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## Obtaining Conservation Liquids Based on Compositions of Co and Ni Salts of Synthetic Petroleum Acids with Amidoamines and Nitro Compounds

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**Abstract:** The article presents the results of a scientific study devoted to the production of preservation fluids based on compositions of Co and Ni salts of synthetic petroleum acids with amidoamines and nitro compounds. Corrosion prevention is a critical issue in industries where metal components are exposed to aggressive environments. The composition of the preservation composition was selected for the synergistic anticorrosive properties of the components, which increases its durability and efficiency. The anticorrosive liquid forms a protective layer on metal surfaces, preventing oxidation and extending the service life of industrial equipment. This paper presents a detailed analysis of the synthesis process, chemical interactions, efficiency assessment and potential application of the prepared liquid. The results show that Ni and Co salts with amido acids and nitro compounds significantly increase corrosion resistance and thermal stability, which makes the resulting composition promising for industrial use.

**Keywords:** conservation liquids, corrosion inhibitors, natural petroleum acids, oxidized liquid rubber, nitro compounds.

## INTRODUCTION

Protecting metal objects from corrosion has become a major issue in both global and local industries. In certain cases, ensuring the corrosion resistance of metal structures becomes even more challenging. Metals, when exposed to aggressive environments, cannot maintain their thermodynamic stability and undergo corrosion. Corrosion leads to not only technical challenges but also significant economic consequences, making it a crucial factor for every industrial sector. According to the kind of base fluid, conservative liquids or other name rust prevention liquids can be categorized as solvent-based, oil-based, or water-based. They are made by combining corrosion inhibitors, film-forming agents, and other additives with a base fluid. For them to achieve optimum performance, corrosion inhibitors are unquestionably essential. The two primary kinds of corrosion inhibitors are inorganic and organic. Nitrite, nitrate, chromate, dichromate, and phosphate are examples of inorganic inhibitors that are frequently used for a variety of metals and base fluids. Conversely, organic inhibitors are substances that have one or more polar groups (with O, N, P, S, and  $\pi$  electrons) and work well to stop corrosion by adsorbing onto the metal surface.

As a result, the development of corrosion-resistant substances and solutions remains a key research focus. Enhancing the corrosion resistance of complex metal-based industrial equipment relies on the use of conservation liquids. The study of inhibitors in conservation liquids is considered one of the most effective methods in terms of economic efficiency and application technology. Inhibitors work by forming a

chemical absorption layer on metal surfaces, preventing chemical reactions that cause corrosion. In this article, conservation liquids were examined using oxidized liquid rubber, petroleum acids with a boiling range of 310–360°C, Co and Ni salts, and C<sub>14</sub>H<sub>28</sub> α-olefins in T-30 turbine oil with various compositions and ratios.

## EXPERIMENTAL PART

The formulation of conservation liquids with inhibitory properties relies on three primary components: metal salts derived from natural petroleum acids, aliphatic nitro compounds, and oxidized liquid rubber. T-30 turbine oil serves as the solvent. In Azerbaijan, salts of Co, Ni, Zn, Mg, and Ba are typically extracted from natural petroleum acids by isolating kerosene and diesel fractions as organic solvents. The compositions of liquid rubber are generated by incorporating aliphatic nitro compounds into the resultant product. The active ingredient is utilized in a 1:1:1 ratio (by weight). Nitro compounds are produced by treating C<sub>14</sub>H<sub>28</sub> α-olefin with nitric acid. The developed conservation liquid was evaluated on steel plates using 7% and 10% T-30 oil solutions. The liquid rubber applied in this investigation was synthesized from 1,4-cis-polybutadiene. These components establish a robust protective shield against corrosion by forming strong attachments to metal surfaces. The aim of this study is to create an efficient, environmentally sustainable corrosion-inhibiting conservation liquid suitable for extensive industrial application.

To develop conservation liquids, it is essential to analyze the synergistic effects of all the components, especially T-30 turbine oil. The metal salts derived from petroleum acids act as primary anti-corrosion agents. For example, naphthenic acids react with nickel and cobalt hydroxides to form corresponding salts. Amidoamines provide additional stability and adhesion to metal surfaces, enhancing the film-forming properties of the formulation. Nitro compounds increase the oxidative stability of the protective layer, improving its resistance to environmental degradation. To ensure a homogeneous application, a mixture of organic solvents is used to dissolve the salts and other components. Surface-active agents and stabilizers are added to improve the viscosity, spreading ability, and storage stability of the liquid.

Petroleum acids are reacted with nickel hydroxide (Ni(OH)<sub>2</sub>) and cobalt hydroxide (Co(OH)<sub>2</sub>) in a controlled environment. The reaction results in the formation of nickel and cobalt salts, which are then purified and dried. The Ni and Co salts are dissolved in a solvent and mixed with amido acids such as stearamide or oleamide. To facilitate the formation of stable complexes, the mixture is heated. Nitro compounds like nitrobenzene or nitrophenol are added to enhance film-forming properties and oxidative stability. The reaction is carried out under controlled temperature and pH conditions to ensure optimal performance. The final product is prepared by dissolving the synthesized complexes in a suitable solvent like ethanol or isopropanol. Surface-active agents and stabilizers are added to improve application properties and shelf life.

The name of samples:

1. T-30 oil + Zn salt of the NPA + liquid rubber-10%
2. T-30 oil + Co salt of the NPA + liquid rubber-10%
3. T-30 oil + Ni salt of the NPA + liquid rubber-10%
4. T-30 oil + Nitro compound + Ni salt of the NPA + liquid rubber-10%
5. T-30 oil + Nitro compound + Co salt of the NPA + liquid rubber-10%

Five different samples selected for the determination of conservation fluids were evaluated using IR spectroscopy. IR spectroscopy is a powerful analytical technique used for molecular structure identification and the determination of functional groups. IR analysis is employed to confirm the interactions between petroleum acids and metal salts, as well as to elucidate the structures of the resulting complexes. In this analysis, an infrared beam is directed at the sample to identify molecular vibrations. Molecular bonds absorb infrared light at different wavelengths, producing characteristic peaks in the absorption spectrum. Based on the spectral analysis of wavelengths, the inhibitor composition (natural petroleum acid Co salt + nitro compounds + liquid rubber) demonstrated the most effective results

## RESULTS AND DISCUSSION

The STA-449 F3, NETZSCH thermal analyzer is used for thermogravimetric analysis (TGA). Thermogravimetric analysis measures the variation in mass as a function of temperature and differential thermal analysis. This technique is employed to characterize the thermal stability of conservation fluids in environments with different electrical conductivities. The TGA instrument, such as STA-449 F3 (NETZSCH), is then set up with a controlled gas atmosphere, usually nitrogen ( $N_2$ ) to prevent oxidation or air/oxygen ( $O_2$ ) for oxidative degradation studies. A gas flow rate of 20–50 mL/min ensures uniform conditions, and the heating rate is commonly set at 10–20°C per minute. The experiment begins by taring the crucible, loading the sample, and initiating the heating program, starting from room temperature (e.g., 25°C) and increasing to a final temperature (e.g., 600°C or higher) at a controlled rate. The instrument continuously records weight loss over time. The analysis of TGA data involves different stages: initial mass loss at lower temperatures (~50–150°C) due to solvent evaporation, main decomposition at medium temperatures (~150–400°C) where organic inhibitors and polymers break down, and the formation of residual mass at high temperatures (~400–600°C), which may indicate the presence of inorganic components. Higher thermal stability (less weight loss at lower temperatures) suggests better performance in high-temperature environments, while stable residue formation may indicate the presence of protective inorganic additives. Comparing different samples provides insights into their relative effectiveness. The process is conducted under a nitrogen atmosphere, with the temperature increasing at a rate of 20°C per minute. In thermal analysis, the thermal analysis curve of the fifth sample, when evaluated without any chemical additives, coincides with its composition at 360°C.

The obtained conservation fluids (a 7% and 10% solution in T-30 turbine oil) were tested on a steel plate. The test was conducted in two phases: condensation and atmospheric. To ensure consistent results, standard parameters were regulated based on electronic devices. For the condensation phase, these parameters included the chamber temperature, the stabilizer temperature of the environmental phase, and the test duration. The atmospheric phase aimed to determine the retention period of the conservation fluid on the steel plate in days. A combination of TNT + nitro compounds + liquid rubber was used, providing corrosion protection for metal layers for 301 days in the condensation phase and 384 days in the environmental phase. At a 10% concentration, the respective durations were 338 and 419 days. A comparative analysis of the results was conducted to assess the impact of liquid rubber. Without liquid rubber, the above-

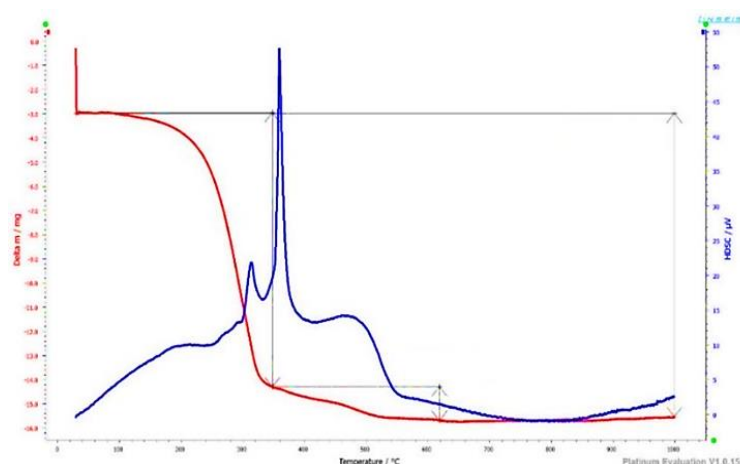


mentioned composition (TNT + nitro compound Co salt) provided corrosion protection for 93 and 201 days in the respective phases.

Table 1

Physical and Rheological Properties of Conservation Liquids

Name of the property	Name of the device	ASTM	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Freezing point (°C)	Stanhope Seta	ASTM D2386	-35	-25	-25	-30	-25
Viscosity (mm <sup>2</sup> /s, °C 40)	TW4000	ASTM D445	60.88	66.93	61.96	56.47	53.99
Viscosity (mm <sup>2</sup> /s, °C 100)	TW4000	ASTM D445	8.31	26.75	8.72	7.98	7.63
Density (g/cm <sup>3</sup> )	DMA 4500 M	D5002	0.9072	0.9112	0.9136	0.9093	0.9090



**Fig 1.** The thermogravimetric analysis curve of the 5th sample

The obtained conservation fluids (a 7% and 10% solution in T-30 turbine oil) were tested on a steel plate. The test was conducted in two phases: condensation and atmospheric. To ensure consistent results, standard parameters were regulated based on electronic devices. For the condensation phase, these parameters included the chamber temperature, the stabilizer temperature of the environmental phase, and the test duration. The atmospheric phase aimed to determine the retention period of the conservation fluid on the steel plate in days. A combination of TNT + nitro compounds + liquid rubber was used, providing corrosion protection for metal layers for 301 days in the condensation phase and 384 days in the environmental phase. At a 10% concentration, the respective durations were 338 and 419 days. A comparative analysis of the results was conducted to assess the impact of liquid rubber. Without liquid rubber, the above-mentioned composition (TNT + nitro compound Co salt) provided corrosion protection

for 93 and 201 days in the respective phases. Composite inhibitors formulated from the combination of TNT-Co salt,  $C_{14}H_{28}$  nitro compounds, and 1,4-cis-polybutadiene rubber demonstrated exceptional resistance to corrosion. The integration of TNT-Co salt provided corrosion protection for steel plates over a period of 401 days under atmospheric conditions. These inhibitors, characterized by their very low sulfur content, exhibit minimal environmental impact, aligning with ecological standards. The anticorrosive properties of the conservation fluids, which include their ability to form protective layers on metal surfaces and maintain thermal stability, suggest a high potential for future applications in corrosion protection. Moreover, the study emphasizes that the inclusion of other metal salts, which play a pivotal role in process optimization, could pave the way for large-scale research into conservation compositions. The use of these conservation fluids for corrosion prevention, within the context of this innovative approach, holds the potential to significantly reduce maintenance costs while prolonging the service life of metal structures and industrial equipment.

## CONCLUSION

This study successfully demonstrates the development of advanced conservation liquids that enhance the corrosion resistance of metal compounds through the synergistic effects of Co and Ni salts derived from synthetic petroleum acids, in combination with amidoamines and nitro compounds. The formulated conservation liquids exhibit remarkable protective properties, forming a durable barrier on metal surfaces that significantly inhibits oxidation and extends the lifespan of industrial equipment.

The experimental results confirm that the incorporation of these specific components not only improves corrosion resistance but also enhances the thermal stability of the formulations. The rigorous testing conducted under controlled conditions, including thermogravimetric analysis and IR spectroscopy, validates the efficacy of the conservation liquids in both condensation and atmospheric environments. Moreover, the findings highlight the economic and environmental advantages of utilizing these innovative conservation liquids. By reducing maintenance costs and prolonging the service life of metal structures, this research contributes to sustainability in industrial operations.

