Nanomodified natural aluminum silicates in technology treatment of industrial waste and the production of building materials

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Summary. The article presents the results of cleaning galvanic drains, etching solutions, waters contaminated water soluble fractions of petroleum products, including seawater. Conducted data testing of technology for recycling products of water treatment in the technology of production of ceramic bricks.

Key words: galvanic drains, etching solutions, water soluble fractions of petroleum products.

INTRODUCTION

Sustainable development (SD) provides such a model of resource use that is aimed to meet human needs while preserving the environment so that these needs can be met not only for the present but also for future generations [1…4].

This paper presents the results of scientific studies and technological tests of sorbents for purification of industrial and household sewage water containing heavy metal ions and soluble fractions of petroleum products, including sea water, such as ballast water of ships [5…7].

Clay minerals have unique colloid-chemical properties and can therefore serve as basic material for adsorbents. Thanks to the large specific surface area, high values of dispersion and cation-exchange capacity of clays, it is possible, after their physical or chemical treatment, to obtain products with an adjustable non-hydratable or hydrophobic surface balance, high adsorption and coagulating properties, which can be successfully used to purify water: industrial, economic, storm water, water containing a colloid-disperse suspensions, sea water containing crude oil and soluble oil products [8…11].

It is proposed to use as an adsorbent some clay modified with ferric hydroxide compounds selected from the series: montmorillonite, hydromica, kaolin.

The term “modified” means creation of a modifier nanolayer on dispersed clay mineral surface with a view to change the nature of the surface, its colloid-chemical and technological properties [12, 20].

The economic feasibility of usage of the nanomodified aluminum silicates at water treatment technologies is based on their effectiveness and low cost at cleaning of large volumes of water, simplicity and reliability of their production and application, possibility of closed manufacture cycle organization, and no less important possibility of spent sorbent and water purification product recycling.

The paper presents the assessing results of modifier impact on clay minerals colloid-chemical properties, as well as the results of scientific studies and industrial testing of clay minerals (natural and modified) used for purification of acid-alkaline, electroplating and domestic sewages and water contaminated with petroleum products (Tab.1).

Table 1. The list of technologies and products obtained by recycling industrial and household waste

The list of industrial waste to be disposed of	Production, derived products
The slurry that is formed by treatment of fresh and sea water contaminated by oil products	Getting organic nanomineral compositions. Raw materials for production of building ceramics
Sludge treatment halvanostokov	Ingredients charge in the production of building ceramics, brick tiles, sanitary ware
The slurry after neutralization etching solution in the production of steel pipes	The component in the production of building ceramics
Products of WWTP sludge	Production of technical ceramics: industrial premises, ceramic gravel
Oxidizer propellant, food processing	Getting nanocomposites batch ingredients in the manufacture of ceramic building materials, fertilizers

OBJECTS OF RESEARCH

Clay minerals with different crystal lattice structures, dispersion, natures of structure formation in aqueous dispersions: montmorillonite, hydromica from the Cherkassy field, kaolin form the Prosyanovskoe field (Ukraine).

THE MATTER THEORY AND THE METHOD TO OBTAIN NANOMODIFIED FORMS OF CLAY

Getting nanomodified clay is based on $FeCl_3$ hydrolysis, theoretical views of the formation of ferric hydroxide colloidal particles α – FeOOH, namely, that part when a solid phase (a centre) is formed, which absorbs forming potential ions from the solution. As an ion absorption result the centre surface acquires a charge. Oppositely charged ions (counterions), presented in water, are grouped near the centre surface by electrical attraction of unlike electrical charges, forming a colloidal particle. Colloidal particles with surrounding diffuse layer are called micelles. If the dispersion medium is water, it is called hydrosol. Depending on the colloidal solution formation conditions the forming potential ions and counterions can change places. Depending on hydrolysis conditions for iron salts, aluminum, the formed sol is positive at low pH values of water and the negative at high ones.

