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# Technological Schemes for Wastewater Treatment and Efficiency Analysis

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**Abstract**

Mechanical treatment remains the predominant method for treating industrial wastewater from oil refineries, focusing on the separation of oil, petroleum products, suspended solids, and water. This approach relies on gravitational forces and utilizes equipment such as sand traps, separators, hydrocyclones, centrifuges, flotation devices, and filters. Despite its widespread use, there is no standardized methodology for selecting or calculating the most effective treatment devices. The choice of treatment method depends on the nature of pollutants in the water, which is determined through rinsing kinetics analysis. The study highlights the importance of understanding the granulometric composition of pollutants, where the proximity of the pollutant distribution curve to the ordinate axis indicates a high dispersion of pollutants, necessitating advanced methods like coagulation, flotation, or filtration to improve sedimentation efficiency. Additionally, the study reviews the influence of hydrodynamic parameters on the efficiency of sedimentation and flotation processes and the need for correction factors in industrial settings. Furthermore, recent advancements in flotation techniques, the design of thin-layer oil traps, and the application of physicochemical methods, including coagulation, electrocoagulation, and adsorption, are discussed. The research demonstrates that advanced methods, such as electrochemical treatment and the use of reagents like polyelectrolytes, can significantly enhance pollutant removal.

**Keywords:** industrial wastewater, petroleum products, oil refining, mechanical mixtures, liquid flow, flotation

## Introduction

Mechanical treatment of industrial wastewater from oil refineries remains the primary and most widely utilized method. This approach is based on the separation of oil, petroleum products, suspended solids, and water through gravitational forces. Mechanical treatment processes are conducted using sand traps, separators, hydrocyclones, centrifuges, flotation devices, and filters. Despite its widespread application, a standardized methodology for the selection and calculation of these treatment devices has not yet been established. The choice of a specific mechanical treatment method depends on the characteristics of the pollutants present in the water, which are determined by analyzing the rinsing kinetics of industrial wastewater (Figure 1).

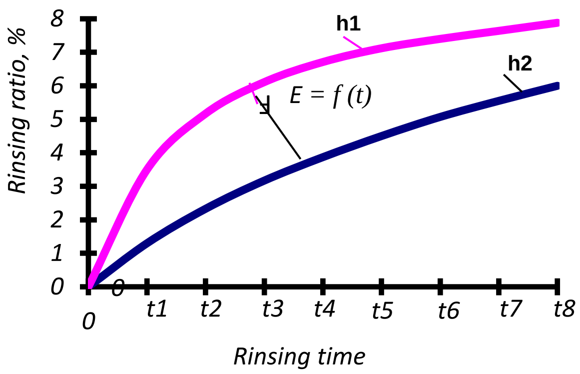


**Figure 1. Production wastewater rinsing kinetics**

According to Figurovsky (1949), the graph illustrates the granulometric composition of mechanical mixtures in water. The proximity of the curve to the ordinate axis indicates a high degree of dispersion of pollutants in water, while its approach to the abscissa axis signifies the predominance of smaller dispersed mixtures. Such conditions necessitate the use of methods that enhance the sedimentation process, such as coagulation, flotation, or filtration, to effectively separate these mixtures from water.

It should be noted that during sedimentation and flotation, the heavier or lighter phases of pollutants may undergo agglomeration. The agglomeration potential of pollutants depends on factors such as their physical and chemical nature, their concentration in water, and the height of the deposition column. Additionally, the hydrodynamic parameters of the flow within the treatment device significantly influence sedimentation and flotation efficiency.

Studies conducted by Naydenko and Zhitanniy (1980) demonstrate that results obtained under laboratory conditions often differ from those observed in industrial settings. To account for these discrepancies, correction factors are incorporated into the formulas used for designing and calculating mechanical treatment systems.

Several researchers have emphasized the importance of rinsing and flotation methods as promising approaches for treating oil-containing industrial wastewater. These methods, when combined with filtration processes, can achieve more advanced levels of treatment (Pokrovskiy and Arakcheev, 1980; Shafi-zade and Kurbanov, 1976). Table 1 presents the trends in the application of rinsing and flotation methods in industrial practices, including their adoption and development up to the year 2000.

