Assessment of territorial impact of industrial mercury pollution and proposal for its solution

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Abstract. The mercury electrolysis plant in Usolye Sibirskoye, which was decommissioned in 1998, is a source of mercury pollution, since measures to prevent mercury pollution of the environment were not implemented after its closure. On the territory of the plant, mercury remained in building structures, in sludge, in soils, in loose sediments. All of them are deposited sources of metallic mercury, from where it continues to spread in the air, soils and groundwater. In order to choose the best method to eliminate the source of mercury pollution, it is necessary to conduct an assessment of the impact on all elements of the environment and to identify the places with the highest mercury contamination. In addition, to propose environmental protection measures those are aimed at eliminating the main sources of metallic mercury release to the environment from the decommissioned mercury electrolysis plant. During the environmental impact assessment of the investigated object, the following tasks were performed: an assessment of the existing environmental situation and the state of the natural environment was carried out; alternative scenarios for achieving the planned activity were considered, with a justification for choosing the best one.

1. Introduction
Worldwide, the production of caustic soda and chlorine on an industrial scale is carried out by electrochemical method. Currently there are about 40 enterprises around the world. In comparison with other man-made sources, the contribution of these industries to mercury pollution is relatively small (1-1.5 %). However, the concentration of significant amounts of liquid mercury in a relatively small area and its constant losses make it possible to attribute this production to objects of very high environmental danger. Their activities over a long period of time lead to mercury pollution of the environment, which is extremely difficult to eliminate [1]. The most acute problem of accumulated mercury-containing waste is at the enterprises ceased its activities. Examples of such objects located in the Irkutsk region near lake Baikal are "Sayanskhimplast" LLC and "Usoleihimprom" LLC.

2. Objects and methods
The state of the environment in Usolie Sibirskoye (Irkutsk region) has been deteriorating for 20 years. Until 1998, the company produced chlorine and caustic soda by electrolysis of an aqueous solution of sodium chloride on electrolysers with a diaphragm and with a mercury cathode [2]. The result of the assessment of mercury pollution of the environment during the application of mercury electrolysis at “Usoleihimprom” LLC is shown in Table 1.
Table 1. The result of the assessment of mercury pollution (1970-1998).

| Source of mercury                      | Mercury (ton) |
|---------------------------------------|---------------|
| Mechanical losses                     | 552           |
| Wastewater                            | 22            |
| Emissions                             | 78            |
| Sulphide mercury in sludge collectors | 668           |
| Flow to the Bratsk reservoir          | 76            |
| Total amount                          | 1396          |

In connection with a reveal in 1997-1998 of mass mercury contamination of fish in the Angarsk part of the Bratsk reservoir, the enterprise had to stop its activities. But the necessary environmental measures to prevent the occurrence of a dangerous situation have not been taken. At the present time, there are a large number of the abandoned production lines, office buildings, warehouses and other structures. The building of mercury electrolysis plant is dilapidated and dangerous. Storage of sludge and construction waste on the territory of the industrial site does not meet sanitary and environmental requirements. The soil and surface water of the territory are characterized by visible contamination of petroleum products [3,4].

The main objective of the environmental impact assessment is to prevent/minimise the effects, that the object under study has on the environmental components: atmosphere, surface water, groundwater, land resources, flora and fauna, human health, components of social and economic spheres of the area [5,6].

3. Results and discussion

To assess the current state of the territory, samples of environmental components were taken: atmospheric air, ground, soil cover, underground and surface water and bottom sediments. The analysis of samples was carried out on the basis of the "Center of laboratory analysis and technical measurements in the Siberian Federal region".

3.1. Assessment of air pollution

As follows from the obtained data, the mercury concentration in the air of the industrial site and the air inside the plant of mercury electrolysis plant varies widely: from 0 to more than 50 000 ng/m³. The upper limit of measurements exceeds the maximum permissible concentration (MPC) of mercury in atmospheric air (300 ng/m³) by 170 times.

