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Experimental Study on the Synergistic Effect between Evaporation Weathering and Emulsification of Oil Spills

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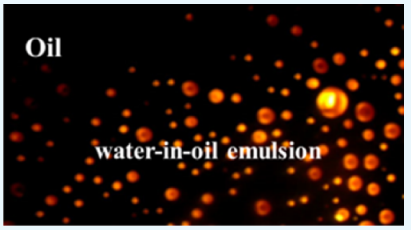
ABSTRACT: First, a range of experiments using a stainless steel shallow plate in a thermostatic oscillator were carried out to simulate evaporation weathering of oil spills under different temperatures, wind velocities, oil film thicknesses, and wave conditions. The information on influencing factors of evaporation weathering could be obtained. Then, evaporation experiments of four oil samples with three emulsification states were conducted, and the effect of emulsification on evaporation of oil spills was investigated. The characteristics of each operation were described, mass loss characteristics of oil spills with time were plotted, and the effects of evaporative weathering processes under different conditions were quantitatively compared. A high-precision visualization system was utilized to simulate experimentally oil spill emulsification processes, and the effect of evaporative weathering on emulsification weathering of oil spills was investigated. The results of evaporation experiments showed that the increase of temperature could promote the evaporative weathering. The thin film thickness was beneficial to evaporation of oil spills. The increment of the wind speed could promote evaporation behavior when the wind velocity was small, but the increase of velocity had little effect on oil evaporation when the wind speed was large. Wave conditions had little effect on oil evaporation under the conditions of this experiment. The effect of different emulsification states on oil evaporation was not consistent. Unstable or semistable water-in-oil emulsions inhibited oil evaporation at the initial stage of evaporation, but water evaporation would increase oil-phase evaporation with the destruction of the emulsion structure. Stable water-in-oil emulsions inhibited evaporation weathering. The evaporation weathering of oil was conducive to the emulsification of oil.



1. INTRODUCTION

At present, the increasing demand for petroleum had promoted oil exploration and oil transport activities in the marine environment. The risk of oil spills always existed in the process of production and transportation.[1,2] Human factors, mechanical failures, ship collision, pipeline explosion, and failure of oil rigs resulted in oil spill accidents, which would have a long-term impact.[3,4] The fate of oil spills in water depended on the complex interactions of physical, chemical, and biological processes, which were jointly determined by the surrounding environment of water and oil properties.[5−7] Under the influence of various environmental factors, oil spills would have very complex physical, chemical, and biological changes, which were usually diffusion, drift, and weathering.[8,9] The diffusion process refers to the process due to which the area of oil film on the water surface increases.[10] The drift process refers to the migration process of oil spills on the water surface under the action of hydrodynamic factors, including horizontal drift diffusion, vertical migration, and suspension.[11] Compared with the diffusion and drift processes of oil spills, the weathering process is more complex.[3,12,13] The weathering process refers to a variety of processes in which oil spills change the composition of crude oil and petroleum products in the environment.[14,15] These processes included evaporation, emulsification, photooxidation, and biodegradation, as well as dispersion and dissolution.[5,15] In short, evaporation and emulsification were the two most important processes in oil spill weathering, which seriously affected the ecological environment and emergency response decision-making.[16,17] Evaporation is the process that caused the most mass loss in the weathering process of crude oil and petroleum fuel. Due to the absorption of a large amount of water, the emulsification process significantly altered the oil spill properties especially density and viscosity, and made it more difficult to remove oil spills.[18−20] Therefore, both in terms of environmental impact and emergency response, evaporation and emulsification were two processes that must be studied.

The main research methods of oil spill evaporation and emulsification included mathematical derivation and experimental methods. Because there were many components in

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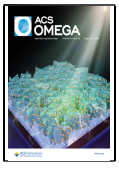

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oil spills, the calculation of oil spill evaporation by a mathematical method needed many parameters and the calculation process was complex. Obviously, physical simulation experiment was the most effective means to study the weathering mechanism in mathematical calculations, numerical simulations, and physical simulations. At present, the research methods of oil spills' evaporative weathering included field observation and laboratory simulation. The field observation method was mainly used to study the change of the quality and component properties of the oil spills by sampling on the site. The field observation method was used to fully investigate the influence of environmental factors on the weathering process when the oil spills occurred. The experimental conditions were true and accurate, and the research results were highly reliable. However, the experimental results obtained using different methods were not the same, and the reproducibility of the results was low. A stainless steel shallow plate was utilized for the experimental study of oil spill evaporation through continuous research and improvement, and the logarithmic relationship between oil spill evaporation loss and time was obtained.[21,22] The evaporation experiment with the stainless steel shallow plate was the most commonly used method, which was used to study the influence of many factors including wind speed, oil spill area, and different oil samples on oil spill evaporation, and the evaporation rate equation considering different factors could be obtained.[23] In conclusion, the shallow plate evaporation method had the following three advantages to study the evaporative weathering. First, it could be used to qualitatively analyze the single factor influence of evaporative weathering, so as to avoid the interference of other factors. Second, the experimental operation was relatively simple, and it was easy to reproduce the experiment and ensure the accuracy of the experimental results. Third, the accuracy of the experimental results was relatively high because of small-scale experimental operation. The stainless steel shallow experiment also had some shortcomings such as it could not completely simulate the environment of oil spill in a water body, which was different from the actual situation. Therefore, the experiment was suitable for analyzing the influence of a single factor on evaporation, but not other weathering behaviors such as emulsification and photooxidation.

Emulsification, as another weathering process of oil spills, has been studied for a long time. It was recognized that the emulsions were formed by the presence of asphaltene and gum in oil. Asphaltene played an important role in the formation of stable emulsified oil, and gum had a certain stabilizing effect.[24,25] More than 3% asphaltene would produce the emulsifying effect, which was further confirmed by experiments. At the same time, the influence of the external environment on the emulsification of oil spills was also studied. The results showed that wave energy could provide enough energy for oil emulsification.[26] Temperature was not an important factor affecting oil spill emulsification.[27] The thinner the oil film thickness was, the better the oil spill emulsification effect was.[28] The higher the viscosity of the oil was, the easier the stable water-in-oil emulsion formed.[29] Photooxidation could produce polar groups, so that water could be effectively retained in oil. Evaporation was helpful to improve the concentration of asphaltene of oil spills and the formation of emulsion.[30,31] In addition, the emulsification rate equation established using the water content, water absorption constant, crude oil viscosity, wind speed, and other parameters for a long time was still adopted by the majority of scholars.[31] Although the emulsification phenomenon of oil spills was very common and has been studied, it still remained a poorly understood phenomenon. To sum up, the influence of external factors on evaporation have been studied in depth, but there seemed to be no experimental study on how evaporative weathering affected emulsification weathering of oil spills.

