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EXPERIENCE IN THE USE OF OIL-MINERAL AGGREGATION FOR LIQUIDATION OF EMERGENCY OIL SPILLS IN ICY SEAS

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Abstract: The influence of the process of oil-mineral aggregation on the emulsification of oil and dark oil products in world practice has been known since the end of the last century. Despite a significant number of studies indicating the applicability of this process for cleaning coastlines from accidental spills, the effectiveness of oil-mineral aggregation in the elimination of oil slicks in open water and in ice conditions of the shelf zone is not well understood. Of particular interest is the study and evaluation of the effectiveness of this process from the point of view of bioremediation, hydrometeorological conditions, physico-chemical properties of the spilled product and the technology of work. This paper provides a brief overview of world studies on the study of the oil and mineral aggregation process to assess its applicability as a response to emergency oil spills in ice seas.
Keywords: oil-mineral aggregation process, oil spill response, icy seas, clay-oil flocculation

INTRODUCTION

Since the widespread use of dispersants as a means of responding to emergency oil spills in ice seas is constrained by a number of factors [1, 2], there are few examples in the world practice of using the oil-mineral aggregation process for these purposes [3].

The process of oil-mineral aggregation (OMA) involves the interaction of oil globules and fine particles of sedimentary rocks, which leads to the formation of new compounds - microaggregates, the structure of which prevents the re-coalescence of oil. Thus obtained oil-mineral microaggregates (OMM) allow, under certain conditions, to disperse oil spills to concentrations below threshold toxic levels, as well as accelerate the natural processes of their biodegradation.

In theory, with sufficient wave energy of mixing, the oil slick disperses in the aqueous phase in the form of micron-sized oil globules (Fig. 1), stabilized, as a rule, on the surface with finely dispersed mineral particles.

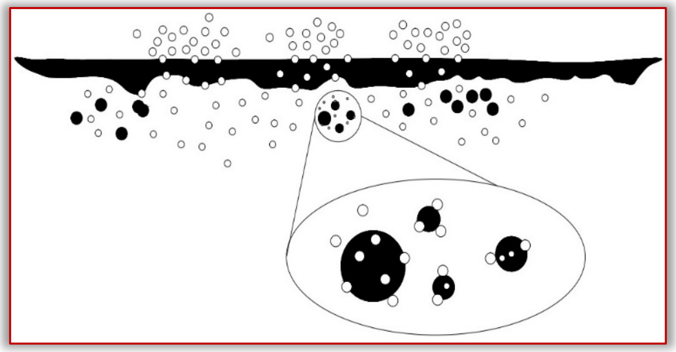

Figure 1. Dispersion of oil slick in the water column by OMA

The resulting petemineral microaggregates reduce the adhesion of oil to solid surfaces, promote the formation of stable globules, preventing re-coalescence of oil, which leads not only to its dispersion in the liquid column, but also to an increase in the rate and degree of microbiological degradation due to an increase in the oil-in-water interface compared to oil slick [4].

The most common type of OMM is an oil globule stabilized over the surface of fine particles of sedimentary rocks. However, the authors of [5] described OMMs, which are a core covered by a layer of oil from a rock particle, as well as large OMMs of a membrane structure. Observed by the authors of the OMM oil-covered clay had an oblong, curved or even branched shape. Membrane OMMs reached several millimeters in length, had a flaky shape (Fig. 2) and positive or neutral (zero) buoyancy.

Figure 2. Flake-type membrane OMM [5]

MATERIAL AND METHODS

— Clay-oil flocculation

A prerequisite for using the OMA-process as a response to emergency oil spills in offshore areas was the Exxon Valdez tanker accident in March 1989.

