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USING HERDERS FOR OIL SPILL RESPONSE IN THE SEA

Abstract. The article is devoted to the study of the capabilities, optimal conditions and efficiency of using herders for in-situ burning of oil as an oil spill response technique in the Kazakhstan Sector of the Caspian Sea (KSCS). The in-situ burning of spilled oil is considered as a preferred approach to fight large-scale oil spills offshore, when the oil slick spreads over large distances under the action of wind and currents, which also results in a greater spill area and greater spilled oil volume due to water absorption. Herders, or chemical oil-collectors, are used in the world practice for contracting oil slicks and their thickening before oil combustion. This study was conducted to determine the feasibility of using in the Kazakhstan sector of the Caspian Sea those herding agents that have proven to be effective for other types of oil and other marine conditions. The herding performance, suitability and efficiency of Siltech OP-40 and ThickSlick 6535 herders were investigated for Kashagan oil in artificial sea water with salinity level of KSCS.

Key words: oil spill, herders, dispersants, Kashagan, Kazakhstan sector of Caspian Sea, salinity, in-situ burning.

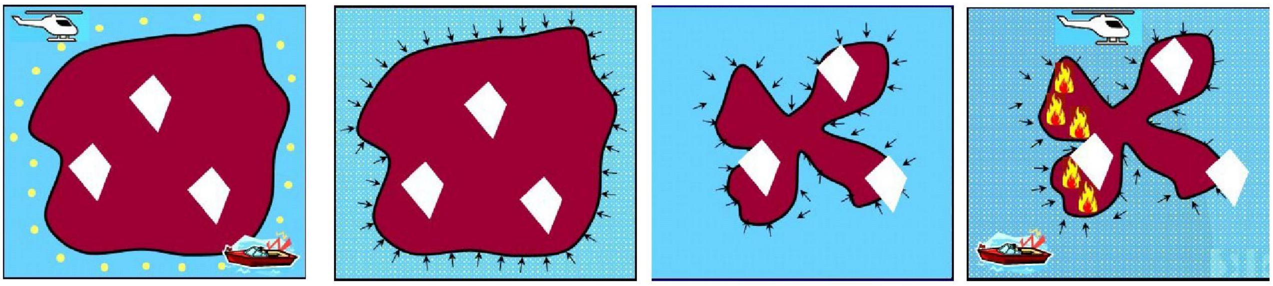
The Kashagan offshore oil field is located in the northern part of the Kazakhstan sector of the Caspian Sea. The distinctive features of the Northern Caspian are low depth of 2-6 m, low salinity of about 6 ‰ and ice cover in winter. Therefore, the methods for oil spills response, developed for open seas with large depth, 33-35 ‰ salinity and minimum fluctuations in water temperature, require significant adaptation to the conditions of the northern part of the Caspian Sea. The above facts necessitate additional studies to select the most suitable methods using chemical agents for oil spill response to find the conditions that provide the greatest positive effect.

Previously, the capability of using dispersants for the oil spills response [1,2] was investigated for Kashagan oil and for the conditions of the northern Caspian [3,4]. Based on the results of these works, the Ministry of Energy of the Republic of Kazakhstan approved the Method for Determination of Dispersants for inclusion on the list of dispersants for the liquidation of oil spills in the sea and inland water bodies of the Republic of Kazakhstan [5]. Also, the Ministry of Energy of the RK approved a list of admissible dispersants, including 5 dispersants [6].

Chemical collectors or herders are surfactants having two ends: hydr and hydrophobic. Herders are designed to contract the oil slick and prevent the oil spreading. The herders are applied to the water surface adjacent to the oil slick, thereby reducing surface tension at the oil/water interface. Reduction of the surface tension of water contributes to the tightening of the oil slick, which in turn leads to an increase in the thickness of the stain to the values sufficiently high for ignition and further combustion of oil.

The possibilities of using herders for oil spill response have been studied since the 1970s, but were considered from the standpoint of their use to restrain oil for subsequent mechanical collection [7,8]. Beginning in 2004, they began to explore more specifically the possibility of using them to contract oil stains before burning oil in cold seawater, especially in ice conditions [8,9].

The principle of the herder action is shown in Fig. 1.