The lowest concentrations of mercury in the air were found at the site free from buildings to the northwest of the mercury plant and at the site to the southwest of the plant (0 – 299 ng/m³). The highest concentrations of mercury were found in the air inside the mercury electrolysis plant (50 995 – 52 760 ng/m³).

At the points opposite the exits of the plant, at a distance of up to 15 meters, mercury concentration in the air ranges from 429 to 37 012 ng/m³. Such a high difference in readings can be a consequence of changes in the direction and force of the wind during measurements. In the case of a windward location of the measurement point relative to the building of the plant, the concentration value will be lower. Conversely, in the case of a leeward finding of a measuring point relative to the building of the plant, the concentration value will be higher.

The results of atmospheric air measurements indirectly confirm the absence of a mercury depot at the open undeveloped site to the northwest of the mercury plant and at the site to the southwest of the plant and the presence of large amounts of mercury in the waste and sludge inside the plant’s building.

3.2. Assessment of surface water, ground water and bottom sediments pollution

Water samples for chemical analysis of water and bottom sediments were taken at the two control points for surface water of the Angara river and the Belaya river (Bolshaya Belaya). Bottom sediments
are one of the most stable components of aquatic ecosystems, which reflect the main physical, chemical and biological processes within water. They play an important role in the cycle of chemical elements and are a kind of indicator of water pollution, as substances from the water mass accumulate and concentrate in the bottom sediments.

Bottom sediment is a zone of concentration of all water pollutants. Insoluble compounds settle to the bottom and bottom sediment is a good sorbent for many substances. Therefore, the content of all substances in bottom sediments, as a rule, is much higher than in water. Since there are no approved standards for the content of chemicals in bottom sediments, the maximum permissible concentrations for soils were used in the analysis of samples.

Groundwater was found at depths from 1.70 m to 6.50 m. The steady-state groundwater level is from 0.10 m to 1.68 m. Mercury content into the groundwater has been investigated by an accredited method. For the analysis, 11 samples were taken from different depths and in different places of the territory [7].

The results of determining the concentrations of pollutants in surface waters, groundwater and bottom sediments are shown in Table 2.

Table 2. Concentration of mercury in surface waters, groundwater and bottom sediments.

| Name of indicator                  | MPC       | Unite     | Angara river            | Belaya river           |
|-----------------------------------|-----------|-----------|-------------------------|------------------------|
| Mercury in water                  | 0.00001   | mg / dm³  | 0.00017±0.00003         | 0.00019±0.00004        |
| Mercury in bottom sediments       | 2.1       | mg / kg   | 14.29±4.29              | 67.84±20.35            |
| Mercury in groundwater            | 0.5       | mkg / dm³ | 1.018 -123.658          |                        |

Analytical data of chemical analysis of surface and groundwater, as well as bottom sediments in the study area indicate that at the time of sampling, the concentration of mercury exceeds the established maximum permissible values many times. Groundwater is particularly contaminated. The upper limit of mercury measurements in groundwater exceeds the maximum permissible concentration (MPC) of mercury in water (0.5 mg/dm³) more than 247 times.

3.3. Assessment of soil pollution

Soil is one of the main objects of ecological and geochemical researches. Unlike water and air, which are only migratory spheres, soil is the most objective and stable indicator of industrial pollution, since it clearly reflects the spread of pollutants and their actual distribution in the components of the natural environment. In this regard, particular attention is paid to the inventory and remediation of contaminated soil, which is a component of the habitat and depositing pollution [8].

The sampling of the surface layer of soil was carried out by employees of "Siberian Mercury Company” and employees of “Center of laboratory analysis and technical measurements in the Siberian Federal region” in June 2018 [9].

The study of samples of the surface layer of soil to a depth of 0.2 m in terms of mercury content showed exceeding the established standard. Additional samples were taken to analyse soil contamination at points where mercury content in the surface layer was exceeded. As follows from the obtained data, the concentration of mercury in the surface layer of the soil and in the ground of the industrial site of the mercury electrolysis plant varies widely: from 0.016 to 248.28 mg/kg. The upper limit of measurements exceeds the maximum permissible concentration (MPC) of mercury in the soil (2.1 mg/kg) by 120 times. However, the vast majority of samples (almost 90%) showed mercury content less than MPC.