**Table 1. Dynamics of application of situational and flotation methods to production**

| Type of polluted water | Purification methods | Scale of application of methods by year, % | | |
|---|---|---|---|---|
| | | 1980 | 1990 | 2000 |
| Water polluted with oil and petroleum products | Sedimentation followed by flotation | 12-17 | 25-35 | 48-54 |
| | Sedimentation by subsequent coagulation | 10-14 | 18-22 | 28-32 |
| | Separation by subsequent sorption | 3-7 | 8-12 | 16-20 |

While all three methods presented in the table have shown increased utilization, the combination of sedimentation and flotation exhibits the highest prevalence, accounting for 48-54% of applications. This approach is based on the separation of pollutants in water according to their mechanical and phase states, including mixed gas phases, water-liquid phases, mixed liquid or solid phases, and water-gas phases.

Currently, many enterprises continue to operate outdated technological schemes and facilities, which are insufficient for adequately treating various types of production wastewater. From a fire safety perspective, the distance between devices within these technological schemes is maintained at a minimum of 10 meters, resulting in the occupation of extensive production areas. Consequently, replacing such outdated equipment with more efficient and compact alternatives could offer significant technical and economic advantages.

Since the second half of the 20th century, various designs of thin-layer oil traps with settling depths of up to 100 mm have been developed and implemented in industrial operations. Our research has demonstrated that these devices offer several advantages over conventional oil traps. The performance of the newly designed devices under production conditions has been thoroughly evaluated, and we have provided well-founded recommendations for their design and operational optimization.

An analysis of existing patent materials (Kangarly and Mirzayeva, 2004) and relevant scientific and technical data reveals that, despite their innovations, the designs and operational guidelines for thin-layer oil traps are often complex. Moreover, in certain cases, their overall dimensions differ minimally from those of traditional oil reservoirs.

## Methodology

The flotation of dispersed water-polluting particles occurs due to their adhesion to hydrophobic surfaces immersed in water (Ksenofontov, 1992; Stakhov, 1984). Air bubbles typically serve as these hydrophobic surfaces. When introduced into the liquid to be treated, air bubbles adhere to pollutant particles and carry them to the liquid's surface, where they are removed as a concentrate.

The collision between particles and air bubbles arises from differences in their individual trajectories and velocities. For the air bubbles to adhere to the particles, they must overcome the resistance of the water layer between them and the forces maintaining the hydrate layer on the surface of the flotation particles. In hydrophobic particles, the absence of such resisting forces facilitates bubble attachment, reducing the energy required for adhesion.

It should be noted, however, that not all collisions between particles and air bubbles result in the formation of flotation aggregates. According to the second law of thermodynamics, flotation aggregates are formed when the free surface energy of the system decreases. When a particle adheres to a gas bubble, the resulting aggregate has a free energy lower than that of the initial system. The free energy of the initial system can be described by the following equation:

$$W_1 = S_{m-q}\sigma_{m-q} + S_{m-nm}\sigma_{m-nm} \qquad (1)$$

Here, $S_{m-q}, S_{m-nm}$ - *liquid-gas* and *liquid-oil (products)* separation surfaces, respectively;

$\sigma_{m-q}, \sigma_{m-nm}$ - surface tension at the *liquid-gas* and *liquid-oil (product)* interfaces, respectively.

The equation for calculating the free energy of the system, in the case where a homogeneous contact surface forms between a particle and an air bubble, can be expressed as follows:

$$W_2 = (S_{m-q} - 1)\sigma_{m-q} + \sigma_{nm-q} + (S_{m-nm} - 1)\sigma_{m-nm} \qquad (2)$$

Here $\sigma_{nm-q}$ - surface tension at the *oil (product)-gas* interface.

If we express the reduction of the free energy of the system by equation (3)

$$\Delta W = W_1 - W_2 = \sigma_{m-q} + \sigma_{m-nm} - \sigma_{nm-q} \succ 0 \qquad (3)$$

or

It is possible to write as following:

$$\sigma_{m-q} + \sigma_{m-nm} \; \phi \; \sigma_{nm-q} \qquad (4)$$

The difference in surface tension at the oil (or petroleum product)-gas and liquid-oil (or petroleum product) interfaces can be described using an equation derived from Laplace's law:

$$\sigma_{nm-q} - \sigma_{m-nm} = \sigma_{m-q} \cos\theta \qquad (5)$$

Here, $\theta$ - contact angle.

