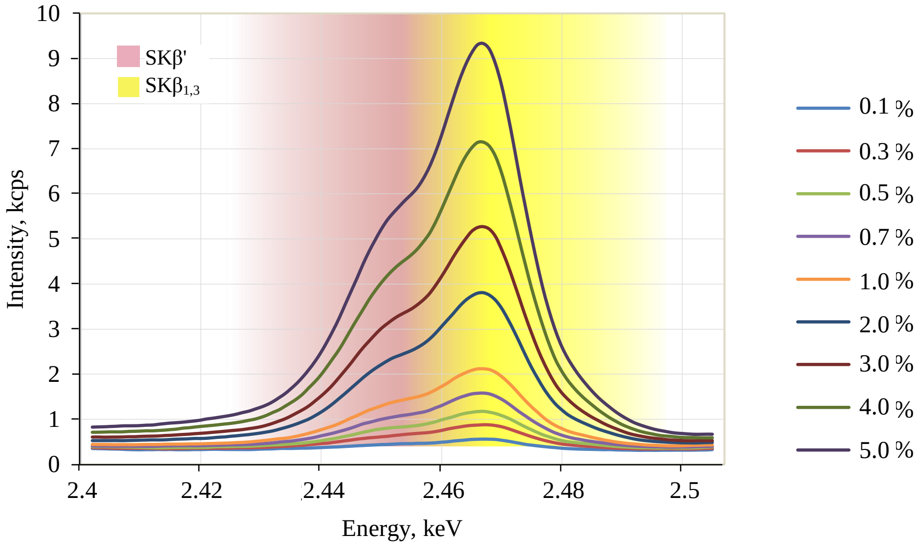

Fig.3. Spectra in the area of the SKβ line

Calibration of the device. To construct the calibration curve, pure anhydrous calcium sulfate was used and mixed with sulfur-free rock dried to an absolutely dry state in the required ratio. A series of samples with different sulfate sulfur content ranging from 0.1 to 5 wt.%, was prepared for calibration. The obtained spectra are shown in Fig.3. For each of the spectra, peaks were selected according to which a calibration curve was built on the intensity of the analytical line and the area under the peak SKβ'. The results of the calibration are shown (Fig.4). As can be seen from the graphs, when calibrating with artificial mixtures, the coefficient of determination is high for both types of calibration: in terms of the intensity of the analytical line and the area under the peak.

Checking the calibration characteristics. To check the calibration characteristics, real objects of various nature: rocks, soils, bottom sediments and mining waste were taken, two of which are standard samples. The content of total sulfur and sulfate sulfur in the selected samples is presented in Table 2. The total sulfur content in the samples varies from 0.10 to 3.44 % and the sulfate content varies from 0.10 to 1.16 % in absolutely dry weight

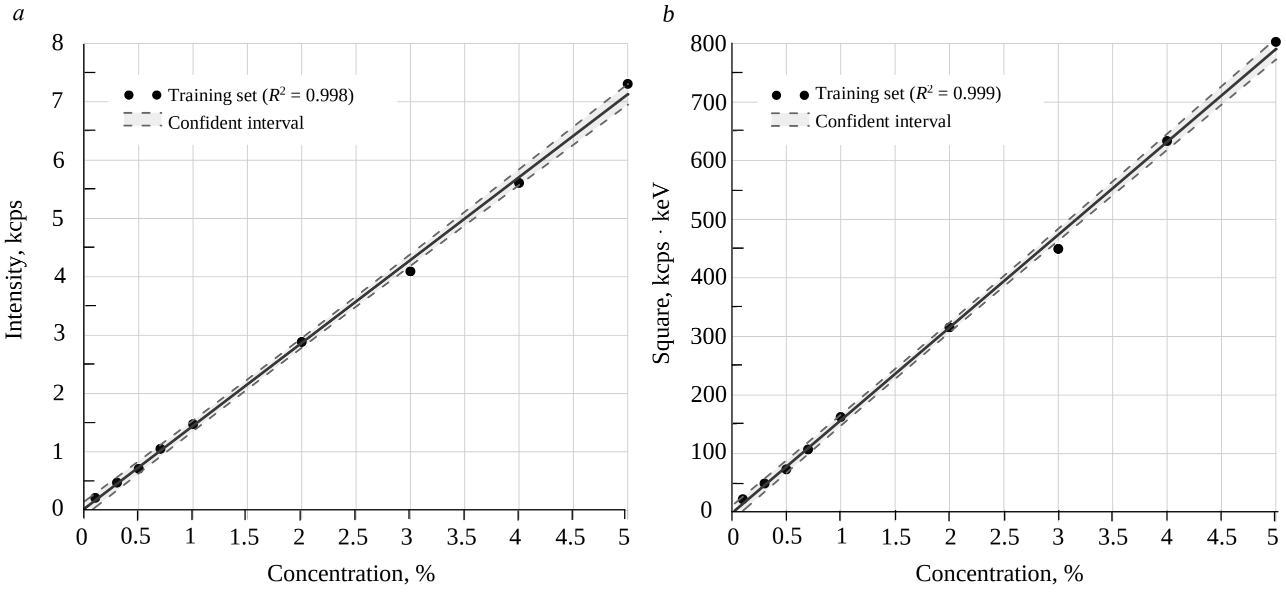

Fig.4. Calibration curves:
a – sulfate sulfur by the intensity of the SKβ′ line; *b* – sulfate sulfur by the area under the SKβ′ peak

Table 2

Samples with known sulfur content, wt.%

Sample	Type	Total sulfur	Sulfate sulfur
SP89	Rock	3.44±0.34	0.18±0.02
SGHM-4	Soil	0.43±0.04	0.23±0.02
1	Mining waste	0.24±0.02	0.23±0.02
2	Mining waste	1.17±0.12	1.16±0.12
3	Bottom sediments	2.14±0.21	0.81±0.08
4	Bottom sediments	0.10±0.01	0.10±0.01
5	Bottom sediments	2.04±0.20	0.73±0.07
6	Bottom sediments	0.61±0.06	0.30±0.03
7	Bottom sediments	0.82±0.08	0.12±0.01
8	Bottom sediments	0.26±0.03	0.24±0.02

The spectra of the SKβ line of rocks, soils, sediments and mining waste after normalization, superimposed on the spectral line of elemental sulfur, are shown in Fig.5. The SKβ’ line characteristic of sulfates is observed in each of the samples. For samples 1 and 2, the intensity of the satellite line is the highest, since almost all of the sulfur in these samples is in the form of sulfates. The spectral line of the SP89 sample almost completely coincides with the line of elemental sulfur and only a small part of it in the SKβ' region goes beyond the region of the line of elemental sulfur, since the proportion of sulfate sulfur in this sample is only 5.2 % of the total sulfur. Sample 4 contains the smallest amount of total sulfur, only 0.1 %. For this reason the satellite line is not pronounced in it, despite the fact that all the sulfur in this sample is presented in the form of sulfates.

For all the obtained spectra, the peaks were adjusted (see Fig.2), their maximum intensities and the areas under the peaks were determined, which were later used to determine concentrations by calibration curves (see Fig.4). The results of the analysis are presented in Table 3.

As can be seen from Table 3, the total sulfur content determined by the intensity of the SK$\alpha_{1,2}$ line of sulfate sulfur practically does not differ from the reference values established by the other method. The content of sulfate sulfur determined by the height of the peak and by the area under the peak SKβ' differs significantly for samples with a high content of other forms of sulfur. If the sample contains sulfur only in the form of sulfates, then both methods show themselves to be effective. Calibration by the area under the peak shows better results with samples containing different forms of sulfur, since this method of calibration depends less on the intensity of the main peak SK$\beta_{1,3}$. A similar pattern is observed on the curves of reference concentrations of sulfur from those measured by the X-ray fluorescence method (Fig.6).

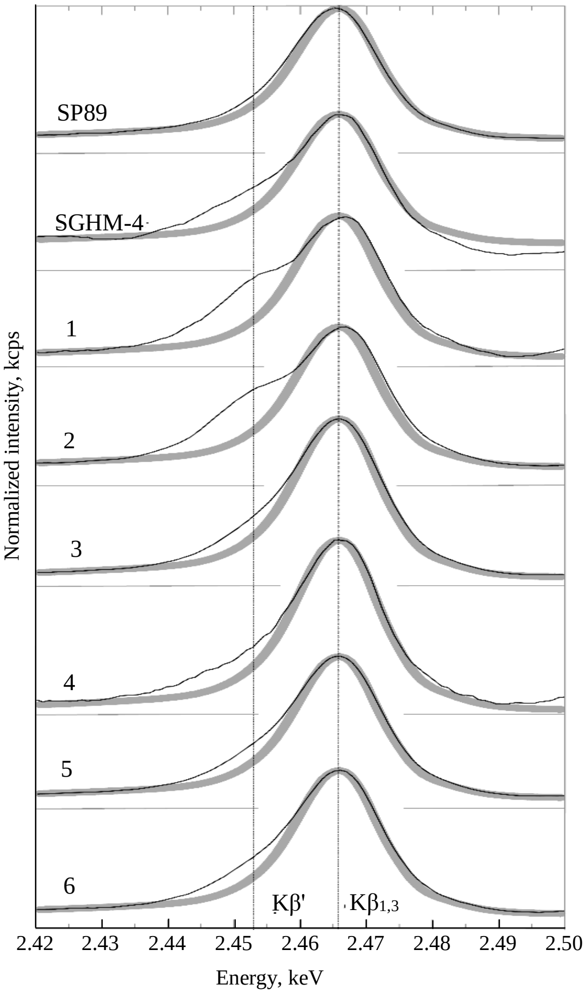

Fig.5. Spectra of various samples superimposed on the SKβ line of elemental sulfur

Table 3

The content of total and sulfate sulfur determined by the intensity of the line and the area under the peak, wt.%

Name of the sample	Total sulfur (according to the intensity of the line $SK\alpha_{1,2}$)	Sulfate sulfur (according to the intensity of the $SK\beta'$ line)	Sulfate sulfur (by area under the peak $SK\beta'$ line)
SP89	3.46	0.58	0.19
SGHM-4	0.42	0.25	0.23
1	0.24	0.27	0.23
2	1.19	1.22	1.19
3	2.14	1.16	1.05
4	0.11	0.11	0.11
5	1.99	1.93	0.82
6	0.64	0.42	0.37
7	0.84	0.22	0.14
8	0.27	0.32	0.28

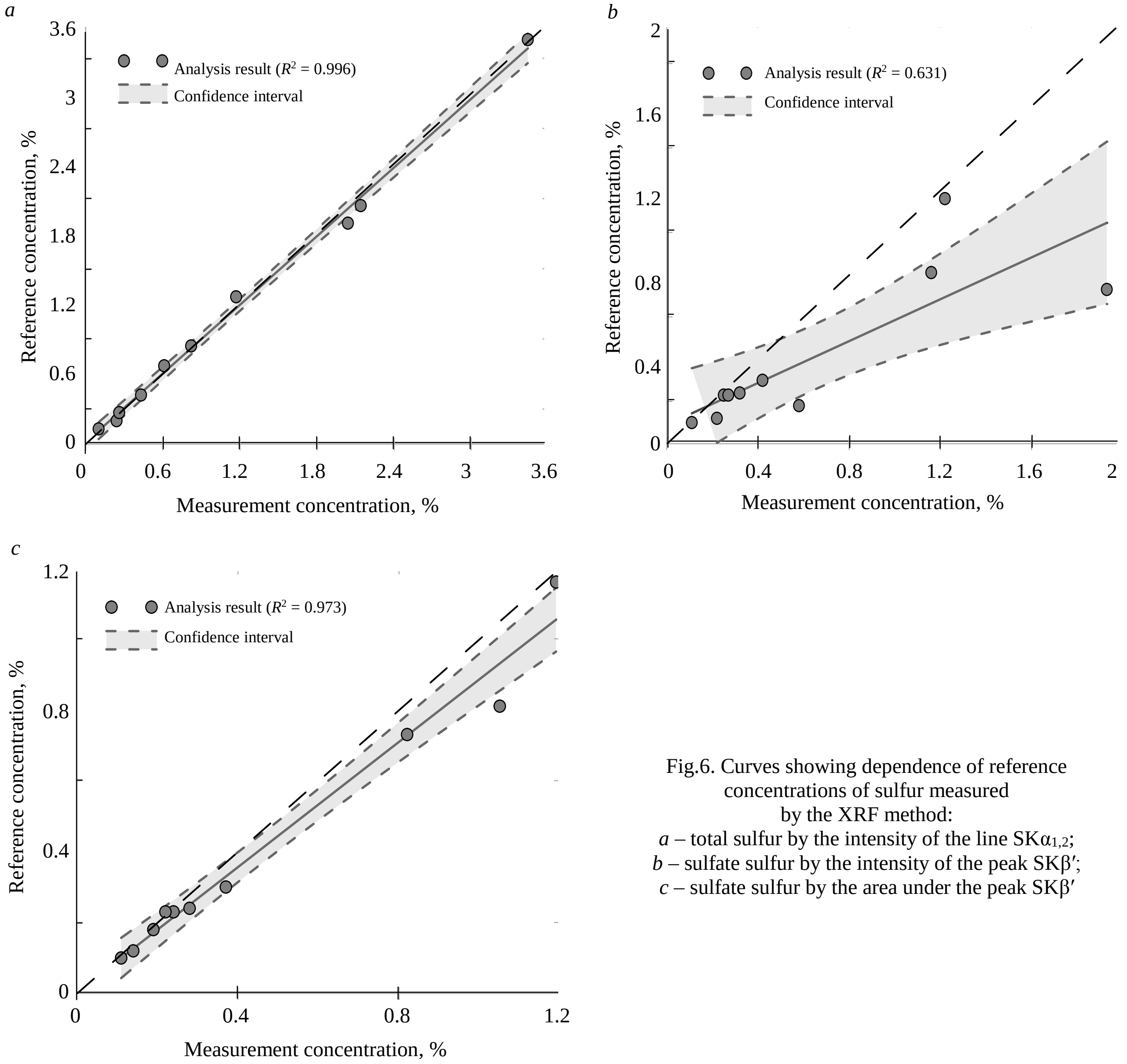

Fig.6. Curves showing dependence of reference concentrations of sulfur measured by the XRF method:
a – total sulfur by the intensity of the line $SK\alpha_{1,2}$;
b – sulfate sulfur by the intensity of the peak $SK\beta'$;
c – sulfate sulfur by the area under the peak $SK\beta'$

As can be seen from the graphs of the determination of sulfate sulfur (Fig.6), the theoretical line along which the points of the analysis results must be located goes beyond the confidence interval both when determining by intensity and by area under the peak. Both ranges of confidence intervals go below that theoretical line. This is due to the fact that the separation of SKβ' peaks from $SK\beta_{1,3}$ in case of high non-sulfate sulfur contents is difficult and the measured results exceed the reference values. However. for sulfate sulfur, which was determined by the area under the peak 95 % confidence interval is much smaller, which means that the range of measured values is also smaller [35, 36]. Determination of sulfate sulfur by the area under the peak can be used for rapid assessment of the content of sulfur forms in samples of different nature.

Conclusion. In this study. a new approach to the quantitative assessment of sulfur forms was developed. Calibration curves for the determination of total sulfur were obtained from the intensity of the $SK\alpha_{1.2}$ line, and of sulfates – after processing the $SK\beta_{1,3}$ lines and the SKβ′ satellite line on the X-ray emission spectra after fitting the peaks. With the help of the presented method, it is possible to determine the concentrations of total and sulfate sulfur in ores, mining waste and bottom sediments with a WDXRF spectrometer using calibration curves constructed on the basis of artificial mixtures. The concentrations of sulfate sulfur determined by the area under the peak SKβ′ are consistent with the concentrations measured by the classical method. Determination of sulfate sulfur by the area under the peak can be used for rapid assessment of the content of sulfur forms in samples of different nature.

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Research article

Acid mine water treatment using neutralizer with adsorbent material

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Abstract. One of the biggest issues in the mining sector is due to acid mine drainage, especially in those abandoned mining operations and active ones that fail to adequately control the quality of their water discharge. The removal degree of copper, iron, lead, and zinc dissolved metals in acid mine drainage was investigated by applying different proportions of mixtures based on neutralizing reagent hydrated lime at 67 % calcium oxide (CaO), with adsorbent material – natural sodium bentonite, compared to the application of neutralizing reagent without mixing, commonly used in the neutralization of acid mining drainage. The obtained results show that the removal degree of dissolved metals in acid mine drainage when treated with a mixture of neutralizing reagent and adsorbent material in a certain proportion, reaches discharge quality, complying with the environmental standard (Maximum Permissible Limit), at a lower pH than when neutralizing material is applied without mixing, registering a net decrease in the consumption unit of neutralizing agent express on 1 kg/m^3 of acid mine drainage. Furthermore, the sludge produced in the treatment with a mixture of the neutralizing reagent with adsorbent material has better characteristics than common sludge without bentonite, since it is more suitable for use as cover material, reducing the surface infiltration degree of water into the applied deposit.

Keywords: bentonite; acid mine drainage; adsorption of metals; water treatment; cover material

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Introduction. The most ecologically harming effluents are those that come from mine discharges with low pH and elevated metal concentrations [1-3]. These conditions lead to ground degradation and hydrology system modification [4, 5], which plays a main role in life development where ecosystems and people are strongly affected by its shortage [6, 7].

In that sense, mining companies face a relevant challenge to run and raise their metal or energy production under a sustainable approach involving economic, social, and environmental spheres [8, 9]. To do so, lead with mine drainage, which mainly is divided into three types: basic, neutral, and acid. The main concern is linked to the acid ones, called acid mine drainage (AMD) due to its characteristic of a less than 3 pH and high concentration of heavy metals [10, 11] Furthermore, as [12, 13] states, AMD impacts can be classified into four groups: ecological, biological, physical, and chemical.

The treatment of AMD is mostly divided into passive or active technologies [14], the latter is commonly applied for effective and rapid toxic material removal reducing environmental impacts due to legal requirements [15], and where materials beneficiation-valorization under a circular economy understanding is trending [16, 17]. Nevertheless, a huge amount of sludge production is inevitable and management could represent a barer in the active application process [18].

AMD treatment strategy must be based on its flow rate, chemistry, logistic capacity, and economic sources as well as legal discharge requirements and receiving body characteristics [19, 20]. Subsequently, AMD neutralization and element immobilizations are quite crucial [21].

There is evidence that companies have been using lime or unactivated attapulgite for AMD neutralization, heavy metal removal [22, 23] and secondary minerals formations in those affected lands by AMD [24].

It is also well documented by [25, 26] that nowadays, it is also important to incentivize production methods to reduce AMD formation at the source and predict environmental harm under a preventive approach, since AMD generation can passively continue over the years [27, 28] and that mining companies should not rely on single technologies to achieve environmental standards [29].

This research aims, despite obtaining good results in the neutralization and metals removal in acid mine drainage, which is measured by the quality of the produced effluent, to adapt the quality of the solid by-product known as neutralization sludge and, to improve its use properties as cover material for tailings and waste dumps, decreasing mine closure costs and environmental liabilities.

In the treatment of AMD, it is very common to use the neutralization process – alkaline precipitation followed by oxidation and sludge separation from the effluent, discharging treated water that reaches the environmental standard. The progress and optimization of the process are based on the sludge recirculation to take advantage of its remaining alkalinity and to increase the sludge sedimentation rate produced with the technology called “High-density sludge” and by the improvements in the flow neutralizing quality that depends on the lime hydration conditions to have the maximum proportion of hydroxyl ions free. Also, equipment works better at homogenizing flows, minimizing “dead zones” and reactor flow short circuits.

The applied concept in the study provides the neutralization process and alkaline precipitation an additional adsorption effect of dissolved metals using an adsorbent material that does not interfere with the main process. It also contributes to the removal of dissolved metals by fixing them on its surface, so that stoichiometrically, the requirement for hydroxyl ions is reduced, in other words, the consumption of lime should be lower.

Bentonite is a rock composed of crystalline clay-like minerals formed by devitrification. The chemical alterations that accompany its glassy igneous material, usually a tuff or volcanic ash often contain variable proportions of accessory glass beads that were originally phenocrysts in volcanic glass. Nevertheless, commercially, bentonites are defined exclusively on a mineralogical basis and they are generally classified according to their cations interlayers and their corresponding capacity for a swell in water as sodium, calcium, or potassium. The study applied sodium bentonite.

Many studies on the simple adsorption of ions in bentonite [30] investigated the capacity of activated bentonite as an adsorbent to remove components under experimental conditions [31] evaluated the adsorption relation of norfloxacin (NOR) and copper Cu^{2+} on bentonite compound elements. The binary adsorption of Cd(II) – Ni(II) on bentonite revealed that both metals presented a very strong antagonism similar to the adsorption of another metal [32]. On the other hand, information on simultaneous adsorption on bentonite multi-component systems or other mineral clay is very rare.

According to [33], using natural bentonite, Cd(II), Cu(II), Ni(II), and Pb(II) ions were removed in systems of one and multiple components under various conditions, with maximum adsorption at 20 min. The pH rise favored the removal of metallic ions. The heavy metal adsorption followed the Langmuir isotherm in both systems of one and multiple components, indicating that Sorption mechanisms do not change under competence conditions. Due to strong antagonism between cations, the solution cation's coexistence reduced adsorption capacity compared to the individually obtained with single metal systems. The adsorption order selectivity was: Cu > Ni > Pb > Cd.

Also, [34] investigated the adsorption of Fe(II) acid drainage from abandoned mine coal in Enugo Okpara – Nigeria, using clay from bentonite. The study was based on an initial concentration of 1308, 62, 49 and 24 mg/l of Fe(II), Cu(II), Zn, and Pb(II)**,** respectively in a 100 ml bottle. In addition, incremented bentonite doses were added from 0 up to 7 g one by one stabilizing the solutions at a constant pH of 2.7 finding that the biggest adsorption occurs under a dose of 4 g in 100 ml. The metal concentration at the end of the process with orbital shaking at 200 rpm for 4 h was 78.50, 0.075 and 0.053 mg/l of Fe(II), Cu(II), and Zn(II), respectively.

Comparably, [35] states about different activations of natural bentonite, including acid activation showing that bentonite compounds have a high potential for pollutant removal in mine wastewater. Linked to acid activation, when the acid concentration is more than 30 %, the bentonite-specific surface area will not increase significantly and bentonite sodium acidification requires a lower concentration than calcium bentonite. As can be seen, there is scientific evidence that sodium bentonite is an abundant and relatively cheap material that can be used in the treatment of AMD.

The main objective of the current study is to reduce the neutralizing reagent consumption, and improve the produced sludge quality by neutralization, making it more suitable for later use as cover material for tailings dumps, clearing, or liability closure state in mining activity.

Different mixing ratios of neutralizing reagent with adsorbent material were applied to identify the most effective, both in metal removal and sludge quality. The investigation is complemented by a sludge waterproofing test as a cover material on the exposed material surface.

Furthermore, the current study is located in Cerro de Pasco, Pasco, Peru at 4300 meters above sea level, and produced by mine dumps with accumulated pyrite belonging to a closed mine after its exploitation phase in an open pit way.

Methods. *Hydrated lime and sodium bentonite*. Hydrated lime was used as neutralizing reagent (NR), sampled from an acid mine drainage neutralization industrial plant which, analyzed in the laboratory results with 66.73 % calcium oxide (CaO), 1.8 % moisture and granulometry of 96 % – 200 mesh.

Bentonite was used as adsorbent material (BE), natural sodium whose chemical name is a silicate of hydrated aluminum – high montmorillonite content white-cream colored powder contained in bags of 25 kg; 94-98 % bentonite, and quartz or silicon oxide of 2-6 % with 2.52 specific gravity and 881 kg/m^3 at 20 °C relative density.

The adsorption capacity of soluble metals, waterproofing, and sealing are the most relevant properties of bentonite for this study.

Acid Mine Drainage. The sample collected from acid mine drainage of 25 ± 0.25 l, was taken following the acid drainage treatment plant sampling procedure, from where the aliquots were taken for the experimental tests: pH (*in situ*) 1.91-1.96; Cu 14.94 mg/l; Fe 836.75 mg/l; Pb 0.32 mg/l; Zn 60.72 mg/l.

Reagent Preparation. As a solid reagent for neutralization and precipitation tests of metals, three powdered mixtures of hydrated lime with bentonite in different proportions were prepared evidenced in Table 1.

Then, 150 g was mixed in 1 l of distilled water for each case. In addition, hydrated lime was prepared by mixing 150 g of it in 1 l of distilled water.

Experimental Tests of Neutralization and Precipitation. The experimental tests were carried out in jar-test equipment of six jars, with a two liter capacity for each one, with adjustable speed agitators and time control. Due to sanitary restrictions, the tests were performed in an isolated environment inside the laboratory located in the environmental operations unit of the Universidad Continental in Huancayo.

Table 1

Mixtures characteristics, %

Mixture	Hydrated lime (NR)	Bentonite (BE)
M1	95	5
M2	90	10
M3	80	20

Table 2

Reagents consumption in the neutralization and precipitation test, g/l

Reagent	Mix	NR	BE
NR 100 %	6.45	6.45	0.00
NR 95 % – BE 5 %	6.35	6.03	0.32
NR 90 % – BE 10 %	6.04	5.44	0.60
NR 80 % – BE 20 %	7.12	5.70	1.42

The used test standard was 1 l of the acid drain, agitator at 300 rpm, a reaction time of 20 min, and the addition of reagent with a graduated milliliter syringe. During the test, the reagent was contained in a beaker with a magnetic stirrer to keep the mixture homogeneous.

Table 2 shows the reagent dosages used in the four neutralization and precipitation tests. The reagents were fed as a solid-liquid mixture.

Additionally, the obtained sludge in the neutralization tests for each dosage with five repetitions was collected and stored in four containers separately, one for each dosage.

Analytical methods. The metals in liquid solutions were analyzed by the following methods: copper (Cu) – SMEWW-APHA-AWWA-WEF. Part 3500-Cu B, 23rd Ed. 2017; zinc (Zn) – SMEWW-APHA-AWWA-WEF. Part 3500-Zn B, 23rd Ed. 2017; iron (Fe) – SMEWW-APHA-AWWA-WEF. Part 3500-Fe B, 23rd Ed. 2017; lead (Pb) – SMEWW-APHA-AWWA-WEF. Part 5210-Pb B, 23rd Ed. 2017.

Experimental coverage tests. The four percolation columns were prepared using 4-inch (10.16 cm) internal diameter PVC pipes, a padding height of 50 cm ± 0.5 cm. A 4-inch PVC cover was placed at the bottom with 1/8 inch drilled from inside to outside to collect percolating liquid by gravity. At the bottom of each column, transparent containers were placed to collect the percolated. Also, the lateral parts were covered with transparent polyethylene to minimize losses by evaporation.

The sludge from each of the four test groups was combined due to its origin similarity, high molecular weight soluble polymer flocculant was added and shaken for 10 min at 60 rpm, then by separating the supernatant liquid obtained a stable thickened sludge whose content of solids is detailed in Table 3.

Table 3

Characteristics of the test group

Test group	Sludge volume, ml	Solids content, %	Column number
NR 100 %	280	32	1
NR 95 % – BE 5 %	275	28	2
NR 90 % – BE 10 %	270	29	3
NR 80 % – BE 20 %	271	27	4

In this first coverage stage of the percolation columns, after 45 min in none of the columns, liquid leakage was observed from the bottom. It was observed that on the surfaces the coloration was turning reddish and without liquids above it as shown in Table 4.

Percolation Experimental Tests. After 18 h of percolation columns were covered with the respective sludge, and cool water was gradually added to the column's surface: 200 ml at 0 min, 150 ml at 10 min, and 100 ml at 20 min.

Volume of supernatant and percolated liquid after 25 min since added last cool water is detailed in Table 5.

Table 4

Coverage data from the percolation columns with thickened sludge

	Column, cm			
	1	2	3	4
Fill Height	50	50	50	50
Sludge Height	3.4	3.5	3.6	3.6
Initial Height	53.4	53.5	53.6	53.6
Reduction 10 min	2.8	2.6	2	1.8
Height at 10 min	50.6	50.9	51.6	51.8

Table 5

Volume of liquid after added water

Column number	Height, cm	Volum of liguid, ml	
		Supernatant	Percolate
1	0.3	24	145
2	1.2	94	142
3	1.6	126	105
4	2.2	177	65

Result and Discussion. *Metals Neutralization and Removal*. Neutralization with unmixed hydrated lime is within the range of consumption (6.45 g/l) that is handled in the industry for acid water with pH between 1.91 and 1.96 as well as the content of analyzed dissolved metals.

In the tests with a mixture of hydrated lime with bentonite, the pH decreases with the increase in the proportion of bentonite – also the concentration of dissolved metals in treated water increases slightly. Nevertheless, still, at lower pH, the removal of dissolved metals occurs while complying with the environmental maximum permissible limit (MLP) standard already mentioned.

It should be noted that to reach the pH range of 7.6 to 8.0 using only hydrated lime as a reagent, although the consumption is low, the concentration of dissolved metals is above the MPL standard (pH 6 to 9, Pb 0.16 mg/l; Zn 1.20 mg/l; Cu 0.40 mg/l and Fe 1.6 mg/l): pH 7.8; Pb 0.18 mg/l; Zn 5.18 mg/l; Cu 1.23 mg/l; Fe 177.78 mg/l.

Furthermore, bentonite has a dissolved metal adsorption effect, decreasing its concentration in the liquid (Table 6) especially iron with which it would have an effect of pretty good adsorption, as mentioned by [34].

Table 6

Liquid characteristics obtained by the acid drainage treatment under different proportions of neutralizer and adsorbent, mg/l

Reagent	pH	Pb	Zn	Cu	Fe
NR 100 %	8.93-9.27	0.03	0.16	0.05	1.21
NR 95 % – BE 5 %	8.72-8.89	0.03	0.28	0.09	1.54
NR 90 % – BE 10 %	7.89-8.15	0.09	0.75	0.25	1.55
NR 80 % – BE 20 %	7.61-8.0	0.11	0.97	0.32	1.58

Coverage and percolation tests. From the results of coverage with thickened sludge, it is observed that at a higher proportion of bentonite in the mixture, the formed layer thickness on the surface is greater 10 min after its application. Also, for up to 45 min, there was no evidence of percolation at the bottom of the column.

By adding fresh water to the top surface of the columns, it is observed that when the coverage is of the sludge from the hydrated lime treatment (column 1), the height of the supernatant is lower and the volume of the percolated is higher. When the proportion of bentonite increases the percolation speed and the percolate volume decrease evidencing that water remains caught in the column.

For purposes of applying sludge mixtures with bentonite contents, it remains to investigate the sequence of its use on mineral deposits, tailings, or dismounts, depending on the characteristics that should eventually have the exposed layer exposed.

Conclusions. Acid water treatment with hydrated lime mixed with bentonite removes dissolved metals at a lower pH than when only hydrated lime is used. Sludge from acid water treatment with hydrated lime mixed with bentonite acquires additional properties of reducing percolation speed directly proportional to the content of bentonite. The use of hydrated lime neutralization sludge mixed with bentonite must be adapted to the type of coverage that is required for the closure of tailings, clearings, or exposed deposits in general.

It is highly expected to reduce AMD effluents at the source to reduce treatment costs, environmental damage, and tedious sludge management under a preventive approach.

Acid water neutralization sludge, currently considered a waste of no commercial value, which on the contrary represents handling and disposal costs, can be used as cover material.

The use of cover material based on neutralization sludge and bentonite on dumps of acid-generating material will gradually decrease the potential for acid generation of the dump by reducing aeration and water infiltration, both essential factors for the oxidation of sulfides and generation of acids and dissolved metals.

Coverage with a mix of bentonite neutralization sludge, unlike geosynthetic coverage, has the advantage of being better incorporated into the landscape environment in the post-closure of deposits generated by mining.

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Research article

Assessment of the efficiency of acid mine drainage purification (using the example of copper-pyrite mines in the Middle Urals)

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Abstract. According to the results of the anti-rating of regions with extreme pollution of watercourses in the Sverdlovsk region, the largest number of polluted rivers has been recorded in recent years – more than a quarter of all high and extremely high pollution. One of the sources of pollution of natural water bodies in the Middle Urals are closed and flooded copper-pyrite mines, where acidic mine drainage continue to form and unload to the surface. Several of them have organized collection and a two-stage acidic drainage purification system, including neutralization with lime milk and settling in a clarifier pond. Despite the identical schemes, different indicators of pollutants are recorded during discharge into water bodies. The aim of the work is to evaluate the effectiveness of the applied acid mine drainage purification system and identify the parameters affecting the quality of treated mine water. Laboratory studies were performed using methods of flame emission spectrometry, flame atomic absorption, atomic absorption spectrometry, mass spectrometry with ionization in inductively coupled plasma, potentiometric, etc. It has been established that the existing mine drainage purification system at the Degtyarskii mine makes it possible to significantly reduce the concentrations of most toxic components of mine waters to almost standard values. At the Levikhinskii mine, the multiplicity of exceeding the maximum permissible concentrations reaches hundreds and thousands of times. To achieve a higher degree of purification, it is necessary that the duration of passive purification is sufficient for the reactant to interact with acidic waters. However, to ensure this possibility, it will require the creation of a cascade of ponds with an area of several thousand hectares. If the current two-stage system is quite effective for the Degtyarskii mine, then for Levikhinskii it is necessary to switch to the use of more modern systems, including three stages of purification.

Keywords: acid mine drainages; hydrosphere; active and passive purification methods; copper-pyrite mines; clarifier pond; reagents

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Introduction. Acid mine drainages (AMD) is one of the most serious environmental problems, closely related to mining activities. The main reason for the formation of these waters is the presence of sulfide minerals in rocks [1, 2]. During mining, the integrity of the rock mass is violated, sulfuric acid weathering of sulfide minerals occurs when interacting with water and air, which leads to the formation of acid mine drains [3-5]. Low pH values in mine waters contribute to the further dissolution of minerals and the release of heavy metals from them. These flows, when entering the landscapes of mining territories, cause significant damage to both the hydrosphere and the entire environment as a whole [6-8].

The main problem with AMD purification is their high acidity (pH = 2.5-4.5), the presence of dangerous chemical elements (Cu, Zn, Mn, Fe, Al), as well as large volumes of water that are formed after flooding of mines and come to the surface for tens and sometimes hundreds of years [9]. The composition of mine waters depends on the time that has passed since the flooding. In the first years, there is a sharp increase in all indicators, sometimes 3-5 times compared to the stage of development. This phenomenon is called the “first flush” and manifested itself, among other things, in the copper-pyrite mines of the Middle Urals [2, 10]. In the future, there is a gradual rather slow decline in mineralization and concentrations of individual components, but at the same time significant fluctuations in their content are noted depending on the season and the water content of the period. These processes significantly complicate the organization of mine water purification and must be taken into account at each specific facility.

In the Sverdlovsk region, at many liquidated copper-pyrite mines (Levikhinskii, Karpushikhinskii, Lomovskii, Degtyarskii, etc.), after the cessation of drainage, concentrated AMD outlets formed, as a rule, in the lowest part of the mining landscape (in sinkholes, pits). Although their consumption is lower than during mining and mine drainage, it can reach several thousand cubic meters per day and, without cleaning, leads to degradation of the landscape and unacceptable pollution of the hydrosphere over significant areas. To prevent environmental pollution of such facilities, since the early 2000s, AMD collection and neutralization has been organized at the expense of the regional budget (for this purpose, the State Government Institution of the Sverdlovsk region “Uralmonatsit” was created). Treated wastewater from the Levikhinskii, Karpushikhinskii and Lomovskii mines is discharged into the Tagil River (Irtysh basin district), below the discharges is the Lenevskii reservoir, which is one of the sources of water supply in Nizhnii Tagil (population 350 thousand people) [11]. Despite the cleaning, the level of water pollution in the mouth of the Levikha River exceeds the permissible norms by thousands and hundreds of times [12].

The Degtyarskii copper-pyrite deposit is located on the eastern slope of the Middle Urals in the municipal district of Degtyarsk, Sverdlovsk region, 45 km southwest of Yekaterinburg, 18 km southeast of Revda. The deposit was mined from 1914 to 1995. The operation was carried out comprehensively by both open and underground methods up to a depth of 610 m. At the end of 1995, due to the liquidation of the mine, the mine drainage was stopped and by 1999 the filling of the depression funnel was completed [13]. From this moment on, AMD with a flow rate of about 180 m^3/h enters the pit hole of the Kolchedannaya mine in the northern part of the field. AMD flowing from the pit enters the Istok River in a dispersed flow, where it is mixed with lime milk, which is piped from the neutralization station. Then the entire runoff of neutralized mine waters along the riverbed enters the Yelchevskii pond sump, built in 1952 to purify the mine waters of an operating mine [14-16]. The design volume of the pond is 9.4 million m^3, with an area of 220 ha [17]. After settling, the water purified from suspension along the riverbed of the Yelchevka River enters the Volchikhinskii reservoir, which is the main source of drinking water supply in Yekaterinburg (population 1.5 million people) (Fig.1) [18].

The degree of purification is much higher here, almost up to the standards of maximum permissible concentrations (MPC). The Volchikhinskoe reservoir is located in the basin of the Chusovaya River (Kama basin District), Yekaterinburg is located on the Iset River (Irtysh Basin District). In fact, the inter-basin transfer of river flow through the Main Ural watershed is carried out. Water from the Volchikhinskoe reservoir is supplied to Yekaterinburg, providing the bulk of the city's domestic water supply, therefore, the state of the hydrosphere in the watershed of the Volchikhinskoe reservoir is the subject of close attention by both supervisory authorities and the public.

The Levikhinskoe copper-pyrite deposit is located 120 km north of Yekaterinburg, on the eastern outskirts of the village Levikha, 30 km northwest of Kirovgrad (Fig.2). The mine was worked out from 1927 to 2003 both open and underground to a depth of 615 m. Until the end of the 1950s, AMD was dumped into the Porokhovoe swamp, located in the north-west of the deposit, without preliminary purification. In 1959, a clarification pond was built in the valley of the Levikha River. Its design volume is 3 million m^3, its area is 142 ha. In 2003, the drainage was stopped, which led to the filling of the depression funnel, and by 2007, a man-made reservoir was formed at the lowest point of the mining outlet in the sinkhole of the Levikha II mine, into which AMD is discharged. The discharge flow rate is approximately 115 m^3/h, which is half what it was during the mining period. Mine water is pumped through a pipeline from a man-made reservoir in the area of the Levikha II mine to a neutralization

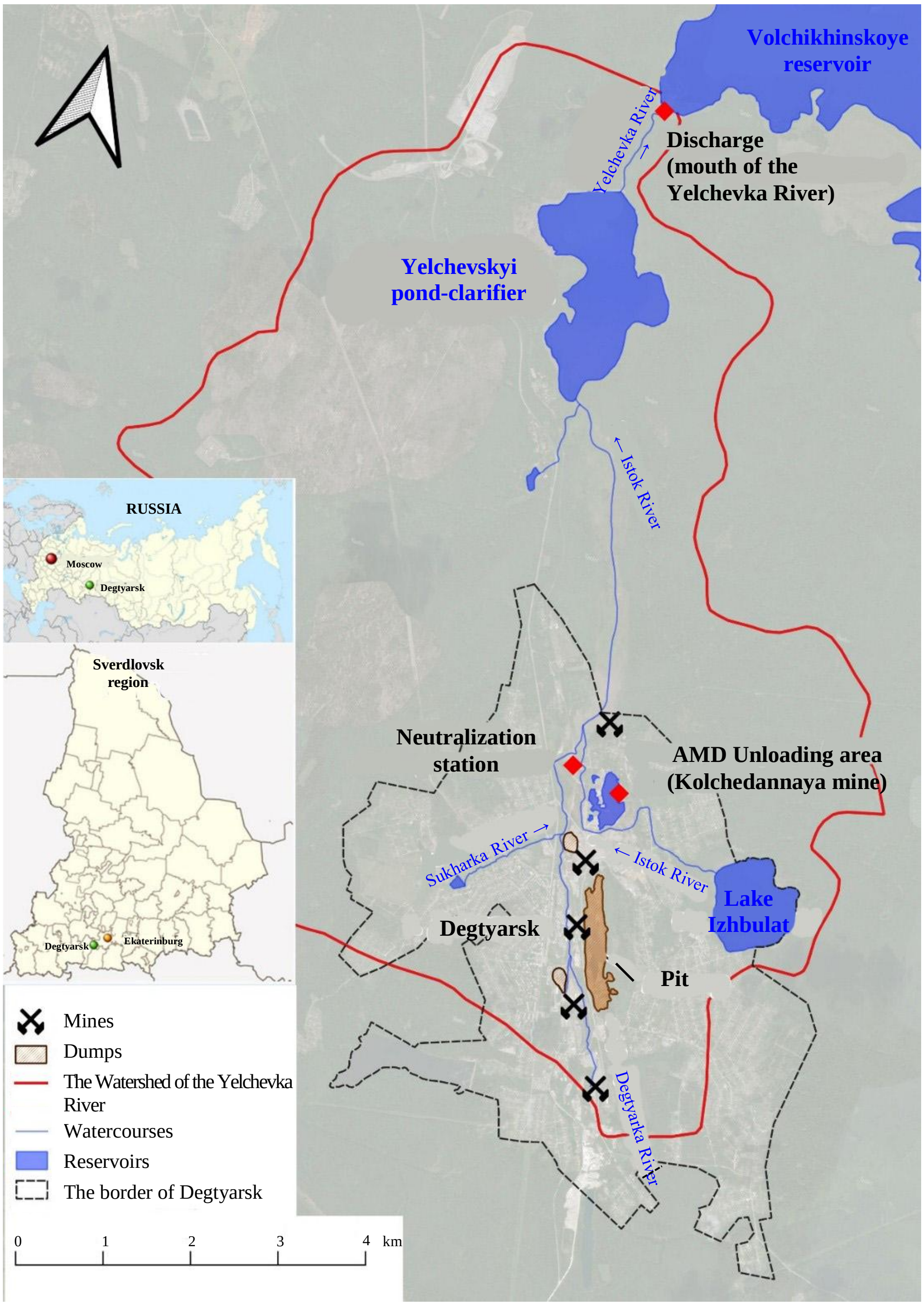

Fig.1. Overview map of the location of facilities at the Degtyarsk mine

station. After adding lime milk, these waters enter the clarifier pond, and then flow by gravity along the old riverbed of the Levikha River into the Tagil River (Fig.2).

A wide variety of technologies are currently used to effectively clean AMD, in general they are divided into active and passive methods [19-21].

Active purification methods are chemical (neutralization), electrochemical, membrane, ion exchange, sorption, oxidation, eutectic crystallization by freezing [22-24]. Active cleaning systems require various equipment (tanks, mixers, pumps and aerators), regular maintenance, continuous dosing of chemicals, and power supply. The main advantages of their use include: effective removal of contaminants from mine drains, precise process control, allowing them to be designed and operated to obtain water of a certain chemical composition, as well as the possibility of use in places with a limited area. The main limitations are the high capital and current costs of operation

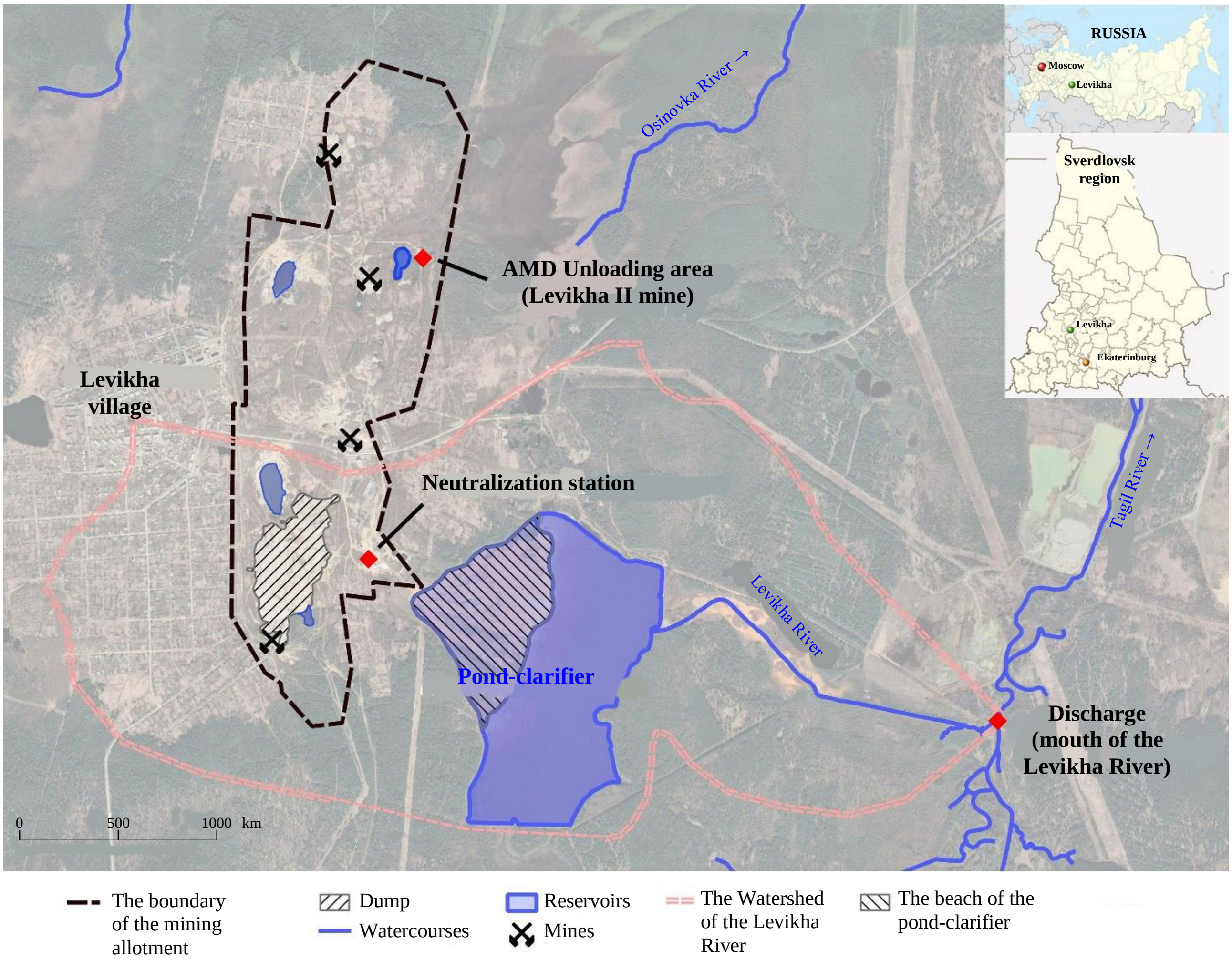

Fig.2. Overview map of the location of facilities at the Levikhinskii mine

and maintenance. Active cleaning is more suitable for operating mines, which usually have a subsurface area for extraction, as well as production facilities and personnel to manage the cleaning system.