The described above mechanism of hydroxide sol formation in the light of the theory of Muller [13] and the theoretical foundations of water technology [14] allows us to determine the conditions of coating formation on the surface of finely dispersed aluminum silicate made of hydroxide nanoparticles. At clay modifying with hydroxide, coagulation takes place mainly under the gravity force and the gradient coagulation induced by mixing of the system: water-clay-hydroxide [14, 15].

Nanomodified aluminum silicates or other finely dispersed materials can be used as efficient absorbents, fillers, structure-formers, as well as an ingredient for many modern composite materials.

RESEARCH METHODS

Clay mineral aggregate stability was determined by the volumetric method on the base of a sediment volume formed during kaolin sedimentation from dilute suspension. Rheological properties of modified clays at a critical concentration for structure formation were determined with a rotary viscosimeter «Rheotest-2". At a gas analyzer «Wleft» there were determined sorption capacity of water-soluble fractions of petroleum and benzene with a flame ionizer, and the presence of atomic adsorption metal cations and their number in water systems with a C-115 spectrophotometer.

RESULTS AND DISCUSSION

The modification of clay minerals. The sediment volume (V_{OC}) of the samples depends on clay mineral nature and a degree of modification (α). The degree of modification is defined as the ratio of the masses of ferric hydroxide and of clay minerals (b %). At kaolin modifying with α from 0,1 to 0,7%, the sediment volume increases from 2,0 to 3,6 cm^3/g (Fig.1). With further α increase up to 5%, V_{OC} decreases, remaining at α 3,0 to 5.0% almost unchanged – 1,96…1,74 cm^3/g (V_{OC} for not modified natural kaolin is in the range of 2°cm^3/g [16]).

Rheological studies to obtain information about the process of structure formation of modified kaolin in aqueous dispersions were carried out at strain rate of 0,33…145,8 s^{-1}. The concentration of solids in the suspension was 33,0%, which corresponds to the concentration at which three-dimensional structuring of a system occurs. These conditions are the best ones to evaluate effectiveness of introduced additives or other type of system processing carried out in order to stabilize its properties.

Fig. 2 shows rheological curves of viscosity dependence on shear stress and curves of sample flow for modified kaolin suspensions. With increasing of a modification degree α from 0,1 to 5,0 % the coagulation structure strength increases also, as it is indicated by viscosity increase at low values of shear stress. The maximum value of shear stress, which is achieved in this range of strain rates, for samples modified on 0,1…1,5% is 3…4 times as high as than that for samples of natural kaolin and kaolin modified on 3,0 and 5,0%. This process is observed more clearly on rheological flow curves. The maximum structure strength in