Thus, the free energy of the system decreases due to the formation of an aggregate between the air bubble and the particles. This reduction is proportional to the contact surface area between the air bubbles and particles, the surface tension at the gas-liquid interface, and the contact angle.

The adhesion of air bubbles dissolved in water to the surface of solid or liquid pollutants is influenced by the wettability of the particle surface, which is characterized by the contact angle, and is quantified by the parameter (insert parameter). As the contact angle increases, the particle surface becomes more hydrophobic, thereby enhancing the likelihood of air bubble adhesion to the surface and increasing the strength of the resulting aggregate. This relationship is clearly illustrated in the graph I have provided (Figure 2).

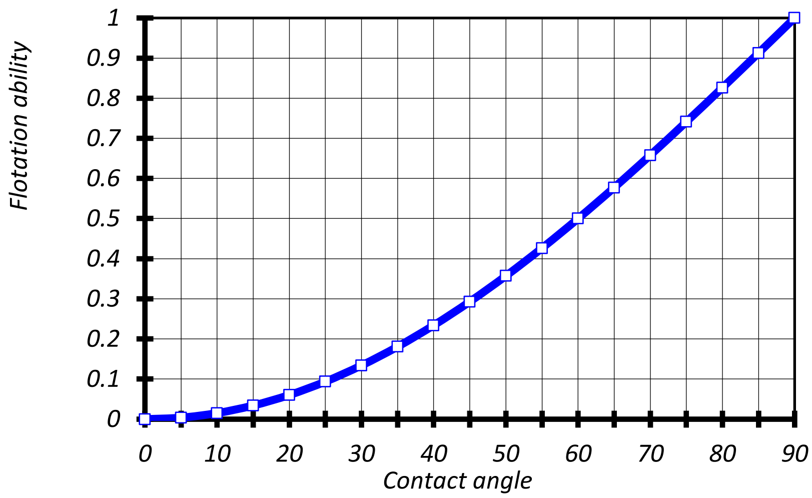


**Figure 2. Dependence of particle flotation capacity on contact angle**

As shown in the graph in Figure 2, the flotation capacity of the particle increases with the contact angle, reaching its maximum value at an angle of 90°. Since oil particles in industrial wastewater possess hydrophobic properties, their flotation capacity is relatively high

(Ponomarev et al., 1985; Kulgskiy et al., 1980).

Physicochemical methods are employed to separate colloidal and dissolved pollutants in industrial wastewater. The concentration of these pollutants typically remains relatively constant after mechanical cleaning. Oil products in the form of emulsions account for 1-5% of the contaminants in the production wastewater of oil refineries. Kulsghky et al. (1974) have found that industrial wastewater after oil separators typically contains 100-150 mg/l of oil products. Water with such a concentration of petroleum products is deemed unsuitable for reuse, and since biological treatment is not effective for their removal, additional treatment methods are required. While numerous physicochemical cleaning techniques and devices exist, coagulation, flocculation, electrocoagulation, and sorption methods are of particular interest in this field.

As a result of my research in the field of enhancing the industrial wastewater treatment process for oil refineries using physicochemical methods, it was found that the addition of polyelectrolytes synthesized from hydrolyzed polyacrylonitrile can improve the efficiency of petroleum product removal by coagulation to 90-95%. The experiments were conducted under laboratory conditions using industrial wastewater containing up to 200 mg/l of petroleum products (Figure 3). However, the results obtained have not yet been tested under production conditions (Guseynov et al., 1982).

**Figure 3. During test studies I conducted in the “Sukanal” Research Laboratory of "Azersu" OJSC**

## Analysis and discussion

The organization and operation of reagent management play a critical role in the physicochemical treatment of wastewater. It is important to note that the use of reagents, as well as the construction and operation of reagent facilities (including storage, solution and consumption tanks, dosing systems, mixing, and reaction chambers), necessitate additional production space and incur significant costs, which ultimately increase the cost of treated water. Similarly, the operation of compressor units for the flotation process requires substantial capital investment, skilled personnel, and ongoing operational costs.

