Combustion of Hydrogen Sulfide-Containing Oil on the Surface of the Water and Possible Applications of Combustion Method at Sea

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Abstract

Oil production in sea conditions is associated with certain difficulties of the field development process due to technological peculiarities of oil production at sea. The Caspian Sea is an enclosed pond with a very sensitive ecosystem, therefore, maritime operations here meet higher requirements than in open ponds. The uniqueness of the Caspian Sea is in the fact that its biological wealth has no analogues in the world, therefore, mining without complying with strict ecological requirements can cause irreparable harm to the environment. This work deals with the analysis of the possibility to use controlled combustion in situ in case of accidents on the Kashagan oil field which is located in the Caspian Sea. The Kashagan oil field is distinguished by a high content of hydrogen sulphide. In order to study the operational possibilities of oil combustion in situ, the process of evaporation and combustion of desulfurized oil from the Kashagan field depending on salinity of water was studied in this work. The process of evaporation of hydrogen sulphide from hydrogen sulphide-containing oil and the peculiarities of its combustion on water surface were studied in this work. It has been stated that the main difference in oil combustion with a high content of hydrogen sulphide is that the oil combustion process leads to the increase of sulfur concentration in oil residue after combustion.

Keywords:
- oil spills
- combustion
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- ppm

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1. Introduction

Almost the entire technological chain on exploitation, production, transportation, storage, processing and usage of petroleum products is associated with severe pollution of the environment [1‒3]. In this regard, all the processes associated with oil represent a significant environmental hazard. Emergency situations during transportation of oil through the water areas by tankers and pipelines, both land and underwater, are hazardous [4]. The latter kind of accidents is especially characteristics of oil producing of CIS countries. The main causes of pipeline ruptures are: metal corrosion (internal – 86%, external – 5.3%). It should be noted that during pumping of oil with a high content of sulfur-containing compounds, in particular hydrogen sulphyde and mercaptans, the risk of pipes corrosion increases. But some Kazakhstan oil and gas fields are characterized by an increased content of the above-mentioned corrosive components. These problems become especially urgent with the beginning of works on the development of Kashagan field. The development of deposit is carried out in complex geological conditions: shelf zone, large depths (up to 4800 m), high reservoir pressure (80 MPa) and the most important factor – is a high content of hydrogen sulphide (up to 19%), which leads to rapid corrosion of pipelines, this fact increasing the risk of oil spills in the field. In this regard, the issues related to scientific developments and aimed at development and creation of effective methods for elimination of oil spills with a high content of hydrogen sulphide become actual.
There are various methods for eliminating of oil spills on the water and ice surfaces. One of the methods is the use of the herders sprayed onto the water surrounding an oil slick result in formation of a monolayer of surfactants on the water surface. Surfactants decrease the surface tension of the water from 73 mN/m to 25–30 mN/m. The best hydrocarbon-based herding agents have spreading pressures in the mid-40 mN/m, contracting the oil into thicker slicks [5, 6]. However, the use of surfactants is time-consuming, which is not always possible at the need for rapid response, and has low efficiency at significant sea waves. Practice shows that the use of various methods of elimination allows to achieve a better result. Combining the possibility of "in-situ burning" and the use of surfactants gives good efficiency value [5, 7].

The response time is important during emergency oil spills in water areas. When oil is spilled on water, it begins to spread, evaporate and emulsify. With time, it becomes more difficult to track, retain, and collect, or process the spilled oil. As a consequence, rapid mobilization and deployment of equipment on oil spill response are essential for the effective management of spill-out effects in general [8]. Controlled combustion of spilled oil in situ is an efficient and quick way to eliminate large volumes of oil from the level of ground, snow, ice or water surface. In this case, carbon dioxide and water are the combustion products.

In [9], the authors presented the results of laboratory tests for burning oil spills on the surface of water. Results show that after 15 min of burning, the degradation ratio made up 36% to the initial oil relatively (Fig. 1).

There are a lot of articles describing the oil combustion, but very few papers are devoted to the study of the effect of sulfur on the process and the effectiveness of the combustion method for elimination of oil spills. Sulfur, hydrogen sulphide and mercaptans as highly corrosive sulfur compounds are the most undesirable components of oils [10]. The study of the combustion of sulfur-containing oils is of great theoretical and practical importance.