A small amount of herder is sprayed onto the water around the perimeter of the oil slick

Herder rapidly spreads over the water surface, forming a monolayer

Herder changes the surface properties of water - the area of the oil film is reduced

After oil compression, the spots are ignited on the windward side using the Helitorch

Figure 1 - Effect of the herder on an oil slick [5]

In our opinion, the largest number of effective studies on chemical collectors - herders was conducted by Jan Buist, who developed a technique for small-scale testing of herders [10-12]. Over the past period, he carried out a number of tests to burn different types of oil in various natural and climatic conditions [6-7], including the use of herders, which allowed him to establish their comparative characteristics. The most effective herders, based on the results of the studies of Buist et al., are ThickSlick 6535 and Siltech OP-40. Both these chemical collectors were included in the list of herders allowed for use by the U.S. Environmental Protection Agency and currently, they are the most well-known in the world and commercially available chemicals.

A brief description of these collectors is presented in the following table [8].

Table 1 - Herders for testing on Kashagan oil

Herder / Indicators	ThickSlick 6535	Siltech OP-40
Manufacturer	Desmi Inc.	Siltech Corp.
Composition	65% sorbitan monolaurate and 35% 2-ethyl butanol	3-(polyoxyethylene)propyl-heptamethyltrisiloxane
Density, г/см^3 (60˚F = 15.6˚C	0.975	0.988
Solubilbity in water	Partial miscibility	Partial miscibility
pH	6.45	10.1
Kinematic viscosity, cSt	24.70	8.27
Dinamic viscosity, mPa*s (cP)	25.35	8.37
Freezing point	-1,7°C (21,2°F)	-59°C (-74,2°F)
Flash Point	> 82°C (180°F)	> 82°C (180°F)

In this regard, we were interested in studying the behavior of these ThickSlick 6535 and Siltech OP-40 as herders for Kashagan oil in the water of the North Caspian.

MATERIALS AND EQUIPMENT

We used crude degassed Kashagan oil, density 0.802 g/ml, viscosity at 15°C 3.02 mPa*s.

In the initial stage of the study, weathering was carried out at 60°C. The density of oil increased to 0.803 g/ml, the viscosity under those conditions was 3.11 mPa*s.

For the second stage of the study, it was used oil stripped at a temperature of 200 °C. The density of the oil was 0.865 g/ml, and the viscosity – 22.6 mPa*s.

The herders are known to act differently on different types of oil. Thus, to establish comparative characteristics, the Buzachi oil with density 0.920 g/ml and viscosity 427.2 mPa*s was chosen as an alternative variant.

The experimental basin with an area of 1 m^2 was used for research. For each experiment, the pool was tightened with a freshly washed new plastic film, fastening them with large clips over the sides of the pool.

The tests were carried out at water temperatures of 5°C (+/- 2°C), 15°C (+/- 2°C). The water temperature of 5°C was maintained by adding ice pieces to water as needed. The water temperature was measured in the persistent extended tracking mode by using a thermometer.

Figure 2 - Pool for experiments with herders, on the right - a thermometer

Water for experiments with a salinity of 6‰, 12‰, 18‰ was prepared by dissolving sea salt in water.

Quantitative experimental data:

- The water volume of the corresponding salinity is 20 liters;
- Oil volume - 100 ml. The exact mass of oil was measured by weighing the cylinder with oil before and after pouring oil out of the cylinder, and calculating the difference between these two values; the exact value of the volume was calculated from the oil density.

The herder volume was 150 μl (micropipettes were used for sampling). Just as in the case of oil, the exact mass of the herder was determined by the difference between the total and empty micropipettes, and the exact value of the volume was determined from the density.

EXPERIMENTAL METHOD

We put water in the pool, create the appropriate temperature, pour 100 ml of oil, let the spot spread over the surface of the pool, add 150 μl of herder at the edges of the spot.

Results of experiments with oil weathered at 60°C

The oil produced from the Kashagan field is very light, quickly spreads over the surface of the water, tending to the edges of the basin, making it difficult to fix the zero point. We had to repeat the experiment several times to introduce the herder in time.

Fig. 3 shows photographs (real and black and white format) characterizing the results of experiments on the use of two types of herders for Kashagan oil, weathered at 60°C, at a temperature of 5°C and a salinity of 6‰.

From Fig. 3 it can be seen that both herders act as oil collectors, since the area of oil spots decreases in all cases. In the course of the test, it was established that the effect of the herder is independent of the salinity of the water. The effectiveness of the action of chemical collectors in these experiments was not very high due to low density of oil. Nevertheless, of the two types studied the OP-40 herder is more effective. In turn, this herder showed the best result at a temperature of 15°C, because it was able to reach the maximum thickness of the oil film.