Four primary methods of electrochemical treatment for industrial wastewater have been identified (Antropov, 1969):

- ✓ Removal of dissolved and suspended organic and inorganic substances through the electrolysis of industrial wastewater using soluble anode electrodes.
- ✓ Elimination of suspended and partially dissolved substances from industrial wastewater using insoluble electrodes.
- ✓ Separation of dissolved organic substances from water, transforming them into non-toxic (or low-toxicity) compounds, and in some cases, insoluble, sediment-forming compounds via oxidation at the anode and reduction at the cathode.
- ✓ Separation of dissolved mixtures, primarily inorganic substances, from water with the potential for subsequent processing via electrodialysis (using semi-permeable membranes).

Electrochemical methods offer several advantages over reagent-based approaches. These include the fact that the salinity of the treated water does not increase, less sludge is generated, the treatment process is simpler, there is no need for reagent management, the technology can be fully automated, and electrochemical treatment devices require minimal production space.

Electrocoagulation is an effective method for separating fine oil, petroleum products, organic substances, and similar pollutants from industrial wastewater. However, substances that are completely dissolved in water cannot be removed by this method. According to Chukov, Mongait and Rodziller (1977), electrocoagulation yields better results in waters with neutral or low alkalinity (pH = 5–9). Given that electrocoagulation requires significant amounts of metal material and electrical energy, it is more suitable as a local treatment technology with relatively low productivity (30–50 $m^3$/hour).

Decanters are essential for separating the products of electrochemical reactions in water passing through the electrolyzer. One of the main drawbacks of this method is the high costs associated with the preparation and operation of electrodes and power supply systems (Leibovskiy and Ushakov, 1979), as well as the accumulation of sediments on the surface of the electrodes. To address this issue, the electrical polarity is periodically reversed, which necessitates that both the cathode and anode be made from the same material, thereby increasing the manufacturing cost of the electrode system. Additionally, during the electrochemical treatment process, a mixture of explosive gases is generated due to the separation of hydrogen and oxygen. To rapidly remove this gas mixture, a specialized ventilation system must be installed, which further increases the overall construction costs and complicates operation. These challenges often result in the rejection of this method in favor of alternatives.

The adsorption of pollutants in wastewater occurs in three sequential stages. The first stage involves the diffusion of organic matter molecules into the liquid layer surrounding the adsorbent, bringing them closer to its surface. This is known as external diffusion. In the second stage, the molecules diffuse into the macropores and micropores on the surface of the adsorbent. In the third stage, pollutants further diffuse into the micropores, completing the adsorption process (Lukinikh et al., 1978.).

Granular activated carbon, with a particle size exceeding 0.1 mm and consisting of 85-99% carbon, is commonly used as an adsorbent due to its ability to be easily separated from water. However, the complexity of its production process, the requirement for large quantities of high-quality materials, energy, fuel, specialized equipment, and highly skilled personnel make activated carbon a costly option (Iskanderov et al., 1974; Genon, 1976). The technological characteristics of the most widely used activated carbons for industrial wastewater treatment are provided in Table 2.

**Table 2. Technological characteristics of activated coals**

| Carbon type | Volume, $cm^3/g$ | | | Casting mass, $t/m^3$ | Wholesale sales price*, *rub /t* |
|---|---|---|---|---|---|
| | micropore | mesopore | macropore | | |
| *KAD* - iodine | 0.28 | 0.05 | 0.32 | 450 | 485 |
| *AQ -3* | 0.26 | 0.09 | 0.55 | 450 | 660 |
| *BAU* | 0.3 | 0.08 | 0.80 | 300 | 1340 |
| *DAC* | 0.19 | 0.04 | 1.23 | 230 | 790 |
| *AQM* | 0.34 | 0.07 | 0.40 | 350 | 1140 |

Note: The prices are for 1985

The deep treatment of industrial wastewater containing dissolved and emulsified oils using the adsorption method is carried out in two stages. In the first stage, the wastewater passes through mechanical filters, followed by activated carbon filters in the second stage. As a result, the residual concentration of petroleum products in the treated water is reduced to 0.1-2 mg/l.

The above indicates that this method is complex and often requires significant labor and resources. As a result, it is typically employed only for the treatment of small volumes of wastewater at production facilities and is not economically viable for large-scale treatment complexes.

The results of studies conducted by me and other authors at enterprises operating within the CIS indicate that, in most cases, the water treated by biochemical methods fails to meet the required standards for several quality indicators. These include water temperatures ranging from 40 to 42°C, mechanical mixtures exceeding 150 mg/l, suspended oil products, oils, and other contaminants. An example is the presence of pollutants that surpass permissible limits.