The experimental results demonstrated that these compositions provide significant protection against metal corrosion, with the most effective formulation ensuring up to 419 days of protection in atmospheric conditions and 338 days in condensation conditions. Thermal and structural analyses confirmed the stability of the synthesized fluids, making them suitable for various industrial applications.

Based on the findings, the following recommendations are proposed:

1. **Expansion of Applications** – Further testing should be conducted in industrial machinery, oil and gas pipelines, and marine environments to explore broader applications.
2. **Optimization of Formulations** – Additional metal salts and polymer-based additives should be introduced to enhance protection and stability.

3. **Sustainability Considerations** – Future research should focus on environmentally friendly and biodegradable corrosion inhibitors to meet regulatory standards.
4. **Commercialization Potential** – The synthesized fluids should be patented and tested for large-scale industrial production to facilitate market adoption.

Overall, this study presents a promising approach to developing high-performance protective fluids with extended durability and industrial applicability. Further research and optimization will contribute to the advancement of corrosion prevention technologies.

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## STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF HEAVY OIL RESIDUES

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**Abstract:** The search for potential applications and the exploration of methods for utilizing heavy oil residues is a highly prioritized and relevant task. In this study, the compositions of heavy oil residues were examined, the optimal conditions for porphyrin extraction were determined, new organic extractants of ketone-alcohol nature were developed, and the most effective one was identified, providing a high yield of porphyrin from the residues. The study of the physicochemical composition was carried out by extraction and liquid chromatography methods using the example of asphaltene-resin-paraffin deposits collected at the Buzovna "Taghiyev Operating Company" Intertek Azəri LTD. To identify the raw materials used and the compounds obtained, modern methods of physicochemical analysis such as X-ray phase analysis, IR and UV spectroscopic, thermographic analysis, as well as scanning electron microscopy were used. Study of the physicochemical composition and structure of asphaltene-resin-porphyrin deposits.

**Keywords:** Bifunctional organic extractants, asphaltenes, IR spectral characteristics, UV absorption spectra, ketone-alcohol nature extractants, 2-hydroxycyclohexanone.

## INTRODUCTION

It is known from literary sources [1-6] that oil with maximum values of vanadium and nickel concentration (in total reaching 300-600 g/t and higher) belongs to the class of heavy oils with an increased content of asphaltene-resinous substances, while asphaltenes contain their maximum amount. In this regard, it seems rational to use asphaltene-resin-paraffin deposits (ARPD) sorbed on the surface of pipes, equipment, and oil-saturated rocks as objects of study.

Petroleum porphyrins can be used as catalysts, semiconductor compositions, sensitizers, dyes, and also in medicine for the production of antitumor drugs [7]. A characteristic feature of metalloporphyrins is their diversity, which, in combination with a unique molecular structure, determines their ability to act as drugs, catalysts, photosensitizers, various dyes, organic semiconductors, etc. As petroleum feedstocks become heavier, attention to the challenges of processing heavy petroleum feedstocks and their deposits increases, both to increase efficiency and reduce oil refining costs, and to produce new chemical systems based on them. In this regard, the development and research of new modified chemical systems based on metalloporphyrins isolated from heavy, highly viscous oil or oil residues are of great interest.

Currently, numerous studies are devoted to searching for the possibilities of using porphyrins in medicine. The development of drugs and other biologically active agents based on porphyrins is, apparently, one of the promising applied areas in the problem of using porphyrins [8-15]. One of the areas that has been intensively developing recently is the fixation of active metalloporphyrins on a polymer matrix. An analysis of the literature data showed that the nature of the attachment of porphyrins to the polymer

matrix can be different. In a number of studies, the immobilization of porphyrins and their complexes was carried out through coordination bonds. The attachment of porphyrins is carried out due to the interaction of functional groups of polymers and porphyrins with the formation of secondary amine, ester and other functional groups. The fact of immobilization of porphyrins and metal complexes in the above works is confirmed by the authors using electron and IR spectroscopy, elemental analysis for nitrogen, as well as a spectrophotometric method for determining the mass fractions of metal in the case of polymer metalloporphyrins. Polymer-bound porphyrins are of significant interest from the point of view of their therapeutic effects. However, studies on the synthesis of polymer derivatives of porphyrins and their metal complexes are scarce, so the development of new methods for immobilizing porphyrins and their metal derivatives on a polymer matrix and expanding the scope of their applications is of undoubted interest. The possibility of modifying metalloporphyrins from heavy petroleum residues may stimulate the further development of more efficient and economical technologies for the production of effective drugs.

## EXPERIMENTAL PART

The study of the physicochemical composition was carried out by extraction and liquid chromatography methods using the example of asphaltene-resin-paraffin deposits collected at the Buzovna "Taghiyev Operating Company" Intertek Azəri LTD. The research results are presented in table 1.

Table 1

Study of the physical and chemical composition of ASPO

Sample	Content, %			
	Mechanical impurities	Asphaltenes	Paraffins	Resins
Sample 1	47.50	21.00	11.60	19.90
Sample 2	43.40	27.00	9,10	20.50

It was found that the samples of ASPO contain a large number of mechanical impurities, which may include clay, sand, metals and complexes based on them. It should also be noted that the deposits of asphalt resin paraffin substances are dominated by asphalt resin components.

According to the data presented in table 1, both research objects are of the asphaltene type, which suggests a high content of vanadium and nickel in them.

### X-ray fluorescence analysis of solid deposits

The presence of metals and their quantitative composition in ASPD were determined using an X-RAY INNOV-X SYSTEMS spectrometer. Sample measurements were carried out in the ranges of 0.0-16.0 keV.

### IR spectrometry method

The IR spectra were recorded at a temperature of 20 °C using a NICOLET 5700 FT-IR Fourier spectrometer in the range of 4000 - 400 cm<sup>-1</sup>.

### UV spectrometry method

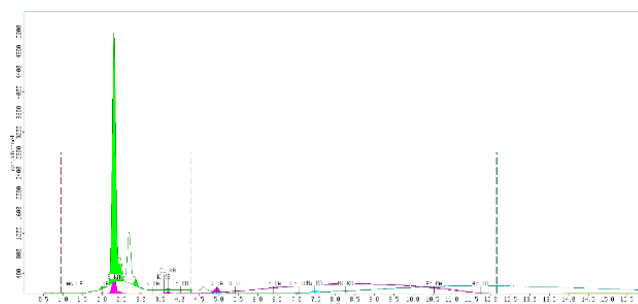
At the exit from the column, free porphyrins were collected in 10 ml portions, which were analyzed by an Evolution 300 UV/VIS spectrophotometer (USA) in a 10 mm thick quartz cuvette in the near ultraviolet and visible regions (300-700 nm). The

spectral type of porphyrins was determined by the intensity ratio of absorption bands I, II, III, IV.

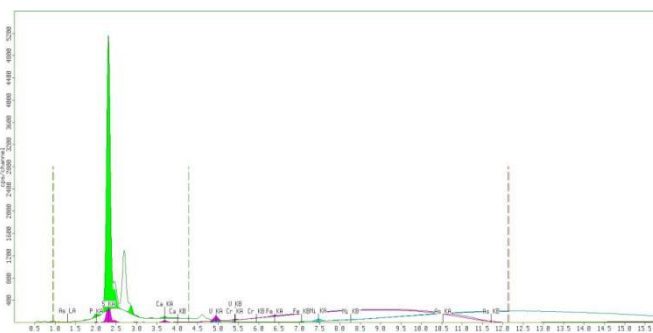
UV spectra of aqueous solutions of medicinal substances were recorded on an Evolution 300 UV/VIS spectrophotometer (USA) in a 10 mm thick quartz cuvette. Scanning electron microscopy (SEM) images of polymer composite systems in the form of films on the Superprobe 733 electrozone microanalyzer.

#### **X-ray fluorescence analysis of asphaltene-resin-paraffin deposits**

The results of determining the presence of metals and their quantitative composition in the studied ASPO samples are presented in figures 1, 2.



**Fig.1.** Spectrogram of ASPO, sample 1



**Fig.2.** Spectrogram of ASPO, sample 2

## **RESULTS AND DISCUSSION**

Using the IR spectral method, differences in the functional groups of asphaltene resin deposits were revealed; the results of the studies are presented in figures 3, 4, 5. Analysis of the IR spectra of ASPD and asphaltenes shows that they contain a high content of C-H bonds of saturated hydrocarbons in the absorption band regions of 1375, 1460, 2850, 2920  $\text{cm}^{-1}$ . The absorption bands in the region of 760  $\text{cm}^{-1}$  characterize the presence of unbranched paraffin chains in hydrocarbons [16].

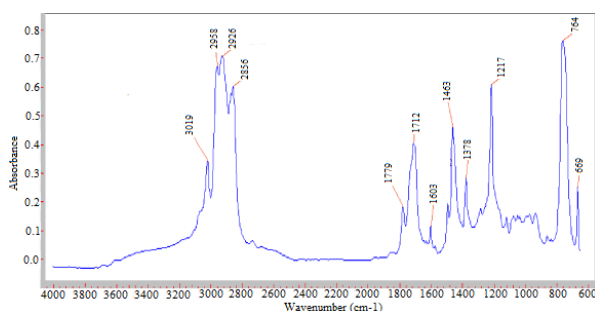
The absorption band in the region of 1600  $\text{cm}^{-1}$  indicates the presence of aromatic structures in the ASPD and asphaltenes. For ASPO sample No.2, the presence of absorption bands of the C=O group in the region of 1215 and 1700  $\text{cm}^{-1}$  is noted; the absorption band in the region of 3400  $\text{cm}^{-1}$  is characteristic of vibrations of the OH group, which indicates the presence of carboxylic acids in the composition of the deposits [17].



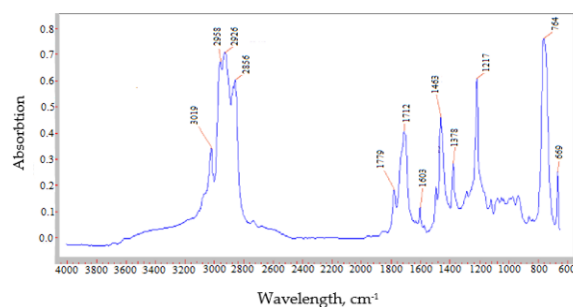
Thus, the physicochemical composition and structure of ASPD were studied using the methods of combined extraction and liquid chromatography, as well as X-ray fluorescence analysis and IR spectroscopy. It was shown that the main component of ASPD are resins and asphaltenes. The IR spectra of asphaltenes isolated from ASPD were also studied. Based on the obtained experimental data, it can be concluded that the studied samples of asphaltene-resin-paraffin deposits can serve as a source of porphyrins [18].

Among natural sources of porphyrins, in addition to plant and animal origin, various residual products of oil refining are promising, including heavy residues of oils with increased content of vanadium and nickel. The significant yield and limited rational use of such oil objects, along with the high content of metalloporphyrins in them, determine the need for a comprehensive study of the possibility of obtaining porphyrins from such raw materials.

At present, there are a large number of works devoted to the extraction of petroleum porphyrins for analytical purposes using extraction methods. At the same time, the possibilities of extraction for the practical use of the obtained concentrates of petroleum porphyrins have been practically unstudied.



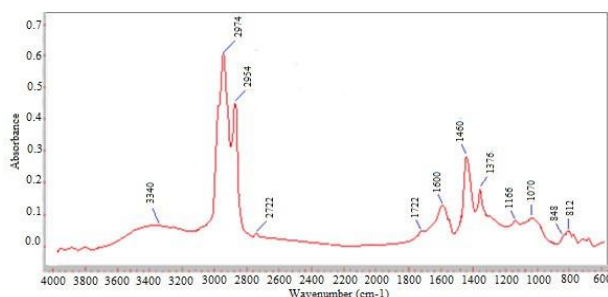
**Fig.3** IR spectra of ASPO, sample 1



**Fig.4** IR spectra of ASPO, sample 2

It is more rational to carry out the extraction of porphyrins from heavy oil residues with an increased content of vanadium and nickel, in which metalloporphyrins are concentrated.

To create a method for efficient concentration of porphyrins, it is necessary to select the conditions for the extraction of porphyrins from heavy oil residues



**Fig. 5.** IR spectra of asphaltenes

Since the composition of the produced heavy oil residues depends significantly on the composition of the raw material and the process conditions, it is necessary to study the features of the composition and content of porphyrins isolated from asphaltenes and resins and paraffin deposits separately.

Asphaltene and asphaltene-resin-paraffin deposits collected at the deposit (sample 1 and sample 2) usually were used for a preliminary assessment of the possibility of extracting porphyrins with acids. Unlike existing methods we synthesized and used extractors of ketone-alcohol nature, listed in table 2.