As a result of the release of oil from an Exxon tanker off the coast of Alaska, about 260 thousand barrels of oil spilled into the water of the Prince William Strait with the formation of a spot with an area of 28 thousand square kilometers. The inaccessibility of the accident area made it impossible to timely localize the oil spill, which led to the spread of the stain to the prince Wilhelm Strait. A day after the accident, a spot on the surface of the water was treated with dispersant sprayed from an airplane, but due to the lack of disturbance at sea, there was no significant effect (only 1% of the volume of spilled oil was transferred to the bottom layer). Incineration measures also did not take effect due to weather conditions. The work of skimmers was limited by the thickness of the slick film and by the fact that the oil managed to mix with brown algae in the water per day. Thus, about two thousand kilometers of the coastline were polluted.

A few years after observing the ecosystems of contaminated territories, researchers [6] found that some of the methods and tools used after the Exxon Valdez tanker accident to eliminate the oil spill on the coastline could be more harmful to the environment than their lack of. At the same time, the researchers for the first time noted the effect of "self-cleaning" of beach areas composed of sedimentary rocks.

A similar effect was observed and was used in response to the emergency spill in Tampa Bay (USA), when on August 10, 1993, as a result of the collision of the ocean-255 tanker barge, the B-155 tanker barge and the Balsa 37 cargo ship South of the Mullet Key Island in the Gulf of Mexico, about 1,000 barrels of diesel fuel and 10,500 barrels of fuel oil were dumped into the water. Most of the resulting hydrocarbon mixture, drifting along the surface of the water along the coast, contaminated almost 21 km of the sandy beaches of Pinellas Park (Florida). [7]

A probable explanation for this "natural self-cleaning" was given by the authors [8, 9] at the XVII Arctic and Marine Oilspill Program (AMOP) in 1994, and the process of the interaction of oil and fine particles of sedimentary rocks was originally called "clay-oil flocculation".

— Wave washing

When liquidating a spill on the coast of the Tampa Bay, an attempt was first made to use the "clay-oil flocculation" process as an additional measure to combat pollution. After excavating 39827 cubic yards of oil-contaminated sand, the remaining soil was mixed and transferred from the upper littoral and supralittoral zone to the lower. Since during the operations the wave action in the surf zone was minimal (breakers with a height of less than 10 cm), the recorded accelerated removal of oil from the soil was associated with the interaction of oil and mineral particles, and not with physical abrasion [7]. These observations were correlated with the results of field tests previously carried out by researchers [10, 11] on beaches with low wave energy surfs, as a result of which it was found that mechanical mixing procedures increase the rate of dispersion of oil from contaminated soils.

Thus, the prerequisites were created for the emergence of a new approach to the elimination of emergency oil spills in coastal environments with insufficient hydraulic energy, which could be used in addition to the traditionally used excavation and mechanical mixing and on rocky beaches.

This method, which consists in transferring oil-soaked soil forming a coastal surface to the surf zone, where a wave action stimulates the formation of oil globules, resuspension of sedimentary rock particles and the formation of OMM (Fig. 3), was called "wave washing" (or "washing of beaches") and was successfully tested in the aftermath of the See Empress tanker accident. [12-14]

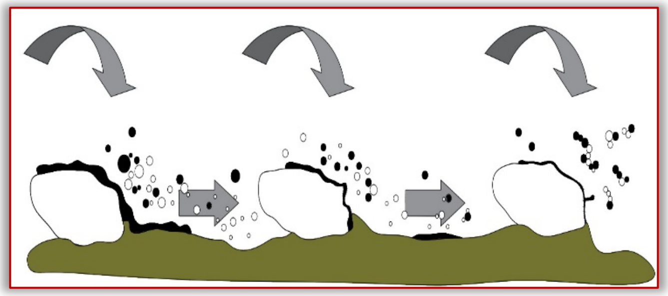

Figure 2. "Wave washing" of pebble contaminated with oil while moving it to the sandy bottom in the surf zone

On February 15, 1996, the Sea Empress tanker ran aground off the southwestern coast of Wales (UK). As a result of the accident, about 73 thousand tons of crude oil spilled onto the water surface and, after the drift of the spot, 201 km of the coastline were polluted, including the territory of the Pembrokeshire National Park and the resort beach Amrot.

