Physical and Chemical Fundamentals of Obtaining Reusable Oil Sorbents Based on Low-Alkali Aluminoborosilicate Glasses and Regularities of Oil Absorption by them

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Abstract
The paper describes the issues of modification of formulations used to produce C52-1 foam glass. Physical and chemical regularities of processes of oil absorption by it are determined and interpreted, and the possibility of its multiple using as the oil sorbent followed by the application in C52-1 glass melting and in producing foam glass (oil sorbent) based on it, is experimentally proved.

Keywords: oil sorbent, foam glass, oil absorption kinetics, multiplicity of using, waste-free production.

INTRODUCTION
Today, environmental issues are of paramount importance worldwide. Threatening environmental pollution has reached the scale affecting the life of the entire planet. One aspect of this issue is the pollution of the earth’s surface and water bodies as a result of accidents related to the deterioration of obsolete tankers carrying oil products, and oil pipelines, as well as unauthorized tapping into pipelines to steal oil and oil products [1].

It is hard to overestimate the role of oil in the modern world economy. It is the primary raw material for the production of modern synthetic materials and transport fuels, occupies an important place in the structure of energy balances, its processing products are used to produce electric energy and heat. However, at all stages of oil use, from exploration and production to disposal of its waste, the environment is polluted. The accidents in water transportation are the most severe in terms of the scale and consequences.

When a man learned to extract oil, so-called black gold, he did not think what intensive production hides. At that time people tried to produce as much of this natural wealth as possible. Thousands of tons of oil are produced every minute in the world. But people do not even think about the near future of our planet.

The most prominent and well-known cases of deplorable consequences of the effects of oil and oil products on the environment are water pollution. Oil spilled at sea represents greater danger than oil spilled on land. Oil affects the structure of the ecosystem of living organisms. Oil pollution changes the ratio of species and reduces their diversity. Microorganisms fed by oil hydrocarbons but toxic to many marine animals develop well.

As noted in [2], about 10 million tons of oil is spilled in the World Ocean each year. Photographic surveying from satellites, direct observations in seas and oceans allow suggesting that about one third of water surface is already covered by the thinnest iridescent film. This situation is accompanied by many troubles of the global scale.

The thinnest oil film on water surface reduces evaporation from this area by 60%. It results in intensification of water surface heating. The temperature difference contributes to more frequent cyclones. Oil causes a lot of troubles to the sea itself. A ton of oil can contaminate about 12 km² of the ocean surface, destroying all living things in it, because plankton, juvenile fish and many adult inhabitants of the ocean spend most of their lives in the near-surface water layers, where it is particularly likely to meet with oil.

In [3], it is noted that the oil film prevents penetration of the light in the sea, which is essential for the life of phytoplankton, resulting in a decrease in the initial food link in the ocean food and reduction in the intensity of the oxygen supply of the atmosphere. Death of marine organisms increases the mass of decaying matter intensively spending the oxygen contained in water, further exacerbating the scarcity of oxygen balance. The lack of food and oxygen affects vital activity of all marine organisms.

Oil pollution affects even those sea inhabitants that reside in the depths, and those who get used to live and feed in the reef area. Oil also annoys ocean mammals: whales, dolphins, seals and birds. If a seal rise to the surface in the area of the oil spill, its stained fur ceases to be a reliable heat insulator. The same thing is happening with the bird plumage [4].
Oil pollution caused by accidents differs from many other man-made impacts in the fact that it provides not gradual, but as a rule, “shock” burden on the environment, causing a rapid response [5].

In all activities related to elimination of pollution, recovery of the ecosystem, one must be based on the main principle: not to cause more damage to the ecosystem than the one that has already been caused by pollution [6]. In assessing the effects of such pollution, one cannot always unambiguously judge the possibility of returning the ecosystem to its stable state. Thick oil films are typically removed from the surface of water areas by using mechanical methods. However, they are unacceptable for removal of thin films. In this case, sorption method is the primary [1; 5]. Additionally, the advantages of sorption method include: the possibility to remove contaminants of extremely broad nature to almost any residual concentration irrespective of their chemical stability, and the absence of secondary pollutions and process controllability [5].

A trend for development of the technology of sorption water treatment is determined by the transition from the activated carbons to the ever-increasing range and number of natural mineral and organic substances, to the creation of new synthetic sorbents and especially sorbents with immobilized hydrocarbon oxidizing microorganisms – biosorbents, the which use to eliminate impurities from water surface refers to biological methods [7].

A quite detailed analysis of sorption materials for treatment of sewage and natural water from oil products is given in [8]. It particularly notes the paper [9], the authors of which have proposed a new type of biosorbent representing the associations of strains – destructors of hydrocarbons immobilized on a porous sorbent – foam glass produced from a dust fraction of glassy AVA phosphorus-containing fertilizer, including potassium, magnesium, calcium, boron, silicon, trace elements, and creating optimal conditions for feeding and life activity of microorganism cells.

