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## PETROLEUM PRODUCTS IN AQUATIC ENVIRONMENTS

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**Abstract.** *In the aquatic environment petroleum products (PP) are in different migration forms: in the homogeneous phase in the form of droplets of various sizes and films with thickness from 1 to 200 microns; in the emulsified form; in the form of molecular solutions. The distribution of PP in water between these forms depends on the way of their entry into water, time of their stay in the aqueous medium, its temperature, dispersion mode and physicochemical composition of the aqueous medium. It is shown that the distribution of droplets of the dispersed phase of the PP is described by the Kolmogorov function. When determining the concentration of PP, it is necessary to pay attention to the presence of benzene groups in them. With increasing duration of contact of gasoline with water the difference of PP solubility in distillate and ordinary water increases. It is connected with sensitivity of benzenes to salt content of water due to formation of solvate complexes and with competition for free water molecules. The decrease in the concentration of dissolved benzene-containing PP increases according to the law  $S^{1/3}$ , where  $S$  is the salt content in water. When designing water treatment systems from PP, it is necessary to use a step system corresponding to the content of different forms of PP in water.*

**Key words:** *petroleum products, phase state, distribution of droplets, solutions in water.*

## 1. Introduction

Petroleum products (PP) are a mixture of low and high molecular weight hydrocarbons, therefore it is conventionally accepted to call non-polar and low-polar compounds soluble in hexane, i.e. the sum of aliphatic, naphthenic (alicyclic) and aromatic hydrocarbons that determine the basic composition of oil [1-4].

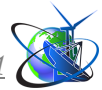
PP is among the most common environmental pollutants. They are found in surface runoffs, rivers and lakes. The last decades are characterized by an increasing spread of oil products in groundwater of the upper horizon. The processes of mixing of mine water with surface runoffs contaminated with oil products and their penetration into formation water in Donbas mines due to the cessation of water pumping due to military operations pose a special danger.

The most significant sources of such pollution are:

- motor vehicles and their infrastructure, various agricultural and military equipment;
- oil refineries, oil depots, fuel terminals and filling stations;
- enterprises of metallurgical and metalworking industries;
- pipeline transportation of crude oil and oil products, railroad and sea transportation;
- energy enterprises.

In the aquatic environment PP are in different migration forms:

- in homogeneous phase in the form of drops of various sizes and films with thickness from 1 to 200 microns;



- in emulsified form;
- in the form of molecular solutions.

The distribution of PP in water between these forms depends on the way they enter the water, the time of their stay in the aqueous medium, its temperature, the dispersion mode and the physicochemical composition of the aqueous medium.

Due to the formation of films on the surface of water bodies, oil products disturb their oxygen regime, slow down the reaeration processes and inhibit the biochemical oxidation of other organic compounds, including life processes. It should be noted that 1 kg of PP can form a film on the water surface with the area from  $10^4$  to  $10^6$  m<sup>2</sup>. In summer time the film of PP decomposes by 50-80% within 7-10 days, and at temperature below +4°C decomposition is suspended. Wastewaters of oil refineries containing more than 15 mg/dm<sup>3</sup> of PP are not suitable for fish and their fry [1,3-6]. At the PP content of more than 1.2 mg/dm<sup>3</sup> the normal development of eggs and some representatives of benthos is disturbed. At the concentration of PP more than 0.1 mg/dm<sup>3</sup> water taste quality deteriorates and fish meat acquires "oil taste". Concentration of PP is determined by the competition between the flow of their input into the water body and the rate of oxidation due to aeration and solar radiation. In spring and summer, due to the increase in water temperature and surface aeration with a constant flow of PP input, their total concentration in water decreases, while in fall and winter it increases. If the total flux of PP input and their corresponding oxygen uptake is greater than the aeration flux of a given water body, its total oxygen balance is disturbed, which leads to the death of flora and fauna [3, 4].

Sanitary norms and rules [2] establish maximum permissible concentrations (MPC) of petroleum products in the water of water bodies of I category (fishery use) and II category (sanitary and domestic use):

$$MPC_I < 0,05 \text{ mg/dm}^3;$$

$$MPC_{II} < 0,1 \dots 0,3 \text{ mg/dm}^3,$$

(0.1 mg/dm<sup>3</sup> for sulfuric oils, 0.3 mg/dm<sup>3</sup> for mineral oils) [2].

Sanitary and chemical control determines the sum of all forms of PP.

Water purification from PP is difficult because a significant part of them (sometimes up to 1-3g/dm<sup>3</sup>) is in emulsified and dissolved states. Particular difficulties arise in the presence of surfactants and emulsion stabilizers.

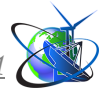
The following methods are used for wastewater treatment: physical, physical-chemical and biochemical methods [3-6].

