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ASSESSMENT OF SOIL SALINITY FROM GALVANIC SLUDGE DURING S LONG-TERM STORAGE IN OPEN AREAS

Abstract: *The article analyzes the ecological state of the soil in an enterprise with a galvanic shop that produces chips and microcircuits. The problem of production waste storage in open areas is investigated. Environmental hazards during long-term storage of sludge have been identified. The composition of the sludge obtained after sewage treatment of the production of the copper line was investigated. A method for predicting the level and depth of soil salinity during long-term sludge storage is proposed. The experience of reuse of copper extracted from sludge is analyzed. Maximum service life of packaging made of polyvinyl chloride to save the sludge was determined.*

Keywords: *galvanic production, sludge, soil salinity, prediction.*

Introduction

Implementation of environmental security is accepted as a basic component of national security for Ukraine, taking into account the systematic nature of environmental problems and their correlation with economic, political and social factors. Under the influence of many anthropogenic factors, a certain ecological environment is formed. Numerous scientific studies [21, 23] indicate that genetically programmed mechanisms of regulation of human behavior are not adapted quickly enough to the conditions of increasing influence of anthropogenic loads. Extra loads on the human body due to poor food, contaminated water and the atmosphere lead to the nervous and endocrine systems damage. Such factors create favorable conditions for the development of traditional diseases and cause new types of serious ailments in humans and animals. Anthropogenic pressure on the environment acts as an independent stress factor, which results in various conflicts in society [17, 20]. Neglecting environmental safety in Ukraine for many years has led to uncontrolled consequences:

- economic: reduction of total production volumes, deterioration of living standard; increase in the number of industrial accidents;
- political: increasing distrust of state structures; inability to effectively counter external economic and military aggression;
- medical: increasing the level and complexity of occupational diseases, which results in loss of working capacity in the able-bodied population; stress; nervousness in relationships, demographic situation worsening.

One of the first places among environmental problems is the problem of water resources [5, 12]. In Ukraine, surface water is polluted mainly by petroleum products, phenols and heavy metals. The most polluted waters are recorded in the Dnieper basin, in the rivers Ros, Goryn, Sluch, Teteriv and others, on the banks of which large industrial enterprises and cities are located [1]. The content of pollutants in these rivers is accordingly: petroleum products – 10÷18 maximum permissible concentrations MPC; phenol – 1÷5 MPC, copper compounds – 4÷17 MPC, zinc – 20÷28 MPC.

Groundwater is subjected to significant techno-genic effects. In the valleys of Siverskyi Donets, the rivers of the Western Donbas, the Kryvyi Rih basin, the Carpathian region, more than 200 centers of permanent pollution of water soil horizons have been fixed. To date, this irresponsible attitude towards the disposal of industrial waste has resulted in complete contamination of 6% and partial contamination of 25% of explored groundwater reserves. Today, in conditions of military aggression in the territories of the Donbas that are temporarily occupied, the pollution levels of the Siverskyi Donets, Krynka and groundwater rivers are at a catastrophic level due to the discharge of untreated liquid industrial waste [19].

Water pollution is inseparably linked to soil pollution. Substantial environmental damage is caused by soils due to their pollution by liquid and solid industrial production. Solid waste, consisting of waste from metallurgical, chemical, electroplating industries, and from mining and mineral processing, is often located on agricultural land. Such wastes are a source of toxic substances and elements that enter the atmosphere, soil, surface and groundwater, causing irreparable damage. In Ukraine, an average of 1 680 million tonnes of solid waste of industrial enterprises are accumulated annually which must be processed, disposed of and stored [22].

According to the Law of Ukraine “On Environmental Protection” [9], an environment is considered to be safe if its condition meets the statutory criteria, standards and allowances. In accordance with the sanitary norms, requirements have been approved that determine its qualitative and quantitative levels of contamination and resource content.

The scale of the annual production and accumulation of solid waste requires the creation of powerful processing plants, which productivity is measured in millions of tons per year. The problem of practical implementation of scientific and technical developments is associated with numerous difficulties of financial, social and technical nature. The problem of industrial waste recycling is an urgent one, caused by the constant increase in the amount of waste and insufficient rates of its processing.