Speaking of a biosorbent described in [9], its main disadvantages should be noted [10], including insufficiently high buoyancy, and the fact that the association of strains – destructors of hydrocarbons can work only at temperatures above 8 °C, while their storage life is less than two years. Thus it is necessary to take into account the fact that biosorbents cannot provide the required efficiency in oil spill response. Thus, even a solution to the issue of buoyancy cannot ensure the required effectiveness of biosorbent described in [9] (as any other biosorbents), for treating water areas from pollution by oil and oil products at accidental spills.

Despite the large number of papers devoted to the development of oil sorbents, the issue of elimination of pollution by oil and oil products cannot be considered resolved to this day. In our opinion, the main reasons for this is the emphasis of the vast majority of papers on production (by trial and error) of oil sorbents for practical use, rather than on identification of physical and chemical regularities of the processes of oil absorption on them that would contribute to the creation of scientific foundations of producing oil sorbents with a given set of physical and chemical properties and operational parameters, as well as failure to use the whole wide range of materials for production of oil sorbents.

Works performed at the Department of General and Physical Chemistry of the National University of Mineral Resources “Gorny” under the supervision of prof. V.E. Kogan, are aimed to overcome two above drawbacks. The most unexplored materials in terms of this aspect include foam glasses – a unique material 100% consisting of glass cells, developed in the 30-ies of the last century in the Soviet Union (D. Mendeleev University of Chemical Technology) and in the early 40-ies in the USA (Corning Glass Works). It sounds somewhat paradoxically, as originally foam glass was intended to be used as a floating material, and buoyancy is one of the essential parameters of oil sorbents. No one studied foam glasses as oil sorbents before our works [11; 12].

**EXPERIMENTAL PROCEDURE**

The obtained samples of oil sorbent were mechanically released from the surface “crust” and were crushed to a fraction of 3 – 8 mm. Buoyancy of the samples and their oil absorption were measured in accordance with technical requirements TU 214-10942238-03-95 “Evaluation of the sorbent effectiveness” [5]. REBCO (Russian Export Blend Crude Oil) oil was used for study – a sort of Russian export blend oil formed in “Transneft” pipe system by mixing heavy sour crude oil of the Urals-Volga region and sweet crude oil of the Western Siberia corresponding to Urals brand in its characteristics.

**RESULTS AND DISCUSSION**

As in [13], we have used C52-1 glass of molybdenum group (its granulate), manufactured by Svetlana-Malovishersky Glass Manufacturing Plant LLC in this study as a low-alkali aluminoborosilicate glass, which according to chemical analysis comprises (mol. %): Na2O – 4.14; K2O – 2.99; Al2O3 – 1.97; B2O3 – 17.90; SiO2 – 73.00.

The choice of this glass, in addition to economic considerations and the features of its structure (it is liquidating) that opens up the prospects of further modification of the porous structure of sorbents (at the nanostructure level) by the method of producing porous glasses [13], was due to its low coefficient of linear thermal expansion (52·10⁻⁷ K⁻¹). The latter favored the high temperature resistance to cyclic loads, which opened up the prospects to achieve great values of multiplicity of using, and as is known [5], multiplicity of using is one of the requirements for oil sorbents.

The aim of this study was to modify formulations used to produce C52-1 foam glass, and testing the possibility of its multiple using as oil sorbent followed by the application of the sorbent in C52-1 glass melting and production of foam glass based on it.

As in case of [13], chalk and diatomite of fractions ≤ 100 microns which were mixed with C52-1 glass of the same faction were used as a main foaming agent in the preparation of foam glass. In [13], positive results – virtually unsinkable opalescent foam glasses, indicating the phase separation – were produced only under the additional use of our developed formulations based on organic substances of vegetable origin in a specially selected solvent, where the total carbon content was not less than 1 mole per 100 g of glass. However, formulations based on organic substances of vegetable origin had their drawbacks.
One part of the components could be introduced only through the use of chemical agents or food products that adversely affected the economic performance, and the other part represented wastes of reprocessing of natural materials with the composition and properties not normalized by the state standards, reducing stability of oil sorbent performance. Therefore, in this paper, the mentioned formulations based on organic substances of natural origin have been replaced by the combustible additive – peat with low degree of decomposition according to GOST 51213-98 [14] (produced by ROSTORFINVEST JSC, Pskov region). Positive results have been obtained using peat in amounts providing compliance with the condition stated in [13] – carbon content in the charge mixture of at least 1 mol per 100 g of glass.

The nature of kinetic absorption curves of the sorbent produced by us (Fig. 1) is correlated with that of the sorbents with the glassy surface [11; 12] (there is a maximum when a sorbent is in oil at the initial period of time). In this case, in contrast to the sorbent considered in [13], for which the maximum occurred at 7.5 minutes, in this case it is shifted to 5 minutes, which is most likely due to the visually observed increase in size of open pores on the sorbent surface when using peat.

