Research of the toxicants sorption-diffusion migration from the accumulated industrial arsenic wastes along the soil profile

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Abstract. With the account of the accumulated environmental damage caused by the mining processing industrial wastes in the country, there is an urgent need in developing a concept for eliminating the related social and ecological consequences. The article presents the research of the sorption properties of the soil in Svirsk that has been long subject to the arsenic wastes pollution. As a result, the ground sorption capacity has been defined for different occurrence depth grounds. It has been found that the ground of 2 to 9 m thick is an important geological lock preventing arsenic and heavy metal penetration in the underlying aquifers. A remediation method for the soils polluted with arsenic and heavy metals has been suggested, which uses an organic-mineral complex developed by Irkutsk National Research and Technical University (INRTU). While interacting with the toxicants, the complex increases the toxicants mobility, facilitating their transfer from the hard soil into the liquid phase and further migration along the soil profile in the form of organic complexes, fine-dispersed suspension and sparingly soluble salts, being absorbed by the clay lock.

1. Introduction

In 2015, within the frames of the Federal Program, National System of chemical and biological safety of the Russian Federation (2009-2014) and of the regional program, Environmental Protection in Irkutsk Region (2006-2015), INRTU completed elimination of the accumulated environmentally hazardous industrial wastes on the Svirsk industrial site of the former Angarsk arsenopyrite-ore processing plant (AAP) that was producing arsenic trioxide for the war industry purposes in 1934-1949 [1].

Most of the industrial output of the arsenic plants in the period from the 1930s right up to 1989 (when the Soviet Union stopped the toxic warfare agents production), was used by the defense industry for the purpose of lewisite, adamsite and diphenylchlorobarsine production. It has been almost 80 years since the large-scale arsenic field development began and the arsenic plants were launched, but the industrial grounds are still uncultivated, being of an immense danger for the population and the environment. Only the landfill sites of the arsenic toxic agents are subject to total control. At the moment, the following zones are polluted with arsenic and heavy metals: Svirsk (arsenic production plant), Vershino-Darasunsky (arsenic production plant, gold mine), Zapokrovsky (arsenic field), Karabash (copper smelting complex), Plast (roasting plant for pure arsenic production), Revda (copper smelting plant). They do not only impact the environment, but also produce public health hazards, with the death rate exceeding the average rate [2].
At the beginning of the work on eliminating the pollution sources, the total amount of the arsenic cinder stored on the Svirsk AAP site (with an area of 13 ha) was 156,900 tons, the arsenic content being about 1%. Next to the slag heaps, there were the remains of the process equipment and production shops, the total volume being 6,600 m³ and the arsenic content being 150 tons. The third source was the arsenic-polluted soil, 48,000 tons. The elimination of the site was done in 2015 by decontamination of all the wastes and their further burial in the spent mines (Severný 5 open-cut mine) 20 km from Svirsk, after which the AAP industrial zone was recultivated.

The 70-year exposure to the arsenic pollution sources impact has aggravated the environmental situation in the whole area of Svirsk and in the adjacent agricultural zones (25 km²), with the arsenic and heavy metals content being hundreds times the norm content. Arsenic is found in the Angara river bed sediments down the stream, 20 km from the pollution source. The public health is also affected, the specific death rate being 20%, the highest in Irkutsk region [3]. This correlates with the obtained data for the children’s hair and nail biological substrates. It has been found that the arsenic content for practically all children examined is 4.7 higher than the allowable reference values, with the maximum being 27 times (for hair) and 36 times (for nails).

In connection with the current large-scale negative impact of the arsenic mining industrial wastes on the ecological situation in many settlements of Russia, a concept of the arsenic pollution sources elimination has been developed, the Svirsk AAP site being a model. The concept includes: monitoring of the natural-technogenic complex subject to the long-term impact of the accumulated arsenic-containing industrial wastes; development of a mathematical model describing the nature, the range and the risks of the toxicants biogeochemical migration into the environmental objects following the “soil-plant-man” trophic chain; development of a regenerative technology for different-morphology toxic waste sources neutralization, allowing extraction of the valuable components and usage of the reactive chemical agents in the neutralization process, with further elimination of the accumulated environmental damage.

