Determining the composition of therapeutic mud and sewage sludge of mud baths for their subsequent disposal

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Abstract. The composition and characteristics of therapeutic mud and sewage sludge of mud baths are studied in the article. The use of the X-ray fluorescence method makes it possible to determine the composition and percentage of elements in the resulting waste of mud baths. The studies are carried out using a sample of natural therapeutic mud from the Sulfatnoe Lake of the Kurgan Region and natural sewage sludge generated after treatment. The study of the elemental composition of natural mud and sludge have shown a high content of silicon dioxide, aluminium oxides, as well as compounds of calcium, magnesium and other elements. Possible options for the disposal of waste mud and sludge by using them in various industries, such as road construction, agriculture, production of structural materials, are proposed. Based on the results of the study, the article also concludes that it is possible to use the sludge in the construction industry. Keywords: mud treatment complex, sewage sludge, sludge conditioning, sludge dewatering

1. Introduction
The aim of the article is to determine possible directions for the disposal of waste mud and sewage sludge of mud baths. The objectives of the article are to determine the composition of waste mud and sewage sludge of mud baths. The research object is waste mud and sewage sludge of mud baths, the subject of research is the composition of waste mud and sewage sludge.

Designing mud treatment complexes is an important stage in the development of sanatorium construction. At present, the sludge of flushing wastewater from mud treatment complexes is not separated from household ones, which excludes their effective use as a commercial product in the future, or they are stored at landfills, which negatively affects the environment [1-2].

In terms of its structure, therapeutic mud is a complex physicochemical system, which consists of three interrelated components - mud solution (liquid part), coarsely dispersed (skeleton) part and finely dispersed (colloidal complex) part [3].

The main part of the therapeutic mud is a crystalline skeleton, consisting of coarsely dispersed fragments of gypsum, calcite, dolomite, aragonite, phosphate, and sometimes fragments of remains of plant or animal origin. The second component of the therapeutic mud is the colloidal fraction, which binds the skeletal parts, including organic substances, organo-mineral compounds, hydrotroillite, silicic acid, sulfur, hydrates of aluminum oxide, iron oxides, and manganese [4-5].

Colloidal iron hydrosulfide, which determines the black color of the mud, is of great importance in this fraction. The colloidal also contains organic acids, lipoids, enzyme-like and hormone-like substances, chlorophyll, and pigments. Mud colloids preserve its therapeutic properties. A mud
solution obtained by squeezing, centrifugation or filtration is a liquid phase of mud and consists of salts, organic substances and gases dissolved in water. This solution basically corresponds to the chemical composition of the brine of the reservoir, in which this therapeutic mud was formed, and, first of all, contains sodium chloride, magnesium sulfate and sodium sulfide [6].

In the mud solution and mud colloids, in addition to the usual mineral salts, there are many biologically active substances (B vitamins, including riboflavin and folic acid, as well as vitamins C and D), as well as such microelements as bromine, iodine, boron, manganese, copper, iron, etc. Salt concentration (mineralization) in a mud solution depends on the type of therapeutic mud, ranging from 0.01 g/l (in peat and sapropel) to 400 g/l or more (in sulphide-silt mud). The amount of mineralization and the amount of salts depend on the ionic composition of the mud solution. The bulk of the salts dissolved in water consists of six ions: chlorine - $\text{Cl}^-$, sulfate - $\text{SO}_4^{2-}$ and hydrocarbonate - $\text{HCO}_3^-$, sodium - $\text{Na}^+$, magnesium - $\text{Mg}^+$, and calcium - $\text{Ca}^{2+}$ [7].

The acidic reaction of the mud solution (pH) depends on the chemical composition and the nature of the flow of biological processes in the therapeutic mud. The following mud can be distinguished: ultra-acidic mud (pH <2.5), acidic mud (pH 2.6 - 5.0), slightly acidic mud (pH 5.1 - 7.0), slightly alkaline mud (pH 7.1 - 9.0), and alkaline mud (pH > 9.0) [8].

Waste mud and sewage sludge produced after flushing should not be stored on the territory of mud baths, since they are waste of hazard class 4. These sludge should be pretreated with their subsequent disposal or use as raw materials. Existing methods of treatment and disposal of sewage sludge do not imply independent use of these sludge as a commercial product [9].

A promising solution in the use of sewage sludge is to put it into circulation in the following industries: road construction, agriculture, and production of structural materials. This is a beneficial solution, since sewage sludge acquires a certain consumer value, moving from the waste category to the raw material category.

After determining the composition of the sludge produced after the sedimentation of mud baths sewage, this study suggests options for the processing and disposal of these sludges, which will make it possible to produce independent commodity products that can be used in the production of structural materials, as well as pottery materials for leisure activities by vacationers of mud treatment complexes [10].

2. Materials and methods

One of the most effective methods of analysis that allows obtaining in a minimum period of time the most complete and reliable information on the elemental composition of complex samples regardless of their state of aggregation and origin is an X-ray fluorescence spectrometry (XRF). This method makes it possible to simultaneously determine more than 80 selection elements up to uranium and can be used to control the content of both matrix elements and trace elements in materials of various compositions [11-13].

An important point is the possibility of implementing standardless analysis in the XRF method, which eliminates the need to use standard samples, the preparation of which is often a difficult problem in analytical chemistry, especially for microgram amounts of substances. The design features of modern X-ray fluorescence spectrometers make it possible to carry out analysis not only in stationary laboratory conditions, but also directly in the technological process, which eliminates many problems associated with the selection, preparation and storage of samples of analyzed materials [14-16].

