Destruction of Oil Pollution on Soils by Ameliorant Based on Peat

L.D. Stakhina1*, T.I. Burmistrova2 and T.P. Alekseeva2
1Institute of Petroleum Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Academichesky Ave., 634021, Tomsk, Russia
2Scientific Research Institute of Peat Problems, 3, Gagarin st., 634050, Tomsk, Russia

Abstract

Biodestruction of crude oils of various chemical types recovered from different regions has been studied. Soil pollution with crude oil and oil products results in serious ecological problems in oil fields, that is especially characteristic for the North regions. Degradation of crude oil components was caused by the communities of micro-organisms obtained from various peat samples of the Tomsk Oblast. The micro-organisms were activated by mineral systems. Oil destruction level was defined by gravimetric determination after extraction from soils by methylene chloride; the elemental composition was also determined. The study has revealed that the efficiency of oil degradation ranges from 60% to 80% depending on peat sample and ambient conditions. In general, the content of alkanes (linear + cyclic) and aromatic hydrocarbons with alkyl chains decreased as a result of crude oil destruction. The content of oxygen compounds decreased 2-3 times. As to nitrogen-containing compounds they completely disappeared in the biodegraded samples.

Introduction

Urgency of ecological problems due to increasing development of oil fields has resulted in search for various methods of oil pollution removal for both water and soil ecological systems. Though the consequence of oil spilling on the pond surface can be removed easily by means of various adsorbents, the soil purification from oil is much more complicated and practically cannot be performed by methods of the productive cultivation.

Lately much attention has been paid to the development of biological cultivation methods based on activation of the processes of oil microbiological destruction in soil. Peat is known to be a high-efficiency adsorbent of oil components; moreover, it contains various species of naturally occurring hydrocarbon-oxidizing community that are capable of oil degradation [1]. Sorption capacity of peat for oil depends on the decomposition degree and is 8-10 for high-moor peats and 6-8 for valley peat per 1 g of oven-dry substance [1]. The aim of the research done by us is to obtain an ecologically pure, wasteless ameliorant based on peat with high sorption capacity and enriched with the active hydrocarbon oxidising micro-organisms.

Analyses of the content of micro-organisms

The analysis of the total number of the micro-organisms in peats studied was performed by inoculating agars nutritive medium, which mineral composition corresponds to the liquid Mounts medium.

Elemental analysis

The contents of carbon and hydrogen were measured by pyrolysis in oxygen flow followed by gravimeter [2]. Sulphur content was determined by Schoeniger’s combustion method. Nitrogen content was determined by method of oxidative destruction over a nickel oxide catalyst [2].

Oil destruction level was determined by gravimeter method after extraction by methylene chloride [3].

Results and Discussion

At the initial stage of the research we studied the changes in oil composition under the action of microbial communities of different peats of the peat fields of the Tomsk Oblast. Using the commercial
oil mixture of the West Siberia we have tried to select a peat, which would be the most active in the destruction of the oil components, among the peat samples of the Tomsk Oblast. The results of the analysis of the population of the hydrocarbon oxidizing micro-organisms (HOM) in 4 studied species of the native peat of the Tomskoye peat field under natural humidity conditions have demonstrated that the maximal HOM number is contained in the valley peats of Taganskoye and Temnoye peat fields (2229.4×10^6 and 1239.9×10^6 cells per 1 g of oven-dry substance (o.d.s.), respectively). Minimal HOM populations are in the valley peat of Kandinskoye field (628.6×10^6 per 1 g of oven-dry substance) and the high-moor peat of the Temnoye field (522.4×10^6 cells per 1 g o.d.s.). It has been found that the number of hydrocarbon oxidising micro-organisms in the native peat from the Tomsk region is 4-5 times higher than the same index for mineral soil. After physical-chemical activation of peat the number of subject micro-organisms in it increases by 100 times and makes 5×10 cells/1 portion of o.d.s in average. Peat hydrocarbon-oxidizing community is rather various in respects of species; mainly it consists of mesophilic bacilli, actinomycetes and pro-actinomycetes.

Figure 1 shows the results of the destruction of the commercial oil mixture of the West Siberia under the action of peats HOM of the Tomsk Oblast.

As seen from Fig. 1, in 3 months a reduction in weight of the commercial oil introduced by from 72 to 85% was observed for all the peat samples studied, which points to an intensive process of its destruction. The most drastic reduction in the weight of an oil sample was noted for Temnoye valley peat, in which the initial oil mass was finally reduced to 15.4%. The least degraded oil sample was observed in the experiment with the micro-organisms of Kandinskoye peat field, the reduction in mass of this sample was 41.3% only.

On the subsequent experiments on destruction of the oil of different compositions, we took the samples of Temnoye valley peat, which had the highest HOM content and possessed the highest degradation activity for oil components.

The crude oils of various fields that significantly differ by physicochemical properties (Table 1).

The initial crude oils differed from each other by elementary and fractional compositions. Commercial mixture of West-Siberian oils (Russia) and crude oils of Vietnam (White Tiger and Dragon) are high-paraffin ones and contain approximately equal amounts of saturated and aromatic hydrocarbons. Crude oil of Liao He oil field (China), by the contrast, contains less amount of hydrocarbons and greater amount of resin-asphaltene structures. The results of the structure analysis are confirmed by high values of H/C ratios (1.7–1.9 respectively) of commercial mixture of West-Siberian oils and crude oils of Vietnam, which evidences, by the difference to the crude oil of Liao He oil field (H/C 1.4), the predominance of alkanes (linear+cyclic) over aromatics. The oils studied also differ by the content of heteroatomic (S, N, O) compounds: their greatest amount is in the commercial mixture of West-Siberian oils and crude oil of Liao He field.