According to the conducted studies of soil pollution assessment, it can be concluded that soil belongs to an extremely dangerous category of pollution, recommendations for the use of soil – removal and disposal at specialized landfills.
3.4. Assessment of building structures and stock sediments of sewage pollution

The concentration of mercury in the building structures of the mercury electrolysis plant varies from 29.0 to more than 250 mg/kg. The lowest mercury concentrations were found in the building structures of auxiliary premises. In the building structures the concentration of mercury was found in very wide range from 145.0 to more than 250.0 mg/kg. The research results of mercury concentrations allow us to conclude that more than half of the building structures are contaminated.

Analysis of the concentration of mercury in the stock sediments of sewage wells of the industrial site of the mercury electrolysis plant showed that the concentration varies within very narrow range - from 417.050 to 1309.50 mg/kg. Stock sediments of sewage wells of the industrial site have high mercury content.

On the territory of the plant there is technological equipment filled with mercury-containing waste in the form of coal-adsorbent, nozzles and sludge. In addition, at the outdoor area there are 4 tanks that served the function of receiving mercury-containing drains. According to the technological process, water was pumped out of them, and mercury-containing sludge accumulated during the entire period of operation of the plant. Significant amounts of mercury were also dumped into these tanks when production was halted. The sludge in these tanks is classified as waste of the first hazardous class.

3.5. Comparative analysis of possible measures to eliminate mercury pollution

An assessment of the environmental impact of the contaminated area showed that this facility is a major technogenic source of environmental pollution with metallic mercury as well as its hazardous compounds. Thus, serious damage is caused to the ecological situation of the Irkutsk region and the basin of the Bratsk reservoir. It is necessary to undertake urgent measures for elimination of deposited mercury sources and block the path of the mercury contamination spread. The studies included the analysis of several scenarios of possible measures of the remediation of contaminated site.

**Scenario 1:** It includes the dismantling of building structures, extraction of mercury-contaminated soil. All wastes of 3-4 hazard classes are subjected to demercurization on the site and then transported for further treatment, using or disposal. Wastes related to the 1-2 hazardous classes to take out to the special places authorized for the placing and dumping of mercury containing wastes.

The following solutions can be selected as demercurization agents: potassium iodide, copper sulfate and calcium polysulfide. A 10% aqueous solution of copper sulfate is sprayed on the identified area of the structures with contamination. It is applied with a high-pressure apparatus with a consumption rate of 0.1 l / m². After 1-2 minutes of impregnation, a 10% aqueous solution of potassium iodide is applied to the same area at a rate of 0.2 l / m² with an exposure of 24 hours.

As a result of the reaction, highly active demercurization agents (CuI₂ и I₂) are formed, the interaction of which with mercury leads to the production of water-insoluble, low-toxic and non-decomposable under normal conditions (to metallic mercury) chemical compounds (HgI₂, K₂[HgI₄], Cl₂[HgI₄]).

The accumulated experience and results of researches carried out by the Institute of Vinogradov Institute of Geochemistry SB RAS show that the most appropriate from an economic and environmental point of view is the processing of industrial mercury-containing waste together with ore processing or mineral filler, which will allow roasting at temperatures above 600 °C [10,11].

However, isomorphic mercury is removed from the soil at temperatures above 800 °C. This work can be performed only the enterprise that has experience with mercury and has special landfills for disposal cinders from the processing with a residual mercury content of 20-40 mg / kg while a standard MPC of mercury in soils is 2.1 mg/kg.

Such an enterprise on the territory of Russia is “Kubantsvetmet” CJSC, located in the Krasnodar region, the distance to which is about 6000 km. The cost of transportation will be 180 million rubles.