Studies of water samples from rocky beaches contaminated during the Sea Empress tanker accident confirmed the presence of natural oil and mineral aggregation. Active wave washing operations on Amroth Beach helped to remove oil not only due to abrasion associated with high waves and surf, but also by stimulating the interaction between oil and fine mineral particles under pebble, which was mechanically mixed excavator and transfer to the surf zone.

The results were so significant that after four days of treatment, the cleaning operations were stopped, since the concentration of the oil emulsion on the pebble was reduced from 15.2 g / kg to 0.94 g / kg. Visual observations showed [13] that 50% of the oil was extracted from the pebble in the form of dispersed drops of oil stabilized by mineral fine particles. The rest of the oil was extracted in the form of a condensed mass, according to the authors [13], obtained due to physical abrasion, weathering and, possibly, with the assistance of some mineral particles in the oil emulsion.

After achieving such significant positive results when cleaning the Amrot beach from oil using the "wave washing" method, it was approved for use on a more environmentally vulnerable and difficult to restore territory - Marros Beach of the Pembrokeshire Coast National Park, where the contaminated soil was transferred to the surf zone manually without application of technology [13, 14].

In the summer of 1997, in the course of field trials to assess the effectiveness of the selected methods for cleaning the coastline with a mixed soil type (sandstone, clay, and pebble) from accidental spills on the Spitsbergen archipelago (Svalbard), Norway, an IFO 30 fuel oil spill was conducted. In total 5500 l of fuel oil was applied to a preformed soil roll 3 m wide in the upper littoral zone of the three experimental sections of the coastline.

A week after the spill, the soil of the contaminated areas was subjected to mechanical mixing (plowing) and "wave washing" for bioremediation. The tests were carried out at water temperatures of 0 ° C - 2 ° C during the absence of ice and low wave energy (the wave height during the tests was less than 0.3 m).

Monitoring of the amount of oil remaining in the soil samples taken from the experimental plots was carried out six times, the latter was carried out 60 days after the "wave wash". The authors of [15, 16] noted that a sharp decrease in the amount of fuel oil was observed during the first five days after soil transfer to the surf zone, as well as the presence of oil-mineral microaggregates in the samples.

— Accelerated biodegradation of oil

Since the total oil-water interface in oil-mineral microaggregates significantly exceeds the same slick area of the same oil volume, the authors of [17, 18] made an assumption about an increase in the rate and degree of microbiological degradation of oil in the presence of oil-mineral aggregation.

Confirmation of an increase in the degree of biodegradation of oil in the presence of fine particles of sedimentary rocks was obtained from field observations of both the natural restoration of contaminated beaches [8, 9] and the results of "wave washing" [12], while monitoring was carried out, including in arctic conditions.

Thus, according to the results of observations in May 1980 - August 1983, after the pilot oil spill response of the BIOS project in the area of Baffin Island, Canada, it was found that in the long term, in most cases, natural cleansing of the coastline of Arctic beaches is observed [19]. It is worth noting here that the author has not yet associated the observed effect with the influence of oil-mineral aggregation. However, the Svalbard field trials, during which "wave washing" was tested under arctic conditions, confirmed the presence of intangible organic matter and its effect on increasing the rate of oil biodegradation [15, 16].

Within the framework of exploratory research under the Canadian Coast Guard program (CCG), aimed at developing methods and means of eliminating spills in the water area of the mouth of the St. Lawrence River, the authors of [20] evaluated the effect of oil-mineral aggregation on the biodegradation rate of oil emulsified using OMM.

The finely dispersed mineral particles used in the experiment were separated in sedimentation columns from sedimentary rocks taken from the Laurentian Depression at the mouth of the St. Lawrence River. X-ray diffraction analysis revealed the main composition of the selected particles: 90% clay with a size of less than 2 nm) and 10% sludge with a size of 2 to 63 nm (including 38% quartz, 22% feldspars, 20% illite and 10% chlorite). Prior to testing, Terra Nova crude oil produced from a research well off the Atlantic coast of Canada was pre-weathered by evaporation for 18 hours.