A slightly modified technological scheme is employed for the treatment of industrial wastewater at the Shell refinery in Houston, USA. This scheme incorporates API-type oil separators, parallel thin-layer oil traps, and biological treatment units (Figure 4).

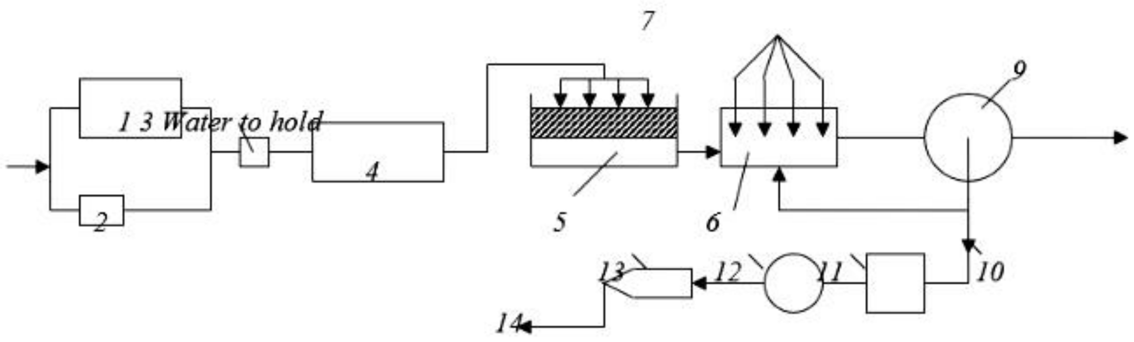


**Figure 4. Technological scheme of wastewater treatment at the Shell oil refinery:**
1-oil separator of ANI type; 2- oil trap with parallel plates; 3- pH control point; 4- soothing basin; 5- biofilter; 6- air tank; 7- mechanical aerators; 8- regenerated sludge; 9- secondary rinser;10- providing sludge for aerobic stabilization; 11- aerobic stabilizer; 12- compressor rinse; 13- centrifugal machine; 14- dewatered sludge

It is important to note that the concentration of petroleum products in the water entering the treatment facility complex at the plant does not exceed 0.5-1.0 g/l, as the production wastewater generated during the plant's technological processes undergoes preliminary on-site treatment (Kazakov et al., 2004). Following 8 hours of mechanical aeration, the biological oxygen demand (BOD) of the treated water is reduced to 20-25 mg $O_2$/l. As evident from the technological scheme, the water treatment process is relatively complex.

The general flow of industrial wastewater is treated in oil traps of various designs. The most employed designs include American Petroleum Institute (API) oil traps and parallel plate traps (Gerome, 1971). According to American experts, parallel plate oil traps offer higher treatment efficiency compared to API traps. Consequently, in subsequent years, these devices were rapidly replaced by parallel plate oil traps (Pret à Poser, 1997; Saint Dizier, 1994).

However, it is also noted that the space between the parallel plates in such oil traps often becomes clogged with fuel oil or sludge, leading to disruption of the unit's normal operation. This results in considerable time and financial expenditure required to flush the space between the plates. Industrial wastewater entering the initial treatment system is predominantly contaminated with oil and petroleum products. These pollutants exist in the form of water droplets, emulsions, and substances dissolved or adsorbed onto the surfaces of solids in the water. The concentration of oil and petroleum products in these waters typically averages 3000 mg/l, with mechanical mixtures reaching up to 300 mg/l, as reported by P.I. Pobegailo and O.V. Kedrov (1972), researchers at VODGEO RF. This finding is supported by research I conducted at one of the oil refineries in the Republic of Azerbaijan (Mirzaeva et al., 2005).

In addition to oil products, the waters of the second treatment system may also be contaminated with phenols, fatty acids, urea, mercaptans, mineral salts, alkalis, acids, sulphides, sulphohydrates, and demulsifiers. The concentration of oil and petroleum products in these waters is generally higher, reaching up to 5000 mg/l. The amount of emulsified oil products depends on the type of demulsifiers used in the electro-preservation process, while the concentration of mechanical mixtures ranges between 300 and 800 mg/l. Given that the production wastewater from oil refineries is contaminated with a wide variety of organic and inorganic compounds, both in terms of quantity and composition, their treatment is highly complex. As a result, separate treatment units are constructed for each wastewater system. The wastewater from the first system is primarily treated through a series of devices designed to remove oil and petroleum products from the water (Figure 5). This treatment unit comprises a drainage system, a sand trap, an oil collector, an additional washing basin, and filters.

