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Investigation of the Possibility of Immobilization of Mobile Forms of Arsenic in Technogenic Soils

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Levels of contamination of three mining industrial zones in Irkutsk Oblast and Zabaykalsky Krai were revealed by means of geoecological and geochemical monitoring. Bulk contents and mobile forms of As in soils, stubs, bricks, and dumps of the mining and processing industry were defined. This allowed revealing features of chemical composition of technogenic substrates for the purpose of a choice of a way of their neutralization. The possibility of chemical immobilization of mobile ionic forms of As in natural and man-made objects by treatment with alkaline reagents was studied. X-ray diffraction (XRD) analysis revealed pharmacolite $CaHAsO_4 \cdot 2H_2O$, calcium arsenate $Ca_3(AsO_4)_2$, and segnitite$Pb(Fe^{3+})_3AsO_4(AsO_3OH)(OH)_6$ that are formed in the obtained solid insoluble precipitates. Formation of new solid insoluble compounds indicates the chemical binding (immobilization) of arsenic-containing compounds and the irreversibility of the process. This allows us to offer an effective way of fixing toxic agents to reduce migration in the environment by stabilizing immobilized forms. Experiments with the use of lignin sludge ash (accumulated waste of the closed Baikal pulp and paper mill) for the neutralization of arsenic-containing waste of mining and metallurgical industries were carried out. Application of modified coal sorbing agents for the sorption of residual mobile forms of As (after treating with an alkaline reagent) allows achieving a decrease in its concentrations to the TLV standard for a hazardous substance. NoritRO 3520 is the most effective sorbing agent. The results are of high applied importance for the implementation of the method of chemical immobilization of mobile ion forms of As in technogenesis zones.

Key words: geoecological and geochemical analysis; technogenesis; soils; technogenic substrates; arsenic compounds; sorption

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Introduction. The increase in the scale of pollution by toxicants of the geological environment leads to the degradation of its natural properties in the zone of technogenesis. This process becomes irreversible throughout the world. Constant disturbance of biochemical processes in the surface soil layer worsens its biosphere function; the increasing flow of pollutants leads to a cumulative effect, which creates the danger of increasing the global geochemical background, leads to the transformation of natural geosystems [1]. Under technogenesis, the natural migration of chemical elements and substances are also violated, which leads to the formation of dangerous technogenic geochemical anomalies. In this regard, in recent decades, studies of the migration and transformation of chemical elements in altered landscapes are relevant [7]. The identification of the causal relationship of geochemical and hydrochemical parameters and the conditions of the disturbed environment contributes to the understanding of the poorly studied distribution, transformation and migration of substances under the technogenesis conditions.

It is essential to develop the methodology for the formation of the geochemical barrier in order to limit the spread of toxicants and their fixation contributing to increase the environmental safety. Therefore, the development of evidence-based recommendations for the normalization and disposal of contaminated geochemical habitat is extremely relevant [14].

The problem of neutralizing hazardous and toxic formations (dumps, sludge storage facilities, tailings, and wastes) containing arsenic compounds (included by the UN in the list of the most dangerous substances) is especially acute in the mining industry [13]. Arsenic-containing compounds can remain active under natural conditions for a very long time, being capable of chemical transformations and migration in the environment [10]. The accumulated environmental damage, the scale and level of arsenic pollution in the area of abandoned mining enterprises necessitate the

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search for ways to consolidate and localize toxicants for the neutralization of disturbed soils, to ensure the environmental safety of natural geosystems and human health [11].

Despite the available developments in this area, the transformation of arsenic-containing compounds in disturbed soil, especially the migration characteristics of mobile forms, is poorly studied. This does not allow us to propose a method for their localization in territories with a high technogenic load [15]. The presence of arsenic of variable chemical valence in substrates also complicates the studies to select methods for its immobilization and removal from migration processes.

The methodological basis for the assessment of soil systems is geoecological analysis and environmental diagnostics, which allow not only to identify areas of pollutants localization within the territory but also develop methods for creating geochemical barriers on the toxicants migration [6].

The aim of the study: Use the methods of geoecological and geochemical analyzes in the technogenesis zone to study the possibility of immobilizing the mobile forms of arsenic in the formed soil-technogenic substrates of the mining operation and to obtain objective criteria for the irreversible chemical binding of arsenic-containing compounds into insoluble compounds.