500 ml Erlenmeyer flasks were filled with 300 ml of seawater with a salinity of 28 ‰, taken from the St. Lawrence River in the area of the proposed OSR works. Then, equal amounts of weathered oil and Bushnell Haas broth were added to each flask (the broth was introduced weekly throughout the experiment). Then, in all flasks, except for the control ones, finely dispersed mineral particles were introduced in a ratio of 1 to 3 with respect to oil, after which the flasks were placed on a horizontal shaker to break the surface tension and ensure the formation of oil-mineral microaggregates. Shaking lasted 24 hours.

Then the flasks were incubated in the dark at a constant temperature of 10 ° C on a rotary shaker. The experiment lasted fifty six days, with oil biodegradation control samples taken from Erlenmeyer flasks on the first, seventh, fourteenth, twenty-eighth and last day of the experiment. For each sampling interval, the flasks of both groups (with and without finely dispersed mineral particles) were randomly selected for detailed chemical analysis. To assess the effect of the interaction of oil with mineral particles on the adhesion of oil to solid surfaces, such as laboratory glassware, samples from each sampling were divided into the fraction of the aqueous phase (dispersed oil, free-floating oil and OMM suspended in the water column) and solid phase fraction (oil particles and / or mineral particles adhering to the surface of glassware).

Changes in the concentration and composition of the aliphatic and aromatic fractions of residual hydrocarbons were determined by gas chromatography and mass spectrometry (GC-MS).

Samples were introduced into a Hewlett-Packard 5890 Series II gas chromatograph equipped with an HP 5972 mass selective detector (MSD). The device worked in selective ion monitoring mode for the quantitative determination of specific components of saturated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). The concentration of specific compounds was determined by comparing the peak heights with the values of the recovery standards during extraction.

RESULTS AND DISCUSSION

Direct observations of samples from experimental flasks using UV-epifluorescence microscopy confirmed the presence of oil-mineral microaggregates consisting of oil droplets stabilized by mineral fine particles. The decrease in the adhesion of oil to the surface of glassware observed during the experiment was not taken into account by the authors of [20] when evaluating the results of chemical analysis, and they note that such dynamics can be explained by the presence of finely dispersed mineral particles in the flask.

Analysis of samples of the aqueous phase showed that mineral particles scattered oil into the aqueous phase (components > n-C25) and enhanced biodegradation (components < n-C25), and analysis of the dynamic series of samples during the experimental period showed that the addition of mineral fine particles increased the rate biodegradation of common aliphatic components.

As a result of analysis of samples on the seventh day of the experiment, the researchers found that the interaction between oil and mineral particles contributes to the start of the biodegradation of oil: 42.2% of the total amount of n-alkanes (from n-C13 to n-C35) decomposed in flasks with oil, treated with fine mineral particles. In the corresponding control flasks (without mineral particles), the same degree of biodegradation was achieved only on the twenty-eighth day.

During the experimental period, the authors of [20] found that the interaction between oil and mineral particles enhances both the rate and degree of biodegradation of oil.

The authors of [20] propose a quantitative increase in the biodegradation rate by statistical analysis, since oil concentrations exponentially decreased over time, but note that a significant increase in the overall rate of loss of n-alkanes was observed only in flasks with oil-mineral microaggregates.

In addition, the authors of [20] note that, contrary to the results of studies conducted earlier [4], the degree of biodegradation of oil during oil-mineral aggregation is not limited to aliphatic components, because their analysis of GC-MS revealed a similar trend in biodegradation and aromatic components.

CONCLUSION

Despite the fact that a number of laboratory studies and field observations indicate a positive effect of oil-mineral aggregation on the removal of oil from contaminated coastlines, including in the Arctic latitudes, the use of this physicochemical process as a separate measure to combat open water spills and with the presence of ice in the ice seas of the Arctic region, it remains today a matter requiring detailed study.

Of particular interest is the study and evaluation of the effectiveness of this process from the point of view of bioremediation, hydrometeorological conditions, physico-chemical properties of the spilled product, production technology, as well as solving the question of the potential for controlling the oil-mineral aggregation process to obtain the required efficiency under certain conditions.

Note:

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