Table 2

Some characteristics of synthesized extractants I-III used for the selective extraction of oil metalloporphyrins

№	The structure and name of ketone alcohols	Molecular mass	Characteristic absorption bands in the IR spectrum, $\nu$ cm <sup>-1</sup>
I	$  \begin{array}{c}  \text{CH}_3 \qquad \qquad \text{CH}_3 \\    \qquad \qquad \quad   \\  \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_3 \\    \qquad \quad    \qquad \quad   \\  \text{CH}_3 \qquad \text{O} \qquad \quad \text{OH} \\  \text{2,2,6-trimethylheptanon-3-ol-5}  \end{array}  $	172	1711 (C=O), 3595 (-OH)
II	$  \begin{array}{c}  \text{CH}_3 \qquad \text{CH}_3 \\  \diagdown \quad \diagup \\  \text{C} - \text{CH}_2 - \text{CO} - \text{CH}_3 \\    \\  \text{OH} \\  \text{2-methylpentanon-4-ol-2}  \end{array}  $	116	1708 (C=O), 3520 (-OH)
III	$  \begin{array}{c}  \text{O} \\     \\  \text{C}_6\text{H}_{10} \\    \\  \text{OH} \\  \text{2-hydroxycyclohexanone}  \end{array}  $	114	1715 (C=O), 3340 (-OH)

A highly effective method for the separation of metalloporphyrin concentrate from heavy oils and oil products using bifunctional organic compounds (ketone alcohols) with respect to metal porphyrins has been developed [19]. The synthesized bifunctional compounds are superior in the efficiency of extraction of metalloporphyrins in comparison with known extractants. The best results were shown by 2-hydroxycyclohexanone.

The amount of porphyrin extract from asphaltene and ASPD with increased content of vanadium and nickel varies within the range of 6.8-18.0 wt. %. Since the difference in the amounts of porphyrin extract yield from asphaltene compared to the

yield from ASPD is insignificant, asphalt resin and paraffin deposits can be used as raw materials for obtaining porphyrins, which does not require preliminary separation of asphaltenes from ASPD. With an increase in the content of vanadium and nickel in both ASPD and asphaltenes, the yield of extracts increases.

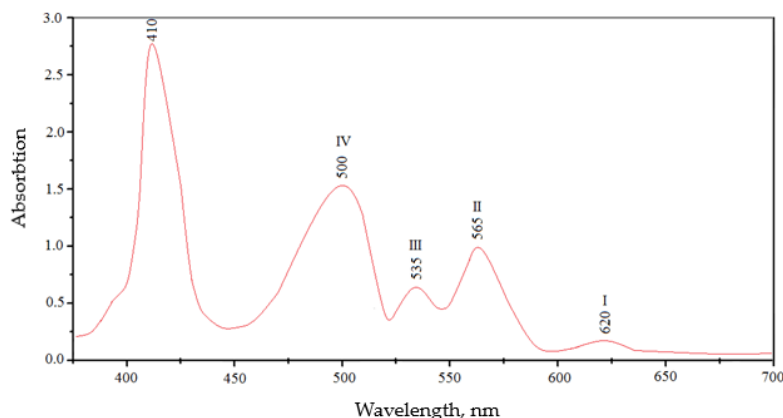
Thus, the obtained results show the possibility of obtaining a higher concentration of porphyrins by extraction from heavy oil residues by reducing the proportion of hydrocarbon and heteroatomic components insoluble in the primary extract.

To obtain data on the composition and types of porphyrins in the extracts, the adsorption chromatographic separation method on ASKG silica gel was used. A mixture of 0.5% isopropyl alcohol and 99.5% benzene was used as an eluent.

In the visible absorption spectra of the primary extract, the 530 and 570 nm bands of metalloporphyrins are absent and bands characteristic of free porphyrin bases are present (fig. 6, 7).

As can be seen from the figures, free porphyrin bases have four Q-absorption bands of relatively low intensity at 620, 565, 535 and 500 nm in the electronic spectra and one band called Soret at 410 nm of very high intensity.

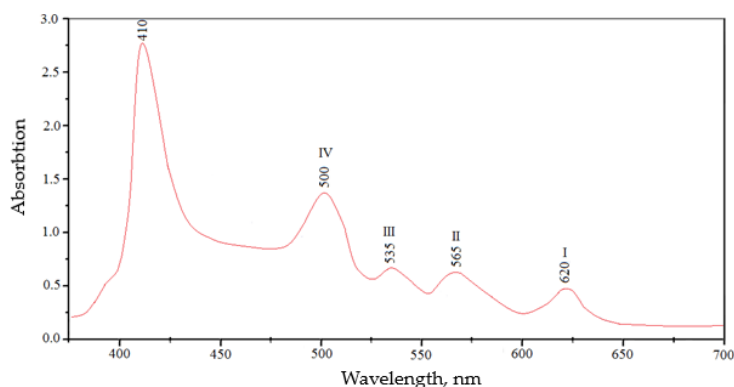
Based on the spectral analysis of porphyrin fractions, the presence of all 4 main types (IV, III, II and I) of porphyrins was detected. In the composition of ASPD, the predominant types are phyllo-type porphyrins, and in the composition of asphaltenes, etio-type porphyrins.



**Fig. 6.** UV absorption spectra of the primary extract of ASPO (sample 1)

Thus, according to the results of spectral absorption in the visible region, the disappearance of characteristic absorption bands of vanadyl and nickel porphyrins and the appearance of absorption bands characteristic of free porphyrin bases were established in all the extracts obtained, which indicates demetallation of metalloporphyrins during the extraction process.

In the IR spectra of porphyrin-containing fractions, absorption bands are observed at 940, 3315  $\text{cm}^{-1}$ , corresponding to the stretching and deformation vibrations of the NH bond, as well as a band at 1458, 1498  $\text{cm}^{-1}$  corresponding to vibrations of the C–N bond of the pyrrole ring.



**Fig. 7.** UV absorption spectra of the primary acid extract of asphaltenes (sample 2)

Thus, it was established that the composition of the primary porphyrin extract obtained by extraction from ASPD differs slightly from the concentrate isolated from separated asphaltenes.

## CONCLUSION

A highly effective method for the separation of metalloporphyrin concentrate from heavy oils and oil products using bifunctional organic compounds (ketone alcohols) with respect to metal porphyrins has been developed. The synthesized bifunctional compounds are superior in the efficiency of extraction of metalloporphyrins in comparison with known extractants. The best results were shown by extrogent-2-hydroxycyclohexanone.

Thus, according to the results of spectral absorption in the visible region, the disappearance of characteristic absorption bands of vanadyl and nickel porphyrins and the appearance of absorption bands characteristic of free porphyrin bases were established in all the extracts obtained, which indicates demetallation of metalloporphyrins during the extraction process.

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## THE INTEGRATION OF RENEWABLE ENERGY INTO THE REVERSE OSMOSIS PROCESS (Review)

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**Abstract:** This article explores the integration of renewable energy sources, including solar, wind, hydro, and geothermal energy, with reverse osmosis (RO) systems and explains how this enhances the sustainability of water purification processes. While reverse osmosis is effective in producing clean water, it requires a significant amount of energy, especially in desalination processes, and contributes to greenhouse gas (GHG) emissions. For example, solar-powered reverse osmosis (SPRO) systems use photovoltaic panels to convert solar radiation directly into electricity and are considered ideal for areas with high solar radiation. Wind energy, on the other hand, is effective in coastal areas with strong wind potential. Technological innovations such as energy recovery devices and preheating of water have significantly improved the energy efficiency of RO systems. This article highlights the benefits of integrating renewable energy sources with RO systems: reduced demand for fossil fuels, decreased environmental impact, scalability, and improved water security. By reducing energy consumption and carbon emissions, these technologies help address global water needs in an environmentally responsible manner.

**Keywords:** Reverse osmosis, Renewable energy, Greenhouse gas emissions, Carbon footprint, Water scarcity.

## INTRODUCTION

Reverse osmosis technology has developed over the last 40 years to control a 44% market share of global desalination production capacity and 80% of the total installed desalination plants worldwide. The application of conventional and low-pressure membrane pretreatment processes for seawater desalination via reverse osmosis has rapidly advanced in the past decade. Since the primary challenge is membrane fouling associated with organic/inorganic compounds, particles/colloids, and biological growth, reliable pretreatment methods are required for the successful operation of seawater reverse osmosis (SWRO) processes. Although traditional pretreatment processes such as coagulation and granular media filtration are widely used for SWRO, there is an increasing trend toward using ultrafiltration/microfiltration (UF/MF) instead of conventional treatment methods. Literature indicates that both conventional and UF/MF membrane pretreatment processes have distinct advantages and disadvantages.

The results of studies on the impact of temperature on productivity, electricity consumption, and the quality of mineralized water in the desalination of Caspian Sea water using reverse osmosis are presented. A series of simulation experiments were conducted to analyze the hydraulic characteristics of membrane elements in a branched hydraulic system and to calculate key design parameters of desalination complexes when multiple factors change in the Caspian desalination complex, allowing for

operational simulation. The quantitative dependencies of the effect of key factors—such as source water temperature and the operational mode of the second desalination stage—on the process's techno-economic indicators were determined. Considering the limitations on boron concentration in drinking water, the optimal operating mode and design of the complex were selected. An analysis of desalination plants operating at the Caspian desalination complex (Aktau, Kazakhstan) with a capacity of 20,000 m<sup>3</sup>/day showed a satisfactory match between calculated and actual characteristics. In industrial conditions, for low-temperature ranges (6-17°C), the temperature dependence of boron selectivity for low-pressure membranes was obtained for the first time [1].

The world has long faced the problem of water scarcity. There is a strong trend toward desalinating seawater from Oman or the Caspian Sea and transferring it to central regions. These projects encounter significant technical, economic, and environmental challenges. In this study, using existing economic theories related to single stage reverse osmosis desalination plants, an analysis was conducted on the cost of a conceptual plant with a production capacity of 200,000 m<sup>3</sup>/day, considering the use of Oman and Caspian Sea water for drinking purposes. The effects of key parameters such as applied pressure, recovery rate, total salinity of the feed water, formation water, and temperature were theoretically studied. The results show that, under the same operating conditions, the cost per cubic meter of fresh water from the Caspian Sea is approximately 50% cheaper, at \$0.69, compared to \$1.24 for Oman Sea water. The main reason for this is the lower salinity of the Caspian Sea, which reduces the cost of the reverse osmosis membrane (by 62%), intake and pretreatment costs (by 20%), and membrane replacement costs [2].

A technological scheme for seawater desalination in two stages (reverse osmosis and thermal distillation) has been proposed and studied. To prevent scale formation during desalination, the method of Na-cationite softening of seawater is used. In the distillation stage, the utilization of waste heat from gas turbine units is proposed. In this case, cation exchange regeneration will be carried out solely with the concentrate from the desalination stage.

Calculations were conducted using the example of the gas turbine power station at the Neft Dashlari oil field. The combination of these cases makes it urgent to establish a multi-purpose desalination complex utilizing heat recovery from existing gas turbine units. The real prerequisites for solving this problem involve equipping each of the four gas turbine units with a waste heat boiler that allows heating water to 150-160°C. However, due to the lack of low-potential heat consumers, practically only one waste heat boiler is used. The remaining waste heat boilers receive combustion products at 450°C and discharge them at the same temperature. These three boilers could be utilized in the seawater desalination scheme.

Calculations show that heat losses with flue gases in each boiler reach 38%, and the corresponding waste heat consumption is 6.7 MW. The study was conducted using the example of a gas turbine power plant. Such a station includes four gas turbine units and is currently operating at the Neft Dashlari oil field in Azerbaijan. By improving waste heat utilization and integrating low-carbon technologies, the project has the potential to contribute to climate change mitigation while addressing the region's water scarcity challenges [3].

One of the key considerations in this process is the impact on greenhouse gas (GHG) emissions. Conventional desalination methods, particularly thermal processes, are energy-intensive and contribute significantly to carbon emissions. By integrating

waste heat recovery from gas turbine units, the proposed system aims to reduce the reliance on additional fossil fuel consumption, thereby lowering GHG emissions. However, if excess waste heat remains unused due to system limitations, it could result in inefficiencies and indirect emissions through energy losses. Implementing carbon capture solutions or optimizing heat utilization across multiple processes could further enhance the sustainability of the desalination complex.

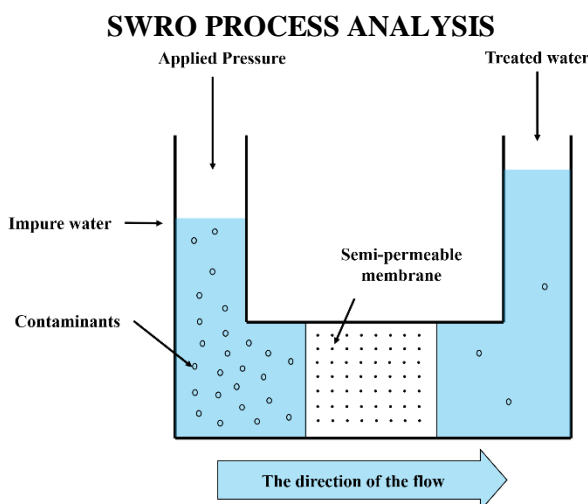
Greenhouse gas emissions are the main cause of climate change, and these changes may lead to irreversible alterations in the planet's climate. According to the International Energy Agency (IEA), approximately 80% of global GHG emissions come from the energy sector [4]. A similar situation is observed in Azerbaijan, where 75% of emissions come from the energy sector [5].

