

Research on destruction of oil-containing emulsion waste by hard solid demulsinators based on industry waste

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Abstract. The article presents experimental data on the destruction of oil-containing emulsion effluents stabilized by solid emulsifiers, that were obtained by heat treatment of ore mining and processing enterprises (GOK) waste and sugar industry. The comparative characteristics on purification of oil emulsion effluents by solid demulsifiers when passing through a filtration layer consisting of solid demulsifiers particles and a layer of sand are given. As well as research into the practical application of oil sludge in the production of lightweight ceramic materials.

1 Introduction

Along with the problem of stable reverse emulsions formation, which is of great importance in many technical processes, the reverse problem is also important-the destruction of emulsions (demulsification) [1-4].

Demulsification is used in such common processes as separation of emulsified water from crude oil and tar, purification of condensate from oil, as well as in the purification of oil wastewater [5-10]. All methods of destruction can be divided into three groups: 1) mechanical or physical; 2) chemical; 3) electrical.

Currently, there are many demulsifiers used for the destruction of oil-containing emulsions. However, a demulsifier suitable for the destruction of one emulsion may be completely unusable for another. Therefore, the development and research of solid demulsifiers obtained on the basis of large-scale industrial waste is an urgent task.

It should be noted that the problem of destruction of oil emulsions in wastewater is no less urgent [11,12]. The purification technology of such effluents should ensure the complete destruction of the stable emulsion structure and the subsequent separation of the oil phase from the aqueous medium.

Therefore, the issues of affordable and high-quality wastewater treatment of metallurgical plants from oils and oil products is one of the priority areas of environmental protection. For wastewater treatment, sorption methods using active carbon and other sorbents (including those based on industrial waste), filters with granular loading, and others are widely used.

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2 Theoretical basis

Demulsifiers are substances with a diphilic structure. Due to the property of diphilicity, demulsifiers are adsorbed on the interfacial boundary surface layers of dispersed phase particles, due to which the globules of water-oil emulsions reduce the interfacial tension and the destruction of natural stabilizers protective layer. The new layers formed, oriented around globules and consisting of demulsifier molecules, have almost no mechanical strength. Consequently, the fusion of the water dispersed phase particles is greatly facilitated, which leads to the subsequent destruction of the emulsion with a clear water and oil layers separation. Emulsions can be destroyed when passing through a filtration layer consisting of adsorption material and sand [9]. The essence of the filtering process through a granular loading layer is the separation of inhomogeneous systems consisting of a dispersion medium (liquid or gas) and solid particles or droplets suspended in it, which are produced in the filter. The emulsion is fed into the filter. Under the action of a pressure drop, the dispersion medium passes through the granular layer, and the particles of the dispersed phase are retained by the granular layer. In the filtering process, the channels of the granular layer become clogged with small particles of the dispersed phase and a sediment layer of increasing thickness is formed from large particles of the dispersed phase.

As a process result, the inhomogeneous system is divided into clarified dispersion medium and sludge. In granular filtration of oil-containing emulsions, the initial surface character of the loading grains is important. At a hydrophobic surface of grains particles adhesion is stronger, than at hydrophilic as on a surface of grains of hydrophilic materials there is a hydrate cover and adhesion of impurity drops occurs only where this cover is broken. The introduction of new technologies for the destruction of persistent oil-water emulsions requires the development of a science-based approach based on a thorough knowledge of the mechanism's formation structure of the interphase layer and the structural features of emulsifiers in the oil-water emulsions stabilization process

The main problem in the treatment of effluents containing petroleum products is the purification of emulsified petroleum products. The complexity of purification is a sufficiently high stability of such systems, which may be the result of the adsorption action of surfactants and the elastic protective layers formation or the electrolytes presence and the stabilizing effect strengthening of the DES layer. At all known methods efficiency of clearing of them is far from 100%.