There were many reports on the mechanism and influencing factors of oil spill evaporation and emulsification. Evaporation and emulsification were the two most important weathering processes in the initial stage of weathering and the synergistic effect between them could not be ignored. However, almost all theoretical studies and all reported physical experimental studies did not refer to the synergistic weathering between evaporation and emulsification, and a significant experimental work was not undertaken to investigate this effect.

This article attempted to provide some qualitative information of characteristics and influence factors on evaporation and emulsification of oil spills and innovative description of the synergistic effect between them. A stainless steel shallow plate was utilized to simulate the evaporation process and obtain apparent mass loss characteristics. A high-precision visualization device was utilized to simulate and gather emulsification information of emulsions. The experimental results revealed a synergistic effect between evaporation and emulsification and presented an in-depth understanding of the weathering process of oil spills.

2. OIL SPILLS EVAPORATIVE WEATHERING EXPERIMENTS

2.1. Experimental Apparatus. The schematic of oil spill evaporation experiment is shown in Figure 1, and the

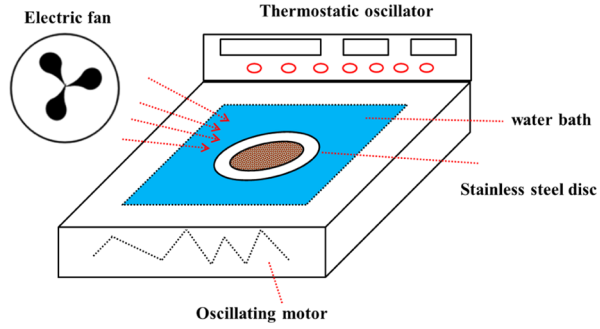

Figure 1. Schematic diagram of oil spill evaporation experiment.

equipment mainly consisted of two parts, an experimental power system and a data monitoring system. The experimental power system consisted of a constant temperature oscillator, a variable frequency electric fan, a stainless steel shallow plate with a diameter of 20 cm, and a lifting clamp. The constant temperature oscillator with the operating temperature ranging from 5 to 80 °C and the operating speed ranging from 30 to 500 rpm could work normally for more than 300 h. The data monitoring system was composed of a high-precision electronic balance, a hot ball intelligent anemometer, a liquid thermometer, etc. The data monitoring system could measure the temperature, wind velocity, viscosity, and other properties of the experimental oil sample.

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2.2. Experimental Schemes. Evaporation was a mass transfer process in which light components of oil spills change from the liquid state to gas state to atmosphere. It was an important weathering process affecting the properties of oil spills, drift and diffusion behavior, and the amount of residual oil on the water surface. There were many factors affecting oil spill evaporation, such that it was not only affected by the nature of the oil sample itself, but also affected by temperature, wind speed, oil film thickness, and wave conditions. In addition, the influence of the emulsification process on oil spill evaporation was also worth studying.

In order to study the influence of the above factors on oil spill evaporation, four types of oil samples were used in this paper, and the composition of the oil samples is summarized in Table 1. 20 groups of experiments were set up to explore the effects of temperature, wind speed, oil film thickness, and wave conditions on evaporation, and the detailed experimental scheme is summarized in Table 2. The shallow plate oscillation was induced by adjusting the speed of the oscillator to simulate the wave condition in the experiment. Considering that the experimental conditions of groups 3, 9, 15, and 18 were the same and the experimental period of a single group was long, four groups of experiments with the same conditions were carried out only once, so the results of the four groups of experiments were completely consistent. 12 groups of experiments were set to explore the influence of emulsification on oil spill evaporation and the detailed schemes are summarized in Table 3. The experimental temperature, wind speed, oil film thickness, and rotating speed were consistent with the experimental conditions of no. 3.

Table 1. Compositions of Oil Samples

oil sample	saturated hydrocarbon (%)	aromatic hydrocarbon (%)	colloid (%)	asphaltene (%)
A	49.5	26	17	4.5
B	40.4	30	24.6	1.9
C	34.6	21.2	32	7.3
D	35.7	18.6	28.4	14.5

Table 2. Experimental Data for the Oil Sample A Evaporation Weathering

run no.	temperature, °C	wind velocity, m/s	oil film thickness, mm	rotating speed, rpm
1	5	2.8	10	50
2	10	2.8	10	50
3	15	2.8	10	50
4	20	2.8	10	50
5	25	2.8	10	50
6	15	0.05	10	50
7	15	0.48	10	50
8	15	1.5	10	50
9	15	2.8	10	50
10	15	5.13	10	50
11	15	2.8	0.5	50
12	15	2.8	1	50
13	15	2.8	3.5	50
14	15	2.8	10	50
15	15	2.8	15	50
16	15	2.8	10	0
17	15	2.8	10	30
18	15	2.8	10	50
19	15	2.8	10	100
20	15	2.8	10	150

Table 3. Experimental Data for the Emulsified Oil Sample Evaporation Weathering

run no.	oil sample	moisture content of emulsion (%)	evaporation time
21	A	0	24, 48, 72, 96, 120
22	A	25	24, 48, 72, 96, 120
23	A	50	24, 48, 72, 96, 120
24	B	0	24, 48, 72, 96, 120
25	B	25	24, 48, 72, 96, 120
26	B	50	24, 48, 72, 96, 120
27	C	0	24, 48, 72, 96, 120
28	C	25	24, 48, 72, 96, 120
29	C	50	24, 48, 72, 96, 120
30	D	0	24, 48, 72, 96, 120
31	D	25	24, 48, 72, 96, 120
32	D	50	24, 48, 72, 96, 120

2.3. Experimental Procedures.

(1) Connecting process. Each device and auxiliary equipment was installed according to Figure 1, and the stainless steel plate was fixed in the middle of the bath. The stainless steel iron plate was fixed in the middle of the water bath, so that the oil sample could be placed in the iron plate to simulate the evaporation weathering process under different experimental conditions.
(2)Material preparation. According to the experimental schemes (Table 3), the mass of oil and water in the emulsion sample could be calculated, and 400 g samples were prepared for each experiment. According to the water content and total mass of the required emulsion in Table 3, the respective mass of oil and water in the emulsion was calculated. The mass of water in the emulsion accounts for 25%, so the mass of oil and water required for this trail is 300 and 100 g, respectively. After the oil and water have been weighed, they were poured into the same beaker and stirred with an electric mixer at 200 rpm for 10 min. In this way, the emulsion with a given water content can be obtained.
(3) Data acquisition. The weight of the stainless steel shallow plate with the experimental oil samples was weighed at set intervals, and the mass loss of the oil samples was calculated.
(4) Data processing and result analysis. Evaporation characteristics under different conditions were plotted in the form of curves. Through data processing, the variation of mass loss with time could be obtained. The factors influencing evaporative weathering could be obtained by analyzing the curves and data.