In order to increase the pH of mine waters, reduce the solubility of pollutants, control the composition of wastewater and reduce the harm caused to the environment by acidic waters, substances such as limestone $CaCO_3$, slaked lime $Ca(OH)_2$, quicklime, or calcium oxide CaO, liquid and solid caustic soda NaOH are used as reagents, soda ash Na_2CO_3, ammonia NH_3 [25]. A certain chemical is suitable for a specific state and conditions. The choice of a specific reagent depends on both technical (pH level, consumption, metal concentration) and economic factors (reagent price, labor, equipment, cleaning time) [26-28].

Passive purification systems are based on natural physical, geochemical and biological processes. These can include: limestone drains or channels, wetlands, systems for reducing and increasing alkalinity, clarification ponds, passive oxidation systems (cascades) [17, 29].

Unlike active methods, which require a continuous supply of reagents to neutralize the acidity of mine waters during the entire period of operation, passive systems are usually designed with such a service life (25 years) of the neutralizing material that no additional costs are required during this period [30]. Most passive systems are based on dissolving a neutralizing material (usually limestone) to increase the pH. In order to effectively interact pollutants with reagents, sufficient residence time in systems is necessary; therefore, large areas of land are usually necessary for the implementation of passive systems [31-33]. The combination of active and passive methods leads to a significant increase in the degree of purification. The most cost-effective and highly effective combination of methods is, for example, the use of reagents to reduce acidity and sedimentation of mine waters in clarification ponds before discharge into water bodies.

The aim of this work is to evaluate the efficiency of AMD purification at facilities in the Middle Urals and identify the main parameters that allow achieving higher water quality indicators at discharge into water bodies. To do this, the following tasks were solved: an array of hydrochemical monitoring data was processed at the Degtyarskii and Levikhinskii mines as the most significant objects; the efficiency of the AMD purification system was evaluated; the main factors on which the reduction of pollution indicators depends were identified, and measures for organizing cleaning at the Levikhinskii mine were proposed.

Research methods. To analyze the chemical composition of water in the area of Degtyarskii and Levikhinskii copper-pyrite mines, monitoring data was used, which was conducted by Uralmonatsit in Degtyarsk and the village Leviha. At these facilities, the most characteristic pollution indicators for AMD are determined monthly (starting from the moment AMD reaches the surface) in the discharge zone and when wastewater is discharged into surface reservoirs: hydrogen index, copper, zinc, total iron, suspended solids, total mineralization (dry residue), chlorides, sulfates, manganese, petroleum products, and arsenic.

The Institute of Mining of the Ural Branch of the RAS has tested an expanded list of components. The analyses were carried out at the Institute of Industrial Ecology of the Ural Branch of the RAS (Yekaterinburg) using methods of flame emission spectrometry (determination of Na, K), flame atomic absorption spectrometry (Ca, Mg), atomic adsorption spectrometry (Fe), mass spectrometry with ionization in inductively coupled plasma (Al, Be, Cd, Co, Mn, Cu, As, Ni, Pb, Se, Zn), determination of nitrogen-containing substances (NO_2), potentiometric with ion-selective electrode (NO_3), gravimetric (SO_4) and argentometric (Cl), photometric in the form of yellow silica-molybdenum heteropolyacid (Si), determination of alkalinity and mass concentration of carbonates and hydrocarbonates. About 16 components were found in each sample. T (°C), Eh (mV), pH, TDS (mg/l), EC (mSm/cm) were measured on site.

To visualize the results of the chemical composition of water and display a variety of indicators, classifications based on Piper and Durov diagrams are most often used. Such graphs are based on the same principle of construction – the image of the sample with two points on two Ferre triangles. The diagrams use three main cations Ca^{2+}, Mg^{2+}, Na^{+} (in our case, the content of Na^{+} is insignificant, therefore $Fe+Al^{3+}$ are taken into account) and three main anions HCO^{3-}, SO_4^{2-}, Cl^{-}. The triangles show the dominant number of cations and anions, and the field shows the classification of the sample. The main difference between the Durov diagram is that it includes the hydrogen index and mineralization. Guided by considerations of unification, visualization and detection of trends in changes in the chemical composition and indicators of water, a classification based on the Durov diagram was chosen for plotting in the work.

The efficiency of the system was evaluated using the formula:

$$\mathrm{E} = \frac{C_{\mathrm{in}} - C_{\mathrm{out}}}{C_{\mathrm{in}}} \cdot 100\,\%, \tag{1}$$

where C_{in}, C_{out} are the concentrations of pollutants in the AMD discharge zone and in wastewater at the mouth of the Yelchevka and Levikha rivers, respectively, mg/l.

To calculate the required volume of an alkaline reagent that will neutralize hydrogen ions, both present in the solution (pH of the solution) and formed during the oxidation of soluble metals and their precipitation, the water acidity formula is used[1] [34]:

$$\mathrm{Acidily} = 50\left(\frac{2\mathrm{Fe}^{2+}}{56} + \frac{3\mathrm{Fe}^{3+}}{56} + \frac{2\mathrm{Mn}^{2+}}{55} + \frac{3\mathrm{Al}^{3+}}{27} + \frac{2\mathrm{Cu}^{2+}}{64} + \frac{2\mathrm{Zn}^{2+}}{65} + 1{,}000\left(10^{-\mathrm{pH}}\right)\right), \tag{2}$$

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[1] Hedin R.S., Nairn R.W., Kleinmann R.L.P. Passive Treatment of Coal Mine Drainage. Washington: United States Department of the Interior, 1994, p. 52.

where the calculated acidity is expressed in mg/l $CaCO_3$; Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+} – metal concentrations in solution, mg/l; 50 – the coefficient for converting mg-eq of acidity to mg/l $CaCO_3$; The content of Fe^{2+} and Fe^{3+} was calculated using the PHREEQC computer program[2].

To assess the degree of exposure of a group of pollutant components, a total pollution indicator is used[3]:

$$Z_c = \sum_{i=1}^{n} \frac{C_i}{C_{\text{MPC}}} - (n-1), \tag{3}$$

where C_i – the actual content of the substance determined in water, mg/l; C_{MPC} – MPC of pollutants for fishery purposes; n – the number of defined summable substances.

The dependence [22] is used to estimate the area of the cascade of ponds necessary for passive purification and sedimentation of water after neutralization

$$F = \frac{Q_d\left(C_i - C_t\right)}{R_a}, \tag{4}$$

where F – required pond area, m^2; Q_d – average daily water consumption, m^3/day; C_t – concentrations of pollutants at final discharge, mg/l; R_a – the rate of removal of pollutants, g/m^2/day.

Results discussion. To assess the effectiveness of mine water treatment, comparative dates were taken – 10 years after the stop of drainage – 2003-2004 at the Degtyarskii, 2015-2016 and Levikhinskii mines. The mine waters at the Degtyarsk mine in the unloading zone (here a man-made reservoir was formed in the pit of the Kolchedannaya mine) are characterized as acidic (pH = 2.3-3.3), Eh = 263 mV, sulfate in anionic composition, aluminum-iron-calcium-magnesium cationic (the order of cations is not constant), mineralization *M* it varies from 1.4 to 16 g/l (Tables 1, 2, Fig.3). At the Levikhinskii mine in the unloading zone (in a technogenic reservoir in the sinkhole of the Levikha II mine), the waters are less acidic (pH = 3.6-3.9), Eh = 188 mV, calcium-magnesium-iron-aluminum sulfate in composition (the ratio of cations may vary), with mineralization from 14.2 to 20.0 g/l.

Table 1

Results of hydrochemical monitoring

Indicators	MPC		AMD Unloading area		Discharge		Cleaning efficiency, %	
	fi*	dw**	Degtyarskii mine	Levikhinskii mine	The mouth of the Yelchevka River	The mouth of the Levikha River	Degtyarskii mine	Levikhinskii mine
pH	6.5-8.5	6.0-9.0	2.3-3.3*** 2.6	3.6-3.9 3.8	7.2-7.5 7.4	6.6-7.6 7.2	–	–
Fe_{total}, mg/l	0.1	0.3	477-2,562 899	994-2,353 1,455	0.1-0.03 0.1	35-245 95	99	93
Cu, mg/l	0.001	1.0	4.6-12 11	16-29 19	0.01-0.01 0.01	0.9-1.3 1.0	99	93

* For reservoirs of fishery importance (Order of the Ministry of Agriculture of the Russian Federation dated December 13, 2016 N 552 “On approval of water quality Standards for aquatic bodies of fishery importance, including standards for maximum permissible concentrations of harmful substances in the waters of aquatic bodies of fishery importance”, as amended on August 22, 2023).

** For centralized drinking water supply systems (SanPiN 1.2.3685-21 “Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors to humans”, as amended on December 30, 2022).

*** The numerator has the minimum and maximum values, and the denominator has the median value.

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[2] Parkhurst D.L., Appelo C.A.J. Description of Input and Examples for PHREEQC. Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. Techniques and Methods 6–A43. Denver: United States Geological Survey: 2013, 2013, p. 497.

[3] MG 2.1.7.730-99. Methodological guidelines “Hygienic assessment of the soil quality of populated areas” (approved by the Chief State Sanitary Doctor of the Russian Federation dated 07.02.1999).

End of Table 1

Indicators	MPC		AMD Unloading area		Discharge		Cleaning efficiency, %	
	fi	dw	Degtyarskii mine	Levikhinskii mine	The mouth of the Yelchevka River	The mouth of the Levikha River	Degtyarskii mine	Levikhinskii mine
Zn, mg/l	0.01	5.0	54-151 121	234-397 280	0.03-0.2 0.1	54-123 107	99	62
Mn, mg/l	0.01	0.1	8-56 39	44-137 82	0.1-0.2 0.2	1.6-73 34	99	52
Cd, mcg/l	5	1	40-100 100	Not defined	0.8-5 0.8	Not defined	99	–
Cl, mg/l	300	350	34-52 42	32-53 33	23-32 28	10-28 20	–	–
SO_4, mg/l	100	500	2,685-8,791 7110	3,710-10,450 7,493	583-826 704	274-5,460 2133	90	71
Dry residue, mg/l	–	1000	4,356-15,990 11,188	14,183-19,942 1,654	930-1,284 628	458-9,296 4,557	–	–
Zc			36,057	64,821	44	15,967		

Table 2

Kurlov's formula

Mine	Unloading AMD	Discharge (mouth of the Yelchevka and Levikha rivers)
Degtyarskii	$M_{9,7}\dfrac{SO_4 99}{Fe36Mg35Ca16Al13}pH2.6$	$M_{1,3}\dfrac{SO_4 95}{Ca65Mg30}pH7.5$
Levikhinskii	$M_{11,5}\dfrac{SO_4 99}{Al32Fe28Mg23Ca16}pH3.8$	$M_{3,5}\dfrac{SO_4 98}{Ca62Mg34}pH7.3$

As can be seen from Fig.3, in terms of cationic and anionic compositions, most points form compact fields, which indicates the similarity of the chemical composition of water at the two objects. According to the cationic composition in the AMD discharge zone at the Degtyarskii mine, most samples do not have a constant content of elements, unlike Levikhinskii. Sulfate is noticeably predominant in the anionic composition at facilities both in the unloading zone and after discharge.

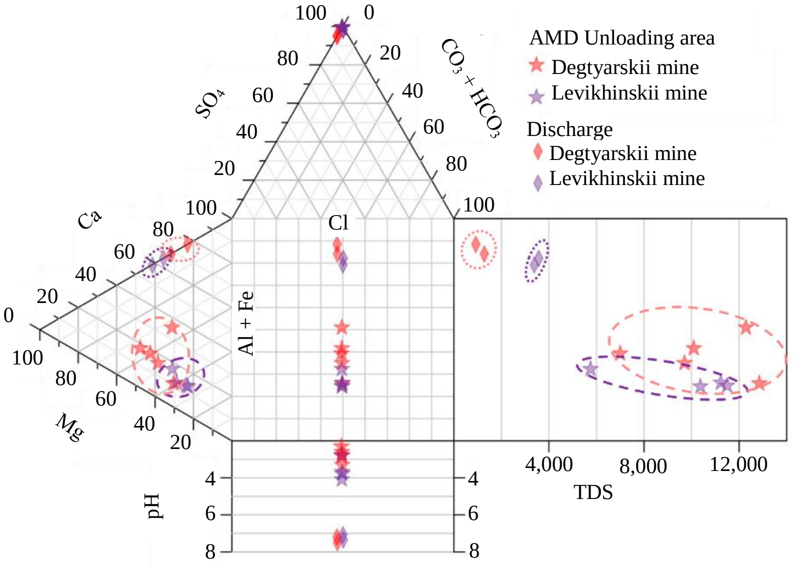

Fig.3. Durov diagram – graph of the chemical composition of water in the AMD unloading zone and after purification, %-eq/l

It is important to note that at the discharge of purified AMD at two sites the pH increases and mineralization decreases. Therefore, based on these two parameters, one can conclude about the effectiveness of the ongoing measures to collect AMD neutralization.

Nevertheless, the metal content in mine waters exceeds the MPC by several orders of magnitude. The most significant (thousands of times) are noted for copper, iron, zinc, aluminum, and manganese at the Levikhinskii mine. On Degtyarskii, there are fewer exceedances for the same elements (Table 3). In general, the mineralization and content of the main polluting components at Levikhinskii is 1.5-3 times higher than in the mine waters of the Degtyarskii mine. To reduce the environmental burden on the hydrosphere and prevent the entry of untreated acidic waters into watercourses at flooded mines, a two-stage AMD purification system operates, which includes neutralization of mine waters with lime milk and sedimentation in a clarifier pond.

Table 3

Exceedances of MPC for reservoirs of fishery importance

Mine	Unloading AMD	Discharge (mouth of the Yelchevka and Levikha rivers)
Degtyarskii	Cu (3600) Fe (2790) Mn (1600) Zn (1960) Al (1275) Co (53) Ni (25) Cd (8) Be (8)	Mn (20) Cu (10) Zn (10)
Levikhinskii	Cu (16300) Fe (12900) Zn (12700) Al (12350) Mn (5830) Co (110) Ni (50) Cd (50) Be (32)	Mn (1437) Zn (444) Cu (256) Al (110) Fe (10) Mg (5) Ca (5) Cd (3) Co (3)

Note. The chemical composition of water is presented in the form of a generalized association, where to the right of the name of the element is the multiplicity of exceeding the MPC for reservoirs of fishery importance.

The estimated acidity of mine waters at the Degtyarskii mine is 1003 mg/l equivalent of $CaCO_3$, at the Levikhinskii mine – 5413 mg/l (Table 4). Consequently, the amount of reagent required to neutralize mine waters differs and according to the calculated data is 1581 and 5462 t/year, respectively (with discharge flow values of 50 and 32 l/s).

Table 4

Calculation of the acidity of mine waters and the amount of lime required for neutralization

Mine	pH, units	Fe^{2+}, mg/l	Fe^{3+}, mg/l	Al, mg/l	Mn, mg/l	Cu, mg/l	Zn, mg/l	Calculated acidity, mg/l $CaCO_3$	Required amount of reagent, t/year
Degtyarskii	2.5	274.4	5.6	51	16	3.6	19.6	1003	1581
Levikhinskii	3.8	1254	36	494	58.3	16.3	127	5413	5462

After clarification in the Yelchevskii clarifier pond at the mouth of the Yelchevka River, the waters are characterized as magnesium-calcium sulfate, pH is 7.2-7.5, which corresponds to a neutral medium, mineralization is 0.9-1.3 g/l. The concentration of cadmium decreases to 0.0008 mg/l, but remains almost an order of magnitude higher than the MPC for drinking purposes. The iron concentrations at the discharge usually do not exceed 0.1 mg/l, which is significantly lower than the MPCfi (see Table 1).

After clarification in the Levikhinskii clarifier pond at the mouth of the Levikha River, the water composition is also magnesium-calcium sulfate. The hydrogen index varies 6.6-7.6, which indicates a neutral environment. Mineralization – 0.5-9.3 g/l. The efficiency of the two-stage mine water purification system at the Degtyarskii mine reaches 99 % for iron, copper, zinc, manganese and cadmium, and 90 % for sulfate ion (see Table 1). Despite a sufficiently high degree of purification, the concentrations of components at the discharge from the clarifier pond exceed the MPC for reservoirs of fishery importance (MPCfi): manganese (20 times), copper and zinc (10 times), sulfate ion (7 times). According to the normative indicators for drinking water supply, exceedances were found for manganese (2 times) and sulfate ion (1.5 times).

The Levikhinskii mine uses the same purification scheme in general, but it turns out to be much less effective: from 59 % for manganese to 93 % for iron and copper. As a result, in the mouth of the

Levikha River at the discharge into the Tagil River, the concentrations of components have significant exceedances of MPCfi: for zinc by 11 thousand times, manganese by 1.4 thousand times, zinc, copper, aluminum – by hundreds of times.

Thus, despite the same AMD purification schemes at the facilities under consideration, the concentrations of pollutants at the discharge into the hydraulic network have different indicators. This can be explained by several factors. Firstly, despite the lower pH values, the acidity of mine waters at the Degtyarskii mine is 5 times lower (see Table 4). Secondly, ponds built in the 1950s, which have been operating without purification for decades, are used to settle water after neutralization. At the same time, the quality of purified water at the Degtyarskii mine is much higher than at Levikhinskii. This is due to the fact that the pond area at the Degtyarskii mine is 1.5 times larger, and its volume is almost 3 times larger. The degree of filling of ponds with sludge after neutralization also varies: 74 % at Yelchevskii and 93 % at Levikhinskii ponds. As a result, the volume of the Yelchevskii pond, which is free for settling, turns out to be 10 times larger. It is obvious that the remaining volume of the Levikhinskii clarifier pond is not enough to settle the water after neutralization and interaction of pollutants with reagents. Thirdly, the stage of passive purification includes sedimentation of water after neutralization in watercourses, the travel time from the neutralization station to discharge is 2.25 times longer at the Degtyarskii mine (Table 5, fig.4).

As a result, according to the total pollution indicator, the degree of purification at the Degtyarskii mine is 300 times higher than at Levikhinskii (despite the fact that this indicator differs only twice in the AMD discharge zone).

Table 5

AMD Cleaning Options

Mine	Consumption, l/s	Characteristics of the clarifier pond				Passive cleaning sites, km		Total pollution indicator *Zc*	
		Area, ha	Volume*, million m^3	Degree of filling, %	Free volume, million m^3	Length**, km	Time, day	Unloading AMD	Discharge
Degtyarskii	50	220	9.34	74	2.43	6.3 (5.0 + 1.3)***	1.26	36057	44
Levikhinskii	32	142	3.30	93	0.23	2.8 (0.5 + 2.3)	0.56	64821	15967
Multiplicity of parameters	1.56	1.55	2.83	0.80	10.57	2.25	2.25	0.56	0.003

* Project-based. ** General. *** In brackets “neutralization – clarifier” + “clarifier – discharge”.

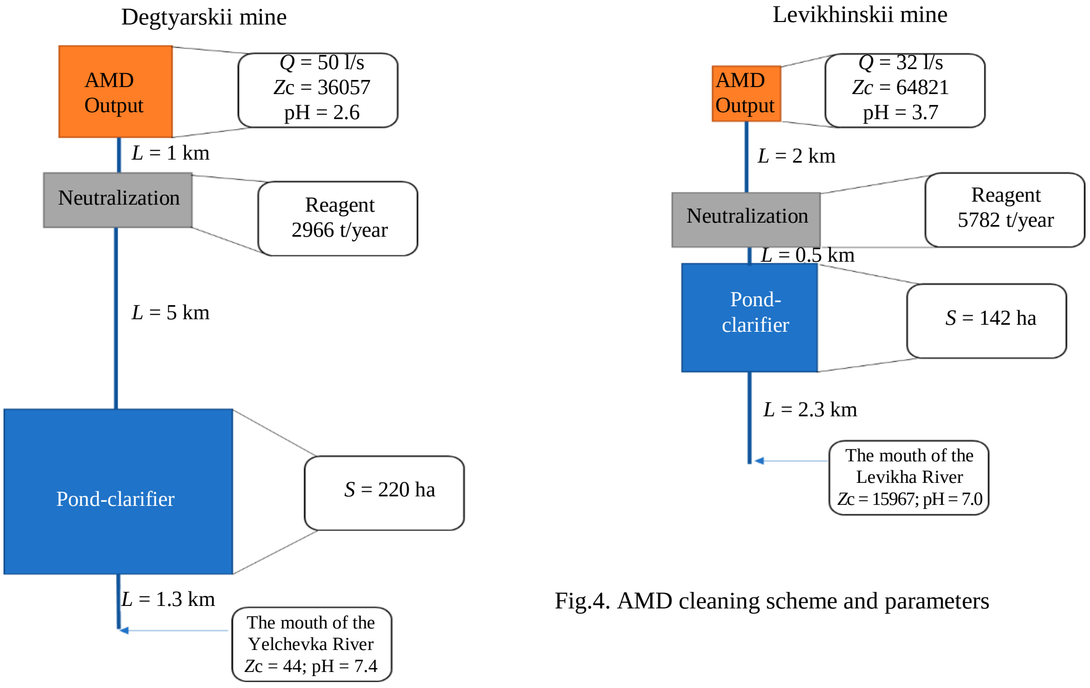

Fig.4. AMD cleaning scheme and parameters

Proposals for the organization of cleaning at the Levikhinskii mine. For the Degtyarskii mine, the current two-stage system is quite effective. For the Levikhinskii mine, it is necessary to switch to the use of more modern systems that include three stages of purification, for example: 1 – sewage treatment plants with aerators, 2 – radial settling tanks, 3 – a cascade of ponds [10].

The first stage of purification is the use of wastewater treatment plants with aerators (for example, FUCHS OxyStar Aerators), which have successfully proven themselves in various enterprises over the past decades. One example of an identical water composition (Fe content up to 700 mg/l) with a low pH value and a flow rate of up to 3,600 m^3/h is the output of AMD from a coal mine in Germany[4]. Aerators are used to supply oxygen to water. In addition to fine bubble deep aeration, they also ensure circulation and thorough mixing of mine waters with the reagent. During operation, aerators draw atmospheric air through a hollow shaft and release it into a stream of water created by a rotating propeller. Due to high turbulence, fine bubble aeration and excellent oxygen transfer efficiency are achieved. When using wastewater treatment plants with aerators (stage 1), the pH of the mine water will increase. As a result of an increase in the mixing rate and the interaction time of acidic waters with lime milk, a precipitate is formed.

According to the results of operation of FUCHS aerators, it was found that purification has an efficiency of 99 % (Mn content from 600 mg/l at the inlet and up to 3 mg/l at the outlet). However, AMD neutralization due to aeration is limited. To achieve a high rate of chemical reactions, increase the efficiency of water purification and reduce the number of aerators, it is possible using a radial type sump with an integrated flocculation chamber (stage 2). Flocculants, when mixed with purified mine waters, will lead to normalization of the pH of the water and its additional purification.

Nevertheless, it is advisable to supplement the active cleaning system with passive cleaning (stage 3). It can be implemented in the form of a cascade of ponds on the section of the riverbed of the Levikha River.

Since December 2020, the clarifier pond of the Neiva prospectors' artel (a worked out pit with an area of 12.9 ha) located below the main clarifier pond has been included in the main process of mine water purification at the Levikhinskii mine (Fig.5).

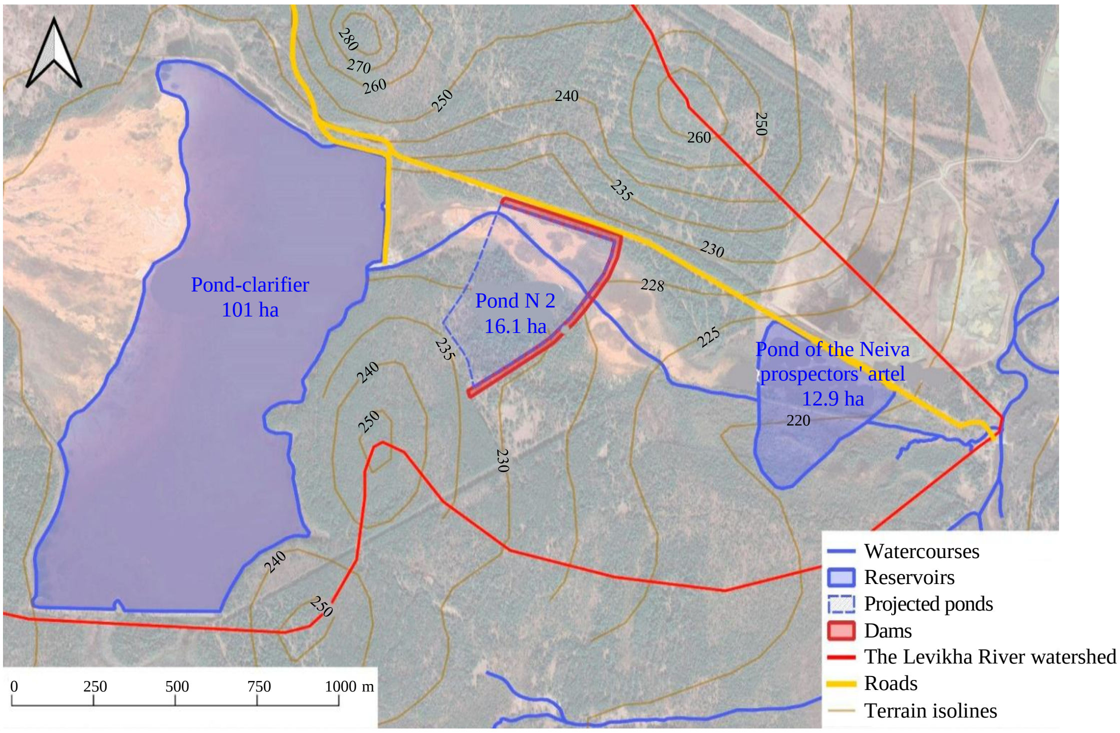

Fig.5. The layout map of the cascade of ponds-clarifiers in the valley of the Levikha River

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[4] FUCHS Mine water treatment. Case studies. Mayen: FUCHS, 2021, p. 10.

In 2021, the concentrations of components at the discharge in the Tagil River decreased significantly compared to the same period in 2020: copper to 0.04-0.5 mg/l (it was 2.2-4.9 mg/l), iron to 0.6-17 mg/l (it was 27-101 mg/l), zinc to 10-20 mg/l (it was 35-96 mg/l), manganese up to 12-16 mg/l (it was 13-38 mg/l), sulfate up to 1515-2115 mg/l (it was 1420-2450 mg/l). Nevertheless, when discharged into the water of the Levikha River, significant exceedances of MPCfi remain: zinc by 1000-2000 times, manganese by 1230-1600 times, copper by 50-500 times, iron by 6-170 times, sulfate ion by 15-21 times (Table 6).

Table 6

Efficiency of mine water purification using the Neiva pond

Month	Year	Object/indicator	Components, mg/l				
			Cu	Fe	Zn	Mn	SO_4
			MPCfi				
			0.001	0.1	0.01	0.01	100
March	2020	The multiplicity of MPC The mouth of the Levikha River	4,900	1,010	9,600	3,800	22
	2021		400	8	2,000	1,230	21
	2020	Cleaning efficiency, %	67	90	40	32	53
	2021		98	99	91	78	67
April	2020	The multiplicity of MPC The mouth of the Levikha River	2,200	367	3,940	1,320	14
	2021		500	170	1,900	1,600	20
	2020	Cleaning efficiency, %	90	96	82	74	–
	2021		97	99	88	71	66
May	2020	The multiplicity of MPC The mouth of the Levikha River	4,900	2,700	6,500	2,600	25
	2021		50	6	1,000	1,300	15
	2020	Cleaning efficiency, %	71	97	62	62	51
	2021		99	99	95	78	81

The use of a second clarifier pond compared to the same period in 2020 led to an increase in purification efficiency for iron 99 % (was 90-97 %), copper 97-99 % (was 67-90 %), zinc 88-95 % (was 40-80 %), manganese 71-78 % (was 32-62 %) and sulfate ion 66-81 % (it was 51-53 %). The use of an additional pond can significantly reduce the concentration of elements.

As a result of the accumulation of large volumes of bottom sediments and a high degree of filling of the existing clarifier pond at the Levikhinskii mine, the issue of sludge disposal is relevant. The main areas of sludge use are considered in [35]: reclamation of waste rock dumps and substandard ores, storage in spent quarries, production of building materials, extraction of valuable components and storage after sludge dewatering in geotubes (Geotube). Unfortunately, each of the options has significant limitations. The option of using sludge as a landfill reclamation is not advisable due to the possibility of leaching elements of hazard classes 2-4 from bottom sediments. The laying of worked out pits is impossible due to the fact that the reserves of the field are still listed in the state balance sheet. To implement the option for the production of building materials, it is necessary to organize a public-private partnership. The extraction of valuable components has not yet been provided with cost-effective technology. In addition, the sludge will still need to be stored in geotubes after dewatering. The main limitation is the formation of waste after the extraction of valuable components, the preparation and waterproofing of the site, the construction of extraction plants and the need for significant alienation of land.

Thus, none of the considered options for sludge purification fully allows cleaning the clarifier pond and it is impossible to achieve regulatory indicators at the discharge in the Tagil River without changing the existing purification system.

A further increase in the degree of purification can be achieved using a cascade of ponds and the decommissioning of an existing clarifier pond (Fig.5, Table 7).

Table 7

Estimated cleaning efficiency, %

Degrees of purification	Cleaning system	Cleaning efficiency
1	Sewage treatment plants with aerators	90-99
2	Radial sump	80-95
3	Cascade of ponds	76-100

It is not enough to operate only the existing clarifier pond of the Neiva prospectors' artel for passive cleaning due to its small area (12.9 ha). For full-fledged passive cleaning, the area of ponds calculated according to the formula (4) is 18 ha. It is advisable to use the Neiva prospector’s pond and add another clarifier pond with an area of 16.1 ha, which together will ensure the deposition of metals due to a decrease in the water flow rate and an increase in the time of interaction of pollutants with reagents.

Conclusion. AMD is being unloaded to the surface at spent and flooded copper ore mines. The waters are characterized by low pH values (2.5 at Degtyarskii and 3.3 at Levikhinskii mines), the composition of the waters is sulfate, aluminum-iron-calcium-magnesium with mineralization up to 12 g/l.

AMD purification at the facilities under consideration is carried out in two stages: neutralization with lime milk and settling in clarification ponds. The efficiency of mine water treatment at the Degtyarskii mine reaches 99 % for the main pollutants. The Levikhinskii mine uses the same purification scheme in general, but it turns out to be much less effective – from 59 % for manganese to 93 % for iron and copper.

Despite the same purification system, at the Levikhinskii mine, the quality of water discharged into the hydraulic network does not reach the standard indicators, the multiplicity of excess reaches hundreds and thousands for manganese, copper, zinc, aluminum.

The reasons for the low cleaning efficiency at the Levikhinskii mine are a complex of natural and man-made factors:

- despite the lower pH values, the acidity of mine waters at the Degtyarskii mine is five times lower;
- ponds built in the 1950s are used to settle the water after neutralization. They have been working without cleaning for decades. The area and volume of the Yelchevskii pond is 1.5-3 times larger. The degree of filling of ponds with sludge after neutralization is 74 % in the Degtyarskii and 93 % Levikhinskii mines. As a result, the volume of the Yelchevskii pond, which is free for settling, turns out to be 10 times larger;
- the settling time of water after neutralization in watercourses at the Degtyarskii mine is 2.25 times longer.

As a result, according to the total indicator of *Zc* pollution, the degree of purification at the Degtyarskii mine is 300 times higher than at Levikhinskii (despite the fact that this indicator differs only twice in the AMD unloading zone).

To increase the efficiency of the purification process, it is necessary to modernize the existing system: firstly, to decommission the existing clarifier pond, and secondly, to use active (aerators, radial settling tanks) and passive (cascade of ponds below the discharge of neutralized wastewater) purification systems. Three-stage purification (including structures with aerators, radial settling tanks and a cascade of ponds) will reduce surface water pollution to normalized levels, significantly improve the environmental situation and reduce damage to the hydrosphere.

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Research article

Natural carbon matrices based on brown coal, humic acids and humine extracted from it for purification of aqueous solutions from low molecular weight organic impurities

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Abstract. Heterogeneous systems including natural carbon matrices in the solid phase and aqueous solutions of low molecular weight organic compounds with positive and negative variations from ideality in the liquid phase are considered. The technical characterization of the considered supramolecular ensembles on the basis of brown coal of the Kara-Keche deposit (Kyrgyzstan), humic acids and humine extracted from it is given. Functional analysis of the samples was carried out using FTIR spectroscopy. The morphology of the surface of the considered carbon matrices has been investigated, in different points of which the local microelement composition has been established. An X-ray phase analysis of Kara-Keche brown coal and humic acids and humine extracted from it was carried out. The isothermal adsorption of bipolar molecules of glycine and urea, neutral D-glucose from aqueous solutions on solid carbon sorbents has been studied. An assumption has been made about the adsorption of low molecular weight organic compounds from aqueous solutions on humine and Kara-Keche coal in irregularities and pores of the carbon matrix of sorbents, for humic acids – on surface reaction centers. Due to its developed pore structure and resistance to acids and alkalis, humine from Kara-Keche coal is recommended for the purification of industrial wastewater from low molecular weight organic ecotoxicants.

Keywords: brown coal; humine; humic acids; urea; glycine; D-glucose; adsorption from solutions; solid carbon sorbents

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Introduction. Purification of wastewater from industrial plants remains one of the main environmental problems, the solution of which will help combat the threat of pollution of natural objects. A material of natural origin – brown coal – is widely used as an absorber of ecotoxicants. The main advantages of this sorbent are high sorption capacity, environmental friendliness and a wide range of applications. It has a heterogeneous structure, which consists of a huge number of different functional groups [1-3]. Brown coal is a potential source of humic substances (HS), which have a wide spectrum of effects. Their content in brown coals ranges from 20 to 90 %. The share of the mineral part is about 52 % [4]. Brown coal from the point of view of solid-state chemistry is an interesting object for mechanochemical oxidation aimed at increasing the content of humic acids and chemical modification of their structure. The most studied is the solid-phase treatment of brown coal with alkalis, leading to an increase in the extractability of humic acids [5].

A large number of reviews are devoted to humic substances [6-8], which have a variety of specific properties that ensure their wide practical use. The works [9-11] note the ability of humic acids

(HA) to effectively bind metal cations. The processes of binding of copper, nickel, cadmium ions, ferricenium cations and methylene blue from aqueous solutions on humine (residual coal) and humic acid of Kara-Keche brown coal have been studied in detail [12,13].

The interaction of organic compounds with HS allows their use in the production of microfertilizers, feed and food additives, and as enterosorbents for water purification and detoxification of land from petroleum products [14-16]. Research continues on the development of technical specifications for the use of products based on recycled organic waste as sorption material for the treatment of domestic, industrial and technological wastewater from organic and inorganic components [17,18]. The interaction of HS with mineral particles of the soil with the formation of organomineral complexes determines their use as structure formers and soil ameliorants [19]. The prospects of using humic preparations for restoration of disturbed areas are investigated by assessing the relationship between their biological activity and structural-group composition [20-22].

Various thermodynamic and kinetic models are used to describe the sorption process involving HS [23-25]. Using these models, as well as ideas about the supramolecular nature of HS, it is possible to understand the mechanism of the process, select the most effective sorbents and optimal conditions for sorption [26-28].

Insufficient attention is paid to adsorption of low molecular weight organic compounds from aqueous solutions on humic acids and especially on humine extracted from brown coals [29-31]. There are few publications in the scientific literature on functional and local trace element compositions, surface morphology of brown coal-based carbon sorbents, humic acids and humine extracted from them [32-34].

The limited information causes the actuality of studies of surface properties in heterogeneous systems including water-organic solutions with positive and negative variations from ideality, which are contained in wastewater of chemical, pharmaceutical, electrical engineering. The treatment of wastewater from low molecular weight organic compounds is an important environmental protection goal. At the same time, humin (residual coal) as a spent carbon sorbent can be utilized by combustion in power plants as a refined fuel.

The aim of the work is the physicochemical characterization of brown coal of Kara-Keche deposit (Kyrgyzstan), humic acids and humine extracted from it, determination of their classification features, study of isothermal adsorption of low molecular weight organic compounds from aqueous solutions on the obtained natural carbon matrices.

Methods. One of the ways to extract humic acids from brown coals is alkaline extraction [35]. At the first stage of humic acid and humine extraction, decalcification of the sample was carried out to free the coal and organic compounds contained in it from calcium ions, which form difficultly soluble humates with humic acids. For this purpose, a sample of coal was filled with 0.005 n solution of H_2SO_4 at the rate of 5-6 liters per 1 kg of coal, stirred for 15 min on a rotator and left for 24 h. After settling, the acid solution was drained and discarded along with the undecomposed plant materials that floated to the surface. Upon exposure to mineral acids, aluminium and iron partially pass into solution, which also contributes to the release of humic substances.

After decalcification, the coal was washed with distilled water and humic acids were extracted with 0,1 n NaOH solution at the rate of 6-7 liters per 1 kg of coal. Stirred for 15-20 min on a rotator, then the suspension was allowed to stand for 24 h followed by separation of the solid phase by centrifugation at 4000 rpm. The mother liquor was sodium humates, the undissolved precipitate was the non-hydrolysable part of the charcoal (humine).

Humine was placed in a 10-litre container, poured with distilled water, mixed thoroughly and allowed to stand for two days. After settling, the upper clear layer was drained (by decantation) and the lower layer was centrifuged on an OS-6M centrifuge at 4000 rpm for 15 min.

The resulting humic precipitate was rewashed six more times to remove residual amounts of humic acids and small dispersed sols, which give colour to the solutions. After final centrifugation, the precipitate was placed on glass and dried at room temperature. It was then dried in a desiccator for one hour at 90-100 °C, crushed and ground in a mortar to a powdery state. The obtained humic sample from Kara-Keche coal was sieved on sieves with 0.25 mm mesh diameter (60 mesh). Humine was stored in tightly corked bouquets for further research.

The solution after coal leaching usually contains some amount of mineral impurities in the form of a fine suspension, from which were freed before the humic acids were precipitated. For this purpose, the alkaline solution was centrifuged at 4000 rpm. To precipitate humic substances a small amount of concentrated H_2SO_4 at the amount of 2.0-2.5 ml per 1 liter of alkaline solution was added to the obtained solution (until the first signs of coagulation). The loose precipitate of humic acids was centrifuged to separate it from the solution, transferred to a filter and washed several times with distilled water to neutral pH value. The crude preparation of humic acids contains a certain amount of himatomelanic acids, for the separation of which the precipitate was washed with ethyl alcohol, and the himatomelanic acids passed into solution.

The wet humic acid precipitate was air-dried for one or two days and then pe-recrystallised. For purification from small amounts of impurities humic acids were again dissolved in a small amount of 0.1 n NaOH solution at the rate of 30 ml of alkali per 10 g of humic acids, stirred for 15 min and stood for 24 hours. The humic acids were further extracted from the alkaline solution. The purified humic acid preparation was then air dried and ground to a powder-like state and sieved on sieves with a mesh diameter of 0.25 mm. The obtained preparation was stored in the desiccator.

Discussion of results. Ash content A^a and moisture W^a of the analysed sample of Kara-Keche coal, humic acids and humine extracted from it were obtained according to the methods of [36] (Table 1).

Table 1

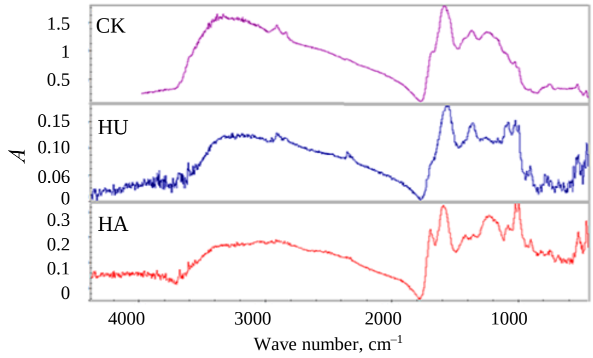
Moisture and ash content of Kara-Keche brown coal, humic acids and humine extracted from it, elemental analysis in count to ash-free, anhydrous mass of samples

Object of the study	W^a, %	A^a, %	C^h, %	S^h, %	H^h, %	N^h, %	O^h, %	H/C	O/C
Brown coal (CK)	2,54	22,90	72,33	1,21	4,72	0,98	20,76	0,78	0,22
Humic acids from coal (HA)	3,63	10,70	70,90	1,22	3,56	0,62	23,70	0,60	0,25
Humine from coal (HU), washed	7,35	20,52	78,75	1,29	3,94	0,00	16,02	0,60	0,15

The carbon content of humine increases and the oxygen content decreases markedly compared to humic acids and coal itself (Table 1). Humic acid structures were estimated from the hydrogen-to-carbon and oxygen-to-carbon content ratios using the Van-Crevelen graph-static analysis method. According to classification criteria, the humic acids extracted from Kara-Keche coal belong to the class of humic acids from brown coals and the black soil.

Functional analysis of Kara-Keche coal, humic acids and humine extracted from it by FT-IR spectroscopy. Near-infrared spectroscopy is widely used in both qualitative and quantitative analyses [37, 38] and is also used in the study of brown coals.

Figure 1 shows the IR spectra of all investigated samples recorded on Varian FT-IR spectrometer in tablets with KBr in the ratio 1:300, frequency range 4000-450 cm^{-1}, as well as the maxima of characteristic absorption bands of the most important atomic groups of the investigated substances.



Optical ratio densities	HA	HU	CK
$A_{O–H\ 3400}/A_{C=C\ 1600}$	0.56	0.45	1.06
$A_{C=O\ 1720}/A_{C=C\ 1600}$	0.74	0.57	0.61
$A_{C–O\ 1225}/A_{C=C\ 1600}$	0.88	0.86	0.83
$A_{Calk\ 2920}/A_{C=C\ 1600}$	0.62	0.55	0.94
$A_{O–H\ 3400}/A_{Calk\ 2920}$	0.90	0.82	1.13
$A_{C=O\ 1720}/A_{Calk\ 2920}$	1.20	1.04	0.64
$A_{C–O\ 1225}/A_{Calk\ 2920}$	1.41	1.56	0.88

Group	Absorption frequencies, cm^{-1}		
	HA	HU	CK
Stretching vibrations of OH-groups connected by intermolecular hydrogen bonds	3394	3398	3399
Stretching vibrations –C–H of aliphatic hydrocarbons	2922	2923 2855	2930 2859
Stretching vibrations of groups $^+NH_2$, C≡N	2363	2363	2348
Stretching vibrations of C=O in carboxyl and carbonyl groups	1707	1710	1700
Stretching vibrations of C=C conjugate with C=O or Ar (aryl) Stretching vibrations of the aromatic ring	1610	1600	1592
Stretching vibrations of ion $–COO^–$	1368	1373	1385
Stretching vibrations of C–O in the carboxyl group	1260 int.	1264 weak	1247
Deformation vibrations of –OH groups in alcohols and carboxylic acids Deformation vibrations Me…OH…O Stretching vibrations Si–O	1094 1031 1008 915	1089 1031 1010 918	1097 1034 1010 914
Deformation vibrations Si–O, Si–O–Me	760 533 473	777 532 470 int.	761 539 471

Fig.1. Infrared spectra, maxima of characteristic absorption bands of the most important atomic groups of the of Kara-Keche brown coal, humic acids and humine extracted from it

Comparative analysis of IR spectra of Kara-Keche brown coal, humic acids and humine showed that all samples contain condensed aromatic systems, aliphatic and alicyclic hydrocarbon groups, as well as oxygen-containing functional groups (carboxyl, carbonyl, hydroxyl).

All samples contain mineral components. The relative quantitative content of functional groups in the studied samples was estimated by the ratio of the peak areas of the absorption bands of oxygen-containing groups to the peak areas corresponding to aromatic polyconjugated systems (1600 cm^{-1}) and aliphatic substituents at 2920 cm^{-1}. The ratio of optical densities of absorption bands of alkyl substituents to aromatic fragments showed the predominance of aromatic fragments (A_{2920}/A_{1600}). Humic acids contain more alkyl substituents than humine. The relative amount of hydroxyl groups (A_{3400}/A_{1600}) in HA and HU is low compared to brown coal. Carboxyl groups (A_{1720}/A_{1600}) are much more prevalent in humic acids than in humine and coal.

From the data of Fig.1, it is also evident that in HA and HU, carboxyl groups are predominant over alkyl substituents, the ratio A_{1720}/A_{2920} for both samples is greater than one. For coal the situation is opposite – the ratio A_{1720}/A_{2920} is much less than unity. It can be stated that IR spectra of Kara-Keche coal, humic acids and humine extracted from it are similar. The main characteristic absorption maxima for humic substances are found in all samples. The differences are observed mainly in intensity – humic acids are dominated by oxygen-containing groups, while coal is dominated by alkyl substituents. More aromatic fragments are observed in the composition of humine. At the same time, differences in broadening and shifts of absorption bands of absorption spectra of Kara-Keche coal, humic acids and humic acid can be associated with both different chemical environment within the structural units of the studied objects and intermolecular interactions. Therefore, and taking into account the fact that the investigated carbon matrices are chemically heterogeneous supramolecular systems, comparative analysis of their IR spectra before and after adsorption will not provide objective information about the nature of the functional groups of coal, humine, and humic acids involved in the binding of urea, glycine, and D-glucose, respectively.

Scanning electron microscopy of Kara-Keche brown coal, humic acids and humine extracted from it. The analytical sample of Kara-Keche coal was examined on a TESCAN VEGA 3 LMH microscope with a secondary electron detector. The surface morphology of humine and humic acid samples was examined on a JEOL JSM 6510 scanning electron microscope using an SEI secondary electron detector and a BEC reflected electron detector.

Figure 2 shows photos of analytical samples of Kara-Keche brown coal, humic acids and humine extracted from it. The conglomerate of the raw coal sample has a lamellar structure, with a partially faceted structure observed for the constituent particles. Upon higher magnification of the sample surface, it can be seen that the coal has a poorly developed porous surface, due to which its negligible adsorption properties can be expected to manifest. Humic acid particles of quasi-crystalline form are grains of various sizes not exceeding 100 μm. The surface of humic acid particles is flat, not penetrated by pores and capillaries, without any kind of roughness.

Humine, in contrast to humic acids, are particles of irregular, splintered shape up to 100 μm. Particles with developed, porous surface are present. The maximum size of individual pores of humic acid reaches 200 nm.