One promising technology that can address both water scarcity and emissions resulting from energy use is reverse osmosis technology powered by renewable energy sources. Although reverse osmosis is a relatively simple process, there are several potential developments to make it more environmentally friendly [6].

A significant feature of reverse osmosis is its integration with renewable energy sources like solar and wind power. These renewable sources have proven their ability to significantly reduce greenhouse gas emissions and are well-established processes. Integrating reverse osmosis with renewable energy sources can offer several advantages [6]:

- Reduction of ecological impact [6];
- Scalability and versatility [7];
- Enhanced water supply security [8].

Depending on the specific features of technology, the list of advantages can expand. This research paper will focus on the aspects of integrating reverse osmosis with renewable energy sources.



**Fig. 1.** Brief overview on the reverse osmosis process

Reverse osmosis is a technique used for purifying water from contaminants. During this process (fig.1), water is passed through a semi-permeable membrane by applying pressure. The process begins by applying high pressure to the contaminated water side, which allows the water to pass through the membrane, while larger particles, contaminants, and salts remain trapped in the membrane. The purified water, called



"permeate", is collected on the opposite side of the membrane. The remaining contaminants on the membrane are called "concentrate" or "retentate". After filtration, the purified water may undergo additional cleaning stages to further improve its quality before storage and distribution [9].

In membrane processes, the principle of filtering seawater through a porous semipermeable element is applied. This element is called a membrane. The term "semipermeable" indicates that, like all filtration materials, the membrane allows certain substances in the mixture to pass through while retaining others. This characteristic is referred to as selectivity. In the initial stage, membrane-based processes share similarities with conventional filtration. Conventional filtration is primarily used to remove coarse and large colloidal dispersed impurities from water. However, in membrane technology, in addition to these impurities, even the smallest colloids, macromolecules, and dissolved substances are also removed.

The fundamental difference between membrane filtration and conventional filtration lies in the structure of the membrane layer. The membrane itself is extremely thin, and unlike traditional filtration materials, the retained impurities do not accumulate within the membrane's volume but instead form an additional filtering layer on its surface, which has significant resistance. This layer is continuously washed away and removed by the flowing water.

Thus, the purification of seawater using membranes is based on the principle of passing the water through a semi-permeable membrane. To achieve this, a driving force is applied to the water containing various impurities, allowing water molecules to pass through the membrane material while the remaining impurities are discharged with the concentrate. The filtered water that passes through the semi-permeable membrane is called permeate or filtrate.

From this perspective, the reverse osmosis process ensures that seawater is purified to a higher degree, removing coarse and colloidal dispersed particles as well as other impurities [10]. This makes it a highly effective method for producing clean water from seawater.

In 1986, plants with a total global capacity of 57,000 t/s were established. Thermal distillation methods accounted for 64.5% of desalination processes, while reverse osmosis desalination plants made up 23.4%. The physical principle of thermal distillation is that seawater is heated and evaporated using an energy source. The resulting vapor is then condensed and utilized as distilled water. Based on this, thermal desalination plants are classified into two main types:

- Boiling type
- Adiabatic type

Depending on the number of stages, these plants can be either single-stage or multi-stage. In boiling-type plants, the number of stages ranges between 5 and 10, whereas in adiabatic plants, they can reach 30 to 40. Various research methods have been developed to reduce the salinity of seawater and make it suitable for domestic use. These methods include distillation, ion exchange, freezing, and membrane technologies. Today, membrane-based salt separation is widely used as an alternative method. Membrane processes are classified based on the size of retained particles into the following main types [11]:

- Ultrafiltration membranes
- Microfiltration membranes
- Reverse osmosis membranes

- Nanofiltration membranes

Seawater desalination systems used on oil platforms are selected based on platform size and water consumption requirements. Recent developments indicate that two primary methods play a significant role in seawater desalination: reverse osmosis and distillation. Research in this field is expanding rapidly. The key difference is that reverse osmosis desalination is typically used for smaller-scale platforms, whereas distillation, despite its higher energy consumption, is more commonly applied to larger platforms due to their greater water demand. Naturally, the choice between these methods depends on energy resources, financial feasibility, and operational convenience.

In some countries, particularly in the Commonwealth of Independent States (CIS), membrane processes are used very sparingly. The primary reason for this is the complexity of both manufacturing and acquiring high-quality membranes. The membranes used in these regions are susceptible to contamination from marine ions, petroleum products, and other corrosive ions present in seawater, which affect their efficiency and longevity.

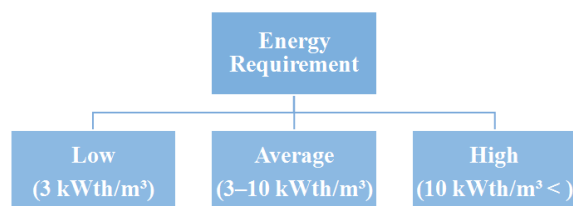
## ENERGY REQUIREMENTS IN THE REVERSE OSMOSIS PROCESS

Energy requirements in the reverse osmosis process are one of the key factors determining its efficiency and sustainability. The operating principle of this method is based on applying high pressure to overcome the natural osmotic pressure of the solution, which is particularly energy-intensive when seawater is converted into drinking water [12].

The energy consumption of reverse osmosis depends on several factors, such as the salinity, temperature, and required flow rate of the feedwater. It is important to note that the pumps used to move the water in the reverse osmosis process also consume a significant amount of energy. Solving these two issues could enhance the application of reverse osmosis in different parts of the world.

Although reverse osmosis is a simple technology, addressing its energy requirements is essential to ensure that it remains environmentally more suitable and economically sustainable in the long term [13].

The high energy consumption of the process also means it has a carbon footprint. On average, desalination through reverse osmosis generates approximately 2.1 to 3.6 kilograms of CO<sub>2</sub> emissions per cubic meter of purified water [14]. However, with the application of renewable energy sources, these emissions can be reduced to approximately 1.53 kilograms per cubic meter [15], making reverse osmosis a more sustainable option among future water purification technologies.



**Fig. 2.** Reverse Osmosis energy requirements

Reverse osmosis can be divided into three categories (fig.2) based on its energy requirements. The following graph illustrates these categories: Low, Average, and High, along with their corresponding energy consumption values:

In Azerbaijan, carbon dioxide (CO<sub>2</sub>) emission factor for electricity generation in 2023 is approximately 0.67 kilograms of CO<sub>2</sub> per kilowatt-hour (kg CO<sub>2</sub>/kWh) [16]. With this in mind, we can calculate the emission amount per cubic meters for different energy consumptions:

**For low energy consumption:**

$$\text{CO}_2 \text{ emission / m}^3 \text{ (low)} = 3 \text{ kWh/m}^3 \times 0.67 \text{ kg CO}_2/\text{kWh} = 2.01 \text{ kg CO}_2/\text{m}^3$$

**For high energy consumption:**

$$\text{CO}_2 \text{ emission / m}^3 \text{ (high)} = 10 \text{ kWh/m}^3 \times 0.67 \text{ kg CO}_2/\text{kWh} = 6.7 \text{ kg CO}_2/\text{m}^3$$

It is planned to build a big **SWRO Desalination Plant** in Sumgayit and it is estimated that 300,000 m<sup>3</sup>/day of water will be treated [17]. With this we get:

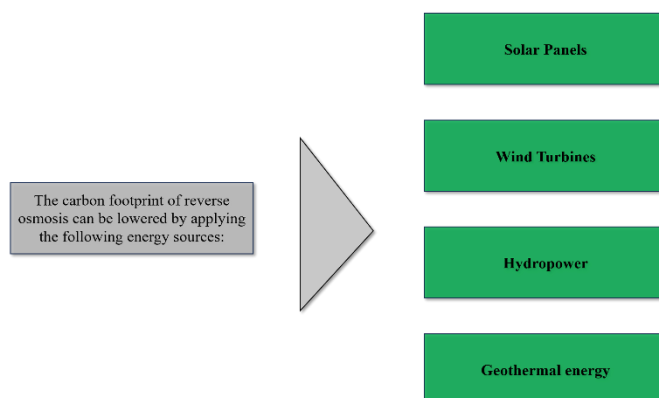
$$300,000 \text{ m}^3/\text{day} \times 365 \text{ days} = 109,500,000 \text{ m}^3$$

Now we can calculate the yearly CO<sub>2</sub> emissions for both low and high energy consumption:

$$\text{Annual CO}_2 \text{ emission (low)} = 2.01 \text{ kg CO}_2/\text{m}^3 \times 109,500,000 \text{ m}^3 = 220,095 \text{ tons CO}_2/\text{year}$$

$$\text{Annual CO}_2 \text{ emission (high)} = 6.7 \text{ kg CO}_2/\text{m}^3 \times 109,500,000 \text{ m}^3 = 733,650 \text{ tons CO}_2/\text{year}$$

For an annual treatment volume of 109.5 million cubic meters, emissions range from 220,095 to 733,650 tons of CO<sub>2</sub> per year, depending on whether low or high energy consumption is assumed. These calculations highlight the substantial carbon footprint associated with desalination.



**Fig. 3.** Reverse osmosis and energy resources

## INTEGRATION WITH RENEWABLE SOURCES

The integration of renewable energy sources with reverse osmosis (RO) systems (fig.3) shows promising results in increasing the sustainability of water purification processes. This integration makes the water purification process more accessible for human use and reduces its negative environmental impact. Solar energy is one of the most widely used renewable energy sources.

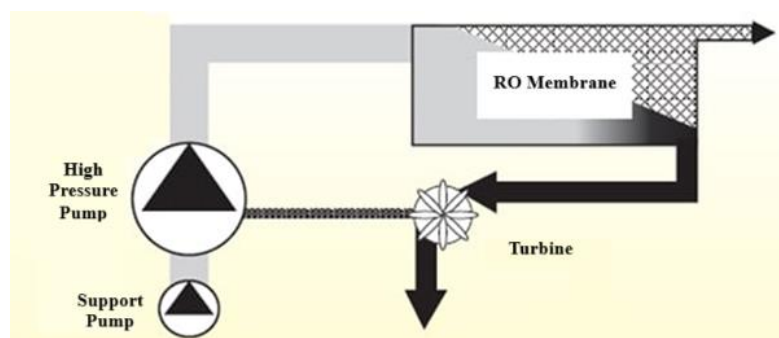
Several possibilities have been explored for integrating solar energy with reverse osmosis (RO) systems. These systems use solar panels to generate the required electricity and are particularly effective in sunny regions, especially deserts and coastal areas. The solar thermal energy produced is used to pre-heat the water, which reduces the energy required for the reverse osmosis process and increases overall efficiency in the entire process, not just in energy usage [18].

Wind energy is also one of the widely used renewable sources. Wind turbines can generate electricity to operate reverse osmosis systems in regions with high wind potential. For example, wind-powered reverse osmosis systems are widely applied in remote islands and communities with isolated energy systems [19], where access to both drinking water and grid electricity is limited [20].

Other renewable sources, such as hydropower [21] and geothermal energy, can also contribute to the operation of reverse osmosis systems, especially in regions with abundant flowing water or geothermal activity. Currently, reverse osmosis systems powered by geothermal energy are being implemented in various regions around the world, and the integration of reverse osmosis with hydropower is actively being researched [22].

Getting some energy back from the process itself is also very important to achieve sustainable solutions and lowering CO<sub>2</sub> emissions. In figure 4 [23] we can see a simple process which helps to get some of the used energy back. It illustrates the energy recovery process in a reverse osmosis (RO) desalination system. The system consists of key components that work together to optimize energy efficiency during water treatment.

A high-pressure pump is responsible for pressurizing seawater or brackish water before it enters the RO membrane, where freshwater is separated from concentrated brine. The pressurized brine, which still contains significant energy, exits the membrane and passes through a turbine or energy recovery device. This turbine captures and transfers a portion of the brine's energy back into the system, reducing the overall power demand.



**Fig. 4.** Energy recovery scheme



A support pump assists in the operation by maintaining necessary flow and pressure levels. The recovered energy helps decrease the energy input required from the high-pressure pump, leading to improved efficiency and reduced operational costs.

### **ADVANTAGES OF INTEGRATING RENEWABLE ENERGY WITH REVERSE OSMOSIS**

The integration of renewable energy sources with reverse osmosis (RO) systems offers several advantages beyond just reducing greenhouse gas emissions.

Existing projects, such as the Chira-Soria project in Gran Canaria [24], have demonstrated the potential for energy savings and a 20% reduction in emissions [25]. In cases involving wind energy, its effectiveness has been well-proven. Wind-powered reverse osmosis desalination is considered one of the most environmentally friendly options among renewable energy sources. Although the variability of wind conditions poses certain challenges, efficiency can be improved through pressure stabilizers or by reducing the turbine load [25].