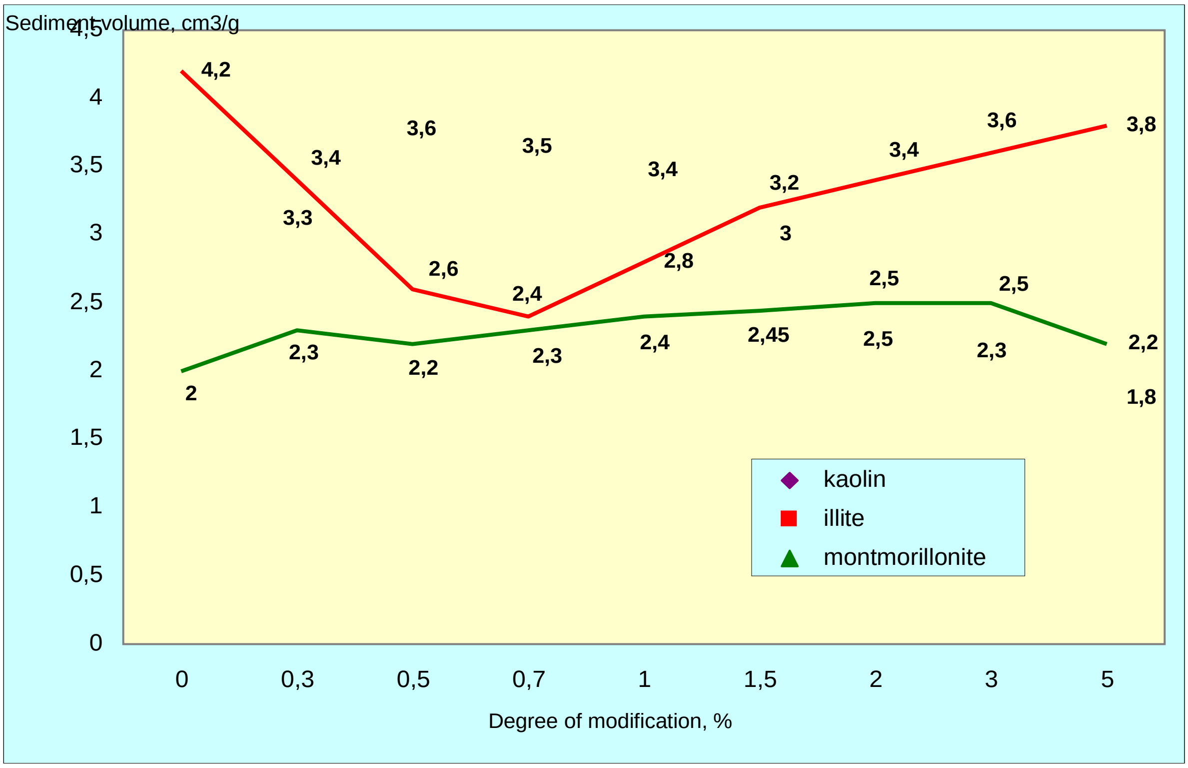

Fig. 1. The dependence of sediment volume for ferric hydroxide-modified clay minerals on the degree of modification

suspension with modified kaolin is achieved at α = 0,3%. At modifier increase from 0,3 to 5%, the strength is gradually reduced, and natural and modified 3% kaolin have practically identical rheological parameters.

At treatment of suspension with natural kaolin by ferric salt solution followed by FeOON precipitation on the kaolin surface, a degree of surface coating with the modifier plays a crucial role in the properties of the clay surface. In a case of partial covering, interaction between particles increases, reaching a maximum value at – 0,3% (see Fig. 2). That is, formation of an uninterrupted hydroxide layer on the kaolin particle surface is completed when FeOON content is equal 3,0%. If α = 5,0% structure formation is determined mainly by free hydroxide particles not bound to the surface of the main dispersed phase of ferric hydroxide aggregates. It can be assumed that the formation of a modifier layer provides stabilization of kaolin suspension.

Hydroxide modifying affects a sedimentation process for montmorillonite and hydromica in a less degree. At hydromica modifying with increasing modifier amounts, after hydroxide layer formation V_{OC} decreases firstly and then increases, that indicates more complex processes of coagulation structure formation. At montmorillonite modifying, a clear V_{OC} dependence on α was not established, but FeOON presence in the montmorillonite – water system has significant effect on suspension rheology, the process of structure formation and the aggregation state of dispersed mineral. At α < 3%, precipitation is completed within 5 h, and not modified montmorillonite and one with α of 5% are deposited over 30 days.