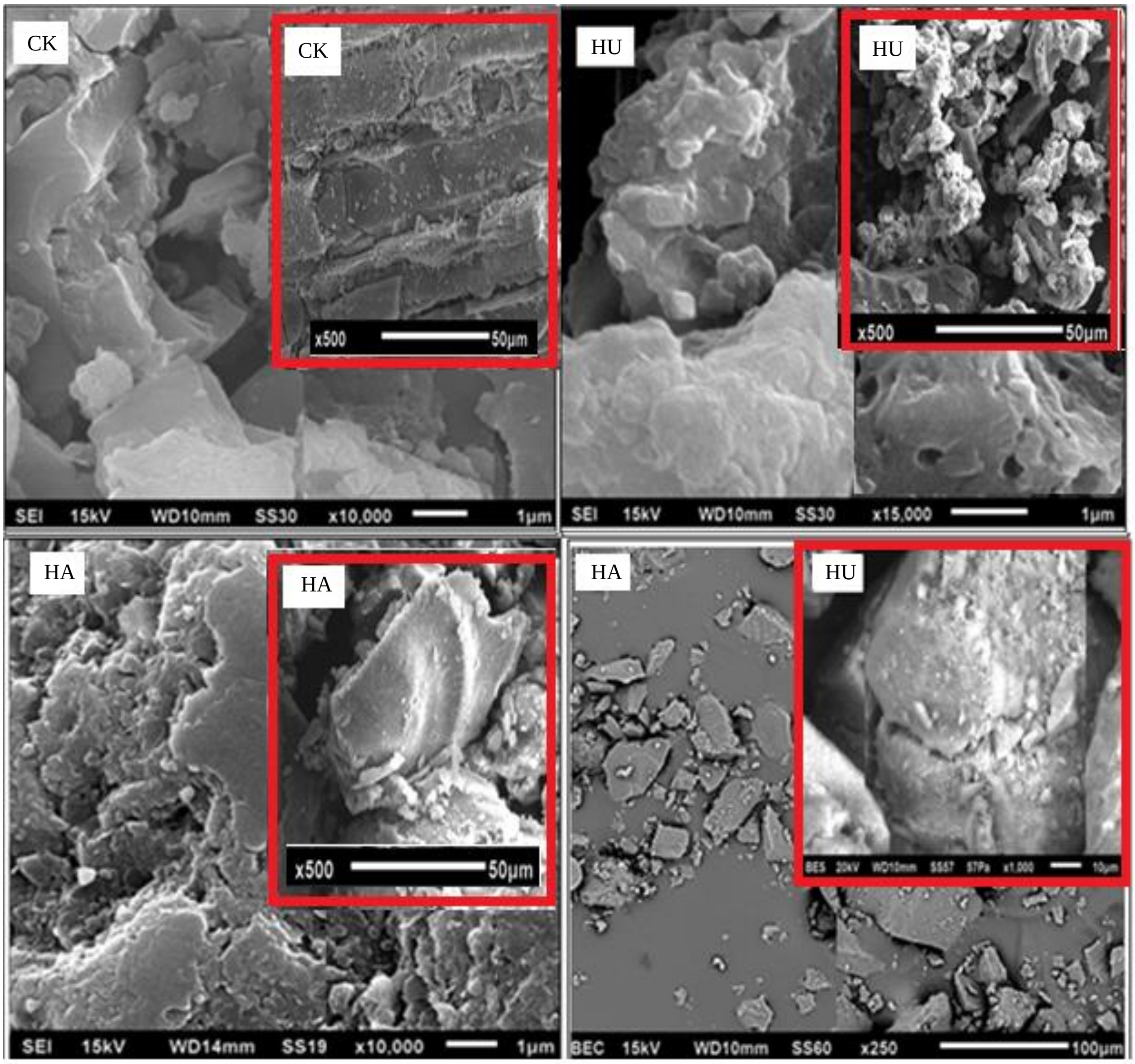


Fig.2. Surfaces of Kara-Keche brown coal, humic acids and humine extracted from it at different magnifications

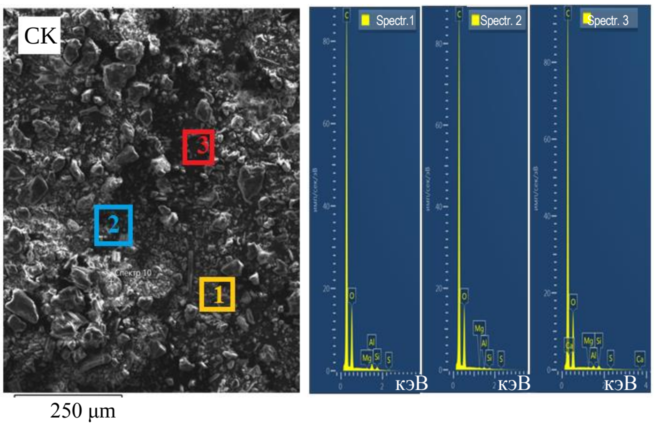
Also shown in Fig.2 are photographs of humic acids and humin from Kara-Keche brown coal, taken using a reflected electron detector. The surface of humic acid and humine is homogeneous grey colour with rare small light inclusions representing more oxidized fragments in the structure of the studied substances or zones with increased content of ash elements.

As a result of the surface evaluation of the studied samples, considering only one physical aspect - the surface configuration, one can expect different adsorption mechanisms – from monomolecular in humic acid, to volumetric filling of micropores – in humine and coal.

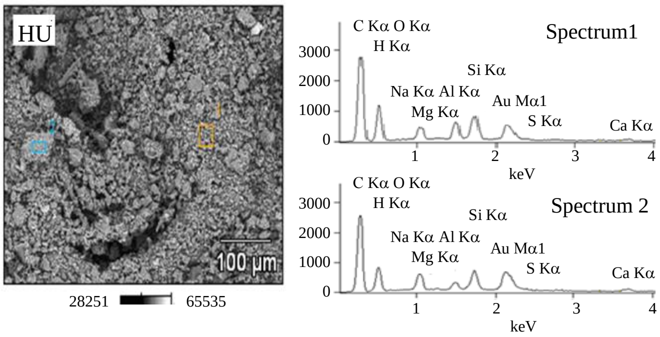
Energy dispersive spectra of Kara-Keche coal, humic acids and humine extracted from it. The analysis of local elemental composition at given points of the studied samples of humic acids and humine was carried out on a JEOL JSM 6510 scanning electron microscope, a nitrogen-cooled energy dispersive spectrometer NSS7 was used as a detector. The local content of various elements in the Kara-Keche coal sample was determined on a TESCAN VEGA3 LMH microscope using an X-ACT EDS analyzer.

The study of the local elemental composition for all three samples was carried out in several morphologically different surface specimens. Data on the relative content of elements of the selected candidates, are shown in Fig.3. The quantitative content of elements at different points of the surface of the investigated samples of coal, humic acids and humine varies considerably (given in atomic per cent). The obtained result indicates that the studied samples of natural carbon matrices are chemically heterogeneous, dispersed, microheterogeneous supramolecular systems.

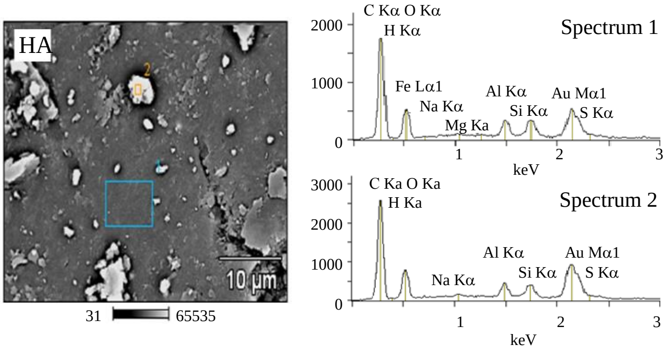
X-ray phase analysis of Kara-Keche coal powders, humine and humic acids extracted from it. An optimal set of methods for analyzing natural substances also includes X-ray phase analysis [39]. The powders of coal, humic acids and humine extracted from it were analysed on a Panalytical X'Pert Pro X-ray diffractometer (Philips) at the wavelength of copper Kα radiation λ = 0.154 nm.



Contents, at. %	C	O	Mg	Al	Si	S	Ca
Spectrum 1	72.92	26.79	0.03	0.18	0.08	–	–
Spectrum 2	72.98	26.93	0.03	0.04	0.02	0.01	–
Spectrum 3	74.38	25.39	0.03	0.08	0.09	0.02	0.01



Contents, at. %	C	N	O	Na	Mg	Al	Si	S	Ca
Spectrum 1	59.04	4.83	29.65	1.86	0.09	1.73	2.42	0.12	0.25
Spectrum 2	62.61	5.06	25.27	3.00	0.10	0.90	2.33	0.36	0.38



Contents, at %	C	N	O	Na	Mg	Al	Si	S	Fe
Spectrum 1	62.04	7.55	26.01	0.30	0.16	1.58	1.91	0.33	0.13
Spectrum 2	59.72	8.60	28.10	0.41	–	1.41	1.48	0.29	–

Fig.3. Energy dispersion spectra at given points on the surface of Kara-Keche brown coal, humic acids and humin extracted from it

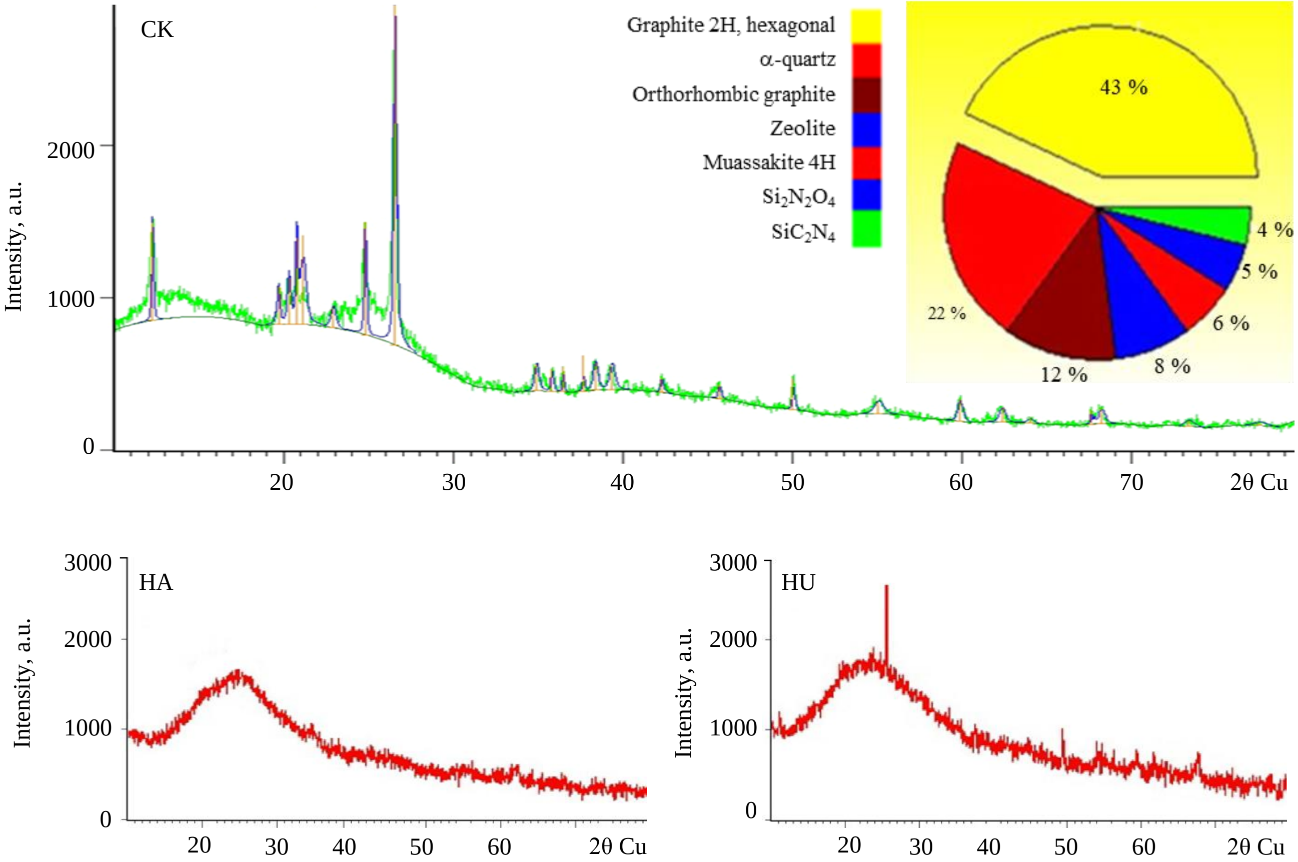


Fig.4. Diffraction spectra of Kara-Keche brown coal, humine and humic acids extracted from it

Figure 4 shows the diagram of mineral composition of Kara-Keche brown coal. The radiographs were recorded in GIXD geometry at 1° and 5° in the range of 20-80° (step 0.05°, time per step 2 s).

The analysis of the diffractograms and the search for candidate matches according to official PDF databases showed the presence of various modifications of graphite, silicon dioxide (quartz), aluminosilicates (zeolite), various carbides, carbide-nitrides and silicon nitride-oxides in the brown coal sample.

X-ray radiographs of humine and humic acids have the view of a broad line (halo) characteristic of amorphous materials (Fig.4). However, the presence of peaks in humine (residual coal) samples indicates the presence of structural formations similar to Kara-Keche brown coal.

Adsorption of low molecular weight organic compounds from aqueous solutions on Kara-Keche coal, humic acids and humine extracted from it. The adsorption studies used carbon sorbents whose particle sizes did not exceed 0.25 mm (60 mesh). Urea, glycine, D-glucose were chosen as adsorbates characterised by different type of variations from ideality in aqueous solutions. They are representatives of different classes of organic compounds that are of interest to specialists in biochemistry, biotechnology, ecology, and materials science. The bipolar molecules of urea and glycine are characterised by self-association in aqueous solutions, which determines their positive variations from ideality. Heteroassociation of the components of the aqueous solution of D-glucose underlying the mechanism of mutarotation of the monosaccharide suggests negative deviations from ideality in this binary system.

Conductivity and liquid chromatography methods were used to determine glycine concentrations in aqueous solutions. The polarimetric method was used to determine the concentration of D-glucose in aqueous solutions. The concentration of urea in aqueous solutions was determined chromatographically on a JASCO-HPLC high-efficiency liquid chromatograph.

Heterogeneous equilibrium in the system sorbent in solid phase – aqueous-organic solution was established during 24 h in dry-air thermostat at $T = 298$ K. The phases were stirred every 15 min for the first two hours. After 24 h the phases were separated on a syringe filter with a pore size of 1-2 μm. Adsorption values were calculated using the equation:

$$a = \frac{(c_0 - c_\text{p})V}{m} \cdot 1000,$$

where c_0 and c_p – initial and equilibrium concentrations of adsorbate, M; V – volume of solution from which adsorption occurs, l; m – mass of adsorbent, g; 1000 – conversion factor of the obtained result in another unit of measurement – mmol/g.

The calculated adsorption values for each composition of the aqueous-organic solution were averages of three or four parallel tests with an accuracy of 10 % relative error.

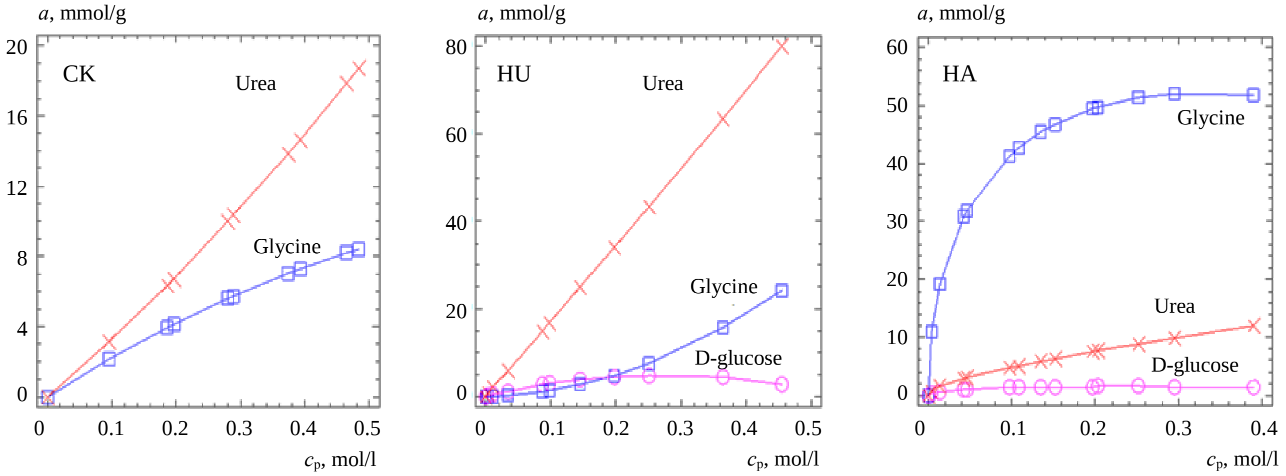
The dependence of the above methods of determining the concentrations of urea, D-glucose, and glycine on the acidity of the medium allowed us to conclude that there were no noticeable changes in the acid-base manifestation in the studied systems after adsorption.

Visualization of experimental data of isothermal adsorption is presented in Fig.5. The series on adsorption of urea, glycine, D-glucose from aqueous solutions on Kara-Keche brown coal, humic acids and humin extracted from it, respectively, are shown. Differences are observed for adsorption of glycine and urea on humic acids compared to brown coal and humine. In this case, the adsorption of D-glucose from aqueous solution on coal was found to be negligible. It can be assumed that for bipolar molecules of urea and glycine both physical adsorption and chemosorption on brown coal, humic acids and humine extracted from it are realised.

For a neutral monosaccharide molecule, only the formation of weak hydrogen bonds can be expected with the adsorption centres of all investigated carbon sorbents.

The reversal of the series for adsorption of urea and glycine on humic acids is due to the binding of glycine to the surface carboxyl groups of the carbon matrix of the sorbent matrix. The greater polarity of urea compared to glycine obviously affects its preferential adsorption in the pores, roughness of brown coal and humine.

In order to evaluate possible adsorption mechanisms in the studied systems, the data of Fig.5 are considered in the framework of ideas about monomolecular adsorption and volumetric filling of sorbent micropores using the Langmuir and Dubinin – Radushkevich equations. The results of calculations are given in Table 2.



$a^\text{CK}_\text{urea(W)} > a^\text{CK}_\text{glycine(W)} >> a^\text{CK}_\text{D-glucose(W)}$ $a^\text{HU}_\text{urea(W)} > a^\text{HU}_\text{glycine(W)} >> a^\text{HU}_\text{D-glucose(W)}$ $a^\text{HA}_\text{urea(W)} \geq a^\text{HA}_\text{glycine(W)} > a^\text{HA}_\text{D-glucose(W)}$

Fig.5. Isotherms of adsorption of urea, glycine, D-glucose from aqueous solutions on Kara-Keche brown coal, humic acids and humine extracted from it at 298 K

Linearisation of experimental data with high correlation coefficients on adsorption of investigated organic compounds from aqueous solutions on lignite, humine extracted from it is provided in coordinates of the Dubinin – Radushkevich equation, and for humic acids – in coordinates of the Langmuir equation.

Table 2

Adsorption of urea, glycine, D-glucose from aqueous solutions on Kara-Keche brown coal, humic acids and humine extracted from it at 298 K in coordinates of the Langmuir and Dubinin – Radushkevich equations

Sorbent	Sorbat	The equations of linear regression in coordinates of Dubinin – Radushkevich and Langmuir equations	Correlation coefficient k_{corr}	Adsorption a_∞, mmol/g
CK	Urea	$\ln a = 7.47 + 1.21\ln(c_p/20)$	0.99	1752.7
	Glycine	$\ln a = 3.20 + 071\ln(c_p/3.4)$	0.78	24.6
HU	Urea	$\ln a = 9.17 + 1.17\ln(c_p/20)$	1.00	9604.6
	Glycine	$\ln a = 8.91 + 2.80\ln(c_p/3.4)$	0.94	7405.7
	D-glucose	$\ln a = 1.85 + 0.08\ln(c_p/4.7)$	0.98	6.4
HA	Urea	$c_p/a = 0.009 + 0.105c_p$	1.00	9.5
	Glycine	$c_p/a = 0.0003 + 0.018c_p$	1.00	55.5
	D-glucose	$c_p/a = 0.011 + 0.610c_p$	1.00	1.6

The obtained result suggests adsorption of low-molecular organic compounds from aqueous solutions on humic and coal mainly in irregularities and pores of carbon matrices of the studied sorbents. On humic acids, on the contrary, the binding of the considered sorbates is provided mainly on their surface reaction centres. It is obvious that adsorption of urea, glycine, D-glucose from aqueous solutions on brown coal, humic acids and humine extracted from it is caused by a number of forces, including physical and chemical interactions of sorbate molecules with functional groups of carbon matrices of the studied sorbents.

The obtained values of the limiting adsorptions of urea, glycine, D-glucose from aqueous solutions on Kara-Keche brown coal, humic acids and humine extracted from it were used to estimate the specific surface area of these carbon sorbents. For this, using the 3D demo version of Chemical Office, the area occupied by sorbate molecules on the solid surface was calculated (Fig.6). From the histogram of Fig.6, it can be seen that humene has the highest specific surface area compared to humic acids and coal. Obviously, the result obtained is due to the developed, porous structure of the humin established by morphological studies.

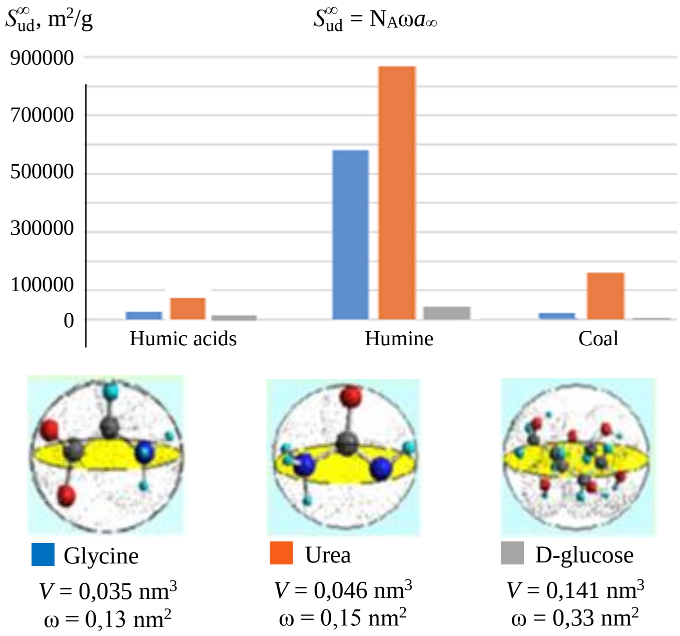


Fig.6. Specific surface area of Kara-Keche brown coal, humic acids and humine extracted from it, determined by glycine, urea and D-glucose

Conclusion. The studied natural carbon matrices – Kara-Keche brown coal, humic acids and humine extracted from it – are amorphous, chemically heterogeneous supra-molecular systems with structural formations.

On humic and Kara-Keche brown coal, volumetric filling of sorbent micropores with urea, glycine, D-glucose from aqueous solutions is carried out. Surface adsorption of investigated low molecular weight organic compounds from aqueous solutions takes place on humic acids.

In the range of considered natural carbon matrices, humine has the highest limiting adsorption capacity with respect to urea, glycine and D-glucose from their aqueous solutions. Due to the developed pore structure, stability in acids and alkalis, humine of Kara-Keche brown coal can be recommended as an effective sorbent for treatment of industrial wastewater from low molecular weight organic compounds.

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Preparation and use of complex titanium-containing coagulant from quartz-leucoxene concentrate

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Abstract. The search for the new high-efficiency reagents for wastewater treatment is a challenging and urgent task. Titanium-containing coagulants represent a new trend in water treatment and have a much higher efficiency that the traditional aluminium and iron-containing coagulants. The high cost of reagents significantly hinders their implementation. Complex titanium-containing reagents are coagulants prepared by modifying the traditional coagulants by adding 2.5-10.0 wt.% titanium compounds. In this work, titanium tetrachloride prepared from quartz-leucoxene concentrate was prehydrolyzed with subsequent double decomposition with sulfuric acid. The resulting mixture of hydrochloric and sulfuric acids was neutralized with aluminium hydroxide/oxide to form a self-hardening mixture (chemical dehydration). The sample of a complex sulfate-chloride titanium-containing coagulant was a mixture of $AlCl_3 \cdot 6H_2O$ – 5-20 wt.%, $Al_2(SO_4)_3 \cdot 18H_2O$ – 70-90 wt.% and $TiOSO_4$ – 2.5-10.0 wt.%. It was proved that by changing the ratio of aluminium oxide/hydroxide and titanium tetrachloride at the stage of prehydrolysis and double decomposition, it is possible to obtain samples of a complex coagulant with different contents of the modifying additive of titanium compounds. An assessment of the coagulation properties of the complex reagent demonstrated its higher efficiency in cold water compared to aluminium sulfate. Studies on the use of the complex titanium-containing coagulant in the process of wastewater treatment from phosphate anions and suspended matter demonstrated its higher efficiency as compared to that of traditional reagents. The advantages of the prepared reagent are a reduction in the effective dose of the reagent, minimization of residual concentrations of pollutants in purified water, intensification of the processes of sedimentation and filtration of coagulation sludge. Purified water can be reused in the recycling water supply system. The use of quartz-leucoxene concentrate and titanium tetrachloride obtained from it as the source material would not only minimize the cost of the resulting complex coagulant, but also take a step towards the implementation of the Zero Waste concept.

Keywords: complex titanium-containing coagulant; quartz-leucoxene concentrate; chemical dehydration; water purification; dephosphatization

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Introduction. Considerable attention is paid to the search for the new high-efficiency reagents for water purification and treatment processes. Most common among the water purification processes is the coagulation and its special case – flocculation. Introduction of the salts of aluminium, iron, titanium, silicon, etc., into the dispersed system leads to hydrolysis with formation of hardly soluble hydroxides of the corresponding metals, which are capable of aggregating dispersed particles around due to neutralization of the surface charge. Depending on the type of reagent used, in addition to neutralization processes, adsorption and flocculation can also occur.

In spite of their relatively high efficiency, the traditional coagulants based on aluminium and iron salts are no longer able to optimally perform their assigned tasks, and also have a number of major disadvantages. The strict residual MPC standard, a narrow pH range and a low efficiency in cold water are the main disadvantages of aluminium salts, while iron salts have strong abrasive properties and can form highly soluble compounds with organic ligands [1-3]. Titanium salts, despite an almost complete lack of shortcomings and the highest efficiency, are not commonly used due to their high cost [4-6].

This situation can be overcome by the use of complex titanium-containing reagents - aluminium or iron salts modified by the addition of titanium compounds in the amount of 2.5-10 wt.%. The key advantage of such reagents is a possibility of producing them from various mineral raw materials and technogenic waste, which will significantly reduce the cost [7, 8]. Titanite (sphene), ilmenite and other concentrates can be used as potential raw materials for preparing complex titanium-containing coagulants. These raw materials are used to produce titanium dioxide from ilmenite as well as tanning agents, sorbents and other products from titanite.

Quartz-leucoxene is a large-tonnage by-product of the development of the Yarega oil-titanium field with titanium compounds content of 7-11 wt.%. In the course of flotation enrichment, a quartz-leucoxene concentrate with titanium dioxide content to 45-50 wt.% was obtained. Reserves of quartz-leucoxene, according to various estimates, are approximately 260 million tons [9].

The chemical nature of the mineral (close intergrowth of silicon and titanium dioxides) determines a high chemical resistance and makes it impossible to use the traditional sulfuric acid processing method [10, 11].

Currently, a number of technologies were developed for the enrichment or processing of quartz-leucoxene concentrate to prepare rutile concentrate:

- Autoclave leaching [9].
- Magnetic separation and reduction roasting [9, 12].
- Plasma-thermal reduction [13].
- Hydrofluoride leaching [14, 15].
- Silicon reduction [16].

Undoubtedly, the most successful trend of processing quartz-leucoxene concentrate is a comprehensive solution developed by a team of authors under the leadership of prof. G.B. Sadykhov at the A.A.Baikov Institute of Metallurgy and Materials Science, RAS. The proposed technology comprises the stages of magnetizing enrichment and autoclave leaching of quartz-leucoxene concentrate to produce rutile concentrate and acicular wollastonite [9, 11, 12].

The rutile concentrate is directed to the stage of selective chlorination to produce a mixture of titanium, silicon, aluminium, etc., chlorides. The resulting $TiCl_4$ after rectification purification can be used to produce technical titanium dioxide [17, 18]. Unfortunately, the multi-stage cleaning system considerably increases the cost of the process.

As an alternative processing trend, one should mention the pyrometallurgical processing of quartz-leucoxene concentrate to produce titanates for the needs of various industries [19].

To increase the economic attractiveness of the chlorination/rectification process, it seems most appropriate to develop an alternative technology for producing innovative reagents with increased cost and market demand.

The main goal of this work is to develop a technology for the synthesis of a complex titanium-containing coagulant using titanium tetrachloride obtained by selective chlorination of quartz-leucoxene concentrate as a raw material. An additional goal is to check the efficiency of the complex reagent in wastewater treatment processes and compare its activity with traditional aluminium-containing coagulants.

Methods. As the initial precursor for the synthesis of the complex reagent, a sample of titanium tetrachloride containing an admixture of silicon tetrachloride was used in the amount up to 0.4 wt.% obtained by selective chlorination of quartz-leucoxene concentrate from the Yarega oil-titanium field.

In the experiment, samples of aluminium oxide and hydroxide produced by Sigma-Aldrich (Germany) and sulfuric acid produced by "Component-Reaktiv" (Russia) were used. Aluminium sulfate and aluminium oxychloride produced by Kemira (Finland) were chosen as a sample for comparison of coagulants.

Identification of the phase composition of solid samples was performed using a DRON 3 N X-ray diffractometer manufactured by NPO "Burevestnik" (Russia) (copper anode Kα-1.5418Å).

The determination of metals in acidic solutions and wastewater was accomplished by atomic emission spectroscopy with magnetic plasma on a “Spectrosky” device manufactured by the GK “Skygrad” (Russia) [20].

Test coagulation (Jar tests of at least three repetitions for each water) was performed on a laboratory flocculator JLT4 Velp Scientifica (Italy). Mixing time of coagulant and wastewater was 2 min, flocculation phase (slow coagulation) 8 min, sedimentation 30 min.

Determination of suspended matter concentration was performed by the gravimetric method, and also on a portable turbidimeter-haze meter Hanna HI 98 703 HANNA Instruments (Hungary).

The filtration rate was determined by passing a given volume of wastewater treated with coagulants through the “White Ribbon” filter (15 μm) for 60 s. Sedimentation time of sludge was estimated using a ZOMS-KFK-3-01 photocolorimeter (Russia).

To assess the coagulation efficiency of complex and traditional coagulants, a sample of river water taken in the warm and cold seasons was used, wastewater from the gas purification unit of the moulding and steel melting shop at the machine-building plant as well as household wastewater subjected to deep biological treatment and directed to the stage of reagent dephosphatization.

Discussion of results. To obtain a solid sample of a complex titanium-containing coagulant, an innovative synthesis technology was applied (Fig.1) including prehydrolysis of titanium tetrachloride, double decomposition and hydrolysis of titanium oxysulfate:

$$\mathrm{TiCl_4 + 4H_2O \rightarrow 4HCl + Ti\,(OH)_4;}$$

$$\mathrm{TiCl_4 + 2H_2SO_4 \rightarrow Ti\,(SO_4)_2 + 4HCl;}$$

$$\mathrm{TiOSO_4 + 3H_2O \rightarrow H_2SO_4 + Ti\,(OH)_4.}$$

Titanium tetrachloride, hydrolytic hydrochloric or sulfuric acid will react with aluminium hydroxide/oxide to form aluminium sulfate and chloride:

$$\mathrm{Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O;}$$

$$\mathrm{Al\,(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O;}$$

$$\mathrm{2Al\,(OH)_3 + 3H_2SO_4 \rightarrow Al_2\,(SO_4)_3 + 6H_2O}\ \text{(12 }\mathrm{H_2O}\text{ moles lacking);}$$

$$\mathrm{Al_2O_3 + 3H_2SO_4 \rightarrow Al_2\,(SO_4)_3 + 3H_2O}\ \text{(15 }\mathrm{H_2O}\text{ moles lacking).}$$

Neutralization of sulfuric acid with aluminium hydroxide or oxide leads to formation of aluminium sulfate; however, since only 18-aqueous crystalline hydrate is in a stable form, the deficient hygroscopic moisture will be absorbed from the reaction mixture, and it would be possible to obtain solid products (chemical dehydration).

The key feature of the proposed technology is a possibility of rejecting the drying processes and obtaining a reagent consisting of two water-soluble metal cations with a charge of 3+ and 4+ for aluminium and titanium, respectively.

Phase composition of the resulting sample of complex titanium-containing coagulant is presented in the diffractogram (Fig.2).

Data on the chemical composition of coagulant samples (a set of results of X-ray diffraction and atomic emission analyses) obtained from aluminium oxide and hydroxide at various ratios of aluminium compounds and sulfuric acid are presented in Table 1.

Comparing the data in Table 1 and Fig.2, it can be concluded that, regardless of the type of the compounds used, the main phase in the complex reagent is aluminium sulfate – 70-90 wt.%, while the product contains aluminium chloride – 5-20 wt.% and water-soluble titanium oxysulfate – 2.5-10 wt.%. The presence of aluminium compounds in the form of sulfate and chloride in the reagent will probably increase the efficiency of coagulation due to a synergistic effect.

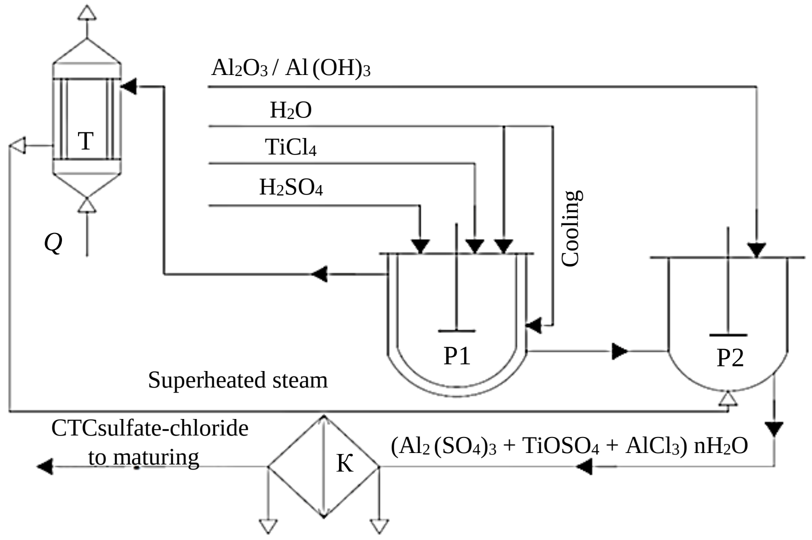

Fig.1. Scheme for the synthesis of a complex titanium-containing coagulant
P1 – double decomposition reactor; P2 – neutralization reactor
(chemical dehydration); T – heat exchanger; K – crystallizer

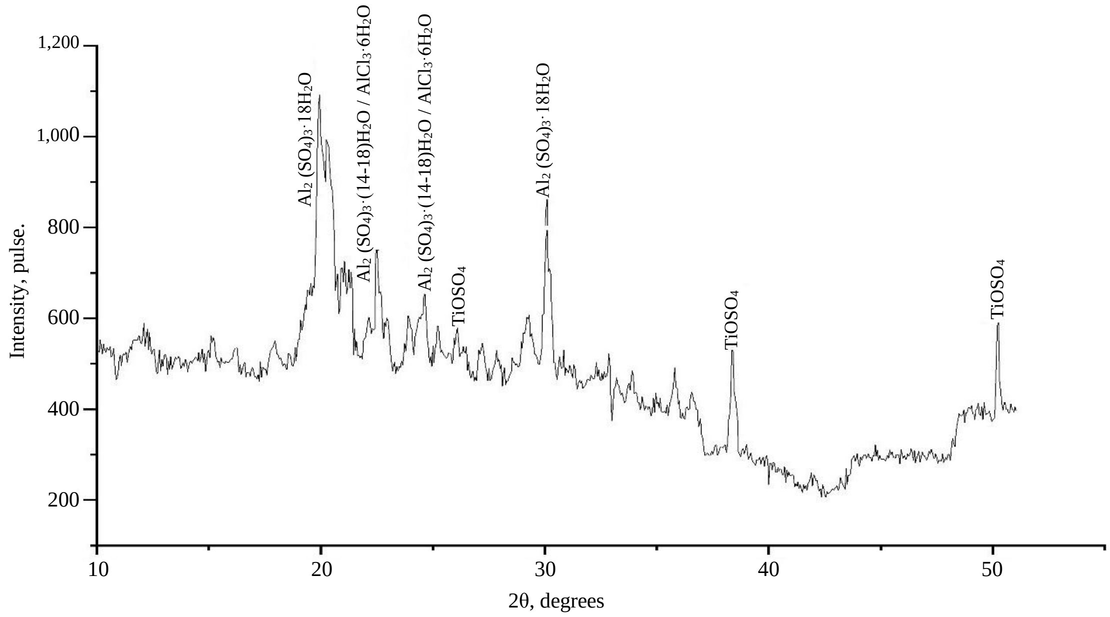

Fig.2. Diffractogram of a coagulant sample

Table 1

Phase composition of samples of complex titanium-containing coagulants

Al-containing component	Mass ratio $(Al_2O_3/Al(OH)_3)/TiCl_4$	Content of main components, wt.%			
		$AlCl_3\cdot6H_2O$	$Al_2(SO_4)_3\cdot18H_2O$	Ti-components	Insoluble part
Al_2O_3	2.3/1	5.5±0.35	91.7±5.78	2.6±0.22	0.2±0.04
	2/1	10.1±0.64	84.6±5.33	5.0±0.42	0.3±0.06
	1.1/1	15.1±0.95	76.8±4.84	7.6±0.64	0.5±0.10
	0.6/1	19.8±1.25	69.4±4.37	10.1±0.85	0.7±0.14
$Al(OH)_3$	7/1	5.7±0.36	91.7±5.78	2.5±0.21	0.1±0.02
	3/1	10.5±0.66	84.6±5.33	4.8±0.40	0.1±0.02
	1.6/1	16.1±1.01	76.2±4.80	7.5±0.63	0.2±0.04
	1.1	21.7±1.37	67.7±4.27	10.4±0.87	0.2±0.04

The final stage of experiments was the assessment of the efficiency of the prepared samples of complex titanium-containing reagents in water purification processes.

The first object of study was water from the surface water intake collected in the warm and cold seasons. The initial content of suspended matter was 6.9 mg/dm^3 (autumn), pH – 6.54 and 12.3 mg/dm^3, pH – 6.71 (summer).

From the data in Table 2 it is clear that the use of the sample of the complex titanium-containing coagulant makes it possible to neutralize the effect of water temperature and significantly increase the efficiency of the base reagent – aluminium sulfate (70-90 % of the composition of the complex reagent). This phenomenon can be accounted for by the expansion of the range of coagulant hydrolysis products, polycondensation (flocculation) processes as well as neutralization (nucleation) phenomena [21-23].

Table 2

Efficiency of natural water purification from suspended matter, %

Coagulant	Coagulant dose, mg (Me_XO_Y)/dm^3	Purification efficiency, %	Suspended matter concentration, mg/dm^3	Filtration rate, ml/min	Sedimentation time, min
	Cold period (water temperature 8-9 °C)				
Aluminium sulfate	15	65.8	2.36	35	8
Aluminium oxychloride	12	84.3	1.08	46	5
CTCsulfate-chloride	10	93.8	0.43	55	4
	Warm period (water temperature 18 °C)				
Aluminium sulfate	12	94.2	0.71	43	5
Aluminium oxychloride	9.5	98.3	0.21	54	4
CTCsulfate-chloride	8	98.4	0.20	60	3

Data on the efficiency of dephosphatization of household wastewater subjected to deep biological treatment are presented in Fig.3.

Fig.3 shows that the use of the complex titanium-containing coagulant allows minimizing the residual content of phosphate ion, which is primarily due to a low solubility of titanium phosphate compared to aluminium phosphate. In addition to the growing efficiency, the use of the complex reagent also allows reducing by 10-25 % the dose of coagulant required to achieve the MPC$_{\text{fish farming}}$ standard.

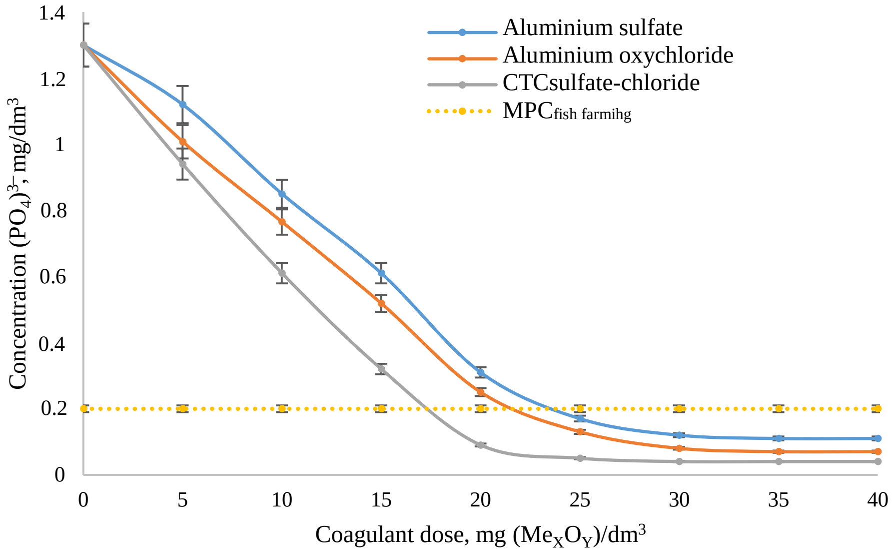

Fig.3. Reagent dephosphatization of wastewater

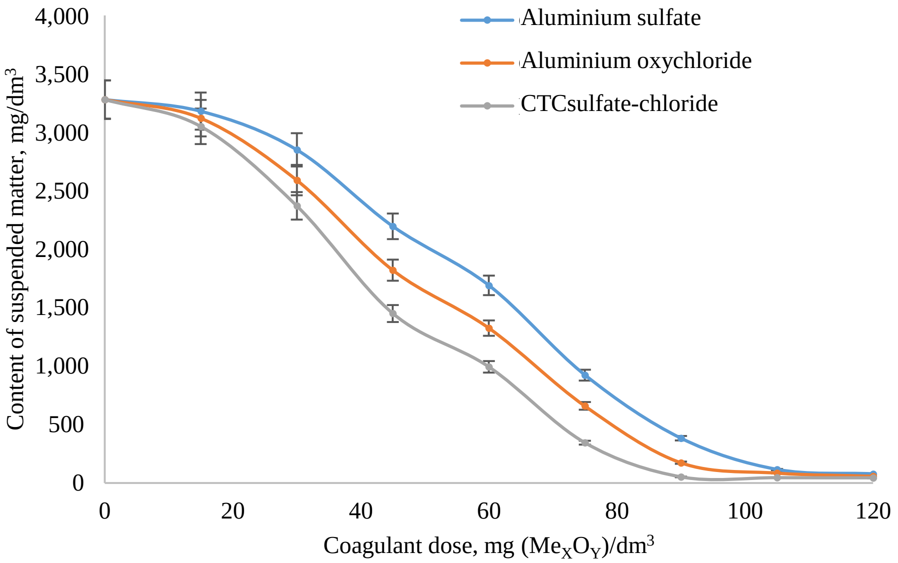

Fig.4. Residual concentrations of suspended matter

The next step was the assessment of the efficiency of the complex coagulant using a sample of wastewater from the area for preparing the core mixture and electro arc steel melting at the machine-building plant in the Moscow Region. The initial content of suspended matter represented by oxides of iron, silicon, aluminium and calcium in water of wet gas purification system was 3,280 mg/dm^3. Data on residual concentrations of suspended matter in wastewater, depending on the type and dose of the coagulant used, are presented in Fig.4.

The graph in Fig.4 clearly shows that the use of the complex coagulant allows not only reducing the consumption of reagents, but also minimizing the residual content of suspended matter in water. Purified water can be sent for reuse in the gas purification system, and, due to the lowest residual concentration of suspended matter in the recirculated water, abrasive wear of the equipment will be much less [24, 25]. The coagulation sludge formed when using the complex reagent settled on average 10-15 % faster, which in the future will significantly increase the productivity of the treatment facilities. Filtration rate of coagulation sludge when using the new reagent was on average 20 % higher than when using traditional reagents.

The composition of coagulation sludge obtained using the complex reagent will be almost identical to coagulation sludge from the use of aluminium sulfate, with the exception of the addition of titanium dioxide in the amount of 5-10 wt.%, while both sludges have the 4th hazard class and can be placed for permanent storage at landfills. In addition, the sludge obtained when using the complex titanium-containing coagulant can be used as a precursor for thermochemical synthesis of titanium aluminates (a component of ceramics, a catalyst) [19].

Conclusion. As part of the work, a technology was proposed for the preparation of innovative complex titanium-containing coagulants using titanium tetrachloride as the raw material obtained from quartz-leucoxene concentrate – large-tonnage mineral waste from the shale oil extraction process at the Yarega oil-titanium field. The use of quartz-leucoxene concentrate will make it possible to take a step towards the implementation of the Zero Waste concept within the framework of circular economy [26, 27].

The possibility of obtaining a solid sample of the complex coagulant including the processes of prehydrolysis of titanium tetrachloride and its double decomposition in combination with chemical dehydration was established. It was proved that the composition of the complex reagent remained virtually unchanged when using both aluminium hydroxide, and oxide. It was proved that the main phase in the complex reagent was aluminium sulfate (70-90 wt.%), while the product contained aluminium chloride and 2.5-10.0 wt.% water-soluble titanium oxysulfate.

Studies on the coagulation ability of the complex titanium-containing coagulant showed that in the efficiency of removing suspended matter, the complex reagent surpassed the traditional coagulants based on aluminium sulfate or oxychloride. It was ascertained that titanium-containing reagents were less sensitive to low water temperatures compared to the base aluminium sulfate.

It was proved that the use of the titanium-containing reagent allowed minimizing the residual concentrations of phosphate anion during after-purification of water that passed the stage of deep biological treatment. The resulting coagulation sludge settled to the bottom faster and had a higher filtration rate, which will significantly increase the efficiency of the treatment facilities.