By reducing dependence on fossil fuels, the environmental footprint of the process is minimized, resources are conserved, and waste associated with conventional energy consumption is reduced.

Another key advantage is the scalability and flexibility of renewable energy systems, such as solar and wind power, which can be adapted to various energy demands. This makes it possible to apply reverse osmosis in both small-scale remote applications and large-scale desalination plants [15].

This integration ensures a sustainable source of clean water. Additionally, adapting technology to the specific characteristics of the location enhances water supply security.

### **CONCLUSION**

The integration of renewable energy sources with reverse osmosis (RO) technology represents a significant advancement in addressing two major environmental challenges: water scarcity and greenhouse gas emissions. As freshwater demand continues to rise, traditional desalination methods contribute to high energy consumption and carbon emissions. By incorporating renewable energy sources such as solar, wind, and hydroelectric power, the environmental impact of RO systems can be significantly reduced while ensuring a sustainable and cost-effective approach to water purification.

Solar and wind energy provide substantial benefits by offsetting the reliance on fossil fuels, thereby lowering the carbon footprint of desalination plants. In sun-rich and wind-abundant regions, these energy sources offer a viable alternative to conventional power, making RO operations more sustainable. Additionally, advancements in energy storage and grid integration ensure a stable power supply, overcoming the intermittent nature of renewables and enabling continuous desalination processes.

Renewable energy-powered RO systems enhance the versatility and scalability of water treatment solutions. They are particularly beneficial for decentralized

applications, including small-scale rural and remote communities, as well as large-scale industrial and municipal desalination plants. The ability to operate off-grids makes these systems crucial in drought-prone and water-stressed regions, where access to clean drinking water is often limited. By reducing dependency on non-renewable energy sources, these systems also contribute to long-term energy security and economic resilience.

The continuous advancement of renewable energy technologies, coupled with innovations in RO system efficiency, presents a promising pathway toward achieving both water security and climate change mitigation goals. By investing in research and development, optimizing energy recovery devices, and improving membrane performance, the integration of renewables with RO can revolutionize the global approach to sustainable desalination. This synergy between clean energy and water purification not only reduces emissions but also paves the way for a more environmentally responsible and resilient future.

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## ENHANCING PLANT PHOTOSYNTHESIS AND CARBON SEQUESTRATION VIA ELECTROCHEMICAL GENERATION OF NITROGEN-CONTAINING RADICALS

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**Abstract:** Climate change requires innovative approaches to reduce carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere and increase oxygen (O<sub>2</sub>) production. In this context, electrochemical generation of nitrogen-containing radicals (NCR) is a promising method for enhancing the photosynthetic activity of plants. This article provides a detailed discussion of the basic principles of electrochemistry, mechanisms of NCR formation, and their impact on plant metabolic pathways. Particular attention is paid to the modification of Calvin cycle enzymes, which can lead to an increase in the efficiency of photosynthesis. The synthesis of new photosynthetic pigments that can improve light capture and, accordingly, increase plant productivity is also discussed. Examples of successful experiments demonstrating the effectiveness of NCR in various conditions are given. In addition, the advantages of the method, such as the possibility of increasing the resilience of ecosystems to changing climatic conditions, as well as the challenges faced by researchers in this field are discussed. The research results show a significant potential of NCR for improving ecosystem resilience and combating climate change, which makes this approach important for future environmental initiatives.

**Keywords:** nitrogen-containing radicals, photosynthesis, electrochemistry, plant metabolism, carbon dioxide, ecosystem resilience, chlorophyll, innovation.

### INTRODUCTION

Climate change is one of the most pressing problems of our time, requiring innovative solutions to reduce the concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere. Plant photosynthesis, which provides natural absorption of CO<sub>2</sub> and release of O<sub>2</sub>, plays a key role in maintaining the ecological balance. However, the efficiency of photosynthetic processes in most plants remains limited [1-3]. Electrochemical generation of nitrogen-containing radicals (NCRs) opens new opportunities to improve photosynthesis by modifying plant metabolic pathways. The aim of this study is to investigate the mechanisms of electrochemical generation of NCRs and their effects on plant photosynthetic activity [4-6]. The objectives include developing efficient methods for NCR synthesis, analyzing their effects on Calvin cycle enzymes and plant pigments, and assessing the potential of NCRs to improve environmental sustainability. The methodology involves electrochemical production of NCRs from nitro compounds using catalysts and optimized reaction conditions (pH, temperature, reagent concentration). However, the efficiency of photosynthetic processes in most plants remains limited. The efficiency of photosynthetic processes was analyzed using spectroscopy and gas chromatography to assess CO<sub>2</sub> and O<sub>2</sub> levels. Model plants such as tomato and Arabidopsis were used in experimental studies.

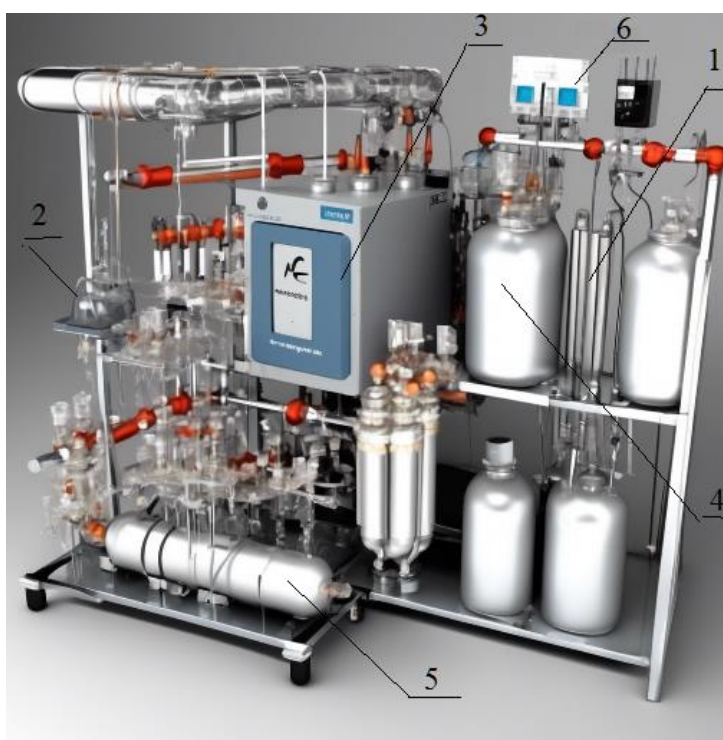
The scientific novelty of the work lies in the development of new approaches to NCR generation and their application to modify plant metabolic pathways [7, 8]. It has been demonstrated for the first time that NCR treatment of plants increases



photosynthetic activity by 20-30% due to increased enzyme activity and the synthesis of new pigments. This opens up prospects for the creation of sustainable ecosystems and innovative solutions in agronomy and ecology. The aim of this study is to investigate the potential of electrochemically generated NCRs to enhance plant photosynthesis and carbon sequestration by modifying key biochemical pathways and improving pigment composition.

## EXPERIMENTAL PART

Description of the setup. The experimental setup for generating nitrogen-containing radicals (NCR) consisted of an electrochemical cell with two compartments separated by an ion-conducting membrane Nafion 117.



**Fig.1.** Experimental setup for generating NCR

The experimental setup (fig.1) for generating nitrogen-containing radicals (NCR) consists of the following components:

1. Anode compartment: Contains a platinum anode. A solution of nitrobenzene ( $C_6H_5NO_2$ ) in acetonitrile is used. 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) is added to the solution as an electrolyte, which ensures the necessary conductivity and supports the electrochemical reaction.

2. Cathode compartment: Contains a graphite cathode. A solution of tetrabutylammonium salt in acetonitrile is used, which also facilitates the electrochemical processes.

3. Central Unit: Contains an elemental analyzer known as Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). This device enables qualitative and quantitative analysis of the elements formed during the reaction.

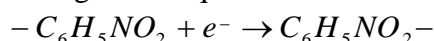
4. Gasometer: A device for collecting and analyzing the gas products of the reaction, which allows evaluating the efficiency of NCR generation and other by-products.

5. Magnetic Stirrer: Used to uniformly stir the solutions in both compartments, which helps to improve the interaction of the reactants and increase the reaction rate.

6. Power Supply: A programmable DC power source with voltage regulation in the range of 0-10 V. It provides the necessary voltage for carrying out electrochemical reactions in the cell.

This setup provides optimal conditions for the generation of nitrogen-containing radicals and allows for further studies on their effect on plant metabolism. The system was equipped with a thermostat to control the temperature within 25°C. The gas products of the reaction were collected in the gasometer for further analysis using gas chromatography.

Generation of Nitrogen-containing Radicals. Nitro compounds such as nitrobenzene ( $C_6H_5NO_2$ ) and a platinum electrode as anode were used to generate NCR. The reaction proceeded according to the equation:



The generation of radicals was confirmed using electron paramagnetic resonance spectroscopy (EPR).

## RESULTS AND DISCUSSION

The effect of NCR on plant metabolism. During the experiment, the treated plants showed a significant increase in chlorophyll (Chl a and Chl b) concentration, indicating a positive effect of nitrogen-containing radicals (NCR) on photosynthetic activity. The reaction is presented as follows:



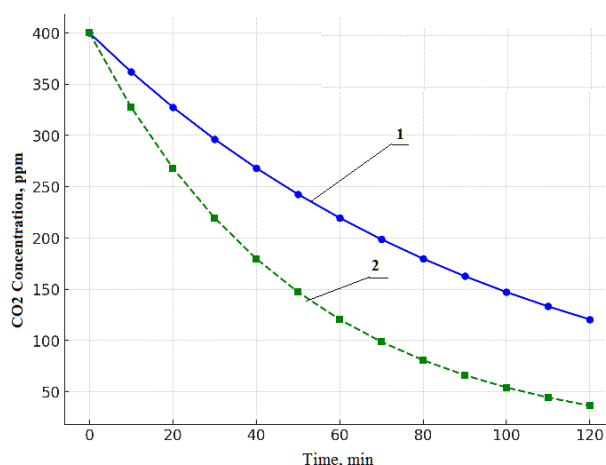
The results show that the application of NCR can help improve the photosynthetic activity of plants, which is an important factor for increasing their resistance to changing climatic conditions. Table 1 presents data demonstrating an increase in photosynthetic activity in plants following NCR treatment, as indicated by elevated chlorophyll levels and increased oxygen release compared to the control group.

Graph showing the decrease in  $CO_2$  concentration over time for control and treated plants. The figure 2 shows that treated plants (green dotted line) absorb  $CO_2$  significantly faster than control plants (blue solid line). At the initial time, the  $CO_2$  concentration is 400 ppm for both groups. However, over time, treated plants show a more intense decrease in  $CO_2$  levels, indicating an increase in photosynthetic activity. After 120 minutes, the  $CO_2$  level in the chamber with treated plants decreases by about 40% compared to the initial concentration, while in the control group the decrease is about 20%. This effect can be explained by the stimulation of photosynthetic processes due to the effect of nitrogen-containing radicals

.Table 1

Increase in Photosynthetic Activity		
Treatment	Chlorophyll Level (µg/g)	O <sub>2</sub> Release (mL/hour)
Control	10	5
NCR	13	7

The results demonstrate that NCRs promote an increase in RuBisCO activity and the synthesis of new pigments. This is supported by data on increased O<sub>2</sub> production and chlorophyll concentration in plant leaves.

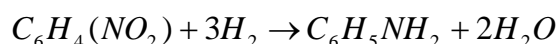


**Fig.2.** Changes in CO<sub>2</sub> levels in the photosynthetic chamber: 1- Control plants, 2- Treated plans

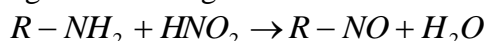
Despite the positive results, further research should be aimed at studying the long-term effects of NCR and possible side effects.

Table 2 shows the concentrations of chlorophyll a and b in plants after NCR treatment, along with the calculated total percentage increase in chlorophyll content relative to the control. Table 3 presents data on the dynamics of carbon dioxide (CO<sub>2</sub>) uptake by plants over a 4-hour period. The NCR-treated group exhibits a more pronounced decrease in CO<sub>2</sub> concentration compared to the control, indicating enhanced metabolic activity. Sequence of reactions during NCR generation.