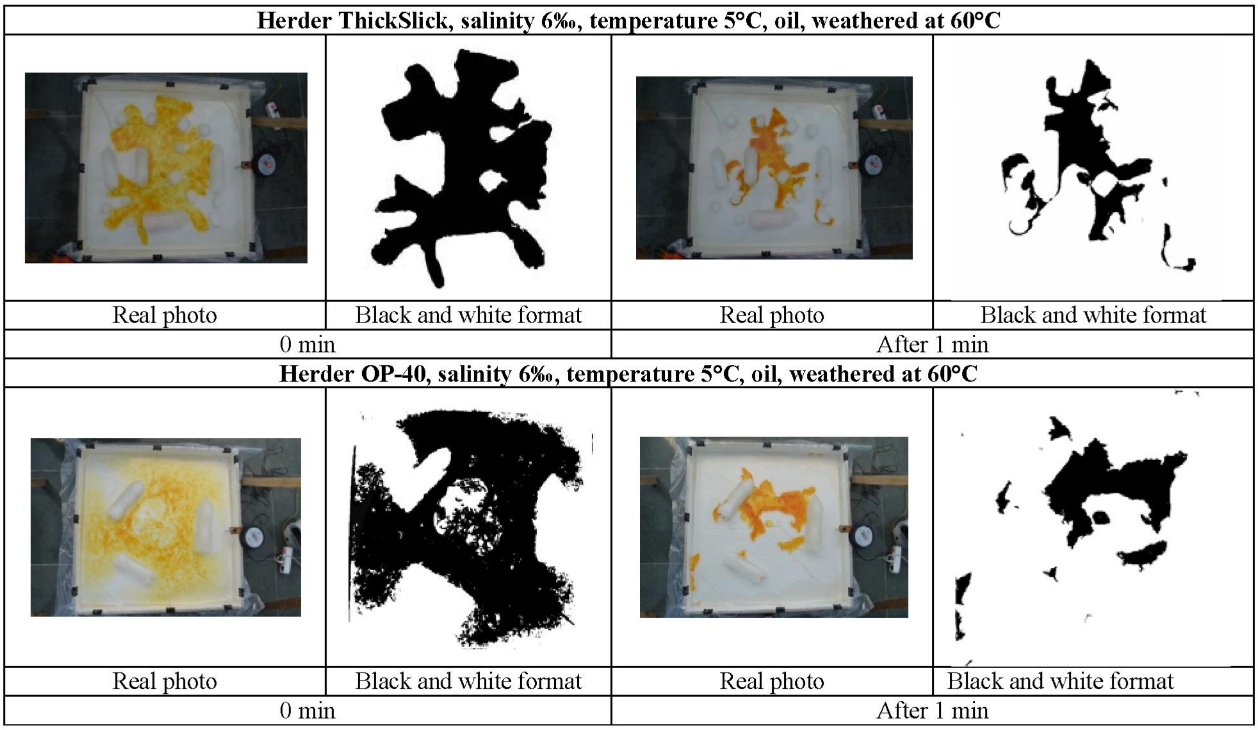


Figure 3 - Images of oil spots before and after the application of two types of herders at a temperature of 5°C and a salinity of 6‰

In Table 2 there are given the results of experiments and their processing on the application of herders to Kashagan oil weathered at 60°C. The areas and thickness of the spots at 15°C calculated are shown.

Table 2 - Experimental and calculated data on the determination of the area and thickness of the spot at 15°C after the application of herders to Kashagan oil weathered at 60°C