Waste containing heavy metals is of particular danger. Such contamination of the soil and water occurs near the enterprises with galvanizing plant [10]. Galvanic production is used previously to various coatings: chromium plated, copper, nickel plated, galvanized. Such productions in Ukraine are located at the enterprises of the military-industrial complex, machine building and electronic equipment

Galvanic production consists of sequential electrochemical processes (galvanizing, nickel plating, chromium, copper plating). As a production result, waste is generated: electrolytes and etching solutions of different composition. Mixed with water during the purification, the electrolytes and etching solutions form toxic wastewater. Heavy metals trapped in water and absorbed by phytoplankton are of particular danger, which can subsequently lead to their ingestion. Regulatory documents set maximum permissible concentrations for metals that get into water [8].

Dry waste (sludge) is formed during wastewater treatment. The most dangerous components of sludge are heavy metal oxides. Depending on the technological features in the waste of various galvanic industries, heavy metals were fixed within the following limits: copper – 500÷5600 mg/kg, iron – 750÷1100 mg/kg, chromium 250÷5000 mg/kg, nickel – 20÷200 mg/kg, zinc – 100÷5500 mg/kg, lead – 130÷600 mg/kg, tin – 1200÷7600 mg/kg [3]. Due to the variety of chemical elements in the sludge and the high level of harmfulness, the problem of their storage, disposal and recycling arose. The difficulty in galvanic waste recycling is that the waste contains different metals, depending on which different technologies are used. For example, the use of the method of electrical coagulation during the treatment of galvanic line sewage. Ferrite method of sewage treatment of galvanic production is based on the reaction of iron oxides formation, in the process of which there is a simultaneous deposition and sorption of heavy metal ions. Improving the precipitation structure makes it possible to intensify the process of separating it from water [11].

However, the issue of storage, purification and reuse of sludge in the production area receives current attention. The reasons for this condition are the lack of a methodology for assessing the contamination levels and effective methods of metal recovery and recycling. Nowadays, the most common ways of using sludge is to add it as a raw material for the production of expanded clay, brick and ceramic tile and to obtain coloured glaze, which is further used in ceramic products. However, a small amount of sludge is recyclable. This results in an annual formation of up to 12 000 tonnes of sludge in the territories of Ukrainian enterprises [4, 7].

Long-term storage of galvanic waste is allowed at special sites in equipped storage facilities. However, as practice shows, artificial repositories have limited capacity and service life. Nowadays, the sludge is stored in open areas with the use of protective coating materials made of clay, polyethylene, polyvinyl chloride. The large waterlogging of territories and the loose permeable soils in Ukraine complicate the choice of landfills for industrial waste and limit their area. Solid wastes under the influence of precipitation, especially acid rain, go into a liquid state. Such phenomena lead to the leakage of reactive elements into the environment. As a result, heavy metal contamination occurs not only adjacent to the soil and surface water storage sites, but also to groundwater horizons. The levels of soil and water pollution in the regions of Ukraine where galvanic and painting shops are located are significant [16].

Contamination of the soil surface brings a number of problems related to soil salinization, soil water contamination and increased water mineralization in surface water bodies. According to the degree of salinization, the soils are divided into weak, medium, strong, and extremely strong saline [6]. It is established that on poorly saline soils the crop yield decreases on average to 25%, on medium-saline soils – up to 50%, on strongly saline soils – up to 75%. Soils with a level of salinity in excess of 75% become practically unsuitable for plants of all kinds and sorts. Regardless of the chemical composition of substances, salts can concentrate in a certain soil horizon. According to the depth of the salt layer from the surface, the soils are divided into four types: surface salinization (0÷30 cm); medium salinization (30÷80 cm), deep salinization (80÷150 cm) and depth (very deep) salinization (> 150 cm) soils. In 2017 there were 4700 million m^2 of medium and heavily saline soils in Ukraine, accounting for 14.3% of agricultural land [2].

Predicting the development of hazardous physical and chemical processes on the surface and deep soil layers is one of the basic requirements for environmental safety. Solving the problem of limiting the negative impact of industrial waste makes it possible to significantly improve working and living conditions for people.

It is important to develop a method for predicting soil salinity levels and the possibility of groundwater contamination by galvanic waste [15].

Purpose and research objectives

The article is devoted to the analysis of the ecological status of the territory of the enterprise with the electroplating workshop, which produces chips and microcircuits. The purpose of the article is to improve the method of predicting the effect of galvanic sludge on soil salinity and groundwater contamination.