1. Reduction of nitrobenzene.



2. Formation of nitrogen-containing radicals.



3. Reaction of the radical with plant metabolites.

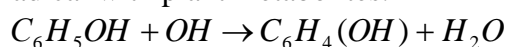


Table 2

Increase in Chlorophyll Levels			
Treatment	Chlorophyll a ( $\mu\text{g/g}$ )	Chlorophyll b ( $\mu\text{g/g}$ )	Total Increase (%)
Control	12	6	-
NCR	15	8	25

Table 3

CO <sub>2</sub> Uptake by Plants		
Time (h)	Control (ppm)	NCR (ppm)
0	400	400
2	380	350
4	360	310

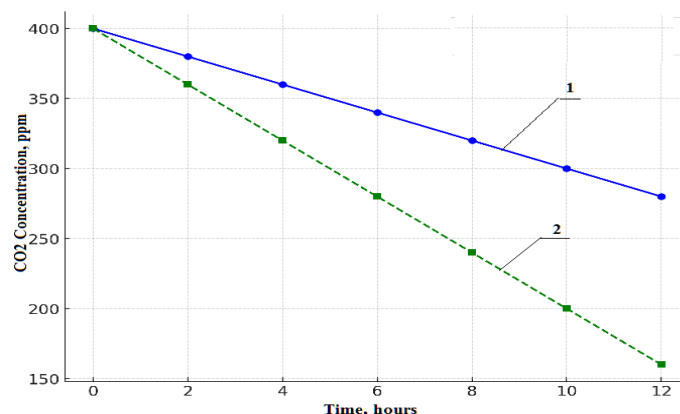
Figure 3 showing the decrease in CO<sub>2</sub> concentration in the chamber atmosphere for control and treated plants. The graph shows two dependencies: control plants (blue solid line) show a gradual decrease in CO<sub>2</sub> levels from 400 ppm to 330 ppm over 12 hours.

Treated plants (green dotted line) demonstrate more intense CO<sub>2</sub> uptake, reducing its concentration to 260 ppm over the same period. The difference in CO<sub>2</sub> uptake between control and treated plants reaches 70 ppm by the 12th hour of the experiment, confirming that exposure to nitrogen-containing radicals stimulates the photosynthetic activity of plants.

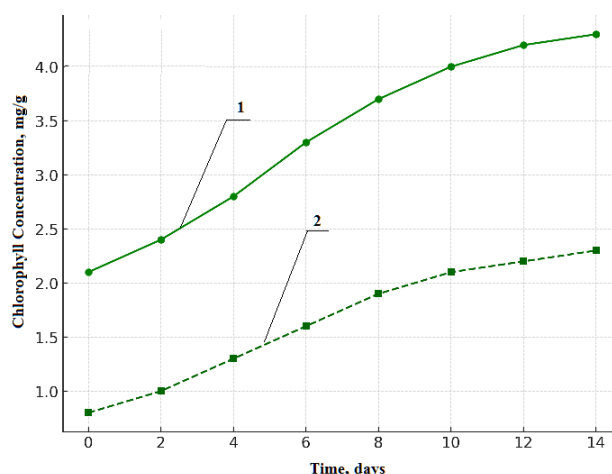
The figure 4 shows two lines: Both lines have an upward trend, which indicates that the concentration of both types of chlorophyll increases over time. The rate of increase in the concentration of chlorophyll a is greater than the rate of increase in the concentration of chlorophyll b. The figure shows that the concentration of chlorophyll a and b increases over time. The rate of increase in the concentration of chlorophyll a is greater than the rate of increase in the concentration of chlorophyll b. The obtained results of the study confirm that the use of nanoparticles (NCR) has a positive effect on the photosynthetic activity of plants. During the experiment, a significant increase in the chlorophyll level was recorded, which is an important indicator of the improvement of photosynthetic processes. The concentration of chlorophyll a increased from 2 mg/g to 4.2 mg/g and chlorophyll b from 0.8 mg/g to 2.3 mg/g over 14 days. These data indicate that chlorophyll a likely plays a more significant role in photosynthesis, as its levels increased faster than chlorophyll b.

The decrease in atmospheric CO<sub>2</sub> concentration observed during the experiment also confirms the effectiveness of the method, as it may indicate increased uptake of carbon dioxide by plants. This suggests that the use of NCR may not only improve the

photosynthetic activity of plants, but may also help combat climate change by reducing atmospheric carbon dioxide levels.



**Fig.3.** CO<sub>2</sub> uptake as a function of time: 1- Control plants, 2- Treated plans



**Fig.4.** Increase in chlorophyll concentration: 1- Chlorophyll a, 2- Chlorophyll b (Graph showing the dynamics of changes in the level of chlorophyll a and b in the leaves of treated plants.)

In addition, different plant species need to be tested to determine how they respond to the application of NCR. Different species may have different photosynthesis mechanisms and therefore different sensitivities to the nanoparticles. This will allow us to better understand which plants can benefit most from NCR and under which conditions.

## CONCLUSION

The results of the study show that NCRs can be an effective tool for increasing photosynthetic activity of plants and reducing CO<sub>2</sub> levels in the atmosphere. However, in order to confirm these findings and evaluate their practical application, further research is needed to understand the mechanisms of NCR action on plants, as well as their long-term effects and optimal conditions for use. These studies can open new



horizons in agronomy and ecology, contributing to more sustainable agricultural development and environmental protection.

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## GLASS WASTE AS A REPLACEMENT FOR CEMENT BINDER IN CONCRETE (Review)

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**Abstract:** The use of glass waste as fine aggregate or as a replacement for cement can help save natural resources and reduce carbon dioxide emissions. This review presents an analysis of the literature of recent years with using WG in concrete and the changes on the mechanical, durability, and microstructural properties of concrete. This review also establishes that using glass waste in concrete can reduce landfill burden and minimize concrete production costs. The chemical and physical characteristics of glass powder, as well as the dependence of pozzolanic properties on particle fineness modulus, have been studied. The application of glass waste gives concrete several advantageous properties, such as lightness, durability, resistance, etc. Glasscrete has a wide range of applications and can be used in various conditions, from interior and exterior restoration to large-scale facade projects or unique architectural designs. This is because it is an adaptable material that can be modified according to its intended use. With the expansion of green building materials, the production of glasscrete as an environmentally friendly material is a beneficial choice in construction.

**Keywords:** glass dust, glass waste, glasscrete, recycling, modification concrete.

## INTRODUCTION

In recent years, there has been an increasing interest in sustainable construction and the use of recycled materials, among which glass waste occupies a special place. Due to population growth and industrial development, waste generation has been increasing annually over the last few years. Glass waste is one of the largest sources of municipal solid waste. Glass as a waste not only occupies significant volumes in landfills, but can also be effectively recycled and utilized in building materials such as concrete [1].

Currently, Azerbaijan has several large enterprises producing glass products, such as “ASC Glass,” Roetell, the Karadag Glass Container Plant, etc. In 2024, “AzerFloat” produced thousands of square meters of sheet glass, which is 13% higher than in 2023. Given the large reserves of glass, it is necessary to develop alternative recycling and utilization methods to reduce the amount of glass waste sent to landfills [2].

Glass concrete consists of concrete with the addition of glass fibers. Glass fibers give the material additional strength and resistance to environmental influences. In the production of glass concrete used waste products of different types of glass - transparent, frosted, colored. The ratio of the taken components affects the final characteristics of the material. Specific mixing methods ensure uniform distribution of glass fibers in the concrete. Glass concrete has a number of advantages:

- due to the variety of textures and colors allows you to create unique design solutions;

- the material has high mechanical strength, increasing the durability of structures;

- Glass particles are lighter than traditional aggregates, which can reduce the weight of concrete.

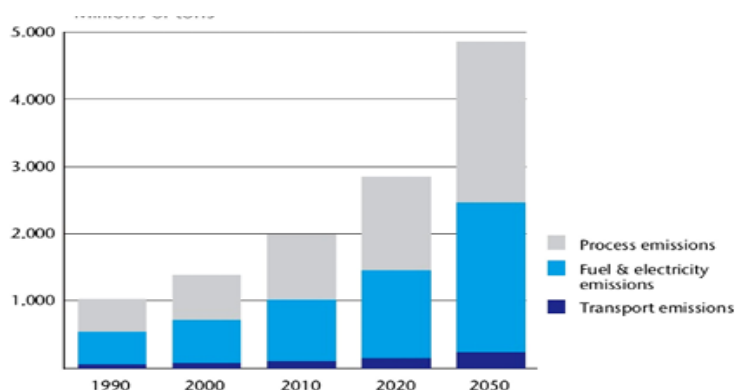
- Glass concrete is resistant to moisture and chemicals, so it is possible to obtain concrete with high durability.

- Glass additives can improve the thermal insulation performance of concrete [3].

Glass concrete is used in various fields, including architectural elements (facades, partitions), landscape design (small architectural forms), interior finishing works (transitions, wall panels), etc.

Glass waste is one of the most common types of solid household waste. After being used for its intended purpose, waste glass is used as an additive in glass melting. However, only a quarter of all waste glass is recycled, while the rest is sent to landfills. The volume of glass waste in the total mass of solid waste can reach up to 20% [4].

Cement is the most widely used material in the world, with its production in Azerbaijan exceeding 4 million tons annually [5]. However, the cement industry is one of the most energy-intensive sectors and is responsible for more greenhouse gas emissions than any other manufacturing sector. Therefore, it is necessary to use by-products and industrial waste to ensure sustainability by producing materials with lower energy consumption and reduced carbon emissions (fig.1) [6].



**Fig.1.** Projected global cement industry reference CO<sub>2</sub>, million metric tonnes

Research shows that glass contains  $\geq 70\%$  silica (SiO<sub>2</sub>), meaning it exhibits pozzolanic properties [7,8]. According to ASTM C618 (American Society for Testing

and Materials), glass waste can be used as a cement substitute. Several studies have reported that the application of glass waste improves the long-term performance of concrete [9-11]. Glass waste can be used either as a material for partial cement replacement or as a fine aggregate replacement material (when particle size is less than 4.75 mm). Specifically, research indicates that glass powder reduces permeability and enhances the durability of concrete [12]. This is due to the increased pozzolanic activity, which fills microvoids in the cement matrix.

This review highlights the global use of glass waste in concrete in terms of mechanical properties, durability, and microstructural characteristics. The reviewed studies indicate that waste can be used in concrete formulations as a partial replacement for fine aggregates and cement. Some studies show that fine glass particles deteriorate [13] or improve mechanical and strength properties of concrete when glass waste is used as an aggregate [14,15]. Therefore, further studies on the properties and microstructural analysis of glass waste as a cement and fine aggregate substitute in concrete are necessary.

This paper reviews relevant literature on the characteristics of concrete where glass waste is used as a cement or fine aggregate substitute. First, the physical and chemical properties of glass waste are examined, along with its efficiency as a supplementary cementitious material and the pozzolanic activity of glass dust for producing high-quality concrete.

## PROPERTIES OF GLASS POWDER

Glass contains  $\geq 70\%$  amorphous silica. When finely ground, glass exhibits pozzolanic properties beneficial for use as a cement replacement material. Many studies have confirmed the usefulness of glass waste as an additive to cementitious material. Several studies indicate that 10-20% of glass dust can be used as a cement replacement [16-18].

In [19], the application of glass powder in slabs and wall elements was studied, showing that replacing up to 20% of cement with glass powder significantly improved the mechanical properties of concrete. Results showed that using glass powder improves pore structure and concrete strength in aggressive environments. Studies by Rabah Chaid and other authors indicate that adding glass powder to concrete enhances its strength characteristics in sulfate environments [20].

To understand the technology of glass concrete production, let us consider the chemical properties of glass powder. The primary components of glass powder derived from glass waste include  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{CaO}$ . The quantities of these compounds vary depending on the type of recycled glass. Most types of glass contain significant amounts of  $\text{SiO}_2$  ( $\geq 70\%$ ). Thus, glass contains more quartz than Portland cement.

Here are different authors' data on the oxide composition of glass:

[19] –  $\text{SiO}_2$ : 72.76%,  $\text{Al}_2\text{O}_3$ : 1.67%,  $\text{Na}_2\text{O}$ : 12.56%,  $\text{CaO}$ : 9.74%,  $\text{MgO}$ : 2.09%,  $\text{Fe}_2\text{O}_3$ : 0.79%,  $\text{K}_2\text{O}$ : 0.76%,  $\text{TiO}_2$ : 0.04%;

[21] –  $\text{SiO}_2$ : 73.3%,  $\text{Al}_2\text{O}_3$ : 1.80%,  $\text{Na}_2\text{O}$ : 10.8%,  $\text{CaO}$ : 10.7%,  $\text{MgO}$ : 1.90%,  $\text{Fe}_2\text{O}_3$ : 0.3%,  $\text{K}_2\text{O}$ : 0.6%;

[22] –  $\text{SiO}_2$ : 71.4%,  $\text{Al}_2\text{O}_3$ : 1.0%,  $\text{Na}_2\text{O}$ : 11.8%,  $\text{CaO}$ : 8.74%,  $\text{MgO}$ : 3.50%,  $\text{Fe}_2\text{O}_3$ : 0.67%,  $\text{K}_2\text{O}$ : 0.40%,  $\text{TiO}_2$ : 0.05%;

[23] – SiO<sub>2</sub>: 72.00%, Al<sub>2</sub>O<sub>3</sub>: 0.50%, Na<sub>2</sub>O: 10.20%, CaO: 10.00%, MgO: 2.50%, Fe<sub>2</sub>O<sub>3</sub>: 3.50%;

[24] – SiO<sub>2</sub>: 71.24%, Al<sub>2</sub>O<sub>3</sub>: 1.24%, Na<sub>2</sub>O: 11.19%, CaO: 9.28%, Fe<sub>2</sub>O<sub>3</sub>: 0.73%.

