The elaboration of environmentally safe way of galvanic sludge deactivation with the use of bentonite clay

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Abstract. On the basis of experimental data, the qualitative galvanic sludge composition has been got after reactant purification of waste water of the machine building enterprise. The research has been carried out on the degree of encapsulation of heavy metals in the system of galvanic sludge (GS) – cement-sand (CS) – bentonite clay (BC) with different percentage ratio of components. It has been stated that it took 28 days to complicate galvanic sludge with the mixture of CS and CS-BC. It has been shown that appending of 5% and 10% bentonite clay into the system GS-CS increases its sorption capacity and leads to decrease of washing heavy metals out of it. It has been defined that initial heat treatment of galvanic sludge with subsequent appending of BC ensures decrease of concentration of chromium ions, cuprum and ferrum in the water which is lower than the level of admissible concentration limit (ACL).

1. Introduction
The introduction of environmentally safe technologies while elaboration processes of industrial waste utilization, decreasing anthropogenic impact on the bioenvironment and providing rational use of natural resources, has remained an important task. The number of researches [1,2,3,4,5] has been devoted to it. So, at the industrial enterprises, being involved in galvanotechnics, after the purification of waste water by reactant way, galvanic sludge (GS) forms. It is one of the most hazardous wastes (II-IV class of hazard) and one of the main resources of heavy metal inputs into the environment.

Together with the problem of galvanic sludge deactivation by creating special land disposals, a more important task will be its economically reasonable recycling, which will allow decreasing the level of waste class hazard. For example, it is shown that the treatment of sludge by solidifiers allows getting the material which is safe for the environment. As a result, insoluble solidified blocks for construction are formed [4].

On this basis there has been an attempt to offer a sorption utilization way of multi-component galvanic sludge with the use of bentonite clay (BC) of Zyryanovskiy mineral asset, which shows sorption activity in relation to ions of zinetum, chromium, cuprum, cadmium [6,7].

2. Methodics of study
The object of the study has been sludge of galvanic production of one of the metallurgic plants of the Urals, belonging to the second class of hazard, received as a result of waste water neutralization.

To get concrete (cemet) mixture the concrete of the company “Werker” Portland PC 400 – D 20, sand of the company “Werker” in proportion 1:3 and water have been used (1 sample set). While appending bentonite clay of Zyryanovskiy mineral asset of Kurgan region in quantity of 5% and 10%
into samples of set 1, sample set 2 has been received, the composition of it is presented in table 1. Before adding into the mixture, the sludge has been dried at the temperature of 105°C. For further researches its heat treatment has been held under temperature conditions from 700 to 900°C in a muffler (brand «SNOL–2.2.5.2/12.5–I1») for an hour. Calcinated and reduced galvanic sludge was added to cement mixture in a quantity from 5 to 10 mass %.

Table 1. Proportions of GS, CS and BC.

| Mass of galvanic sludge, m(GS), g | Percentage of galvanic sludge in the sample, ω (%) | Mass of mixture of CS, m(CS), g | Mass of bentonite clay, m (BC), g | Percentage of bentonite clay in the sample,ω(%) |
|----------------------------------|-----------------------------------------------|--------------------------------|---------------------------------|-----------------------------------------------|
| 17.5                            | 5                                             | 332.5                          | 17.5                            | 5                                             |
| 35                               | 10                                            | 332.5                          | 17.5                            | 5                                             |
| 17.5                            | 5                                             | 315                            | 35                              | 10                                            |
| 35                               | 10                                            | 315                            | 35                              | 10                                            |

Test cylinders have been made of the received concrete mixtures with different percentage ratio of components, after their hardening, they were reduced into pieces of the size of 1–3 mm, then they were poured with water in ratio in mass (1:10) and were left for the contact with water for 2 or 4 weeks to check the washing-out of ions. After the prescribed time, the precipitation was separated by centrifuging (centrifuge brand «OPn – 3.02 DASTAN»), and the water was analyzed for containing ions of cuprum (II), chromium (III) and ferrum (III) photometrically. The control of the value of pH was carried out with the use of ionomer «Expert» –001–3.0.1.