The goals of the study:

1) to identify the extent of pollution of three industrial zones of mining in Siberia based on geochemical monitoring;

2) to determine the contributions of mobile forms of elements to the chemical composition of such technogenic substrates as soils, remains of bricks, cinders of metallurgical production and mixtures thereof;

3) to evaluate the possibility of chemical immobilization of arsenic mobile forms by reagents processing and obtain analytical criteria for the process effectiveness;

4) to study the possibility of sorption of residual contents (after reagent treatment) of mobile forms of arsenic using a series of modified carbon sorbents for the most complete extraction of a toxic agent.

Objects, materials and methods. The research methodology was based on an interdisciplinary systems approach, including:

– geochemical monitoring of territories in the zone of abandoned industrial mining facilities;
– a complex of physical and chemical analytical methods;
– statistical approach;
– optimization of the obtained experimental results and revealed dependencies;
– comparative analysis.

The objects of research were three abandoned technogenic zones of the mining industry in Siberia: Angarskiy Metallurgical Plant (AMP), Svirsk, Irkutsk Oblast (1 object), Vershino-Darasunskiy (facility 2) and Zapokrovskiy (facility 3) villages in Transbaikalia (Fig.1, 2).

1. Angarskiy Metallurgical Plant (Svirsk), specializing in the arsenopyrite ores roasting to produce arsenic oxides, is located in Irkutsk Oblast on the shore of the Bratsk reservoir. After the plant closure, the elimination, disposal of accumulated arsenic-containing wastes, and the remediation of the contaminated territory of the plant and the surrounding area were not carried out.

2. The Vershino-Darasunskiy mine in Transbaikalia is one of the oldest gold mining enterprises in Transbaikalia (Fig. 2, *a*). Arsenopyrite ore was supplied to the Angarsk metallurgical plant for beneficiation (Svirsk, Irkutsk Oblast). Subsequently, a plant for the white arsenic production was opened in the village. It was revealed that the industrial site and nearby territories are heavily contaminated with arsenic. At the same time, several significant anomalous geochemical zones of severe pollution formed. However, no remediation works were carried out.

Fig. 1. Space imagery of the AMP industrial site, Svirsk, the Angara river bank (Yandex maps, 2011)

Fig. 2. Location of industrial sites of arsenic waste in the villages of Transbaikalia: Vershino-Darasunskiy (*a*) and Zapokrovskiy (*b*) (Yandex maps, 2016)

3. The Zapokrovskiy mine and the beneficiation plant are located 27 km away from the regional center. Currently, the main sources of arsenic pollution remain tails, ruins of the old factory and the formed technogenic mixtures of soil, bricks, and cinders from old dumps.

Methods. We studied both contaminated soil, cinders from dumps, bricks from the destroyed workshops, and a technogenic mixture consisting of these three components. Sampling and analytical determinations were carried out in accordance with the methods approved in the Russian Federation (PND F 12.1: 2: 2.2: 2.3: 3.2-03. Sampling of soils, bottom sediments, silts, industrial sewage sludge, and industrial and household waste). The As content in the samples was determined using an ICPE-9000 inductively coupled plasma-atomic emission spectrometer and a Shimadzu AA-7000 atomic absorption spectrophotometer, and the XRD analyses (D8 ADVANCEBRUKER diffractometer) was used to study the chemical composition of the solid samples.

The subject of the study is the analysis of accumulated environmental damage in the form of chemical pollution of industrial sites with arsenic; the ratio of the content of bulk and mobile forms of arsenic in contaminated substrates (soils, bricks, cinder in dumps and a technogenic mixture of these components); experimentally obtained physical, chemical

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and analytical parameters of the substrates and reagents interaction; sorption isotherms and results of XRD analysis.

The approach allows to:

– conduct a geoecological assessment of the potential migratory properties of arsenic in the area of technogenic impact;

– identify new opportunities for the immobilization of mobile forms of arsenic in technogenic substrates to ensure environmental safety;

– determine objective analytical criteria to evaluate the effectiveness of the arsenic ionic compounds transition into a bound state to obtain insoluble mineralized forms.