#	Test conditions	Number of white pixels	Number of black pixels	Spot area,%	Spot area, cm^2	Spot thickness, mm
Thick Slick						
1	00 min, 15°C, 6‰ TS	1088629	7625048	0,1249	1249,33	0,8004
2	01 min, 15°C, 6‰ TS	1246566	7349821	0,1450	1450,10	0,6896
3	05 min, 15°C, 6‰ TS	828634	7908811	0,0948	948,37	1,0544
4	30 min, 15°C, 6‰ TS	728408	7962083	0,0838	838,17	1,1931
5	60 min, 15°C, 6‰ TS	703439	7869412	0,0821	820,54	1,2187
6	90 min, 15°C, 6‰ TS	703546	7987086	0,0810	809,55	1,2353
7	120 min, 15°C, 6‰ TS	716835	7926290	0,0829	829,37	1,2057
OP-40						
1	00 min, 15°C, 6‰ OP-40	1425047	7218113	0,1649	1648,76	0,6065
2	01 min, 15°C, 6‰ OP-40	381624	8714547	0,0420	419,54	2,3835
3	05 min, 15°C, 6‰ OP-40	320863	8559331	0,0361	361,32	2,7676
4	30 min, 15°C, 6‰ OP-40	356232	8467190	0,0404	403,73	2,4769
5	60 min, 15°C, 6‰ OP-40	511166	7921378	0,0606	606,18	1,6497
6	90 min, 15°C, 6‰ OP-40	669823	8139010	0,0760	760,40	1,3151
7	120 min, 15°C, 6‰ OP-40	669648	7973795	0,0775	774,75	1,2907

Fig. 4 presents the data characterizing the effectiveness of two herders on Kashagan oil weathered at 60 °C. It is clear that the OP-40 is a more effective herder. It is also seen that after 40 min the activity of the OP-40 herder decreases, while the ThickSlick herder retains this feature for 2 hours.

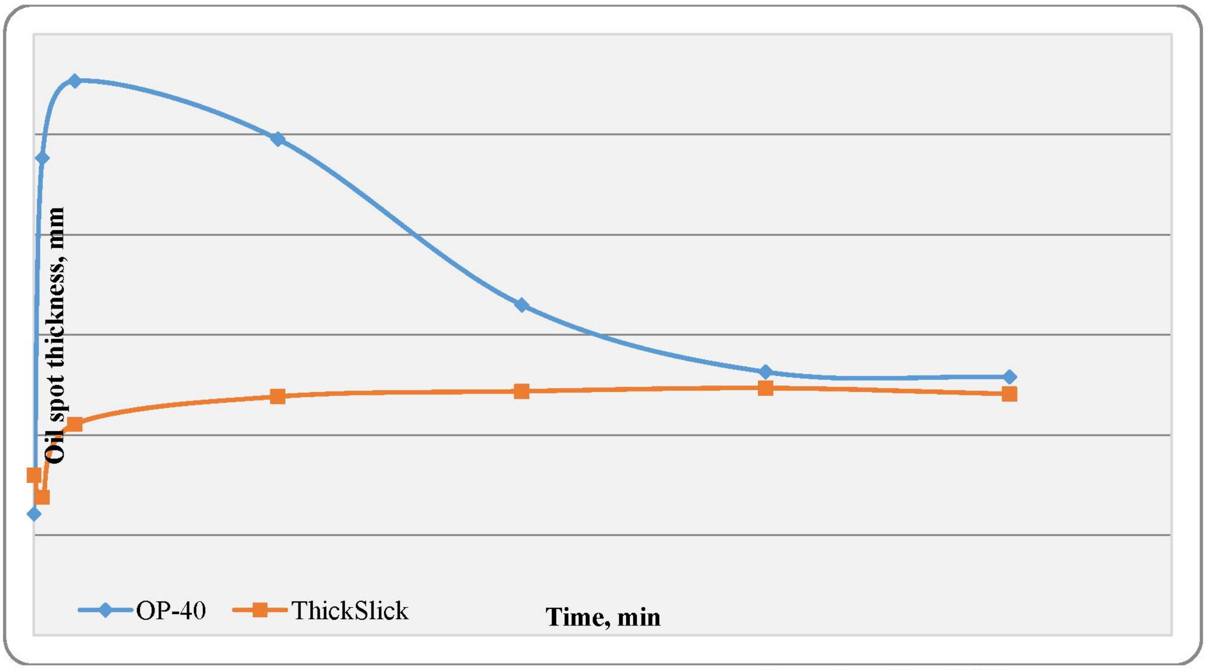


Figure 4 - Efficiency of herders in relation to Kashagan oil weathered at 60°C

Results of experiments with oil, stripped at 200°C

In real-life conditions, after an oil spill, a certain time passes before the response begins, during which the light fractions can evaporate and the oil becomes more viscous. To bring the experimental data closer to the real conditions, the oil was stripped at 200°C. The oil density increased to 0.865 g/ml, and the viscosity increased to 22.6 mPa*s.