Within the concept-development frames, the sorption-diffusion mechanism and the sorption properties of the Svirsk soils have been studied for the purpose of refining on the arsenic-polluted soils remediation.

2. Research methods

The tests were done at the INRTU Environmental Monitoring Accredited Laboratory (RU.0001.518897). The following certified techniques were used: Procedure of elements mass concentration measurement for drinking, nature, waste and precipitation water samples using inductively coupled plasma atomic spectrometry; Procedure of metal content measurement for solid objects using inductively coupled plasma atomic emission spectrometry; Procedure of moving metal mass content measurement for soils, wastes, composts, cakes and waste water suspension using inductively coupled plasma atomic emission spectrometry with atomization in argon.

3. Research results and analysis

Both the former AAP industrial site and the city of Svirsk are situated on the surface of II-III above-the-flood-plain terraces of the Angara River. These are alluvial sediments with a sharp stratigraphic inconformity on the carbonate rocks of the lower Cambrian rock sets of both Angara and Litvinzevo. The Litvinzevo rock set cross-section is composed by dolomites and lime-stone. In the upper part of the cross-section, there are 2-3 gypsum and anhydrite interlayers. The Angara rock set is composed by grey, light-grey, fine- and close-grain, thin-plate, and less often, solid body dolomites. There are multiple breaking tectonic abnormalities registered in the ‘Cambrian carbonate’ sediments. As a result of the geological research of Svirsk territory, the clay layer thickness has been defined, varying from 2 to 9 m. The layer has low permeability, which allows it being a barrier prohibiting into-the-depth penetration of the toxic elements from the former AAP site. Under the sandy clay soil, there are clay sand soils with fine-grain clayey sand lenses, sometimes brownish, sometimes, greenish-grey. The presence of the sand allows the ground waters entry into the core bore holes. The aquifer’s upper
boundary coincides with that of the sand sediments, its thickness varying from 0 to 6.5m. Under the sand layers, there are sand-pebble sediments that are 50-60% fine pebble of rare-occurrence rocks, and 40-50%, light-grey different-grain akrosic sand. The layer is strongly water-encroached [4].

To define the migration degree and the mechanism of dissolvable arsenic forms penetration in different-type soils, research of the soil sorption characteristics has been done. The soil sorption capacity is the ability of the ground to keep water and nutrients, including toxic compounds, e.g., arsenic ones. It depends on the clay minerals presence as the latter have a developed specific surface due to their layered and porous structure.

For the research purposes, the ground types have been selected that are characteristic of the city of Svirsk. For the sake of convenience, let us divide the research territory grounds into 4 types: Type 1 – 0-44 cm, dark-grey color, recent, middle dense, mid clay sand, inclusions – plant roots; Type 2 – 44-80 cm, grey-brownish with a yellow tint, recent, very dense, heavy clay sand - clay; Type 3 - 80-390 cm, yellow-whitish, recent, very dense, heavy clay sand – clay, carbonate infiltration; Type 4 – sand clay lower 390 cm, dense, pebble inclusions. Arsenic trioxide from the AAP refining shop waste has been used as a toxicant source, the ground-to-process solution ratio being 1:10. The initial arsenic concentration in the filtrate was 3000 mg/dm³. It was used to obtain the process solution arsenic concentration of 2,500, 2,000, 1,500, 1,000, 500, 100 and 50 mg/dm³. The suspension was stirred for 1 hour and afterwards, left for 24 hours. Then it was filtered, the filtrate being used to define the arsenic content using a standard inductively coupled plasma spectrometry technique (Figure 1).

As one can see in Figure 1, the clay soil types (Type 3, 80-390 cm) have the highest affinity to arsenic compounds, the statistic volume capacity of the sorbent being 12.5 mg/g. Close are Type 2 grounds (44-80 cm), their sorption capacity being a little lower, 10 mg/g. Type 1 grounds (0-44 cm) have the lowest sorption capacity.