To achieve this goal, one needs to solve the following problems:

1. To analyse the experimental data on the qualitative and quantitative composition of the sludge that are formed in the galvanic shop during the chips production.
2. To develop a mathematical model of the distribution process of heavy metals, high-density metals in the soil, which lead to salinity of the soil and pollution of groundwater. Based on the model, create a methodology for predicting the depth and concentration of contamination.
3. Check the reliability of the developed mathematical model and methodology, created on its basis.
4. Suggest proposals for implementation of the obtained results.

Research matter and results

Copper is widely used in chips and microcircuits production and electroplating because of its high electrical conductivity. The article investigates the production processes of "copper etching" during chips and microcircuits manufacturing. The process of "etching copper" is used to create and secure the images on the surfaces of chips and microcircuits. The processing of individual parts is accompanied by the use of a large amount of water and, accordingly, the generation of waste. The spent technological solutions of chemical and electrochemical degreasing, as well as alkaline sewage, after cascading washing, fall into acidic drains. The spent electrolyte of the copper line is partially directed to regeneration and the recovered solution is reused in the technological process. Solutions are dehydrated mechanically. The received slurry has a humidity of 75÷85%.

The technological processes in the galvanic shops promote the formation of liquid waste with metals in the process of digestion and solid waste (sludge) – during disposal.

Experimental data

The authors carried out experimental studies of the sludge accumulation process at the enterprise during the operation of copper etching lines during chips and microcircuits manufacturing. The research was carried out on the territory of the enterprise for the production of electronic equipment in Cherkasy region of Ukraine. The company has been operating for 48 years. The average production capacity is up to 2500 m^2 of chips per month. With the productivity of the digestive line 14 m^2/h, the amount of sludge in 8 hours reaches 100÷120 kg. For one month during work in one shift accumulates up to 2500 kg and for two shift work – up to 5000 kg. According to the analysis of chip production waste, the percentage of a number of metals was determined (Table 1).

TABLE 1*. Metal content of the sludge in test specimens*

Indicators	**Metal content in sludge**					
Type of metal	Copper	Calcium	Iron	Chromium	Nickel	Zinc
Metal content, % wet soil	16	8	9	2	2	1
Harm class [18]	3	4	3	3	3	3
Limit concentration in water, mg/dm^3	1.0	3.5	0.3^3	0.05	0.1^3	1.0

The enterprise, which productivity ranges from 2,000 to 4,000 m^2 of chips, accumulates from 30 to 48 tonnes of waste annually. In previous years, the sludge was stored on the territory of the enterprise in landfills in open areas. For the last 20 years, the sludge has been stored in polyvinylchloride packages.

Storing sludge with particle sizes 0.1÷50 μm with metal oxides, the soil is salted and this has the corresponding negative effects [11]. Under the influence of atmospheric precipitation, metal ions are washed out and transferred to soils, surface and ground waters due to easy dissolution in acidic environment. The zone of aeration of the soil is saturated with salts of metals, which gradually move to the groundwater level. Soil salinity is measured as a percentage of the dry soil density: in the presence of metal salts, less than 0.1% of the soil is considered unsalted; 0.1÷0.3% – poorly salted; 0.3÷0.5% – average salinity; 0.5÷0.75% – strongly salted [15].

Model description

A method for predicting soil contamination in the sludge storage area is proposed. Simulation of the process of movement of salts from the surface of the earth to the below-located layers of the zone of aeration occurs according to the laws of molecular diffusion.

Soils in the area have the following structure: loam – $h_1 \le 1.5$ m; sand – $h_2 \le 0.3$ m; groundwater – $h_3 \le 0.8$ m; clay – $h_4 \le 1.2$ m; then the interlayer water begins (Fig. 1). The pores are up to 40 per cent of the volume of the soil layer.

The research methodology is based on the use of the theory of physicochemical hydrodynamics of porous media. The process of metal salts cycling can be described by the differential equation of motion and the conservation of mass of matter for the vertical transfer of mass of matter [13].

