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Obtaining light technogenic soil as a result of the utilization of sulfurous-alkaline waste

V.G. Ofrikhter[1], A.S Grishina[2], A.A. Ketov[3], Y.A. Ketov[4], Y.I. Vaisman[5], E.I. Korolev[6]

[1]Professor, Perm National Research Polytechnic University, Perm, Russian Federation, email: ofrikhter@mail.ru

[2]Senior lecturer, Perm National Research Polytechnic University, Perm, Russian Federation, email: koallita@mail.ru

[3]Professor, Perm National Research Polytechnic University, Perm, Russian Federation, email: alexander_ketov@mail.ru

[4]PhD Student, Perm National Research Polytechnic University, Perm, Russian Federation, email: ketov1992@internet.ru

[5]Professor, Perm National Research Polytechnic University, Perm, Russian Federation, email: eco@pstu.ru

[6]PhD Student, Perm National Research Polytechnic University, Perm, Russian Federation, email: 89223504492@mail.ru

ABSTRACT

The article deals with an innovative light technogenic soil obtained by utilization of sulphur-alkali desulfurization waste. The environmental safety of the lightweight technogenic soil has been proved. The granulometric composition of the product, its density, moisture and compaction ability in comparison with natural soils have been studied. Based on the determination of physical and mechanical characteristics, the conclusion about the possible use of the obtained material as a technogenic soil was made. The most important advantage of the product is its density, which is on average 30% lower than the density of natural disperse soils. Also noteworthy is the increased strength properties of the lightweight soil established in laboratory tests.

Keywords: light technogenic soil, sulphur-alkali waste disposal

1 INTRODUCTION

Sulfur-alkali wastes are formed during cleaning of pyrolytic gases from hydrogen sulfide and carbon dioxide with a sodium hydroxide solution. The effluents are generated in a number of processes: during the purification of liquefied gases, the production of lower olefins, the purification of kerosene and gasoline fractions and some other petrochemical processes. The resulting sulfur-alkaline wastes are aqueous solutions of a usually yellow-brown color with a pungent bad smell and alkaline reaction of the medium. In chemical terms, sulfur-alkaline wastes contain, in addition to sodium sulfide, a complex mixture of polysulfide, mercaptide and carbonate sodium salts, sodium phenolates, as well as mechanical impurities and various oil products in a dissolved or colloidal form.

Among the sulfurous compounds found in oil products are hydrogen sulfide (H_2S), mercaptans (C_nH_{2n-1}-SH), carbon disulfide (CS_2), carbon oxide sulfide (COS), sulfides (R-S-R) and disulfides (R-S-S-R) [Narzullaev 2017, Rakhimov 2018], all of them being highly toxic.

Thus, sulfur compounds negatively affect both people and the environment. The analysis of the morbidity of workers with temporary disability in one of the oil refineries has reliably established that the number of disease cases in workers for certain diseases is reliably higher than in the comparison group [Sushinskaya 2017].

Besides sulfur compounds sulfur-alkali wastes contain a great deal of sodium hydroxide which also has an extremely adverse effect on the human body [Melnikova 2014]. Moreover, sodium hydroxide water solution is a lye, but alkalis are unacceptable in the environment [Petrova 2015].

The alkalis pH values above 9.2-12.8 are the reason for classifying the residue as a hazardous material, which, along with significant concentrations of sodium ions, is why the solutions are toxic to living organisms [Gräfe 2011], and the high alkali concentration makes it impossible to lower the pH by simple dilution.

Thus, sulfur-alkaline wastes constitute a twofold ecological hazard: they contain toxic sulfur compounds (II), primarily of the organic sulfur type, and have a high pH due to the high content of sodium hydroxide in the solution.

2 PRODUCTION OF LIGHT TECHNOGENIC SOIL

2.1 Choosing the sulphur-alkali waste disposal method

There are various methods for the decontamination of sulphur-alkali waste (Budnik 2019, Ksandopulo 2009), the most acceptable of which are physical or reagentless, chemical, and integrated treatment methods. As a result, sulphur (+2) compounds are usually concentrated and converted to less toxic compounds. Thus, oxidation of sulphur-containing odorants by ozonation allows us to utilize them, obtaining less dangerous compounds (Neretin 2016).