The results of the study of the temperature mode influence on the sorption process are presented in Figure 2.
The chart shows that the apparent maximum is at the temperatures of 20 - 30 °C. Applying Arrenius equation $K = K_0 \cdot e^{-E/R \cdot T}$ and the sorption isobar (Figure 2) in coordinates $\ln C/f(1/t)$ by the straight line slope ratio, physical sorption activation energy has been defined in the temperature interval 4 - 30 °C. The calculated activation energy values for the four ground types are: 6.2; 26.9; 38.2; 11.4 kJ/mol. The values are characteristic of physical connection types, that is, physical adsorption.

**4. Discussion**

In the course of the research, there has been found that Type 3 grounds (80-390 cm, yellow-whitish, recent, very dense, heavy clay sand – clay, carbonate infiltration) and Type 2 grounds (44-80 cm, grey-brownish with a yellow tint, recent, very dense, heavy clay sand – clay) have the biggest sorption capacity. As the clay layer thickness in the whole Svirsk territory is 2 - 9 m, the layer is a strong geological lock prohibiting penetration of the pollutants in the underlying aquifers.

The available data of the previous research show that the maximum total concentration values for the surface soil layer in Svirsk territory are 9 times the arsenic norms, 2.7 times the copper norms, 14.8 times the zinc norms, and 10 times the lead norms. The average concentration of the migration forms (maximum accessible for plants) in the agriculture and settlement zones is about 10% of the total content. This shows that over the 5 years after the pollution source elimination, the migration forms went down to the underlying soil levels under the precipitation influence and got adsorbed by the clay lock starting at a depth of 0.4-0.7 m. Based on the obtained data on arsenic and heavy metal content for different soil profile levels, their graphical dependence chart has been built (Figure 3).
Figure 3. Distribution of the toxicant total content by the soil profile depth.

The chart shows that the maximum content of the toxicants is concentrated at a depth of 0.4 - 0.7 m (accessible for the plants root system). Below 1 m, there is no significant change in the arsenic and heavy metal concentration. This indicates that there is minimum additional entry of the pollutants into this soil level due to the high sorption capacity of the above-lying clay lock at a depth of 0.6-1 m, and that the toxicant content reaches the natural content values [5].

5. Conclusion
The obtained results have become a basis for developing a remediation technology for the soils polluted by arsenic and heavy metals. The remediation presupposes the use of an organic-mineral complex developed at INRTU [6] which, while interacting with the toxicants, causes an increase in their mobility, their transfer from the hard soil into the liquid phase and their further migration in the form of organic complexes and fine-dispersed salts along the soil profile, being adsorbed at the clay lock having the highest sorption capacity. The clay lock is to a big extent represented by Type 3 ground: 80-390 cm, yellow-whitish, recent, very dense, heavy clay sand – clay, carbonate infiltration, sorption capacity of 12.5 mg/g, activation energy of 38.2 kJ/mol.

References
[1] Bogdanov A V, Kachor O L, Fedotov K V and Chaika N V 2014 Elimination of the consequences of the industrial arsenic production Ecology and industry in Russia 5 pp 31–35
[2] Petrov I M, Volfson I F and Petrova A I 2014 Arsenic discharge by metallurgical plant in Russia and its influence on the environment and public health Ecology Bulletin of Russia 12 pp 44–49
[3] Koval P V, Chernyago B P, et al. 2010 State Report on the environment state in Irkutsk region in 2009 Irkutsk p 585
[4] Bogdanov A V, Fedotov K V and Kachor O L 2014 Development of scientific and practical foundations for the recuperative concrete-casting technology of arsenic-containing wastes in mining industry (Irkutsk: ISTU)
[5] Grebenshikova V I, Lustenberg A E and Kitajev N A 2008 Geochemistry of Pribaikalje Enviroment. Baikal Geo-ecological Test Field (Novosibirsk: Geo) p 235
[6] Bogdanov A V, Kachor O L and Chaika N V 2015 Patent 2546903 Russian Federation, C05G1/00 (2006.01). Recultivatation compound and Composition of the compound for arsenic-polluted soils recultivation (options) Published: 10.04.2015