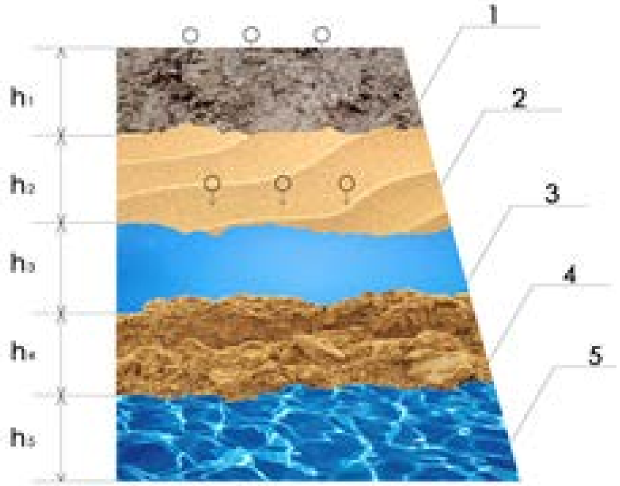

FIGURE 1. *Structural diagram of the soil: 1 – loam; 2 – sand; 3 – groundwater; 4 – clay; 5 – interlayer water*

The presence of sludge on the soil surface corresponds to the first-order boundary condition.

$$D\frac{d^2C}{dX^2}=\Theta\frac{dC}{dT} \tag{1}$$

where:

D – molecular diffusion coefficient, m^2/s;

C – salinity of rocks, %;

Θ – volume humidity, %;

X – spatial coordinate, m;

T – time coordinate, s.

The analytical solution of equation (1) has the form:

$$C_{hx}=\left(C_s-C_0\right)erfc\frac{1}{2}\frac{h_x}{\sqrt{\frac{D\cdot T}{\Theta}}} \tag{2}$$

where:

C_{hx} – predicted level of salinity at a depth of h_x, %;

C_s – surface salinity of the aeration zone at $h = 0$;

C_0 – initial level of soil salinity before the start of storage at $T = 0$;

h_x – distance of the calculated points from the origin, i.e. from the surface of the earth, m;

T – term of the predicted calculation, year;

erfc – tabulated function.

The predicted salinity level is determined by the following target setting:

1. The level of salinity for 20 years during the sludge storage in the open area.
2. Salinity level for 20 years during the packed sludge storage in an open area.

In the course of prediction, the following assumptions are made: the process of accumulation of metals is cumulative; annual seasons of soil moisture change are not taken into account. One year (365 days) is accepted for the billing period. The total prediction time is 20 years.

Input data

The molecular diffusion coefficient D characterizes the movement of metal ions as a result of thermal motion in the soil and depends on the properties of the metal molecules, temperature and pressure. In the calculations, the reference value D was taken at a temperature of 20°C [14].

Volume humidity Θ is determined by the moisture content of the soil and is calculated by the formula:

$$\Theta = \frac{m_{sw}}{\left(V_{hs} + V_{is} + V_{sw}\right)} \tag{3}$$

where:

m_{sw} – mass of water in the soil;

V_{hs} – volume of hard soil;

V_{is} – volume (interstices of soil) of pores;

V_{sw} – volume of subsoil water.

At the first formulation of the problem, the following baselines were adopted:

- salinity of the soil surface prior to the beginning of storage is $C_0 = 1\%$;
- the soil has pores up to 40% of the volume. We accept the maximum value of $C_s = 40\%$ on the boundary of "air – soil surface", which corresponds to a constant layer of slag on the soil surface;
- the molecular diffusion coefficient is defined as the mean value per day $D = 1 \cdot 10^{-5}$ m^2/day;
- volumetric humidity is taken as the average value during the year $\Theta = 0.23$.

In the second formulation of the problem, it is necessary to consider changes in the levels of surface salinity during the calculation period, i.e. $C_s\big|_{h=0} \to$ var.

Sludge storage in polyvinyl chloride packages results in gradual contamination of the surface layer. This is due to packaging damage, primarily due to the failure of the joints obtained by high-frequency welding. Seams under the influence of mechanical stress, changes in external temperatures, UV radiation and precipitation are cracked, which leads to the formation of a constant layer of sludge in the storage areas. It should also be noted that the guaranteed service life of this type of packaging does not exceed 15 years.

The value of the surface salinity of the soil is determined based on the results obtained in the previous iteration

$$C_s\big|_{h=0}^{i} = C_0\big|_{T=0} + \Delta C_s\big|_{h=0}^{(i-1)} \tag{4}$$

where

$C_s\big|_{h=0}^{i}$ – level of soil salinity on the surface in the i-th iteration;

$C_0\big|_{T=0}$ – initial level of soil salinity before the start of storage at $T = 0$;

$\Delta C_s\big|_{h=0}^{(i-1)}$ – increase in the level of salinity of the soil surface during storage of sludge during the previous year, which corresponds to (i–1) iteration.