In some cases, the technical solution involves the utilization of sulphur-alkali wastes as a single material, without sequential conversion into safe products of sulphur compounds and an alkaline component. An example is the production of a mineral additive based on sulphur-alkali waste to improve the properties of concrete (Badikova 2020). The introduction of such a mineral additive from sulphur-alkali waste significantly improves the properties of concrete compositions, as well as reduces the consumption of resources for the production of concrete mixture and structures based on it (Murtazaev 2017, Batrakov 2006).

However, the necessity to utilize significant volumes of sulphur-alkali waste requires searching for a form of the obtained stuff that allows for a safe disposal of the resulting multi-tonnage product in the environment (Vaisman 2018). For this reason, the technology of waste recycling into anthropogenic soils, which minimizes the migration ability of ecotoxicants while creating an equilibrium and durable structure of the resulting material, has a long-term perspective. It has been proposed to utilize sulfur-alkali wastes using amorphous trepel oxide and obtaining a cellular silicate material (Knat'ko 2015). It was shown that as a result of heat treatment, sulphur (II) from sulphur-organic compounds oxidized to sulfur (IV), and after water detachment, sodium hydroxide was a part of the obtained glassy cellular silicate material. Therefore, the purpose of this work was to study the characteristics of the resulting product as a man-made soil, and to determine the fundamental possibility of applying it for the erection of earthworks in difficult geotechnical conditions, on weak soils (cohesive soils with I_L>0.75 or wetlands). After the first studies of physical and mechanical characteristics, of additional interest was the density of the obtained technogenic dispersed soil, which was on average 30% lower than that of natural soils, and its significant strength properties. The material obtained by the thermal treatment of sulphur-alkali desulfurization solution and trepel was chosen as the object of the study. Earthen structures erected from such a man-made soil will significantly reduce the load on the environment by decreasing the load on the underlying soils and downsizing the geometric dimensions of the structure due to steeper slopes, which will require a smaller area to accommodate such a bulk structure.

2.2 Selecting the initial product composition and the utilization process parameters

Industrial sulphur-alkaline effluent was used for the research; according to the chemical analysis, it contains 8.6 wt.% sodium hydroxide and 1.4 wt.% sulphur (II). The density of the solution is 1.094 kg/m^3. Silica gel KSKG was selected to study the possibility of binding sulphur-alkali effluents into a silicate. Trepel with an average chemical composition (wt.%): SiO_2 - 76.16; Al_2O_3 - 9.33; Fe_2O_3 - 4.10; CaO - 1.05; MgO - 1.01 and SO_3 - 0.31 was used as a natural analog of amorphous silicon oxide.

The toxicity class of water and aqueous extracts was determined according to the "*Methodology for determining the toxicity of water and aqueous extracts from soils, sewage sludge and wastes by mortality and changes in the fecundity of daphnia*", Federal Register (FR) FR.1 .39.2007.03222 and in accordance with the "*Methodology for determining the toxicity of water, water extracts from soils, sediments, sewage and wastes by changes in chlorophyll fluorescence and algae cell number*", Federal Register (FR) FR.1.39.2007.03223.

At the first stage, the task was set to determine the conditions for obtaining an environmentally safe product. Samples of pellets heat-treated at different temperatures were subjected to the standard procedure of biotesting. As a result, it was found that heat treatment of pellets at temperatures above 700°C allows obtaining a material with zero toxicity and acidity of the aqueous extract not higher than pH = 8.5. For a preliminary study of the physical and mechanical characteristics of the obtained environmentally safe granules, tests recommended by national and interstate standards for natural and man-made soils were carried out.

Acceptable quantities of the test material were obtained from a pilot plant designed and tested for the disposal of up to 200 litres of the sulfur-alkali solution per shift. The general view of the light technogenic soil is shown in Figure 1.