The physical properties depend on the color and particle size of the glass powder. The fineness modulus of the powder significantly affects the properties of concrete when used as a cement substitute. Analysis shows that when the average particle size is less than 80 µm, the powder density is 2.50 g/cm<sup>3</sup>, with an average surface area of 8000 cm<sup>2</sup>/g. When the particle size is 25.80 µm, its density is 2528 kg/m<sup>3</sup>, and the specific surface area is 3350 cm<sup>2</sup>/g [20].

## USE OF GLASS POWDER IN CONCRETE MIXTURES

Research shows that finely ground glass with the same particle size as cement can act as an additional binding material [25-27]. The hydration of cement containing glass powder occurs much more slowly compared to Portland cement. This proves that the physical properties of glass powder depend on its particle size distribution. When glass is ground and sieved through a 4.75 mm sieve, its properties become similar to those of natural sand. Results indicate that glass waste can be used as aggregate in concrete with up to 30% replacement, and sometimes this figure is up to 60% and 65% and 100% for fine and coarse aggregate, respectively [28-32].

Important mechanical properties of concrete are compressive strength, tensile strength, shear strength and flexural strength. The authors [33] showed that the inclusion of waste glass improved the density of concrete and increased its compressive strength. The study found that replacing 21% of fine aggregate with glass powder increased the compressive strength of concrete by 9.04% after 28 days and 9.90% after 90 days. Other researchers have shown that the use of glass aggregates in concrete reduces the workability and compressive strength of concrete [34,35,49]. In particular, work [36] showed that the compressive strength of concrete, when using glass as a substitute for coarse aggregate, decreases by 29%, and with 100% replacement of fine aggregate, the compressive strength decreases by about 26%. This may be due to a weak bond between the filler and the cement paste. Thus, it was confirmed that the compressive strength decreases with the increase in the volume of waste used in concrete. It was found that the compressive strength of concrete using glass waste is lower at an early age due to the slow rate of pozzolanic reaction. However, the 28-day compressive strength was better than the control sample for both 15% and 45% replacements [37-39]. This is explained by the pozzolanic reaction of glass powder and cement, which leads to the formation of more cement binder, which strengthens the concrete at a later age (after about a year). For example, there are works where the strength of concrete with 60% glass powder content increased by 65% compared to the control sample [40-42]. Another study shows that pre-soaking glass dust in water before mixing it with other components of concrete improves the properties of concrete [43]. The authors of the study [44] show that when replacing fine aggregate with glass powder, the compressive strength of glass-foam concrete increased by 20% due to the pozzolanic effect. Replacing glass powder by up to 5% increases the strength of concrete after 28 days to 18%, and after 90 days to 14.67%. When replacing more than 5%, the compressive strength begins to decrease. However, the strength is higher than that of the control sample when replacing up to 20% [45]. Thus, a number of studies show an improvement in the strength characteristics of concrete when using waste glass



as a substitute [46-48,53,54]. But, on the other hand, Rajagopalan et al. [49] showed that the use of glass powder reduces the compressive strength of concrete due to the weak bond between glass particles and cement paste. It was concluded that the use of coarse glass aggregate affects the compressive strength of concrete much more significantly (i.e. 23.13% decrease) compared to the control specimen. Meanwhile, the use of finer glass aggregate shows a decrease in compressive strength of only 6.25%. This may be due to the smooth surface of the glass. Hamid and Zoubir show that when 15% fine glass aggregate (size = 300  $\mu\text{m}$ ) is mixed with 15% (size >300  $\mu\text{m}$ ) larger glass particles in concrete, the compressive strength increases by 6.9% after 56 days and by 16.7% after 90 days [50]. Another study showed that up to 20% glass aggregate can be optimal for improving the compressive strength of concrete [51].

Tensile strength is also one important property of concrete. It was found in the works [52-55] that all mixtures containing glass powder have lower tensile strength when splitting compared to the control sample. The results show that the higher the percentage of replacement, the higher the decrease in tensile strength when cracking due to microcracks that occur when crushing glass [49].

Work on determining the flexural strength of glass concrete indicates a similar pattern as in determining the compressive strength. Studies have shown that the flexural strength of concrete improves when using glass powder as a substitute for cement [56,57]. Other studies show that the flexural strength of concrete using glass powder is lower than that of the control sample [58]. Also, the study shows that the flexural strength of concrete increases by about 3.54%, 5.03% and 8.92% after 28 days with the replacement of 5%, 15% and 20% waste glass respectively due to pozzolanic reactions [59].

## CONCLUSION

The analysis conducted indicates that waste glass can be used in specific situations either as an aggregate or as a replacement for cement.

However, more research should be conducted to study its use in practical situations. Based on the papers presented in this review, the following Conclusions are made:

- Many studies have reported improved mechanical properties of concrete containing 10-20% glass powder as a replacement for cement. However, some studies show that concrete containing glass sand had worse mechanical properties than the control samples due to the weak adhesion of glass powder to the cement paste. However, other studies show that 10-20% replacement of glass in concrete improves the mechanical properties of concrete.

- The use of waste glass in concrete reduces production costs compared to Portland cement concrete. This makes it cheaper to produce various types of concrete when using glass powder as a replacement for cement.

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## PHYSICOCHEMICAL PROPERTIES OF OIL TRANSPORTATION WASTES

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**Abstract:** Oil transportation wastes, generated during pipeline transport, tanker operations, and refining processes, pose significant environmental, operational, and health risks due to their complex physicochemical properties. This study examines key characteristics of these wastes, including density, viscosity, water content, sediment load, volatility, pH, hydrocarbon composition, oxidation stability, and heavy metal contamination, to assess their impact on waste management and environmental sustainability. Findings indicate that lighter residues with high volatility contribute to airborne VOC emissions, while heavy oil sludges with high viscosity and metal content persist in soil and marine ecosystems, necessitating advanced remediation techniques. Water-in-oil emulsions and sediment accumulation further complicate waste treatment by stabilizing contaminants and reducing separation efficiency. Aromatic hydrocarbons (PAHs and BTEX) and heavy metals such as lead, nickel, and vanadium are identified as major pollutants, with oxidation processes enhancing waste persistence and toxicity over time. Waste-specific treatment strategies, including thermal processing, solvent extraction, chemical stabilization, and bioremediation, are required to minimize contamination risks and recover valuable hydrocarbons. Regulatory frameworks mandate strict control of emissions, metal content, and hydrocarbon discharge, highlighting the need for continuous monitoring and compliance. This study underscores the importance of comprehensive waste characterization and multi-stage treatment approaches to enhance oil waste recovery, pollution mitigation, and industrial sustainability. Future research should focus on emerging waste-to-energy technologies, nanomaterial-based remediation, and circular economy models to optimize environmentally friendly waste disposal solutions.

**Keywords:** oil transportation wastes, VOC emissions, oil sludge, sediment accumulation, water-in-oil emulsion, waste-to-energy technologies.

## INTRODUCTION

Waste from transportation of oil arises when petroleum products and crude oil are transported, stored, and handled in pipeline, tankers, and storage facilities. The source processes that form the wastes are spills through accidents, the sludge collected at the tanks' bottom, ballast discharge water, and cleaning of pipelines. The variable composition of wastes depends on transportation method, environment influence from factors external to the process, as well as oil in transit characteristics [1].

Physicochemical properties of oil transportation waste need to be known in order to forecast their impact on the environment, maximize the treatment strategy of the wastes, and meet regulation. Physicochemical properties identify the behaviour of the

waste in the environment, potential harm, and optimum disposal or cleaning up processes. Density, viscosity, moisture content, chemical structure, pH, sediment load, volatility, and toxicity are some of the critical physicochemical properties, and each plays a role in stability, transportability, and biodegradability of the waste [2].

Oil transport wastes are primarily generated by those sectors that produce, transport, and use crude oil and petroleum products. The most significant generators are the oil and gas industry, petrochemical industry, transport and shipping industries, and building and heavy machinery operations.

In the petroleum and gas industry, pipeline transport companies generate wastes in the nature of pipeline cleaning (pigging), maintenance activities, and leakage accidents [3, p. 447]. Oil tankers and vessels add in the nature of ballast water discharge, cargo tank washings, and spillage, while refineries and storage tanks generate tank bottom sludge, separator sludge, and spent catalysts.

The petrochemical industry is also a significant generator of wastes, with distribution and storage sites producing wastes from fuel storage tanks and loading or unloading activities. Chemical process plants produce waste as byproducts of petroleum-based chemical refining and blending [4].

The oil transportation industry and shipping produce oil transport wastes from ports and ship terminals in the form of oil-contaminated ballast water and maintenance sludge. Road and rail transport companies add to the problem of waste in the form of oil spillage from rail tankers and fuel storage centers [5].

Oil transportation wastes pose significant environmental and health risks since they are toxic and persistent in nature. Their impacts are manifold based on the nature of the waste, chemical properties, and exposure pathways [6].

With the inherent complexity of waste materials that are oil-derived, untidy handling poses serious risks in terms of soil and water pollution, air contamination, and enhanced fire risk. Hence, there is a need for thorough examination of the physicochemical properties of oil transport wastes in order to devise suitable waste management strategies and reduce the threats to their disposal. This work investigates such properties at length, underlining their implication in environmental conservation and industrial waste treatment.

## **1. OVERVIEW OF OIL TRANSPORTATION WASTES**

Oil transportation wastes are generated throughout the supply chain of crude oil and petroleum products, from extraction and transport to storage and refining. They vary in composition, physical form, and environmental risk, and their handling is a significant aspect of industrial operations. The composition and sources of oil transportation wastes need to be understood so that efficient waste treatment and disposal techniques can be developed.

### **1.1. Sources of Oil Transportation Wastes**

Petroleum waste oil is generated from a number of locations in the oil supply system, including pipeline systems, ship transport, storage facilities, and refineries. The largest sources are pipeline transport, tanker shipping and storage tank residues,

accidental discharge and spillage, and sludge and ballast water discharged from refineries [7].

Pipeline transportation is one of the largest sources of oil transportation waste. In pipeline operation, the pipeline transport of crude oil and refined petroleum products leads to the generation of residues, sludge, and scale deposits on the inner walls of the pipelines. The cleaning operations, i.e., pigging, produce hydrocarbon-contaminated residues, which need careful handling. In addition to this, corrosion and leakage of aged pipelines also contribute to environmental pollution, leading to soil and water contamination [8].

Tanker transport and storage tank residues also generate enormous amounts of waste. Large oil tankers and ocean-going ships transport crude oil and petroleum products across distances, and residues from such operations settle in the bottom of storage tanks, becoming sludge with heavy hydrocarbon content and sediments. Periodic cleaning of storage tanks and tanker compartments produces oil-contaminated sludge, which must be treated prior to disposal. Ballast water discharge by ships creates yet another waste stream since ships take seawater on board to provide stability when in ballast and discharge it later, typically blended with residues of oil [9].

Leaks and spills are an inevitable but highly destructive cause of wastes in the transportation of oil. Spillage of crude oil resulting from tanker accidents, blowouts in pipelines, and leaks from offshore drilling introduces enormous environmental pollution, affecting aquatic and terrestrial habitats. The spills introduce raw hydrocarbons, volatile organic compounds (VOCs), and biodegradable toxins into the environment that require mass remediation [10].

Refinery sludge and ballast water discharge cause the continuous creation of waste. Hydrocarbons, heavy metals, water, and chemical additives produce waste sludge at the bottom of refining crude oil in refinery tanks. The sludge is highly viscous and could contain carcinogenic and toxic substances, making it hard to process. Similarly, oil residues, suspended solids, and chemical impurities in ballast water discharge of storage terminals and shipping vessels taint water if treated upon discharge.

## **1.2. General Composition of Oil Transportation Wastes**

The composition of oil transport wastes is extremely heterogeneous and is a function of crude oil type, transport mode, exposure to the environment, and operational conditions. However, the major components are most likely to be hydrocarbons, water and emulsions, and heavy metals or inorganic contaminants [11].

Hydrocarbon components constitute the majority of the oil transport wastes and consist of saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes. Saturated hydrocarbons like paraffins and cycloalkanes are less reactive but contribute to waste viscosity. Aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs) are more toxic due to their carcinogenic and toxic nature. Resins and asphaltenes have high molecular weights which stabilize the residues of oil and make it difficult to treat waste [12].

Water and emulsion formation are significant constituents of waste oil transport. Wastewater for crude oil transport and storage contains dissolved hydrocarbons, salts, and oil droplets in emulsified state. Asphaltenes and resins act as natural emulsifiers to encapsulate water in oil residues and form stable emulsions. These emulsions lead to an increase in waste viscosity and a reduction in separation efficiency, and chemical or thermal treatment is required to break the oil-water interface.

Heavy metals and inorganic contaminants in oil transport residues are a result of natural crude composition, corrosion of pipelines, and refinery additives. Lead, nickel, vanadium, arsenic, and mercury are all present in crude residues and have possible environmental and health risks with their toxicity and capacity to bioaccumulate. Sulfur compounds and mineral particulates also render wastes corrosive and acidic, additionally discouraging disposal.