Results and discussion. The total level of As pollution (bulk content) of soils, cinder dumps, old building's bricks within the studied territories and the morphological composition of the technogenic mixture are presented in the Table.

The average bulk content of As in soils, cinders, bricks and the morphological composition of the technogenic mixture (2016)

Area	As, ppm			The morphological composition of the technogenic mixture cinders: soil: brick, %
	Cinders	Soil	Brick	
Svirsk, Irkutsk Oblast.	19500	4910	4194	70.9 : 21.6 : 7.5
vil. Vershino-Darasunskiy	12095	6080	3006	79.8 : 10.4 : 9.8
vil. Zapokrovskiy	17310	3031	840	80.1 : 15.2 : 4.7

Note. The percentage ratio of components in the natural-technogenic soil mixture was determined during geodetic surveys taking into account the depth of arsenic migration in the soil profile up to 1 m up until the persistent clay layer.

It is known that arsenic belongs to hazard substances of the first class and its content in the soil of more than 15 ppm (an approved hazard indicator) characterizes it as extremely dangerous (MU 2.1.7.730-99. Hygienic assessment of soil quality in inhabited places).

So, for the plant in Svirsk, Vershino-Darasunskiy and Zapokrovskiy industrial sites this indicator is 72.7, 78.7 and 55 times higher respectively (see table). The neutralization techniques at such an extremely high level of pollution involve the removal of the soil layer and its processing at specialized landfills. However, the extent of contamination, financial challenges, and the lack of safe neutralization technologies and specialized enterprises in this region do not allow to carry out such works.

The soil and technogenic substrate that has formed over the course of decades is 70 % of cinder. Therefore, the physical and chemical properties of the technogenic mixture are determined mainly by cinder. However, the forms of arsenic-containing compounds in the individual components of the technogenic mixture can differ significantly and make a different contribution to the molecular and more mobile ionic forms of the element in the formed soil and technogenic substrate.

So, the specifics of production at factories in Svirsk and Vershino-Darasunskiy village provided the arsenopyrite ores roasting with the sublimation of volatile forms of arsenic. Therefore, in these samples, it is expected the presence of neutral molecular forms of arsenic in the form of insoluble oxides, in particular, As_2O_3, and mobile ionic forms of arsenic-containing compounds. This necessitates the determination of the, H_2, H, and As^{3+} ions contents.

Unlike the plants of Svirsk and Vershino-Darasunskiy village, in the beneficiation plant of the Zapokrovskiy village, more sulfide forms of arsenic in the form of arsenopyrite FeAsS and scorodite $FeAsO_4 \cdot 2H_2O$ entered the environment.

Figure 3 shows the contributions of arsenic mobile ionic forms to the chemical composition of the studied samples. It was revealed that brick fragments accumulated the largest number of mobile forms.

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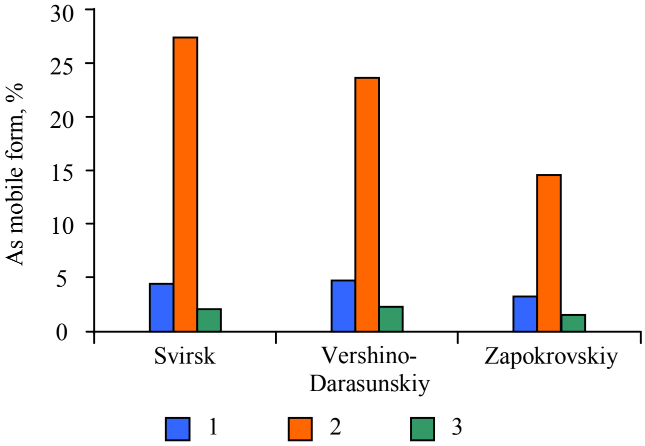

Fig.3. The dynamics of the As mobile form distribution in substrates within the territories of objects 1 – soil; 2 – brick; 3 – cinder