Granules were prepared by mixing trepel powder and the sulfur-alkali solution, 400 g of the sulfur-alkali solution was added to 1000 g of trepel and the granules were pelletized in a disk granulator. The silicate material obtained from trepel and sulfur-alkali wastes consists of strong granules. A photo of such a pellet, heat-treated at 700°C, is presented in Figure 1.

Some areas with remnants of diatomite microorganisms can be traced in the structure of the material, but in general, it has a high porosity and homogeneity. To analyse the hazard of the initial waste and the resulting product, standard techniques were used.

Figure 1. *Light technogenic soil: left – general view; right - micrograph of a chipped silicate pellet obtained by utilizing a sulphur-alkali solution through interaction with trepel.*

The proposed technological scheme was implemented as follows. The initial sulphur-alkali solution of waste is mixed with trepel powder in a disk granulator in the ratio of 400 ml of the sulphur-alkali solution per 1000 g of trepel powder (Fig. 2).

Figure 2. *Production of a technogenic soil: left - production of raw pellets from sulphur-alkali waste and trepel in a pan pelletizer, right – the drum kiln.*

The obtained raw pellets are fired in a drum furnace at 700°C with a calculated residence time in the firing zone of 25 minutes. The organosulphur compounds in the form of water vapor, carbon monoxide (IV) and sulphur monoxide (IV) are removed from the raw pellets, and the obtained pellets form a strong glassy silicate material. The proposed technology was implemented in practice on a pilot scale. Figure 2 shows the external view of the firing furnace.

The technology of sulphur-alkali waste recycling makes it possible to receive an environmentally safe material from the alkaline component of sulphur-alkali waste and to transform highly toxic sulphur-organic compounds into sulphur oxide (IV) of a low hazard class. In this connection, the physical and mechanical properties of the material were investigated for the possibility of its application as a technogenic soil.

3 GEOTECHICAL INVESTIGATIONS OF OBTAINED TECHNOGENIC SOIL

3.1 Physical properties of light soil

3.1.1 Granulometric composition

The granulometric composition of the material was determined according to GOST 12536-2014 by the sieve method with water washing. Samples weighing 100 g in an air-dry condition were taken. At the first stage, the sample was placed on a sieve with a hole diameter of 0.1 mm and washed under a stream of water until the water flowing out of the sieve became clear. The particles remaining on the sieve were dried in a desiccator and sifted through 10, 5, 2, 1, 0.5, and 0.25 mm diameter sieves. The results of partial determination of the particle size distribution are shown in Table 1.

Based on the sieve analysis it was concluded that, in accordance with GOST 25100-2020 "Soils. Classification", the obtained material corresponds to the dusty sand by particle size distribution (the content of particles with a diameter of more than 0.1 mm is less than 75%).

Table 1. *Particle size distribution*

Size of fractions, mm	Share of total mass, %
>10	0
5-10	0
2-5	0.11
1-2	3.72
0.5-1	14.02
0.25-0.5	11.96
0.1-0.25	14.19
<0.1	56.00

3.1.2 Density of solids

Next, an attempt was made to determine the density of solid particles of the material using the pycnometric method according to GOST 5180-2015. The test involves boiling a soil sample with distilled water in a sand bath to remove the absorbed air. When testing the man-made soil, the boiling reaction was very violent, so the water was replaced by a neutral liquid - acetone, which does not contradict GOST. As a result, a preliminary value of the particle density of the technogenic soil was obtained, which was 1.83 g/cm^3. Thus, it can be concluded that the density of the technogenic soil particles is about 30% lower than the density of natural soil.

3.1.3 Compaction ability

The next test of the product was a preliminary study of its ability to compact and finding the maximum density by the method of standard compaction according to GOST 22733-2016. The method consists in determining the dependence of the dry soil density on its moisture content during compaction. For the test, we used a device for mechanized compaction of soil by a falling load from a constant height and samples of man-made soil, the moisture content of which was sequentially increased.