During liquidation of oil spills, when direct participation of people is necessary, the high content of hydrogen sulphide in spilled oil has its negative impact. At a concentration of 500 ppm, hydrogen sulphide causes breathing disorders, and the concentration of 800 ppm leads to death during five minutes. The combustion method of oil spills does not require direct participation of people on site, and this refers to another advantage of incineration, as a method for elimination of oil spills containing hydrogen sulphide. In this regard, in proposed work the processes of hydrogen sulphide evaporation from hydrogen sulphide-containing oil were studied. Also, some processes of combustion of oil containing hydrogen sulphide on the surface of water at its various salinity were studied.

2. Experimental

The process of evaporation of desulphurized Kashagan oil at various temperatures as well as, the process of combustion of Kashagan oil at different values of water salinity were studied. To carry out investigations, a special installation was assembled (Fig. 2).

In order to study evaporation and combustion of oil, we used a bath (4) with the volume of 12 l and the surface size of 120 cm² which was placed on the balance (3) to take measurements of the oil mass both in the process of evaporation and before and after combustion. To maintain the desired temperature, the balance with bath was placed into the cooling chamber (1). Also there is used a fan (7) allowed to create imitation of wind with constant speed and airflow direction which is 1.4 m/s over the surface of oil film. Oil was poured into the bath through the branch pipe (2), but unburned oil was discharged through the branch pipe (5). The temperature of water was measured with the help of a thermocouple (6), water in the experiments was used at 5, 18 and 25 °C.

Salinity of water was provided by addition of the estimated amount of NaCl into water. The experiments were performed at salinities of 0, 18, 35‰.
In experiments there were used different oil volumes for thickness variation of burned oil film – 300, 600, 900 ml. Oil volume of 300 ml provided the formation of oil film with thickness of 3 mm, when the implementation of oil combustion at the surface of the water is possible [8].

After pouring water and oil into the vessel, the mass was registered on the balance, the mass of oil was determined by the difference between the total mass and mass of water used in experiments.

To study evaporation and burning, we took readings of oil mass every 10 min during the first hour, every 20 min during the second hour and every 30 min during the third hour, before and after burning. Burning was realized after 3 h of evaporation. The measurement accuracy of the balance made up ±5 g.

Regardless of the temperature and salinity of the water there is observed one peculiarity – if the oil lies on the water long time, more light oil is evaporated (Fig. 3).

However, if the temperature water is higher, the evaporation effectiveness of light oils is better. In accordance with our experimental data the increase of temperature water from 5 °C to 25 °C lead to the fact that the percentage of evaporated light oil is increased two-fold Fig. 4.
We have investigated the oil combustion efficiency on the surface of water with different salinity after evaporation process of light oil for 1, 2 and 3 h. For determination of oil combustion efficiency, upon completion of experiment, the mass, volume and thickness of unburnt oil film were measured. The results of these studies are shown in Fig. 5.

The obtained results have shown that the combustion effectiveness depends on the content of light oil in oil. If the oil lies on the water long time, less light oil remain in oil and combustion efficiency decreases. The experiments carried out by us also revealed that the degree of water salinity has significant effect on oil combustion efficiency. In order to understand this process we have studied the dependence of oil combustion effectiveness on water salinity at different temperatures of water Fig. 6.

The experiment carried out by us allowed to state that salinity of water exerts a negative effect on the efficiency of oil burning, i.e. the increase in salinity of water results in the decrease in efficiency of oil burning on the surface of water.

In the previous experiments we stated that the efficiency of dispersants decreases with the decrease in salinity [11, 12]. In open water basins, salinity of sea water is known to make up 35‰ and in the region of the Caspian Sea (location of Kashagan) it varies within 6‰. Therefore, the efficiency of using dispersants under the conditions of Kazakhstan sector of the Caspian Sea becomes significantly lower than in other open water ponds. The experiments performed by us showed that the method of burning becomes most effective when salinity of water is low as under such conditions oil yields to effective burning. Besides, it is stated that the efficiency of oil burning decreases by minimum 10% with the increase in salinity of water from 0‰ to 35‰. Consequently, this fact conditions the necessity of a more careful study of the method of oil burning at sea as the most acceptable one under the conditions of the Northern Caspian.