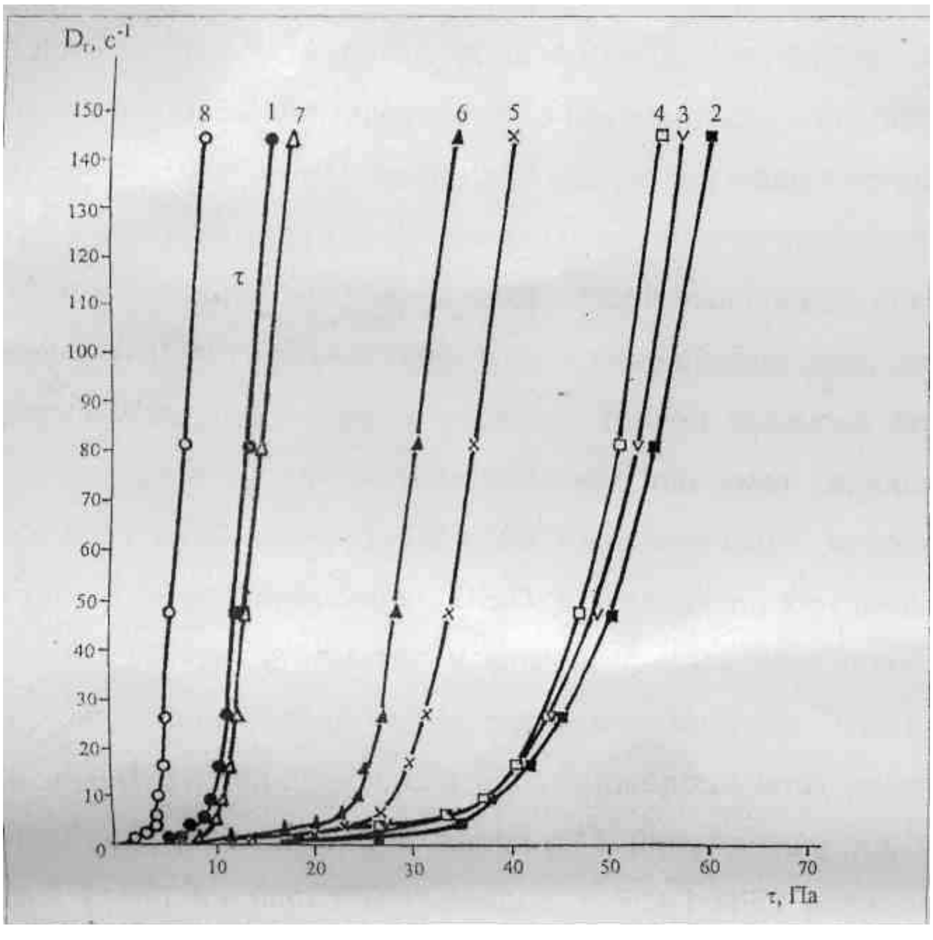

Fig. 2. Rheological flow curves (Dr − τ) for suspensions with modified kaolin:
1 – natural kaolin; *2* – 0,3; *3* – 0,5; *4* – 0,7; *5* – 1,0; *6* – 1,5; *7* – 3,0;
8 – 5,0 % weight of FeOOH

Industrial testing of natural and modified bentonite as adsorbent for industrial wastewater purification at existing facilities showed positive results, tests were carried out at the neutralization centre of the Antonov aircraft company (Kiev). The company "Dashukovskie Bentonity" together with the Research and Design Technological Institute of Municipal Services (Kiev) conducted studies of bentonite for domestic sewage treatment in one of the shops of the Nikopol stainless tube mill (Nikopol). There are also experimental results of assessment of possibility to use natural sorbents for water treatment from soluble fractions of petroleum products, made within the research program INTAS Call, 1996, Brussels, Belgium (Tables 2 – 5).

The purification scheme for chromium-bearing wastewater using modified bentonite is as follows: the adsorbent is fed to a reactor tank, where wastewater is stirred for 15 min, then it is pumped into settling tanks and deposited for 3 – 4 hours till water clarification (adsorbent amount required for wastewater treatment is determined by content of pollutant substances). Wastewater treated with adsorbent can be used again as purified water, or it can be discharged into a sewer network, because, under bentonite powder influence, pollutant content decreases and becomes several times lower than specified in sanitary norms or maximum permissible concentrations.

The purification scheme for domestic sewage is similar to the above described one: after rough machining or complete biological treatment, water is fed into tanks equipped with agitators (adsorbent amount is also determined by pollutant quantity). Then waste water enters into settling tanks for secondary settling, where impurities precipitate and water clears (at necessity, adsorbent is added). Such wastewater neutralization allows dumping of it into water bodies.

The results of the scientific and technological studies show viability, technological and economic feasibility of bentonite application for domestic sewage treatment.