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Research article

Rationale for a possibility of using humic preparations production waste for wastewater purification from metals (Cd^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}) aimed at developing efficient measures on environmental rehabilitation

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Abstract. Results of studying optimal conditions and parameters for afterpurification of underspoil waters from metal ions using humic acids production waste are presented with a view to develop the efficient measures on environmental rehabilitation of ecosystems disturbed by the development of copper pyrite deposits. The influence of contact time and waste dosage on the purification process was analysed, changes in the pH of wastewater and its impact on the growth and development of plants were studied. The key factors were identified allowing to achieve the efficiency of the purification process – the optimal contact time in the range from 120 to 180 min and waste dosage of 10 g/l. The study showed that the use of waste resulted in a neutral pH value of 7.03 compared to the initial pH value of 5.95. It was ascertained that the use of iron-magnesium production waste in combination with waste from humic preparations production made it possible to achieve the MPC of commercial fishing importance (with the exception of magnesium). Wastewater after the afterpurification process with high magnesium concentrations did not have a stimulating effect on the growth and development of *Lepidium sativum L.* plants. From biotesting results it can also be stated that there is no negative impact on the growth and development of *Lepidium sativum L.* The results obtained indicate a potentiality of using afterpurified wastewater for watering plants in the process of initiating the environmental rehabilitation of the disturbed ecosystems.

Keywords: heavy metals; wastewater; removal of ions from solution; waste; environmental rehabilitation; biotesting

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Introduction. The development of solid mineral deposits in the Ural region, the occurrence of abandoned or sealed-off mining facilities as well as objects of accumulated environmental damage predetermine a complicated environmental situation in the region; therefore, progressing degradation of the natural environment is still a major challenge at present, despite the fact that the environmental factor is gradually becoming one of the fundamental issues in decision making [1, 2].

According to the governmental report on the state and protection of environment in the Sverdlovsk Region[1], mining industry was the main source of waste generation in 2022. The share of mining waste in generation, disposal and availability at the end of the year was 90.1; 87.4 and 93.2 % of all generated, recycled and accumulated production and consumption waste in the Sverdlovsk Region. Generation of

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[1] On the state of environment in the Sverdlovsk Region in 2022. Governmental report. Ekaterinburg: Ministry of Natural Resources and Environment of the Sverdlovsk Region, 2023, p. 366.

waste from this group increased by 8.147 million tons (5.24 %) compared to 2021 and amounted to 163.6 million tons, mainly due to the growing overburden volume. It should be noted that the share of recycled waste also increased. The amount of recycled mining waste compared to 2021 increased by 2.01 million tons (3.1 %) and reached 67.5 million tons (41.2 % of the generation of this group of waste) due to the use of hard rock overburden for own needs.

Despite a positive dynamics, the presence of large-tonnage waste from the mineral raw materials complex, of both operating and sealed-off production facilities, is one of the reasons for the negative processes occurring in the environment [3, 4]. In 2022, in the Sverdlovsk Region, water of water bodies at 26 % of observation stations was classified as "polluted", at 57 % as "dirty", at 13 % as "very dirty", and at 4 % of stations as "extremely dirty". The main ingredients from the list of extremely high surface water pollution levels at the stations of the national observation network in the Sverdlovsk Region for 2022 are zinc, copper, and manganese. As regards groundwater quality, cases of exceeding the MPC for cadmium and lead can be recorded.

The relevance of solving the environmental problems of disturbed territories is obvious in connection with accumulation of a huge amount of waste from mining and metallurgical industries stored in sludge and tailings dumps, dumps of overburden rocks, slags and substandard raw materials [5-7]. Therefore, identification of the pattern of mining facilities impact on the deposit environment in respect of studying the processes that determine the accumulation and migration of pollutants, the use of reclamation techniques for soil detoxification, the development of measures on environmental rehabilitation of water bodies with the help of plants and sorption materials produced from natural and technogenic raw materials is an intensely developing field of research [8-10]. A great number of publications illustrate the broad range of materials used for removing metals from wastewater solution including red mud [11-13], ash [14-16], steelmaking slags [17], biochar [18-20], vermiculite [21], and different waste of plant origin [22-24]. Among them, the industrial waste is attracting more and more attention, since it is expected that the use of waste for environmental purposes will be low-cost [25].

The earlier experiments [8] confirmed the possibility of using iron-magnesium production waste to neutralize industrial wastewater from metal ions (Cd^{2+}, $Zn^{2+,}$ Co^{2+}, Cu^{2+}). The dependence of purification efficiency on the dose of waste introduced, contact time, initial concentration of metals and acid-alkaline balance was experimentally determined. Optimal conditions are the 120-180 min contact time, dosage of 4-10 g/l and an initial concentration of metal ions not exceeding 500 mg/l.

The purpose of the work is to assess the possibility of using waste generated in production of humic preparations as a material for afterpurification of wastewater to the MPC level of commercial fishing importance from metal ions (Cu^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}) in concentrations obtained as a result of experimental research on redistribution of heavy metals in the "wastewater – waste" system using iron-magnesium production waste [8]. In addition, the task was set to assess the impact of already purified water on the growth and development of agricultural biological plant resources.

Analysis of the initial concentration of metals in solution and pH of solutions was accomplished. The optimal contact time and dosage of materials were determined. An assessment was made of the effect of water following afterpurification on the growth of *Lepidium sativum L.* watercress plants.

Materials and methods. *Waste* used in this study was obtained from the production of humic preparations (HPW). As the source raw material for the production of a humic preparation (potassium humate), the following ratio of components by weight of dry matter is used, %: high-moor peat – 40-60; sapropel (TU 0135-001-94744244-2007) – 25-38; diatomite (TU 5761-001-59266087-2005) – 14-20; KOH – the rest. The main inorganic compounds of peat

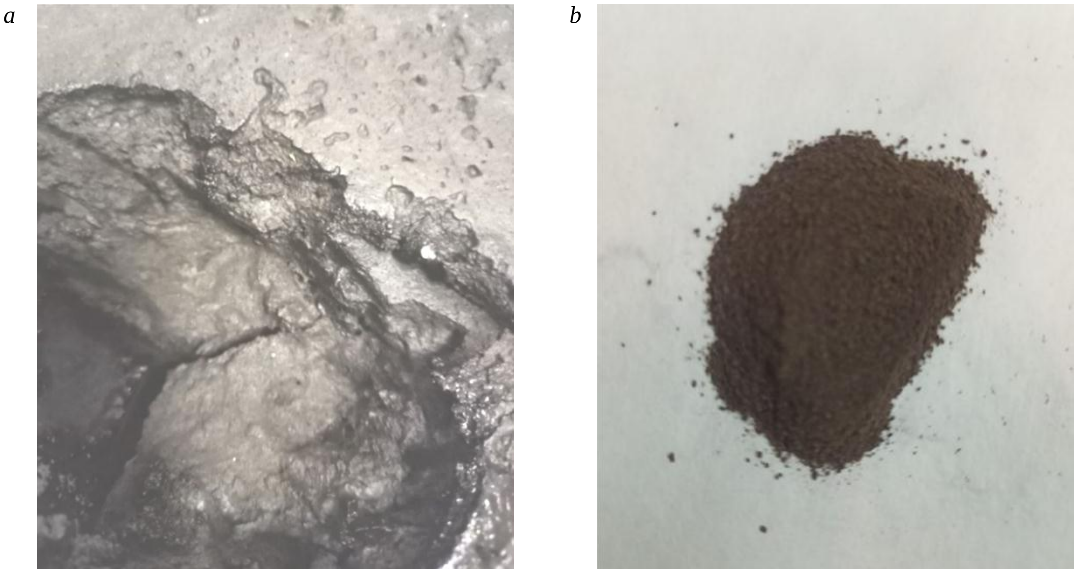

Fig.1. Humic acids production waste: *a* – before treatment; *b* – after treatment

are nitrogen to 1.5 %, phosphorus, potassium, calcium (in total) to 0.6 % (N:P:K). The content of humic substances in peat is 7.4-7.9 %. Diatomite is by more than 80 % composed of silica.

HPW is a pasty substance of dark grey colour which forms as a result of solid phase separation from the target product by centrifugation (Fig.1).

The waste was dried at a temperature of 95 °C and crushed to a fraction of 1 mm. A drying cabinet (ShS-80-01-SPU, OOO PriborUfa, Russia) was used for drying the samples, and laboratory sieves and a porcelain mortar and pestle were used for grinding. Bulk density of the HPW is 400-450 kg/m^3, humidity – 3-5 %, pH – 8.0-8.5.

Wastewater is underspoil water from the exhausted copper pyrite deposit Kaban-1 within the boundaries of the Sverdlovsk Region, 190 km from Yekaterinburg. Wastewater was investigated after interaction with iron-magnesium production waste applying the procedure [8], pH = 5.95. Elemental composition, mg/l: Cd^{2+} – 0.01 (MPC – 0.005); Zn^{2+} – 0.2 (MPC – 0.01); Mg^{2+} – 849.60 (MPC – 40); Cu^{2+} – 0.1 (MPC – 0.001) [8]. The MPC was adopted by Order of the Ministry of Agriculture of Russia dated December 13, 2016 N 552 (as amended on 10.03.2020) "On approval of water quality standards for water bodies of commercial fishing importance including the standards for the maximum permissible concentrations of harmful substances in waters of water bodies of commercial fishing importance".

Elemental analysis and sample preparation. To ash the samples, a MARS 5 Digestion Microwave System by CEM Corporation (USA) was used in accordance with methodology EPA 3052[2]. The process started with addition of 0.5 g sample to which 9 ml of HNO_3 (GOST 11125-84, 70 %) and 3 ml of HF (GOST 10484-78, 45 %) were added. Then, the mixture was stirred, after which it was left for 15 min, and the vessels were closed. Special vessels were used recommended by the manufacturer – EasyPrep. The time required to heat to 180 °C was 6 min, the time to maintain the temperature was 10 min, and the power was 1,800 W. After treatment with dilution to 50 ml, a transparent sample without colour and foreign particles was obtained. 1 M HNO_3 was used to determine the mobile forms of metal.

Air-acetylene flame atomic absorption spectroscopy (AAS) (Varian AA 240 FS by Varian Australia Pty Ltd. Australia) was applied to determine metal concentrations in wastewater, mineralized samples and leachates. Specific wavelengths were used for different elements: Cd – 228.8;

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[2] MARS 6. Microwave Acid Digestion. Method Note Compendium. CEM, 2018, p. 320.

Zn – 213.9; Mg – 202.6; Cu – 324.7 nm. The detection limits of elements in solution were: Cd – 1.5; Zn – 1.6; Cu – 1.2; Mg – 0.3 μg/l.

Experiments. *Redistribution of metals in the "wastewater – HPW" system*. The effect of HPW dosage on the degree of metal ions removal from solution was investigated. In the experiments, samples of 0.1; 0.2; 0.5; 1.0; 1.5 and 2.0 g were weighed and placed in conical falcon tubes. Wastewater in a volume of 50 ml was poured to the samples. Then, the samples were mixed (at a frequency of 99 rpm) for 120 min using a rotary mixer ELMI RM-1L manufactured by ELMI LTD (Latvia). Afterwards, the resulting solutions underwent filtration using "Blue ribbon" filters.

Determination of the optimal contact time for removing metal ions from solution. Wastewater in a volume of 50 ml was poured to 0.2 g weighed quantities. Samples were mixed at different time intervals from 5 to 180 min. The resulting solutions underwent filtration using "Blue ribbon" filters.

To assess the influence of the initial concentration of metal ions Cu^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} on wastewater purification process, solutions with different concentrations were prepared: 5, 10, 50, 100, 300, 500 and 1,000 mg/l. The solutions were prepared using test-grade "high purity" reagents and the state standard samples (with concentrations from 1 to 10 g/l). The experiment was conducted with contact time of 120 min, a 0.2 g weighed quantity was applied, the solution volume was 50 ml, at room temperature. In the experiment, the static exchange capacity of waste (SEC) and the degree of pollutant recovery from the solution (E) were determined, and the standard error of the mean value was calculated.

Determination of static exchange capacity and degree of pollutant recovery from solution:

$$qe = (C_i - C_e)V / m; \tag{1}$$

$$E = (C_i - C_e) / C_i \cdot 100, \tag{2}$$

where C_i is the initial concentration of ions in solution, mg/l; C_e, the equilibrium (residual) concentration of copper ions in leachate determined in water after mixing water and substrate, mg/l; V – volume of model solution added to waste, l; m, mass of dry weighed quantity of the substrate, g.

Biotesting of wastewater. The seed germination experiment was performed according to the procedure in SanPin 2.1.7.573-96. Watercress *Lepidium sativum L.* seeds (30 pcs.) were placed evenly on filter paper in a Petri dish. Then, 5 ml of wastewater obtained after interaction with waste was poured into each dish. As control – wastewater from the Kaban-1 deposit with initial elemental composition (concentrations before purification using iron-magnesium production waste: Cd^{2+} – 0.20 (MPC = 0.005); Zn^{2+} – 50.12 (MPC – 0.01); Mg^{2+} – 322.50 (MPC – 40); Cu^{2+} – 78.10 (MPC – 0.001); Fe^{3+} – 147.71 (MPC – 0.1); Co^{2+} – 1.73 (MPC – 0.01); Ca^{2+} – 33.20 (MPC – 180); K^{+} – 5.26 (MPC – 50) and distilled water [8]. Dishes were covered with lids and left for 72 h at room temperature. The experiment was repeated three times. Root length and germination power of seeds as well as the contents of the investigated chemical elements in individual plants were measured on completing the experiment. Before the chemical analysis, the seeds were washed with distilled water. The seeds were considered germinated if their length was at least 2 mm. Based on these data, the indicators of relative seed germination power (RGP) and relative root growth (RRG) were obtained:

$$\mathrm{Gs} / \mathrm{Gc} \cdot 100 = \mathrm{RGP}, \tag{3}$$

where Gs – is the number of germinated seeds in the sample; and Gc – the number of germinated seeds in control (distilled water);

$$\mathrm{Ls} / \mathrm{Lc} \cdot 100 = \mathrm{RRG}, \tag{4}$$

Ls – root length of germinated seeds in the sample; Lc – root length of germinated seed in control (distilled water).

Discussion of results. To confirm the possibility of using the HPW as a material for afterpurification of wastewater from metal ions, the influence of initial concentration of metals in solution, contact time between the material and the solution, dosage of the HPW and acid-alkaline state of the aqueous medium (pH) were studied. Analysis of the influence degree of each factor helps to prove the efficiency and potential of the HPW for wastewater purification from metals [26-28]. The results obtained can serve as a rationale for the use of production waste as a material for purification and afterpurification of industrial wastewater in terms of developing the efficient measures on environmental rehabilitation of water bodies.

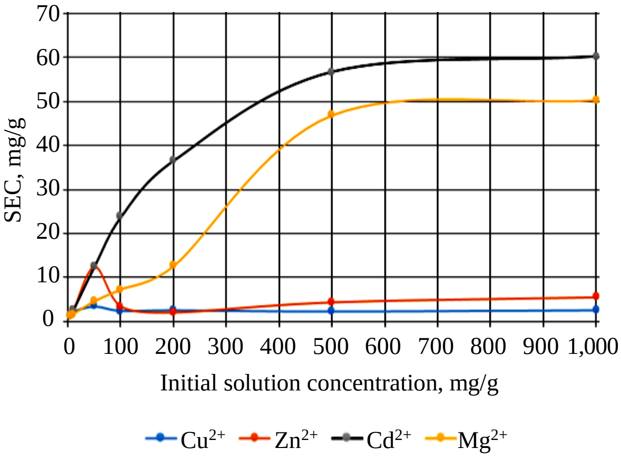

Fig.2. Effect of initial concentration of metal ions in solution on the HPW wastewater purification process (monometallic solutions)

Influence of initial concentration of metal ions on wastewater purification. Initial concentration of metal ions controls the removal of metal ions from aqueous solution. This allows evaluating the influence of metal concentration in solution on the interaction processes and to understand, what concentrations are most important for an efficient removal from solutions [29]. The dependence of the static exchange capacity of the HPW with respect to the metals under study (Cu^{2+}, Zn^{2+}, Cd^{2+}, $Mg^{2+)}$ relative to their initial concentration in monosolution is shown in Fig.2. State standard samples were used to dilute solutions from 5 to 1,000 mg/l.

The graph in Fig.2 shows that the processes of removal of metals such as copper, cadmium, magnesium, and zinc have a certain dynamics. The initial stage (from 5 to 50 mg/l) is characterized by a rapid recovery of metals (Cu^{2+}, Zn^{2+}), which points to a high formation rate of metal compounds with waste [30, 31]. After this stage, there is a period (50-200 mg/l) of a marked decrease for Cu^{2+}, Zn^{2+}. As a result (from 500 mg/l), the equilibrium sets in when the absorption rate of metals and their removal becomes approximately the same, which signals the completion of this process and the attainment of a certain stability of the system. The process of magnesium and cadmium absorption by the HPW is increasing with growing initial concentration of these elements in solution, which is shown in Fig.2 by a concave curve.

Therefore, it can be stated that it is impossible to use the HPW for purification of wastewater containing high concentrations of the elements under study (Cu^{2+}, Zn^{2+} more than 50 mg/l); however, they can be used at the final stages for bringing the quality of purified water to the MPC level of commercial fishing importance.

The mechanism for removing elements from wastewater can be described in several stages. At the first stage, metal ions move from solution to the outer surface of waste. This process corresponds to film diffusion, when metal ions move from solution surface to the waste surface. At the second stage, metal ions penetrate into the waste structure. This process involves movement of metal ions through internal channels or pores of the material, which can lead to their deeper fixation inside the material [32, 33]. All this plays the key role in understanding the processes of metal removal as well as for the development of efficient water purification technologies in terms of introducing measures on environmental rehabilitation of water bodies including the elimination of discharge of highly mineralized water into them.

Effect of contact time and dosage. The study of the process of ion recovery from solution included a change in the waste mass from 0.1 to 2 g in 50 ml of solution with constant concentration. This process was performed at a constant stirring speed of 99 rpm and lasted 120 min at room temperature. To evaluate the recovery of metal ions from wastewater, underspoil water of the Kaban-1 deposit treated with iron-magnesium production waste was used as model solution [8]. The results are shown in Table 1 and Fig.3.

Table 1

Results of chemical analysis of obtained leachates (50 ml wastewater, contact time 120 min)

Weighed quantity, g	Content of chemical elements in leachate, mg/l				pH
	Cd^{2+}	Zn^{2+}	Mg^{2+}	Cu^{2+}	
0.1	0.007±0.001	0.15±0.02	953.14±55.16	0.073±0.01	6.25±0.01
0.2	0.003±0.001	0.1±0.02	857.11±47.21	0.039±0.01	6.78±0.01
0.5	< 0.0015	< 0.0016	931.10±45.24	< 0.0012	7.03±0.01
1.0	< 0.0015	< 0.0016	932.05±43.42	< 0.0012	6.99±0.01
1.5	< 0.0015	< 0.0016	946.41±40.56	< 0.0012	6.9±0.01
2.0	< 0.0015	< 0.0016	992.94±44.15	< 0.0012	6.78±0.01

The results of the study showed that the efficiency of removing these metals with the use of the HPW increased with its growing dosage, until almost complete purification (100 %) was achieved. This suggests that a higher dosage of the HPW favoured the increasing number of active sites for metal binding, which, in turn, increased the overall efficiency of the removal process [34-36]. Further, the ability of the HPW to remove copper, cadmium and zinc from solution does not change with increasing dosage. Considering the presence of silica in the source raw material for the production of potassium humate (diatomite), virtually insoluble compounds form as a result of the HPW interaction with wastewater.

At the next stage of research, the influence of duration of contact between the HPW and wastewater on the efficiency of metal ions removal was determined, which makes it possible to verify the optimal exposure time to the HPW for purifying wastewater from the investigated elements to the MPC level.

Table 2

Results of chemical analysis of obtained leachates (50 ml of wastewater, 0.2 g weighed quantity)

Contact time, min	Content of chemical elements in leachate, mg/l				pH
	Cd^{2+}	Zn^{2+}	Mg^{2+}	Cu^{2+}	
5	0.009±0.001	0.18±0.03	995.45±52.14	0.08±0.02	6.05±0.01
10	0.007±0.001	0.17±0.02	994.51±54.21	0.07±0.02	6.11±0.01
15	0.006±0.001	0.15±0.02	854.25±56.12	0.05±0.02	6.25±0.01
30	0.005±0.001	0.12±0.02	966.32±50.11	0.05±0.02	6.52±0.01
60	0.005±0.001	0.11±0.01	854.55±56.87	0.04±0.01	6.70±0.01
120	0.003±0.001	0.10±0.02	857.11±47.21	0.03±0.01	6.78±0.01
180	0.003±0.001	0.10±0.02	905.84±67.14	0.04±0.01	6.82±0.01

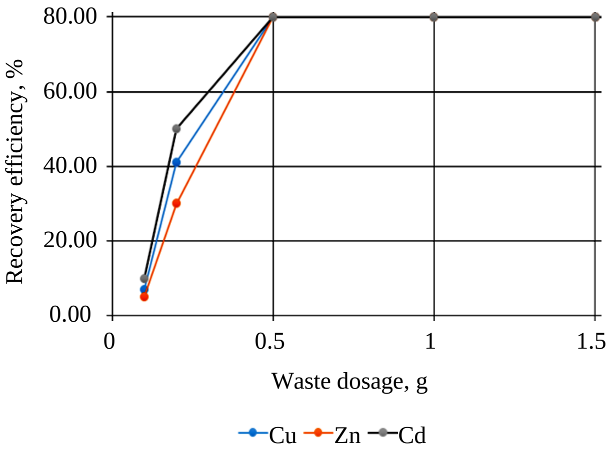

Fig.3. Influence of waste dosage on degree of metal ions recovery from solution

An experimental study of the effect of contact time on wastewater afterpurification process was conducted at constant solution concentration (Table 2) within different time intervals from 5 to 180 min at room temperature (Fig.4).

Elemental composition of leachates obtained as a result of the HPW interaction with wastewater allows evaluating changes in concentration of different elements in leachates depending on contact time, which is important for understanding the dynamics of the process and determination of the optimal conditions for wastewater purification to the MPC level (Table 2). Residual concentration of metals in leachates after interaction at these contact time conditions varied from

0.009 to 0.003 mg/l for cadmium, from 0.18 to 0.10 mg/l for zinc, from 995.45 to 854.55 mg/l for magnesium, and from 0.08 to 0.04 mg/l for copper.

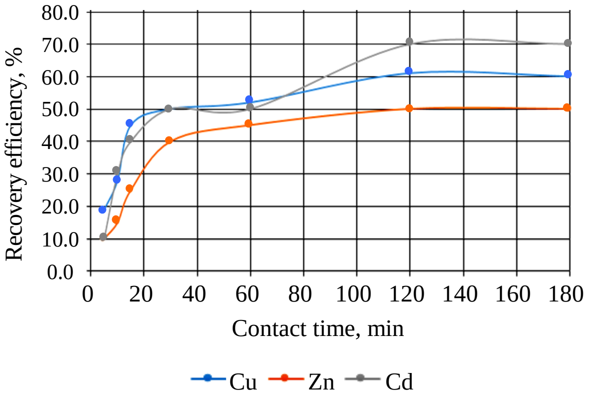

Fig.4. Effect of contact time on recovery rate of metal ions from solution

It can be concluded that in the time interval from 120 to 180 min. the maximum values of the efficiency indicator for copper, cadmium and zinc are recorded; further increase of the interaction time of solutions with the HPW will not lead to major changes in the investigated indicator. It should be noted that magnesium values in the resulting leachates were higher than the initial magnesium values in wastewater. This indicates that the process of removing magnesium ions from polymetallic wastewater is not as efficient as in artificially created model solutions from the SSS, which indicates the need for further research related to formation of a cascade of biological ponds considering the material composition of the bed and filtration dam sensitive to this chemical element.

Further, to assess the risk of secondary pollution when using the HPW, the chemical analysis of the samples obtained after interaction with wastewater was accomplished. Concentrations of metals in the material before the start of the experiment are given (Table 3).

Table 3

Results of chemical analysis of HPW after interaction with wastewater

Element	Gross forms, mg/kg (before interaction)	Gross forms, mg/kg (after interaction)	Mobile, mg/kg (after interaction)	MPC, mg/kg[*] (gross/mobile forms)
Cu	0.81±010	9.68±1.58	1.53±0.25	33/3
Zn	4.38±0.98	21.75±4.58	4.25±0.89	55/23
Cd	< 0.0015	< 0.0015	< 0.0015	0.5/Undetermined
Co	0.20±0.05	4.35±1.25	0.98±0.10	–/5.0
Mg	1,504.31±354.44	1,305.40±299.45	602.93±154.45	Undetermined
Mn	21.27±3.47	22.03±3.33	4.03±0.78	1,500/700
K	36,540.38±3,548.21	3,628.68±454.68	1,245.39±248.45	Undetermined
Fe	2,485.93±384.49	2,490.38±335.24	1,300.58±224.87	Undetermined

Initially, the HPW contains a large amount of magnesium – 1,504.31 mg/kg; potassium – 36,540.38 mg/kg; manganese – 21.27 mg/kg and iron – 2,485.93 mg/kg. At the end of experiment, a decrease in gross forms of magnesium to 1,305.40 mg/kg, potassium to 3,628.68 mg/kg was recorded, iron and manganese remained at the same values. At the same time, there is a significant accumulation of copper from 0.81 to 9.68 mg/kg; zinc – from 4.38 to 21.75 mg/kg, cobalt – from 0.20 to 4.35 mg/kg.

Experiments on afterpurification of pre-treated underspoil water from the Kaban-1 deposit, when determining the optimal conditions and time parameters for the purification processes, indicate the range within which the process reaches its highest efficiency – from 120 to 180 min, at material dosage 10 g/l (0.5 g weighed quantity).

Biotesting of wastewater. Despite a major excess of the MPC of commercial fishing importance for magnesium, in this study, a biotesting technique was applied for in-process monitoring of acute toxicity of samples including the use of watercress as a test object. This method is based on the study of behavioural response of plants to exposure to wastewater. Response of plants (seed germination

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[*] SanPiN 1.2.3685-21 "Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors to humans".

rate, root system development, and total biomass) can serve as an indicator of the negative impact of various pollutants on the ecosystem.

One of the main advantages of using watercress as a test object is a relatively short duration of experiments due to the rapid cycle of plant growth and development [37, 38].

Seeds of *Lepidium sativum L.* were germinated in Petri dishes (Fig.5) on filter paper within 72 h with addition of the investigated aqueous solutions: 1) wastewater from the Kaban-1 deposit (untreated); 2) wastewater from the Kaban-1 deposit (after interaction with iron-magnesium production waste) [8]; 3) wastewater from the Kaban-1 deposit (after interaction with iron-magnesium production waste and the HPW); 4) distilled water.

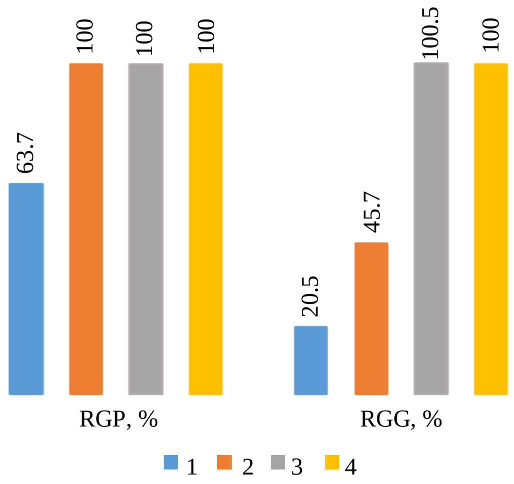

Fig.5. Effect of different wastewater compositions (1-4 in Table 4) on germination power (RGP) and root growth (RGG) of watercress *Lepidium sativum L.*

Table 4

Influence of different wastewater compositions on germination power and growth of watercress, elemental analysis of individual plants after interaction

Element	Untreated wastewater	Wastewater after interaction with iron-magnesium production waste. Waste dosage – 10 g/l, contact time – 120 min	Wastewater after interaction with iron-magnesium production waste and HPW. Waste dosage – 10 g/l, contact time – 120 min	Distilled water
	1	2	3	4
Number of germinated seeds, pcs.	19.00±2.00	30.00±0.00	30.00±0.00	30.00±0.00
Root length, mm	4.30±4.00	9.64±2.65	21.11±6.00	21.06±1.53
Total biomass, mg	15.00±2.89	27.15±4.04	40.09±4.36	45.66±1.15
RGP, % (germination percentage)	63.33±2.00	100.00±0.00	100.00±0.00	100.00±0.00
RGG, % (relative root length)	20.50±4.00	45.74±2.65	100.50±6.00	100.00±1.53
Cu, mg/kg	662.67±30.00	16.80±1.33	8.75±1.02	8.40±1.11
Zn, mg/kg	1,478.40±218.04	174.32±6.56	53.10±3.11	45.12±1.85
Cd, mg/kg	1.87±0.46	1.00±0.27	< 0.0015	< 0.0015
Fe, mg/kg	1,442.47±117.90	234.80±33.50	206.15±25.51	246.40±29.42
Mg, mg/kg	2,042.13±211.00	15,064.00±667.18	11,956.00±468.01	1,996.00±127.42
K, mg/kg	< 0.0008	13,108.00±452.28	15,419.50±709.10	13,704.00±394.22
pH	2.33	5.95	7.05	6.51

Experimental studies revealed that *Lepidium sativum L.* seeds exposed to untreated wastewater from the Kaban-1 deposit displayed a major decrease in seed germination power, total biomass and root system development compared to control values (Table 4, Fig.5).

It was found that seed germination decreased by more than 30 %, and total biomass by 65 %, indicating a deterioration in seed viability under the influence of this wastewater. Development of the plant root system was 80 % less compared to control values. These data indicate the negative impact of wastewater on plant development, which is a serious signal of its potential toxicity and impact on living systems.

The study showed that compositions 2 and 3 containing wastewater taken after interaction with waste, demonstrated a high efficiency compared to composition 1 containing untreated wastewater.

The number of germinated seeds in these solutions was similar to the control sample and amounted to 100 %.

In plants germinated in composition 2 (containing iron-magnesium production waste 10 g/l), relative length of the root system was 45.74 %, which is 2.2 times greater than in plants from composition 1. However, this length of roots was 2.1 times less than that of plants from composition 3 which included water prepared first using iron-magnesium production waste, and then waste from humic acids production.

When analysing the elemental composition of plants, it is important to note a decrease in the content of all studied metals in samples 2 and 3 compared to untreated wastewater, with the exception of magnesium and potassium. This indicates a potential impact of wastewater treatment process using waste on reducing concentrations of different metals in plants. It is potassium and magnesium that play an important role in vital activity of plants, especially in conditions of technogenically altered or polluted ecosystems. These elements are macronutrients and are necessary for plants in relatively large amounts compared to micronutrients [39, 40].

Potassium plays the key role in the process of photosynthesis, activates many enzymes, participates in regulation of plant water balance, and also affects plant resistance to stress conditions such as drought and frost. On the other hand, magnesium is no less important for plants, since it plays an important role in photosynthesis and chlorophyll synthesis, participates in metabolic processes, in the absorption and transport of phosphorus, which is important for ensuring plant growth and development [39, 40].

In conditions of anthropogenic influence on the environment, where plants can encounter unfavourable conditions, sufficient levels of potassium and magnesium in soil and their availability become critical for ensuring normal growth and development, and, therefore, is essential for the renewal and maintenance balance in such ecosystems, although it should be clarified that purified wastewater does not have any stimulating effect on *Lepidium sativum L.* plants [39, 40].

Also, iron is one of the most important and indispensable micronutrients for the plants. Insolubility of iron salts and difficulty of their transition into a soluble form create problems for the absorption of iron ions by plant roots. Iron is an important element for many reactions and processes in plants, and its deficiency or excess can negatively affect their development and productivity [41]. In wastewater samples from the Kaban-1 deposit (compositions 1 and 2), iron concentration is much higher than in other samples including compositions treated with waste.

It is especially important that cadmium was not found in composition 3, which indicates a possible decrease in cadmium availability for the plants when using the treatment process including iron-magnesium production waste and the HPW.

In the study of chemical composition of germinated watercress seeds, it was found that the plants exposed to untreated wastewater absorbed more micronutrients, such as iron, zinc, copper, and cadmium, compared to other samples. Since most plants have the root type of metal accumulation, the accumulation process, most likely, occurred in the underground part [42-44]. The detected high concentrations of iron, zinc, copper, and cadmium appeared to be toxic for plants, and this affected the characteristics of the germinated seeds, root length and total biomass.

In addition, in samples 1chlorosis was recorded associated with a lack of chlorophyll, which led to a change in colour (yellowing) of plants. Low pH level (2.33) in samples 1 also affected the availability of magnesium and potassium macronutrients which are essential for healthy plant growth [45, 46]. Macronutrients including nitrogen, potassium, calcium, magnesium, and sulfur are known to be better absorbed at pH values between 6.0 and 6.5. Micronutrients become less available to plants at higher alkaline pH values exceeding 7.0 [45, 46].

Potassium and magnesium micronutrients, being antagonists, compete with each other in the processes of assimilation of nutrients by plants [47]. In samples with low pH level plants do not receive enough essential macronutrients, such as potassium and magnesium, but accumulate an excess of iron, zinc, cadmium, and copper micronutrients. This imbalance has a negative effect on plant growth and development.

Therefore, maintaining the optimal soil pH level is the key to preventing chlorosis and ensuring healthy plant growth. The results obtained indicate a possibility of using wastewater purified by a complex of iron-magnesium production waste and the HPW of wastewater for irrigation of biological plant resources when initiating the processes of ecological rehabilitation of ecosystems disturbed by development of copper pyrite deposits.

Conclusion. In this study, the optimal conditions were identified for the efficient use of the HPW in afterpurification processes of pre-treated underspoil water of the Kaban-1 deposit from copper, cadmium, and zinc ions. The most efficient parameters include the following:

- Contact time ranging from 120 to 180 min, indicating the importance of prolonged exposure to attain the maximum efficiency of the purification process. Long contact time allows intensifying the interaction between waste and wastewater, which promotes a more complete removal of metal ions from solution.
- Waste dosage of 10 g/l indicates the optimal amount of waste to achieve the desired purification effect. This parameter affects the degree of interaction between waste and solution as well as the overall efficiency of the process.

Using waste, a neutral pH value (7.03) was attained compared to the initial value (5.95). However, waste appeared to be inefficient for the afterpurification of natural wastewater from magnesium ions, and the process of releasing Mg^{2+} into solution was also recorded. Purified wastewater, despite a significant amount of magnesium, does not have a negative effect on the growth and development of *Lepidium sativum L.* plants; however, no stimulating effect was recorded.

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Iron ore tailings as a raw material for Fe-Al coagulant production

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Abstract. The paper presents the results of experimental research into the recovery of Fe-Al coagulant from iron ore tailings (IOTs). The variables investigated in the laboratory tests included sulphuric acid concentration, temperature, leaching time, solid/liquid phase ratio (S:L) and the presence of stirring. The experiment determined the composition of the coagulant and the solid residue after leaching. The maximum iron content in the solution after leaching was obtained using 40 % H_2SO_4 at a temperature of 100 °C (or with stirring at 75 °C) and a contact time of 60 minutes. In this case, the iron yield was at the level of 25 % of the total content in the iron ore tailings. Chemical analysis of the solution obtained after leaching showed Fe and Al sulphate contents of 11 and 2 % respectively. In the next step, the efficiency of the coagulant was evaluated on model solutions of colour. The experimental results showed that the coagulant obtained from the iron ore tailings can be used for wastewater treatment in a wide pH range from 4 to 12 pH units. The solid residue after leaching is a fine-grained powder rich in silica, which can potentially be used as an artificial raw material in the construction industry. The research carried out in this thesis has shown that the extraction of coagulants from iron ore tailings can be considered as a way to extend the production chain of iron ore mining and to minimise the amount of tailings to be stored in tailing ponds. The technical solution presented in this work allows to comprehensively solve the problem of environmental protection by creating new target products for wastewater treatment from IOTs.

***Keywords*:** coagulant; waste disposal; wastewater treatment; iron ore tailings; acid leaching; sulfuric acid

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Introduction. The storage of mineral processing wastes in tailings ponds has been a significant environmental problem for the mining and processing industries worldwide for many years [1]. The mineral resource sector in the Russian Federation is no exception [2-4]. Despite continuous improvements in iron ore processing technologies [5], the increase in iron ore production has led to a corresponding increase in waste generation. According to the Federal Service for Supervision of Natural Resources, by the end of 2023, approximately 2.5 billion tonnes of iron ore tailings[1] will have accumulated in man-made massifs across the Russian Federation. Meanwhile, only about 15 %[1] of the newly generated IOTs each year is destined for recycling. Therefore, the development of ecologically and economically efficient technologies for the secondary processing of iron ore tailings is becoming increasingly important.

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[1] Rosprirodnadzor. Information on formation, treatment, utilisation, disposal, neutralisation, disposal of production and consumption wastes. URL: rpn.gov.ru (accessed 13.05.2024).

According to «The scientific and technological forecast up to the year 2030», one of the main directions of current state policy is the integrated development of mineral resources and technogenic raw materials on an industrial scale. “The Strategy for the Development of the Industry of Treatment, Utilisation and Neutralisation of Production and Consumption Waste for the Period up to 2030” states that ferrous metallurgy enterprises are among the main types of industrial facilities that generate waste and use processed secondary raw materials in production. Consequently, ferrous metallurgy enterprises are fundamental to the creation of an up-dated system focused on the integration of industrial waste into the economic cycle. The expected result of this policy will be the rational use of the mineral resource base.

In order to address the challenges of iron ore tailings generation and storage, numerous researches have been carried out by scientists worldwide, focusing on the disposal and multipurpose use of IOTs. Both Russian and foreign scientists have explored the potential applications of iron ore tailings in various fields, including fertiliser production [6-8]; wastewater treatment reagents [9-11]; production of building materials – cement [12-14], concrete [15-17], materials for underground construction [15, 18, 19]; road construction [20-22].

However, most of these developments have not been applied in practice, despite the importance of addressing the environmental problems caused by operating and decommissioned technogenic facilities. This is mainly because the processing of IOTs in a market economy must be both efficient and profitable. This can only be achieved by developing zero-waste technologies that extract valuable constituents and utilise tailings to produce marketable products. The main valuable component in iron ore tailings is iron itself, due to the shortcomings of existing technologies. Currently, modern iron extraction technologies are not widely used in our country due to lack of interest from both iron ore concentrate producers and consumers.

A review of the aforementioned utilisation methods for ferrous tailings indicates that existing scientific work has not adequately explored the potential for recovering coagulants from IOTs. Coagulation is a crucial process in water treatment and industrial wastewater purification [23]. The reagents used in this process are generally divided into aluminium-based and iron-based coagulants [24]. Iron (III) salts have several advantages over aluminium salts, including higher coagulation efficiency at low water temperatures, operation over a wide pH range, and a high sedimentation rate of coagulated particles. However, over-dosage of iron-based coagulants can result in iron ions remaining in the treated water. This problem can be mitigated by adding aluminium salts either simultaneously or sequentially. Thus, mixed coagulants containing both aluminium and iron compounds provide optimal water treatment results. Analysis of the composition of tailings from various deposits, according to open sources, shows that aluminium is present in almost all such wastes at levels of a few percent [25-27]. Consequently, iron ore tailings have the potential to be used as a raw material for the production of high-performance coagulants.

Coagulants play a critical role in wastewater treatment worldwide, making the search for alternative materials for their production, including the use of iron ore tailings, an urgent task. Currently, methods for the production of iron-based coagulants from materials such as rolling mill scale, electric arc furnace dust and ferrous metallurgy slag are well known in academia and industry [28-30]. The objective of this study was to produce a Fe-Al coagulant from iron ore tailings and to evaluate its efficiency and environmental safety. To achieve this goal, a series of experimental studies were conducted at the Scientific Centre for the Assessment of Technogenic Transformation of Ecosystems, located at the Empress Catherine II Saint Petersburg Mining University.

Methods. *Study of the composition and properties of iron ore tailings*. In order to study the composition and properties of iron ore tailings, a composite sample was collected from the tailings dump of a mining and processing plant located within the iron ore basin of the Kursk Magnetic Anomaly. Sampling was carried out during the 2022 field season in accordance with the methodological recommendations[2].

In the first phase of the laboratory studies, the chemical composition of the iron ore tailings was determined by X-ray fluorescence (XRF) using the Shimadzu XRF-1800 [31]. Based on the chemical composition data, the phase composition was investigated by X-ray diffraction using the Shimadzu XRD-6000 with high temperature chamber NA1001. The phases were searched using the JCPDS international file system [31]. The granulometric analysis of the tails was carried out by laser diffraction on the Horiba LA-950 particle size analyser [32]. For a comprehensive assessment of the studied iron ore tails, the grain morphology was also studied using a JEOL JSM-7001F scanning electron microscope [33].

Obtaining a coagulant using sulfuric acid. At present, the majority of iron-containing coagulants used in industry are produced on the basis of iron chloride and iron sulphate. Considering the disadvantages of hydrochloric acid, such as high volatility, vapour toxicity and cost, in this study it was decided to focus on the leaching process using sulphuric acid. However, despite the aforementioned drawbacks, the production of iron chloride as a coagulant for the purification wastewater from iron ore tailings shows promising prospects and will be further explored by the authors in subsequent research.

The leaching process of iron ore tailings was investigated in laboratory conditions, where various factors were successively studied: acid concentration, temperature, contact time, solid-liquid phase ratio (S:L), and the presence of forced stirring. Each experiment was repeated three times to ensure statistical reliability and the final results presented in the following section are reported as averages.

Theoretical calculations were carried out to determine the amount of sulphuric acid required to dis-solve the iron present in the tailings studied, based on their chemical and phase composition and using the reaction equation:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2\,(SO_4)_3 + 3H_2O.$$

For example, the theoretical specific consumption of 30 % sulphuric acid to leach all the iron con-tained in the IOTs is 1 cm^3/g, corresponding to an S:L ratio of 1:1. However, not all of the iron in the IOTs studied may be in an accessible and reactive form when in contact with 30 % sulphuric acid. Therefore, experiments were carried out to determine the optimum concentration of sulphuric acid for maximum extraction of iron and aluminium from the IOTs, in the range of their mass concentrations from 20 to 50 %, with an S:L ratio of 1:1. The contact time was 3 hours, without heating or stirring (t = 20 ºC).

Having selected the optimum concentration of sulphuric acid, the next stage of laboratory research focused on investigating the influence of reaction mixture temperature on the yield of iron and aluminium. Temperature is one of the key parameters in leaching reactions and significantly affects the extraction of components [34]. During the experiment, the reaction temperature ranged from 20 to 100 °C, while the contact time and phase ratio were chosen similarly to the previous experiment.

To determine the minimum contact time, leaching experiments were carried out for 15, 30, 60, 120 and 180 min. The acid concentration and temperature of the reaction mixture were set based on the results of previous experiments, while the S:L ratio was kept constant at 1:1.

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[2] PNDF 12.1:2:2:2:2.3:3.2-03 refers to the Russian standard “Methodological Recommendations for Sampling Soil, Grounds, Bottom Sediments, Sludge, Industrial Wastewater Sediments, Production and Consumption Waste”. URL: https://library-full.nadzor-info.ru/doc/37518 (accessed 13.05.2024).

In addition, a laboratory experiment was carried out with solid-liquid phase ratios of 1:1, 1:3 and 1:5 to confirm the empirically selected optimum phase ratio.

The final external factor investigated under laboratory conditions was the presence of stirring during the leaching process. Stirring significantly increases the surface area of solid particles in contact with the reagent, thereby improving the efficiency of the leaching process. Stirring was performed using an IKA KS 3000 i control laboratory shaker-incubator at a speed of 150 rpm. The experiment was carried out within a temperature range of 20 to 75 °C.

At the end of each leaching experiment, the solution was filtered through a paper filter to separate the unreacted portion of the IOTs, and the filtrate was subjected to quantitative chemical analysis using inductively coupled plasma atomic emission spectrometry on a Shimadzu ICPE-9000 instrument. The aim of this analysis was to evaluate the content of the desired components in the solution and to determine the leaching efficiency, which was determined by comparing the iron and aluminium content transferred to the solution with their content in the IOTs.

Coagulant efficiency evaluation. To test the performance of the solution after leaching, a sample obtained under the optimum leaching parameters established in the previous experimental stages was used as a coagulant.

The evaluation of the coagulation properties of the obtained Fe-Al coagulant was carried out in ac-cordance with GOST R 51642-2000 “Coagulants for domestic drinking water supply. General requirements and method for determining efficiency”. For this purpose, a model colour solution based on sodium humate was prepared. A 50 g of sodium humate was taken and placed in a 2 dm^3 flask, to which 1 dm^3 of distilled water at a temperature of 40 °C was added. The solution obtained was stirred and kept for 24 hours in a flask with a closed stopper, then filtered through a paper filter. The solution was then diluted with distilled water to obtain a colour equal to 50° on the standard chromaticity scale according to GOST 3351-74 “Drinking water. Methods for determining taste, odor, color, and turbidity”. The chromaticity of the model solution was determined by the spectrophotometric method using the DR5000 from HACH-LANGE. The solution obtained was used as a model colour solution to determine the effectiveness of the coagulant. In accordance with GOST R 51642-2000, the dose of coagulant that reduces the chromaticity from 50 to 20° is considered the minimum dose for the model colour solution.

To determine the minimum dose of coagulant, 1.0 dm^3 of the prepared model chromaticity solution was placed in beakers, stirrers were lowered into the beakers and the stirring speed was set at 140 rpm. The samples were thermostated until the suspension reached the test temperature of (20±1) °C. Then the working solution of the coagulant was dosed into them in the range of mass concentrations from 3 to 6 mg/dm^3 with a step of 0.5 mg/dm^3 in terms of the basic substance (ferric oxide (III). The working solution of the coagulant was prepared by adding an aliquot of the coagulant obtained after leaching, containing 1.0 g of the main substance in terms of ferric oxide (III), to a 1 dm^3 flask and making up the volume with distilled water. The model solution was stirred with the working coagulant solution for 3 min, after which the stirring speed was automatically reduced to 40 rpm and the contacting lasted another 15 min. The solution was then allowed to stand for 30 min, filtered and colour measured.

As the efficiency of the coagulant depends significantly on the pH of the treated water, the pH range in which the coagulant obtained was most efficient was determined. For this purpose, 50 cm^3 of model colour solution was poured into five glass beakers. An equal dose of coagulant (6 mg/dm^3) was then added to each beaker and the pH of the solution was adjusted from 1 to 12 pH units in steps of 1 pH unit using 0.1N NaOH and HCl solutions. The solutions were then stirred for 3 min and filtered. The filtrates were analysed for colour.