The results of the herder effect on the oil stripped at 200°C at 5°C are shown in Table. 3.

Table 3 - Experimental and calculated data on the determination of the area and thickness of the spot at 5°C after the application of herders to Kashagan oil stripped at 200°C

#	Test conditions	Number of white pixels	Number of black pixels	Spot area,%	Spot area, cm^2	Spot thickness, mm
Thick Slick						
1	00 min, 5°C, 6‰ TS	4932840	2747585	0,6423	6422,61	0,1557
2	01 min, 5°C, 6‰ TS	3074019	4786767	0,3911	3910,57	0,2557
3	05 min, 5°C, 6‰ TS	3085968	4956569	0,3837	3837,06	0,2606
4	10 min, 5°C, 6‰ TS	3063227	4664084	0,3964	3964,16	0,2523
5	30 min, 5°C, 6‰ TS	3036094	4758240	0,3895	3895,26	0,2567
6	60 min, 5°C, 6‰ TS	2958613	4592571	0,3918	3918,08	0,2552
7	90 min, 5°C, 6‰ TS	2959968	4901942	0,3765	3764,95	0,2656
OP-40						
1	00 минут, 5°C, 6‰ OP-40	2151907	6627301	0,2451	2451,14	0,4080
2	01 min, 5°C, 6‰ OP-40	1538319	7386747	0,1724	1723,59	0,5802
3	05 min, 5°C, 6‰ OP-40	1199200	7327123	0,1406	1406,47	0,7110
4	10 min, 5°C, 6‰ OP-40	1107462	7552195	0,1279	1278,88	0,7819
5	30 min, 5°C, 6‰ OP-40	1024073	7735862	0,1169	1169,04	0,8554
6	60 min, 5°C, 6‰ OP-40	1022606	7714868	0,1170	1170,37	0,8544
7	90 min, 5°C, 6‰ OP-40	1016577	7767356	0,1157	1157,31	0,8641

Fig. 5 demonstrates the data characterizing the effectiveness of herders at 5°C in relation to Kashagan oil stripped at 200°C. The data show firstly, that the efficiency of the herders quite quickly reaches a peak (maximum) value; secondly, both herders retain the oil collecting ability for an hour and a half, and thirdly, the OP-40 is more efficient than ThickSlick. In the course of this experiment, the OP-40 herder was able to achieve a maximum thickness of the oil film of 0.85-0.86 mm.

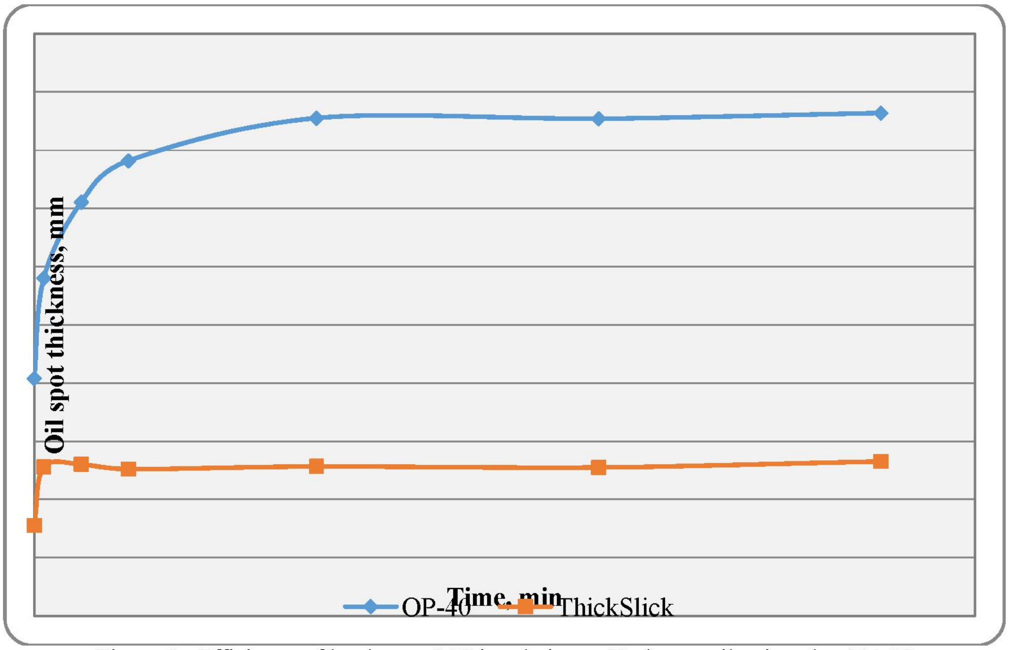
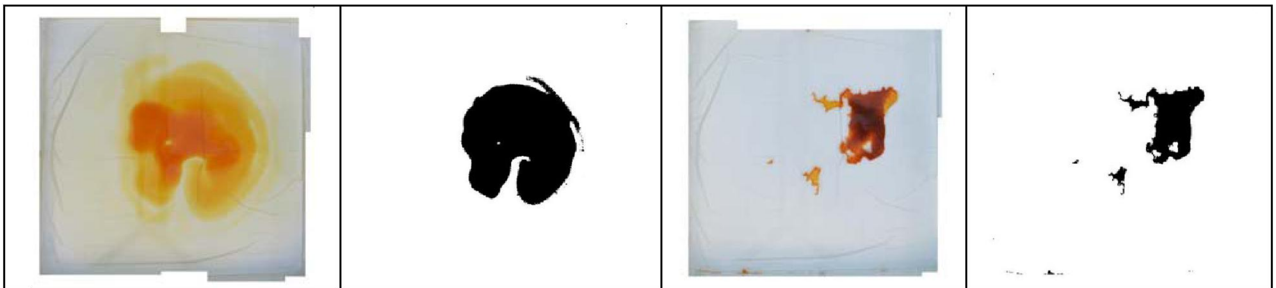