3. Results
It is known that the composition of sludge is not constant and depends on the used solutions in the galvanic shop and the used reactants at the waste treatment plant [8].

The conducted qualitative analysis has shown that in the composition of the studied waste there are cations – Cu²⁺, Mn²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Cr³⁺, Sn²⁺, Ca²⁺, Mg²⁺, Al³⁺, Fe³⁺, and anions – CO₃²⁻, PO₄³⁻, SO₄²⁻, SiO₃²⁻, Cl⁻, NO₃⁻.

It is stated that the appending of bentonite clay at the rate of 5% into the system GS-SC has led to the decrease of containing metal ions in out wash in comparison with concrete mixture, not having sorbent agent. However, the metal concentrations remained significant. The appending of bentonite clay in the quantity of 10% encouraged the decrease of the ferrum ion concentration in the water by 1,5 times, cuprum ions by 1,2 times, chromium ions almost by 2 times in comparison with samples, in which there was no clay. The concentration of the studied ions exceeded the level of admissible concentration limit (ACL) insignificantly.

At the decrease of the quantity of the appending galvanic sludge into the mixture CS (1:3) and CS-BG from 10% to 5%, the decrease of the concentration of the defined ions was observed in the analyzed solution.

The similar decrease of the concentration happened on the condition of the increase of time of sample fixation with cement mixture from 14 to 28 days.

The heat treatment of the galvanic sludge may ensure mineralizing of waste organic element, as well as the change of heavy metal salts into more stable compositions – oxides and help of fixation of galvanic sludge sample by cement mixtures.

The comparative analysis of a high and low temperature regimes of preparation of galvanic sludge samples has been carried out to define the degree of fixation of ions of chromium, cuprum and zinetum by concrete mixtures of two series. So, for chromium ions (III) (figure 1) at the contact time with water of 28 days and 5% presence of galvanic sludge, while not having bentonite clay, the sample without heat treatment, there was chromium ion yield (III) into the solution in the quantity, 3 times
more than the admissible concentration limit (ACL). The rise of calcination temperature up to 700°C has led to the decrease of chromium ion concentration (III) in the analyzed solution to the level, exceeding the admissible concentration limit insignificantly. Only the calcination of the sample at 800°C encouraged the decrease of chromium ions (III) in the analyzed solution to the admissible concentration level. The appending of the clay and the calcination together influenced the degree of fixation of chromium ions (III) positively. At the temperature of 700°C in the mixture GS-SC-BC the decrease of chromium ion concentration already reached the level lower than the admissible concentration limit. The similar dependence was observed for the ions of ferrum and cuprum (figure 2,3).

For samples, not having bentonite clay, the increase of time contact with water led to an insignificant increase of defined ion concentrations in out wash. In samples, which had bentonite clay in the composition, additional washing out of heavy metal ions did not happen on condition of time increase of contact with water.

The increase of galvanic sludge treatment to 900°C did not affect significantly on the presence of heavy metal ions in the water after the contact with all the samples and was similar to the one treated by t = 800°C. At the temperature of 900°C the sample agglomerates and becomes difficult for the further processing.

In the course of preliminary qualitative analysis, it was stated that galvanic sludge contained nitrates, silicates, carbonates, silicates, sulfates, phosphates. It is known that at the temperature of 800 °C nitrates, sulfates and carbonates (cuprum, zinetum and chromium) resolve with the formation of oxides, so: partial change of salts into oxides most probably encouraged more effective fixation of metal cations. Silicates, silicates, phosphates remained unchanged.
Overall, optimal temperature of galvanic sludge calcination is 800°C; the time of fixation of galvanic sludge with cement mixture is 28 days.

Optimal percentage of bentonite clay in cement sample is 10%, of galvanic sludge is 5% and 10%.

The developed sorption-thermic way of utilization of multi-component galvanic sludge will allow using the material, received on the basis of concrete mixtures for industrial purposes.

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