Stabilization of the soil bases contaminated with peracetic acid

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Abstract. The solution of the urgent problem, which is connected with the substantiation and development of the method of fastening of soil bases, acidified by industrial flows of food industry enterprises, is formulated and substantiated. It was established that in the food industry widespread use was made by washing and disinfectant Oxonia Active-150 on the basis of 25 % peracetic acid. This substance as a result of leakage and sewage emissions, getting into the soil basis, reacts with the chemically active substances of the soil, which leads to swelling of the base. It has been found out that the most effective way of stabilizing the behavior of soils of the bases contaminated with industrial effluents is the injection methods of fixation, in particular, silicification. It is established that for today there is no method of fixing soils contaminated with solutions of peracetic acid, which would solve the problem not only improving the mechanical characteristics of contaminated soils, but also would take into account the environmental aspect of the problem. For this purpose, the main approaches to solving the problem of fastening and ecological cleaning of soils contaminated with solutions of peracetic acid have been developed and substantiated. A scientifically and experimentally grounded method for calculating the chemical fixation of soils, which are prone to contamination with solutions of peracetic acid, is proposed. The model of the grounded choice of method of fastening and clearing of soils, which takes into account all requirements, which are advanced to arrays of fixed soils, is offered. The basic technological and chemical criteria for choosing a method for fixing a contaminated soil mass are determined.

1. Introduction
In the modern world, the issues of environmental contamination are very serious. Recently, they started to take the first place in world relations and in cooperation with various world economic objects. States allocate significant funds both for measures to prevent environmental contamination, and to combat its consequences.

Experience of operation of multiple enterprises showed that, as a result of dangerous soaking of soils with industrial effluents, chemically active solutions of various concentrations enter into the bases of buildings, under the influence of which the soils substantially change their properties [1-3]. Thus, as a result of physicochemical processes and exchange reactions there is an increase in the volume of soils, the so-called "chemical swelling" [4-8]. Currently, in the food industry, washing and disinfecting substance Oxonia Active-150 has gained widespread use, the basis of which is 25 % peracetic acid. This substance as a result of leaks, sewage emissions, entering into the soil base, reacts with the chemically active substances of the soil, which leads to swelling of soil bases.
When designing or reconstructing buildings and structures on the swelling soils, it is necessary to clearly visualize the pattern of their behaviour in order to be able to predict the behaviour of the “basis-foundation-building” system in the future. The most effective way of stabilizing the behaviour of the bases that are contaminated with industrial effluents is the injection methods of fixation, in particular, silicification [2, 9]. The stabilization of such foundations is a set of various measures that take into account resolving both technical and environmental issues.

The foregoing indicates the need to solve a relevant scientific problem, which is related to the experimental substantiation and the development of a scientifically grounded method for stabilization of the soil massifs that were contaminated with wastewater from the food industry, in particular, with peracetic acid.

2. The purpose of the work
The purpose of the work is to study the changes in the physical and mechanical properties of soil bases contaminated with peracetic acid, and to develop a method for their stabilization.

3. Methods
To determine the value of free swelling, soil samples of the experimental group were pre-soaked till full saturation in 0.6 %, 1.0 %, 1.5 %, 2.0 %, 3.0 % peracetic acid solutions. Samples of the soil of each of the four groups of approximately the same humidity (difference 1.0-1.5 %) and volume weight were placed in the standard device PNG-1, which allows to determine the value of free swelling of the soil.

Chemical stabilization of experimental soil samples was carried out using the special equipment LPZ-2, developed on the recommendations of V. E. Sokolovich and V. P. Ananiev.

The concentration of peracetic acid in soil pores is established by titration of a water extraction of soil according to B. O. Rzhanitsyn and Yu. V. Lurie. Characteristics of the strength of stabilized samples were determined at the manual press, and the degree of chemical swelling of the soil was determined on a device designed by Litvinov, type PNG-1, in accordance with the requirements of the GOST method B.V.2.1-4-96 [10].

Testing and research of silicate gels based on peracetic acid was also conducted. Experimental samples of gels were made according to technique by V. V. Askalonov. Solutions of the input components were mixed in various volume ratios of acid to silicate $\Omega = 2.0-18.5$. During studying the properties of silicate-peracetic gels, the input materials were: liquid glass, silicate module $M = 2.75$; peracetic acid 0.6 %, 1.0 %, 1.5 %, 2.0 %, 3.0 %. The data obtained were used for further calculations.