Predicting the salinity depth, the calculation points are selected in 0.1 m steps from the surface.

Results

The first formulation of the problem calculates the annual changes in soil salinity levels by the depth of penetration. The results of changing the depth of penetration of metals into soil layers by years are shown in Figure 2.

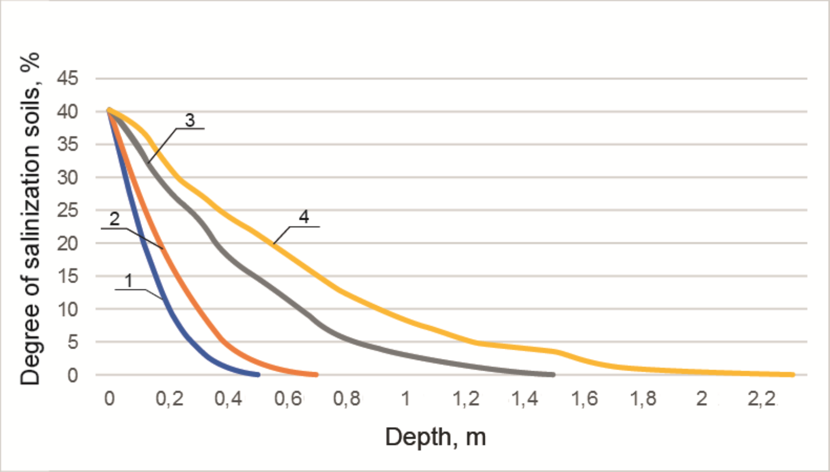

FIGURE 2. *The level of soil salinity at the depth of penetration during storage of sludge in the open area: 1 – one year storage; 2 – five years; 3 – ten years; 4 – twenty years*

According to the graphs (Fig. 2), the storage of sludge in open areas annually results in the increase in the depth of soil salinity.

Storing the sludge in polyvinyl chloride packing, a long-term soil contamination prediction is obtained as a result of an iterative calculation according to formula (2). The level of soil salinity decreases substantially in the first ten years of storage, but complete soil protection is not ensured (Fig. 3).

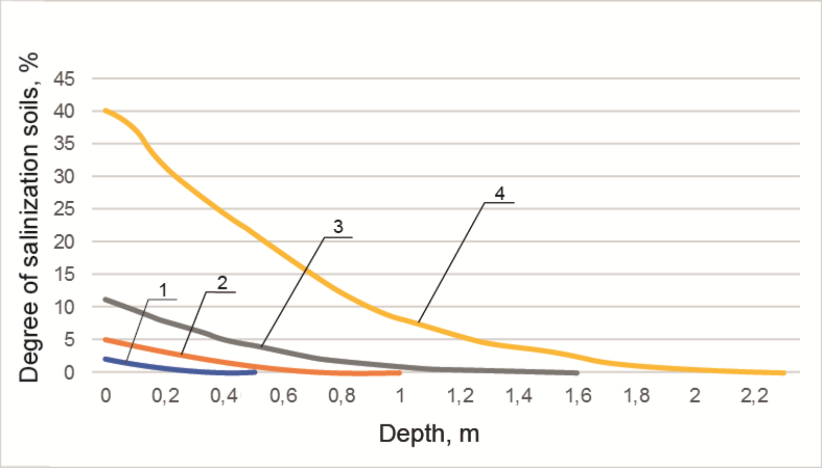

FIGURE 3. *The level of soil salinity at the depth of penetration during storage of sludge in the package: 1 – one year of storage; 2 – five years; 3 – ten years; 4 – twenty years*

As shown in Figure 3, the soil salinization process is slowed down during storage of the sludge in polyvinyl chloride packing, but practically reaches the previous levels due to the destruction of the packing after 20 years.

According to the force regulations, the salinity level exceeding 0.3% is already a danger to the environment. Figure 4 shows the soil depth with a salinity level of 0.3÷0.344% during long-term storage of sludge in open areas.

As follows from Figure 4, when the sludge is placed on the open surface in a year, the soil 0.65 m thick goes into the category of poorly saline, in four years such a layer reaches a depth of 1 meter, in 15 years the depth reaches two meters, which creates conditions for groundwater contamination. The contamination process is slower when the sludge is stored in the package. However, if the service life exceeds 15 years, the process of polymer destruction packaging takes place and further storage leads to contamination of soil and groundwater.

