Efficiency Sorbents Comparative Analysis for Heavy Oil Products in the Conditions of Low Temperatures

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Abstract. At the present time ecological safety questions occupy one of priority positions. This is especially important when objects in the Arctic water areas and the freezing seas are projecting. Nature and climatic features of these areas limit use of traditional methods of oil spill response. The analysis of response activities in various climatic and natural conditions has shown that one of the well-proven methods is sorption purification. The laboratory data have served the preliminary stage for correcting sorbents (Lessorb, Exfoliated Graphite Sorbent (EGS), Peat Dust Oil Sorbent (PDOS), Biomatrix technical passports and selecting their best quantities for oil spill response under various temperatures including low value in the marine environment.

1. Introduction

In the context of stepping up transportation of oil and oil products by sea the risks of their entry into the environment are increasing. Spills, particularly in the arctic seas, are major ecological disasters, their impact being highly destructive and not predictable to a full degree for sensitive coastal-marine ecosystems [1, 2, 6]. State-of-the-art oil spill response toolbox includes various oil pickup methods; however most of these are characterized by low efficiency [2, 3]. This is accounted for, first of all, by physical-chemical properties of oil, which also determine the peculiarities of its behavior during the spill and its impact on the environment.

The outcomes of numerous researches make it possible to predict oil behavior at sea water area and give recommendations on the use of specific response techniques [4, 5, 8, 9, 10]. The analysis of response activities in various climatic and natural conditions has shown that one of the well-proven methods is sorption purification [7, 9, 10]. Nevertheless the practice of applying various sorbing materials has shown that the specifications as provided by the manufacturers have been somewhat different from the actual performance when deployed in sea waters.

The range of sorbents for various ends is rather wide. But it is the sorbent powders that are of the best performance, as these have sufficiently high oil capacity, combined with hydrophobic property and environmental friendliness.

2. Materials and methods

When studying production range of materials available with the Russian Far East emergency response teams it is found out that the most popular powders are the following brand names of sorbent materials: adsorbents: «Lessorb», Exfoliated Graphite Sorbent (EGS), Peat Dust Oil Sorbent (PDOS),
and absorbent: «Biomatrix». All the said has predetermined the selection of test pieces for assessing the efficiency in marine environment. Heavy fuel oils of \( M_{40}, M_{40}, M_{100} \) grades were selected as sorbates, as the likelihood of their entry into sea water areas is the greatest. Accounting probability of spills under varying natural environment and climatic conditions the temperature scenarios have been selected to most closely resemble the natural ones at \(+23^\circ C, +5^\circ C, -9^\circ C\).

The sorbent material is selected based on three key criteria: oil capacity, water-holding capacity and buoyancy. Standard assessment techniques (efficiency assessment is determined as per TR 214-10942238-03-95) allowed assessing the efficiency of selected materials for absorbing various grades of heavy fuel oils [11].

The principle of oil capacity assessment is as follows. 5 grams of sorbent in micromesh are dipped into heavy fuel oil poured in Petrie dish. 10 minutes later the micromesh is removed, the surplus heavy fuel oil drains, after which the material is weighed on analytical balances.

To have water-holding capacity assessed dishes of various diameter filled with sea water are also used. The sorbent layer in the largest diameter dish is 3mm, thickening to 30 mm in the smallest diameter dishes. In three hours the removed sorbent is weighed to determine the weight of the wet sorbent.

To determine sorbent’s buoyancy it is also placed into dishes half filled with sea water, the sorbent layer thickness being the same as in the previous experiment. Five series are made: 12, 24, 36, 48 and 96-hour duration. Upon termination of each time series the sorbent remaining afloat is removed and dried. The amount of sunken sorbent is determined through the difference of weights.

3. Findings and Discussion

Therefore experiments with tested sorbents and sorbates were carried out under 3 temperature modes as recommended by guidance materials. Summaries of oil capacity are given in Table 1.

| Sorbent | \( C, \%\), \( T_0 = +23^\circ C \) | \( C, \%\), \( T_0 = +5^\circ C \) | \( C, \%\), \( T_0 = -9^\circ C \) |
|---------|----------------------------------|----------------------------------|----------------------------------|
|         | \( M_{10} \) | \( M_{40} \) | \( M_{100} \) | \( M_{10} \) | \( M_{40} \) | \( M_{100} \) | \( M_{10} \) | \( M_{40} \) | \( M_{100} \) |
| Biomatrix | 540 | 280 | 300 | 520 | - | - | 440 | - | - |
| PDOS | 280 | 320 | 340 | 240 | - | - | 220 | - | - |
| EGS | 1000 | 1800 | 1200 | 1300 | - | - | 1300 | - | - |
| Lessorb | 540 | 300 | 340 | 560 | - | - | 400 | - | - |

Oil product behavior is governed not only by the ambient temperature, but also by its composition. The experiments have proved that at temperatures of from \(+5^\circ C\) heavy fuel oils of grades \( M_{40}, M_{100} \) set solid, and the effect of sorbents vanishes.

On the whole the best performance as to oil capacity has been demonstrated by EGS, its sorption capacity was approximately 5 times higher compared to all other sorbents at all the temperatures and was from 1: 10 to 1: 18. The worst capacity was typical with PDOS.