Figure 5 - Efficiency of herders at 5 °C in relation to Kashagan oil stripped at 200 °C

Fig. 6 shows photos describing the effect of the OP-40 herder at 15°C and a salinity of 6‰ on Kashagan oil stripped at 200°C.



Real photo	Black and white format	Real photo	Black and white format
0 min		After 1 min	

Figure 6 - Photographs and black and white images of oil spots for oil stripped at 200°C: OP-40 herder, 15°C; salinity 6‰

The results of the herder impact on the oil stripped at 200°C at 15°C are shown in Table. 4.

Table 4 - Experimental and calculated data on the determination of the area and thickness of the oil spot at 5°C after herder application to Kashagan oil stripped at 200°C

#	Test conditions	Number of white pixels	Number of black pixels	Spot area,%	Spot area , cm^2	Spot thickness, mm
1	2	3	4	5	6	7
Thick Slick						
1	00 min, 5°C, 6‰ TS	1711573	7457102	0,1867	1866,76	0,5357
2	01 min, 5°C, 6‰ TS	1212779	7786793	0,1348	1347,60	0,7421
3	05 min, 5°C, 6‰ TS	1227626	7965183	0,1335	1335,42	0,7488

Продолжение таблицы 4						
1	2	3	4	5	6	7
4	10 min, 5°C, 6‰ TS	1018576	8198153	0,1105	1105,14	0,9049
5	30 min, 5°C, 6‰ TS	1237076	7883121	0,1356	1356,41	0,7372
6	60 min, 5°C, 6‰ TS	1003368	8164454	0,1094	1094,45	0,9137
7	90 min, 5°C, 6‰ TS	1013537	7097312	0,1250	1249,61	0,8003
OP-40						
1	00 min, 5°C, 6‰ OP-40	1563154	7531985	0,1719	1718,67	0,5818
2	01 min, 5°C, 6‰ OP-40	369848	8534342	0,0415	415,36	2,4075
3	05 min, 5°C, 6‰ OP-40	272525	8895435	0,0297	297,26	3,3641
4	10 min, 5°C, 6‰ OP-40	271338	8701935	0,0302	302,38	3,3070
5	30 min, 5°C, 6‰ OP-40	271229	8848742	0,0297	297,40	3,3625
6	60 min, 5°C, 6‰ OP-40	272666	8798668	0,0301	300,58	3,3269
7	90 min, 5°C, 6‰ OP-40	275081	8965908	0,0298	297,67	3,3594

Fig. 7 shows the efficiency of the herders when exposed to Kashagan oil stripped at 200°C at 15°C. The nature of the action of the herders in time is approximately the same for both temperatures: the area of the spot decreases and becomes stable for 1.5 - 2 hours, while the thickness of the oil spot increases.