Physical methods are used to separate film and coarse-dropped forms of PP. They include: sedimentation, centrifugation, flotation, filtration, exposure to acoustic, electric and magnetic fields.

Physicochemical methods include coagulation, sorption, ozonation and chlorination.

Biochemical methods include oxidation of PP by microflora of activated sludge in aeration tanks, ponds and various types of biofilters. Recently, special non-pathogenic bacterial strains have been used for this purpose.

As a rule, water purification devices from PP are characterized by multi-stage purification, including to a greater or lesser extent the previously mentioned methods.



For example, at the initial concentration of PP in water  $C_0 = 30\text{mg/dm}^3$  to achieve  $\text{MPC}_1$  requires a five-stage purification system with  $k_1 = 0.3$ ;  $k_2 = 0.2$ ;  $k_3 = 0.3$ ;  $k_4 = 0.2$ ;  $k_5 = 0.4$ . Then the total purification factor will be

$$K = k_1 \cdot k_2 \cdot k_3 \cdot k_4 \cdot k_5 = 0.3 \cdot 0.2 \cdot 0.3 \cdot 0.2 \cdot 0.4 = 1.4 \cdot 10^{-3}, \quad (1)$$

$$C = C_0 \cdot K = 0.043.$$

Therefore, the operation of such devices is rather complicated and the technological regime is sensitive to random deviations from the regulations. The capital costs for manufacturing and operating costs are also higher than the average costs related to wastewater treatment.

## 2. Distribution of oil products by phase-dispersed composition and determination of their content in water

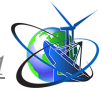
Analysis of water treatment methods shows that they are determined by the phase-disperse state of impurities [4, 5]. Petroleum products are not an exception in this respect, which in water can be in three states:

- homogeneous, in the form of a film on the water surface or large droplets;
- heterogeneous, in the form of finely dispersed suspensions or stabilized emulsions;
- molecular, in a dissolved state.

The main feature of a heterogeneous state is the presence of an interface between the dispersion medium and the dispersed phase, i.e., petroleum products. Accordingly, the surface energy is associated with the interface, the value of which depends on the structure of the boundary interfacial layer and the presence of surfactants [4, 8]. For PP droplets with a size of  $r < 10^{-5}$  m, the value of the surface energy depends on their size ( $r$ ) and increases with its decrease according to the law  $\sim r^{-1}$ . Aqueous emulsions of PPs with  $r > 10^{-6}$  m are unstable with respect to gravitational forces or other types of physical separation. If the particle size of the emulsion  $r < 10^{-6}$  m, kinetically stable colloidal systems are formed. For them, the processes occurring in electrical double layers, as well as molecular and polarization interactions between particles are of primary importance. Since PP droplets have a negative charge, their coalescence can be accelerated by lowering the pH of the medium. When the dispersion particles reach a size of  $r < 10^{-9}$  m, molecular solutions of petroleum products are formed. Due to the hydrophobicity of PP they have some properties of colloidal-disperse systems, namely:

- delayed diffusion;
- light scattering;
- double refraction during flow (optical activity);
- low osmotic pressure;

Dissolution of PP is accompanied by the interaction of PP molecules with the aqueous medium through induction and dispersion forces. For some fractions of PP, hydrogen bonds may be formed between water molecules and hydrogen-oxygen groups of PP molecules. The distribution of PP between phase-disperse states depends on the type of PP and the method of dispersion formation, its temperature and salt content. For example, a study of the distribution of PP between droplets and emulsions [6], allows us to conclude, taking into account the solubility of PP, that the distribution of the mass content of dispersion fractions is as follows:



$$\text{droplet mass : emulsion mass : solution mass} = 1 : 0.1 : 0.009.$$

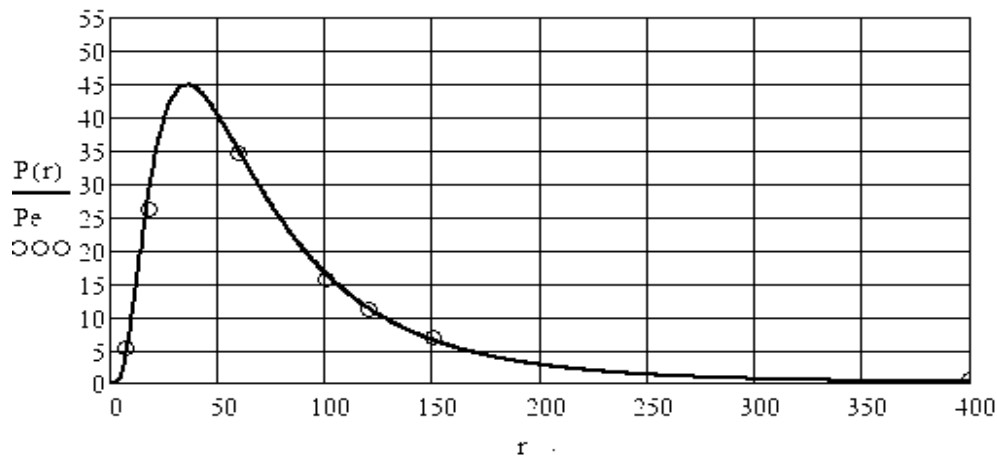
If the total PP content of water is 2000 mg/dm<sup>3</sup>, then:

$$\begin{aligned} \text{mass of droplets (homogeneous phase)} &= 1817 \text{ mg/dm}^3; \\ \text{mass of emulsified PP} &= 182 \text{ mg/dm}^3; \\ \text{mass of dissolved PP} &= 1.6 \text{ mg/dm}^3. \end{aligned}$$

Such a distribution by phase states can occur in cases where PPs enter water under intense mechanical mixing, thus forming a dispersed phase.

The result of determining the size of the droplets of the PP dispersion formed in this way is shown in Fig. 1, where the logarithmic Kolmogorov distribution function corresponding to the random fractionation of particles is depicted as a solid line, and the experimental data are represented by dots.

$$P(r) = c_0 \cdot \exp \left[ -c_1 \cdot \left( \ln \left( \frac{r}{r_0} \right) \right)^2 \right], \tag{2}$$



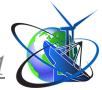
**Fig.1. Distribution functions of droplet dispersion of PP by size.**

The vertical axis is the percentage of PP particles of a given size in μm.

Pe - experimental points; P(r) - Kolmogorov distribution function (2) corresponding to random particle splitting.  $c_0 = 44.89$ ;  $c_1 = 0.95$ ;  $r_0 = 36 \mu\text{m}$ .

Comparing the Kolmogorov distribution and field data, we see that the most likely particle size of the PP is 36 microns. This allows us to conclude that in this case, the droplet phase of petroleum products can be effectively removed by a coalescing filter with a hydrophilic loading.

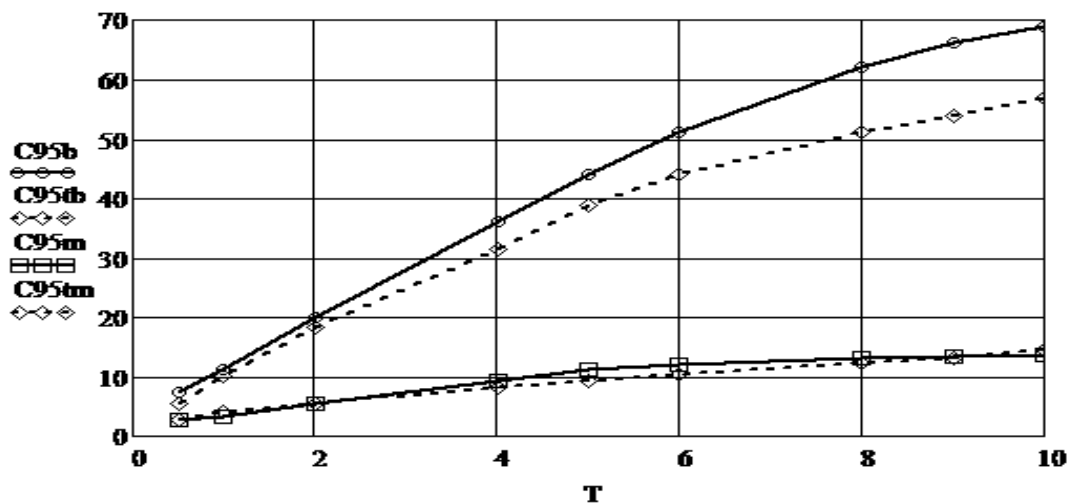
The situation is quite different when, as a result of long-term storage, water is released from the PP, forming the so-called "sub-commodity water". In such water, the content of emulsified and dissolved PP can be equal to the amount of droplets and reach 2-3 g/dm<sup>3</sup>. In addition, "sub-commodity water" can be enriched with fractions of PP containing benzene groups, and therefore the concentration of dissolved PP determined by conventional methods can significantly differ from the total concentration of petroleum organic matter contained in the water, since the solubility of benzene-like compounds in water is much higher than that of classical PP.