The process of evaporation of hydrogen sulphide from hydrogen sulphide containing oil and peculiarities of its combustion on the surface of water were studied. The studies were carried out with the oil from Tengiz field, which was artificially saturated with hydrogen sulphide. To obtain gaseous hydrogen sulfide and for saturation of oil with hydrogen sulphide, the installation was assembled, Fig. 7. The apparatus for producing hydrogen sulphide consists of hermetic vessel (2) welded from iron with the wall thickness of 0.3 mm with a branch pipe (1) for output of gas and a heater (3). To obtain hydrogen sulphide, a standard procedure was used: 100 g of paraffin was mixed with 60 g of ground sulfur, heated to the melting point of paraffin, and mixing was carried out until a homogeneous mass was obtained. The resulting mass was poured into an iron vessel and heated to a temperature above 170 °C, the hydrogen sulphide emission was determined by the indicator paper impregnated with lead acetate. In the process of chemical reaction, paraffin (namely, hydrogen in paraffin) reacts with sulfur with the release of hydrogen sulphide and formation of carbon.

The reaction proceeds according to the following equation:

\[
C_{40}H_{88} + 41S \rightarrow 41H_2S + 40C.
\]

In order to saturate the oil with hydrogen sulfide, an aerator (4) was placed in a sealed vessel with oil (6), the operational principle lies in the fact that with the help of a branch pipe the oil runs at a rate of 600 l/h, and due to the output of oil with a high flow rate from the pipe, hydrogen sulphide with a volume of the order of 300 cm³/min is captured. The mixture of oil and hydrogen sulphide is forced out through the diffuser-sprayer and thus oil is saturated with hydrogen sulfide in the form of small bubbles (7). The conducted studies showed that there takes place intensive evaporation of hydrogen sulphide bubbles from oil, therefore, the oil was launched into the unit immediately after saturation with hydrogen sulphide.

3. Results and discussion

Investigations on the study of the dynamic process of evaporation of hydrogen sulphide from oil, depending on residence time on the surface of water were carried out. The percentage content of evaporated hydrogen sulphide in the Installation volume.
was evaluated using a standard linear-colorimetric express method of analysis. The linear-colorimetric method is based on pulling of the investigated gas mixture through glass indicator – tubes and measuring the length of colored powder column depending on the concentration of hydrogen sulfide. When measuring the concentration of hydrogen sulphide, the indicator tubes for hydrogen sulfide TU-RU-AZ-415522505 were used. The measurement was carried out in the following order:

- the measurement was made in 15–30 sec after injection of oil;
- the measurement was performed in 15 min after injection of oil;
- the accumulated hydrogen sulphide was evacuated by the exhaust system and the next measurement was made after 15 min from extraction. The measurements were carried out until the concentration of hydrogen sulfide was reduced to the minimum.

The process of oil combustion with hydrogen sulphide content was studied under the following conditions:

- the volume of water was 12 l, the volume of oil was 360 ml. The volume of the combustion plant is 0.8 m$^3$;
- ignition was carried out immediately after the branching of oil containing hydrogen sulphide;
- ignition was carried out after evaporation of hydrogen sulfide to the minimum;
- during the combustion process with the help of thermocouple sensors, the temperature was measured at 3 points in the water layer and 6 points in the flame volume continuously until the end of the burning every 600 ms. The measurements were carried out by automatic monitoring system with recording of the temperature output data to the computer. For flame temperature measurements, the permanently installed chromel-alumel thermocouples were used, but for water temperature measurement the resistive sensors were used;
- after completion of the combustion process, the volume of oil residues was measured and the samples of oil residues were taken for analysis of sulfur content.

The first stage of the conducted experimental studies was determination of the hydrogen sulphide evaporation dynamics from the surface of oil containing hydrogen sulphide and measurement of hydrogen sulfide concentration in unit volume. The studies have shown that the dynamics of hydrogen sulphide evaporation from the surface of oil saturated with hydrogen sulfide does not undergo significant changes depending on water salinity. The temperature of water was maintained in the range of 18–20 °C. The average time of hydrogen sulphide evaporation to minimum value was 1 h 30 min. Just after pouring of oil, the concentration of hydrogen sulphide in the volume unit was from 600 to 700 mg/cm$^3$. After 15 min, the concentration of hydrogen sulphide reaches 2000 mg/cm$^3$. After next 15 min hydrogen sulphide is extracted, and newly measured concentration reaches 500–550 mg/cm$^3$. In the following next 15 min, the concentration of hydrogen sulphide decreases to 350–400 mg/cm$^3$. In the next 15 min after drawing, and after 1 h from the beginning of the experiment, the concentration of hydrogen sulfide decreases to 50–100 mg/cm$^3$.

