Wastewater Treatment for Mercury and Arresting Mercury Contaminants Movement Within Industrial Soil

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Abstract. We have proposed optimal methods of treating both the waste- and stormwater for metallic and soluble mercury within the soil of mercury-based chlorine- and sodium-hydroxide production sites. The problem has been solved by combining physical, chemical and physicochemical treatment methods. Through the use of various filtering materials, coagulants and flocculants followed by sorption through AB-17-8 and Lewatit TR-214 ion exchangers, the level of mercury within wastewater has been decreased by about 99.9%. Demercurization of mercury-contaminated areas to the complete extraction of metallic mercury has been carried out by draining and the subsequent transfer of water-based compounds into a stable form through chemical immobilization without any prior soil removal. To achieve the aforesaid result we have treated the soil with stearic-acid salts solutions, which resulted in almost complete arrest of mercury within the soil.

1. Introduction
The mercury-cathode-based chlorine- and sodium hydroxide production is a multi-ton one, hence there is a need for a large amounts of highly desalted water for the electrolysis. Such production results in large volumes of wastewater contaminated with mercury mixed with other pollutants.

Mercury is a first hazard class substance. Technogenic pollution of soil, water and air with mercury leads to deterioration of the environment. Almost all water sources, soil and biota contain a certain background amount of mercury, which is the result of its use in the chemical industry, in the production of paper, synthetic silk, viscose, metals extraction in the mining industry, and in mercury-based electrolysis. For a long time, most chemical plants dumped mercury waste in special sections of their sludge collectors, while the polluted wastewater was poured into an industrial collectors and water bodies.

Over the past decades, part of the waste mercury has been reclaimed and returned into the production cycle of the plants generating such waste or handed over to specialized plants. Accumulation of mercury in the plants' sludge collectors negatively affects the state of the surrounding areas. This is particularly noticeable in turf and soil.

2. Relevance, scientific significance, literature review
The objective of this publication is to develop ways of mercury-containing waste water after-treatment, as well as means of arresting the mobility (immobilization) of all types of mercury contaminants within the soils at the production site.
The area of mercury-contaminated territories expands annually and takes up hundreds of square kilometers. Taking this fact into account, as well as growing mercury pollution of industrial sites, it is necessary to arrest the in-soil mercury contamination by creating a barrier against the movement of soluble and insoluble forms, including those present in storm- and melt-water [1, 2]. The total amount of mercury waste accumulated in the soil of chlorine and sodium hydroxide extraction mercury-based electrolysis workshops reaches hundreds of thousands of tons [3,4]. To date, there is no universal technology of treating waste- and groundwater for soluble mercury forms. The conventional reagent-based wastewater treatment is not able to reduce mercury ions content in water to the requirements of the established standards [5-7]. In addition, there is a risk of excess of the general salts content in the solution due to the introduction of additional reagents [8-10]. The problem can be solved by combining reagent-based and physicochemical treatment methods [11-14]. In publication [8] the possibility of using sorbents to treat mercury-containing wastewater of various compounds has been reviewed. An important task in demercurizing the mercury-contaminated areas is complete extraction of metallic mercury and its subsequent transfer of water-based compounds into a stable form through chemical immobilization [15,16]. However, practically all methods of chemical mercury immobilization are efficient in treating solid waste evacuated from the contaminated areas. For example, the solid waste can be treated with a solution of hydrogen peroxide and carbon dioxide in autoclave at high pressure or with calcium polysulfide and active-chlorine-containing oxidizer.

Due to the extensive and uneven mercury-waste contamination of soil at an operating plant, there is no possibility of moving the soil for its further demercurization [17,18]. To reduce the negative impact of soil mercury pollution on the environment, certain ways of arresting the movement of mercury contaminated soil and turf should be developed [15,19,20].

3. Problem statement and theoretical part
The process of mercury-containing water treatment was studied by converting soluble mercury forms into poorly soluble salts and complex compounds. The study was performed on storm water and treated waste water at the GaloPolymer Kirovo-Chepetsk, Ltd plant, as well as on the Hg(NO$_3$)$_2$+H$_2$O salt-containing reference water-sample. To measure the mercury content in the waste water we used a complexometric method.

To treat chlorine and sodium hydroxide mercury-based-production waste water we resorted to the following methods: physical ones (coagulant/flocculant sedimentation, decanting and filtration), and physicochemical ones (sorption on the surface of ion exchange resins). Pollutants analysis of industrial storm wastewater revealed, along with mercury contaminants, the presence of significant amounts of suspended salts of strong acids, ammonium salts, oil products and other substances.

Industrial storm wastewater didn't not meet the requirements for waters of fishery reservoirs: suspended solids exceeded the MPC by 2 times, gross mercury - by 2.7 times, soluble mercury forms - by 52 times, and petroleum products - by 5 times.

