The Use of Water Treatment Sludge Containing Clay with Adsorbed Copper and Nickel Ions in the Production of Ceramic Bricks

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Abstract. The paper presents the results of research on the use of water treatment sludge, which is formed during the processing of model copper and nickel containing water by activated clays as an additive in the manufacture of ceramic products. It was found that with the addition of sludge, the compressive strength of experimental samples increases from 1.8 to 2.5 MPa. The results of bio testing using *Daphnia magna* Straus crustaceans showed that the aqueous extract does not have an acute toxic effect on the test objects.

1. Introduction

Adsorption sewage treatment is traditionally one of the most effective and in demand in the world practice [1-7]. It allows extracting almost all types of pollutants, does not require high energy costs, depending on the type of sorbent used, material costs can be quite low.

A significant drawback of this method of water purification is the formation of waste sorption material, which requires either regeneration or utilization. In the case of the use of inexpensive materials, regeneration is because its cost can exceed the cost of the sorbent. The optimal solution to the problem would be the use of water treatment sludge as a secondary raw material. Clays, both natural and modified, are a common sorbent. With their help, it is possible to achieve high efficiency of treatment from a wide range of pollutants [8-15].

A method of modifying natural clays by electromagnetic treatment is promising and ecologically justifiable, since there is no formation of sewage and the consumption of reagents [16].

In the course of previous studies it was found that clays modified with ultraviolet radiation are effective sorbents for sewage treatment from copper and nickel ions [17].

It is necessary to make utilization for the sludge formed as a result of water treatment. The traditional way of processing the sludge is using it in the production of building materials. It is necessary to take into account the influence of adsorbed components on the properties of the final product, as well as its potential danger to the environment and human health. Heavy metals can be harmful, even in small concentrations, so the maximum allowable concentration of copper ions for water objects in the fishery category is 0.001 mg / dm³, and nickel ions 0.01 mg / dm³ [18].

Therefore, bio testing is a necessary stage in the development of materials using industrial wastes. *Daphnia magna* Straus is a commonly used test object in determining the potential toxicity of aquatic environments, since it has a high sensitivity to most pollutants [19].
2. Material and methods
The concentrations of Cu\(^{2+}\) and Ni\(^{2+}\) ions were determined by a spectrophotometric method using sodium diethyl dithiocarbamate and dimethyl glyoxime, respectively, with a spectrophotometer "KFK-3" according to standard techniques [20].

To determine the chemical composition of clays, a device such as ARL9900 Intellipower Workstation was used, which allows X-ray fluorescence analysis of elements from B (boron) to U (uranium) with the use of an X-ray tube with Rh-anode and X-ray phase analysis in the range of double angles 2θ 8-80°, using a tube with Co-anode. A study of the peculiarities of the chemical composition and internal structure of the sample was carried out on a high-resolution scanning electron microscope TESCAN MIRA 3 LMU.

To clear up the degree of toxicity of clay samples, a bio testing method was used using Daphnia magna Straus crustaceans [21].

Clays, used in the work, belong to Tavrovo and Ternovka deposits of the Belgorod Region (Russian Federation), and often used in local building industry.

3. Results and discussion
The mineral composition of the clay of Ternovka deposit is represented by such substances as illite (d = 10.069); kaolinite (d = 7.202, 4.842, 2.567, 2.497, 2.336); montmorillonite (d = 5.001, 3.259, 3.097); there are impurities of quartz (d = 3.352, 2.286); calcite (d = 3.3871) and anorthite (d = 4.270). The clay of Tavrovo deposit is represented by illite (d = 10.050, 7.112); kaolinite (d = 2.659, 2.495, 2.399); montmorillonite (d = 5.016, 3.253, 3.039); and sometimes there can be quartz impurities (d = 4.270, 3.352, 2.285).

When adding the investigated clays to solutions containing Ni\(^{2+}\) and Cu\(^{2+}\) ions, the pH of the medium increases, which leads to the creation of favorable conditions for the formation of sparingly soluble copper and nickel compounds (Figure 1).

![Figure 1. Roentgenogram of precipitation after purification of model solutions from nickel and copper ions using clay deposits: a - Ternovka, b – Tavrovo.](image)

For the purpose of utilization of the sludge containing hydroxides Ni(OH)\(_2\) and Cu(OH)\(_2\), to prevent the getting the toxic substances into the environment, as well as to exclude land from cultural and agricultural use for industrial landfills for the keeping precipitation (sludge) water treatment, we investigated the possibility of using sludge as a strengthening additive to clay mixtures in the production of ceramic bricks.
In the experiments, a precipitate was used after purification of model solutions with a content of Ni\textsuperscript{2+} and Cu\textsuperscript{2+} ions of 40 mg/dm\textsuperscript{3} respectively. The addition of clay to the solution was 2.5 g/dm\textsuperscript{3}. The precipitation after purification in the dried form contained about 1.8% nickel and the same amount of copper. The moisture of the received sludge was 95%. The sludge was dried in the open air, and when the moisture level reached 50%, it was added to the natural clay (pure dry clay of Tavrovo and Ternovka deposits) instead of the water in accordance with Table 1.