3. OIL SPILL EMULSIFICATION WEATHERING EXPERIMENTS

Emulsification was the second important feature of oil spills after evaporation. After the oil spill was mixed with water, the two weathering processes of evaporation and emulsification

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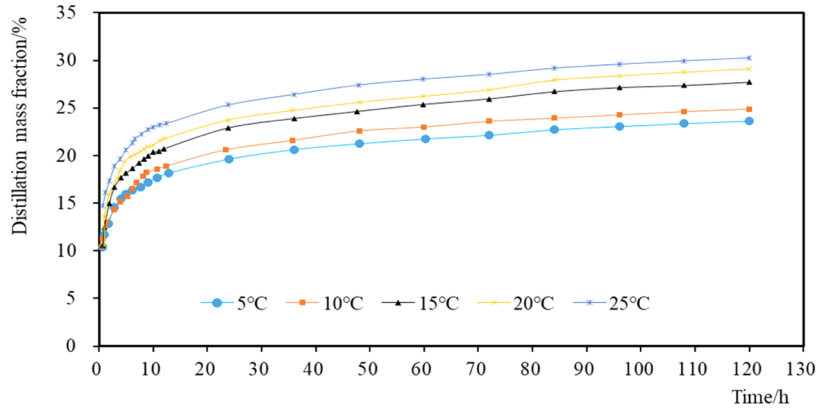

Figure 2. Effect of temperature on the evaporation process.

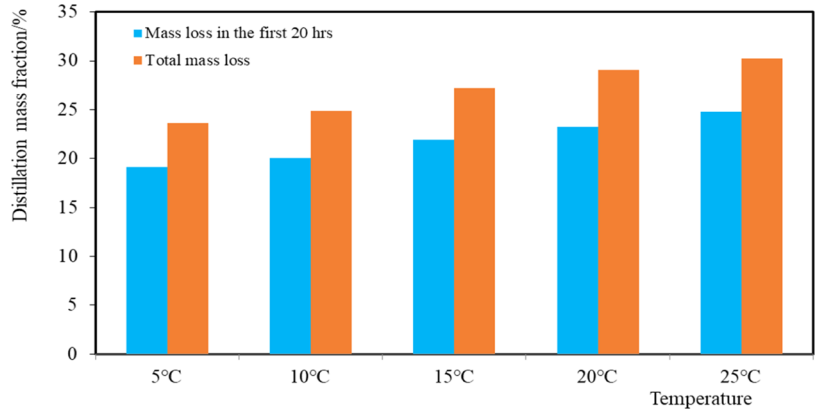

Figure 3. Evaporation characteristics at different temperatures.

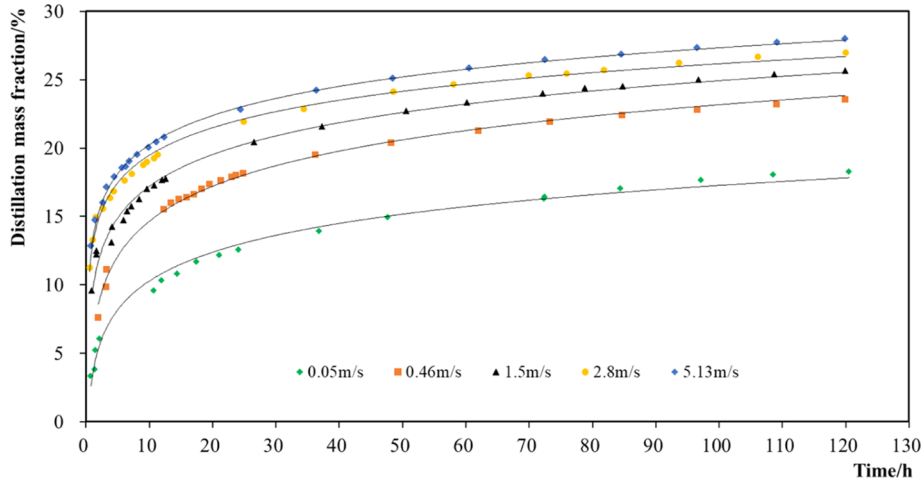

Figure 4. Effect of wind velocity on the evaporation process.

occurred simultaneously. The evaporation process would change the components of the oil spills, and the emulsification process could change the form of the oil spills. Emulsification would seriously affect the evolution process of oil spills, so it would inevitably affect the evaporation process of oil spills. The influence of evaporation on the oil spill and the influencing factors of the evaporation weathering have been studied in depth, and the influence of emulsification on the oil spill and the influencing factors of emulsification weathering have also been studied in depth. However, there was no systematic experimental study on the impact of evaporation and emulsification synchronization on the fate of oil spill, which means that the synergistic effect of the two processes on the fate of oil spill and oil spill emergency response was not explained. Because the evaporation and emulsification of oil spills occurred simultaneously, there was a dynamic interaction between the two processes, and the experimental conditions were difficult to reproduce completely. In order to better study the influence of oil spill evaporation on oil spill emulsification, the oil samples after evaporation for different times were quickly transferred into the emulsification visualization

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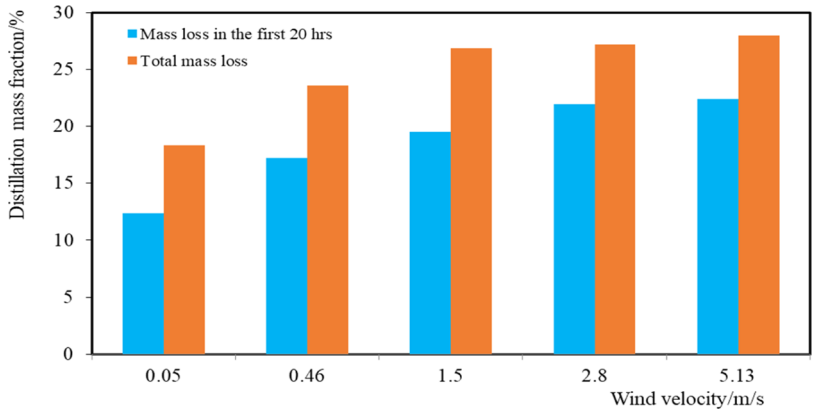

Figure 5. Evaporation characteristics with different wind velocities.

experiment, and the influence results were judged by observing the emulsification morphology of oil samples.