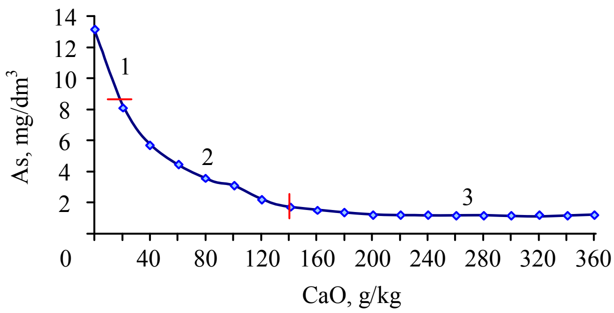

Fig.4. Dynamics of the arsenic concentration decrease in the filtrate depending on a lime dose for a technogenic mixture

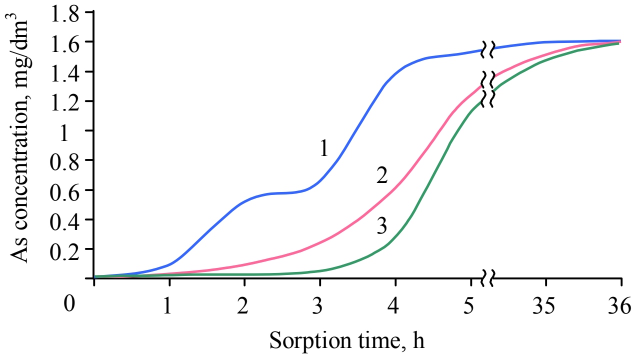

Fig.5. Kinetic curves of arsenic sorption for lime treated technogenic mixture

1 – CAD (anionic sorbent); 2 – SCT (cationic sorbent); 3 – NoritRO 3520 (apolar sorbent)

It is known that various reagents and materials [2, 8, 9, 12, 17], as well as biological methods, are used for the neutralization of arsenic-contaminated soils [5]. The prevalence of cinders with high acidity (pH = 2.7) in the morphological composition of the technogenic mixture (see table) determines the use of an alkaline medium for neutralization [16].

Neutralization of the substrates by means of lime was carried out in the laboratory conditions. Samples (soil, cinder, scrap brick) weighing 20 g were placed in a beaker, a 5 % solution of lime milk with a dose of 20-350 g/kg was added, mixed, filtered in a Buchner funnel after a constant pH regime, and analyzed for arsenic content by atomic absorption.

In the case of cinder, the decrease in the arsenic content in the aqueous extract after treatment with lime reaches 0.09 mg/dm^3 compared with the initial concentration of 1.5 mg/dm^3 (a 16-fold decrease). The dose of lime (CaO) was 40000 ppm.

For soils, there is also a decrease in the arsenic content in the filtrate after treatment with lime to 0.62 mg/dm^3 compared to the initial 5.8 mg/dm^3 (9-fold decrease). The dose of lime (CaO) was already 90000 ppm.

For contaminated bricks, the arsenic content of 139.3 mg/dm^3 in the initial aqueous extract decreases to 18.7 mg/dm^3 (a 7-fold decrease) in the filtrate after treatment with lime. The dose of lime (CaO) was already 1100000 ppm.

For the technogenic mixture, the As concentration in the filtrate is 1.6 mg/dm^3 compared to the initial value of 13.2 mg/dm^3 (decreased by 7 times). This is achieved by adding lime at concentration values of 140 g/kg (CaO). A comparative analysis of the analytical results made it possible to determine the optimal ratio of lime used to select the neutralization mode of the technogenic mixture (Fig.4). As can be seen from the figure, the curve showing variations in the arsenic concentration in the filtrate can be divided into three sections: the first is a straight section of a sharp decrease in the arsenic concentration in the filtrate at a dose of lime by CaO of 20 g/kg; the second is exponential curve section, when the arsenic concentration in the filtrate changes smoothly with increasing of calcium hydroxide dose; the third section of the curve has a straightforward character and begins at a dose of lime by CaO of 140 g/kg.

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We found a general decrease in the As concentration in all filtrates after treatment with lime, which is due to the content of the ionic form of arsenic and correlates with the lime dose.

XRD patterns of a solid insoluble residue show peaks corresponding to the following compounds: pharmacolite $CaHAsO_4{\cdot}2H_2O$, magnetite Fe_3O_4, goethite FeO(OH), calcium arsenate $Ca_3(AsO_4)_2$, segnititePb$(Fe^{3+})_3AsO_4$ (AsO_3OH) $(OH)_6$, which were absent in the initial untreated samples. The formation of new solid insoluble compounds indicates the effectiveness of chemical binding (immobilization) of arsenic-containing compounds and the irreversibility of the process.