Data obtained in the study of adsorption of water-soluble fractions form petroleum products are very interesting. Under adsorbent – water system stabilization, organic matter adsorption increases. Sorption capacity with respect to toluene increases with increasing adsorbent specific surface area, such dependence for water-soluble fraction of kerosene is not observed. The adsorption value with modified clay minerals increases by several times, considerably exceeding the values of organic sorption (see Fig. 3) [19]. The results show high efficiency of water purification from soluble fractions of petroleum products.

At an optimal sorbent aggregative state in water, which corresponds to the system stabilization, an integral adsorption value of organic substances increases?

Depending on a nature and a method of sorbent preparation, its sorption capacity as for soluble fractions of petroleum products is within the range of (80…140) mg/l.

It should be noted that sludge obtained as a result of petroleum products purification can be recycled, which eliminates environment pollution.

Obtained slurry can be used in recycling technologies for building materials such as bricks or clayite. Laboratory studies to obtain bricks, clayite, and light-weight brick based on perlite were performed.

During studies, the next technological factors were controlled: water absorption, flexural and compression strength, porosity. These results indicate that sludge addition to bricks or clayite blend in the amount of (1…3) % of total mass leads to a higher fluctuation of these factors, in the range of (1…2) %, which does not affect significantly the product performance parameters. And at sludge content increasing, even some improvement of the parameters is observed.

Proposed sorbent application showed a new way to solve the problem of water treatment product disposal.

The sequence of technical operations for water treatment is presented in the next figure.

Table 2. Results of spent etching solutions treatment

Nr	Parameter name	Parameters of waste nitrogen-fluoric solution, g/dm^3	Parameters of purified etching solution, g/dm^3	Purification efficiency, %	Ingredient content in solid residue after treatment, %
1	Iron content	56,1	0,001	99,998	18,8
2	Chrome content	9,05	Less then 0,001	99,998	3,4
3	Nickel content	7,54	0,12	98,41	2,5
4	Iron total	50,18	0,00636	99,987	
5	Fluorides	100,4	3,7	96,32	

Table 3. The results of technological tests for modified bentonite for industrial waste water treatment at “Avianit" plant, Kyiv

Parameters of industrial wastewater	Before treatment, mg/l	After treatment, mg/l	Treatment time
Water of galvanic production			
Cr	28	<0,02	
Cu	34	<0,05	
Cd	2,4	absent	1,5-2,0
Fe	38	0,02	
Ni	12	<0,05	
Suspensions of different dispersion			
<0,1 µm	55	0,8	0,5
>10 µm	250	1,5	0,5
Polydisperse suspension	7500	4,0	1,0
Soluble fractions of petroleum products			
$C_8 – C_{26}$	5…35	0,03	2,0
Benzene	Up to 150	0,1	2,0

Table 4. Evaluating of sorbent effectiveness on the base of modified clays for water purification from soluble fractions of petroleum products

Soluble fractions of petroleum products	Quantity of fractions before treatment, mg/l	Quantity of fractions after treatment, mg/l	Treatment time, hours	Purification efficiency, %
$C_8 – C_{26}$	5…35	0,03	2,0	99,99…91,43
Benzene	Up to 150	0,1	2,0	99,99

Table 5. Bentonite effectiveness for domestic sewage treatment

Parameter	Value
Appearance	Light grey finely dispersed powder
Mass fraction of montmorillonite, %	50…70 and more
Mass fraction of clay component having particle sizes less than 0,02 mm, %	86…99
Residue, % not more, on sieves with mesh size, mm:	
- 0,4	3,0
- 0,16	10,0
Mass fraction of moisture, %	6,0…10,0
The reduction degree of contamination indexes for raw wastewater, %:	
- suspended matter	94…95
- biological oxygen demand in 5 days	92…93
- chemical oxygen demand	88
- phosphates	63…65
The reduction degree of contamination indexes for biologically treated wastewater, %:	
- biological oxygen demand in 5 days	74…82
- chemical oxygen demand	32…39
- phosphates	11…83