4. Results
It is established that the soils’ mineralogical composition and mainly the content of clay particles have the great influence on the swelling of the soils. The author has introduced the indicator $L$ - content of clay particles in the soil, expressed as a percentage (%).

Table 1 shows the dependence of the value of free chemical swelling, both on the content of clay particles in the soil, and on the concentration of peracetic acid. Also, a comparison was made between the value of free swelling upon immersion of experimental soil samples with water [11].

| The $L$ indicator, % | Free chemical swelling $\varepsilon_{sw}$ both on the concentration of peracetic acid | Free swelling $\varepsilon_{sw}$ both on the water | Soil characteristics |
|---------------------|------------------------------------------|---------------------------------|-------------------|
| < 3 %               | 0.066 - 0.310                           | -                              | Medium-swollen    |
| 3 – 10 %            | 0.200 – 0.420                           | 0.007                          | Strongly swollen  |
| 10 – 30 %           | 0.250 – 0.570                           | 0.044                          | Strongly swollen  |
| > 30 %              | 0.600 – 1.700                           | 0.090                          | Strongly swollen  |
Based on the results obtained, soils contaminated with peracetic acid solutions, can be considered as structurally unstable and classified as moderately and strongly swelling. The proposed classification provides an opportunity to predict the behaviour of soil bases in the event of their contamination with peracetic acid solutions, and to apply the appropriate measures.

The process of chemical swelling of clay soils under the influence of acid solutions of different concentrations can be conditionally divided into two periods. In the 1-st period of swelling occurs due to the absorption of moisture in the pores of the soil and the emergence of the negative stretching pressures in its core. The 2-nd period begins with the chemical interaction between the clay soil fractions and acid, and lasts as long as the concentration of the products of interaction does not reach the maximum value. Also, a comparison was made between the value of free swelling upon immersion of experimental soil samples with water. The results of the study are presented in Table 2.

| Experimenta 1 soils | The L indicator, % | Free relative swelling $\varepsilon_{sw}$ at various concentrations of peracetic acid | Free relative swelling $\varepsilon_{sw}$ when soaked with water |
|---------------------|------------------|--------------------------------------|--------------------------------------|
| Soil I              | < 3              | 0.066 0.158 0.176 0.280 0.309         | -                                     |
| Soil II             | 3 – 10           | 0.200 0.250 0.256 0.323 0.419          | 0.007                                 |
| Soil III            | 10 – 30          | 0.253 0.394 0.559 0.563 0.570          | 0.044                                 |
| Soil IV             | > 30             | 0.580 1.150 1.420 1.615 1.710          | 0.090                                 |

The study was carried out on the possibility of stabilizing of sandy and clay soils using silicate-peracetic solutions. An effective way for stabilization of chemically swelling soil bases is considered the method by M.F. Bronzhaev, which was further developed in the works by T.V. Mishurova [1]. To address the issues of stabilizing the soil bases contaminated with peracetic acid solutions it became necessary to study the nature of the influence of this acid on the formation of stabilizing silicate gels.

The studies were carried out on the following basic parameters: the time of the start of gel formation $t_g$; Gel strength limits with uniaxial compression $R_{compr}$; hydrogen index (pH) of the gel-forming mixture; durability of stabilized soils in aggressive environments, stabilizing solutions should be characterized by adjustable gel formation time. When choosing the optimal calculated value of the start time of gel formation, it is necessary to remember that the calculated value of the gel formation time cannot be less than the total duration of the technological operations. However, the studies have shown that the estimated time of gel formation can be arbitrarily long. The main limitation is the state of instability of the calculated parameter $t_e$. Therefore, when designing the parameters of the time gel formation, there should be distinguished: minimum gel formation start time $t_{gmin}$; technologically minimum gel formation time $t_{tech}$; estimated start time of gel formation $t_{gen}$.
The estimated start time of gel formation is the designed amount of time during which no significant structural formation occurs in the injected solutions. The estimated time of gel formation \( t_{\text{start}} \), of course, should exceed the value \( t_{\text{max}} \) for reasons of reducing the risk of premature gel formation of the injected solutions. Input materials were the aqueous solutions: sodium silicate with a silica module 2.75 and a density of 1.25 g/cm\(^3\)-1.05 g/cm\(^3\), which corresponds to GOST 13078-87; 25\% peracetic acid (Oxonia-Active 150), which corresponds to GOST R 51696-2000. Properties of silicate gels obtained on the basis of sodium silicate and peracetic acid were studied according to V.V. Askalonov’s method. The reaction of formation of gels on the basis of sodium silicate and peracetic acid is presented in the following way:

\[
2\text{CH\text{-}C\text{-}O} + 2n\text{Na}_{2}\text{SiO}_{3} \rightarrow (n\text{Na}_{2}\text{O})_{2}(\text{SiO}_{2})n + 4\text{CO}_{2} + 4\text{H}_{2}\text{O}
\]

Based on the time dependence of gel formation on the ratio of volumetric components peracetic acid/sodium silicate \( \Omega \), the graphs are built (figure 1).