### 3. Solubility of petroleum products in water

The concentration of hydrocarbons with methyl and methylene groups was determined by the calibration graphs for the infrared absorption band  $2926\text{ cm}^{-1}$  [8, 9], and the concentration of aromatic hydrocarbons was determined by the absorption band of benzene -  $3030\text{ cm}^{-1}$  and the calibration graph of benzene in  $\text{CCl}_4$  [9]. We can see from Fig. 2, that the concentration of aromatic hydrocarbons in water is continuously increasing, see curve C95b, and saturation was not reached within the study time (10 hours). It should be noted that the concentration of PPs with benzene groups in ordinary water, curve C95tb, is 10-15% lower than in distillate, curve C95b.

The concentration of A-95 gasoline with methylene groups is significantly, 4.7 times, lower than that with aromatic groups, see curves C95m and C95tm in Fig. 2, and the solubility of such PPs practically does not depend on the salt content of water.



**Fig. 2. Dissolution curves of PP A-95,  $\text{mg/dm}^3$ , with benzene groups C95b and methylene groups C95m in distillate and tap water C95tb and C95tm.** In Fig. 2 on the OX axis is time in hours. The conductivity of the distillate is  $5\text{--}7\ \mu\text{S/cm}$  and that of tap water is  $690\text{--}720\ \mu\text{S/cm}$ . Dissolution was performed at a temperature of  $18\text{--}19^\circ\text{C}$  without stirring.

At the same time, the difference in solubility of NPs with benzene groups increases with the duration of contact with the solvent (water) in distillate and ordinary water. In our opinion, the reason for this is related to the high solubility of benzene in water and their sensitivity to the salt content in water. The solubility of benzene is associated with the formation of solvate complexes and with an increase in the salt content of water, competition for free water molecules between benzene and salts occurs. The change in the time difference reflects the dynamics of salt hydration. The decrease in the concentration of dissolved benzene-containing PP should increase as  $S^{1/3}$ , where S is the salt content of water

*The sensitivity of the solubility of PPs to benzene content is important because traditional methods for determining the concentration of PPs [4,8] do not take into account benzene content, which can distort the results of determining the*



concentration of PPs in wastewater.

Therefore, when analyzing wastewater, it is necessary to pay attention to the concentration of aromatic hydrocarbons in it. In addition, Fig. 2 shows that the solubility of PPs containing benzene is much higher than that of PPs with methyl and methylene groups. In particular, the saturation concentrations for PPs with methyl groups are [6, 7]:

DF	A-80	AI-95
$0.65 \text{ mg/dm}^3$	$5-6 \text{ mg/dm}^3$	$12-15 \text{ mg/dm}^3$

and the higher the content of low molecular weight organic substances in the PP, the higher their saturation concentration. Thus, under normal conditions, without the presence of surfactants and intensive dispersion, the solubility of PPs with methylene groups at  $t \sim 20^\circ\text{C}$  does not exceed  $15-20 \text{ mg/dm}^3$ . At the same time, the solubility of benzene or benzene-like compounds is much higher and its limit value has not been determined under experimental conditions.

As already mentioned, a special class of waters contaminated with oil products is "sub-commodity waters". In such waters, the content of emulsified and dissolved oil products can be  $2-3 \text{ g/dm}^3$ . In addition, the "sub-commodity water" may be enriched with benzene groups, and therefore the concentration of dissolved PPs determined by traditional methods may differ significantly from the total concentration of petroleum organic substances contained in the water, since the solubility of benzene-like compounds in water, as noted earlier, is much higher than that of classical PPs. Therefore, it is advisable to use oxidative methods to determine the concentration of PPs in such waters [9, 10].

### Conclusions

1. It has been shown that droplets of an emulsion of PPs in water are distributed according to the Kolmogorov random fractionation law.
2. For A-95 gasoline with benzene groups, the solubility of PP is several times higher than in low-octane gasoline or gasoline with methylene groups.
3. The solubility of gasoline with benzene groups depends on the salt content of water. As the time of contact of gasoline with water increases, the difference in solubility of PP in distillate and ordinary water increases.
4. The solubility of benzene is associated with the formation of solvate complexes and with an increase in the salt content, competition for free water molecules occurs. Therefore, the decrease in the concentration of dissolved benzene-containing PPs increases according to the law  $S^{1/3}$ , where S is the salt content in water.
5. A special class of waters contaminated with oil products is called "sub-commodity waters". In such waters, the content of emulsified and dissolved oil products can be  $2-3 \text{ g/dm}^3$ . In addition, they are enriched with benzene groups and therefore the concentration of dissolved oils determined by traditional methods may differ significantly from the total concentration of oil organic matter.
6. Since the MPC for PPs is  $< 0.05 \text{ mg/dm}^3$ , and their concentration in wastewater sometimes exceeds tens of  $\text{mg/dm}^3$ , it is necessary to apply a multi-stage process based on various physical and chemical principles for their treatment.



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