Fig. 7. Installation diagram for investigation of hydrogen sulphide evaporation process from hydrogen sulfide-containing oil and its combustion process at water surface: 1 – a branch pipe, 2 – pressure vessel, 3 – heater, 4 – aerator, 5, 9, 12 – taps, 6 – pressure vessel with oil, 7 – aerators, 8 – tube for oil supply, 10 – temperature sensor, 11 – balance, 12 – water tap, 13 – exhaust system.
After 1 h and 15 min the concentration of hydrogen sulfide decreases to 25–30 mg/cm$^3$. The last measurements taken after 1 h and 30 min showed that the concentration of hydrogen sulfide is less than 10 mg/cm$^3$. The last measurements showed the absence of hydrogen sulfide within the sensitivity of the UG-2 instrument. After 1 h and 30 min, the ignition of oil was carried out.

The second stage of the investigations was the study on the combustion process of hydrogen sulphide containing oil in sealed installation with constant extraction of combustion products. The essence of the research is the study of combustion temperature regimes and degree of oil combustion, depending on water salinity. Flame temperature measurement was made permanently with six chromel-alumel thermocouples arranged along the flame height every 4 cm, the first thermocouple was also located at a level of 4 cm from the surface of oil film. The water temperature measurement was made by special sensors which were resistive elements located at a distance of 2 cm from the surface of the lower part of the oil film and lower at a level of 4 cm and 12 cm. The results of measurements in real mode were recorded every 600 ms on the computer with an automatic monitoring system. Figure 8 shows the scheme of installation on which the combustion process of oil containing hydrogen sulphide was carried out.

Concentration saturation of oil with hydrogen sulphide was estimated as follows: the mass of initial oil (1 l) and container were measured, then the oil was saturated with hydrogen sulfide in accordance with the described methodology and the mass of saturated oil was measured. The difference in weight is 4 g, this corresponding to the content of hydrogen sulfide in oil 4 g/l. The calculations showed that in 360 ml of poured oil at normal atmospheric pressure there are about 1000 cm$^3$ of gaseous hydrogen sulphide in the form of bubbles. The combustion of sulfur-containing oil was carried out in completely sealed installation, the air required for combustion was supplied through a special branch pipe, and the waste gases generated during evaporation of hydrogen sulphide and combustion of oil were pulled by the exhaust system. The exhaust system is equipped with a carbon filter designed to trap hydrogen sulphide. Under such conditions, the process of oil combustion differs from the combustion process in open space. The intensive air flow through the branch pipe forms vortex flows in flame and resulted in more complete combustion with the formation of a small amount of soot in the flame. This condition did not allow to collect soot for analysis. Investigation of temperature regimes of the flame shows a strong change in the temperature gradient throughout the entire volume of the flame. The temperature gradient ranges from 300 °C in the lower part of the flame up to 920 °C in the upper part of the flame. The temperature of water at a level of 2 cm from the surface of the oil film rises by 2–3 degrees, and the temperature of the lower bed of water practically does not change. The main goal of researches was the study of combustion degree of the oil film containing hydrogen sulphide with maximum saturation and after its evaporation, as well as examining of oil residues after burning for the content of sulfur. First of all, the controlled combustion of initial Tengiz oil was made, which was not saturated with hydrogen sulfide at 0% of water salinity. The residue of oil after combustion made up 70 ml, the burning time was 4 min and 17 sec, the temperature in the flame volume varied between 300–900 °C. Table 1 shows the research results on combustion of Tengiz oil saturated with hydrogen sulphide. The ignition was carried out in 1 h and 30 min after the oil was injected.

In these experiments, the influence of water salinity on oil film combustion process is observed. With increasing of water salinity there remains a large amount of unburned oil. This phenomenon is
explained by the inhibitory effect of salt in water composition on combustion process.

Two mechanisms can be distinguished for water salinity effect on combustion process. The first is the formation of powdered salt during evaporation of water droplets, which rises to the flame due to boiling water. Powdered salt has an inhibitory effect mainly due to removal of heat from the combustion zone and insulating action on fuel. Secondly, the salt acts as a combustion inhibitor and is a negative catalyst, inhibiting the reaction at a constant combustion temperature. The mechanism of salt action on the combustion process is in breaking of reaction chains during oxidation of fuel, the salt reacts with active centers of the reaction and converts them into stable products, thus leading to the decrease of intensity of combustion.