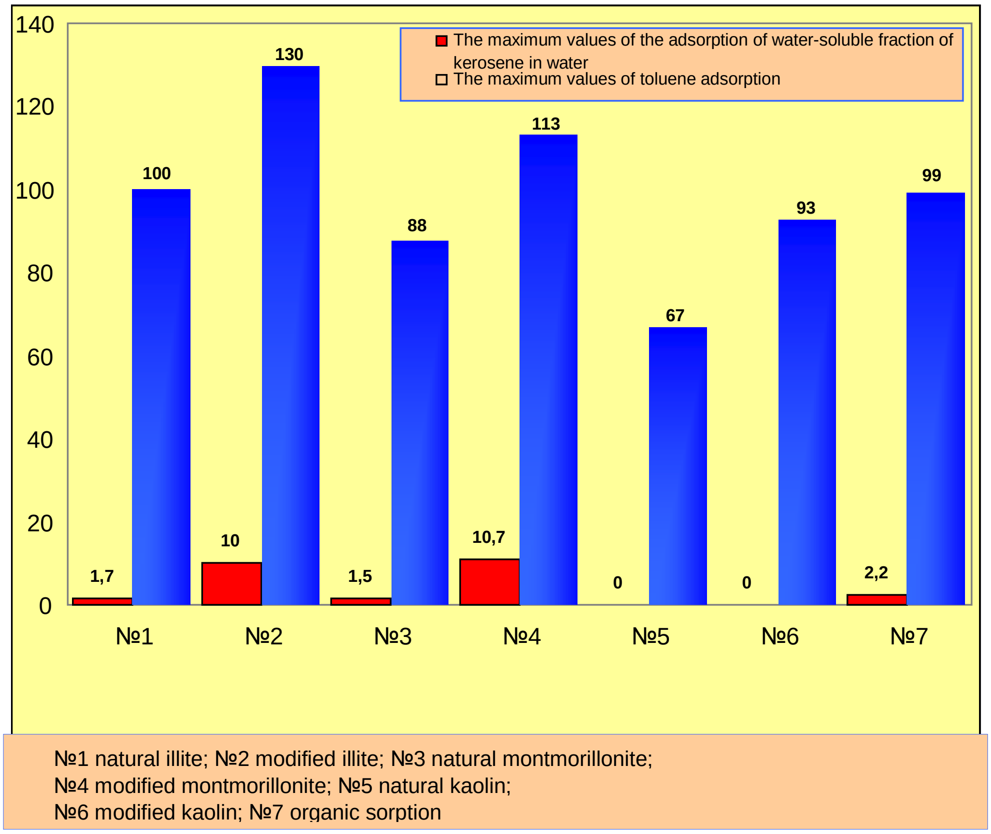

Fig. 3. The maximum values of the adsorption of toluene and soluble kerosene fractions out of water at the optimum degree of clay nanomodification

STAGES OF IMPLEMENTATION OF THE WATER TREATMENT TECHNOLOGY

Industrial technology implementation requires passing a series of stages, namely:

- Estimation of pollutant chemical composition and drain flow volume
- Familiarization with an existing technological scheme and equipment for industrial wastewater treatment
- Selection of optimal ways to modify the selected sorbent according to the criteria of minimal mass picking by means of tests
- Development of a technical project for modernization of the existing technological scheme of industrial wastewater treatment
- Development of a new technological scheme for industrial wastewater treatment using new or existing equipment, if modernization is chosen
- Development of production schedules for industrial wastewater treatment

ENVIRONMENTAL PERFORMANCE OF THE TECHNOLOGY

The technology usage will significantly improve employee working conditions due to the fact that the technology does not require chemicals that are usually needed at a reagent way of industrial wastewater treatment.

Spent sorbent does not require special warehouses for storage, as it is required for highly toxic sludge obtained at a reagent method of industrial wastewater treatment.

Spent sorbent is not environmentally harmful materials and can be used as an additive for ceramic building material manufacture.