**Table 1. Composition of the liquids mixed with the clay [%].**

| № of the mixture | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 |
|------------------|----|----|----|----|----|----|----|----|----|----|----|
| Water            | 100| 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0  |
| Water treatment sludge | 0  | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100|

In accordance with the given compositions of the liquid mixed with the clay, ceramic masses were prepared, from which plastic cylinders with a diameter of 20 mm and a height of 20 mm were then made by plastic pressing. After drying in natural-air conditions, the samples were burnt in a muffle furnace at a temperature of 1000 °C for 60 min. Evaluation of the effect of water treatment sludge on the quality of ceramic samples was carried out on the compressive strength of the cylinders. The test results of the samples showed that under partial replacement of the liquid mixed with the clay water with the water treatment sludge, the strength of the samples increases with an increase in the amount of added sludge to 40%, both with the use of clay from the Ternovka deposit and clays of the Tavrovo deposit. With further increase the sludge content in the mixture, the strength does not change.

![Figure 2](image2.png)

**Figure 2.** The dependence of the compressive strength of the samples on the sludge content.

This can be explained by the fact that the clay that is part of the sludge has a higher dispersion and porosity due to modification and prolonged residence in the aqueous medium, as a result there is more dense packing of the raw mixture, which leads to the overall hardening of the structure.

One of the characteristics of building materials is water absorption. Samples with 40% addition of water treatment sludge and without additives (control) were chosen to determine this index. The results of the experiments presented in Table 2 show that the addition of sludge to the raw mix slightly increases the water absorption of the samples, which probably can be explained by the decomposition of hydroxides during burning and the formation of fine pores in the sample body (Figures 3).
Table 2. Water absorption of samples.

| Clay deposit | Control, C | With addition of sludge, S | Percentage increase, C/S |
|--------------|------------|----------------------------|--------------------------|
| Ternovka     | 10         | 10.6                       | 1.06                     |
| Tavrovo      | 11         | 11.4                       | 1.04                     |

Figure 3. Micrograph: a - of a control sample, b - of a sample with 40% additions of clay sludge from the Ternovka deposit.

Table 3. Ni$^{2+}$ and Cu$^{2+}$ elution from ceramic samples.

| Concentration of the sludge [%] to water | Ni$^{2+}$ concentration [mg/dm$^3$] | Cu$^{2+}$ concentration [mg/dm$^3$] | Ni$^{2+}$ concentration [mg/dm$^3$] | Cu$^{2+}$ concentration [mg/dm$^3$] |
|-----------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| pH 4                                    |                                      |                                     |                                     |                                     |
| 10                                      | 0.001                               | 0                                   | 0.001                               | 0                                   |
| 20                                      | 0.001                               | 0.001                               | 0.001                               | 0                                   |
| 30                                      | 0.001                               | 0.001                               | 0.001                               | 0.001                               |
| 40                                      | 0.002                               | 0.002                               | 0.002                               | 0.002                               |

| pH 5                                    |                                      |                                     |                                     |                                     |
| 10                                      |                                      |                                      |                                      |                                     |
| 20                                      |                                      |                                      |                                      |                                     |
| 30                                      |                                      |                                      |                                      |                                     |
| 40                                      |                                      |                                      |                                      |                                     |

Short-term bio testing makes it possible to determine the acute toxic effect of heavy metals solutions on daphnia. The toxicity criterion is the death of 50 or more percent of the crustaceans over a period of up to 48 hours in the test water compared to the control one.

The results of the studies showed the absence of toxic effect. Thus, when testing daphnia, the criterion of acute lethal toxicity is the death of 50% or more of the crustaceans in the experiment compared to the control for 48 hours of bio testing. The results of the bio testing using *Daphnia magna Straus* as a test object are indicated in Table 4.
Table 4. Bio testing results for determination of the toxic effect of water extract of the samples on the test object *Daphnia magna Straus*.

| Experiment     | Averaged value | Mortality [%] |
|----------------|----------------|---------------|
| Control        | 10,0           | 0             |
| Undiluted extract | 8,3           | 17            |
| 1:1            | 9,0            | 10            |
| 1:3            | 9,7            | 3             |
| 1:5            | 9,9            | 1             |
| 1:7            | 10,0           | 0             |
| 1:9            | 10,0           | 0             |

Based on the results of the studies, the analyzed water extract does not have toxic effect on the test object *Daphnia magna Straus*, since the percentage of dead daphnia is below 50%.

4. Conclusion

The investigations carried out showed that the water treatment sludge formed after extraction of copper and nickel ions by modified clays from model waters can be used as a strengthening additive in production of ceramic products. Hardening is achieved due to a more dense packing of the raw mix, which appears due to the high dispersion and a larger number of micro pores in the sludge.

Studies of ions elution from crushed samples with content of the sludge up to 40% made it possible to establish that at neutral and alkaline pH their concentration in undiluted extract does not exceed 0.002 mg / dm³.

The results of the bio testing showed that the water extracts from the crushed material of the samples do not have acute toxic effect on the *Daphnia magna Straus* test object.

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