The maximum density of the dry soil according to the preliminary tests of standard compaction was ρ_d = 0.98 g/cm^3 at moisture content w = 56%. At these parameters, the natural density of soil is ρ = 1.53 g/cm^3. Thus, one can make a preliminary conclusion that the density of man-made soil is about 25% lower than the density of natural soil, and the optimum humidity, at which maximum density is reached, is higher compared with the optimum humidity of natural sandy and clayey soils approximately by 4.5 and 2.5 times respectively. In this case, the nature of the compaction process is similar to that of natural soils.

It should be noted that the resulting product does not have the plasticity characteristic of clay soils, that is, the man-made soil does not have the ability to deform under external pressures without disturbing the continuity and does not retain the given shape after unloading.

3.1.4 Filtration ability

To assess the ability of man-made soil to pass water, we determined the filtration coefficient k according to GOST 25584-2016. A filtration device for determining the filtration coefficient of sandy soils at a variable head gradient was used for the test. A sample of the material with a density ρ = 1.48 g/cm^3 and moisture content w = 62%, which corresponds to the compaction factor = 0.93, was placed in the device. As a result of the test, the material filtration coefficient k = 0.013 m/day was obtained. In accordance with GOST 25100-2020 "Soils. Classification", the technogenic soil can be preliminarily classified as “low permeable”. In terms of the permeability characteristic, the obtained product is close to dense loams and sandy loams.

3.1.5 Degree of heaving

To assess the degree of material heaving, tests were carried out to determine the relative deformation of frost heaving on the device UPG-MG4 "Soil" according to GOST 28622-2012. A sample of the material was prepared in the device casing using layer-by-layer tamping. Density was ρ = 1.38 g/cm^3 with moisture content w = 62%, which corresponds to the compaction factor = 0.87. As a result of the test, the relative deformation of swelling was ε_{fh} = 0.1, according to which the man-made soil can be tentatively classified according to GOST 25100-2020 "Soils. Classification" as "strongly heaving soil". By the degree of heaving the obtained product is close to clayey soils.

3.2 Mechanical properties of light soil

3.2.1 Results of compression tests

The deformability characteristics were obtained from the preliminary compression tests. A sample of the material with density ρ = 1.51 g/cm^3 and humidity w = 56%, which corresponds to the compaction factor = 0.99, was placed in the device,. The load on the samples was transferred in stages equal to 25, 50, 100, 200 kPa. Transition to every next stage was realized when the conditional stabilization of soil was achieved, the criterion for which was strain increment not exceeding 0.05 % in 6 hours.

The compression curve is plotted in Figure 3. The curve shows that the nature of deformation of the technogenic soil is similar to that of the natural soil. The compression tests gave the normative value of the oedometric deformation modulus in the interval of construction pressures of 0.1-0.2 MPa E_{oed} = 5.8 MPa. In order to switch from the oedometric modulus to the strain modulus, which is used in calculating strains of soil masses, according to SP 22.13330.2016 "Foundations of buildings and structures" we need an empirical factor m_{oed}, which depends on the type of soil and is taken, based on the physical state of soils, equal to 1.0-3.0. Since the test material is not a natural soil, further research, including large-scale one, is required for a full assessment of its deformation characteristics. Another deformation characteristic by which the deformability of the material can be estimated is the compressibility factor m0. In the pressure range of 0.1-0.2 MPa, the average compressibility factor of the tested samples was m_0 = 0.34 MPa^{-1}, which allows us to classify the soil as “highly compressible”.

3.2.2 Strength characteristics of light soil

The strength characteristics of the technogenic soil were obtained by the method of single-plane direct shear test (fast shearing mode), which allows obtaining the values of the angle of internal friction and cohesion in the unstabilised state. Results of a direct shear test are shown in Figure 3. Samples for the shear test were prepared with a density ρ = 1.44 g/cm^3 at moisture content w=59%, which corresponds to the compaction factor = 0.92. The shear test was conducted in a kinematic mode with a given shear rate of 0.5 mm/min. Samples were tested at normal pressure values of 100, 200 and 300 kPa. The choice of this testing method (fast shearing mode) was based on its suitability for the characterisation of the soils to be placed in embankments