ECONOMIC PERFORMANCE OF THE TECHNOLOGY

At technology application, the cost of industrial wastewater treatment will be substantially less in comparison with the reagent purification method which is used now in industry.

Table 5. Testing processing properties of ceramic bricks charge, containing of sludge additives industrial waste water treatment

Name of the index	Batch index component content					
	X_0	X_1	X_2	X_3	X_4	X_5
Forming humidity, %, a/b	23,35/20,22	24,63/19,80	25,19/20,80	24,49/19,70	25,24/19,80	25,80/20,40
Sensitivity to drying, C	>180	>180	> 180	>180	>180	>180
Air shrinkage, %	6,61	6,40	6,24	6,62	6,54	6,70
Overall shrinkage, %	6,70	6,54	6,74	6,72	7,04	7,02
The average density, g/cm3	1,55	1,58	1,58	1,54	1,58	1,50
Ultimate compressive strength, MPa	18,4	19,2	20,0	19,8	20,4	21,8
water absorption, %	22,28	21,50	21,20	21,44	21,0	20,54

Note: X_0 − charge for ceramic brick factory;

X_1, X_2 – samples of the charge additionally contains a slurry consisting of water treatment products of galvanic production wastes 1 and 3 % by weight respectively;

X_3, X_4 – 1,3% by weight sludge after cleaning water contaminated with water-soluble fractions of oil;

X_5 – 3% sludge after cleaning ballast water (seawater)

The cost of the modified sorbent, which will be made by an executive, will not be higher than 5,00 UAH per 1 kg.

Modified sorbent volumes used in the technology are ranged from 0,3 kg to 1,0 kg per $1m^3$ of industrial wastewater.

For example, an enterprise neutralization station with cleaning capacity from 20 m^3 to 30 m^3 of industrial wastewater per day requires about 20 kg of the modified sorbent.

The above data allow us to state with confidence that nanomodified natural aluminum silicates can generally be used for solving of global problems of water purification from heavy metal ions and soluble fractions of crude oil and petroleum products.

The obtained results of scientific studies and technological tests, part of which is shown in this report, provide a basis to offer them to interested parties as an innovative project to address specific problems at different industries and businesses.

In today received results of the preliminary assessment of the physical and mechanical, consumer properties of ceramic building materials samples, which charge as a plastic component along with clays containing sludge. As a batch of ingredients used in the sludge produced in the process of purification of water contaminated with water-soluble fractions of petroleum, electroplating industrial waste, ballast water (seawater) nanomodified natural aluminosilicates (NMPAS). Test samples of ceramic material on the basis of the charge for the ceramic brick, modified by the addition of sludge produced in the purification of industrial waste water, carried out in accordance with the State Standard 2.7-2695 BV, DTSU B.V.2.7-4297. Analyzing the results discussed above, it is possible to conclude that the proposed project has an innovative perspective of implementation. The effectiveness of cleaning effluent is high, cost-effective. Batch tests for ceramic bricks containing sorbents nanomodified samples showed the effect of increasing the mechanical strength during storage within an acceptable range of other important process parameters. There is an assumption that the manipulation of the composition of the basic charge and the number of NMPAS supplements, carrying out preliminary testing technology will be able to find other useful, unpredictable effects that many scientists and technologists find when working with nanosystems. Optimization of the amount and nature nanomodifier when processing natural aluminum silicates (clays) makes it possible to consciously regulate technology, consumer properties of ceramic products for various purposes, to create modern cost-effective and environmentally appropriate innovative projects.

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Наномодифицированные природные алюмосиликаты в технологии очистки промышленных стоков и производстве керамических строительных материалов

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Аннотация. Представлены результаты очистки гальванических стоков, травильных растворов, загрязненных вод, растворимых фракций нефтепродуктов, в том числе морской воды. Приведены результаты испытания технологии по утилизации продуктов очистки воды в технологии производства из керамического кирпича.

Ключевые слова: гальванические стоки, травильные растворы, водорастворимые фракции нефтепродуктов.