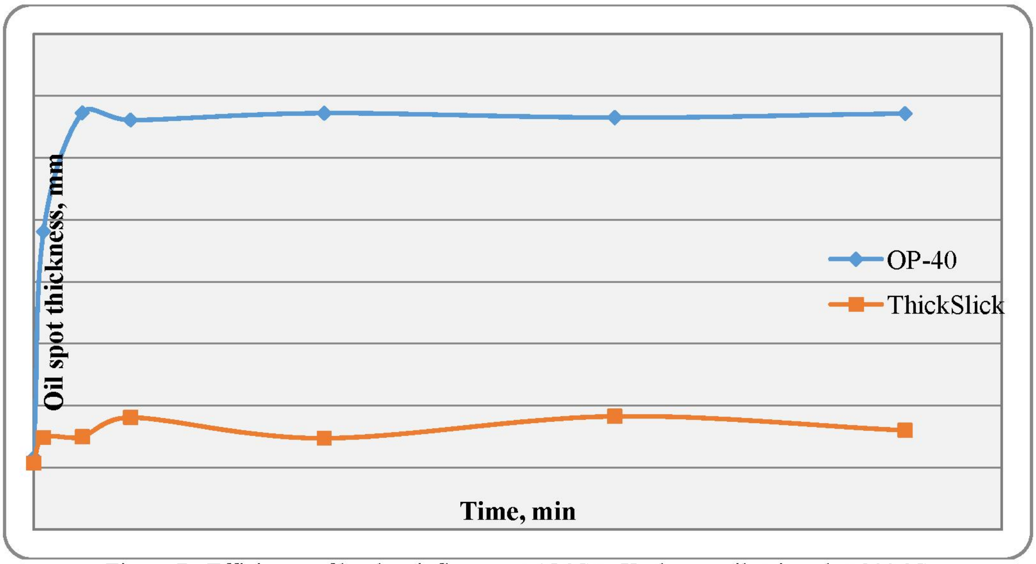


Figure 7 - Efficiency of herders influence at 15 °C to Kashagan oil stripped at 200 °C

With increasing temperature, both herders become more effective. Thus, for the temperature rising from 5 to 15°C the thickness of the oil slick increased from 0.26 to 0.80 mm for Thick Slick herder and from 0.86 to 3.36 mm for OP-40 herder. The effect of water temperature on the effectiveness of herders is shown in Table. 5.

Table 5 - Effect of temperature on the efficiency of herders applied to stripped Kashagan oil

#	Herder	Herder action time, min	Temperature	Spot thickness, mm
1	ThickSlick	60	5°C	0,2552
			15°C	0,9137
2	OP-40	60	5°C	0,8544
			15°C	3,3269

To assess the impact of herders on different types of oil, experiments were conducted with oil from the Buzachi field at 15°C. The results of calculating the efficiency are shown in the Fig. 8. As the data of this figure show, the efficiency of both herders applied to Buzachi oil is higher as compared to the results of Kashagan oil. Of the two herders, ThickSlick herder in this experiment showed a better result than the OP-40.

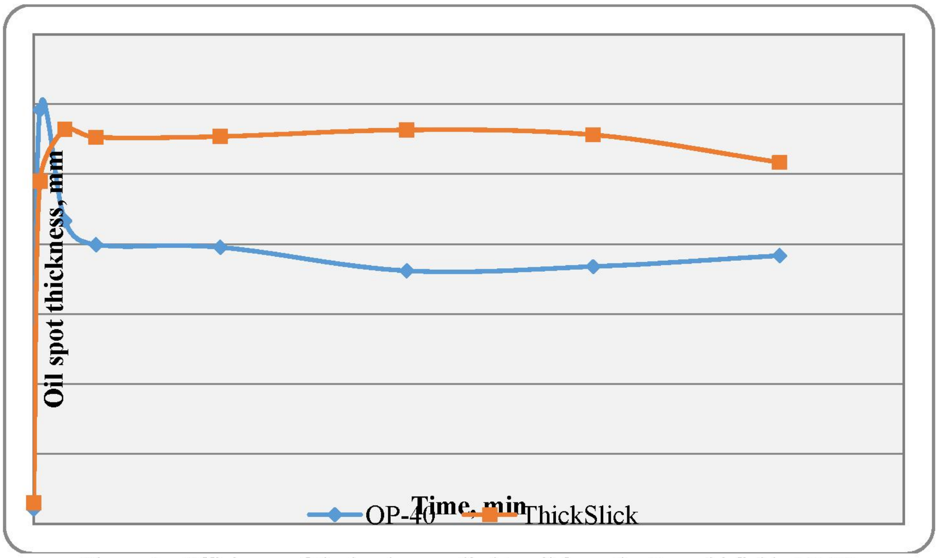


Figure 8 - Efficiency of the herders applied to oil from the Buzachi field at 15°C