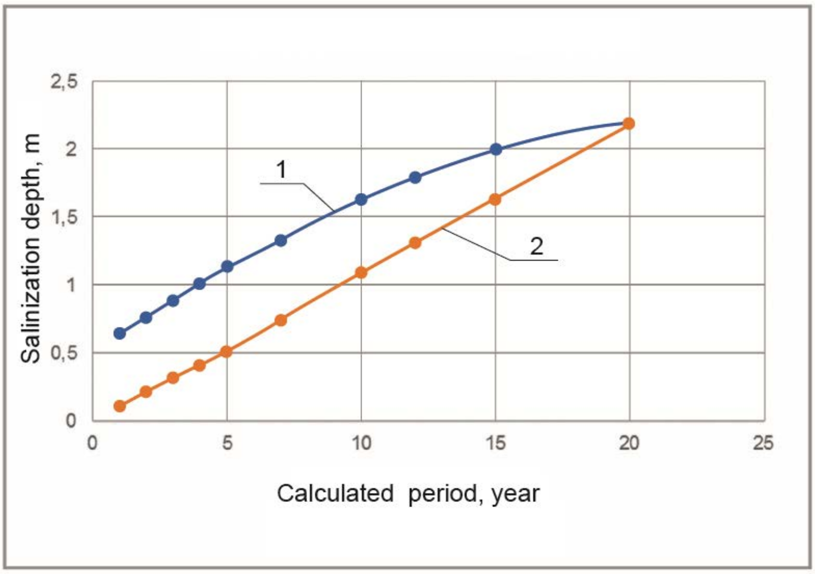

***Figure* 4.** *Depth of distribution of soil salinity within* C_{hx} *= (0.3÷0.344) during long-term storage in the open area: 1 – storage of sludge without packaging; 2 – storage of sludge in polyvinyl chloride packaging*

Future work will be dedicated to developing and implementing effective wastewater treatment and sludge extraction methods. Ukraine has a high demand for copper, which is used in the electrical, aircraft, and defence industries. Prospective deposits of copper ores have been discovered in the Volyn region, on the Donbass in the Dnipro-Donetsk surface valley. The total resources of ores of the Volyn region are estimated at 28 million tons of metal with an average copper content of 1.0%. Ukraine's annual demand for copper is 120÷140 thousand tons, twenty per cent of which is provided with its own copper scrap, and additional ones in the form of raw copper are imported from Poland [4]. In the current economic and technological conditions, it is advisable to use sludge as a secondary raw material. The required copper raw material can be obtained by galvanic wastewater treatment.

Nowadays in Ukraine, up to 20% waste and extraction of mineral resources and sludge are reused. Many countries around the world have accumulated the experience of disposal and sludge metals, including electroplating. For example, in Germany the reuse of iron reaches up to 38%, tin – 34% and zinc – 33%; in the USA copper reaches up to 43%, in the UK – lead 60%, aluminium – 33% [4]. As the results of the research showed, the separated copper from wastewater meets the requirements of industrial production. Copper can be used for smelting or metallization in appropriate processes.

Conclusion

1. On the basis of full-scale research at the enterprise for the manufacture of chips and microcircuits of the process of accumulation of sludge during the operation of the "copper etching" lines the conditions of their storage are analysed. It was found that the sludge samples contained heavy metal oxides: copper up to 16%, iron up to 9%, chromium up to 2%, nickel up to 2%, zinc up to 1%.
2. A method for predicting the depth of penetration of heavy metals and increasing the level of soil salinization based on the theory of physical and chemical hydrodynamics of porous media is proposed.
3. Information on soil structure and its characteristics (molecular diffusion coefficient, volume humidity), annual volumes and conditions of sludge storage within the enterprise were used as initial data for prediction.
4. According to the results of the calculations it is determined: during the placement and storage of sludge in the open area for a year, the soil 0.65 m thick goes into the category of poorly saline, in four years such a layer reaches a depth of 1 meter, in 15 years the depth reaches two meters, which creates conditions for groundwater contamination.

5. During the use of packaging made of polyvinyl chloride to save the sludge, the contamination process is slower. However, if the service life exceeds 15 years, the process of polymer destruction packing takes place and further storage leads to soil and groundwater contamination.

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