**Scenario 2:** It includes the work on the burial of structures impregnated with mercury in sarcophagus and the transporting of part of waste with low mercury content to treatment. These activities include the construction of a foundation pit with a clay lock and a reinforced special insulating film bottom on the site of the abandoned mercury electrolysis plant of “Usoliehimprom”
LCC. Mercury-contaminated soil and industrial structures will be placed in it. A top of the foundation pit will be closed with the concrete sarcophagus.

This scenario is developed on the basis of the experience of demercurization of a mercury electrolysis building of the Pavlodar Chemical Plant, implemented in 2002–2004. During the work, about 15 million US dollars were spent. In addition to high financial costs, disposal will not solve one of the most important problems - pollution of groundwater, since the steady-state level of groundwater at the site of sarcophagus ranges from 0.10 m to 1.68 m. If an emergency of man-made or natural character will lead to a violation of the integrity of the sarcophagus, environmental disaster cannot be avoided [12].

Scenario 3: The application of the technology of gravitational extraction of mercury from soil and sludge. This technology was developed and implemented on a pilot scale by Company “Merkom”[13].

Samples of mercury electrolysis sludge and soil were taken on the territory of “Usoliehimprom”. These samples were processed with a gravity separator. The mercury content in the initial samples was determined by the material balance based on the analysis of processed products. The concentration of mercury was determined in the analytical laboratory of chemical analysis of the research center “Kurchatov Institute”3. The results, presented in Table 3, were obtained during the processing of the soil sample.

| Sample | Mass (kg) | Initial mercury content (%) | Residual mercury content (%) | Mercury recovery (%) | Extracted metallic mercury (kg) |
|--------|-----------|-----------------------------|-------------------------------|---------------------|-------------------------------|
| Soil   | 829       | 2.42                        | 0.4-0.75                      | 75.13               | 15.2                          |
| Sludge | 139.5     | 20.65                       | 15.47                         | 84.53               | 24.35                         |

The high residual mercury content in the soil after processing is explained by the fact that it was not possible to extract the soil sample free from sludge.

Extracted in the processing of metallic mercury is cleaned from mechanical impurities by filtering. Then it can be directed for refining to produce marketable mercury brand R-1 and R-0 [14]. In this scenario, in addition to reducing the impact on the environment through the treatment of contaminated areas, we can obtain metallic mercury, which is further used in the industry. In recent years, the use of hazardous waste as secondary resources has become increasingly popular in Russia [15].

As a result of research conducted by “Merkom” LLC, the possibility of extracting a significant amount of metallic mercury from sludge and soil was confirmed. When using this technology, it is possible to reduce the environmental load by reducing the risk during the transportation of waste for treatment and disposal [16].

4. Conclusion

“Usoliehimprom” LLC was a company that produced chlorine and caustic soda using two technologies: electrolysis of an aqueous solution of sodium chloride on electrolytic cells with a diaphragm and with a mercury cathode. Currently, the mercury electrolysis plant is not functioning. Production was suspended on September 22, 1998. To assess the current state of the territory, samples of environmental components were taken: atmospheric air, soil cover, ground, groundwater and surface water, and bottom sediments.

The main source of mercury contamination at the plant is mercury-containing building structures of the former mercury electrolysis plant, accumulated waste in the form of mercury contaminated sludge and materials that were formed during the operation of the plant, contaminated with mercury soils located under the plant building and on the territory adjacent to the plant. Disposal of waste does not solve the problem of mercury contamination of territories, a “time bomb” is created and any man-made events in the disposal area can lead to the spread of mercury pollution. Even the most modern materials used in the creation of landfills have a warranty period of not more than 50 years. Clay locks
do not guarantee the penetration of groundwater through them. In addition, valuable, readily available raw materials for the production of mercury necessary for domestic industry are being withdrawn from circulation. Besides that, the transportation of waste over long distances is unprofitable from a financial point of view, as well as environmental, since long distance transport increases the likelihood of mercury contamination. Therefore, the most economical and environmentally acceptable is the treatment of mercury pollution at the place of formation.

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