Foam glass is a volume-porous material with closed-cell structure. Open pores in the samples studied are mainly on the surface thereof. Oil absorption is caused by two mechanisms: oil absorption by open pores on the surface of phase separation (oil is a sorbent) and capillary forces acting in particular in the porosity space between the sorbent samples. The absence of long-range orders in glasses and their chemically microinhomogeneous structure, substantiated by R.L. Muller [15; 16], most likely cause the capillary potential gradient in the capillaries with the glassy surface (in particular in the porosity space between the samples). The above contributes to the displacement of the absorbed oil from the capillaries followed by its flow-over to the entire oil volume. In this case, a stationary balance is reached in a particular period of time: the amount of oil drawn into the capillary (the porosity space between the samples) becomes equal to the amount of oil returning from the sorbent into its total volume. The above stipulates the presence of a maximum on the kinetic curve of oils absorption in the initial period of time (Fig. 1).

Reusability of the sorbent was studied on samples at the holding time in oil of 2.5; 5; 7.5; 10; 15; 30; 60 and 120 min. To regenerate the sorbent, it was placed on a brass mesh and ignited (Fig. 2). In the process of oil burning, the sorbent was periodically stirred. The regenerated sorbent (completion of the combustion process) was spontaneously cooled in air. As a result of recovery, some part of oil was desorbed in a cup under the mesh and the other part burned. However, when using the above sorbent regeneration technology, we failed to achieve its complete release from oil with all multiplicities of use. In this case, the amount of oil remaining in the sorbent samples depending on the multiplicity of their use varied uncontrollably. The above was the main reason for the scatter of data on the curves of oil absorption VS multiplicity of using (Fig. 3).

The most specific of all these dependencies is the dependence characterizing the sorbent regeneration while it is in oil for 5 minutes (Fig. 3, e), i.e. in case when there is a maximum at the initial sorbent kinetic curve (Fig. 1). The most decrease in oil absorption values during increase in multiplicity of using is observed for this case. The above is most likely due to the fact that in the process of heating – cooling taking place during regeneration, the sorbent structure has no time to fully relax and at the same time the contribution of capillary forces in oil absorption decreases. However, even in case of sevenfold using of the sorbent in oil for 5 min, oil absorption is 53% of the initial absorption, which is comparable with that criterion for porous-elastic materials that may be used for picking oil and oil products from water surface [5]. It must be emphasized that no visible signs of destruction of the sorbent (at any holding times in oil) after the
multiplicity of using equal to 30 were observed, i.e. this multiplicity is not the limiting value.

Some summarized values of the oil sorbent from C52-1 glass reduced to 10 g of it according to thirtyfold use are given in the table.

**Summarized values of the oil sorbent from C52-1 after its thirtyfold use**

<table>
<thead>
<tr>
<th>Holding time in oil, min</th>
<th>Weight of oil absorbed, g</th>
<th>Weight fraction of oil absorbed, %</th>
<th>Oil burned in the process of regeneration, Weight, g</th>
<th>Weight fraction of oil absorbed, %</th>
<th>Oil hold by the sorbent in the process of regeneration, Weight, g</th>
<th>Weight fraction of oil absorbed, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>9736</td>
<td>21.08</td>
<td>21.7</td>
<td>74.11</td>
<td>76.1</td>
<td>2.17</td>
</tr>
<tr>
<td>5</td>
<td>201.42</td>
<td>14.43</td>
<td>7.2</td>
<td>182.53</td>
<td>90.6</td>
<td>4.46</td>
</tr>
<tr>
<td>7.5</td>
<td>191.95</td>
<td>36.71</td>
<td>19.1</td>
<td>149.77</td>
<td>78.0</td>
<td>5.47</td>
</tr>
<tr>
<td>10</td>
<td>184.85</td>
<td>21.28</td>
<td>11.5</td>
<td>161.68</td>
<td>87.5</td>
<td>1.89</td>
</tr>
<tr>
<td>15</td>
<td>222.66</td>
<td>28.03</td>
<td>12.6</td>
<td>191.01</td>
<td>85.8</td>
<td>3.62</td>
</tr>
<tr>
<td>30</td>
<td>185.50</td>
<td>23.61</td>
<td>12.7</td>
<td>156.98</td>
<td>84.6</td>
<td>4.91</td>
</tr>
<tr>
<td>60</td>
<td>185.45</td>
<td>21.55</td>
<td>11.6</td>
<td>161.62</td>
<td>87.2</td>
<td>2.28</td>
</tr>
<tr>
<td>120</td>
<td>185.72</td>
<td>21.17</td>
<td>11.4</td>
<td>158.07</td>
<td>85.1</td>
<td>6.48</td>
</tr>
</tbody>
</table>

The advantages of the oil sorbent that we have developed should include the absence of the need to address the issue of its disposal. Laboratory studies have shown that in the amount of 40% by weight it can be successfully used as cullet glass when melting C52-1 glass, and also in the amount of 10% by weight in production of the oil sorbent from C52-1 glass.

**CONCLUSION**

Based on the conducted physical and chemical study, the oil sorbent was developed, which allows implementing a closed loop and providing waste-free production. This fact allows minimizing the amount of the oil sorbent, which should be provided for various facilities of oil spills, especially oil tankers and ships, while simultaneously equipping them with stand-alone devices providing the sorbent regeneration directly at the spill site. The main field of use of the sorbent is removal of oil films from the water surfaces, as well as treatment of wastewater and natural waters from pollution by hydrocarbons.

**REFERENCES**