Of all the tested sorbents the most moisture-resisting were Biomatrix and PDOS, their index being 1:0.4. «Lessorb» can also be referred to as hydrophobia one with the index of 1:0.6. The lowest moisture-resisting index is that of EGS – 1:6. Table 2 shows the results of water-holding capacity assessment.

To determine sorbent buoyancy, sorbent sample weights were placed in 5 Petrie dishes, half filled with water. In this case five series were made: 12, 24, 36, 48 and 96-hour duration in compliance with guidance materials’ requirements. As the test results show (Table 3), PDOS and EGS keep floating longer than all other sorbents deployed. Their buoyancy is the greatest (100 %) and exceeds 96 hours. 100 % of «Lessorb» sorbent stay afloat for 36 hours, after 48 hours approximately 20 % sink, and after
96 hours 40% of the original mass sank. Sorbent Biomatrix behaved satisfactorily: 100% buoyancy is retained for more than 48 hours. After 96 hours of staying in sea water 10% of the material sank.

Table 2. Water-holding capacity of sorbent powders.

| Sorbent | Weight of dry material, g | Weight of wet material, g | Water-holding capacity, % |
|---------|---------------------------|---------------------------|---------------------------|
| Biomatrix | 5                         | 7                         | 40                        |
| PDOS    | 5                         | 7                         | 40                        |
| EGS     | 1                         | 7                         | 600                       |
| Lessorb | 5                         | 8                         | 60                        |

Table 3. Sorbent powder buoyancy assessment.

| Sorbent | Weight of sorbent, g | Series No. | Amount of sorbent sunk, g | Amount of sorbent staying afloat, g |
|---------|----------------------|------------|--------------------------|-----------------------------------|
| Biomatrix | 5                    | 12 hrs.    | 0                        | 5                                 |
|          |                      | 24 hrs.    | 0                        | 5                                 |
|          |                      | 36 hrs.    | 0                        | 5                                 |
|          |                      | 48 hrs.    | 0                        | 5                                 |
|          |                      | 96 hrs.    | 0.5                      | 4.5                               |
|          |                      | 12 hrs.    | 0                        | 5                                 |
|          |                      | 24 hrs.    | 0                        | 5                                 |
| PDOS    | 5                    | 36 hrs.    | 0                        | 5                                 |
|          |                      | 48 hrs.    | 0                        | 5                                 |
|          |                      | 96 hrs.    | 0                        | 5                                 |
|          |                      | 12 hrs.    | 0                        | 1                                 |
|          |                      | 24 hrs.    | 0                        | 1                                 |
| EGS     | 1                    | 36 hrs.    | 0                        | 1                                 |
|          |                      | 48 hrs.    | 0                        | 1                                 |
|          |                      | 96 hrs.    | 0                        | 1                                 |
|          |                      | 12 hrs.    | 0                        | 5                                 |
|          |                      | 24 hrs.    | 0                        | 5                                 |
| Lessorb | 5                    | 36 hrs.    | 0                        | 5                                 |
|          |                      | 48 hrs.    | 1                        | 4                                 |
|          |                      | 96 hrs.    | 2                        | 3                                 |

Laboratory data have demonstrated that by the key efficiency indices for sea water application the best results were achieved by Exfoliated Graphite Sorbent, evidenced by Figure 1. In the meantime its water-holding capacity indices are the lowest ones (1:6). Furthermore, there are difficulties when applying it to a spill due to its specific structure, which is especially vivid in oil spill response under Arctic conditions.
Analysis of sorbent technical passports has revealed significant discrepancy between their sorption capacity as per technical requirements and that as per given experimental parameters (Table 4). Thus EGS passport characteristics indicate the formulation capacity to be equal to 1:50 (1 part of sorbent per 50 parts of oil). The tests done have shown that in the marine environment the sorption capacity reduced to index 1 : 18, i.e. practically 2.7 times less, which should be taken into account when planning oil spill preparedness and response and when calculating the sorbent – oil ratio when carrying out emergency response.

![Figure 1. Sorbent powders’ key efficiency indices.](image)

**Table 4. Sorbent technical specification comparative indices.**

| Sorbent | Sorption capacity, sorbent/oil, kg/kg | Buoyancy, hrs |
|---------|--------------------------------------|---------------|
|         | Technical passport | Actual data | Technical passport | Actual data |
| EGS     | 1:50       | 1:18       | 2,400           | 96           |
| PDOS    | 1:7        | 1:3.4      | 168             | 96           |
| Lessorb | 1:10       | 1:5.6      | not less than 72| 36           |
| Biomatrix | 1:3.9    | 1:5.4    | not less than 1 | 48           |

Unexpected were the results for «Biomatrix» sorbent. Its sorption capacity in sea water turned to be 1.5 times more than specified in the technical passport. The buoyancy index for this sorbent was also significantly greater than by technical requirements, therefore widening the range of its application. Consequently, the laboratory data have served the preliminary stage for correcting sorbent technical passports and selecting their best quantities for oil spill response under various temperatures in the marine environment.
4. References

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