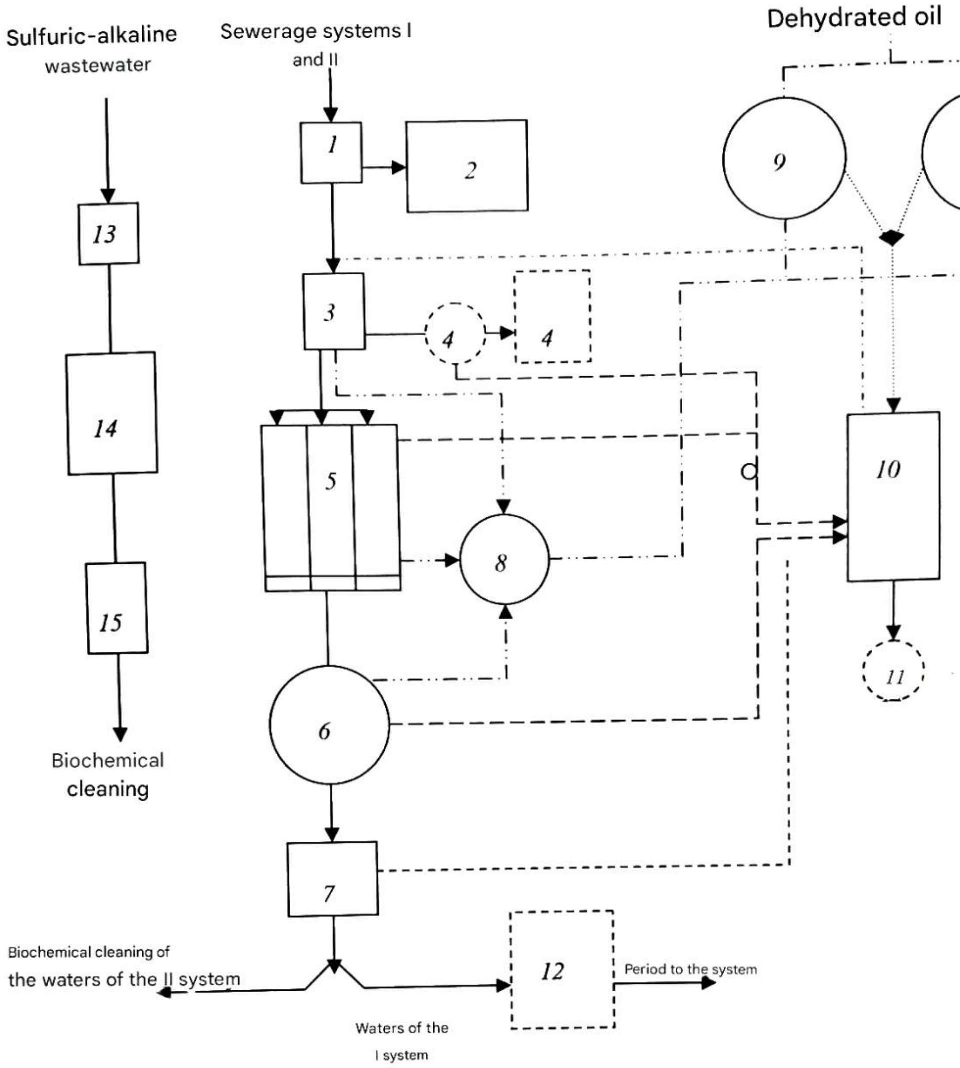


**Figure 5. Technological scheme of the unit of devices for wastewater treatment from oil and petroleum products**: Devices for systems I and II: 1- rainwater harvesting; 2- accident warehouses; 3- sand traps; 4- hydrocyclones and sand fields; 5- oil traps; 6- addition rinsers; 7- sand filters, or floaters

Common devices for systems I and II: 8- a pumping station equipped with a tank to receive oil; 9- tanks to separate trapped oil from water; 10- sludge collection basins; 11- sludge incinerator; 12- System I collection basin or aeration basin for sulphur-alkaline water

Networks: Wastewater from systems I and II; 13- oil traps; 14,15- a collection tank that ensures uniform distribution of pollutants throughout the water volume; pipe transporting filter wash water; a pipeline system that transports trapped oil; pipe system transporting sludge; a system of pipes transporting settled water and oil; pipe system that transports water separated from sediment and oil.