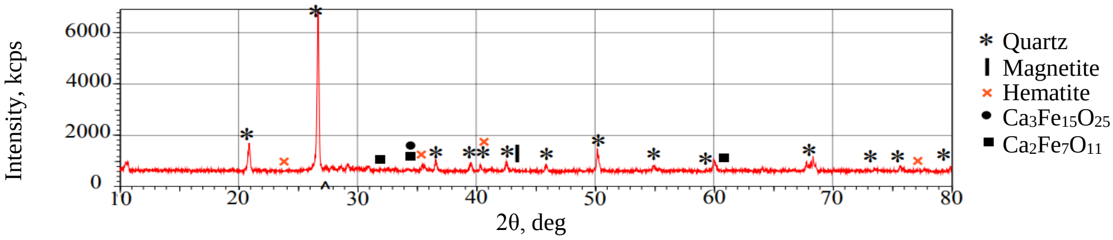

Fig.1. X-ray phase analysis of iron ore tailings

Environmental Safety Assessment of the Coagulant. In order to assess the environmental safety of the coagulant obtained, the qualitative and quantitative identification of matrix and impurity components in the coagulant composition was performed using atomic emission spectrometry on a Shimadzu ICPE-9000. Qualitative and quantitative identification of matrix and impurity components in the coagulant composition was performed by atomic emission spectrometry on the ICPE-9000 of Shimadzu company. Secondary contamination of treated water as a result of coagulant use was then evaluated by chemical analysis of the model colour solution before and after coagulant use. The model solutions were also analysed by atomic emission spectrometry. The results obtained were interpreted by comparing the concentrations of the constituents with the approved water quality standards.

Study of the solid precipitate after leaching. After the leaching products were filtered, a solid precipitate remained on the filter, representing the unreacted portion of the IOTs. The sludge on the filter was washed with distilled water and then air dried. In order to assess the prospects of its further use in industry as a technogenic material, its chemical and particle size distribution was studied by the methods used in the work on the analysis of initial samples of iron ore tailings and described above.

Results discussion. The chemical composition of iron ore tailings according to RFA data: SiO_2 – 69.0; Fe_2O_3 – 18.0; MgO – 4,1; CaO – 3.2; Al_2O_3 – 2.0; K_2O – 0.73; Na_2O – 0.62; P_2O_5 – 0.21; MnO – 0.089; TiO_2 – 0.051; LOI – 2.0 wt.%. According to the results of the X-ray fluorescence analysis, the studied IOTs should be classified as high-silicon type, which is one of the most common types of iron ore tailings [35]. In addition, a high iron content and the presence of aluminium at the level of 2 % were noted in the composition, confirming the theoretical studies carried out on the prospects of using processing waste as a raw material for the production of a mixed coagulant.

According to the results of the X-ray phase analysis, as shown in Fig.1, the mineral composition of the IOTs consists mainly of quartz (SiO_2), with traces of magnetite (Fe_3O_4), hematite (Fe_2O_3) and polymorphic modifications of complex calcium and iron oxide (iron of different valences). The intensity of the diffraction peaks attributed to quartz is significantly higher than those of the other minerals, indicating that quartz is the predominant mineral. This interpretation of the diffractogram is supported by the chemical composition of the sample.

The chemical and phase composition results obtained formed the basis for experimental studies on the production of a Fe-Al coagulant.

The analysis of the particle size distribution showed that the dominant fraction in the IOTs composition is 0.5-1 mm (Table 1). According to the document "Recommendations on the design of tailings facilities of metallurgical industry enterprises", the processing waste in question should be classified as medium-grained. Additional grinding of the IOTs to intensify the leaching process was not carried out.

Table 1

Particle size distribution of iron ore tailings

Indicator	Fraction, mm							
	< 0.005	0.005-0.01	0.01-0.05	0.05-0.1	0.1-0.25	0.25-0.5	0.5-1	1-3
Fraction yield, %	2.41	4.45	13.5	9.98	9.6	18.4	30.1	11.5
Total yield, %	2.41	6.87	20.4	30.3	39.9	58.4	88.5	100

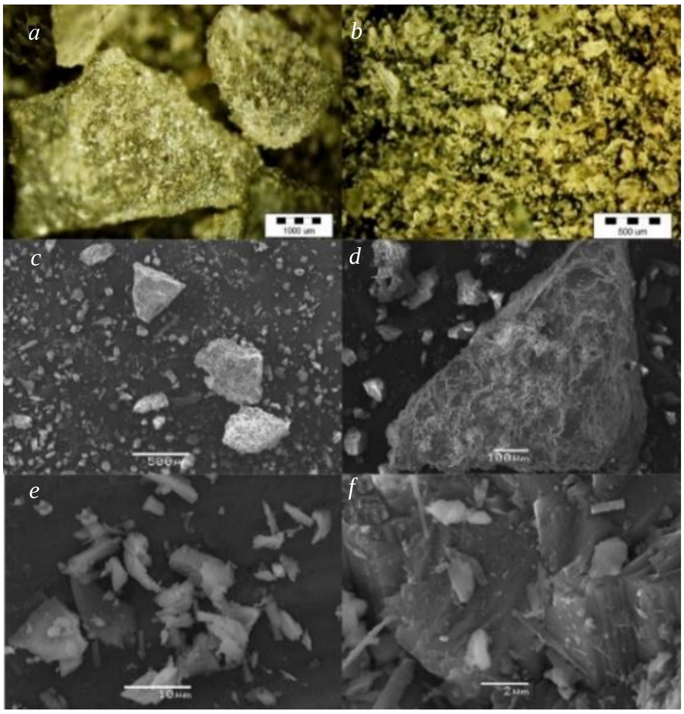

Fig.2. Micrographs of iron ore tailings obtained by scanning electron microscopy

Examination of the sample by scanning electron microscopy (Fig. 2) revealed several noteworthy features in the morphology of the samples. In particular, the particles exhibit angular and irregular shapes (*a*, *d*), while closer inspection reveals protrusions and an uneven surface (*b*, *d*, *e*, *f*). These characteristics contribute to an increase in the specific surface area of the tailings particles and consequently significantly affect the leaching process.

A comprehensive study of the composition of the tailings sample investigated has shown that, un-der suitably selected leaching conditions, a solution suitable for the preparation of a coagulant for wastewater treatment can be obtained.

Experimental investigations to determine the optimum parameters for leaching the desired constit-uents from the IOTs have shown that the highest percentage of iron and aluminium extraction, all else being equal, is observed when sulphuric acid with a mass concentration of 40 % is used (Fig.3).

Investigation of the next key factor, leaching temperature, revealed that the maximum yield of iron and aluminium in solution is achieved at a moderate temperature of 100 °C (Fig.4). Furthermore, increasing the temperature from 75 to 100 °C results in a significant increase, with the efficiency of iron leaching increasing by 10.6 %. Further temperature escalation within the experiment was not pursued due to the proximity to the boiling point of sulphuric acid (113.9 °C).

The results of the experiment to determine the minimum contact time required for the maximum release of iron and aluminium into solution showed a stabilisation of the results after 60 min (Fig.5).

Increasing the liquid phase did not affect the leaching efficiency, as the iron yield remained at 24-25 % at all liquid/solid (S:L) ratios investigated (1:1, 1:3 and 1:5).

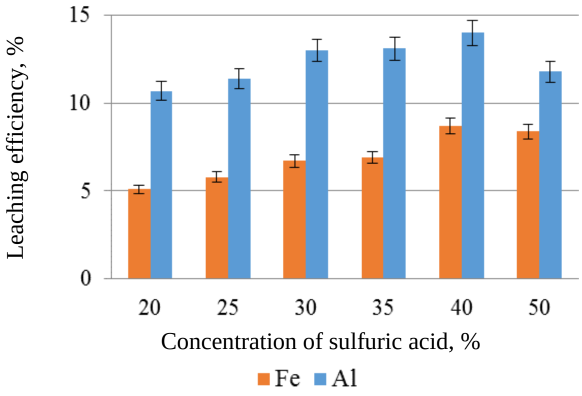

Fig.3. Efficiency of leaching iron and aluminium from IOTs as a function of the sulphuric acid concentration, all other things being equal (leaching time 3 h, solution temperature 20 °C, S:L= 1:1, without stirring)

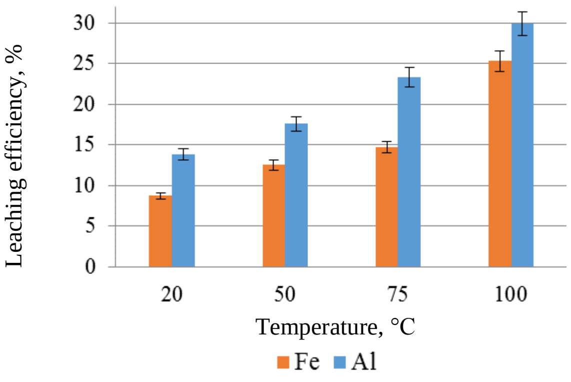

Fig.4. Efficiency of iron and aluminum leaching from the IOTs as a function of temperature, other conditions being equal (sulfuric acid concentration 40 wt.%, leaching time 3 h, S:L 1:1, without stirring)

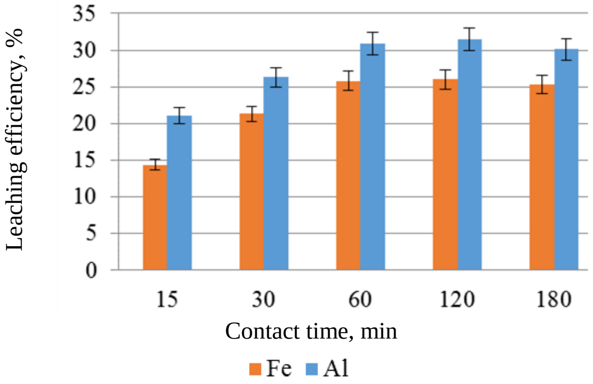

Fig.5. Efficiency of iron and aluminum leaching from the IOTs as a function of contact time under other equal conditions (sulfuric acid concentration 40 wt.%, temperature 100 °C, S:L ratio 1:1, without stirring)

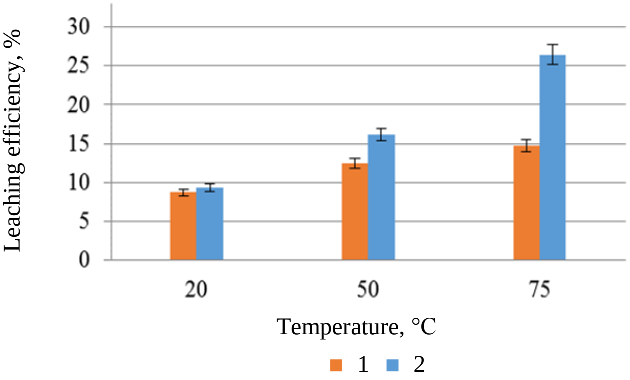

Fig.6. Efficiency of iron leaching from IOTs without stirring (1) and with forced stirring (2) of contacting media at different temperatures (sulfuric acid concentration 40 wt.%, S:L ratio 1:1, leaching time 3 h)

Finally, the effect of forced stirring of the contacting media was investigated. Figure 6 graphically shows a comparison of the results obtained in the temperature range of 20 to 75 °C with and without stirring. It can be seen from the figure that forced mixing increased the percentage of extracted iron by almost 2 times at a temperature of 75 °C.

Laboratory research has shown that maximum leaching efficiency is achieved using sulphuric acid at a concentration of 40 wt.%. The minimum contact time at a temperature of 100 °C was 60 min. A comparative evaluation of the leaching efficiency at different S:L ratios showed that this parameter had no influence on the transition of the desired components into solution. Therefore, the S:L ratio of 1:1 was empirically determined as the minimum for media contact and the establishment of reaction conditions. It was also found that mixing the mixture significantly increases the output of components into solution, with the difference becoming substantial as the temperature increases. For example, at a reaction mixture temperature of 75 °C and with forced mixing, a solution was obtained with an iron content comparable to that obtained in the experiment at a temperature of 100 °C without mixing. Due to technical limitations, forced mixing experiments at higher temperatures have not been carried out in laboratory conditions.

According to the results of quantitative chemical analysis, the test sample contains 11 and 2 % of Fe and Al in the form of sulphates. During the test to evaluate the coagulation properties, it was found that the colour of the solution begins to decrease at a working solution dose of 4.5 mg/dm^3. The graphical representation of the results of the change in colour of the model solution as a function of the dose of coagulant added is shown in Fig.7. From Fig.7 it can be seen that the minimum dose of coagulant according to GOST R 51642-200055 is 5 mg/dm^3 of the working coagulant solution for a model solution with a colour intensity of 50°. To prepare a working solution with such a concentration, 0.12 cm^3 of the initial coagulant solution is required per 1 dm^3 of purified water.

The coagulant obtained showed efficacy over a wide pH range from 4 to 12 pH units. It showed the highest efficiency at pH = 7,

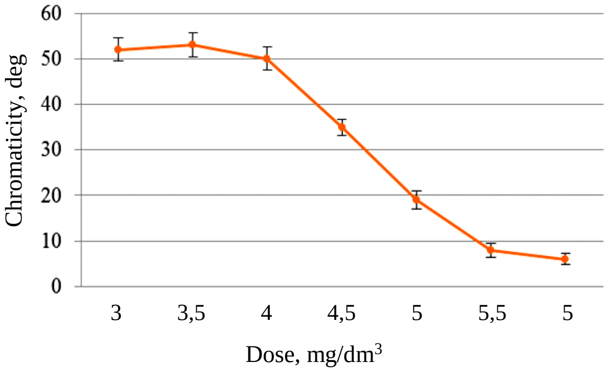

Fig.7. Determination of the minimum coagulant dose in a model solution of colour

where a decrease in colour intensity from 50 to 6 degrees was observed. Based on the results of experimental studies, the invention was patented in the Russian Federation [36].

Having established the functionality of the coagulant, its environmental safety was assessed by studying the matrix and impurity composition: matrix elements Mg – 6800; K – 1970; P – 801; Mn – 210; Na – 81; Ca – 57; impurity elements Zn – 7.0; V – 6.9; Cr – 4.8; Cu – 3.2; Sr – 1.3; Ba – 0.8 mg/dm^3.

As can be seen, the coagulant contains heavy metals such as Mn, Zn, V, Cr and Cu. Therefore, an assessment of the secondary contamination of the treated water as a result of the use of the working coagulant solution was carried out. The results of the quantitative analysis of the composition of the model colour solution before and after the addition of the minimum dose of coagulant (5 mg/dm^3) are presented in Table 2.

Table 2

Chemical composition of the model colour solution before and after water treatment, mg/dm³

Element	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	SO_4^{2-}	Sr	Zn
Before treatment	0.022	0.003	1.36	< 0.001	0.047	1.25	0.2	0.002	0.8	1.0	0.003	< 0.005
After treatment	0.022	0.001	2.03	< 0.001	0.052	1.89	0.7	0.009	20.7	50.7	0.014	< 0.005
$PCL_{b.s.}$[3]	0.5	0.1	–	1.0	0.3	–	–	0.1	–	–	7.0	5.0
$PCL_{f.s.}$[4]	0.04	0.74	180	0.001	0.1	50	40	0.01	120	100	0.4	0.01

From Table 2 it can be seen that several components are introduced into the solution after coagulation process. There is a significant increase in the content of Na, Sr and SO_4^{2-}. However, the recorded concentrations remain below maximum permissible values for all water use categories, indicating the acceptability of using the coagulant obtained as a reagent for wastewater treatment.

The final stage of the laboratory investigations was to examine the composition of the residue after leaching. Chemical analysis of the solid residue after leaching (SiO_2 – 79.7; Fe_2O_3 – 10.5; MgO – 2.7; CaO – 2.5; Al_2O_3 – 1.5; K_2O – 0.45; Na_2O – 0.43; P_2O_5 – 0.059; MnO – 0.048; TiO_2 – 0.013; LOI – 2.1 %) showed a significant increase in the proportion of silica compared to the original IOTs. There was also a decrease in the amount of impurities.

Assessing the changes in the particle size distribution of the IOTs before and after leaching, a significant reduction in particle size can be concluded (Table 3). When analysing the content of the fractions, it is worth noting the absence of the largest fraction (1-3 mm) in the precipitate after leaching. In addition, the content of the 0.5-1 mm fraction, which was predominant in the original IOTs sample, has significantly decreased. This is one of the key points to be considered when discussing possible options for the utilisation of the post-leaching precipitate.

Table 3

Particle size distribution of the solid residue after leaching

Indicator	Fraction, mm							
	< 0.005	0.005-0.01	0.01-0.05	0.05-0.1	0.1-0.25	0.25-0.5	0.5-1	1-3
Fraction yield, %	2.19	4.32	27.3	24.1	21.4	13.3	7.47	–
Total yield, %	2.19	6.50	33.8	57.9	79.2	92.5	100	–

In addition, the second factor limiting the choice of residue utilisation may be the iron content of 10.5 %. However, a study by the authors [37-39] has shown that the use of technogenic material

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[3] SanPiN 1.2.3685-21 "Hygienic standards and requirements to ensure safety and/or harmlessness of environmental factors for humans". URL: https://base.garant.ru/406508041/ (accessed 13.05.2024).

[4] Order of the Ministry of Agriculture of Russia dated December 13, 2016 N 552 "On approval of water quality standards for water bodies of fishery significance, including standards of maximum permissible concentrations of harmful substances in the waters of water bodies of fishery significance" (registered by the Ministry of Justice of the Russian Federation on 13.01.2017 N 45203).

with a higher iron content, including fine-grained material, in the construction industry is possible if additional laboratory studies are carried out and a formulation is developed on a case-by-case basis. The evaluation of the chemical composition and particle size distribution indicates a high potential for the use of leachate residue as artificial sand.

Conclusion. The continuous development of iron metallurgy, as well as the gradual transition to the development of low-grade ore reserves, leads to an increase in the amount of processing waste each year. For this reason, iron ore tailings as a secondary resource have recently attracted considerable attention from researchers, including the authors of this paper.

In this work, the composition and properties of iron ore tailings were studied on the example of one of the objects of the mineral raw materials complex located in the Kursk Magnetic Anomaly, which indicated the prospects and formed the basis for the development of the formulation of Fe-Al coagulant for wastewater treatment. Thus, the iron ore tailings were characterised by high iron content (18 % in terms of Fe_2O_3), represented mainly by magnetite and hematite, aluminium content at the level of 2 % (in terms of Al_2O_3), high content of fine and medium particles, as well as complex particle morphology.

The laboratory studies allowed the determination of the optimum conditions for IOTs leaching to obtain a Fe-Al coagulant: sulphuric acid concentration 40 wt.%, Solution temperature 100 °C without stirring and 75 °C with forced stirring, leaching time 60 min, S:L ratio 1:1.

Tests of the coagulant for efficiency of its use in the process of wastewater treatment on a model colour solution showed a sufficient degree of purification at pH = 4-11. The maximum purification efficiency (88 %) was achieved at pH = 7. In the course of laboratory studies, the minimum dose of coagulant was also determined on the example of a model colour solution according to GOST R 51642-2000.

The assessment of the environmental safety of the use of Fe-Al coagulants showed that, despite the multi-component composition, including the presence of heavy metals, no secondary water pollution occurs due to active precipitation and co-precipitation of components in solution. The maximum increase in concentrations in the model solution after treatment was observed for Na, Sr and SO_4^{2-}, but the recorded values remained below the level of maximum permissible concentrations for all categories of water use.

A comprehensive study of the post-leach solid sludge allows us to recommend it as a potential raw material for the construction industry, subject to further testing of the material in a specialist construction laboratory.

The study has shown that the production of coagulants from iron ore tailings is a worthy alternative to known methods and has promising prospects as it can be considered as a way of extending the production chain of iron ore mining. In this case, the secondary use of IOT as a technogenic raw material will minimise the amount of waste to be stored in tailings ponds and increase the degree of treatment of discharged and recycled water both in the facilities of the mineral and raw materials complex and in other industries.

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Research article

Assessing the effectiveness of sewage sludge in the reclamation of disturbed areas in the Kola subarctic zone (a case study of a sand quarry)

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***Abstract*.** An assessment was made of the effectiveness of reclamation using sewage sludge for the accelerated formation of a stable erosion-proof vegetation cover on the unproductive anthropogenic soil of a sand quarry in the context of the Kola North. The experiment, launched in 2017, included three treatments: control – no treatment, experiment 1 – fragmentary (50 %) application of sewage sludge, experiment 2 – continuous application. In the sixth growing season, anthropogenic soil samples were examined, and measurements of CO_2 emissions were carried out. It was shown that the application of sewage sludge had a positive effect on the physicochemical and agrochemical properties of the soils: *in situ* pH and density decreased, hygroscopicity increased, available phosphorus and potassium increased. Significant differences ($p < 0.05$) were found between CO_2 emissions in the control and experimental treatments. The content of organic carbon in the control treatment was lower than in the experimental ones; under fragmentary application of sewage sludge, it was three times lower, and under continuous application, it was nine times lower. Significant ($p < 0.05$) differences in the content of carbon and nitrogen in cold and hot water extracts between control and treatment samples were found under continuous application of sewage sludge. At the same time, by calculating the C/N ratio, a very low level of nitrogen was found in the humus. The main factors behind the variability of the estimated parameters were identified – the treatment itself and the method of its application, the contribution of the treatment alone was 60 %, the contribution of the application method was 14 %. Taking into account the economic factors, fragmentary application of sewage sludge onto the anthropogenic sand quarry soil is recommended to support the establishment of a stable erosion-proof phytocenosis.

***Keywords*:** landscape; sand quarry; anthropogenic soil; ameliorant; sewage sludge; CO_2 emissions

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Introduction. Mining operations in Russia's Murmansk region involving open-pit mining of sand, crushed stone, block stone, and others mineral resources widely used in the construction and production of construction materials industry has led to the emergence of numerous small and large quarries. This approach optimizes the economics of the region's construction industry but involves a number of environmental problems associated with the emergence of new anthropogenic landscape forms with low biological productivity and distinct geomorphological, hydrophysical, and geochemical properties. The mineral reserves of Murmansk region include 68 deposits of sand and gravel mixture with estimated reserves of 92,690 thousand m^3 in categories A + B + C1, while the reserves under active development amount to 48,721 thousand m^3. [1]

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[1] Current state of the mineral resource base of the Murmansk region. URL: https://mpr.gov-murman.ru/activities/napravleniya/10.mineral/00.current/ (accessed 28.03.2024).

Quarry mining is in greatest demand close to urban areas, but lead to air pollution, soil disturbance, and upset surface and groundwater and biota balance, which also negatively affects human health [1-3].

In Russia, in accordance with the Law on Subsoil[2], upon completion of the development of a deposit in areas disturbed by mining operations, mandatory reclamation measures are required to prevent negative environmental impacts and bring the area to a condition suitable for further use. However, unproductive anthropogenic soils typical of former quarries are unsuitable for reclamation both in terms of physical properties and chemical composition (GOST 17.5.1.03-86) [4-6], especially in the harsh climatic conditions of the Far North. Reclamation is problematic without additional investment in expensive materials and fertilizers, therefore it is necessary to search and develop non-conventional, science-based methods adapted to the region's environment and economics involving the use of alternative ameliorants that improve the biogenicity of human-modified soils [7, 8].

In this context, the products of regional water and sewerage treatment facilities – sewage sludge (SS) – are of great relevance [9, 10]. Many Russian and international researchers are studying the possibilities of using SS as ameliorants to restore vegetation cover at tailings storage facilities of bauxite [11], copper [12, 13] and rare metal mines [14, 15]. The introduction of SS, characterized by a high content of organic matter and nutrients in bioavailable forms, helps to improve the edaphic factors of reclaimed soils [16-18]. However, the material needs to be carefully studied on a case-by-case basis due to the potential presence of heavy metals and pathogenic microorganisms [19].

The use of organic ameliorants for the establishment of erosion-proof phytocenoses on the sandy soils of quarries in the Arctic context without conventional land cultivation can help solve the dusting problem. A number of indicators should be studied – available forms of nutrients (nitrogen, phosphorus, potassium), organic carbon, dissolved organic matter, soil respiration (CO_2 emissions from the soil) – widely used to assess the state and productivity of the resulting ecosystems [20].

The purpose of this study is to assess the effectiveness of soil reclamation using SS for the accelerated establishment of stable erosion-proof vegetation cover in sand quarries. The practical goal of the research is to develop a cost-effective ecotechnology for reclaiming disturbed landscapes using an unconventional organomineral ameliorant that otherwise requires disposal.

Methods. *Description of experimental sites and experimental design*. In 2017, at the model site of a sand quarry operated by the regional water utility AO Apatityvodokanal, staff of the Federal Research Center KSC RAS laid out a small-plot field experiment on the establishment of erosion-proof grass cover by applying SS. The ameliorant was provided by the indicated utility. According to earlier studies, SS of AO Apatityvodokanal was considered waste of hazard class 5 fully compliant with the requirements of GOST R 54534-2011 for SS when used as engineered soils for biological or engineering reclamation (Table 1) [8, 21, 22]. The content of organic matter was 62 %, of potassium 0.38 %. The approximate age of the applied SS was 3 to 5 years of storage in aeration tanks.

The experiment was carried out on 18 plots measuring 1 m^2 each, laid at a distance of 0.5 m from each other. The experimental design included three treatments ($n = 6$): control plot (no SS applied), experimental treatment 1 – fragmentary application of SS (50 % of the area – pointwise, in a checkerboard pattern on each of the plots), experimental treatment 2 – continuous application of SS (100 % of the area). The thickness of the applied SS layer was about 5 cm. The SS had a creamy texture, eliminating the possibility of sediment spreading beyond the treatment area. The humidity of the

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[2] Law of the Russian Federation "On Subsoil" dated February 21, 1992 N 2395-1. Article 22. Basic rights and obligations of the subsoil user. URL: https://www.consultant.ru/document/cons_doc_LAW_343/ed644f2f2ff8ea426789b6895057ff6ddd4807d3/ (accessed 28.03.2024).

applied material was 95-97 %. A grass seed mixture was used as seed material, including zoned seeds of cereal and legume plant species. During the first three years, the quality of the established phytocenoses was assessed annually: height of plants, projected area of cover, density of the grass cover, above-ground phytomass, thickness of the grass turf, increase in plant biodiversity in the established phytocenoses, and later, photosynthetic efficiency [8, 21, 22]. Condition of vegetation in the experimental plots from 2019 to 2023 is presented in Fig.1.

Table 1

Comparative analysis of the chemical composition of the SS of AO Apatityvodokanal compared to GOST R 54534-2011

Parameter	SS	Terms of use	
		Technical reclamation	Biological remediation
Environmental hazard class	V	IV, V	IV, V
Pb, mg/kg	< 30	1000	500
Zn, mg/kg	186	7000	3500
Ni, mg/kg	< 30	800	400
Cu, mg/kg	< 30	1500	750
pH_{KCl}	5.50	5.0-8.5	5.0-8.5
N_{total}, %	0.19	Not standardized	0.5
P_{total}, %	0.02	Not standardized	1.5

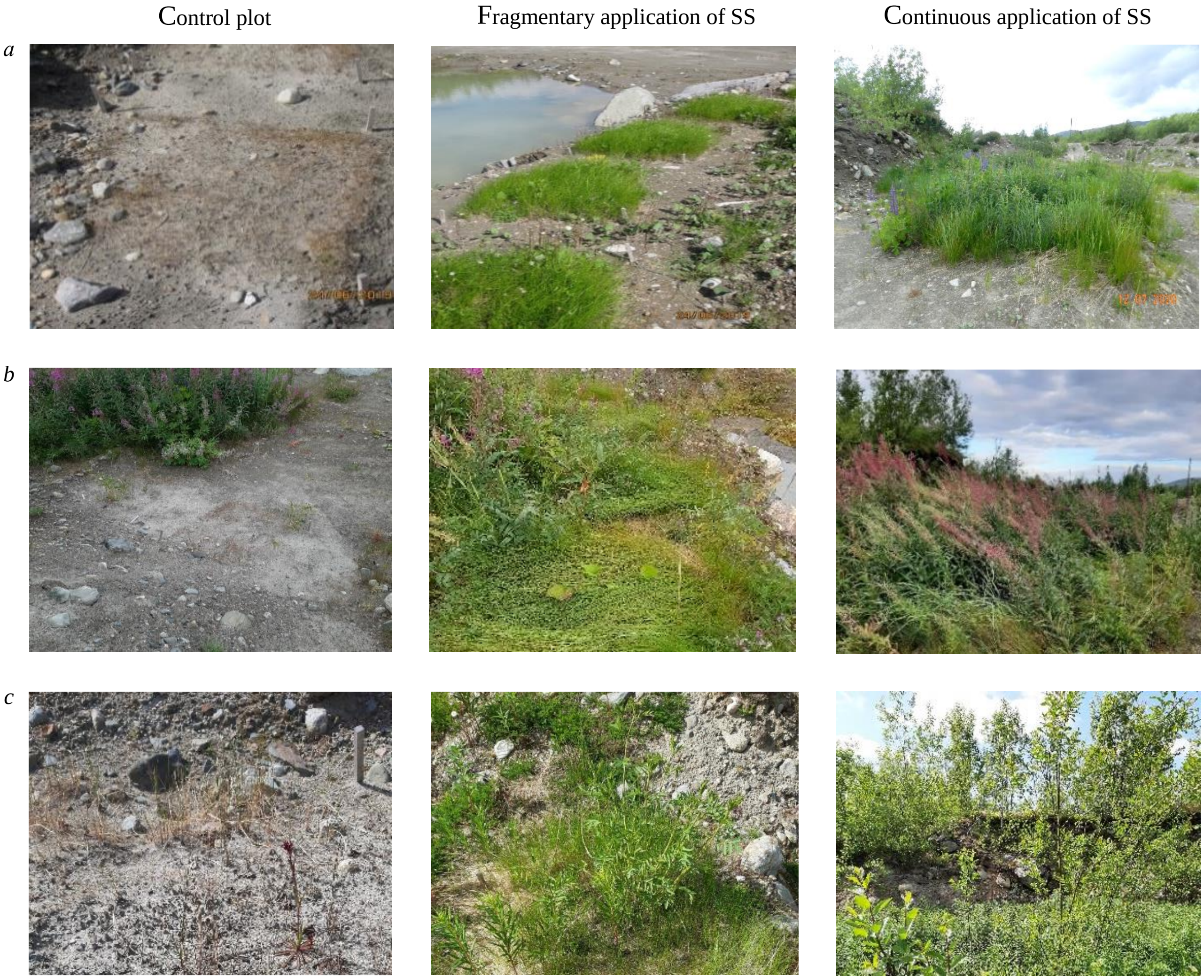

Fig.1. State of vegetation on experimental plots in 2019 (*a*), 2020 (*b*) and 2023 (*c*)

Sampling and analysis. Samples of soil and anthropogenic soils at the experimental site in the quarry were taken in the sixth growing season using a cutting ring with a diameter of 10 cm and a height of 5 cm. Samples were taken one at a time in each sampling round, i.e. for each treatment, six samples were collected, $n = 6$. Soil density was calculated as the ratio of the dry mass of the sample to the volume of the sampler.

Laboratory ion meter I-160MI fitted with glass laboratory electrode ES-10603 and reference electrode ESr-10103 was used to measure the pH of the aqueous and salt (KCl) extracts. The extract for measuring pH_{H_2O} was prepared at a solid to liquid ratio (S : L) of 1 : 5, stirred for three minutes, settled for five minutes in accordance with GOST 26423-85.

The extract for measuring pH_{KCl} was prepared at an S : L ratio of 1 : 25, stirred in a laboratory shaker for one hour in accordance with GOST 26490-85. The determination of the hygroscopicity coefficient of the samples was carried out at the Shared Resource Center, INEP KSC RAS, in accordance with GOST 28268-89.

Mobile phosphorus and exchangeable potassium were determined using the Kirsanov method as modified by TsINAO (GOST P 54650-2011). 0.2 N HCl solution was added to the soil sample (S : L 1 : 5), the mixture was stirred in a laboratory shaker for 15 minutes, then filtered through a blue ribbon paper filter. The resulting solutions were analyzed at the Shared Resource Center, INEP KSC RAS, using atomic absorption spectrometry (atomic absorption spectrometer Quantum-2mt) and photometry (photoelectric photometer KFK 3-01).

Organic carbon in solid samples was determined using the Tyurin method (GOST 26213-91). The content of labile forms of carbon and nitrogen was analyzed after extraction with cold and hot water [23]. Extraction with cold water was carried out at room temperature (distilled water as extractant, S : L ratio 1 : 10, extraction time 30 min), the solutions were centrifuged (universal laboratory centrifuge Dlab DM0636, 3500 rpm, 30 min) and filtered through a Vladipor membrane filter with a pore size of 0.45 μm. For hot water extraction, a fresh portion of distilled water was added to the remaining solid phase and kept in a thermostat at 80 °C for 16 h. The resulting extracts were centrifuged and filtered as described. The concentrations of nitrogen and carbon in the resulting filtrates were determined using an elemental composition analyzer Topaz NC.

Measurements of CO_2 emissions from soils were carried out twice during the growing season using a portable gas analyzer EGM-5 with an SRC-2 camera (PP Systems). One hour before the measurement, the open chambers were deepened into the soil by 3-4 cm with the preliminary removal of living biomass. At the same time, soil temperature was measured at a depth of 1 and 10 cm with a thermometer Checktemp-1 (Hanna Instruments) and soil moisture was measured at a depth of 10 cm with a moisture meter SM-150 (Delta-T Devices) [24].

Statistical processing of the results was carried out in MS Excel 2016, StatPlus suite (v7, AnalystSoft Inc.). The statistical significance of differences in measured parameters among the treatments was assessed using one-way analysis of variance ANOVA ($p < 0.05$).

Results and discussion. The results of measuring the basic physicochemical and agrochemical properties of soil samples taken from the experimental plots and their statistical processing are presented in Table 2.

Table 2

Physicochemical and agrochemical properties of samples

Parameter	Control sample	Sample with fragmentary application of SS	Sample with continuous application of SS
Density, g/cm^3	1.48 ± 0.07^a	1.11 ± 0.04^b	0.99 ± 0.04^b
Hygroscopicity coefficient	1.006 ± 0.0001^a	1.008 ± 0.001^{ab}	1.012 ± 0.002^b
pH_{H_2O}	6.37 ± 0.05^a	6.40 ± 0.03^a	6.20 ± 0.04^b
pH_{KCl}	5.84 ± 0.08^a	5.36 ± 0.03^b	5.03 ± 0.10^c
K, mg/kg	15.60 ± 0.89^a	38.01 ± 2.85^{ab}	59.35 ± 11.12^b
P, mg/kg	81.28 ± 15.32^a	72.13 ± 1.50^{ab}	229.92 ± 63.46^b

Note. Means ± standard errors are shown; letters in superscripts mean the reliable presence (letters are different) or absence (letters are the same) of differences between the experimental options at $p < 0.05$.

The application of SS and its long-term deposition led to a significant decrease in soil density and an increase in its hygroscopicity on the experimental plots. The density of anthropogenic soil samples in comparison with the control area decreased by 1.3 and 1.5 times on the experimental plots with fragmentary and continuous application of SS, respectively. Significant differences were found ($p < 0.05$) in soil density between the experimental and control treatments without a significant difference between the treatment methods. The hygroscopicity coefficient was statistically significantly different for samples from control plots and continuous application plots. Previous research [19, 25, 26] noted the positive effect of SS on the physicochemical properties of soils, in particular density and water-air exchange.

According to the pH of the aqueous extract, all samples are classified as slightly acidic, close to neutral. The application of SS significantly reduced ($p < 0.05$) the actual acidity in the continuous application samples. The pH values of the salt extract changed significantly: the quarry soil was close to neutral, while the soil from the experimental plots was close to being slightly acidic. Not only the fact of treatment, but also the area exposed to the SS treatment did affect the potential acidity level.

Chemical analysis showed a natural increase in the content of mobile potassium along the gradient control treatment < fragmentary application of SS < continuous application of SS. Similar results were obtained during an experiment on apatite-nepheline tailings [21]. However, the content of available phosphorus was significantly higher than in the control only in the continuous application treatment.

When comparing the content of mobile phosphorus and potassium in the soil with the scale of soil nutrient supply presented in the guidelines[3], it was found that anthropogenic soils belonged invariably to the very high phosphorus supply class. In terms of potassium content, the soil of the continuous application plots showed a very high level, while that of the fragmentary application plots demonstrated an elevated level, and the control plots – an average level. Thus, the content of mobile nutrients in the soil six years after a single application of SS allows one to judge the prolonged action of the treatment.

Levels of carbon and nitrogen in various fractions and the statistical processing results are presented in Table 3. The amount of organic carbon naturally increased along the gradient control treatment < fragmentary application of SS < continuous application of SS. Significant differences were found between the control and experimental treatments involving continuous application of SS ($p < 0.05$).

Table 3

Carbon and nitrogen content in various fractions

Parameter	Control sample	Sample with fragmentary application of SS	Sample with continuous application of SS
C_{org}, %	0.29 ± 0.05^{a}	0.90 ± 0.20^{ab}	2.89 ± 0.93^{b}
C_{cold}, mg/kg	199.7 ± 54.7^{a}	358.8 ± 119.1^{ab}	556.1 ± 60.5^{b}
N_{cold}, mg/kg	4.64 ± 0.71^{a}	12.6 ± 1.6^{ab}	27.4 ± 10.1^{b}
C/N_{cold}	46.1 ± 22.0^{a}	26.7 ± 8.1^{a}	26.83 ± 9.4^{a}
C_{hot}, mg/kg	811.5 ± 92.2^{a}	1675.1 ± 425.2^{ab}	2420.3 ± 476.2^{b}
N_{hot}, mg/kg	19.9 ± 4.3^{a}	36.4 ± 1.1^{ab}	227.6 ± 102.3^{b}
C/N_{hot}	51.0 ± 12.7^{a}	45.1 ± 10.3^{a}	21.0 ± 7.2^{a}

The fraction of carbon extracted by distilled water at room temperature characterizes the content of water-soluble organic matter, which is a substrate for soil microflora and vegetation [27-29]. As expected, the content of carbon and nitrogen increased with increasing amount of added SS. Significant ($p < 0.05$) differences in the content of water-soluble carbon and nitrogen were found between the control and experimental samples with continuous application of SS.

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[3] Guidelines for conducting comprehensive monitoring of soil fertility in agricultural lands. Moscow: FGNU "Rosinformagrotech", 2003, p. 241.

The carbon and nitrogen content in the extract prepared using hot water as an extractant characterizes the carbon and nitrogen content of microbial biomass [30-32]. Similarly to the cold-water extracts, the content of carbon and nitrogen in the hot-water extracts increased along the gradient control treatment < fragmentary application of SS < continuous application of SS. Significant differences were also found in the carbon and nitrogen content in the experimental treatment involving continuous application of SS when compared to the control.

An additional indicator of the humus status of soils is the C/N ratio. As found in [33], soils whose C/N ratio exceeds 14 correspond to a very low level of nitrogen in the humus. The C/N ratio of water-soluble varieties in the cold-water extract of the studied samples was significantly higher than the indicated value. At the same time, in both experimental treatments using SS, this indicator is two times lower than in the control one, which may be due to an increase in the nitrogen content together with carbon and correlated with the treatment method. The value of the C/N ratio in the hot-water extract decreased along the gradient control treatment – fragmentary application of SS – conti-nuous application of SS.

The lowest values of CO_2 emission in June were observed on the control plots at 0.15 ± ± 0.05 mg $CO_2/m^2 \cdot h$ at an average humidity of 2,2 % (Fig.2). On the fragmentary treatment plots, this figure was significantly higher at 0.69 ± 0.08 mg $CO_2/m^2 \cdot h$ at an average humidity of 10.7 %, and on the continuous treatment plots, 0.49 ± 0.04 mg $CO_2/m^2 \cdot h$ at an average humidity of 3.8 %.

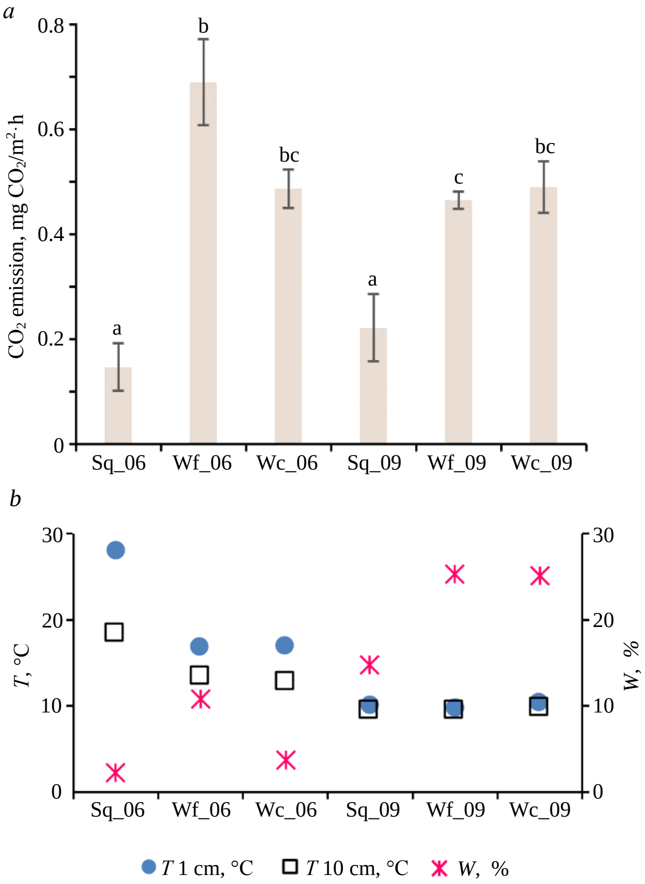

Fig.2. CO_2 emission from soil (*a*), soil moisture and temperature in the surface layer and at a depth of 10 cm (*b*) in June and September

Sq – control; Wf – fragmentary application of SS; Wc – continuous application of SS; 06 – June; 09 – September
Letters above the columns – reliable presence (letters are different), no differences (letters are the same) between experimental variants at $p < 0.05$

At the end of the vegetation season, CO_2 emission was 0.22 ± 0.06 mg $CO_2/m^2 \cdot h$ (at a humidity of 14.7 %) from the control plot; 0.47 ± 0.02 mg $CO_2/m^2 \cdot h$ (at a humidity of 25.3 %) from the fragmentary treatment plots; 0.49 ± 0.05 mg $CO_2/m^2 \cdot h$ (at a humidity of 25.2 %) from the continuous treatment plots. In the control plots, no significant difference was found between the results obtained in different measurement periods. At the same time, emissions from the control plots were significantly ($p < 0.05$) lower compared to the experimental treatments both in June and September. On the fragmentary treatment plots, CO_2 emissions in June were statistically significantly higher than at the end of the season, whereas on the continuous treatment plots, no such trend was found. High values of CO_2 emissions in June from the fragmentary treatment plots were due to increased soil moisture at the beginning of the growing season [34, 35].

Our analysis of the correlations between CO_2 emissions and other labile soil parameters showed a high level of correlation between soil respiration, humidity, and the content of carbon and nitrogen in the hot-water extract (Table 4). A similar pattern was reported in [36].

Table 4

Pearson correlation coefficients for some parameters (n = 18)

Parameter	CO_2 emission, mg $CO_2/m^2 \cdot h$	Humidity W, %	Content of nitrogen in hot-water extract N_{hot}, mg/kg
W, %	**0.7147**	–	–
p	0.0013	–	–
N_{hot}, mg/kg	**0.5165**	**0.6712**	–
p	0.0338	0.0023	–
C_{hot}, mg/kg	**0.6145**	**0.6539**	**0.7814**
p	0.0087	0.0032	0.0001

Our analysis revealed two main factors that explain over 74 % of the variability in the parameters being examined – the application of SS and the treatment method (Fig.3, Table 5). The contribution of the first factor – the application of SS – was 60 %. The greatest effect on this factor was exerted by the content of bioavailable phosphorus, potassium, carbon, nitrogen, CO_2 emission from the soil, potential acidity, density, humidity, and hygroscopicity coefficient. Nearly all parameters had a direct relationship, and only soil density and pH of the salt extract had an inverse relationship [35].

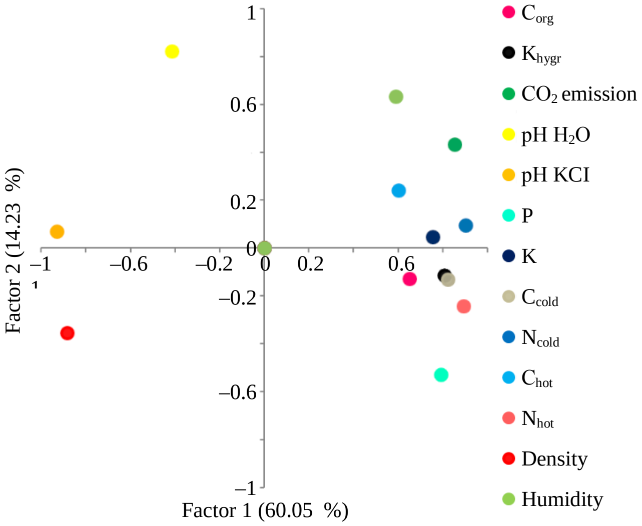

Fig.3. Diagram of factor analysis results

Table 5

Contributions of individual components to the factor analysis

Variable	Factor 1	Factor 2
C_{org}, %	**0.65**	–0.13
K_{hygr}	**0.81**	–0.11
CO_2 emission, mg $CO_2/m^2 \cdot h$	**0.85**	0.43
pH H_2O	–0.41	**0.82**
pH KCl	**–0.93**	0.07
P, mg/kg	**0.79**	**–0.53**
K, mg/kg	**0.75**	0.05
C_{cold}, mg/kg	**0.82**	–0.13
N_{cold}, mg/kg	**0.90**	0.09
C_{hot}, mg/kg	**0.60**	0.24
N_{hot}, mg/kg	**0.89**	–0.24
Density, g/cm^3	**–0.88**	–0.35
Humidity, %	**0.59**	**0.63**

The second factor – the treatment method, whose contribution is 14.2 % – was driven by the pH of the water extract, volumetric humidity, and the content of mobile phosphorus. An inverse relationship was found only for the content of the mobile factor.

The most important condition is the presence of a layer of ameliorant, which leads to loosening of the soil and an increase in its hygroscopicity, a decrease in the pH of the salt extract, an increase in the content of bioavailable phosphorus, potassium, carbon, nitrogen, and an increase in CO_2 emissions from the soil. The second factor is the area of application of SS.

Analysis of the study results indicates that SS can be recommended as a promising ameliorant promoting the accelerated establishment of a stable erosion-proof vegetation cover in sand quarries. Taking into account the economic effect, we find it reasonable to recommend fragmentary application of SS to increase the biogenicity of the soil and create a stable erosion-proof phytocenosis in sand quarries

Conclusion. Adding SS had a positive effect on the physicochemical and agrochemical properties of the sand quarry soil, expressed in a decrease in its *in situ* density, a slight increase in hygroscopicity, a decrease in the pH of aqueous and salt extracts, and an increase in the content of available phosphorus and potassium even after six years after the treatment.