3.1. Experimental Apparatus. The schematic of visualization experiment of oil spill emulsification is shown in Figure 14, and the equipment mainly consisted of two parts, an injection system and an image acquisition and recording system. The injection system was divided into two parts, including an oil spill injection device and a water injection device. Each injection device consisted of an ISCO pump and an intermediate container. A constant speed pump with a flow accuracy < 0.01 mL/min and a pressure accuracy < 0.5% could deliver liquids to the apparatus at a preset, constant volumetric flow rate. The image acquisition and recording system consisted of a visualization device, a planar light source, a high-precision microscope with 200-fold magnification, and a computer with intelligent acquisition software. The high-definition (HD) visualization device was composed of two pieces of transparent glass. The stainless steel frame was used to seal the glass to avoid the influence of evaporation on oil. There was a certain thickness gap between the glasses to facilitate fluid flow. During the experiment, oil and water were placed in a gap. Oil floated on top of water because of its light density. This process was used to simulate oil floating on the water surface. The light could cover the entire window, and the HD microscope could capture the emulsion status in the gap.

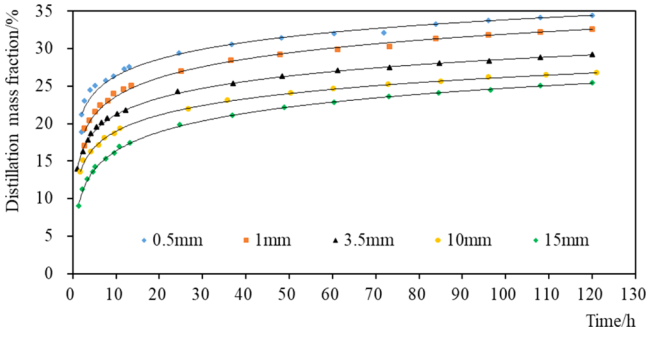

Figure 6. Effect of the oil film thickness on the evaporation process.

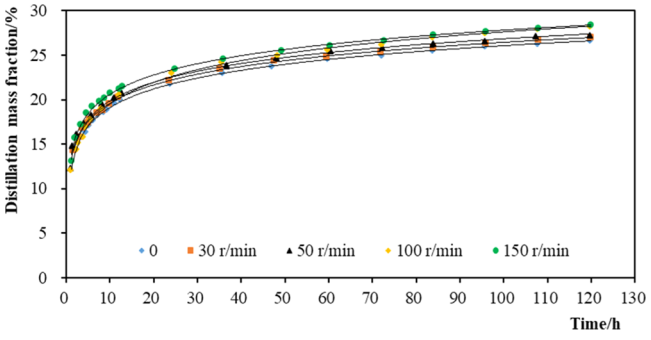

Figure 8. Effect of the rotating speed on the evaporation process.

3.2. Experimental Schemes. Oil spill emulsification usually referred to the process of oil and water mixed together to form water-in-oil emulsion or oil-in-water in the

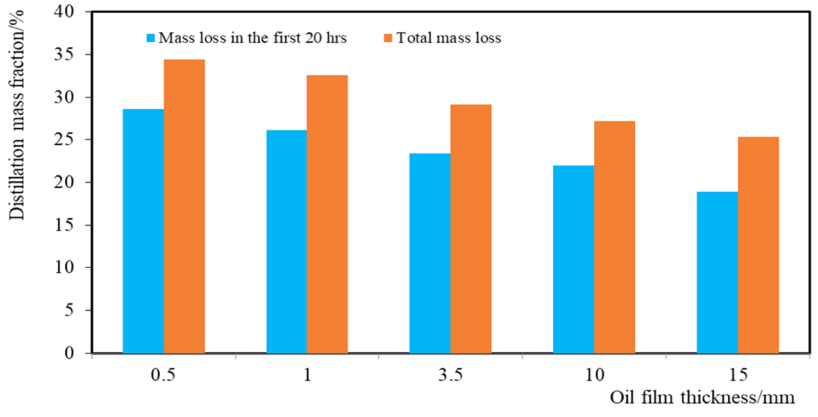

Figure 7. Evaporation characteristics with different oil film thicknesses.

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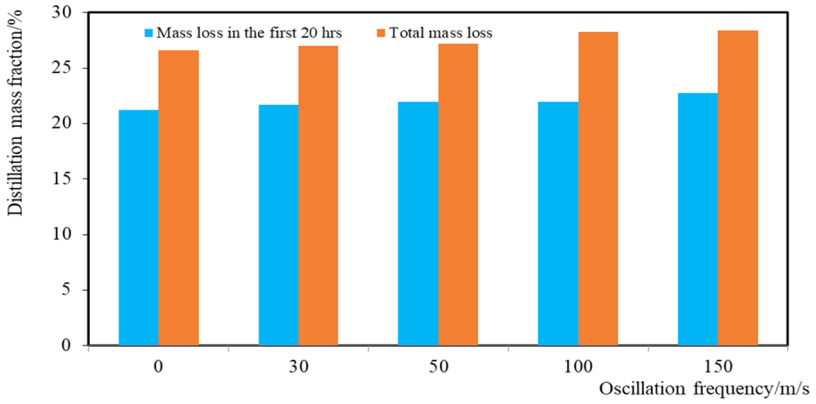

Figure 9. Evaporation characteristics with rotating speed.

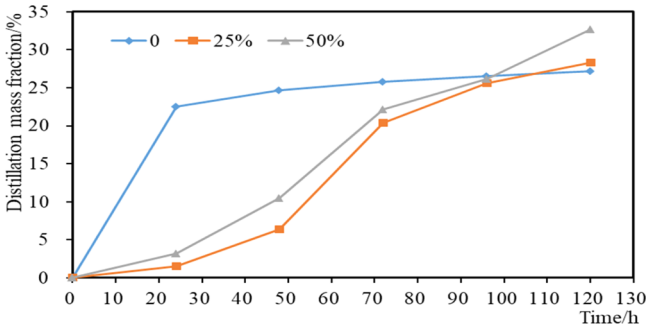

Figure 10. Evaporation curve of emulsion of oil sample A.

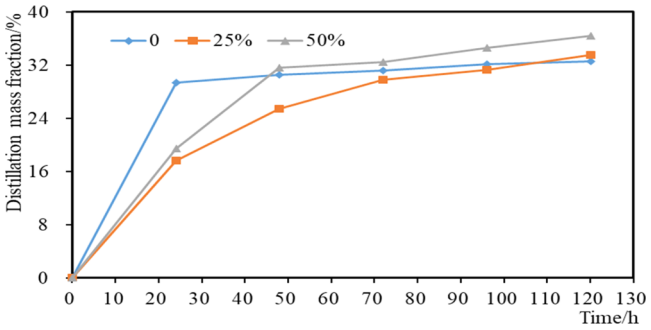

Figure 11. Evaporation curve of emulsion of oil sample B.

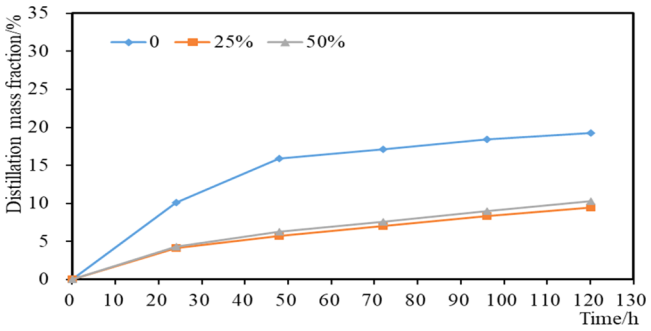

Figure 12. Evaporation curve of emulsion of oil sample C.