CONCLUSIONS

Thus, the following conclusions are drawn on the basis of the experimental studies :

1. ThickSlick 6535 and Siltech OP-40 herders are effective for contracting and thickening Kashagan oil spot.

2. Herders showed the best result on Kashagan oil, stripped at 200°C: oil density increased to 0.865 g/ml.

3. Of the two herders studied the most effective is Siltech OP-40.

4. The herder's action is independent of the salinity of the seawater.

5. The maximum effect of the herder is reached in 40 minutes. Herders retain their activity for one hour from the time they are applied to the water surface.

6. The efficiency of herders increases with rising temperature.

7. Both herders produce higher impact on Buzachi field oil, which has higher density of 0.920 g/ml and viscosity 427.2 mPa*s.

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ТЕҢІЗГЕ ТӨГІЛГЕН МҰНАЙДЫ ЖОЮДА ХЕРДЕРЛЕРДІ ПАЙДАЛАНУДЫҢ МҮМКІНДІКТЕРІ

Аннотация: Бұл зерттеу Каспий теңізінің қазақстандық секторында (КТҚС) мұнай төгілуін жою үшін өртеу әдісін пайдаланған кезде, хердерлерді қолдану мүмкіндіктерін, оңтайлы шарттарын және тиімділігін зертеуге арналған. Теңізге төгілген мұнайды жоюдың өртеу әдісі теңізде үлкен төгіліс болған жағдайда, жел мен ағын әсерінен мұнай жолағы үлкен қашықтыққа тез тарап, жайылу аймағы және төгілген мұнай көлемі суды сіңіру арқылы айтарлықтай ұлғайған кезде ерекше басымдыққа ие болатын әдіс. Дүниежүзілік тәжірибеде су бетіне төгілген мұнайды өртер алдында жиыстырып, қалыңдығын арттыру үшін хердерлер немесе химиялық жинағыштар пайдаланылады. Зертеу, басқа теңіздер мен мұнайларда жақсы нәтиже көрсеткен хердерлерді Каспий теңізінің қазақстандық секторында пайдалану мүмкіндіктерін анықтау мақсатында жүргізілді. Тұздылығы КТҚС жағдайына сәйкес келетін жасанды теңіз суында қашаған мұнайы үшін Siltech OP-40 және ThickSlick 6535 хердерлерін оңтайлы әрі тиімді пайдалану шарттары анықталды.

Түйін сөздер: мұнайдың төгілуі, хердерлер, диспергенттер, Қашаған, Каспий теңізінің қазақстандық секторы, судың тұздылығы, мұнайды өртеу.

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ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ХЕРДЕРОВ ПРИ ЛИКВИДАЦИИ РАЗЛИВОВ НЕФТИ НА МОРЕ

Аннотация: Исследование посвящено изучению возможностей, оптимальных условий и эффективности применения хердеров при сжигании нефти в качестве метода ликвидации разливов нефти в казахстанском секторе Каспийского моря (КСКМ). Метод сжигания нефти на море является одним из предпочтительных методов в случае больших разливов нефти на море, когда под действием ветра и течений нефтяное пятно быстро распространяется на большие расстояния, при этом значительно увеличиваются и площадь разлива, и объем разлитой нефти вследствие поглощения воды. Хердеры, или химические собиратели, используются в мировой практике для стягивания нефтяного пятна и его утолщения перед проведением сжигания. Исследование проведено с целью определения возможности применения наиболее эффективных, используемых с другими нефтями и в других морских условиях хердеров в условиях казахстанского сектора Каспийского моря. Определены условия и эффективность хердеров Siltech OP-40 и ThickSlick 6535 для кашаганской нефти в искусственной морской воде с соленостью, характерной для КСКМ.

Ключевые слова: разлив нефти, хердеры, диспергенты, Кашаган, казахстанский сектор Каспийского моря, соленость воды, сжигание нефти.

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