## Conclusion

Modern technology enables the separation of sand and other mechanical particles larger than 0.15–0.2 mm from water in a sand trap. Finer particles are directed to the oil trap, which is the primary device used to separate oil products and mechanical mixtures from water. The water remains in these devices for approximately 2 hours. Oil products that rise to the surface are removed by rotating slotted pipes, while the sludge that settles at the bottom of the device is removed using a hydro-elevator.

After the water remains in the additional flushing tanks for 12-24 hours, the oil products that rise to the surface are removed through specialized oil pipelines. The reservoir is cleaned of sediment every 1.5 to 2 years, a process that requires significant time, labor, and resources.

In this technological scheme, filters serve as the final purification device. After filtration, the residual oil products in the water are reduced to 20-30 mg/l, and mechanical impurities to 10-15 mg/l, allowing the treated water to be returned to the enterprise's water supply system. The composition of the treatment facilities in the main oil-receiving unit of System II is identical to that of the first system.

Based on my experience at the production facility, design and technological limitations prevent the complete removal of dissolved organic compounds from water in the oil trap, which serves as the primary treatment unit. The residence time of water in such devices is typically 2 hours, with a flow rate ranging from 3 to 8 mm/sec. In a 36-meter-long section of the oil trap, the water depth is 2 meters at the inlet and 1.2 meters at the outlet. The number of sections required depends on the volume of water to be treated, with each section designed to handle a flow rate of 198 $m^3$/hour. The effectiveness of subsequent wastewater treatment facilities is closely linked to the efficient operation of these initial units.

An analysis of the performance of operating treatment facilities reveals that the concentration of oil in the wastewater from both I and II systems after passing through the oil traps ranges from 50 to 450 mg/l, whereas current standards stipulate that this value should not exceed 100 mg/l. In some cases, after mechanical treatment, the oil concentration in the water is significantly higher than the permissible limit. According to Ponomarev et al. (1985), the concentration of oil products in water entering the oil reservoirs is between 1000 and 15,000 mg/l, with treated water containing oil levels ranging from 150 to 350 mg/l.

The results of the research indicate that oil tanks in operation are not uniformly distributed throughout the treatment unit due to the formation of working flow bubbles, which arise from malfunctions in the cooling system. One contributing factor to this issue is the formation of convection currents with varying densities, resulting from uneven temperature and contaminant concentrations across the flow layers (Karelin et al. 1970; Pushkarev et al. 1980). The greater the disparity in these factors, the more pronounced the agitation of the working flow becomes, leading to turbulence. Turbulent flow, in turn, complicates the sedimentation and flotation processes within the system, thereby reducing the efficiency of water treatment and leaving higher concentrations of oil products and mechanical impurities in the water.

Additionally, the formation of these currents increases the velocity of the working flow, significantly reducing the residence time of the water in the treatment unit. Approximately 50% of the oil tank volume in operation is effectively utilized for treatment at the stations, while the remaining 50% consists of dead or circulating zones that do not contribute to the treatment process. The residual concentration of oil products in treated water after passing through the oil traps ranges from 50 to 150 mg/l for wastewater from the first system and from 100 to 200 mg/l for the second system. The efficiency of mechanical mixture removal does not exceed 50%. The captured oil products are composed of 40-70% oil, 1-5% solids, and 30-60% water. The sediments formed consist of 20-25% mechanical mixtures, 10-15% oil products, and 60-70% water.

The preceding discussion highlights that the existing technological schemes and purification devices offer both advantages and limitations. Consequently, the development of equipment and technological schemes that are more cost-effective, occupy less production space, and exhibit higher purification efficiency remains a critical challenge in modern industrial practice.

Theoretical and experimental studies demonstrate that oil traps equipped with reversible and direct-flow thin-layer blocks exhibit superior cleaning efficiency compared to existing designs (Mirza, 2023). The use of this unit for treating oil-containing industrial wastewater at the facility, which occupies minimal space while offering adequate capacity, enhances the overall productivity of the plant's treatment facilities. Additionally, it mitigates air pollution from evaporative emissions on the premises, captures a greater number of hydrocarbons from the water, and facilitates recycling.

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