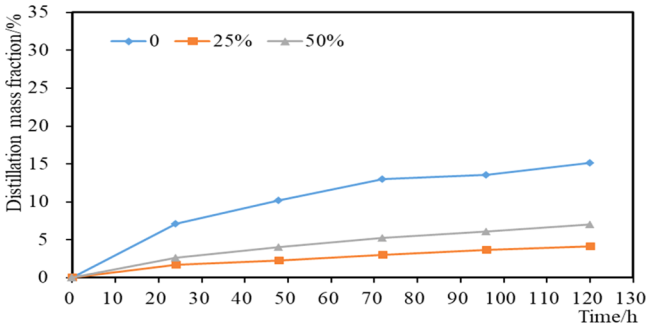

Figure 13. Evaporation curve of emulsion of oil sample D.

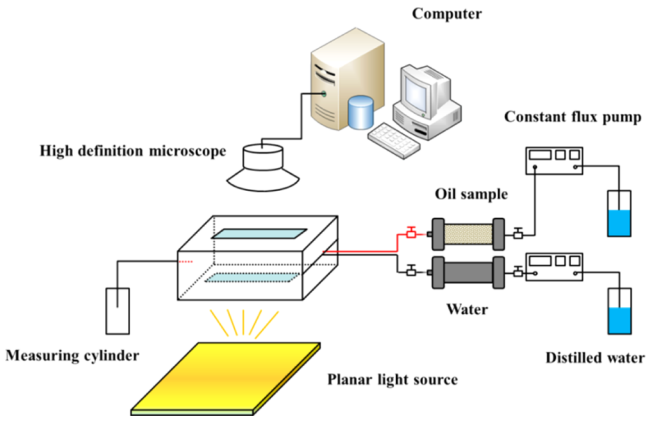

Figure 14. Visualization experiment flow chart of oil spill emulsification.

Table 4. Mass Loss of Oil Samples with Different Oil Film Thicknesses

oil film thickness, mm	0.5	1	3.5	10	15
mass loss in the first 20 h	28.6%	26.11%	23.4%	21.96%	18.87%
total mass loss	34.44%	32.59%	29.16%	27.21%	25.38%
proportion	83.04%	80.12%	80.25%	80.71%	74.35%

process of oil spill weathering. The formation of emulsified oil will go through three processes: oil spill diffusion, oil−water mixing, and emulsion formation. However, it was not easy to distinguish between oil−water mixing and emulsion formation. In order to effectively observe the emulsification phenomenon after oil spill evaporation, six groups of visualization experiments have been performed to investigate the emulsification behavior of the oil spills under different conditions, and the detailed experimental scheme of oil spill emulsification is shown in Table 5. Four different oil samples were used in the experiment, and the composition of the oil samples is shown in Table 1.

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Table 5. Experimental Data for Emulsification Weathering

run no.	evaporation time	oil sample
1	0	A
2	20	A
3	120	A
4	0	B
5	0	C
6	0	D

3.3. Experimental Procedures.

(1) Connecting process. Each device and auxiliary equipment was installed as shown in Figure 9, and HD visualization equipment was installed on the shelf so that the light emitted by the plane light source can pass through the visual window.
(2) Pre-experiment preparation. According to the experimental scheme, water and oil spills were injected into the visualization system to simulate the spreading of oil spills floating on water.
(3) Data acquisition. The flow state of emulsions could be observed through a high-precision visualization window and terminal image acquisition software. The microscope terminal equipment recorded the emulsification characteristics of the oil spills and collected HD images every 1 min.
(4) Data processing and result analysis. Emulsification characteristics under different conditions were recorded as HD images. Different behaviors could be observed from these pictures.

4. RESULTS AND DISCUSSION

4.1. Experimental Results and Analysis of Evaporative Weathering. The oil spills were placed in a stainless steel shallow plate to simulate the evaporation process, and the effect of the temperature on the oil spill evaporation was studied. Experiments 1−5 had the same experimental conditions except for temperature, and the experimental temperatures were 5, 10, 15, 20, and 25 °C, respectively. Mass loss was monitored at selected time intervals and a graph of percentage weathering as a function of time at five different temperatures was plotted, as shown in Figure 2. With the increase of weathering time, the mass loss became more and more. The rate of mass loss within 10 h was very fast, it gradually slowed down from 10 to 20 h, and then tended to be stable, 80% mass loss occurred in the first 20 h, as shown in Figure 3. Figure 2 depicts that the higher the ambient temperature was, the greater the mass loss was. Petroleum was a mixture of saturated hydrocarbon, aromatic hydrocarbon, resin, asphaltene, and other hydrocarbons, in which the volatile properties of each component were different, and the light components had strong volatility. Therefore, the oil spills had their particularity in the evaporation process. The evaporation of hydrocarbon mixtures could be divided into three steps. The molecules first move from the liquid phase to the surface, then from the liquid phase barrier layer to the gas-phase boundary layer, and finally from the gas-phase boundary layer to the atmosphere. Temperature obviously affected the three processes of evaporation. The higher the temperature was, the more intense the molecular thermal movement would be, so the liquid molecules would be easier to migrate from the liquid phase to the liquid phase surface, and the gas molecules would also be easier to diffuse from the boundary layer to the atmosphere. Meanwhile, with the increase of ambient temperature, the molecular thermal movement of oil accelerated, which made it easier to escape from the oil surface and enter the gas-phase space, thus increasing the saturated vapor pressure of oil and the evaporation loss.

Experiments 6−10 had the same experimental conditions except for wind velocity, and the experimental wind velocities were 0.05, 0.46, 1.5, 2.8, and 5.13 m/s, respectively. Mass losses were monitored at selected time intervals and a graph of percentage weathering as a function of time at five different wind velocities was plotted, as shown in Figure 4. This series of experiments confirmed the same rule, showing that the mass loss increased with weathering time and rapid evaporative loss occurred in the first 20 h. For example, when the wind velocity was 0.05 m/s, a weathered fraction of experimental oil sample with a mass loss of 12% after 20 h of weathering was recovered. Then, the evaporation rate slowed down, and the remaining weathered fraction of the sample oil was prepared by extending the weathering time to 120 h, resulting in a mass loss of 18.3%. Based on the graph in Figure 5, it took 20 hours to evaporate the initial two-thirds of the mass loss (12%)and 100 hours to evaporate the remaining third (12−18.3%), respectively.