The purification process of oil wastewater on the granular loading layer is divided into two stages: delivery of droplets to the loading grains (contact with the grain surface and displacement of water from the grain surface by oil products) and filling narrow channels of the filter layer with oil products and moving along them in the filtration direction. When the emulsion is filtered, the internal loading space continuously changes as a result of oil sticking to the grains surface. The efficiency of water purification from undissolved petroleum products is determined, among other things, by the level of hydrophobicity of the granular loading, filter material properties (grain size, shape, surface roughness), layer geometric structure (layer porosity, grain homogeneity), filter layer height, and filtration rate. Quartz sand, crushed anthracite, foamed vermiculite, expanded clay, ceramic chips, thermolysis defecation (TD600) are used as filter materials [9] and others [6].

3 Purpose and objects of research

The aim of the work is to study the destruction of oil-containing emulsion effluents using solid demulsifiers and the use of spent oil sludge in the ceramic materials production. it is proposed to use GOK waste as demulsifiers - ferrous quartzite enrichment tailings (HOZHK)

modified by heat treatment at a temperature of 600° C, and for comparison, the known demulsifier - thermolysis defecation TD₆₀₀.

HOZHK is a fine-grained powder from waste generated by dry and wet separation of crushed iron-containing quartzites [13]. The composition HOZHK includes up to 10% hematite and magnetite and about 72% silica. This is a fine powder with light gray color and an average particle size of 0,1 to 0,05 mm. In accordance with the classification of harmful substances, this waste belongs to hazard class IV - low-hazard substances. Thermal activation of HOZHK is carried out in electric furnaces. The sample is placed in a special metal cell, and heat treated without oxygen at temperatures of 400 - 600° C [13].

Since the predominant part in the waste composition is silica, during heat treatment the structure of HOZHK becomes porous, with a very developed network of capillaries, which increases the adsorption properties, and, consequently, increases the degree of water purification. Defecation is a waste of sugar production, containing on its surface up to 18-20% of various organic substances adsorbed as a result of sugar beet diffusion juice purification at the stages of saturation [14].

Thermolysis defecation (TD₆₀₀) is produced by heat treatment in electric furnaces or fluidized bed furnaces at low temperatures (450-600°C) [15-19].

As a heat treatment result on the surface of the defecation there is incomplete combustion of organic substances and the charred substances formation, mainly consisting of carbon. A significant component of TD₆₀₀ is calcium, magnesium carbonates, trace elements: silicon, potassium, sodium, nitrogen, phosphorus, toxic substances and heavy metal ions are absent.

4 Materials and methods

The oil-water emulsion containing insoluble impurities was purified in laboratory conditions using a plant consisting of a filter with a downward water flow and a purified water receiver, which is a cylindrical vessel of 4,5 cm in diameter with two openings (a two-layer filter with a granular charge). The resulting thermolysis defecation TD₆₀₀ and Volsky sand were used as loading. As well as the obtained thermolysis HOZHK and Volsky sand. In laboratory conditions, was selected the optimal loading height, which was 7 cm, and the optimal layer ratio, which was 1: 1.

5 Results and discussion

Comparative data on the efficiency of the proposed demulsifier (HOZHK) and thermolysis defecation (TD₆₀₀) wastewater treatment are given in table 1. From the table 1 it follows that HOZHK proposed as a filter material has a high degree of purification from organic and suspended substances and is practically not inferior to TD₆₀₀.

Since HOZHK thermolysis particles have a greater hydrophilicity than TD₆₀₀ and the particles are much larger in size, this can explain the lower interaction of HOZHK particles with the oil phase and, therefore, a lower purification compared to thermolysis defecation.

Table 1. Comparative characteristics of the physico-chemical characteristics of the oil-water emulsion before and after filtration

Filter material	COD, mgO / dm ³		COD Cleaning Efficiency, %	Suspended matter, mg/dm ³		Suspended Cleaning Efficiency, %
	Source water	After filtering		Source water	After filtering	
HOZHK	5020	301.2	94	5250	210	96.5
TD ₆₀₀	5020	140.56	97.2	5250	105	98

For disposal of oil sludge formed during the filtration of a water-oil emulsion, the possibility of using it as a burnable additive in the ceramic materials production was investigated.