The study of the micro-organisms of the peats of the Tomsk Oblast gave positive results also at the destruction of the oils from other regions of a chemical composition differing from West-Siberian oils (Table 2).

As seen from the data of the Table 2, the initial oil samples had various contents of alkanes (linear + cyclic) and aromatic hydrocarbons (H/C ratio was about 1.4 and 1.9 for Liao He oil and Vietnam oils, respectively). The highest content of heteroatomic compounds was in Liao He oil, the lowest one – in Vietnam oils. In one month, in accordance with the data of elemental analysis, C, N and H contents in oils decreased under the microbiological action. The decrease in C and H contents evidences a preferential destruction of aliphatic hydrocarbons or alkyl substitutes in the nuclei of aromatic and cyclic rings. As known [4], n-alkanes degrades with rapid growth rates would out-compete the slow-growing decomposers of the more recalcitrant hydrocarbons for the nutritional resources until the n-alkanes are depleted. These organisms would then be replaced by microbes...
Table 1
General characteristics of oils

| Characteristics | Values |
|-----------------|--------|
|                 | Com. Mixture of West-Siberian oils (Russia) | White Tiger (Vietnam) | Dragon (Vietnam) | Liao He (China) |
| Density, g/cm³  | 0.8634 | 0.8328 | 0.8526 | 0.9629 |
| Composition, %: |
| C               | 86.83  | 86.01  | 86.13  | 86.71  |
| H (H/C)         | 12.53 (1.7) | 13.61 (1.9) | 13.37 (1.9) | 10.46 (1.4) |
| N               | 0.11   | 0.11   | 0.19   | 0.53   |
| S               | 0.44   | 0.03   | 0.04   | 0.19   |
| O               | 0.09   | 0.24   | 0.27   | 2.18   |
| Hydrocarbons:   | 92.3   | 98.1   | 91.3   | 74.2   |
| Alkanes         |
| (linear + cyclic) | 65.4   | 90.1   | 80.7   | 54.3   |
| Aromatic        | 26.9   | 8.0    | 10.6   | 19.9   |
| Resins          | 5.3    | 1.2    | 6.0    | 20.0   |
| Asphaltenes     | 2.4    | 0.7    | 2.7    | 5.8    |

Table 2
Characteristics of the initial and biodegraded (1 and 6 months) oils

| Oil, oil field | Sample | Content, wt.% |
|----------------|--------|---------------|
|                |        | C  | H  | H/C | N  | S  | O  |
| Commercial mixture of West-Siberian oils (Russia) | Initial | 86.83 | 12.53 | 1.7 | 0.11 | 0.44 | 0.09 |
|                | Biodegrad. 1 m | 86.60 | 12.38 | 1.7 | Traces | 0.85 | 0.17 |
|                | Biodegrad. 6 m | 86.92 | 11.56 | 1.6 | Traces | 1.42 | 0.10 |
| White Tiger (Vietnam) | Initial | 86.01 | 13.61 | 1.9 | 0.10 | 0.03 | 0.25 |
|                | Biodegrad. 1 m | 85.50 | 12.83 | 1.8 | Traces | 0.16 | 1.51 |
|                | Biodegrad. 6 m | 86.66 | 12.30 | 1.7 | Traces | 0.40 | 0.64 |
| Dragon (Vietnam) | Initial | 86.13 | 13.37 | 1.9 | 0.19 | 0.04 | 0.27 |
|                | Biodegrad. 1 m | 85.62 | 13.14 | 1.8 | Traces | 0.63 | 0.61 |
|                | Biodegrad. 6 m | 86.29 | 12.25 | 1.7 | Traces | 1.21 | 0.25 |
| Liao He (China) | Initial | 86.71 | 10.46 | 1.4 | 0.53 | 0.12 | 2.18 |
|                | Biodegrad. 6 m | 85.58 | 9.29  | 1.3 | 0.01 | 0.32 | 4.80 |

with slower growth rates but greater metabolic flexibility to degrade the more recalcitrant hydrocarbons. The nitrogen compounds in oils may be the source of organogenic elements for the micro-organisms, which leads to the decrease and a complete disappearance of N in the samples at the biodegradation.
The increase in sulphur compounds in biodegraded samples obviously occurred due to the decrease in the fraction of hydrocarbon components. In 6 months one observed a high degree of oil degradation (70-80%) due to the action of peat microorganisms resulted in a more intensive destruction of the hydrocarbons and nitrogen-containing compounds. In the residual oils one observed some increase in sulfur-containing hydrocarbons, which could be thiophenic, benzothiophenic structures – due to lower degradation of these compounds.

In 6 months there was observed a deep destruction of all the oils studied: the reduction in the weight of the initial samples was from 65% (Liao He oil) to 76% (White Tiger oil) (Fig. 2).

Conclusions

It was established that the most fast and deep destruction of the oils of various chemical types and from different stratigraphic complexes is caused by the communities of micro-organisms of valley peats of Temnoye peat field of the Tomsk Oblast.

Quantitative changes of the oil components during destruction depend both on the content and activity of hydrocarbon-oxidizing micro-organisms isolated from the peats.

References

1. Alekseeva, T.P., Tereschenko, N.N.,Perfilieva, V.D., First Russian Setac Symposium on Risk assessment for Environmental contamination, St.-Petersburg, Russia, 1998, pp. 19-21.
2. Klimova, V.A. General micromethods of the analysis of organic compounds. Khimiya, Moscow, 1975, p. 47.
3. McGill, W.B., Rowell, M.J. The Science of the Total Environment, 1980, 14, 245.
4. Eve Riser-Roberts, Ph.D. Remediation of petroleum contaminated soils. Biological, Physical and Chemical Processes. Boca Raton. Boston, London, New York, Washington, 1998, p. 115.

Received 25 October 2002.