According to the experiments, a generalized empirical formula was obtained, which allows us to calculate the design value of gel formation time.

\[
t_{\text{g}} = a \cdot \Omega^b,
\]

where \( \Omega \) – ratio of volumetric components peracetic acid/sodium silicate used in gel formation process; \( a, b \) – numerical coefficients. The values of the numerical coefficients \( a \) and \( b \).

![Figure 1. A general view of the graph of dependence of gel formation time on \( \Omega \)](image)

A study was conducted on the mechanical characteristics of silica gels based on peracetic acid. It is shown that with an increase in the value of the density of sodium silicate \( \rho_s \) increases the value of the strength limit of silicate gels upon compression \( R_{\text{compr}} \). For the value of environmental safety, the value of the hydrogen pH indicator of the synaeresis liquid in the range of 5.0-8.5 was adopted, which corresponds to the state of underground water used for drinking purposes.

Stabilization of acidic soils of the bases is possible using the chemical stabilization methods. The author carried out laboratory work on the study of stabilization with chemical solutions based on sodium silicate and peracetic acid. In the course of work, sandy and clay soils, acidified with peracetic acid, were studied for stabilizing ability with the sodium silicate solutions of different densities. In sequence, stabilization of four groups of soils was carried out. The basic design parameters of the stabilizing compositions for each of the four sample groups were the same \( (t_g, \Omega, \rho_s, \rho_k) \). The results of the studies are presented in Table 3.
Table 3. Mechanical characteristics of soils before acidification and after it

| Experimental soils | The value of mechanical characteristics of soils for acidification | The value of mechanical characteristics of soils after acidification |
|--------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| Soil I             | $\phi = 36.3^\circ$                                         | $\phi = 33.0-35.6^\circ$                                     |
|                    | $E = 31.5$ MPa                                               | $E = 21.5-22.03$ MPa                                         |
|                    | $C = 8.0$ kPa                                                 | $C = 2.096.0$ kPa                                            |
|                    | $R = 270$ kPa                                                | $R = 186$ kPa                                                |
| Soil II            | $\phi = 32.1^\circ$                                         | $\phi = 27.8-31.3^\circ$                                     |
|                    | $E = 22.6$ MPa                                               | $E = 19.9-21.9$ MPa                                          |
|                    | $C = 5.0$ kPa                                                 | $C = 3.0-4.3$ kPa                                            |
|                    | $R = 230$ kPa                                                | $R = 123$ kPa                                                |
| Soil III           | $\phi = 33.2^\circ$                                         | $\phi = 26.7-29.3^\circ$                                     |
|                    | $E = 26.7$ MPa                                               | $E = 16.9-24.8$ MPa                                          |
|                    | $C = 9.4$ kPa                                                 | $C = 5.2-6.3$ kPa                                            |
|                    | $R = 256$ kPa                                                | $R = 196$ kPa                                                |
| Soil IV            | $\phi = 26.4^\circ$                                         | $\phi = 22.0-24.2^\circ$                                     |
|                    | $E = 22.4$ MPa                                               | $E = 18.9-21.9$ MPa                                          |
|                    | $C = 29$ kPa                                                 | $C = 32.0-35.3$ kPa                                          |
|                    | $R = 332$ kPa                                                | $R = 219$ kPa                                                |

In the course of laboratory studies, the issues of stability of soils stabilized by sodium silicate solutions in relation to aggressive environments were considered. As an aggressive environment, tap water with a concentration of ions $\text{pH} = 8.1-8.3$ and 3% peracetic acid solution were used. On the basis of the conducted studies, a table of strength limits was composed for stabilized soil compression after being in aggressive environments.