It could also be concluded from Figure 4 that the wind velocities had a great influence on the evaporation behavior of the oil sample. The increased mass loss was different under different wind velocities. When the wind velocity was 0.05, 0.46, 1.5, 2.8, and 5.13 m/s, the evaporation mass loss of oil spills in the first 20 h is 12, 17.2, 19.5, 22, and 22.4%, respectively. For the first 20 h of evaporation weathering, with the increase of wind velocity, the increased loss of oil spills increased rapidly and then tended to be flat. Based on the above analysis, hydrocarbon evaporation was controlled by three steps, and wind velocity may affect the latter two steps, including molecules entering the gas-phase boundary layer from the liquid-phase boundary layer and molecules spilling into the atmosphere from the gas-phase boundary layer. With the increase of wind velocity, the volatilization rate of molecules from the liquid phase boundary layer to the gas-phase boundary layer increased, and the concentration of molecules in the liquid phase boundary layer also decreased, which will lead to a gradual decrease of the impact of the wind speed on molecules from the liquid phase boundary layer to the gas-phase boundary layer.

Experiments 11−15 had the same experimental conditions except for the oil film thickness, and the experimental oil film thicknesses were 0.5, 1, 3.5, 10, and 15 mm, respectively. Mass losses were monitored at selected time intervals and a graph of percentage weathering as a function of time at five different oil film thicknesses was plotted, as shown in Figure 6. This series of experiments confirmed the same rule, showing that the mass loss increased with weathering time and rapid evaporative loss occurred in the first 20 h. Table 4 presents the mass loss of oil samples at different times and the proportion of mass loss in the first 20 h to the total evaporation time for different oil film thicknesses. It could be seen that the mass loss in the first 20 h was about 80% of that in the whole evaporation weathering process under different experimental conditions. For example, when the oil film thickness was 0.5 mm, a weathered fraction of the experimental oil sample with a mass loss of 28.6% after 20 h

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of weathering was recovered. Then, the evaporation rate slowed down, and the remaining weathered fraction of the sample oil was prepared by extending the weathering time to 120 h, resulting in a mass loss of 34.44%, and the mass loss in the first 20 h is 83.04% of the whole evaporation and weathering process. It can also be observed that the thinner the oil film thickness was, the greater the mass loss in the first 20 h (Figure 7). When the oil film thickness is 0.5, 1, 3.5, 10, and 15 mm, the proportion of mass loss in the first 20 h to the total evaporation time is 83.04, 80.12, 80.25, 80.71, and 74.35%, respectively. This is because the greater the oil film thickness, the slower the liquid molecules will migrate from the phase to the gas−liquid boundary layer, which affects the first step of evaporation weathering.

Experiments 16−20 had the same experimental conditions except for oscillation frequencies, and the experimental oscillation frequencies were 0, 30, 50, 100, and 150 rpm respectively. In these experiments, different wave conditions were simulated at different rotational speeds. Mass losses were monitored at selected time intervals and a graph of percentage weathering as a function of time at five different oscillation frequencies was plotted, as shown in Figure 8. This series of experiments also confirmed the same rule, showing that the mass loss increased with weathering time and rapid evaporative loss occurred in the first 20 h. It can also be concluded from Figure 9 that the rotating speed has little effect on evaporation weathering. This may be due to the high content of alkanes and low content of asphaltenes and colloid in the oil sample, so the oscillation does not affect the entire evaporation process under the experimental conditions.

From the above experimental results, it could be seen that oil spill evaporation was affected by temperature, wind speed, and the oil film thickness. The higher the temperature was, the greater the evaporation capacity was. Because the temperature had a great influence on the first step of evaporation, it speeded up the molecular thermal movement, improved the escape of liquid molecules from the gas−liquid surface, and increased the evaporation capacity. When the wind speed was small, the evaporation increased with the increase of the wind speed. When the wind speed increased to a certain extent, the evaporation of oil spills would not increase any more because the wind speed mainly controlled the third step of evaporation behavior, that is, the diffusion of hydrocarbons from the gas phase to the environment. The oil film thickness had a greater impact on evaporation. The thicker the oil film thickness was, the faster the evaporation speed was, and the greater the evaporation loss was. This was because it could control the first step of evaporation. Wave conditions had little effect on the evaporation of pure oil under the experimental conditions.

Several experiments have been performed to investigate the oil sample A evaporation behavior under different emulsification states. Experiments 21−23 had the same experimental conditions except for the water content in emulsion, and the experimental water contents were 0, 25, and 50%, respectively. In order to calculate the evaporation of oil in water-in-oil emulsion, it was necessary to separate the oil−water mixture. A new emulsion evaporation experiment was needed to be conducted to calculate the mass loss of oil in water-in-oil emulsion at different times, such as experiments 22, 23, and so on. It can be seen from Figure 10 that the evaporation curves of oil sample A and emulsions of oil sample A present different behaviors. In the early stage of evaporation, the evaporation rate of pure oil was faster than that of water-in-oil emulsion. After 24 h, the evaporation of pure oil almost finished, and the evaporation rate of water-in-oil emulsion increased significantly 48 h later. It could be seen that the evaporation behavior of oil in emulsion was delayed in the early stage. The results showed that the oil mass loss of water-in-oil emulsion with a water content of 50% for 120 h evaporation weathering was the largest, followed by the loss of emulsion with a water content of 25%, and the loss of pure oil evaporation was the smallest.

At the beginning of the experiment, the structure of the semistable emulsion was not destroyed, which delayed the evaporation of the oil phase and the water phase. After 48 h, the structure of the semistable emulsion was destroyed, and the oil phase and water phase were evaporated, respectively. The evaporation rate of the oil phase increased subsequently, and the light components gradually evaporated. Meanwhile, the water phase also evaporated, and the water phase would carry part of oil. The higher the water content in the emulsion, the stronger the ability of water to carry oil.

Several experiments have been performed to investigate the oil sample B evaporation behavior under different emulsification states. The experimental water contents used in experiments 24−26 were 0, 25 and 50% respectively. In the early stage of evaporation (Figure 11), the mass loss of oil in pure oil was faster than that in water-in-oil emulsion. The evaporation behavior of oil in emulsions was relatively slow in the first 24 h, but the evaporation of pure oil almost finished. Similar to the above experimental results, the mass loss of oil in water-in oil emulsion with a high water content was high. Different from oil sample A, the oil sample B began to evaporate at the beginning of evaporation because of the unstable structure of water-in-oil emulsion, and the evaporation of the oil phase in the emulsion was almost not delayed. Due to the simultaneous evaporation of the oil phase and the water phase in the oil−water mixture, the evaporation rate of the oil phase is lower than that of the pure oil phase. Obviously, the unstable emulsions had little effect on evaporation.