The average carbon content in the soil samples of the control treatment was 0.29 ± 0.05 %, which is three times lower than in the experimental fragmentary treatment with SS and nine times lower than in the continuous treatment. An increase in the content of carbon and nitrogen in cold- and hot-water extracts was observed along the gradient control treatment – fragmentary treatment – continuous treatment. At the same time, the estimated values of the C/N ratio correspond to a very low level of nitrogen in the humus.

Significant differences were found ($p < 0.05$) between CO_2 emissions in the control and experimental treatments in both measurement periods. A high level of correlation was revealed between soil respiration, moisture, and the content of carbon and nitrogen in the hot-water extract.

Our factor analysis identified two main factors controlling the change in the estimated parameters – the application of SS and the method of application. Moreover, 60 % of the variability in physicochemical, agrochemical, and labile soil parameters is explained by the first factor.

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Research article

Comprehensive utilization of urban wastewater sludge with production of technogenic soil

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Abstract. The article presents the analysis of the existing approach to wastewater sludge treatment and justifies the selection of the most promising management technology that allows maximum use of wastewater sludge resource potential. To obtain a useful product (biocompost) suitable for use as part of technogenic soil, experimental studies of aerobic stabilization of organic matter of dehydrated urban wastewater sludge with the addition of other waste by using passive composting technology were carried out. The technology is included in the list of best available technologies (BAT). The selection of the most optimal components for the mixture was based on the results of determining the C and N content, humidity and pH of the components used that ensured the composting of organic waste. The results of laboratory studies of the obtained biocompost according to the main agrochemical and sanitary-epidemiological indicators are presented. Testing was carried out according to the criterion of toxicity of the biocompost's aqueous extract. The assessment of the technogenic soil was performed when using biocompost in its composition for compliance with existing hygienic requirements for soil quality in the Russian Federation. Based on the results of the vegetation experiment, optimal formulations of the technogenic soil were determined, i.e., the ratio of biocompost and sand, under which the most favorable conditions for plant growth are observed according to a combination of factors such as the number of germinated seeds, the maximum height of plants and the amount of biomass. The conducted research makes it possible to increase the proportion of recycled urban wastewater sludge in the future to obtain soils characterized by a high degree of nutrient availability for plants and potentially suitable for use in landscaping, the biological stage of reclamation of technogenically disturbed lands, as well as for growing herbaceous plants in open and protected soil.

Keywords: urban wastewater treatment plants; wastewater sludge; passive composting; integrated utilization of organic waste; fertile technogenic soil

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Introduction. According to the officially published data based on the results of the last All-Russian Population Census in 2020, there is continued growth of the population combined with urbanization of society: between 2010 and 2020, the population increased by 1.4 % (147.2 million people), and 74.8 % of the total population of the Russian Federation are urban residents. (In 2010, the ratio of urban and urban the rural population was 73.5 and 26.5 %, respectively)[1]. The growth of the urban population, in turn, leads to an increase in the amount of the generated wastewater flowing to urban wastewater treatment plants. For example, the annual intake of water in Russia from natural water sources, including the water used for household needs, increased from 54523 million m^3 to 56531 million m^3 between 2020 and 2022.[2]

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[1] Federal State Statistics Service: The results of the General Population Census of the Russian Federation 2020. Vol. 1. The number and location of the population. URL:https://rosstat.gov.ru/vpn/2020/Tom1_Chislennost_i_razmeshchenie_naseleniya (accessed 22.04.2024).

[2] Federal State Statistics Service: Main indicators of environmental protection. Statistical Bulletin. Moscow, 2023, p. 105. URL: https:// rosstat.gov.ru/storage/mediabank/oxr_bul_2023.pdf (accessed 22.04.2024).

Wastewater generated as a result of human economic and industrial activities enters wastewater treatment plants, where the process of removing mechanical impurities and pollutants using various technologies is organized, as well as further discharge or use of treated wastewater [1-3]. It should be noted that urban wastewater treatment plants often receive mixed wastewater instead of household wastewater in its pure form. It comprises a mixture of household, industrial and stormwater in various proportions. The composition of these waters has a wide range of insoluble and soluble pollutants [4, 5].

The classical wastewater treatment method includes the stages of mechanical, chemical, physicochemical and biological treatment, as well as measures for the treatment, neutralization and disposal of wastewater sludge[3]. Mechanical cleaning is usually a preparatory stage and is used to remove insoluble impurities mainly using gratings, sand traps, grease traps, oil traps, etc., as well as settling tanks, where suspended solids settle under the influence of gravitational forces and light substances float to the surface [6, 7]. Chemical and physicochemical treatment ensures the removal of most pollutants and includes a variety of approaches, such as the addition of reagents for the deposition of pollutants, coagulation, flocculation, sorption, as well as ion exchange and reverse osmosis [8, 9]. Special attention has recently been paid to technologies using alternative sorbents that are effective from an environmental and economic point of view [10, 11]. The final stage is biological treatment, the essence of which is the mineralization of organic pollutants of wastewater in the form of finely dispersed undissolved and colloidal substances, as well as in a dissolved state, using aerobic biochemical processes [12-14].

The adoption of a particular treatment method depends on many factors and requires consideration depending on the specifics of the generated wastewater. For example, for industrial wastewater, the key stage is often chemical and physicochemical treatment aimed at removing dissolved chemical compounds and heavy metals. For urban wastewater treatment plants, it is biological treatment and disinfection, which is due to large amount of organic impurities in incoming household and sewage effluents.

Nevertheless, regardless of the adopted water treatment system, wastewater sludge occurs, which is a mixture of solid fractions of organic and mineral substances containing a significant number of pathogenic microorganisms and heavy metals formed during mechanical treatment, as well as excess activated sludge (a complex of microorganisms involved in the process of biological wastewater treatment and derived from the technological process) [15, 16]. According to data published on the portal on the practice of water supply and wastewater treatment of settlements and industry, in Russia the annual formation of wastewater sludge (by dry matter) is about 1.37-1.51 million tons[4], and the annual sludge from urban buildings with its average humidity of 96 % is more than 100 million m^3, while the organic to mineral ratio is 80 : 20 [17, 18].

When handling wastewater sludge, there are two main stages: dehydration and further disposal of the dehydrated sludge. Dehydration is carried out by mechanical processing (filter pressing, centrifugation, vacuuming, filtration through geotubes, etc.) or in natural conditions on sludge pits [17, 19]. It should be noted that, despite the development and the introduction of mechanical dehydration technologies, sludge pits are still widely used today due to their ease of operation and low cost, however, this process is long-term and requires alienation of large territories. In addition, sludge pits are often overcrowded due to insufficient utilization of dehydrated sludge, which negatively affects the components of the environment due to the high content of pathogenic viruses and bacteria, gases and dangerous chemical compounds, including heavy metals [18, 19]. It is known that in Russia's million-plus cities alone there are more than 50 sludge pits with a total area of more than 1.5 thousand

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[3] Belokonev E.N., Popova T.E., Puras G.N. Vodootvedenie i vodosnabzhenie: Rostov-na-Donu: Fenix, 2012, p. 379.

[4] Wastewater sludge as a by-product of production: new possibilities. URL: https://vodanews.info/osadki-stochnyh-vod-kak-pobochnyj-produkt-proizvodstva-novye-vozmozhnosti (accessed 22.04.2024).

hectares[5]. According to the state register of waste disposal facilities[6], the technology of sludge pits is used everywhere, regardless of natural and climatic conditions, including in the territories of the Arctic zones of the Russian Federation vulnerable to anthropogenic impact.

Concerning the methods of disposal of dehydrated wastewater sludge, it should be noted that the most common approaches today are heat treatment to obtain secondary waste in the form of solid residues that are further disposed of, and the production of fertilizers and soils [4, 16, 20].

Thermal disposal methods make it possible to neutralize sewage sludge against pathogenic viruses and bacteria. However, they lead to a concentration of non-volatile toxic substances, especially heavy metals, in solid residues, which limits the scope of their further application. In addition, these methods are associated with high economic costs [4]. Thus, the most common uses of solid residues in the form of combustion ash are the production of composite materials (concretes, asphalt concrete, expanded clay gravel, wall ceramics) [21, 22], and solid residues in the form of pyrolysis products are the production of carbonaceous materials (coal, semi-coke, or pyrocarbon) [23].

The development of technologies for obtaining fertilizers based on sewage sludge [24, 25] and soils [26, 27] is primarily due to the high content of organic substances in these wastes, which provides a supply of nutrients for plants. Unlike thermal recycling, the use of these technologies is characterized by lower economic costs, minimal environmental consequences during implementation (there is no concentration of toxic compounds, including heavy metals), as well as the absence of secondary waste formation [4, 16]. It should also be noted that this approach makes rational use of the resource potential of sludge (as a fertile substrate for plants), which meets modern requirements for sustainable development in combination with the restoration of disturbed lands [28]. However, special attention should be paid to the sanitary and epidemiological assessment of the products obtained due to the presence of pathogenic microorganisms in urban wastewater sludge.

It thus becomes obvious that it is necessary to increase the options for the disposal of dehydrated urban wastewater sludge and intensify the processes of its introduction in order to avoid overflow of existing sludge pits and the need to alienate new territories for newly formed precipitation, which helps to minimize negative consequences for the components of the natural environment. At the same time, the purpose of this study is to obtain a product (technogenic soil) potentially suitable for use in greening of territories, the biological stage of reclamation of technogenically disturbed lands, as well as for growing herbaceous plants in open and protected soil.

Methods. To obtain a product containing urban wastewater sludge that would be safe in sanitary and epidemiological aspect, the technology of aerobic fermentation of organic matter of dehydrated sludge (passive composting) was selected, which is included in the list of the best available technologies[7]. According to some studies [29, 30] and regulatory documents[8], for the effective course of the composting process of organic waste, the following parameters must be observed:

- the optimal moisture content of the compostable material should be 60 %, but the process can also take place in the range from 40 to 70 %. With a moisture content above 70 %, the rate of organic de-composition decreases, anaerobic conditions are formed, and a putrid smell appears;
- the C/N ratio of the compostable material should be from 25 : 1 to 35 : 1. At a higher C/N ratio, the process speed decreases, and at a lower one, nitrogen loss occurs;

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[5] Geospatial analytics: Reclamation of sludge pits in Russia. URL: https://geonovosti.terratech.ru/social/rekultivatsiya-ilovykh-poley-v-rossii (accessed 22.04.2024).

[6] Federal Service for Supervision of Environmental Management: State Register of Waste Disposal Facilities. URL: https://rpn.gov.ru/activity/regulation/kadastr/groro (accessed 07.03.2024).

[7] RG: Abandoned lands are being developed for growing grain and potatoes in Pomerania. URL: https://rg.ru/2022/03/29/reg-szfo/v-pomore-osvaivaiut-zabroshennye-zemli-dlia-vyras hchivaniia-zerna-i-kartoshki.html (accessed 22.04.2024).

[8] An information and technical guide to the best available technologies. Wastewater treatment in the production of products (goods), performance of works and provision of services at large enterprises. Moscow: BAT Bureau, 2015, p. 129.

- the optimal pH levels of the compostable material range from 7.0 to 8.0. However, the composting process can also take place at a wider range of pH values (from 6.5 to 9.0 pH units).

The result of composting organic waste is a fermented mixture, which is a stabilized biocompost with a high nutrient content [31, 32]. Also, during the course of organic decomposition, the compostable material is self-heated (above 60 °C), which leads to the death of most pathogenic microorganisms dangerous to humans and plants, as well as weed seeds [29, 33].

Compliance with the optimal ranges of the parameters presented above was obtained by selecting the composition of the compostable mixture. The classical approach to obtaining fermented wastewater sludge consists in adding organic carbon-rich components (e.g. sawdust, straw, peat) during composting to compensate for the high nitrogen content in the sludge and obtain an optimal C/N ratio [26, 34, 35]. It should be noted that when selecting the composition of the compostable mixture in this study, the task was in organizing co-disposal of several types of waste, as well as choosing easily available additional materials for that, which is most effective from an environmental and economic point of view.

In addition to the selected classic and available components (sawdust and peat), the possibility of adding feed waste (residues of grain raw materials obtained during the cleaning of technological lines in the production of combined fodder) and soil waste during open excavation was considered. The availability of feed waste is due to the presence of 25 largest companies of the agro-industrial complex for the production of combined fodder in Russia with established logistics lines throughout the country, while recently there has been growth and development of this industry, including in the Arctic territories, which is associated with the intensification of the import substitution process. For example, in the Arkhangelsk region, abandoned lands are being developed for the cultivation of forage crops in order to further develop their own production of compound fodder[9]. The advantage is that feed waste is characterized by a high content of organic carbon, nitrogen, protein, vitamins and trace elements, which makes it suitable for composting in order to obtain nutritious substrates for plants. The availability of soil waste is conditioned by the widespread carrying out of open excavations.

Thus, the following materials were used as components for the production of biocompost: wastewater sludge (waste from urban wastewater treatment plants from sludge pits), pure wood sawdust (waste from the woodworking industry), feed waste, peat and soil waste during open excavation. The appearance of the components is shown in Fig.1.

Fig.1. The appearance of the compostable mixture components: wastewater sludge (*a*), sawdust of pure wood (*b*), feed waste (*c*), peat (*d*), soil waste (*e*)

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[9] AgroInvestor: Analytics. Combined fodder is still profitable. The top 25 largest players produced over 19 million tons of products over the year. URL: https://www.agroinvestor.ru /analytics/article/37844-kombikorm-poka-v-plyuse-top-25-krupneyshikh-igrokov-za-god-proizveli-svyshe-19-mln-t-produktsii (accessed 22.04.2024).

The ratio of components in the mixture to ensure the flow of the composting process was determined based on laboratory studies using the following indicators:

- humidity of the components (using the LECO TGA701 thermogravimetric analyzer in accordance with the user manual);
- carbon and nitrogen content in the components (using the LECO CHN-628C carbon, hydrogen, nitrogen analyzer in accordance with the user manual);
- actual and metabolic acidity – reaction of the medium (determination of the pH of the aqueous and salt extract from the components using the pH meter-ionomer Expert-001 in accordance with GOST 26423-85, GOST 26483-85, GOST 27979-88, GOST 11623-89).

The characteristics of the components according to the above indicators are presented in Table 1. The C and N contents are presented taking into account the moisture content of the components. It was found that with a mass ratio of components (wastewater sludge, sawdust of pure wood, feed waste, peat, soil waste) in the compostable mixture of 32.5 : 35 : 6.5 : 13 : 13, respectively, optimal conditions for the composting process are achieved: humidity – 61 %, C/N ratio – 25 : 1, the actual and metabolic acidity is 7.0 and 6.7 pH units, respectively. It has been established experimentally and computationally that with an increase in the proportion of sawdust of pure wood and/or peat, both the actual and metabolic acidity decreases (less than 6.5 pH units), while it is impossible to compensate for the pH level of the mixture by adding wastewater sludge, feed waste, and soil waste without reducing the C/N ratio beyond the optimal the range. With a decrease in the proportion of sawdust, the pH level is in the acceptable range. However, there is a need to reduce the proportion of wastewater sludge due to the high nitrogen content in them, which is impractical, since this type of waste is the main recyclable component.

Table 1

Characteristics of composting components according to the main indicators

Component	C content, wt.%	N content, wt.%	C/N	pH_{aq}	pH_{KCl}	Humidity, wt.%
Wastewater sludge	8.1	1.1	7:1	7.5	7.1	80
Pure wood sawdust	26.1	0.02	1305:1	5.5	4.5	55
Feed waste	41.5	2.3	18:1	8.0	7.5	13
Peat	19.2	1.1	17:1	6.0	5.7	80
Soil waste	3.7	0.3	12:1	7.0	6.1	35

The experimental clamp was laid on the territory of Saint Petersburg Mining University in the summer. The composting site was a fenced area protected from direct sunlight, intense wind load and precipitation (in order to avoid excessive evaporation of moisture and overmoistening of the compostable material). Preliminary preparation of the site was also carried out, which consisted in covering the place where the experimental clamp was laid with a layer of straw, which prevents premature cooling of the compostable material due to the relatively small volume (about 100 dm^3).

The composting experiment lasted for 90 days to fully stabilize the biocompost. The compostable mixture was stirred occasionally (1 time every 10 days) in order to increase the air flow to eliminate the development of anaerobic processes. Also, temperature control inside the clamp was carried out using Thermochron portable loggers. Humidity control of the composted mixture was implemented by periodic sampling and using a MOS-120H moisture analyzer (in order to add water, if necessary, to maintain humidity at an optimal level of 60 %). The appearance of the experimental clamp in different time periods is shown in Fig.2.

After receiving the biocompost, its multifactorial assessment was carried out according to the main agrochemical and sanitary-epidemiological indicators, as well as testing according to the criterion of toxicity of aqueous extract. Laboratory studies of the biocompost and its quality assessment were carried out according to the relevant regulatory documents currently provided for soils, since on the basis of the resulting biocompost, the composition of technogenic soil was developed, the quality of which should meet modern environmental safety requirements.

Fig. 2. The appearance of an experienced clamp during the composting period

From the group of agrochemical indicators, the following laboratory studies were carried out in order to determine the fertility of the resulting product according to the degree of availability of nutrients (macronutrients) for plants[10]:

- organic matter content (using the LECO TGA701 thermogravimetric analyzer in accordance with GOST 26213-2021);
- mineral nitrogen content – ammonium and nitrate (using the DR5000 spectrophotometer in accordance with GOST 26489-85 and GOST 26488-85);
- mobile phosphorus content (using the DR5000 spectrophotometer in accordance with GOST 54650-2011);
- exchangeable potassium content (using the Shimadzu AA-7000 atomic absorption spectrometer in accordance with GOST 54650-2011);
- actual and metabolic acidity – the reaction of the medium.

Laboratory studies were also conducted to determine the main indicators for assessing the sanitary and epidemiological condition in accordance with SanPiN 2.1.3684-21:

- content of gross forms of metals (mesoelements and trace elements), including heavy ones (using the Shimadzu AA-7000 atomic absorption spectrometer in accordance with M-MVI-80-2008);
- petroleum products content (using the liquid analyzer “Fluorat-02-3M” in accordance with PND F 16.1:2.21-98);

All of the above laboratory studies were carried out on the basis of the Scientific Center “Assessment of technogenic transformation of ecosystems” at Saint Petersburg Mining University. The study of the following sanitary and hygienic, bacteriological and parasitological indicators was carried out by the Federal State Budgetary Institution “Center for Hygiene and Epidemiology in Saint Petersburg and the Leningrad Region”:

- mass fraction of volatile phenols (in accordance with PND F 16.1:2.3:3.44-2005);
- cyanide content (in accordance with M 4-2017);
- coli-index of lactose-positive E. coli (in accordance with MUC 4.2.3695-21);
- coli-index of fecal enterococci (in accordance with MUC 4.2.3695-21);
- presence of pathogenic bacteria, including salmonella (in accordance with MUC 4.2.3695-21);
- presence of eggs and viable larvae of helminths (in accordance with MUC 4.2.2661-10, clause 4.2);
- presence of oocysts and cysts of intestinal pathogenic protozoa (in accordance with GOST R 57782, item 12);
- presence of larvae and pupae of synanthropic flies (in accordance with MU 2.1.7.2657-10, paragraph III).

Additionally, testing was performed according to the toxicity criterion of the aqueous extract of the biocompost in accordance with PND F T 14.1:2:3:4.10-04 taking *Chlorella vulgaris* algae culture as a test object using a set of biotesting equipment: cultivator KV-05, multi-cell cultivator for algae KVM-05 and photoelectric colorimeter IPS-03.

The final stage of the laboratory research was the implementation of a vegetation experiment, which is the cultivation of plants in vessels filled with test and control substrates. At the same time, homogeneous conditions are provided (except for the studied factors), which eliminates accidental

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[10] Methodological guidelines for conducting comprehensive monitoring of soil fertility of agricultural lands. Moscow: Federal State Budgetary Institution “Rosinormagrotech”, 2003, p. 240.

effects on plant growth and development[11]. The value of vegetation experiments lies in the prompt receipt of information about the influence of various factors, which are selected depending on the objectives of the study [26, 36, 37].

The main studied factor influencing the growth and development of plants was the composition of technogenic soil obtained by mixing biocompost with quartz sand in various mass ratios. Mixing of biocompost with sand in the production of technogenic soil is caused by the need to balance the mineral and organic parts (creation of a soil skeleton) to ensure optimal conditions for plant growth and development, while sand is chemically inert. It does not contain heavy metals, petroleum products, nutrients, pathogenic microorganisms for humans and plants. The biocompost performs the function of a structure-forming agent when obtaining a ready-made technogenic soil: sand particles are packed into the pore space of the biocompost with stirring.

Before conducting the vegetation experiment, additional studies were conducted to determine the actual and metabolic acidity of the sand used in accordance with GOST 29234.6-91 and GOST 26483-85, as well as the volumetric (bulk) density of all prepared substrates in accordance with GOST 5180-84. The use of a standard for determining the exchange acidity in soils is due to the absence of an appropriate standard for sands.

During the experiment, lawn grass of the Lolium perenne family of grasses (perennial ryegrass) was used as a test object. The planting rate was determined according to the recommendations of the manufacturer of the seeds used. To create homogeneous growing conditions, the NLO 79-03-04 LD plant stand was used with the ability to adjust the power of LED phytolamps and the daily schedule, and the humidity of the substrates was maintained at 60 % of the total water capacity. Figure 3 shows the soil substrates studied during the vegetation experiment. Sod-podzolic soil, which is a subtype of podzolic soils common in the Leningrad region, was used as a control soil sample[12].

As a result of the vegetation experiment, results were obtained on seed germination (in percentage terms), as well as an assessment of the maximum height of lawn grass and the amount of its biomass. At the same time, the number of germinated seeds was determined on the 10th day of the experiment, which corresponds to the recommendations for determining the germination rate of perennial ryegrass according to GOST 12038-84, and the maximum height of plants and the amount of biomass were estimated on the 21st day. The biomass was cut in an identical manner for all samples at a level of 2 cm from the surface.

Fig.3. Experimental substrates during the vegetation experiment
The figure corresponds to the mass fraction of the corresponding component in the substrate
BC – biocompost, S – sand, SPS – sod-podzolic soil

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[11] Krasnoyarsk State Agrarian University: Fundamentals of scientific research in agronomy. URL: http://www.kgau.ru/distance/agro_02/belousov_oni-110201/01_05.html (accessed 22.04.2024).

[12] Unified State Register of Soil Resources of Russia. URL: http://egrpr.soil.msu.ru/egrpr.php?show=RUREG & valueId= 1001 (accessed 23.05.2024).

Discussion of the results. During the composting of the mixture using portable loggers, the moment when self-heating began (after 26-28 h) and the maximum temperature (on the 3rd day) were recorded, which was about 71 °C. That indicates the course of the process of thermal destruction of organic substances and the death of microorganisms pathogenic to humans and plants, as well as weed seeds. Figure 4 shows the change in the average daily temperature inside the experimental clamp and the composting stage. Minor fluctuations in the average daily temperature in the passive stage of composting are caused by fluctuations in atmospheric air temperature.

The finished biocompost is characterized by the absence of putrid, ammonia or hydrogen sulfide smell and has an earthy smell, which indicates the completion of the composting process. The results of determining the main agrochemical parameters of the finished biocompost: organic matter content 60 %; mineral nitrogen content (ammonium and nitrate) 145 mg/kg; mobile phosphorus content (in terms of P_2O_5) 3500 mg/kg; exchangeable potassium content (in terms of K_2O) 1700 mg/kg; reaction of the medium (actual acidity) 7.3 pH unit, reaction of the medium (metabolic acidity) 6.8 pH unit. The biocompost has a very high supply of nutrients available to plants[13].

The results of determining the main sanitary and hygienic indicators of the finished biocompost are presented in Table 2. It was found that according to SanPiN 1.2.3685-21, there are no exceedances in the biocompost for any indicators for which the maximum permissible (MPC) or approximate permissible concentrations (APC) have been established to date, except for zinc. The ratio of the concentration of the element to APC was 1.2). However, this excess is neutralized by mixing the biocompost with sand when obtaining the final product (technogenic soil). There was also no excess in the content of petroleum products, the permissible level of which is 1000 mg/kg[14].

The results of determining the main bacteriological and parasitological parameters of the finished biocompost: lactose-positive E. coli (coli-forms)10 CFU/g; enterococci (fecal streptococci)10 CFU/g; pathogenic bacteria, including salmonella, eggs and larvae of helminths (viable), cysts of intestinal pathogenic protozoa, larvae and pupae of synanthropic flies – not detected. Based on the results obtained, it was found that according to MU 2.1.7.730-99, technogenic soil produced by mixing biocompost and sand belongs to the category of clean soils and can be used in the territories of recreation areas (parks, squares, etc.), sanitary protection zones of reservoirs, sanitary protection zones, etc.

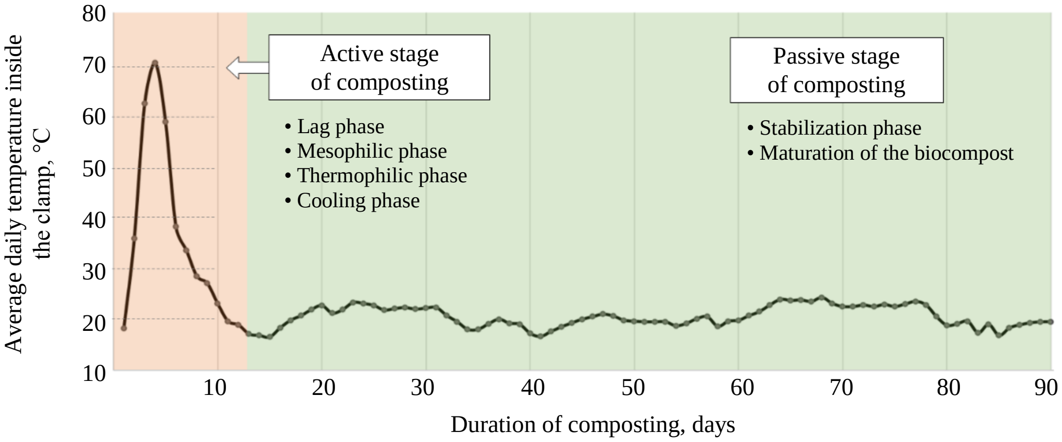

Fig.4. Change in average daily temperature

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[14] On the procedure for determining the extent of damage from land pollution with chemicals: Letter N 04-25 dated December 27, 1993 from the Ministry of Natural Resources of the Russian Federation (Ministry of Environmental Protection and Natural Resources of the Russian Federation).

Table 2

Characteristics of the biocompost according to the main sanitary and hygienic indicators (including the content of mesoelements and trace elements), mg/kg

Indicator	C_i	MPC_i	APC_i	C/MPC(APC)
Zinc	265	–	220	1.2
Lead	35	–	130	0.3
Copper	123	–	132	0.9
Cadmium	0.7	2.0	–	0.4
Mercury	Less than 0.02	2.1	–	0.2
Manganese	639	1500	–	0.4
Molybdenum	4.4	–	–	–
Iron	30900	–	–	–
Aluminum	48500	–	–	–
Magnesium	11200	–	–	–
Calcium	38700	–	–	–
Petroleum products	160	–	–	–
Volatile phenols	1.8	–	–	–
Cyanides	Less than 0.5	–	–	–

When testing according to the toxicity criterion of an aqueous extract of a biocompost (biotesting using a culture of *Chlorella vulgaris* algae), it was found that there was no manifestation of toxicity. There was no decrease in the average optical density compared to the control variants by 20 % or more in the case of suppression of the growth of the test culture or its increase by 30 % or more in case of stimulation of the growth processes. The results of the bioassay are presented in Table 3.

Table 3

The results of bioassay of the aqueous extract of the biocompost

Sample number	Dilution ratio	Number of repetitions	D	$D_{\text{average value}}$	I %	Has/does not have an acute toxic effect
Control	0	1	0.138	0.151	0	–
		2	0.152			
		3	0.156			
		4	0.158			
1	1	1	0.195	0.188	–24.50	Does not have
		2	0.182			
		3	0.191			
		4	0.184			
2	3	1	0.178	0.171	–13.25	Does not have
		2	0.169			
		3	0.170			
		4	0.167			
3	9	1	0.171	0.162	–7.28	Does not have
		2	0.158			
		3	0.160			
		4	0.159			
4	27	1	0.160	0.158	–4.64	Does not have
		2	0.147			
		3	0.166			
		4	0.159			
5	81	1	0.149	0.153	–1.32	Does not have
		2	0.158			
		3	0.145			
		4	0.160			

The vegetation experiment made it possible to evaluate the suitability of the obtained biocompost as a source of nutrients for plants in laboratory conditions and to determine the optimal ratios of biocompost and sand in technogenic soil. It should be noted that the first shoots of the test culture appeared on the 3rd day of the vegetation experiment already. Figure 5 summarizes the stages of biomass formation on experimental substrates during vegetation experiment.

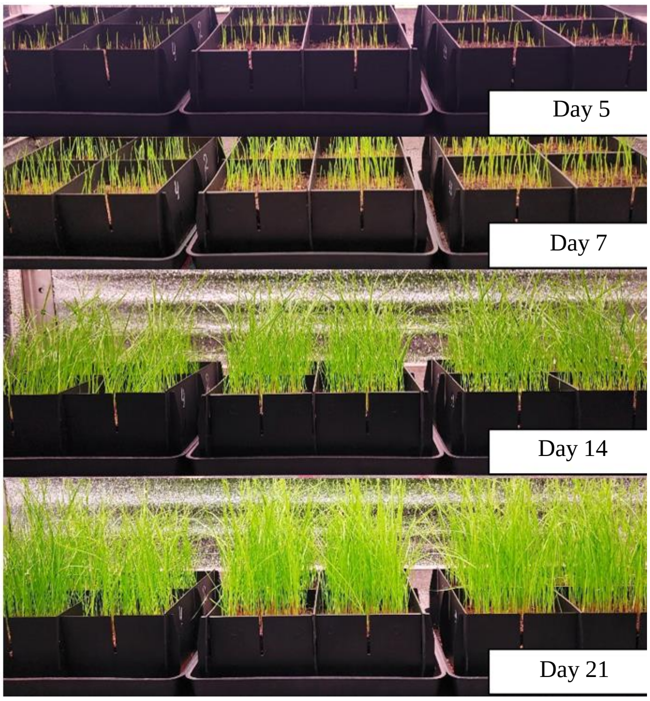

Fig.5. Stages of biomass formation on experimental samples of substrates for the entire period of the vegetation experiment

According to the obtained results of the vegetation experiment, optimal formulations of technogenic soil were identified, i.e. the ratio of biocompost and sand, in which the most favorable conditions for the growth of the test crop are observed based on the combination of all factors (Table 4, Fig.6). It should be noted that the actual and metabolic acidity of the sand used is 7.0 and 6.6 pH units, respectively. Therefore, the finished technogenic soil is neutral (pH_{KCl}: more than 6.0 pH units) regardless of the ratio of biocompost and sand.

Thus, with a biocompost: sand mass ratio equal to (20-60) : (80-40), the following positive trends are observed: an increase in seed germination (over 95 %), the maximum height of lawn grass and the amount of its biomass compared with both control samples and samples with a higher or lower content of biocompost. These trends may be due to the influence of factors such as nutrient content and substrate density, both individually and in combination with each other. For example, with an increase in the biocompost content of more than 60 wt.% despite the increase in the amount of nutrients, there is a deterioration in the studied indicators, which may be due to a decrease in the density of substrates.

Table 4

The results of the vegetation experiment

Experimental substrate	Number of seeds sprung up, %	Maximum height of plants, cm	Biomass amount, g	Bulk density, cm^3/g
Control 1: BC100	89.1	25.3	4.31	0.46
Control 2: S100	74.6	22.5	2.74	1.26
Control 3: SPS100	83.8	25.0	5.09	0.82
BC10:S90	83.0	24.5	3.94	1.18
BC20 : S80	95.1	25.8	5.07	1.10
BC30 : S70	95.5	25.9	5.56	1.02
BC40 : S60	97.3	26.5	5.97	0.94
BC50 : S50	97.4	27.8	6.19	0.86
BC60 : S40	95.8	28.8	6.26	0.78
BC70 : S30	89.3	28.1	5.36	0.70
BC80 : S20	89.4	26.5	5.15	0.62
BC90 : S10	89.8	25.1	5.01	0.54

An insufficient amount of the mineral component (sand), which serves as the basis of the soil skeleton, critically affects the air and water regime, leads to violation of capillary bonds, leaching of macronutrients and trace elements, excessive evaporation of moisture, as well as instability in the formation of root systems.

With the biocompost content of less than 20 wt., in addition to reducing the amount of nutrients, substrate compaction can also play an important role. It complicates the formation of root systems, worsens the diet due to a decrease in the number of pores and capillary bonds, and impedes the circulation of soil air [38].

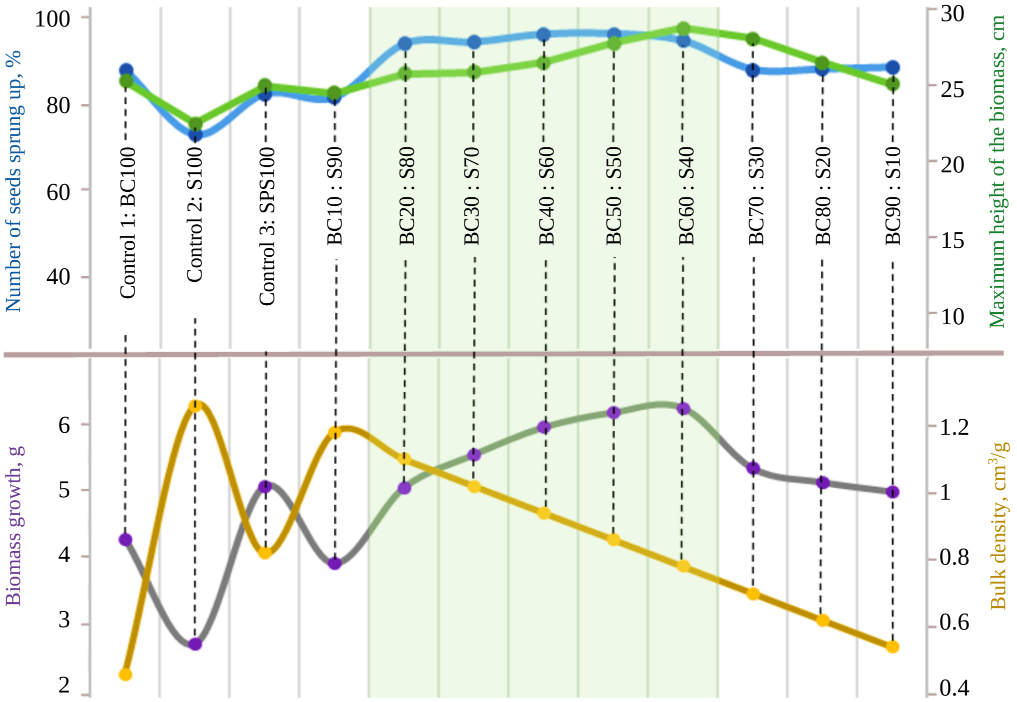

Fig.6. The results of the vegetation experiment

It has been experimentally established that the resulting technogenic soil can be stored in air-dry form, which greatly simplifies its transportation if necessary, and also eliminates the need to use insecticides, fungicides and/or preservatives. It is also possible to store and/or transport the biocompost separately with the further production of technogenic soil of the required composition directly at the site of its intended use, while available sandy soils can be used as a mineral part [38].

Conclusion. The conducted research and the presented results allow us to speak about the possibility of integrated utilization of urban wastewater sludge with sawdust of pure wood, feed waste, peat and soil waste. Moreover, the resulting useful product in the form of a biocompost is characterized by a high content of organic matter, nitrogen, phosphorus, and potassium in forms accessible to plants. When mixing biocompost with sand, optimal ratios are obtained, at which the most favorable conditions for the growth of herbaceous plants were revealed using the example of perennial ryegrass.

Increasing the options for recycling urban wastewater sludge will reduce the number of sludge pits, which in turn helps to reduce the negative impact on environmental components. However, it is important to take into account that, when implementing this method of disposal, it is necessary to monitor each batch of the resulting biocompost or the finished composition of technogenic soil according to sanitary, hygienic, bacteriological and parasitological indicators to confirm the safety of their use for various purposes in accordance with current regulatory documents.

To establish the suitability of using the resulting technogenic soil for a long-time during landscaping, the biological stage of reclamation of technogenically disturbed lands and the cultivation of herbaceous plants in closed or open ground conditions, it is advisable to conduct long-term vegetation experiments in laboratory conditions and pilot tests.

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Research article

Potential use of water treatment sludge for the reclamation of small-capacity sludge collectors

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Abstract. In small settlements, collectors for the sludge produced during water treatment processes are small-sized and located in the vicinity of drinking water storage reservoirs or in coastal areas. Sludge removal is not economical. Besides, the relief depressions formed after sludge disposal are required to be reclaimed. In ore mining regions, where the main settlements of the Urals are located, sludge produced in water treatment has high contents of heavy metals typical of ore mining provinces. Consequently, places of sludge accumulation are potential sources of water pollution. The article discusses the possibility to mix sludge with slaked lime and local overburden with the help of special equipment. So far water treatment sludge in the region has been used to reclaim the surface of solid waste landfills by creating anaerobic conditions for waste decomposition. When placed inside the embankment dams as an independent object, sludge needs to be improved for the increase of its bearing capacity and the ability to bind heavy metals. The article aims at the substantiation of the composition and properties of the reclamation material made of the water treatment sludge mixed with local overburden and slaked lime (technosoil). For this reason the paper describes the composition of the sludge in a sludge collector, the composition and properties of the overburden rocks as a component of the mixtures with water treatment sludge, the composition and properties of the mixtures of water treatment sludge with overburden rocks and $Ca(OH)_2$ as a component dewatering sludge and neutralizing toxicants. Furthermore, the research work provides the technology created for the optimal processing of the water treatment sludge in the process of the reclamation of a sludge collector. The research results and the experience obtained in reclamation of disturbed lands in the region have confirmed the possible use of technosoil for the reclamation of small-capacity sludge collectors. The analysis of the chemical composition and physical and mechanical properties of the mixtures under study has shown that the most economical and environmentally sound reclamation material is a mixture of water treatment sludge, loose overburden dump soils and $Ca(OH)_2$ in a ratio of 60 : 30 : 10 %.

Keywords: water treatment sludge; sludge collector; reclamation; technogenic soil; sustainability; environmental safety

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Introduction. Surface waters are the main source of domestic water supply. Their reactant purification is accompanied by coagulation and sedimentation of a significant amount of suspended material. Waste from water clarification includes high-moisture organic and mineral sludge consisting of suspended solids contained in the treated water and flocculent hydrolysis products called coagulants with adsorbed organic and mineral compounds [1-3].

The generation of such waste characterized by high moisture content (up to 99.9 %) and very low compaction (dehydration) ability is quite large scaled. For example, the USA generates about 10 million tons of water treatment sludge per year while the Russian Federation annually produces about 500 thousand tons of dry sludge or 100 million m^3 of sludge with moisture content of 99.5 %. A water treatment plant with the capacity of 750 thousand m^3 per day on average generates up to 12 thousand tons of dry sludge per year [4]. According to the Municipal Unitary Enterprise “Yekaterinburg Vodokanal”, the main water treatment station in Yekaterinburg – the Western Filtration Station – operates with the capacity of 400 thousand m^3 per day. In accordance with the design scheme, about 60 thousand m^3 of wash water generated during the water treatment process used to be discharged into the sludge collector. Due to a long-term water discharge, the sludge collector built in the 1970s overflowed, which led to excessive water discharge at the outlet [5].

The problem of environmentally safe storage and disposal of water treatment sludge is extremely relevant for Russia, where the main sources of centralized water supply are surface waters, whose share in the total volume of water intake accounts for 68 % [6]. The water supply of many large cities of the country (Moscow, Saint Petersburg, Saratov, Samara, Yekaterinburg, Chelyabinsk, Novosibirsk, etc.) is entirely based on surface water sources such as rivers and water storage reservoirs. Centralized water supply for half the cities with the population of over 100 thousand people is either entirely based on surface waters or accounts for more than 90 % of the water consumption balance. About 90 % of surface water coming into a water treatment plant is treated (most often by coagulation) to remove excess impurities and pathogenic microorganisms. At the same time, most water treatment stations neither process wash water nor dispose of the resulting sludge [7-9]. As a rule, water treatment sludge is stored in sludge collectors and on sludge beds [10-12]. The use of sludge ponds for storage and partial dewatering of sludge during its long-term gravitational compaction and drainage of clarified water has become widespread in many countries of the world [4, 13, 14].

Water treatment sludge is less dangerous for the environment and humans than, for instance, municipal wastewater sludge [15-17]. The presence of contaminants in sludge largely depends on the quality of wastewater coming for purification [18]. At the same time, water treatment sludge especially that formed during the purification of high-coloured, low-turbidity waters has higher filtration resistivity values and requires greater costs of thickening and dewatering [19, 20]. The storage of water treatment sludge in the sludge ponds or on the dewatering sites leads to the alienation of significant land areas withdrawn from economic use for many years to come. All this requires the search for optimal methods for environmentally safe waste disposal and reclamation of disturbed lands.

Currently, in Russia and abroad, water treatment sludge is mainly used as a component of building materials, as a sorbent for soil and water purification, as a raw material for the production of iron-containing powders, and as a soil component [6, 15, 21].

All these uses of water treatment sludge serve as a basis for the development of technologies for production of cement, mortar, concrete [15, 22, 23], brick [24-26], roofing tiles, and ceramics [15, 27, 28]. Due to its component composition, water treatment sludge can be used as a substitute for natural clay minerals in the production of terracotta ceramics [29]. Agricultural use of water treatment sludge is considered to be the most accessible and large-scale option for its disposal [15]. Other known alternatives for the disposal of water treatment sludge include the reuse of a coagulant or its use as an inexpensive adsorbent for heavy metals such as mercury, lead [30-32], selenium and arsenic [33].

The use of water treatment sludge is one of the effective ways to reclaim disturbed lands. In accordance with GOST R 54534-2011 “appropriately controlled sludge from water treatment, wastewater treatment and water use” can be used as a secondary material resource for the reclamation of disturbed lands. Water treatment sludge can be used either to fill quarry excavations at a technical stage of reclamation [34-36] or to create top soil of the earth and to reclaim contaminated and depleted soils at a biological stage of recultivation [32, 37].

The processing of water treatment sludge for the production of secondary products is rather expensive because big costs are required to determine the composition and properties of the sludge as well as to select and develop technologies for its utilization. When water treatment sludge is produced in big amounts, its utilization can have a beneficial economic impact on the enterprises of housing and communal services. In large cities, a significant part of the budget of organizations operating water treatment plants goes to the removal and deposition of sludge generated in large amounts [37]. In small towns where small amounts of water treatment sludge are generated, the use of sludge treatment technologies or its removal to specialized waste disposal sites is often economically ineffective.

In small settlements of Sverdlovsk region, water treatment sludge collectors are of small capacity (up to 100,000 m^3), but they are commonly located in the vicinity of drinking water storage reservoirs or in coastal zones of surface water bodies. In ore mining regions, where the main settlements of the Urals are located, sludge produced during water treatment processes has increased contents of heavy metals typical of ore mining provinces. All this requires the reclamation of sludge collectors by means of inert material prepared for the reduction of the anthropogenic pressure on the environmental components.

For this reason one of the sludge collectors of the water intake station in Sverdlovsk region has been selected with the aim of studying the possibilities of its reclamation *in situ* and through the use of special equipment mixing sludge with slaked lime ($Ca(OH)_2$) and local overburden soils for the increase of the bearing capacity of the resulting mixtures and the reduction of the environmental hazard from the sludge.

The study aims at the substantiating the composition and properties of the water treatment sludge as a material for the reclamation of the sludge collector. The analysis of the literature on the projects implemented in Russia and abroad and related to the disinfection and stabilization of the sewage sludge has shown that one of the economically feasible, technologically advanced, and relatively simple ways to reduce sanitary and environmental hazard from the sludge is the use of lime as the main reagent. Lime addition leads to the sludge dewatering and structuring, which contributes to the immobilization of heavy metals [12].

The research sets the task to describe the composition of the sludge accumulated in a sludge collector in its initial state; the composition and properties of the overburden rocks as a component of mixtures with water treatment sludge; the composition and properties of the mixtures of water treatment sludge with overburden rocks, and $Ca(OH)_2$ as a component dewatering sludge and neutralizing toxicants. Moreover, the paper focuses on the creation of the technology for optimal processing of water treatment sludge during the reclamation of a sludge collector.

In order to develop a sludge disposal technology for obtaining an optimal sludge composition with characteristics for the reclamation of a sludge collector, several tests have been made. They have resulted in the selection of the technogenic soil composition and the main parameters of the technology for its production. The properties of the composition have made it possible not only to reclaim the sludge collector but also to ensure the safety of the resulting soil for the environment in accordance with regulatory documents.

Research object. The object of research is a sludge collector of the Chernoistochinskiy hydroelectric complex. It is used for the storage of water treatment sludge, that is, suspended solids resulted from washing water treatment facilities such as microfilters and filters, emptying and washing sedimentation tanks, washing the tanks of the reagent facilities of the Chernoistochinskiy hydroelectric complex, a structural division of OOO Vodokanal-NT (a limited liability company under the laws of the RF), which supplies the population and industrial enterprises of Nizhniy Tagil with drinking water.

The sludge collector is located on the border of the landscape reserve of regional significance “Chernoistochinskii pond with Ushakovskaya ditch and surrounding forests” within the water protection zone of Chernoistochinskii water storage reservoir and on the territory of the II and III belts of the sanitary protection zone of the Chernoistochinskii hydroelectric complex. The location of the waste disposal facility within the boundaries of the sanitary protection zone and the water protection zone determines the need for the reclamation of the sludge collector as well as the reduction of its negative impact on the environment.

The collector for the water treatment sludge is a pit consisting of one section up to 4.18 m in depth. It is filled with water treatment sludge. The total capacity of the sludge collector is 75900 m^3. At the base of the sludge collector there are eluvial loams having thickness of more than two meters and filtration coefficients n equal to 10^{-7} cm/s.

The initial water treatment sludge accumulated in the sludge collector demonstrates slightly increased measured values of zinc, lead, arsenic, copper, nickel, and oil products in relation to background values for the soils in the area under study. Tentative allowable concentrations (TAC) of arsenic for soils are also exceeded (Table 1). Increased values are associated both with the natural processes of the sludge concentrating at the particulate surface water phases in complexes with organic substances and with technogenic processes during the sludge treatment at the Chernoistochinskii hydroelectric complex.