Table 4. Strength limit upon the compression of the stabilized soil after being in aggressive environments

| Experimental soils | Aggressive environment | Strength at compression $R_{st}$, kPa, at the time of storage in an aggressive environment, days. |
|--------------------|------------------------|--------------------------------------------------------------------------------------------------|
|                    |                        | 30                                              | 90                                              |
| Soil I             | Water $\text{pH}=8.3$  | 288                                            | 238                                            |
|                    | Peracetic acid 3%      | 301                                            | 337                                            |
|                    | Water $\text{pH}=8.3$  | 199                                            | 143                                            |
| Soil II            | Peracetic acid 3%      | 286                                            | 217                                            |
|                    | Water $\text{pH}=8.3$  | 196                                            | 140                                            |
| Soil III           | Peracetic acid 3%      | 216                                            | 185                                            |
|                    | Water $\text{pH}=8.3$  | 342                                            | 290                                            |
| Soil IV            | Peracetic acid 3%      | 348                                            | 335                                            |

Thus, after stabilizing the soils, their strength increases, mechanical characteristics are improved. In certain cases, the mechanical characteristics of the stabilized soil exceed their value in the natural state. In clay, the strength of the soil $R_{compr}$ increases by 1.81-3.01 times. Specific traction $C$ in sandy loams increases by 9.6 times, and the module of deformation $E$ increases by 2.48 times. The internal friction angle $\phi$ of all studied soils, on average, increases by 1.56 times.

The scientific novelty of the results obtained is as follows:
- for the first time, a general scheme for the formation of silica-peracetic gels was established, and the most effective recommended ratios of components of one-soluble, two-component technology for stabilizing the soil bases contaminated with peracetic acid were determined;
- for the first time, a model of the behaviour of the soil base contaminated with peracetic acid in the conditions of reconstruction was suggested;
- the calculation of parameters of chemical stabilization of the soil bases of foundations contaminated with peracetic acid is improved;
- for the first time, physical and mechanical properties of acidified soils fixed with silicate-peracetic solutions were studied.

The practical value of the obtained results is:
- improvement of the quality of chemical stabilization of the soils contaminated with acid industrial effluents, in the case of applying the recommended recipes;
- improvement of the ecological state of contaminated soils due to cleaning the pollutant out of them;
- the model of behaviour of the soil basis contaminated with peracetic acid is suggested;
- the compositions of the process stabilizing solutions are developed, allowing to provide the massifs of contaminated soils with the strength close to the natural values, and durability.

5. Conclusions
1. The most effective compositions of silicate-peracetic gels, which meet the criteria of strength, water resistance and level of ecological purity are established.
2. The boundary conditions for the most effective and qualitative stabilization of the soils contaminated with peracetic acid solutions are determined, taking into account the environmental aspect of the issue.
3. The influence of peracetic acid on the physical and mechanical properties of sandy and clay soils is comprehensively examined. From the results of studies, it is clear that the value of free relative chemical swelling of the soil increases by 2.94-4.68 times compared with swelling from water, the strength of soils under the influence of peracetic acid decreases by an average of 11%-60%.
4. The boundary criteria for formulations are obtained, which allow to obtain reliable stabilization of soils contaminated with peracetic acid solutions. It has been determined that the practical application of the stabilizing solutions based on sodium silicate having density below ρ<sub>c</sub>=1.05 g/cm<sup>3</sup> is inexpedient because of the small buffer area. It was established that with a decrease in the density of sodium silicate solutions, the stabilization radius increases from 0.52 m at ρ<sub>c</sub>=1.25 g/cm<sup>3</sup> to 0.85 m at ρ<sub>c</sub>=1.10 g/cm<sup>3</sup>.
5. Eco-friendly compositions of silicate-peracetic gels (pH=6.0-8.0) have been isolated, which provide an opportunity to guarantee the ecological cleaning of contaminated soil massifs.
6. After stabilizing the soils, their strength increases, mechanical characteristics are improved. In certain cases, the mechanical characteristics of the stabilized soil exceed their value in the natural state. In clays, the strength of the soil R<sub>compr.</sub> increases by 1.81-3.01 times. Specific traction C in sandy loams increases by 9.6 times, and the module of deformation E increases by 2.48 times. The internal friction angle φ of all studied soils, on average, increases by 1.56 times.
7. The performed laboratory tests indicate that the stabilized samples of acidified soil are resistant to aggressive media over a long period of time. The reduction of compression strength of samples of stabilized soil after exposure to water is 36-47%, and under the influence of 3% of acid – 26-42%.

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