Several experiments have been performed to investigate the oil sample C evaporation behavior under different emulsification states. Experimental water contents used in experiments 27−29 were 0, 25, and 50%, respectively. It can be seen from Figure 12 that the evaporation curves of oil sample C and emulsions of oil sample C present different behaviors. Due to the high content of heavy components in oil sample C, the emulsion is relatively stable, resulting in the oil loss of emulsions for 120 h is only about 10% in the evaporation process.

Several experiments have been performed to investigate the oil sample D evaporation behavior under different emulsification states. The experimental water contents used in experiments 30−32 were 0, 25 and 50%, respectively. It can be seen from Figure 13 that the evaporation curves of oil sample D and emulsions of oil sample D present different behaviors. The formed emulsion was relatively stable because of a high content of heavy components, so the oil loss in the evaporation process was smallest and the evaporation loss for 120 h was less than 7%.

Four groups of water-in-oil emulsion evaporation experiments showed that emulsification could inhibit evaporation, and the more stable the oil spill emulsions was, the stronger the inhibition was. In the evaporation process of unstable (oil

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sample B) and semistable emulsions (oil sample A), because the emulsion structure was not destroyed at the initial stage of evaporation, the evaporation of the oil phase was obviously inhibited, and the evaporation rate was low. The emulsion structure was destroyed after evaporation for a long enough time, and the oil phase and water phase began to evaporate at the same time. After evaporation for a long enough time, the emulsion structure was destroyed and the oil phase and water phase begin to evaporate at the same time. The evaporation of the water phase carried part of the oil components at the same time, resulting in more evaporation loss of the oil phase than pure oil. In the evaporation process of stable emulsions (oil samples C and D), the emulsions would inhibit evaporation for a long time because of the stable emulsion structure. Considering that the natural demulsification time of stable emulsion was long, this experiment could not last long enough due to the limitation of experimental conditions, and it was a pity that the evaporation behavior of stable emulsion after 120 h could not be tracked for a long time. At the same time, it was also the direction of future research.

4.2. Experimental Results and Analysis of Emulsion Weathering. The visualization experiments of oil spill emulsification were carried out by using a visualization device according to the experimental scheme. The emulsifying effect of oil samples under different conditions could be observed through the visualization window with the help of a high-precision microscope. The emulsification characteristics could be real-time captured and recorded in the form of HD images. The emulsification characteristics are shown in Figures 15−20. There were light transmission points with different sizes, colors, and shapes in the captured pictures of six groups of emulsion visualization experiments. What is the light transmission point? Because at the beginning of the experiment, the gap between the upper and lower visual windows was filled with oil and water, the oil was completely floating on the water surface, and the water was under the oil layer. In the initial state, the light could not pass through the oil−water double-layer visual window, and the photo should be completely black, so the light transmission point was the oil−water mixture.

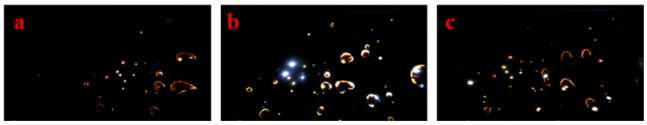

Figure 15. Emulsification for 31 (a), 53 (b), and 97 min (c) of oil sample A without evaporation.

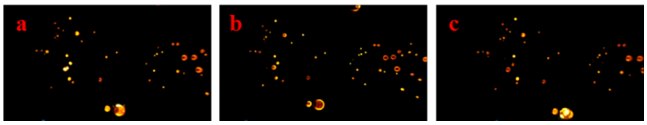

Figure 16. Emulsification for 29 (a), 49 (b), and 102 min (c) of oil sample A after evaporation for 20 h.

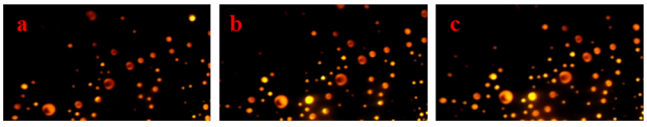

Figure 17. Emulsification for 17 (a), 51 (b), and 120 min (c) of oil sample A after evaporation for 120 h.

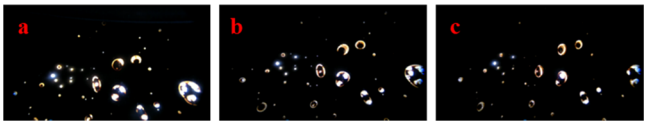

Figure 18. Emulsification for 39 (a), 61 (b), and 123 min (c) of oil sample B without evaporation.

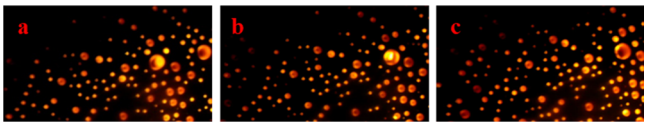

Figure 19. Emulsification for 9 (a), 60 (b), and 120 min (c) of oil sample C without evaporation.

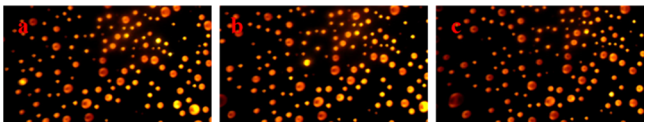

Figure 20. Emulsification for 7 (a), 60 (b), and 120 min (c) of oil sample D without evaporation.

Figure 15 shows the mixture of unevaporated oil sample A with water, and single or multiple water-in-oil emulsions were observed to form in the experiment 1. The three small pictures in Figure 15 show the oil−water emulsification state at the same position at different times, and it was obvious that the three pictures showed great differences. Figure 15a shows only a small part of the oil−water emulsification phenomenon, and the remaining area was of the single-phase oil film state. The water phase was distributed in the oil phase in the form of dots or lines, and the color of emulsion was black or brown. The emulsification area in Figure 15b was more than that in Figure 15a. It could be seen that the water droplets were covered with the thin black oil film, but the size of emulsion was irregular. Water was also distributed in oil in point or line shape, and stable emulsion and unstable emulsion appear at the same time in Figure 15c. Obviously, the oil sample A without evaporation weathering could form a semistable water-in-oil emulsion after mixing with water, and the emulsion was black or brown.

Figure 16 shows the mixture of oil sample A after evaporation weathering for 20 h with water, many stable yellowish brown or reddish water-in-oil emulsions of different sizes were observed to form in the experiment 2. The three small pictures in Figure 10 show the oil−water emulsification state at the same position at different times, and the shape and size of emulsions in the three pictures of Figure 16 were similar in addition to the change of the distribution position. Obviously, the oil sample A with evaporation weathering for 20 h could form locally a stable water-in-oil emulsion of different sizes after mixing with water, and the emulsion is yellowish brown and reddish brown.