Irkutsk Oblast is characterized by the abundance of industrial production and large volumes of generated wastes [11]. The most urgent task is the elimination and disposal of accumulated waste from the Baikal pulp and paper plant (BPPP) in the form of lignin sludge ash (LSA). We have previously shown that these sludges belong to IV hazard class, have ion-exchange and complex-forming properties, contain up to 70 % Al_2O_3 (a binding agent and a sorbent) and can be used as potential material for neutralization of toxic soil and industrial substrates [4]. We carried out experimental verification of the LSA applicability for immobilization of the ionic form of arsenic. It was found that when ash is treated with lignin sludge of an arsenic-containing technogenic mixture, the maximum effect of their neutralization is achieved at LSA dose of 335 g/kg. And although this amount is 2 times more than the detected dose of lime (140 g/kg), the arsenic content in the treated filtrate decrease in comparison with the initial one 3 times and reach 4.86 mg/dm^3. In other words, such additional possibilities were revealed for the fixation of mobile water-soluble forms of arsenic. For example, it is proposed to use BPPP wastes, which makes it possible to consider lignin sludge ash as an alternative not only to immobilize arsenic but also to obtain a positive side effect in Irkutsk Oblast.

However, the obtained arsenic content in the filtrates in both cases when treated with lime and LSA exceeds the TLV standard for hazardous substance by 0.05 mg/dm^3 (standard for fishery reservoirs). We set the task to find a way to bring the arsenic content in the filtrate to an approved safe level [11]. For this purpose, the processes of sorption of arsenic residual amounts from an aqueous medium using non-amphoteric (SCT, CAD) and amphoteric activated carbons (NoritRO 3520) have been studied [3]. Kinetic curves of dynamic sorption processes on carbon composites in an aqueous medium with respect to As ions are presented in Fig.5.

In accordance with the classification of isotherms (BET theory), most of them belong to one of five types (from I to V). Step isotherms are relatively rare and are of theoretical interest in physical chemistry. In most cases, the formed monomolecular adsorption layer on the sorbent's surface does not fully compensate for the excess surface energy and surface forces can affect second, third and subsequent adsorption layers.

The obtained isotherms are of type IV and are characteristic of multilayer adsorption when the attractive forces between the molecules of the sorbent substance and the sorbent are higher than the attractive forces between the molecules of the sorbent substance itself. The first bend of the curve corresponds to the full filling of the first monolayer, and the entire curve characterizes the process of poly-molecular sorption. This allows us to conclude that the process is multi-stage and As ions are in maximum contact with the sorbent's surface. NoritRO 3520 is the most effective for sorption of the ionic form of arsenic compounds. Moreover, the duration of NoritRO 3520 protective action is 3.3 and 1.4 times longer than other KAD and SCT sorbents, respectively. The maximum dynamic capacity of NoritRO 3520 is 1.1 and 0.9 times greater than that of KAD and SCT, respectively.

The arsenic content in the filtrate after sorption on NoritRO 3520 before the «breakthrough», which is fixed after 3 hours of sorption, is 0.03 mg/dm^3, which is significantly less than the sanitary and hygienic TLV standards for a hazardous substance.

Conclusions. Thus, the obtained results and the observed effects indicate the high effectiveness and scientific validity of the proposed methods for technogenic substrates processing, as well as methods for assessing the effectiveness of processes and controlling the toxic arsenic removal from soil and technogenic mixture with the goal of its neutralizing. We estimated the contributions of mobile forms to the chemical composition of the formed technogenic substrates, which made it possible to determine the method of chemical immobilization of arsenic mobile forms and to obtain analytical criteria for its effectiveness. It was demonstrated the usefulness of lignin sludge ash (wastes of Baikal PPP) for neutralizing toxic soil mixtures. It turned out to be possible to sorb the residual (after treatment with the reagent) contents of the arsenic mobile forms using modified carbon sorbents for the most complete extraction of the dangerous toxicant up to the TLV. The obtained results are of great practical importance for the implementation of chemical immobilization of As mobile ionic forms in the technogenesis zone.

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