Table 1

Chemical composition of the water treatment sludge in the sludge collector

Indicator name	Test result	Background in the soil	MAC/TAC for soils according to Sanitary regulations and norms 1.2.3685-21	Norms of the GOST R 54534-2011	
				Technical reclamation	Biological reclamation
pH of the salt extract (pH_{salt})	6.4	–	Not regulated	5.0-8.5	5.0-8.5
Total nitrogen, %	>0.6	–	Not regulated	Not regulated	No less than 0.5
Total phosphorus, %	2.1	–	Not regulated	Not regulated	No less than 1.5
Dense residue of water extract, %	0.30	–	Not regulated	–	–
Ash content, %	91.0	–	Not regulated	Not less than 65	65-85
Exchange (mobile) aluminum, mmol/100 g	0.072	–	Not regulated	–	–
Cadmium (g), mg/kg	<0.8	<0.8	2	60	30
Chromium (g), mg/kg	<10	<10	Not regulated	2000	1000
Copper (g), mg/kg	69	45	132	1500	750
Manganese (g), mg/kg	76	632	1500	–	–
Nickel (g), mg/kg	21	14	80	800	400
Lead (g), mg/kg	23	<20	130	1000	500
Zinc (g), mg/kg	83	81	220	7000	3500
Arsenic (g), mg/kg	**12**	3.6	10	40	20
Mercury (g), mg/kg	0.033	0.11	2.1	30	15
Petroleum products, mg/kg	47.0	23.0	1000	–	–
Benzpyrene, mg/kg	<0.005	<0.005	0.02	–	–
Class of danger	V	–	–	IV-V	–

The main macrocomponents of the water treatment sludge of the research object are inert oxide compounds of silicon (20.88 %), aluminum (14.58 %), iron (4.38 %), calcium (4.27 %), magnesium (4.14 %). They can be constituent elements of sand, clay and mineral particles. The rest components include organic substances, fertilizing macroelements (nitrogen, phosphorus, potassium) and microelements. According to the tests results, the content of exchange (mobile) aluminum in the sludge is 0.072 mmol/100 g, the mass fraction of total nitrogen is >0.6 %, the mass fraction of gross phosphorus is 2.1 %, the mass fraction of the ash content is 91.0 %, the dense residue of the water extract is 0.3 %. Water extracts of water treatment sludge samples are not toxic. They are attributed to the V class of danger according to the degree of their negative impact on the environment.

Methods. The properties of the water treatment sludge have been studied in laboratory conditions by means of standard techniques and engineering survey equipment. The same methods have been used to study the overburden rocks of local deposits and technosoil. Judging by plasticity index and flow index the water treatment sludge refers to fluid clays. Taking into account its granulometric composition, the water treatment sludge belongs to heavy clays. According to the studies, the maximum molecular moisture capacity of the sludge W equals to 206.4 %, total moisture capacity of the sludge W_0 accounts for 720.4 %, and soil density is 1.07 g/cm^3.

The strength properties of the soil have been studied in laboratory conditions using a non-consolidated-undrained shear scheme. The value of compression modulus of deformation of the sludge with natural moisture content is 0.4 MPa. Strength indicators of the sludge with natural moisture content C and φ account for 0.002 MPa and 9° respectively.

The main factors affecting the use of sludge for reclamation are high moisture content and, consequently, low values of strength and deformation properties, increased levels of arsenic (above the established maximum allowable concentrations (MAC) for soils); slightly increased values of zinc, lead, arsenic, copper, nickel, and petroleum products in relation to background values for soils in the area under study.

These tests results have influenced the development of a technology for processing (recycling) the sludge into artificial technogenic soil which can be subsequently used for the reclamation of disturbed lands by means of reducing the moisture content of the sludge, increasing the mechanical properties of the soil and lowering the concentrations of contaminants in the sludge to maximum allowable ones.

The soil from loose overburden dump of the Glavnyi quarry of the Vysokogorsk deposit is another material, whose chemical and granulometric compositions as well as moisture content have been studied. The soil can be used for reclamation as a filler for mixtures with water treatment sludge accumulated in the loose overburden dump located in the Glavnyi quarry of the Vysokogorsk iron ore deposit 20 km north of the sludge collector. The chemical, granulometric composition and soil moisture content of the dump of loose overburden of the Glavnyi quarry of the Vysokogorsk iron ore deposit, selected for use as a reclamation agent, have been studied. The article provides the study of the composition, chemical and physical-mechanical properties of the mixtures of water treatment sludge with overburden rocks of the Vysokogorsk deposit and calcium hydroxide $Ca(OH)_2$ (slaked lime) as a component dewatering high moisture sludge and ecotoxicants (Table 2).

Table 2

Ratios of mixed components, wt.%

Water treatment sludge	Calcium hydroxide $Ca(OH)_2$ (slaked lime)	Soil from the loose overburden dump of the Glavnyi Quarry of the Vysokogorsk deposit
90	10	–
70	30	–
50	50	–
70	–	30
50	–	50
30	–	70
45	10	45
30	10	60
60	10	30

The prepared mixtures of water treatment sludge with overburden rocks of the Vysokogorsk deposit and $Ca(OH)_2$ have the determined contents of gross and water-soluble forms of metals (Cu, Zn, Ni, Al, Mn) and arsenic as well as the determined pH of salt and water extracts. The list of chemical substances determined by the quantitative methods was made taking into account the geochemical specifics of the area under study. The quantitative chemical analysis was performed according to the standard techniques GOST 26483-85, RD 52.18.685-2006, PND F 16.1:2.2:3.17-98, GOST 26485-85, M-MVI 80-2008. The toxicity of mixtures was determined using the method of PND F T 16.1:2.3:3.8. The research was made in the testing laboratory of OOO Test-Expert in Yekaterinburg.

Laboratory tests of the physical and mechanical properties of the mixtures included determining density, moisture content, deformation modulus, angle of internal friction, and specific adhesion in accordance with GOST 30416-2020, GOST 5180-2015, GOST 12536-2014, GOST 12248-2020. The strength properties of the mixtures were studied under the conditions of non-consolidated undrained shear. The deformation properties were determined by the compression method. The studies were carried out in the testing laboratory of OOO Uralgeoproekt in Yekaterinburg.

The bearing capacity of technosoils composed of water-saturated organomineral and organic soils was determined in accordance with the paragraphs 5.1.9 and 5.7.5 of SP 22.133302016 with the calculation of the ultimate resistance of the base N_U under vertical load on linear models.

Results and Discussion. The conducted research has shown that adding recultivants such as loose overburden rocks of the Vysokogorsk deposit and $Ca(OH)_2$ (slaked lime) to the water treatment sludge leads to the fact that the sludge is dewatered and the concentrations of ecotoxicants in it are reduced.

The studies of the chemical composition of the soils from the loose overburden dump of the Vysokogorskoye deposit reveal the following contents of elements and compounds in mg/kg: copper 107.0, zinc 114.0, lead less than 20, arsenic 3.8, nickel 27, mercury 0.097, cadmium less than 0.8, chromium less than 10.0, manganese 124.0, benzopyrene less than 0.005, petroleum products 14.0. The overburden rocks are characterized by a permissive category of contamination ($Zc = 3.8$); increased contents of metals and arsenic are not detected; the soils are not toxic.

The addition of slaked lime ($Ca(OH)_2$) and overburden rocks to water treatment sludge changes the chemical composition of the material. The contents of water-soluble forms of metals and arsenic are significantly lower than those of their gross forms, which proves the binding of ecotoxicants in the form of complex poorly soluble and insoluble mineral and organomineral compounds (Table 3).

Table 3

Content of ecotoxicants in the mixtures

Sample characteristics	pH_{aqu}	pH_{salt}	Elements content											
			Cu		Zn		As		Ni		Al		Mn	
			Gross, mg/kg	Water-soluble, mg/kg	Gross, mg/kg	Water-soluble, mg/kg	Gross, mg/kg	Water-soluble, mg/kg	Gross, mg/kg	Water-soluble, mg/kg	Exchange (mobile), mmol/100 g	Water-solubla, mg/kg	Gross, mg/kg	Water-soluble, mg/kg
Mixture of sludge + $Ca(OH)_2$ (90 · 10 wt.%)	10.2	9.7	143.0	26.0	120.0	<1	3.6	<1	25.0	1.3	0.26	<5	152	5.9
Mixture of sludge + $Ca(OH)_2$ (70 · 30 wt.%)	12.5	12.3	63.0	4.7	57.0	<1	0.3	<1	17.0	2.3	<0.05	<5	62.0	<1
Mixture of sludge + $Ca(OH)_2$ (50 · 50 wt.%)	12.4	12.4	53.0	<1	30.0	<1	1.7	<1	14.0	<1	<0.05	<5	41.0	<1
Mixture of sludge + soil (70 · 30 wt.%)	9.8	8.2	317.0	<1	122.0	<1	6.6	<1	15.0	<1	<0.05	<5	950	14.0
Mixture of sludge + soil (50 · 50 wt.%)	8.4	6.9	427.0	<1	131.0	<1	5.0	<1	14.0	<1	<0.05	<5	1225	12.0
Mixture of sludge + soil (30 · 70 wt.%)	8.3	7.5	289.0	<1	135.0	<1	4.2	<1	<10	1.3	<0.05	<5	777	7.4
Mixture of sludge + soil + $Ca(OH)_2$ (45 · 45 · 10 wt.%)	12.4	12.4	275.0	11.0	109.0	<1	5.1	<1	20.0	<1	<0.05	<5	1479	1.7
Mixture of sludge + soil + $Ca(OH)_2$ (30 · 60 · 10 wt.%)	12.5	12.4	254.0	<1	118.0	<1	4.9	<1	12.0	<1	<0.05	<5	1220	4.0
Mixture of sludge + soil + $Ca(OH)_2$ (60 · 30 · 10 wt.%)	12.0	11.9	200.0	42.0	118.0	<1	0.9	<1	14.0	2.2	0.26	<5	847	16.0

The addition of slaked lime increases the pH of aqueous extracts of the mixtures under the study to 9.7-12.4 and contributes to the decrease of the arsenic content (Fig.1)

The research results emphasize that the mixture of water treatment sludge, overburden rock and calcium oxide in a percentage ratio of 60 : 30 : 10 % proves to be the safest from the environmental point of view (with the arsenic content being below the relevant MAC). In this case, the most favorable conditions are created due to the absence of the components exceeding the maximum permissible concentrations for soils.

The addition of slaked lime and overburden rocks to the water treatment sludge changes physical and mechanical properties of the initial material. (Table 4).

According to the research results, the increase in the sludge density from 1.07 to 1.26 g/cm^3 is observed with the addition of up to 50 % of $Ca(OH)_2$; with further addition of $Ca(OH)_2$, the density of the mixture almost fails to increase. When clay material is added, the density of the mixture increases up to 1.78 g/cm^3.

With the addition of up to 50 % of $Ca(OH)_2$, the moisture content of the mixture decreases from 700 to 65 %. With the addition of up to 70 % of clay soil, the moisture content decreases even more from 700 to 47 %.

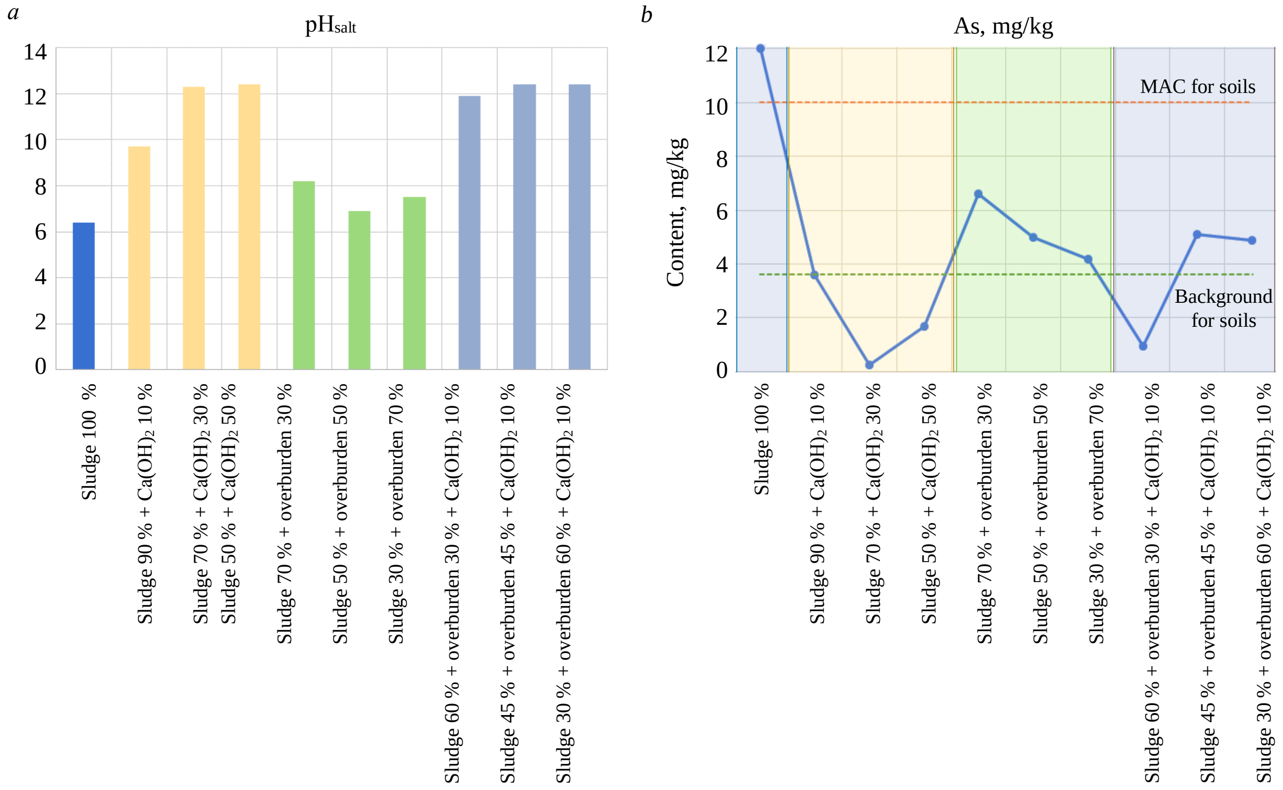

Fig.1. Change of pH_{salt} (*a*) and arsenic content (*b*) in the mixtures of water treatment sludge with $Ca(OH)_2$ and overburden rocks

Table 4

Results of the study of physical and mechanical properties of the mixtures

Sample characteristics, %	Natural moisture content *W*, %	Soil density ρ, g/cm^3	Deformation modulus *E*, MPa	Angle of internal friction φ, deg.	Specific adhesion *C*, MPa
Sludge 100 %	700.0	1.07	0.4	9	0.002
Mixture of sludge + $Ca(OH)_2$ (90 · 10 wt.%)	249.6	1.20	0.7	10	0.003
Mixture of sludge + $Ca(OH)_2$ (70 · 30 wt.%)	135.3	1.25	0.8	20	0.023
Mixture of sludge + $Ca(OH)_2$ (50 · 50 wt.%)	64.4	1.26	2.9	35	0.035
Mixture of sludge + soil (30 · 70 wt.%)	46.6	1.78	0.9	27	0
Mixture of sludge + soil (50 · 50 wt.%)	89.8	1.50	1.3	16	0
Mixture of sludge + soil (70 · 30 wt.%)	169.5	1.28	0.7	10	0
Mixture of sludge + soil + $Ca(OH)_2$ (30 · 60 · 10 wt.%)	46.7	1.68	1.3	36	0.004
Mixture of sludge + soil + $Ca(OH)_2$ (45 · 45 · 10 wt.%)	71.9	1.51	1.3	38	0.006
Mixture of sludge + soil + $Ca(OH)_2$ (60 · 30 · 10 wt.%)	113.8	1.35	0.9	29	0.008

The strength characteristics of the mixture with $Ca(OH)_2$ are higher than those of the mixture with clay material. The decrease in the moisture content occurs more intensely with the addition of $Ca(OH)_2$.

The assessment of the soil according to its bearing capacity for the reason of ensuring the movement of equipment during the reclamation activities has revealed that with an embankment width of up to one meter only the sludge mixed with 30 and 50 % of $Ca(OH)_2$ satisfies the calculation of the bearing capacity. With a strip width of two meters, this condition is satisfied by the mixtures including overburden rocks in different proportions and 10 % of $Ca(OH)_2$. This result imposes restrictions on the use of equipment. Thus, the formation of a dump from freshly prepared technosoil requires the use of the equipment exerting the least pressure on the ground (B10MB bulldozers with an increased width of tracks), and the choice of technology for placing technosoil in a sludge collector should be made in favour of that which does not suggest the need for dump trucks to drive onto the surface of a dump made from technosoil.

The analysis of the results of the chemical composition and physical and mechanical properties of the mixtures under study has provided the reasons why the mixture of water treatment sludge, overburden rock and $Ca(OH)_2$ at a ratio of 60 : 30 : 10 % proves to be the most economical and environmentally friendly option for the preparation of the recultivation material for the reclamation of a sludge collector. The reasons are as follows:

- the initial sediment sample contained arsenic in an amount of 1.2 TAC;
- quantitative analysis of the overburden rocks of the Vysokogorskoe deposit showed that the contents of the gross forms of the metals did not exceed the established maximum permissible concentrations (MAC);
- in the sample containing overburden rocks (30 %), $Ca(OH)_2$ (10 %), and sludge (60 %), the arsenic content decreases below the TAC; in the water extract the arsenic content is also below the MAC;
- the mixture is not toxic;
- according to physical and mechanical characteristics, the mixture in a ratio of 60 % sludge, 30 % overburden rock and 10 % $Ca(OH)_2$ has a high load-bearing capacity for technological operations aimed at the reclamation of a sludge collector with a reclamation strip being of at least two meters wide.

The results of the research have formed the basis for setting up the regulations for the preparation of the technogenic soil recommended for the reclamation of the sludge collector of the Chernoistochinskii hydroelectric complex.

Technogenic soil (technosoil) is the water treatment sludge accumulated in a sludge collector and mixed with slaked lime and natural soil for the improvement of its bearing capacity and the reduction of the contaminant migration. To create technosoil, it is planned to use the entire volume of the accumulated sludge. The embankment formed by the techno-soil is expected to have a convex shape to ensure the drainage of the atmospheric precipitation from the territory of the reclaimed sludge collector.

To avoid dusting, the sludge can be mixed with lime by means of a paddle mixer in the cement truck-mixer system or with soil on a kart freed from the sludge (Fig.2).

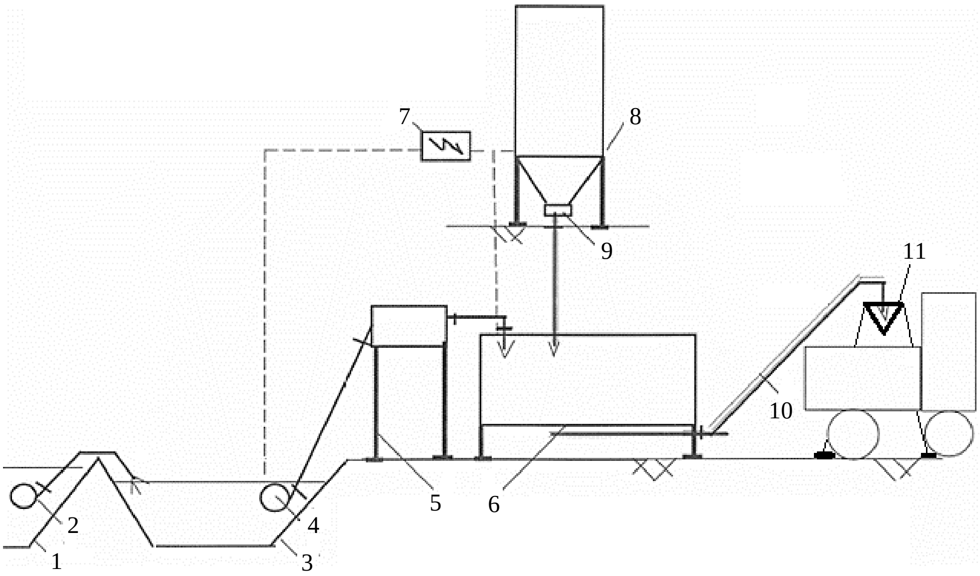

Fig.2. Scheme of equipment for mixing sludge with lime

1 – sludge collector; 2, 4 – sludge pumps; 3 – process unit; 5 – flow divider; 6 – mixer; 7 – control cabinet; 8 – silo – lime bunker; 9 – screw doser for feeding lime; 10 – screw for unloading mixture from the mixer; 11 – bunker device

Fig.3. Twin-shaft paddle mixer SMK-126

The work was carried out in a process unit of the sludge collector. The process unit, whose volume ranges from 900 to1300 m^3, is located next to the technological platform where sludge disposal equipment is installed. The technological platform is situated on board the sludge collector and includes a site covered with reinforced concrete road slabs and two loading areas for the access of cement trucks used for loading lime into the silos and dump trucks used for unloading sludge mixed with lime. The sludge from other remote process sections is fed to the process unit with the help of a high-performance sludge pump. From the process unit the sludge by means of a sludge pump enters the flow divider and then goes through two channels to twin-shaft paddle mixers. Industrial enterprises usually use a twin-shaft paddle mixer SMK-126 for watering and mixing clay (Fig.3). Lime is fed using a screw doser. In the mixer, the sludge is constantly mixed with lime and moves from the inlet hatch to the unloading hatch into the lower part of the mixer. The movement of the entire mass is regulated by blades mounted on the shafts. All work is carried out in summer.

Technosoil resulting from the mixture of sludge and lime is moved to the overburden on the karts. After that the primary planning or leveling is done. The use of $Ca(OH)_2$ has some disadvantages. For instance, the pH medium of the resulting technogenic soil can significantly change from neutral one (pH 6.4) to alkaline (up to pH 12.3), which prevents the restoration of local plant species in the reclaimed areas. This fact determines the need to use potentially fertile and fertile soil as the top layer.

Conclusion. Sustainable development of mining areas is associated with the reclamation of the lands disturbed as a result of industrial activities and their subsequent return to economic use. The increased content of pollutants (arsenic) and low bearing capacity of water treatment sludge accumulated in the sludge collector of the Chernoistochinskii hydroelectric complex have necessitated the search for methods and materials both for binding pollutants to avoid their leaching upon contact with surface waters, and for increasing the bearing capacity of the material for the reclamation of the facility under study.

The analysis of the results of the chemical composition and physical and mechanical properties of the mixtures under study has shown that the mixture of water treatment sludge, loose overburden dump soils and $Ca(OH)_2$ in a ratio of 60 : 30 : 10 % proves to be the most economical and environmentally friendly for the preparation of the reclamation material.

The resulting technosoil with approved material specification 08.92.10-001-97921764-2020 will make it possible to reclaim facilities with small amounts of water treatment sludge and, consequently, to improve the environmental situation in the sanitary protection zone of the water supply source.

The rational use of water treatment sludge as a technogenic secondary raw material ensures environmentally safe waste disposal and reclamation of disturbed lands.

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Research article

Lithification of leachate from municipal solid waste landfills with blast furnace slag

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Abstract. The article presents an alternative method of utilization of blast furnace slag and leachate from solid municipal waste landfills, the formation of which occurs during the infiltration of atmospheric precipitation through the thickness of deposited waste. The method is based on the conversion of leachate from the liquid phase to the solid aggregate state by lithification using blast furnace slag as an astringent material. The hydraulic activity of slag, which depends on the amount of oxides contained in it, has been estimated. The investigated slag belongs to the 3rd grade, which confirms the possibility of its use as an astringent material. The filtrate was analyzed for the content of various elements, and the maximum permissible concentrations for each element were found to be exceeded. Chemical and biological oxygen demand were determined, and critically high values were installed (17200 mgO_2/l and 4750 mgO_2/l, respectively). The lithification process was divided into two stages. The first stage was to reduce the organic component in the filtrate using a coagulant, aluminum sulfate; the second stage was slag hydration. The optimum ratio of lithificate components in terms of mixture solidification rate was established at 1:0.03:1.25 (leachate, coagulant, blast furnace slag). The obtained material was analyzed for the solubility and content of various forms of metal. It is established that at infiltration of atmospheric precipitations through lithificate only 3 % of material will be washed out; concentrations of gross and mobile forms of heavy metals do not exceed the maximum permissible, except for the gross content of arsenic, mobile, and water-soluble forms of which were not found. The values of chemical (687 mgO_2/l) and biological (173 mgO_2/l) oxygen demand in the aqueous extract from lithificate decreased more than 25 times in comparison with the initial filtrate. According to the results of toxicological studies, lithificate was assigned an IV class of waste hazard, which confirms the possibility of its use as bulk material at landfills.

Keywords: metallurgical waste; blast furnace slag; municipal solid waste; leachate from solid municipal waste landfills; utilization of technogenic waste; lithification; bulk material

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Introduction. Currently, the Russian Federation is experiencing steady growth in industrial production. According to Federal State Statistics Service, industrial production grew by 3.5 % in 2023 compared to the previous year[1]. At the same time, the basic branch of the economy that provides life support was and remains the metallurgical industry, which annually becomes the leader of the positive dynamics of the rate of development, where the growth in 2023 amounted to 9.5 % compared to 2022 [1, 2]. The volume of pig iron smelting in Russia in December 2023 amounted to 4.4 million t, which is 3 % higher than in December 2022; over the year it increased by 5.8 % and reached 54.6 million t [3]. Non-alloy steel output in December 2023 increased by 13 % to 4.9 million t compared to the same period in 2022; total growth for the year was 7.9 % (60.2 million t).

A negative factor in the development of industrial production is the increase in the volume of waste generation, which is especially characteristic of enterprises of mineral and raw materials complexes, where during the extraction and processing of minerals, multi-tonnage wastes are generated

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[1] Industrial production in Russia. Moscow: Federal State Statistics Service, 2023, p. 259.

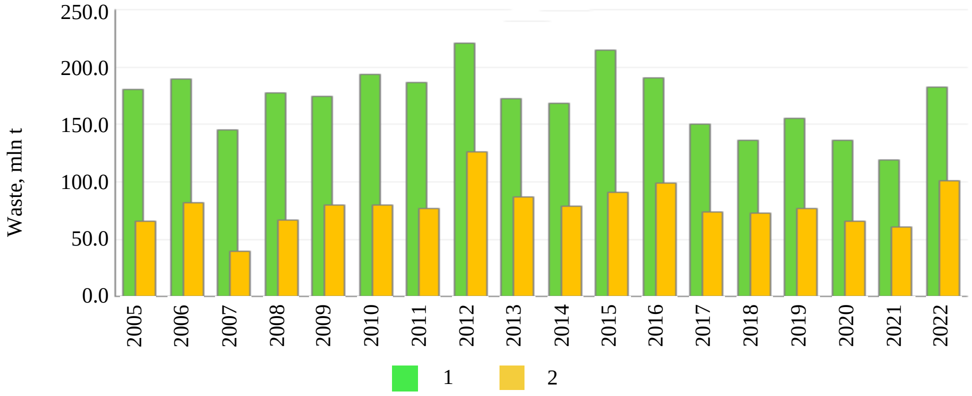

Fig.1. Quantity of generated (1), utilized, and neutralized (2) wastes in the metallurgical production by years

and accumulated – overburden, tailings, as well as processing wastes [4]. A significant position in the formation and accumulation of industrial waste is occupied by the metallurgical processing of iron and steel [5]. According to statistical data[2], currently less than half of the generated wastes from metallurgical production are utilized, which leads to their accumulation in the form of man-made massifs on the territories of industrial enterprises (Fig.1) [6].

The main wastes of ferrous metallurgy are slag from blast furnaces and steelmaking [7]. The output of blast furnace slag can reach 600 kg per 1 t of pig iron, and that of steelmaking slag is 200 kg per 1 ton of steel [8].

Slags formed during iron smelting are products of the interaction of initial components under the influence of a high-temperature regime – ore, fuel, and flux [9]. Fuel provides heating of charge materials up to temperatures of 1400-1600 °C and is a catalyst for chemical reactions in ore melting. Coking varieties of hard coal – coke – are used as fuel [10, 11]. Waste rock from the ore part of the charge and ash from coke combustion are converted into slag by adding flux, a material that reduces heat consumption for the melting of some oxides [12]. The melting temperature of such oxides can be 1700 °C and higher, which is impossible to realize in the conditions of blast furnace operation. At a certain ratio of oxides composing the main part of the ore waste rock (SiO_2, Al_2O_3, CaO, and MgO), by adding flux, compounds with a melting point of 1300 °C are formed, which makes it possible to separate the useful part from the waste part in the ore charge. Depending on the composition of the ore charge, one or another flux is used: basic, acidic, or alumina. In most cases, the ore mined contains acidic rock, which implies the use of basic flux, represented by limestone.

Thus, the composition and properties of the obtained slag depend on the chemical and mineral composition of iron ore, ash from coke combustion, added flux, and the operating condition of the blast furnace [13-15]. The chemical composition of blast furnace slag is mainly represented by such elements as silicon, calcium, aluminum, and magnesium, and, to a lesser extent, iron, manganese, and sulfur. The mass fraction of blast furnace slag components is, %: SiO_2 – 33.0-44.0; CaO – 30.0-49.0; Al_2O_3 – 4.5-20.0; MgO – 1.5-15.0; FeO – 0.5-3.0; Fe_2O_3 – 0.3-0.8; MnO – 0.3-3.0; SO_3 – 0.4-2.5.

One of the peculiarities of slag is its similarity in component composition to cement in terms of lime, silica, and alumina content. For this reason, the main methods of handling this waste can include its use as a binder material or aggregate in the production of cement and concrete, as well as in road construction [16-18]. Less frequently, slag is used in the production of slag wool as a thermal insulation material and mineral fertilizer [19, 20]. In this case, the amount of slag produced significantly exceeds the volume of utilization, which leads to its accumulation and, as a consequence, the formation of technogenic massifs. This determines the relevance of the search for new ways of utilizing the waste under consideration.

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[2] Education, utilization, neutralization, and disposal of production and consumption waste in the Russian Federation. Moscow: Federal State Statistics Service, 2023, p. 209.

The article considers an alternative method of utilization of blast furnace slag together with the liquid waste of municipal solid waste (MSW) landfills – leachate, which is formed as a result of biological and physicochemical transformations in the body of the array under the influence of infiltrating precipitation (Fig.2) [21]. The composition of this leachate, characterized by diversity and variability, includes an extensive list of pollutants – compounds of various heavy metals and a number of toxic, hard-to-oxidize organic substances. The migration of landfill leachate outside the landfill causes irreparable damage to all components of the environment. There is pollution of surface and underground water bodies with salts of heavy metals and organic compounds coming from leachate, soil pollution, and, as a consequence, changes in their composition and reduction of plant communities [22, 23].

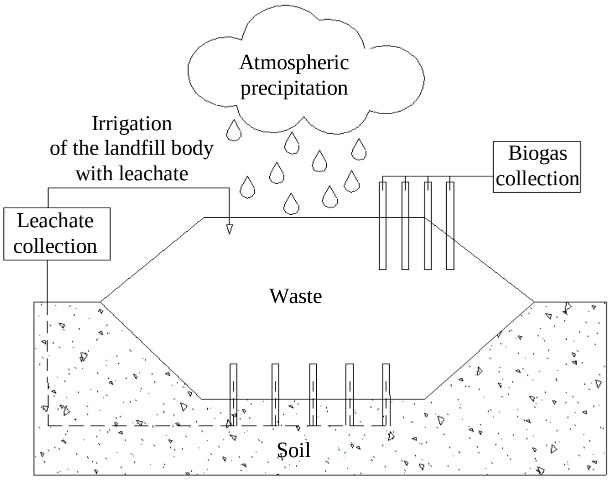

Fig.2. Scheme of landfill leachate formation

To treat leachate from landfills, it is possible to use various methods of effluent treatment – mechanical, physical-chemical, biological, and combined, which are insufficiently effective and economically inexpensive [24]. Therefore, leachate is often collected and used in the irrigation of the landfill body to accelerate the process of decomposition of accumulated waste, which leads to its re-accumulation.

One of the possible options for leachate utilization is the conversion from the liquid to the solid phase. This method of stabilization is called lithification of landfill leachate. Up to now, various methods of leachate lithification have been considered, in particular the method of mixing leachate with shale ash and ash from the incineration of MSW as a binding material [25-27]. The development of this direction is difficult due to the lack of sufficient quantities of binder material of anthropogenic origin (shale ash). The main disadvantage of using ash from the incineration of MSW remains the difficulty of continuous regulation of the composition of municipal waste incoming to incineration plants in order to control the concentration of heavy metals in the ash. The Saint Petersburg Mining University developed a formulation of technology from landfill leachate with the use of binding material based on steelmaking slag [28]. However, the volume of formed steelmaking slag is two times lower than the volume of blast furnace slag formation. At the same time, blast furnace slag has better hydraulic activity due to the increased content of CaO, which should lead to an increase in the strength characteristics of the resulting lithificate. Therefore, it seems promising to use blast furnace slag as a binding material.

Methods. The object of the study is blast furnace slag from a metallurgical plant in the Lipetsk region. Hot liquid slag masses are discharged into trenches and cool down naturally [29]. Sampling was carried out in the area of slag discharge after its cooling on a uniform network according to PND F 12.4.2.1–99 “Waste of mineral origin. Recommendations on sampling and preparation of samples. General provisions”. The site is characterized as homogeneous by the composition, coarseness and moisture content of the material (Fig.3). Selected 22 point samples (marked in red on Fig.3) were combined into one and delivered for further analysis to the laboratory of Saint Petersburg Mining University.


Fig.3. Blast furnace slag sampling scheme at the primary processing site

Blast furnace slag as additives in cement production should meet the requirements of GOST 3476-2019 “Blast furnace slag and electrothermophosphorus granulated slag for cement production”. Assessment of slag hydraulic activity is carried out by the quality coefficient, which depends on the content of some oxides. At the content of magnesium oxide (MgO) of more than 10 %, the coefficient is determined by the formula

$$K = \frac{\mathrm{CaO} + \mathrm{Al_2O_3} + 10}{\mathrm{SiO_2} + \mathrm{TiO_2} + (\mathrm{MgO} - 10)}.$$

The component composition of slag was determined according to GOST 5382-2019 “Cements and cement production materials. Methods of chemical analysis” by X-ray fluorescence (XRF) method using a sequential wave dispersive X-ray fluorescence spectrometer XRF-1800 by Shimadzu [30]. A laboratory sample of blast furnace slag was selected for analysis. The material was crushed to particles less than 30 μm and then pressed into tablets.

The leachate was sampled at the landfill located in Gatchina district, Leningrad region. The leachate is collected by means of a drainage system, passing through the thickness of the deposited waste, and is further directed to a storage pond, from which it is used for irrigation of the body of the massif to accelerate the decomposition process of the deposited waste. In this case, there is a re-accumulation of leachate and an increase in concentrations of pollutants: heavy metals, hard-to-oxidize organics, etc. The content of metals and metalloids in the leachate was determined by atomic absorption spectroscopy according to the method M-02-2406-13[3] using an optical emission spectrometer with inductively coupled plasma Shimadzu ICPE-9000 (Japan). Mass concentrations of anions were measured by ion chromatography according to the method M-02-1805-09[4] using an ion chromatograph Shimadzu (Japan) LC-20 Prominence.

The normal process of slag hydration is hindered by the presence of a high content of organic substances in the leachate. To determine the content of organic substances in the leachate, chemical and biological oxygen demand (COD and BOD) were determined. COD was determined by the spectrophotometric method according to FR.1.31.2013.16588[5], and BOD was determined by the manometric method according to FR.1.31.2015.20690[6].

The lithification process is divided into two stages and consists of mixing leachate and blast furnace slag with the addition of a coagulant to activate the solidification process of the mixture by precipitating suspended solids and some organic compounds.

At the first stage of experimental studies, the selection of coagulant was carried out according to the highest rate of mixture solidification. For this purpose, different coagulants were added to four samples of filtrate in a ratio of 1:0.05 (200 ml of filtrate and 10 g of coagulant). The resulting solution was stirred until the gassing reaction was stopped. The most widely used reagents for wastewater treatment were used as coagulants: slaked lime, aluminum sulfate, iron (III) chloride, and iron (III) sulfate. At the end of the coagulation process, one part of slag (200 g) was added to the obtained mixture, after which the mixture was stirred to form a homogeneous mass. According to the curing time of the mixture, the best coagulant was determined. To determine the effectiveness of the coagulant, a comparison sample without the addition of coagulant was additionally prepared in a 1:1 ratio (200 ml of filtrate and 200 g of slag).

The second stage of research consisted of the selection of the optimal ratio of components – coagulant and blast furnace slag. For this purpose, the coagulant selected in the first stage was added

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[3] M-02-2406-13. Methods of quantitative chemical analysis. Determination of elements in drinking, mineral, natural, waste water, and atmospheric precipitation by the atomic absorption method. St. Peterburg: Analyt, 2013, p. 25.

[4] M-02-1805-09. Methodology for measuring the mass concentration of nitrite, nitrate, chloride, fluoride, bromide, sulfate, and phosphate ions in natural, drinking, and waste water samples by ion chromatography. St. Peterburg: Analyt, 2009, p. 20.

[5] FR.1.31.2013.16588. Methodology for measuring bichromate oxidizability of water (COD) in drinking, surface natural, sewage, sea water, swimming pool water, and process water by spectrophotometric method. Moscow: Ecoinstrument, 2013, p. 15.

[6] FR.1.31.2015.20690. Methodology for measuring biochemical oxygen consumption in natural and waste water samples by gas phase pressure change (manometric method). Moscow: Ecoinstrument, 2015, p. 30.

to five samples of filtrate in the ratio of 1:0.05 and different amounts of slag parts: 1, 1.25, 1.5, 1.75, and 2 (200, 250, 300, 350, and 400 g).

After determining the optimum amount of slag introduced by the rate of solidification of the mixture, the determination of the minimum required amount of the selected coagulant was carried out. For this purpose, coagulant in the amount of 0.01 to 0.05 parts (2, 4, 6, 8, and 10 g) and the previously selected optimal amount of slag were added to five samples of filtrate.

The obtained lithificate was analyzed for solubility by the gravimetric method according to GOST 33135-2014 “Public roads. Viscous petroleum road bitumen. Method for determining solubility”. For this purpose, an aqueous extract of lithificate was prepared according to GOST 26423-85 “Soils. Methods of determination of specific electrical conductivity, pH, and dense residue of water extract”. The solubility was calculated by the formula

$$P = \frac{100\left(m_2 - m_1\right)}{m_{\text{smpl}}},$$

where m_1 is the mass of the weighing cup with filter dried, g; m_2 is the mass of the weighing cup with filter dried with sediment, g; m_{smpl} is the mass of the lithificate sample taken for analysis, g.

Toxicological studies of the lithificate were carried out to establish its hazard class by biotesting on a testing culture of *Chlorella vulgaris* algae. For this purpose, the multiplicity of the dilution of water extract from the obtained waste, at which there is no harmful effect on hydrobionts, was determined. The study was carried out according to the method of PND FT 14.1:2:3:4.10-04[7] and consisted of recording the difference in optical density between the test culture of Chlorella algae grown in a medium containing no harmful substances (the control) and the test sample of water extract, which may contain harmful substances. An aqueous extract of lithificate was prepared, and dilutions of 10, 100, 1000, and 10,000 times were carried out according to the methodology for production and consumption waste. The toxicity criterion is considered to be a decrease in the value of optical density compared to the control variant (distilled water) by 20 % or more, as well as in algae growth stimulation by 30 % or more.

In cases of growth suppression by more than 20 %, the toxic dilution rate is calculated according to the formula

$$\text{TDR} = 10\frac{\left(\lg P_{\text{h}} - \lg P_{\text{l}}\right)\left(I_{\text{l}} - 0,2\right)}{I_{\text{l}} - I_{\text{h}}} + \lg P_{\text{l}},$$

where P_{h} is the dilution rate (the highest) at which the percentage of deviation was below the toxicity criterion (20 %); P_{l} is the dilution rate (the lowest) at which the percentage of deviation was above the toxicity criterion; I_{h} and I_{l} are the deviations from the control corresponding to these dilutions, shares.

In order to establish the degree of leachability of the organic component from the lithificate, COD and BOD were determined in the aqueous extract using the same methods as for the leachate.

The determination of the gross concentrations of metals and metalloids, as well as their mobile and water-soluble forms, in the lithificate was carried out by atomic absorption spectrometry. To determine the gross forms of elements, microwave decomposition of pre-crushed lithificate in a mixture of concentrated acids (nitric, hydrochloric, and hydrofluoric) For the determination of water-soluble forms, an aqueous extract was prepared according to GOST 26423-11 “Methods of determination of specific electrical conductivity, pH, and dense residue of aqueous extract”. For the determination of mobile forms, an extract from lithificate with an acetate-ammonium buffer solution with a pH of 4.8 was prepared according to RD 52.18.289[8].

Results. The presented method of utilization of blast furnace slag together with landfill leachate is based on the transition of leachate from a liquid aggregate state to a solid, stable form using crushed blast furnace slag with particle sizes up to 5 mm instead of cement as a binding material (Fig.4).

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[7] PND F T 14.1:2:3:4.10-04. Methodology for measuring the optical density of *Chlorella vulgaris Beijer* for determining the toxicity of drinking, fresh natural, and waste water, water extracts from soils, sewage sludge, production, and consumption wastes. Moscow, 2014, p. 36.

[8] RD 52.18.289-90. Methods of measuring the mass fraction of mobile forms of metals (copper, lead, zinc, nickel, cadmium, cobalt, chromium, and manganese) in soil samples by atomic absorption analysis. Moscow: State Committee on Hydrometeorology, 1990, p. 36.

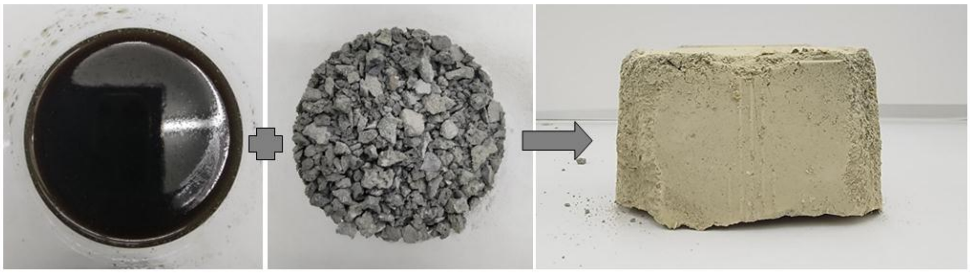

Fig.4. Landfill leachate, blast furnace slag, and lithification product obtained

Blast furnace slag is well studied as a material used as a mineral additive to cement and concrete. It can be used as a binding component and as an aggregate instead of crushed stone [31, 32]. Its use as an additive solves two main environmental problems: the reduction of carbon dioxide emissions into the atmosphere during cement production as well as the partial utilization of waste and its recycling.

The composition of the investigated slag, as well as the quality coefficient calculated on its basis, are presented in Table 1. According to the data obtained, the studied slag belongs to the 3rd grade, which indicates its low activity and unsuitability for use as a binding material in the manufacture of cements and high-strength concrete [33, 34]. Thus, there is a need to find an alternative way of utilizing blast furnace slag. It is proposed to use it as a hydraulic binder for the stabilization of liquid waste from landfills.

Table 1

Chemical composition of blast furnace slag

Sample	Mass fraction of components, %									
	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	MnO	SO_3	TiO_2	Cl	K
Norm for grade 3	n/r*	n/r	n/r	Not more than 15.0	n/r	Not more than 4.0	n/r	Not more than 4.0	Not more than 0.1	Not less than 1.20
Blast furnace slag	40.5	38.1	5.8	10.5	0.47	0.33	2.4	0.39	Less than 0.0001	1.30

* No regulation.

The composition of landfill leachate depends largely on the composition of stored waste and its storage conditions, climatic conditions and the time of landfill operation [35]. The composition of leachate used in this study is presented in Table 2.

Table 2

Indicators of leachate from landfills

Indicator	Significance	MAC[9]
pH	7.8	6.0-9.0
Electrical conductivity, µSm/cm	46,000	n/r*
BOD5, mgO_2/l	4,750	2
COD, mgO_2/l	17,200	15
Solid residual, mg/dm^3	13,405	1,500
Chlorides, mg/dm^3	6,075	350
Sulfates, mg/dm^3	252	500
Hydrocarbonates, mg/dm^3	12,501	n/r

* No regulation.

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[9] SanPiN 1.2.3685-21. Hygienic standards and requirements for ensuring safety and (or) harmlessness to humans from environmental factors. Moscow: Ministry of Health and Social Development of Russia, 2021, p. 419-510.

End of Table 2

Indicator	Significance	MAC
Nitrates, mg/dm^3	51.9	45.0
Nitrites, mg/dm^3	13.8	3.0
Ammonium-ion, mg/dm^3	1,894	1.5
Potassium, mg/dm^3	1,266	n/r
Sodium, mg/dm^3	2,384	200
Calcium, mg/dm^3	365	180
Magnesium, mg/dm^3	168	50
Total iron, mg/dm^3	9.8	0.3
Copper, mg/dm^3	0.3	1.0
Cadmium, mg/dm^3	0.267	0.001
Mercury, mg/dm^3	<0.005	0.0005
Cobalt, mg/dm^3	<0.05	0.1
Chromium, mg/dm^3	2.31	0.05
Lead, mg/dm^3	<0.1	0.01
Arsenic, mg/dm^3	<0.01	0.01
Zinc, mg/dm^3	6.5	5.0
Nickel, mg/dm^3	0.40	0.02
Manganese, mg/dm^3	0.2	0.1
Aluminum, mg/dm^3	5.1	0.2

Thus, exceedances of the maximum admissible concentration (MAC) established for water in underground and surface water bodies of economic and drinking water use are observed almost for each of the above indicators. Thus, the content of ammonium ions exceeded MAC more than 1,000 times.

The high content of organic substances in leachate (COD = 17200 mgO$_2$/l) slows down the process of blast furnace slag hydration. According to GOST 23732-2011 “Water for Concrete and Mortars: Specifications” the oxidizability of water used for the preparation of concrete mixtures should be no more than 15 mg/l. Therefore, the lithification process was divided into two stages. The first stage is represented by the process of particle coagulation [36, 37]. The high intensity of precipitation is visually observed when aluminum and iron (III) sulfates are used, which indicates their high coagulating ability (Fig.5). Aluminum sulfate was chosen for further studies due to its lower toxicity compared to iron (III) sulfate.