Figure 17 shows the mixture of oil sample A after evaporation weathering for 120 h with water, many stable reddish water-in-oil emulsions of different sizes were observed to form in the experiment 3. The three small pictures in Figure 17 show the oil−water emulsification state at the same position at different times, and the shape and size of

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emulsions in the three pictures of Figure 17 were similar in addition to the change of the distribution position. Obviously, the oil sample A with evaporation weathering for 120 h could also form locally a stable water-in-oil emulsion of different sizes after mixing with water, and the emulsion is reddish brown. Compared with experiment 2, the area of emulsion formed in experiment 3 was relatively larger.

Figure 18 shows the mixture of unevaporated oil sample B with water, and single or multiple water-in-oil emulsions were observed to form in the experiment 4. The three small pictures in Figure 18 show the oil−water emulsification state at the same position at different times, and it was obvious that the three pictures showed great differences. In Figure 18a−c, only a small part of the oil−water emulsification phenomenon was present, and the remaining area was of the single-phase oil film state. In the oil−water mixing area, it could be seen that the water droplets were dispersed in the oil as dots, or the oil droplets were dispersed in the water, and did not form stable water-in-oil emulsion or oil-in-water emulsion. Obviously, the oil sample B could not form stable and semistable water-in-oil emulsion after mixing with water.

Figure 19 shows the mixture of oil sample C with water, many stable reddish water-in-oil emulsions were observed to form in the experiment 5, and the size distribution of the emulsion is relatively uniform and the sizes were approximately the same. The three small pictures in Figure 19 show the oil−water emulsification state at the same position at different times, and the shape and size of emulsions in the three pictures of Figure 19 were similar in addition to the change of the distribution position. Obviously, the oil sample C could also form a stable water-in-oil emulsion of the same size after mixing with water, and the emulsion is reddish brown.

Figure 20 shows the mixture of oil sample D with water, many stable reddish water-in-oil emulsions were observed to form in the experiment 6, and the size distribution of the emulsion was relatively uniform and the size was approximately the same. The three small pictures in Figure 14 show the oil−water emulsification state at the same position at different times, and the shape and size of emulsions in the three pictures of Figure 20 were similar in addition to the change of the distribution position. Obviously, the oil sample D could also form a stable water-in-oil emulsion of the same size after mixing with water, and the emulsion was reddish brown. Although the morphology of emulsion in experiment 4 was not completely consistent with that in experiment 3, it showed the same behavior on the whole.

Due to different oil samples, pictures of six groups of experiments were also different, and the oil−water emulsification phenomenon revealed was also different. In experiments 1−3, oil sample A was not evaporated and weathered, oil sample A was evaporated and weathered for 20 h, and oil sample A was evaporated and weathered for 120 h, respectively. The results showed that black or brown unstable emulsions appeared in experiment 1, yellowish brown or black brown stable emulsions appeared in experiment 2, and reddish brown stable emulsions appeared in experiment 3. In experiment 1, because the oil sample was not evaporated, the content of light components was higher, and the content of asphaltene was relatively less, which was 4.5%, forming an unstable emulsion. In experiment 2, the oil sample evaporated and the content of light components decreased, which led to the increase of the asphaltene content and the formation of a relatively stable emulsion. In experiment 3, the oil sample evaporated and the evaporation process basically ended, which further increased the asphaltene content and formed a very stable emulsion.

The emulsion droplets formed in experiment 2 were dispersed, and the emulsion droplets formed in experiment 3 were relatively dense. This is because the oil sample in experiment 2 was obtained after evaporation of oil sample A for 20 h. Due to the evaporation process, the evaporation of oil sample A is uneven, which will lead to the inconsistency of the original oil composition in the oil sample after evaporation of the oil sample A for 20 h, resulting in the instability and dispersion of the emulsion. The oil sample in experiment 3 was obtained after oil sample A was fully evaporated for 120 h. The evaporation of the oil sample was relatively sufficient, and the components of the oil sample basically tended to be the same, so the asphaltene content of each component was relatively consistent, which was convenient for the formation of stable water-in-oil emulsions. From another point of view, evaporation weathering promotes oil spill emulsification.

Experiments 1 and 4−6 had the same experimental conditions except for components, and the detailed components are presented in Table 1. The results of experiment 4 showed that when the asphaltene content of the oil sample is 1.9%, the oil−water mixture could not form a stable emulsion. In Figure 15, there are several broken oil films. The whole picture was black and white, and the water phase could be clearly seen. The oil film strength was not enough to wrap small water droplets, so the water droplets could be seen to crush the oil film. The results of experiment 1 showed that when the asphaltene content of the oil sample was 4.5%, the oil−water mixed flow formed part of stable oil-in-water emulsion and part of unstable oil-in-water emulsion, and the unstable emulsion was black or brown, which indicated that with the increase of the asphaltene content, the oil film strength could wrap small water droplets, but it was not stable. The results of experiment 5 showed that when the asphaltene content of the oil sample was further increased, the formed emulsion was more stable, and the emulsion was reddish brown. Only a few emulsions had the signs of water droplets crushing the oil film, which indicated the asphaltene content was not enough to form a stable oil film. The results of experiment 6 showed that when the asphaltene content of the oil sample was 14.5%, the emulsion was more stable, which means that the particles of the emulsion were more uniform, and there was no phenomenon of water droplets breaking the oil film. This experiment further showed that the higher the asphaltene content was, the easier for the oil spill to emulsify. These experiments further proved that the evaporation of oil spill could promote emulsification.

5. CONCLUSIONS

In view of the findings in this study, the following conclusions could be drawn.

1. On the basis of a series of stainless steel shallow plate oil sample evaporation experiments, the influencing factors of oil evaporation were researched. By measuring and analyzing the mass loss of oil samples with time during the evaporation, the influences of temperature, the wind speed, the oil film thickness, and the rotating speed on oil spill evaporation were

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obtained. The increase of temperature could promote the evaporation of the oil sample. The thin film thickness was beneficial to oil evaporation. The increment of the wind speed could promote oil evaporation when the wind velocity was small, and the increase of the wind speed had little effect on oil evaporation when the wind velocity was large. Wave conditions had little effect on oil evaporation under the experimental conditions.

2. On the basis of a series of stainless steel shallow plate evaporation experiments of oil samples after emulsification, the effect of emulsification weathering on evaporation weathering was studied. The effect of different emulsification states on oil evaporation was not consistent. Unstable or semistable water-in-oil emulsions inhibited oil evaporation at the initial stage of evaporation, but water evaporation would increase oil evaporation with the destruction of the emulsion structure. Stable water-in-oil emulsions inhibited evaporation weathering of oil.
3. On the basis of microscopic visualization experiments of oil emulsification after evaporation, the effect of evaporation weathering on emulsification weathering was investigated. The characteristics of water-in-oil emulsions formed by oil samples of different components were different. The higher the content of asphaltene was, the more stable the water in oil emulsion was. The evaporation weathering of oil is conducive to the emulsification of oil.

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Notes

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