To determine the influence of hydrogen sulphide on oil combustion process, some experiments on combustion of hydrogen sulphide containing oil were conducted, immediately after pouring it at different salinities. Significant visual changes during the oil combustion were not observed, the temperature in the flame volume ranged from 300 to 900 °C, the burning time was about 4 min, and oil residue was 70‒130 ml.

The third stage of the study was analysis of total sulfur percentage in oil residues after combustion. The studies were carried out using analyzer «Spectrascan S» that determined the content of sulfur in oil and oil products. Table 2 shows the results of the studies.

Combustion of hydrogen sulfide-containing oil leads to an increase in sulfur concentration in composition of unburned oil residues. This is explained by the fact that the initial content of sulfur has passed to a smaller volume of oil, because during combustion, from 4 to 5 the parts of oil are burnt. The increase of sulfur concentration in unburned oil residue can be explained by the formation of stably sulfur compounds, which are formed during combined combustion of hydrogen sulphide and oil. During combustion of sulphur there is occurred the formation of sulphur dioxide:

\[ S + O_2 \rightarrow SO_2 \]

Transformation of sulphur into sulphur dioxide is a chain reaction with the formation of a series of intermediate products such as: sulphur monoxide \( S_2O_2 \), molecular sulphur \( S_2 \), free sulphur atoms \( S \) and free radicals of sulphur monoxide \( SO \) that remain in oil. Comparatively lower content of sulfur in Sample #7 is explained by large volume (130 ml) of oil residues after combustion.

### Table 1

<table>
<thead>
<tr>
<th>Water salinity</th>
<th>Volume of injected oil, ml</th>
<th>Volume of oil residues, ml</th>
<th>Temperature gradient in flame volume at high, t, °C</th>
<th>Combustion time of oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0‰</td>
<td>360</td>
<td>70</td>
<td>300‒920</td>
<td>4 min 15 sec</td>
</tr>
<tr>
<td>6‰</td>
<td>360</td>
<td>80</td>
<td>300‒920</td>
<td>4 min 27 sec</td>
</tr>
<tr>
<td>12‰</td>
<td>360</td>
<td>100</td>
<td>300‒920</td>
<td>4 min 32 sec</td>
</tr>
<tr>
<td>18‰</td>
<td>360</td>
<td>110</td>
<td>300‒920</td>
<td>4 min 24 sec</td>
</tr>
<tr>
<td>35‰</td>
<td>360</td>
<td>130</td>
<td>300‒920</td>
<td>4 min 40 sec</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th># Tests</th>
<th>Sample</th>
<th>Sulfur content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test #1</td>
<td>Original Tengiz oil</td>
<td>0.565%</td>
</tr>
<tr>
<td>Test #2</td>
<td>Original Tengiz oil after combustion</td>
<td>0.979%</td>
</tr>
<tr>
<td>Test #3</td>
<td>Original Tengiz oil is saturated by hydrogen sulfide</td>
<td>0.632%</td>
</tr>
<tr>
<td>Test #4</td>
<td>Original Tengiz oil is saturated by hydrogen sulfide and burned immediately after pouring</td>
<td>1.176%</td>
</tr>
<tr>
<td>Test #5</td>
<td>Original Tengiz oil is saturated by hydrogen sulfide and burned immediately after 1 h and 30 min</td>
<td>1.151%</td>
</tr>
<tr>
<td>Test #6</td>
<td>Original Tengiz oil is saturated by hydrogen sulfide and burned immediately after pouring on water with salinity 6‰</td>
<td>1.183%</td>
</tr>
</tbody>
</table>
4. Conclusions

The conducted studies have shown that with water salinity from 0‰ to 35‰, the oil combustion efficiency of on the surface of water decreases to 10%. Two mechanisms can be distinguished for the effect of water salinity on the combustion process. First, the formation of a powdery salt occurs during the evaporation of water droplets, which rise to the flame by boiling water. Powder salt has an inhibitory effect mainly due to the removal of heat from the combustion zone. The second mechanism of the effect of salt on the combustion process is the breakage of reaction chains in the flame, which leads to a decrease in the intensity of combustion.

Combustion of hydrogen sulfide-containing oil leads to the increase in sulfur concentration in composition of unburned oil residues. The increase of sulfur concentration in unburned oil residue can be explained by the formation of stably sulfur compounds, which are formed during combined burning of hydrogen sulphide and oil.

References