An important feature of the XRF is that it is a non-destructive analysis method. It is extremely useful for analyzing near-surface layers of materials and works of art. In the latter case, the XRF method is often irreplaceable due to the availability of portable spectrometers with radioactive sources and detectors with energy dispersion. Such devices can be easily delivered directly to the analyzed object [17-19].

The XRF method makes it possible to determine both the main components and the accompanying ones, as well as trace components after concentration process [20].
The essence of the X-ray fluorescence method is as follows: atoms excited by the primary X-radiation in the sample emit X-rays (X-ray fluorescence), which have a characteristic wavelength. The value of the intensity of the spectral lines is proportional to the concentration of elements in the sample.

The therapeutic mud of Sulfatnoe Lake in the Kurgan Region was taken as an mud sample. The lake was included in the catalog of mud deposits of the USSR (the year 1970) and is a popular tourist destination.

3. Research progress

Let us consider the course of experiments to determine the composition of mud and sewage sludge of mud baths using the X-ray fluorescence method.

The first stage was the collection and drying of mud and sewage sludge of mud baths.

At the second stage, using a press, the mud and sludge samples were formed into tablets of 2 cm in diameter, which were placed in special cuvettes. The sample surfaces were tightly adhered to the inner part of the cuvette and had no possibility of deformation during measurements. All samples were installed in the spectrometer in special holders and cuvettes included in the instrument set.

The third stage was X-ray fluorescence analysis and obtaining the elemental composition.

4. Research results

Analysis of the mud and sewage sludge composition showed the presence of elemental composition and the possibility of drawing conclusions about their further disposal.

The results of determining the elemental composition are presented in Table 1.

| Element | Concentration (%) | Element | Concentration (%) |
|---------|------------------|---------|------------------|
| Na₂O    | 2.232            | Na₂O    | 2.017            |
| MgO     | 3.332            | MgO     | 2.294            |
| Al₂O₃   | 12.334           | Al₂O₃   | 15.642           |
| SiO₂    | 62.931           | SiO₂    | 61.245           |
| P₂O₅    | 2.237            | P₂O₅    | 2.156            |
| SO₃     | 2.368            | SO₃     | 2.532            |
| Cl      | 2.731            | Cl      | 2.291            |
| K₂O     | 3.294            | K₂O     | 3.178            |
| CaO     | 2.251            | CaO     | 2.146            |
| TiO₂    | 0.949            | TiO₂    | 0.839            |
| V₂O₅    | 0.031            | V₂O₅    | 0.028            |
| Cr₂O₃   | 0.067            | Cr₂O₃   | 0.054            |
| Fe₂O₃   | 5.177            | Fe₂O₃   | 5.612            |
| SrO     | 0.044            | SrO     | 0.037            |
| Br      | 0.014            | Br      | 0.012            |
| CuO     | 0.008            | CuO     | 0.007            |

As a result of the X-ray fluorescence analysis, it was found that after the mud treatment procedure there is a large amount of silicon dioxide (SiO₂≈60%) in the composition of sewage sludge and mud of the Sulfatnoe Lake.

Natural silicon dioxide is used in the following industries:
- food industry;
- production of household chemicals, medicines;
- production of ceramics, glass, abrasives, concrete products;
• as a filler in the production of rubber, silica refractories;
• in microelectronics, where dioxide (a product of silicon oxidation) finds application in the field of chromatography;
• in ultrasonic installations and radio engineering due to its piezoelectric properties;
• fused dioxide is used in the production of fiber-optic cables and insulators.

One of the important characteristics of silicon dioxide is its ability to thicken (increase the viscosity) fluid compositions up to a free-flowing state (depending on the required degree of thickening, from 1.5% to 33% is added to the composition). The substance is used in the production of glass, ceramics, concrete products, and abrasives. In the construction industry, silicon dioxide is used as an additive in concrete and cement mortar.

In addition to the use of waste mud and sewage sludge as additives in structural materials, it is possible to use them as a raw material for the manufacture of fine ceramics, since the aluminum oxide (Al₂O₃) contained in this waste is a refractory oxide that increases the refractoriness of clays and the strength of fired products.

The results of the study of the effect of SiO₂ and Al₂O₃ on the characteristics of lightweight aggregates (LWA) have shown that these elements are potentially important additives that can control the physicochemical properties of LWA. The study results showed that LWA with the highest compressive strength, lowest porosity and best solidification can be obtained with a SiO₂ content of 30% to 45% and an Al₂O₃ content of 11% to 19% [21]. The use of these sludges as additives to lightweight aggregate is another possible way for their disposal.

5. Findings
Waste mud and sewage sludge produced after flushing should not be stored on the territory of mud baths, since they are waste of hazard class 4. These sludge should be pretreated with their subsequent disposal or use as raw materials.

As a result of the X-ray fluorescence analysis, it was found that after the mud treatment procedure there is a large amount of silicon dioxide SiO₂ ≈ 60% in the composition of sewage sludge and mud of the Sulfatnoe Lake. One of the important characteristics of silicon dioxide is its ability to thicken (increase the viscosity) fluid compositions up to a free-flowing state.

6. Conclusion
When determining the composition of mud and sewage sludge, the presence of chemical elements in them was established, which make these wastes suitable for further use in various industries. The high content of such elements as SiO₂ and Al₂O₃ allows using the sludge as an additive to increase the viscosity of building mixtures for the manufacture of fine ceramics. It can also be used as an additive for lightweight aggregates. The final choice of the method of disposal of this waste can be carried out depending on the needs of neighboring industrial enterprises.

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