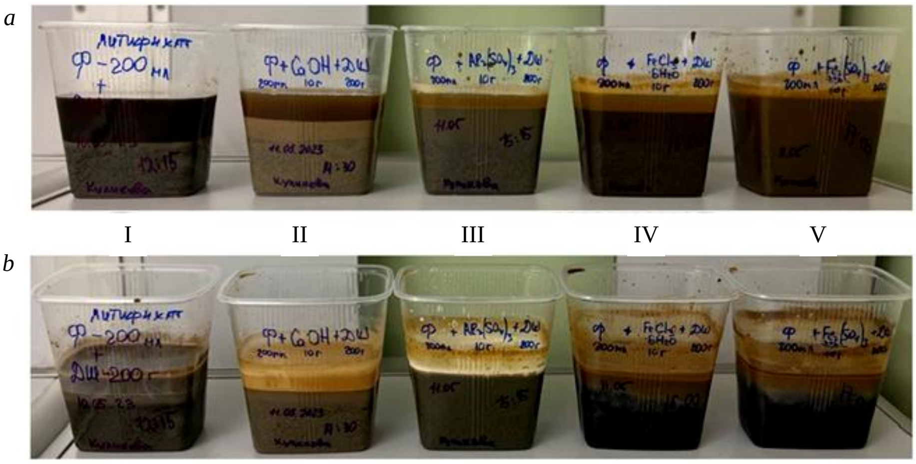

Fig.5. Selection of the optimal coagulant according to the speed of curing of the mixture:
a – on the day of mixture preparation; *b* – on the 10th day of curing;
I – without coagulant; II – Ca(OH)$_2$; III – Al$_2$(SO$_4$)$_3$; IV – FeCl$_3$; V – Fe$_2$(SO$_4$)$_3$

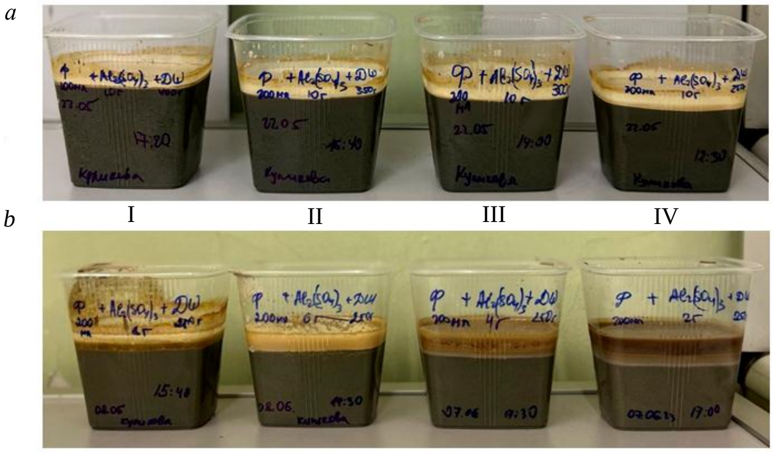

Fig.6. Selection of lithificate formulation:
a – the optimal amount of slag introduced: I – 400 g; II – 350 g; III – 300 g; IV – 250 g;
b – the optimal amount of coagulant added: I – 8 g; II – 6 g; III – 4 g; IV – 2 g

Preliminary coagulation triggers the second stage of lithification: the direct solidification of the mixture with the help of blast furnace slag. Based on the results of laboratory studies, the optimal formulation of lithificate in terms of solidification time was selected: 200 ml of filtrate, 6 g of aluminum sulfate, and 250 g of blast furnace slag (Fig. 6). The ratio of components – filtration, coagulant, and blast furnace slag – was chosen because, at the introduction of more slag, the rate of solidification does not change, and at a lower dosage of $Al_2(SO_4)_3$, the coagulation process is not started. The complete solidification of the lithificate occurred after 14 days from the beginning of the experiment. The highest rate of strength gain of the mixture was noted for the slag fraction smaller than 1 mm.

Based on the results of experimental studies on the solubility of lithificate, it was found that only 3 % of the resulting material would be leached by the infiltration of precipitation through it.

The results of studies of the obtained lithificate for the content of gross, mobile, and water-soluble forms of metals and metalloids are presented in Table 3. The pH of the lithification salt extract was over 12. The determined concentrations were compared with MAC for loamy and clayey soils with a pH of salt extract greater than 5.5.

Table 3

Elemental content in lithifacate

Element	Gross concentrations, mg/kg	Concentrations of mobile forms, mg/kg	Concentrations of water-soluble forms, mg/kg	MAC of substances in soil, mg/kg	MAC[10] of mobile forms of substances in soil, mg/kg
Total iron	2,531	146	0.9	n/r	n/r
Zinc	3	0.3	0.1	220	23
Aluminum	4,967	198	17	n/r	n/r
Chromium	126	1.6	0.1	n/r	6.0
Nickel	55	1.6	0.4	80	4.0
Cadmium	Less than 0.01	Less than 0.05	Less than 0.05	2.0	n/r
Copper	2.2	Less than 0.5	0.5	132	3.0
Manganese	1,471	410	1.9	1,500	100
Lead	Less than 0.05	Less than 0.5	Less than 0.5	130	6.0
Cobalt	Less than 0.01	Less than 0.5	Less than 0.5	n/r	5.0
Calcium	223,963	75,728	3,528	n/r	n/r

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[10] SanPiN 1.2.3685-21, p. 541-545.

End of Table 3

Element	Gross concentrations, mg/kg	Concentrations of mobile forms, mg/kg	Concentrations of water-soluble forms, mg/kg	MAC of substances in soil, mg/kg	MAC of mobile forms of substances in soil, mg/kg
Barium	798	156	2.1	n/r	n/r
Magnesium	31,374	7,200	48	n/r	n/r
Sodium	7,036	2,500	1,687	n/r	n/r
Potassium	8,132	2,091	967	n/r	n/r
Strontium	525	318	16.2	n/r	n/r
Vanadium	28	1.6	Less than 5.0	150	n/r
Mercury	Less than 0.01	Less than 0.005	Less than 0.005	2.1	n/r
Arsenic	31	Less than 0.05	Less than 0.05	10.0	n/r
Titanium	3,048	Less than 5.0	Less than 5.0	n/r	n/r

It follows from the obtained data that concentrations of gross content of heavy metals and their mobile forms in lithificate do not exceed MAC in the soils of settlements, except for the gross content of arsenic. According to the research conducted, mobile and water-soluble forms of arsenic in extracts from lithificate were not found. In the case of atmospheric precipitation impacting lithificate, arsenic migration into the natural environment does not occur [38].

The obtained values of COD (687 mgO_2/l) and BOD (173 mgO_2/l) for the aqueous extract from the lithificate water decreased more than 25 times compared to the same values in the leachate.

According to the results of toxicological studies, the toxic dilution multiplicity of aqueous extract from the obtained waste was established, at which the growth suppression occurs in comparison with distilled water by 20 % – 48.5 (Table 4). According to the order of the Ministry of Natural Resources of Russia[11] at the dilution multiplicity of aqueous extract from 1 to 100, the waste can be referred to the IV class of danger.

Table 4

Biotesting on Chlorella algae culture (*Chlorella vulgaris*)

Multiplicity dilution	Optical density after 22 h of cultivation*	Medium optical density after 22 h of cultivation medium	Deviation out of control, %	Quality assessment
Control	0.048	0.048	–	–
1	0.016	0.015	76.1	Affects
10	0.036	0.036	25.0	Affects
100	0.040	0.040	17.7	Doesn't affect
1000	0.042	0.042	13.6	Doesn't affect
10000	0.044	0.044	9.4	Doesn't affect

* Minus the optical density after the addition of chlorella before culturing.

Based on the results of studies of the composition and properties of lithificate, it is proposed to use it as a techno-soil (Fig.7) to create an insulating intermediate layer for waste storage in accordance with the instructions for the design, operation, and reclamation of landfills for solid municipal waste[12]. Limestone waste, slag from TPPs, gypsum-containing waste, etc. are used as insulating materials at landfills for solid municipal waste storage. Other industrial waste in the IV class of hazards is allowed. Insulation with the material is carried out daily with a layer thickness of 0.15 to 0.25 m. Thus, the use of lithificate

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[11] Order of the Ministry of Natural Resources and Environment of the Russian Federation N 536 dated December 4, 2014, “On Approval of Criteria of Waste Attribution to I-V Hazard Classes by Degree of Negative Environmental Impact”.

[12] Instructions on the design, operation, and reclamation of landfills for solid municipal waste. Moscow: Ministry of Construction of the Russian Federation, 1996, p. 39.

in the research as an alternative insulating material is relevant to the activity of landfills for solid waste [39-41].

Fig.7. Bulk material based on landfill leachate and blast furnace slag

Conclusion. As a result of the conducted research, the method of utilizing blast furnace slag together with landfill leachate was developed. The method is based on solidification of leachate by adding blast furnace slag as a binding material.

Before introducing the crushed slag, a coagulant is added to the liquid waste to reduce the high concentrations of organic compounds in it. Aluminum sulfate was chosen as a coagulant – a reagent with the highest coagulation ability compared to other tested compounds. The conducted experiments allowed us to establish the optimal dosage of coagulant and blast furnace slag introduction into the leachate in the ratio 1:0.03:1.25 (filtrate, aluminum sulfate, blast furnace slag). The formulation can be applied to other objects of the study. However, fluctuations in the composition of filtrate and blast furnace slag can slightly affect the lithification, which requires some adjustment of the doses of the introduced components.

The application of the obtained material was found to form an insulating layer in the filling of production and consumption wastes [42]. The IV class of hazard of the obtained lithified material was established, as well as the absence of mobile and water-soluble forms of toxic elements in it, which confirms the possibility of its use. As a result, the negative impact on the environment will be reduced due to the utilization of two types of accumulated waste at once.

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Research article

Anomaly detection in wastewater treatment process for cyber resilience risks evaluation

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Abstract. Timely detection and prevention of violations in the technological process of wastewater treatment caused by threats of different nature is a highly relevant research problem. Modern systems are equipped with a large number of technological sensors. Data from these sensors can be used to detect anomalies in the technological process. Their timely detection, prediction and processing ensures the continuity and fault tolerance of the technological process. The aim of the research is to improve the accuracy of detection of such anomalies. We propose a methodology for the identification and subsequent assessment of cyber resilience risks of the wastewater treatment process, which includes the distinctive procedure of training dataset generation and the anomaly detection based on deep learning methods. The availability of training datasets is a necessary condition for the efficient application of the proposed technology. A distinctive feature of the anomaly detection approach is a new method of processing input sensor data, which allows the use of computationally efficient analytical models with high accuracy of anomaly detection, and outperforms the efficiency of previously published methods.

Keywords: water treatment systems; industrial cyber-physical systems; cyber resilience; risks; anomaly detection; training datasets; test bed

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Introduction. Wastewater treatment plant systems belong to critical infrastructure facilities, the sustainable functioning of which determines the safety of the population. Violations in the technological process of water treatment plants can lead to irreparable consequences for health and ecology [1, 2].

Water treatment plants are equipped with automated control systems for monitoring and timely control of water treatment processes [3-5]. The usage of such systems leads to new risks of cyber resilience breaches as a result of cyber attacks. For example, in 2000, a cyberattack was conducted on water treatment facilities in Maroochy (Australia). As a result, one million liters of untreated wastewater were discharged into the rainwater drainage system over a three-month period. Recently, a number of cyber threats targeting water treatment systems is constantly growing. In 2021, a cyberattack was launched against the Oldsmar water treatment plant in the US, the attacker managed to increase the level of sodium hydroxide in the water[1]. In 2022, malefactors attacked South Staffs Water in the UK using the ransomware Clop[2].

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[1] 21-015 Detectives Investigate Computer Software Intrusion at Oldsmar’s Water Treatment Plant. URL: https://pcsoweb.com/21-015-detectives-investigate-computer-software-intrusion-at-oldsmar%E2%80%99s-water-treatment-plant (accessed 07.03.2024).

[2] South Staffs Water is victim of botched Clop attack. URL: https://www.computerweekly.com/news/252523856/South-Staffs-Water-is-victim-of-botched-Clop-attack (accessed 07.03.2024).

To monitor the water treatment processes’ state, automated control systems collect and analyze various process data. This data can be used to identify anomalies caused by different threats, predict their occurrence and assess the risks associated with systems’ cyber resilience compromise. Timely detection, prediction and processing of such anomalies and related risks ensures the continuity and resilience of the technological process [6-8].

Recently, a large number of different methods have been proposed to detect anomalies in the functioning of cyber-physical objects [9], and the main focus in scientific research is done on the application of deep neural networks due to their ability to model complex nonlinear dependencies between different object parameters and reveal temporal and spatial patterns in the data [10]. In particular, in [11], a model of a variational autoencoder MTS-DVGAN based on two long short-term memory networks (LSTM-networks) is proposed to detect anomalies in data from water distribution systems and wastewater treatment facilities. The performed experiments showed that the application of such a model allows to detect deviations in the functioning of the water treatment system with a high level of efficiency (up to 97.84 %). The study [12] presents the MTAD-CAN model consisting of an autoencoder and two decoders with a coupled attention mechanism designed to extract both temporal dependencies between the parameters of a multidimensional time series and correlation relationships between the parameters themselves. Experiments with data from a water treatment plant system showed an anomaly detection accuracy of up to 92 %. Time series spectral analysis methods has also shown their efficiency in detection of defects in process equipment that can lead to breach of system’s cyber resilience [13], and in [14] a solution combining visual data analysis and machine learning methods has been proposed.

Detected anomalies can be used to assess and predict risks of cyber resilience breach of a technological process [15-17]. Event logs and network traffic, as well as data from physical sensors, are often used as input data [18-20]. To analyze and predict system’s cyber resilience risks, it is necessary to consider the probability of successful threat implementation and the possible damage in case of its success [21]. To determine the probability of successful implementation of threat, various threat models have been proposed [22-24]. To define a threat model, it is necessary to first determine the model of the analyzed system or technological process.

Threat models can be represented as graphs and Markov chains, and can be built using machine learning techniques to identify anomalies. Tabular, graph-based and probability-based methods can be used for risk estimation. One of the existing problems is the analysis of damage caused by destructive activity on water treatment systems (or other automated control systems), this stage is one of the risk components [25]. For this purpose, expert assessment of potential damage or modeling of contamination spread with subsequent consideration of the cost of its elimination can be used.

To determine cyber resilience risk, integral qualitative and quantitative metrics of risk level are used. When forming integral metrics, a tabular approach, a weighting function, a minimax approach, etc. can be used. In this case, the tasks to be solved include determination of metrics to be considered in the integral assessment, development of a methodology for their integration into the risk assessment procedure and analysis of sensitivity of the proposed integral assessment.

Threat models constructed using machine learning techniques can accurately detect and predict anomalies caused by various types of threats. However, there are two key practical challenges to their application: the existence of a dataset to train the analysis model and the availability of computational resources. Training dataset must be realistic structured data that contain annotations describing object state at different periods of time. Analysis of publicly available datasets has shown that there are very few such datasets [26, 27]. Moreover, the anomalies presented in them are trivial and their detection does not require the usage of machine learning methods [28]. One of the possible reasons for the lack of reliable, labeled datasets describing the functioning of cyber-physical systems is the lack of a unified methodology for their creation. This paper proposes a methodology for generating datasets modeling the functioning of wastewater treatment plants at the process level. It specifies stages starting with the selection of the technological process finishing with specification of the malefactor model and possible destructive activities.

The application of anomaly detection methods based on deep learning places high demands on computational resources, which are not always available in practice. Thus, the task of developing anomaly detection and prediction methods optimized for devices with limited computational resources, such as industrial microcomputers, which are not equipped with graphical processing units, while providing anomaly detection performance comparable to classical deep learning models, is highly relevant practical task. In this paper, such a problem is solved by using a special transformation of the data vector into an image, which allows the application of "lightweight" convolutional neural networks with small number of layers.

The aim of the research is to improve the accuracy of anomaly detection in wastewater treatment process for system's cyber resilience risk assessment, considering the limitations of the available computational resources.

The research tasks include development of a methodology for detecting and assessing risks in the technological process of wastewater treatment based on machine learning; development of a methodology for generating data sets modeling the functioning of wastewater treatment facilities at the process level; development and testing of a methodology for detecting anomalies in the data flow from process equipment in real time; development of a method for transforming the input vector of data into images.

The methodology of detection and risk assessment in the technological process of wastewater treatment based on machine learning is developed. This methodology includes the stages of a training dataset generation, identification of anomalies in the data flow from process equipment in real time and calculation of dynamic risk assessments considering the detected anomalies. To identify anomalies in the technological process, the authors propose a method transforming the input data vector into images, which allows using convolutional neural networks with small number of layers.

Methods. A methodology for identification and assessment of cyber resilience risks in wastewater treatment process based on machine learning is proposed. It includes a methodology for generating a training dataset required for anomaly detection using machine learning, and a methodology for analyzing data from sensors of the wastewater technological process.

Methodology for identification and assessment of cyber resilience risks in the wastewater treatment process. It is based on the analysis of data received from the automated control system of the wastewater treatment process (Fig.1). The methodology includes two modes of application – design mode and operation mode – and three main stages – train dataset generation, anomaly detection and cyber resilience risk assessment. The stage of dataset generation is represented by the methodology of training dataset generation. The output of the methodology is a train dataset that serves as input data for the next stage – training analytical models to detect anomalies in the technological process in the design mode, this stage is represented by the anomaly detection methodology. In operation mode, the trained models and data from sensors/actuators of the process control system are used to detect anomalies in data streams from sensors. The output data of this stage are the identified anomalous processes and sensors/actuators. In turn, this data serve as the input for the next

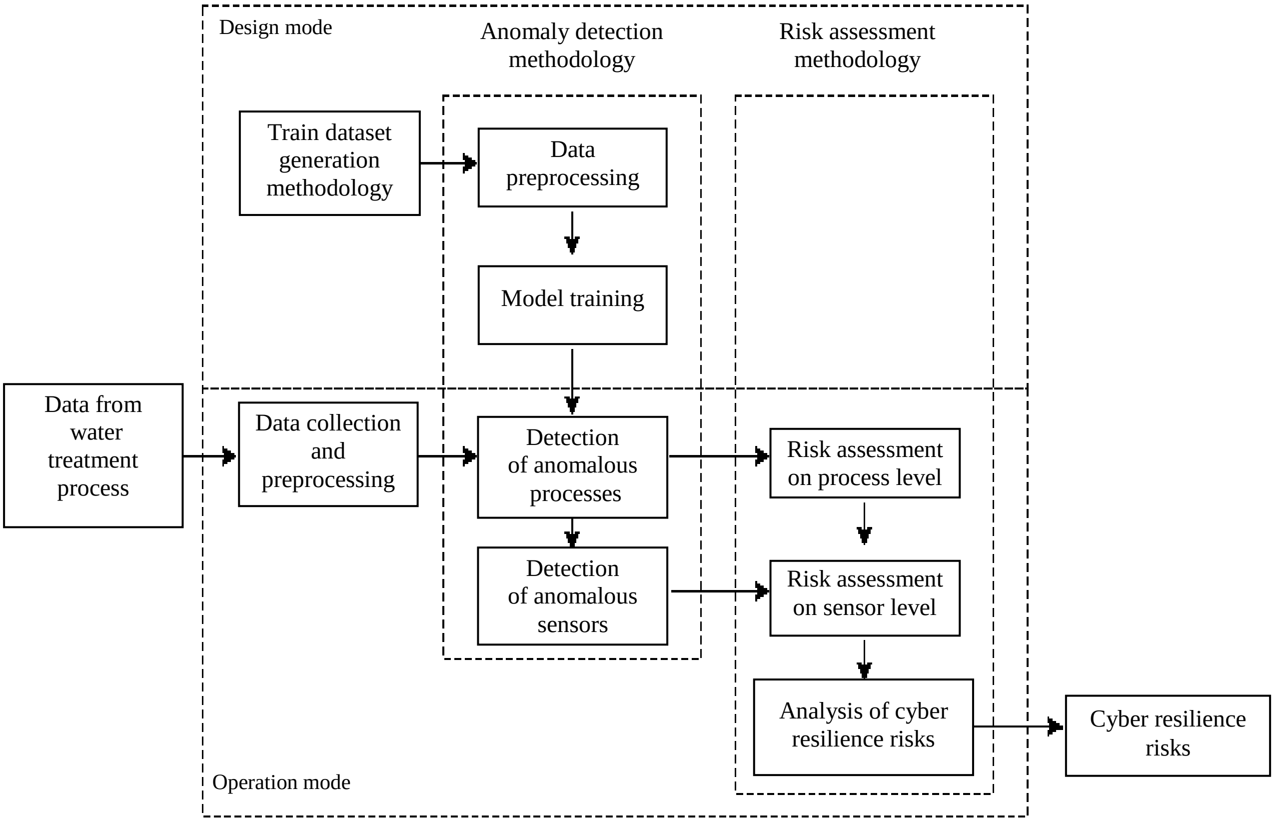

Fig.1. Scheme of methodology for identification and assessment of risks in the wastewater treatment process

step – cyber resilience risk assessment, represented by the cyber resilience risk assessment methodology proposed for the wastewater treatment process.

Methodology of training dataset generation. The developed methodology takes into account the requirements formulated in [27-29]:

- Inclusion of data from both technological equipment and the communication and computing infrastructure of the system, i.e., network traffic data, logs of automated control systems, etc.
- Availability of annotations and a structured annotation scheme that explains the annotations and includes information about anomalies in the technological process, including the possible cause – intentional or unintentional impact on the process.
- Closeness of generated data to real world data, and limitations, due to the use of simplified mathematical models or the limited hardware capabilities should be documented.

Thus, the methodology for generating datasets modeling the functioning of the technological process consists of the following steps:

- process definition and specification;
- determination of the type of testbed and its implementation;
- generation of data consistent with the normal operation of the system;
- development of a threat model to continuity and fault tolerance of the technological process taking into account the possible consequences of their violation;
- development of scenarios of threat implementation considering the used technological stack for modeling the technological process;
- implementation of threat scenarios and collection data;
- evaluation and validation of the generated dataset.

The methodology defines the input and output of each step, including documentation, since each step depends on the result of the previous one. In addition, it allows, if necessary, to reproduce the modeled process, validate the obtained data and explain the obtained results. For example, during the first stage of the methodology a formal model of the technological process with a given set of significant parameters affecting its continuity and fault-tolerance and a technological scheme are formed. Based on the results of this stage, the type of the test bed to be created is determined. According to [27], there are three types of test beds: software (virtual), hardware and hybrid. The software only is used to design virtual test beds for modeling the technological process. Such test beds have a low cost of implementation and a high level of reproducibility. In some cases, for example, when modeling processes performed in hazardous conditions, the use of such stands is the only possible solution. However, mathematical modeling of many processes is an extremely difficult task, for example, when describing the flotation process of water treatment it is necessary to build a hydrodynamic model of the process with a large number of controls and monitored variables taking into account the physical and chemical interaction of substances [30, 31], so the results of their use may be less accurate and reliable. Hardware test beds are built using specialized equipment and software, so the data obtained with their help are more reliable. They reflect possible delays and inaccuracies in the data arising from the use of physical devices and sensors. A significant disadvantage is the cost of developing such test beds and, as a consequence, the low level of reproducibility. Hybrid test beds are a compromise between software and hardware test beds. They are partly constructed using software tools and technological equipment. Thus, at the second stage of methodology, the implementation characteristics of the experimental test bed are elaborated, as well as the format of collected data and the interval of their acquisition are determined.

The results of the first step also have impact on definition of threat model and malicious scenarios. For example, the following potential attacker's targets can be identified for the flotation process of water treatment: stopping raw water mixing; damage to raw water flow meter, reagent pump, acidity sensors; lack of coagulant in the tank, flocculant in the tank, soda in the tank, etc. Threats can be implemented at the physical, information and communication level. The physical level includes physical devices such as water flow sensors, air flow sensors, digital converters, controllers and telecommunication equipment. The targets at the information and communication level are represented by information flows from sensors to controllers, and from controllers to SCADA-system, etc, while the targets at the logical components' level are firmware and software.

The final stage includes evaluation and validation of the generated dataset. They include statistical analysis of the obtained data, and if real data are available, comparative analysis of generated and real data by evaluating the difference between the probability distributions of real and synthetic data.

The collected dataset can be used to analyze technological data.

Anomaly detection technique based on the transformation of tabular data into an image. The proposed technique is based on the idea of using convolutional neural networks, which are good at extracting spatial relationships between attributes. Their application requires transforming the input data vector to a two-dimensional matrix, since the two-dimensional convolution operation extracts spatial relationships better. Let $\bar{v} = \{v_0, v_1, \dots v_k\}$ be the input vector of values from k analyzed sensors and actuators of the system, then the proposed methodology consists of the following steps:

- transformation of each one-dimensional feature vector $\bar{v}$ into a two-dimensional matrix Im_v, usually considered as a grayscale image;

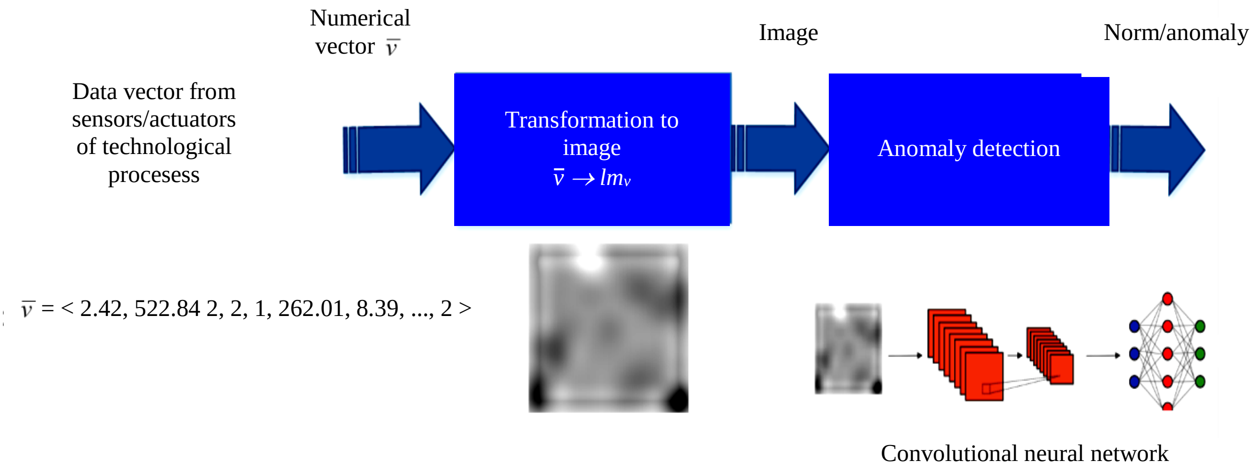

Fig.2. Diagram of anomaly detection in technological processes

- anomaly detection using convolutional neural network (CNN).

The key steps of the methodology are presented in Fig.2.

To construct an image based on a one-dimensional vector $\overline{v}$, the following steps are performed:

- initial preprocessing of feature values, which consists in normalizing them to the range [0,1] for numeric attributes or one-hot encoding the values for categorical attributes;
- preprocessed feature values are interpreted as 8-bit values for a grayscale image;
- layout pixels according to a given algorithm into an image.

To determine coordinates of attribute-pixels direct layout algorithms as well as algorithms can be used based on a nonlinear transformation depending on similiarity of attributes [32-34].

The direct pixel layout algorithm is the most common approach to image generation. The key point in its operation is to determine the dimensionality of the generated image. Usually the input for convolutional neural networks are $n \times n$ images, so the following approach is proposed to determine the image size. Let N be the number of numerical attributes to be analyzed and M be the number of values that all categorical attributes can take, then $n = \mathrm{ceil}\,(N + M)/2$, where ceil is the rounding function to the nearest integer. The image is then generated line by line, with each row generated sequentially. Unused pixels are usually filled with the value 0x00 (black). Thus, in direct pixel layout, the order of features in the vector and the shape of the image determine the position of the corresponding pixel in the image, as a result the neighboring pixels may have no correlation with each other.

Application of algorithms based on non-linear transformation, such as DeepInsight [33, 35] allows taking into account the relationships between features and placing similar attributes close to each other. The basic idea is to use techniques for projecting multidimensional data into a lower dimensional space to determine the position of a given feature on a two-dimensional plane. The scheme of this approach is presented in Fig. 3.

Let $V = \{\overline{v}_i\}_{i=0}^{m}$ – the initial (training) dataset represented as a matrix, where m rows correspond to m vectors with k attributes. Then the procedure of image creation using DeepInsight algorithm includes the following steps:

- Transposion of the matrix V so that each feature is represented by a vector of m elements, i.e. the corresponding row of the transposed matrix V^{T}.

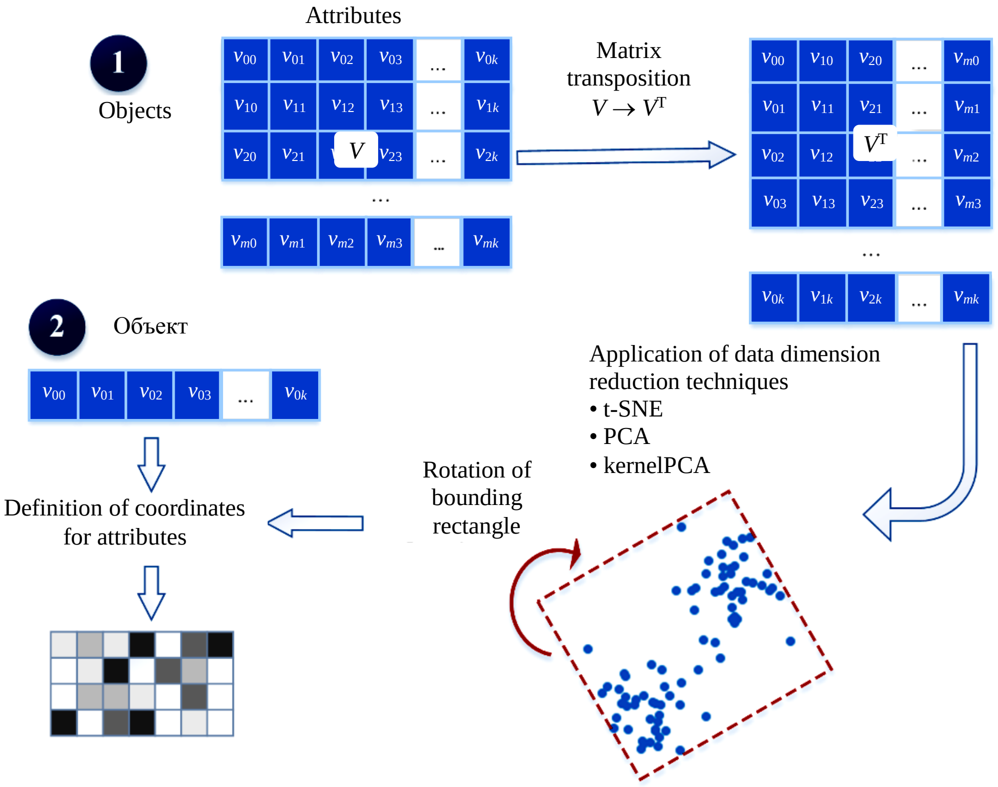

Fig.3. Scheme for determining attribute coordinates using nonlinear transformation

- Application of data dimension reduction technique to map each feature to a two-dimensional plane. This step uses nonlinear dimension reduction techniques such as kernelPCA, t-SNE [36]. The resulting projections determine the position of the features, but not their values.
- Construction the smallest rectangle that bounds all attribute projections and rotation of their coordinates in Cartesian space to get the pixel coordinates for the features.
- Matching attributes to pixel coordinates in the generated projection.

The transformation of tabular data into a matrix structure (image) is characterized by additional computational and time costs required to determine the location of features on the image grid. However, this transformation is performed only at the training stage and does not affect the computational and time characteristics of the real-time anomaly detection process.

To detect anomalies, it was proposed to use a two-layer convolutional neural network, the structure of which is shown in Fig.4. It consists of two convolutional and two fully connected layers. The ReLU function is used as the activation function in the subsampling layers and the sigmoid function is used in the last fully connected layer. The Adam optimizer is used in training and the logarithmic loss function is used as the loss function.

Methodology for assessing cyber resilience risks of wastewater treatment process. Detected anomalies in wastewater treatment processes can lead to cyber resilience breaches. Therefore, they are used to assess risks of breach. In this case, the presence of a single anomaly does not indicate the realization of cyber resilience risks, the risk score grows with the increase in the number of anomalies. Note that risks are identified for processes and individual sensors/actuators measuring various process parameters. The cyber resilience risks are defined based on the criticality of the processes and, therefore, the damage that can be caused to the water treatment process in the case of a breach of process's cyber resilience.

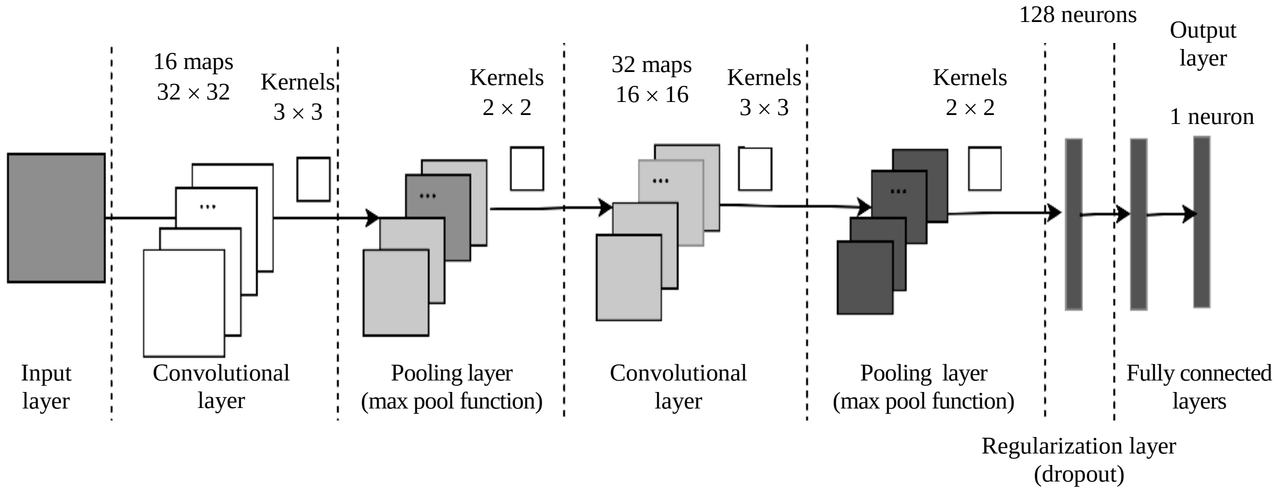

Fig.4. Structure of convolutional neural network used for anomaly detection

The input data for the methodology are the identified anomalies, as well as a description of wastewater treatment processes, their criticality and sensors/actuators measuring various technological parameters. An algorithm is developed to assess cyber resilience risks. It is based on the following assumptions: the risk level is higher for processes that are more likely to exhibit anomalous behavior; the risk level is higher for more critical processes. In addition, a model of the analyzed system is introduced:

$$M = < P_i: R_i, Pr_i, Cr_i, S^i >,$$

where P_i – wastewater treatment process, $i \in \{1:n\}$; n – number of processes implemented in wastewater treatment system; S^i – set of sensors/actuators; Pr_i – probability of anomaly in process P_i; Cr_i – criticality of process P_i, $Cr_i \in \{1,2,3\}$, determined expertly on a scale: 1 – low, 2 – high, 3 – critical; R_i – risk, $R_i \in \{0:3\}$.

Risk is determined by a combination of the criticality of the process and the probability of cyberthreat realization, which depends on the number of anomalies detected. Note that each anomaly also has a probability associated with the confidence score produced by machine learning algorithms. The inputs to the algorithm are the total number of records containing sensor/process actuator readings collected over the entire monitoring period; the number of consecutive records allocated for analysis, called a batch, m; and the total number of batches over the entire monitoring period n. The risk level R is defined on the scale [0, 6], initially $R = 0$. Algorithm for calculating the risk level is as follows:

1. $Pr = 0$ // the initial probability of cyber threat realization.
2. $R = 0$ // the initial level of risk.
3. If $R = 0$, go to step 4, otherwise go to step 5 // if the risk for the process has not yet been assessed ($n = 0$).
4. $R = R\_proc = Cr$ // risk is calculated based on the criticality of the process.
5. If $n = 0$, $Pr = 0$, go to step 9.
6. If $w_i > 0$, go to step 7, otherwise go to step 10 // there were anomalies in the current batch.
7. $w = \frac{\sum_k Pr_k}{n}$ // $\sum_k Pr_k$ – sum of anomaly probabilities for anomalous batches, from the batch we take max Pr; w – share of batches with anomalies, $0 \le w \le 1$.

8. If $Pr + \log_n(1 +) \leq 1$, $Pr = Pr + \log_n(1 + w)$, otherwise $Pr = 1$ // the likelihood of a cyber threat materializing is increasing.

9. $R = R + Cr \cdot Pr$.

10. If $norm > N\_norm$, go to step 11 // *norm* – number of consecutive batches without anomalies, $N\_norm = 10$.

11. $coeff = (n - an)/n$ // *an* – total number of batches with anomalies.

12. If $coeff > R\_coeff$, go to step 13, otherwise go to step 14 // *R_coeff* – coefficient determining the maximum possible risk reduction, $R\_coeff = 0.3$, experimentally determined.

13. $coeff = R\_coeff$.

14. $Pr = Pr - coeff$.

15. $R = R - Cr \cdot Pr$.

The outputs of the methodology are scores for cyber resilience risks for individual processes, sensors/actuators and the wastewater treatment process as a whole.

Discussion of results. Anomaly detection is one of the most important steps in detecting and assessing cyber resilience risks in wastewater treatment process. An open dataset which was generated using the methodology the closest to the proposed by the authors was used as a train dataset. Secure Water Treatment (SWaT) dataset [37] was created using a hardware-software testbed, which represents a reduced copy of a real system for water treatment and disinfection. The simulated process consists of six consecutive sub-processes: raw water intake, addition of necessary chemicals to it, filtration, dechlorination using ultraviolet (UV) lamps, feeding into the reverse osmosis system, and removal of clean water and sludge. Fig.5 shows the scheme of the modeled technological process, subprocesses are marked by letters P1-P6, respectively.

The communication part of the SWaT test bed consists of a multilevel communication network, programmable logic controllers, supervisory control and data acquisition (SCADA) server and workstation, as well as historian server. The test bed architecture allows operational personnel

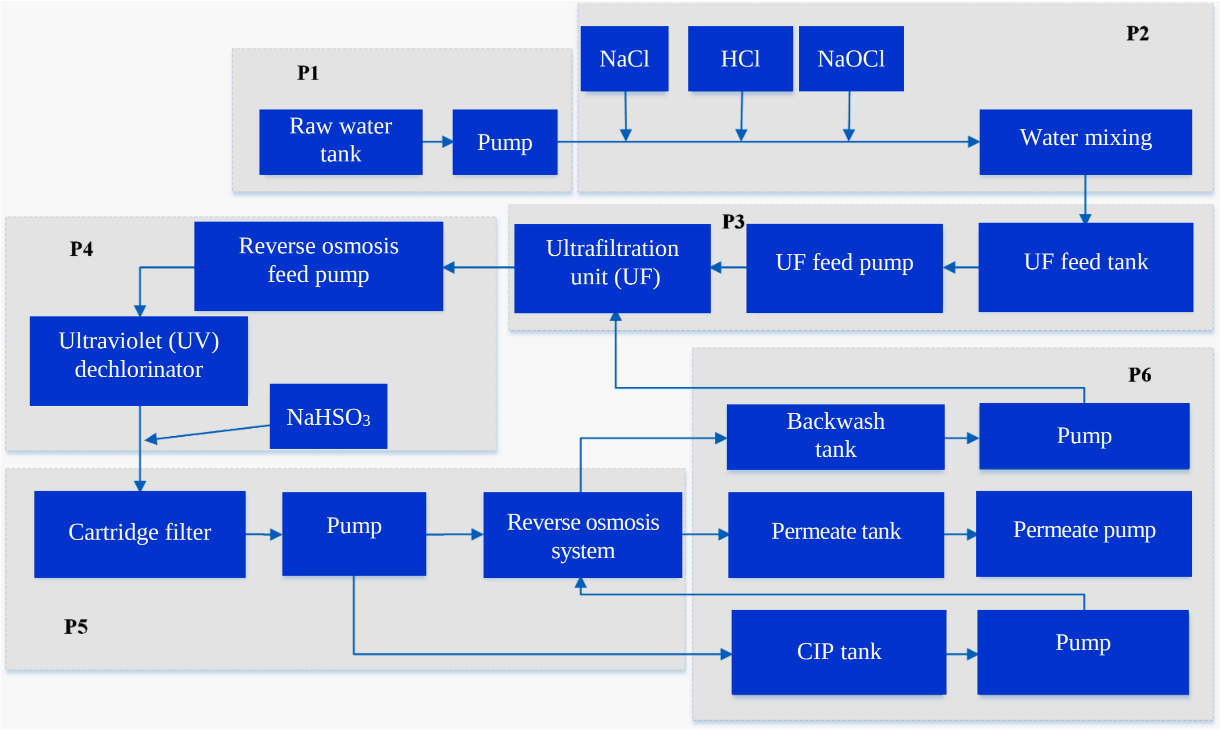

Fig.5. Diagram of the technological process modeled by the SWaT testbed [37]

to connect remotely to the facility infrastructure. The dataset has several versions, differing in the types of data collected, the disruptive impacts conducted and the total duration of the test bed functioning.

In the performed experiment, a variant of the dataset containing 36 different attack scenarios for spoofing the transmitted data was used. The destructive activity targeted different physical devices belonging to different technological sub-processes. The dataset contains 19 attacks modifying the values of one sensor, six attacks spoofing the values of two and three sensors; and seven attacks on sensors belonging to different technological subprocesses (Table 1).

Table 1

Characteristics of anomalies in SWaT dataset

Type of record in dataset	Number of processes targeted for destructive impact	Processes	Number of records
Norm	0	0	399157
Anomaly	1	P1	4053
	1	P2	1809
	1	P3	37860
	1	P4	1700
	1	P5	1044
	2	P3, P4	1691
	2	P1, P3	1445
	2	P3, P6	697
	2	P4, P5	463

To evaluate the performance of anomaly detection, we used the following metrics: precision and recall. The precision metric determines the proportion of records that are classified as anomalous and are true anomalous. The recall metric reflects the ratio of anomalous records that are detected by the algorithm correctly. The higher the values of these metrics, the better the anomaly detection performance. Since the dataset under study is unbalanced, i.e., the number of normal records far exceeds the number of anomalous records, the $F1$-measure, which is the harmonic mean between precision and recall, was also used. The plots of accuracy and loss functions are shown in Fig.6. An analysis of the inference time and the number of model parameters was performed. The latter metrics allow estimating the required computational resources. The authors also performed a comparative analysis of the results with methods presented in the literature, namely solutions based on autoencoder MTS-DVGAN [12] and MTAD-CAN [13], as well as long short-term memory neural network (LSTM) and autoencoder with 1-class support vector machine (deepSVDD), trained on the same dataset (Table 2). It should be noted that there is no information on the inference time and number of model parameters for the MTS-DVGAN and MTAD-CAN models, so a dash is indicated in the columns of the table.

The experiments show that the proposed anomaly detection model shows the highest recall, while the precision is only slightly inferior to the MTS-DVGAN model. At the same time, the proposed solution is characterized by a small number of parameters, and the inference time for one record is $2.07 \cdot 10^{-5}$. Although these data are not available for the MTS-DVGAN model, however taking into account the architecture of the neural networks used in it – variational autoencoder with two short long memory networks – it is possible to assume that the number of parameters is not less than the parameters of the LSTM model. Consequently, the proposed model has high efficiency and low computational complexity and can be used in systems with limited computational resources.

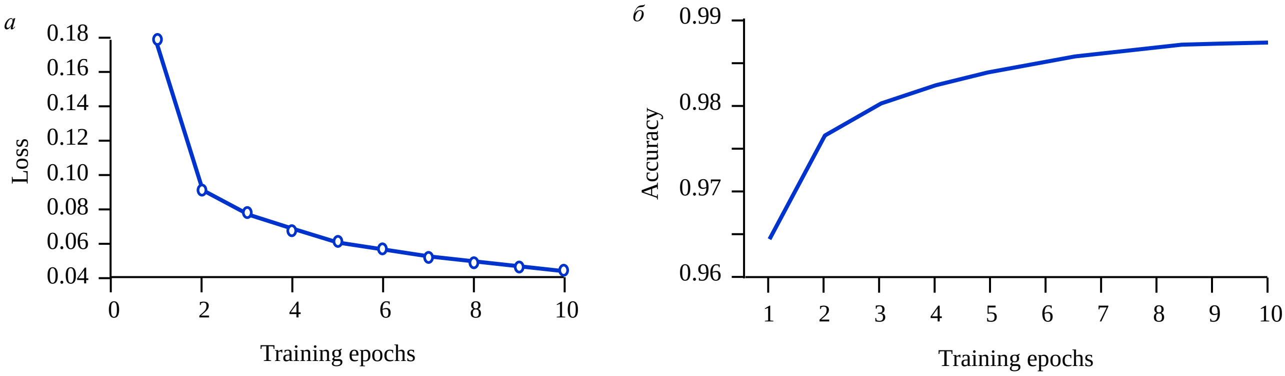

Fig.6. Loss function (*a*) and accuracy (*б*) of convolution neural network during training

Note that the models trained in the design mode are further used to detect anomalies, calculate the probabilities of successful cyber resiliency threat implementation, and assess the cyber resilience risks of the wastewater treatment process.

Table 2

Experimental results for anomaly detection in the SWaT dataset

Approach to anomaly detection	Precision	Recall	*F*1-measure	Number of model parameters	Model inference time, c
Proposed by authors	0.98	0.96	0.97	10 561	$2.07 \cdot 10^{-5}$
DeepSVDD	0.95	0.68	0.82	11 648	$2.43 \cdot 10^{-5}$
LSTM	0.98	0.71	0.82	66 035	$4.37 \cdot 10^{-5}$
MTS-DVGAN [10]	0.99	0.93	0.79	–	–
MTAD-CAN [11]	0.91	0.94	0.92	–	–

Conclusion. The paper presents the methodology for identification and assessment of cyber resilience risks of wastewater treatment process. The stages of the methodology, including the generation of a training data set, anomaly detection and risk assessment are described. Each stage is presented by a separate methodology. The stage of anomaly detection in the technological process is the key stage, since the risk assessments depend on its performance. A new approach to preprocessing the input data for subsequent anomaly detection is proposed. The experiments have shown that this approach uses fairly simple neural network with low inference latency, which allows processing intensive data streams. Due to the small number of model parameters, it can be used in devices with limited computational resources, such as industrial controllers, microcomputers, etc. Thus, the research goal of improving the accuracy of anomaly detection in the wastewater treatment process for system's cyber resilience risk assessment, considering the limitations of the available computational resources, has been achieved.

Further directions of research work relate to the optimization of the image generation procedure by determining a sufficient amount of data samples, investigation of approaches on data from technological processes and development of methods for detecting anomalies in the processes themselves. Experiments with the calculation of cyber resilience risks as well as generation of own dataset are planned.

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