To determine the optimal conditions for the disposal of oil sludge, it was added to the clay mass before molding ceramic samples by plastic pressing. The molded products were fired at a temperature of 900° C for 90 minutes. The ceramic masses composition is presented in table. 2.

The obtained samples were subjected to physical and mechanical tests. The data of the studies are presented in table 3.

From the table 3 it follows that with an increase in the percentage of oil sludge in ceramic samples, the average density (volume weight) decreases, and the true density (specific gravity) remains almost constant; the porosity increases and the strength of the products decreases.

Table 2. The ceramic masses composition

No composition	Clay, %	Oil sludge, %	Water, %
1	100	0	20
2	85	15	20
3	75	25	20
4	65	35	20
5	50	50	20

Note. The moisture content of oil sludge after filtration was 27% wt.

Table 3. Physico-chemical properties of the obtained samples

Indicators	No composition (sample)				
	1	2	3	4	5
Air shrinkage, %	1.21	1.75	1.86	2.24	2.72
Fire shrinkage, %	3.34	3.67	4.41	4.78	5.15
Average density, kg/m ³	1420	1412	1386	1312	1279
True density, kg/m ³	1950	1950	1950	1950	1950
Porosity, %	27.2	27.6	29.0	32.7	34.5
Water absorption, %	16.51	17.92	18.4	19.73	21.6
Limit strength at compression, MPa	12.32	12.24	11.52	8.71	7.21
Thermal conductivity, W/m-K	0.2167	0.2143	0.2105	0.2041	0.2015

Based on the test results, graphs were constructed of the density and strength dependences of the products on the added amount of oil sludge (Fig. 1 and 2).

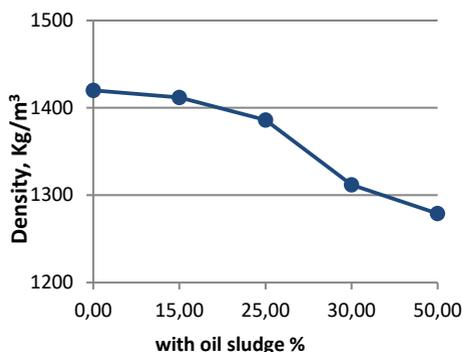


Fig. 1. The dependence of the obtained samples density on the content of oil sludge

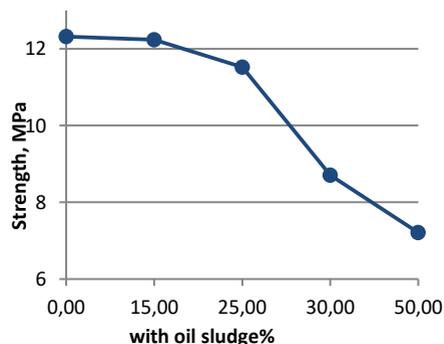


Fig. 2. The dependence of the obtained samples strength on the content of oil sludge

Fig. 1 and 2 shows that the optimum is the addition of oil sludge in an amount of 25% by raw materials weight, since a further increase in the waste content leads to a sharp decrease in these indicators.

Based on the results of experimental studies, it was possible to obtain building ceramic bricks with a density of 1455-1272 kg/m³ and strength of 8,0-12,0 MPa, which, according to regulatory requirements, belongs to the effective class (GOST 530-2012 Ceramic brick and stone. General specifications)

Moreover, the use of oil sludge in the ceramic masses composition does not require special preliminary preparatory technological processes, and this contributes to the disposal of a significant amount of sludge generated during the water-oil emulsions filtration.

6 Conclusion

Thus, the proposed demulsifier (thermolysis HOZHK) can improve the quality of wastewater treatment by COD and almost completely remove suspended solids, as well as reduce the cleaning process cost through the use of large-scale production waste. In addition, the applied filter material will expand the raw material base, abandon scarce toxic materials. It is cheap, domestic, and its application can solve the environmental problem of the region in the utilization of technogenic waste from GOK.

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