4. Practical significance and results of experimental studies
Waste water treatment for suspended solids was done through sedimentation followed by filtration in the presence of aluminum sulfate (4%), as a coagulant, and polyacrylamide (0.02%), as a flocculant. The degree of sedimentation purification (2 hrs) and bank sand filtration at 1.5-2.0 m$^3$/hr-m$^2$ flow rate exceeded 99.2 %. Simultaneously, the gross mercury forms were filtered out of the water. The test results are given in table 1.

| Mercury concentration, mg / l | degree of purification,% |
|-----------------------------|--------------------------|
| after sedimentation | after filtration |
| source | <0.0005 | >54.5 |
| 0.0011 | 0.0006 | 0.0370 |
| 0.0042 | 0.0009 | 0.0370 |
| 0.0011 | 0.0006 | <0.0005 | >98.6 |

Table 1. Wastewater treatment for mercury by coagulation, flocculation with sedimentation, filtration.
Maximum filtration of gross mercury out of the production-site storm water turned out to be 98.6%. To improve treatment for gross mercury and to remove its water-soluble forms, AV-17-8 and Lewatit TR-214 ion-exchange resins were used. We used dynamic treatment of mercury-based production shop waste water as well as the storm water after their bank-sand filtering. The treatment results can be seen in Fig. 1.

![Figure 1](image.png)

**Figure 1.** Dependence of mercury content in mercury workshop wastewater after ionite resin treatment: ● - Lewatit TR-214, ○ - AB-17-8.

The figure shows that with an increase in the volume of water treated with ion exchangers, the concentration of mercury in it increases and exceeds the MPCₖ (MPC for fishery). At the same time, the efficiency of Lewatit TK-214 resin under dynamic conditions exceeds that of AB-17-8 ion exchanger. Therefore, for the mercury concentration meeting the MPCₖ, one should retreat the effluent or increase the resin volume and the height of its layer in the column, as well as reduce the rate of water flow through the column.

The mercury- and mercury compounds immobilization on vast contaminated areas is a complex task that can be solved by drastically reducing the mercury in-soil mobility without further damaging the environment. We researched into the possibility of immobilizing mercury compounds using both the mercury salts and anhydride of organic acids having 15 or more carbon atoms in their chains. The salts of these acids are usually water soluble. For example, sodium or calcium stearates. When interacting with in-soil mercury ions these salts form insoluble mercury stearate.

\[
2C_{17}H_{35}COONa + Hg^{2+} \leftrightarrow (C_{17}H_{35}COO)_{2}Hg \downarrow + 2Na^{+} \\
(C_{17}H_{35}COO)_{2}Ca + Hg^{2+} \leftrightarrow (C_{17}H_{35}COO)_{2}Hg \downarrow + Ca^{2+}
\]

To increase the reaction rate, the stearate salts solutions can be heated up to 50 – 60°C. In this case, the destruction of the soil humus components does not occur. At the same time some calcium cations reacting with anions of carboxic or phosphoric acids, present in acidic in-soil solutions, form poorly soluble calcium carbonate and calcium phosphate salts (In-soil solution (ISS)₉CaCO₃= 4.8-10⁻⁹ and ISS₉Ca₃(PO₄)₂ = 2.0 -10⁻²⁹). This fixes calcium ions, imparting some carbonate hardness to the in-soil solution. The analysis results of in-soil solutions of pH 4.5 - 5.0, containing 180 - 1440 mg/l of mercury ions are presented in Table 2.

| Mercury ion concentration, mg/l | Treatment efficiency, % |
|---------------------------------|-------------------------|
| source                          | after treatment          |
| 180                             | <0.0005                  | 100                     |
| 770                             | <0.001                   | 99.9                    |
| 1440                            | 280                      | 80.6                    |
The results obtained demonstrated that at mercury ions concentrations of 180 - 770 mg/l, the immobilization was almost complete; however, with an increase in its concentration to 1440 mg/l, the efficiency dropped to 80.6%.

Figure 2 illustrates mercury immobilization in contaminated in-soil solutions with sodium stearate as a way of processing industrial sites soil without its removal.

Metallic mercury, which is also present in the soil, is a great hazard by itself. The metallic mercury vapors concentration in the air above the surface can be many times higher than the MPC for a residential area. Stearic acid salts proved to be ineffective to scrub in-soil metallic mercury. To decontaminate soil and turf, there is a need for a technique to remove them, simultaneously decreasing the influx of soluble and insoluble mercury salts. Hence, we have proposed a technique to physically remove liquid mercury out of the soil. Figure 3 illustrates the process.

5. Conclusion
The optimal conditions for the treatment of mercury-containing wastewater have been determined.

A technique to immobilize insoluble mercury in soil and turf on the territory of an operating plant has been devised. The aforesaid technique makes it possible to greatly lessen the impact of hazardous waste on the environment of an industrial hub.

Methods of immobilizing the in-soil mercury solutions as well as the metallic mercury without extracting the soil on the territory of an operating plant have been developed.
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