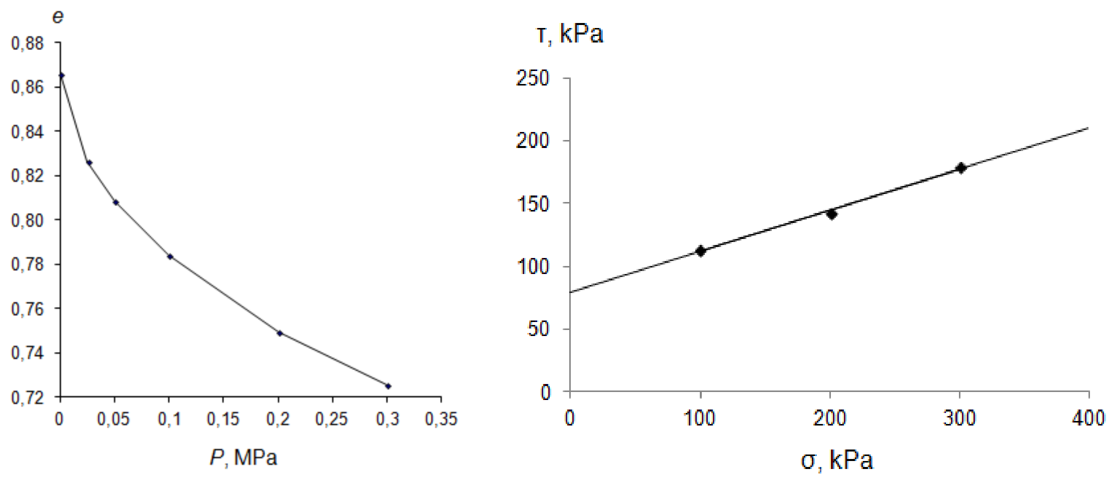

Figure 3. *Mechanical tests results: left – compression test; right – direct shear test (fast mode)*

As a result of single-plane shear tests we obtained the normative values of strength characteristics of the material: the angle of internal friction φ = 18° and cohesion c = 79 kPa. Thus, we can make a preliminary conclusion that the obtained material has a high shear resistance, and the resulting strength parameters are close to the normative values of semi-solid clays according to SP 22.13330.2016 "Foundations of buildings and structures".

4 CONCLUSIONS

Based on the preliminary tests, we can conclude that the resulting material has the characteristics of both cohesive and non-cohesive soil. The granulometric composition of the product is close to silty sands. It is also united with the non-cohesive soil by the lack of plasticity. At the same time, the technogenic soil has high strength and low water permeability, typical for cohesive soils. The material is highly compressible as per the compressibility coefficient, and as per the degree of heaving - highly heaving, which is also close to cohesive soils. The density of the material is about 25% lower than that of natural soil.

When studying the properties of the technogenic soil, attention was also paid to the density of solids, which was on average 30% lower than that of natural soils. It should be noted that the soil is characterized by the properties of both non-cohesive and cohesive soils. The strength characteristics of this soil obtained in conditions of direct shear tests are of certain interest: the angle of internal friction φ = 18° and the cohesion c = 79 kPa.

The initial void ratio at the compaction coefficient of 0.99 was 0.9, which corresponds to 47% porosity. The optimum moisture content was 56%, which exceeds the average values of this indicator for natural sandy and clayey soils by about 4.5 and 2.5 times, respectively.

Thus, the conducted research has established in principle the possibility of recycling sulfur-alkali wastes of gas purification into a safe silicate material. The obtained material has the characteristics of light technogenic soil and can be placed in the environment without restrictions. According to the preliminary studies, the most important feature of the resulting technogenic soil was found to be its lower density, which was on average 30% less than that of natural soil, thus making it possible to build earth structures on weak soils without additional improving measures and to substantially reduce the impact on the environment. The significant strength characteristics of the obtained product in comparison with natural soils also attract attention. Increased strength properties allow us to construct embankments with steeper slopes from such soil, which in turn reduces the area occupied by the earthworks on the ground surface.

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