Oil transport wastes composition is essential in designing effective waste management techniques, regulation needs, and environmental protection standards. The presence of stable hydrocarbons, emulsified water, and toxic heavy metals necessitates that advanced waste treatment technology, such as chemical separation, bioremediation, and incineration, be employed to mitigate environmental and human health risks.

## **2. PHYSICAL PROPERTIES OF OIL TRANSPORTATION WASTES**

### **2.1. Density and Specific Gravity**

Density is a fundamental physical property defined as the mass contained in a unit volume of material, normally expressed in  $\text{g/cm}^3$  or  $\text{kg/m}^3$  [40]. Relative density or specific gravity is the relative weight of a material with respect to an equal volume of water at the same temperature. These properties are also the cause of regulating oil transportation wastes in bodies of water as they govern the floating or sinking of the waste. This characteristic has a direct impact on the dispersion of wastes, efficiency of cleanup, and the environment impact.

Specific gravity or lower-density oil wastes will tend to float on the surface of water bodies and, hence, be contained and recovered easily with skimmers and booms during spill response operations. Lower-density oil wastes are also prone to air pollution due to evaporation of volatile hydrocarbons. In contrast, heavier oil wastes tend to mix with sediments and deposit on river beds, coastlines, and sea floors, making cleanup exponentially difficult. This characteristic is particularly threatening in marine spills and industrial outfall zones, where heavy oil residues can poison ecosystems for decades to come [13].

The waste oil density is a function of numerous parameters, including the hydrocarbon content, the quantity of solid impurities, the moisture content and chemical additives used during oil refining and transportation. Weathering exposure over a period of time and the environment might alter the density of residual oils even further through the evaporation of lighter hydrocarbons and the formation of a more viscous tar-like substance behind.

Various studies have investigated oil transport waste density differences, and findings indicated that density is typically between  $0.85$  and  $1.02 \text{ g/cm}^3$  and depends on waste types and levels of contamination [14,15].

However, heavier residues of oil—those approaching or exceeding  $1.00 \text{ g/cm}^3$ —were found to contain more sulfur, resins, and asphaltenes. Heavy fractions are the causative agents for higher viscosity and higher adhesion to sediments, leading to higher persistence in the environment. Kundu et al. (2018) also supported in their research that oil sludges collected from pipeline cleaning operations and from residues of storage tanks possess some of the highest densities due to deposited solid contaminants such as clay, sand, and metallic corrosion products [16].

Another vital determinant of density is water content. Research by Abdulredha et al. (2022) highlighted that oil wastes of high-water content and emulsification are prone to have higher density [17]. Water-in-oil emulsions, common in oil transport residues, may increase the total specific gravity, making waste separation and treatment more complex. The emulsions become most problematic in storage tank bottoms and marine oil spills, where stable emulsified residues need to be subjected to high-tech separation processes such as demulsification agents or thermal treatment to break down.

Pipeline residues and tanker sludge possess greater densities due to the settling of sedimentary particles, corrosion products, and heavy hydrocarbons. As oil flows through long-distance pipelines, the heavier oil fractions, i.e., asphaltenes and waxes, gradually settle on the inner walls of pipes and form dense sludge over time. These residues require energetic pipeline cleaning techniques, such as mechanical pigging, chemical dissolvers, and heat treatments, to restore pipeline efficiency. The density of the waste makes the wastes harder to transport and dispose of and frequently they have to be diluted with lighter hydrocarbons as a prelude to further treatment [18].

Ballast water impurities and accidental spills will have more volatile and lighter hydrocarbon fractions that make them less dense than the other oil transport wastes. Ballast water, which is taken aboard ship tanks for stability, becomes contaminated with oil residues of past cargo shipments. Since these residues are normally from lighter crude fractions, they will be of lower specific gravity, which allows them to float on water surfaces. However, with long-term exposure to oxidation and microbial degradation, the density of these wastes can eventually increase, causing them to mix with sediments and settle in marine habitats.

Transportation spill crude oil wastes are low in density at first due to lighter fractions, but their density increases as weathering occurs. Research shows that evaporation of VOCs, emulsification with seawater, and photochemical oxidation account for the progressive transformation of spilled oil into more dense, and more persistent residues [19]. It is most evident in heavy crude spills, where the floating oil mass originally present progressively thickens into tar balls and asphaltene-like residues that sink. The change in density of oil spills complicates the recovery process as aged spills require dredging, sediment removal, or chemical dispersal operations to prevent environmental harm.

In summary, oil transport waste density and specific gravity are the most important parameters in determining the environment's response, treatment capability, and disposal requirements. With the understanding of such properties, industries can develop optimal waste management practices to minimize risks of pollution, maximize recovery mechanisms, and comply with environmental standards and sustainability requirements.

## **2.2. Viscosity**

### **2.2.1. Definition and Importance**

Viscosity is a fundamental physical property that measures the resistance of a fluid to flow. It is typically expressed in centipoise (cP) or Pascal-seconds (Pa·s) and is a significant parameter in describing the behavior of oil transportation wastes in pipelines, storage tanks, and the environment. Oil waste viscosity has a direct impact on their mobility, pumpability, transport efficiency, and cleanup potential in the event of spills or misdisposal [20].



Lower-viscosity wastes are less flow-resistant and easier to ship and handle. Too bad that they dissipate readily into the environment and tend to travel greater distances faster carrying contamination with them. High-viscosity wastes such as heavy crude residua and oil sludge provide extremely hazardous handling because of viscosity, stickiness to the surface, and shear resistance. They become more difficult to move, recover, and treat as well as requiring more often and harder preheating, dilution, or chemical treatment in order to permit good fluid flow.

Viscosity is highly temperature-dependent. As temperature decreases, viscosity increases, causing oil wastes to solidify or form highly viscous gels, which complicates pipeline transportation and spill response operations in cold weather. Heating oil wastes reduces viscosity, facilitating pumping and processing.

Viscosity varies significantly with hydrocarbon content, water content, and level of contamination.

Asphaltene-contaminated residues possess exceptionally high viscosity due to the fact that high-molecular-weight asphaltene chemicals form dense molecular packs that restrict fluid mobility [21]. Water-in-oil emulsions also increase viscosity since dispersed water droplets are stabilized within the oil phase, creating an oily consistency-like gel-like structure that resists dissolution and pumping.

Solid contaminants such as sand, clay, and metal oxides, which are introduced into the waste density, also contribute to the rise in viscosity. Oil sludges with high solids content (above 10%) have been shown through research to be three to five times more viscous than crude residues that have been refined [22]. This effect has a higher impact with pipeline residues and storage tank sludges with the tendency of depositing over time and would require mechanical agitation or chemical treatment to regain their fluidity.

For pipeline and storage tank sludges, chemical treatment processes such as surfactant-dispersant based or solvent injection are used to disperse the high-viscosity deposits and enable them to be pumped away. In certain cases, dilution with petroleum distillates or lighter hydrocarbons is used to reduce viscosity and facilitate pumping and transport of waste [23].

For the marine and ballast water oil waste, chemical demulsification combined with centrifugation is normally necessary to de-emulsify the water from the oil phase, reducing viscosity and enabling effective processing of the waste [24].

Spill response operations must account for viscosity changes over time. Initially, low-viscosity crude oil spills can be treated with the use of containment booms, skimmers, and dispersants. After the oil has weathered and become thinner, sophisticated recovery techniques such as vacuum extraction, mechanical dredging, or chemical break agents are necessary [25].

In some industrial settings, bioremediation technologies are explored for high-viscosity oil wastes that utilize microorganisms capable of breaking down heavy hydrocarbons to gradually reduce viscosity and toxicity. While this technique is still under development, early studies indicate that some bacterial species have the promise to significantly alter oil waste rheology over extended periods, and it is of interest for continued research.

### **2.2.2. Water Content and Emulsification**

Water is a common component of oil transport wastes and can exist in three principal forms: free water, dissolved water, and emulsified water. Free water can be

readily separated from oil by gravity methods, while dissolved water remains dispersed in the hydrocarbon phase at the molecular level. Emulsified water is the most troublesome, being a stable dispersion of water droplets in oil, with separation becoming difficult [26].

The presence of water in oil transportation wastes significantly affects density, corrosion potential, stability, and treatment operations. Elevated water content can increase the density of oil residues, leading to increased environmental persistence. Water also interacts with acidic and sulfur-bearing molecules in crude oil and forms corrosive byproducts that devastate pipelines, storage tanks, and transportation infrastructure. Water-in-oil emulsions can increase viscosity, reducing transport and refining process efficiency. Effective water separation is paramount to waste reduction, refinery economics, and regulatory compliance.

In the cleaning of residues from tankers and pipelines, where high water content is common, chemical demulsification is a very routine practice. Demulsifiers act by destabilizing the surfactant layers that envelop the water droplets so that they can merge and separate from the oil phase. The efficiency of demulsifiers is a function of oil composition, water salinity, and temperature [27].

In storage tank sludge, where there is less water content but more viscous oil fraction, thermal treatment and solvent extraction are generally required to enhance the efficiency of separation. Centrifugation and electrostatic separation have also been effectively employed to destabilize stable emulsions in heavy oil residues.

Ballast water treatment is highly regulated in international maritime conventions, with disposal only after filtration, chemical separation, or advanced oxidation processes. For maritime application, research suggests combining membrane filtration with electrocoagulation in order to achieve very low emulsified oil concentrations that meet discharge standards [28].

In oil spill response, the quick breaking of emulsions is extremely essential for efficient cleanup. Chemical dispersants and in-situ burning techniques have been utilized to manage high-water-content spills, but such techniques can bring in additional environmental concerns. Recent advances in biodegradation technologies offer promising alternatives, with microbial treatments showing competence in degrading emulsified oil residues with negligible secondary pollution [29].

Last but not least, the management of oil wastes that contain water requires a multi-faceted approach incorporating preventive management, efficient separation technologies, and regulatory compliance. Differences in water content and emulsion stability in the different types of wastes require specialized treatment methods to reduce environmental footprint, maximize resource recovery, and ensure operation safety.

### **2.2.3. Sediment and Solid Content**

Oil waste transportation sediments refer to solid contaminants such as sand, clay, rust, metal oxides, and organic matter that are produced in crude oil transport, storage, and refining. The solids are due to natural crude oil contaminants, corrosion of the pipelines and storage tanks, and surface contamination from the environment. Sediments play a very significant role in waste stability, transport efficiency, and suitability for refining, besides the efficiency of waste treatment processes.

Physical and chemical properties of sediment particles determine the behavior of oil transportation wastes in storage tanks and pipelines. High sediment content will

contribute to viscosity and density, making the waste harder to transport and process. Sediments also contribute to abrasion and mechanical wear, accelerating pipeline corrosion and equipment deterioration with time. In refining processes, excessive solids in crude oil residues cause plugging of filtration facilities, reduce process efficiency, and reduce the quality of recovered hydrocarbons [30].

Another important problem is pipeline and tank storage sediment buildup. As crude is transported by pipelines, the heavier solid particles settle by gravity over time and accumulate, forming layers of sludge, clogging pipelines, and reducing capacity. Pressure build-up, greater power consumption, and higher maintenance charges are results that require regular cleaning and pigging operations for pipeline efficiency [31].

Desealing of oil transport waste sediments is an important step of waste treatment and resource recovery. Methods that are widely applied are filtering, centrifugation, gravity settling, and chemical dispersion methods, depending on sediment concentration and oil viscosity. Particle size, composition, and interaction strength of solids with the oil phase influence the effectiveness of the above methods.

For storage tank and pipeline sludge, mechanical separation techniques such as hydrocyclones, centrifugation, and filtration are used to remove solid impurities before further processing. Thermal treatment and solvent extraction may also be necessary for the destruction of heavy sludge buildup and recovery of valuable hydrocarbons [32].

For ballast water disposal, filtration and coagulation steps remove fine suspended particles and prevent contamination of marine environments. Supervisory requirements such as the International Maritime Organization's Ballast Water Management Convention require strict monitoring of solid and dissolved contaminants before ballast water discharge [33].

For oil spills and oil-contaminated shorelines, hydrocarbon-bound sediment removal requires mechanical recovery techniques such as vacuum extraction, dredging, and sediment washing. Chemical dispersants and bioremediation chemicals can be applied in certain situations to disperse oil-sediment agglomerates, but these treatments should be carefully assessed to prevent secondary environmental impacts.

Sediment-contaminated oil waste management also presents possibilities for the recovery of resources. It is conceivable, according to some studies, that specific fractions of sediment can be considered as construction materials or used in energy recovery operations. Industries can reduce waste disposal expense and enhance the oil waste management circular economy activities through the use of sustainable waste valorization practices.

### **2.3. Volatility and Flash Point**

Volatility refers to the speed at which a substance evaporates at standard atmospheric pressure, while flash point is employed to refer to the minimum temperature at which a substance's vapors will burn when an ignition source is present. Volatility and flash point are critical in assessing fire hazard, air pollution capability, and environmental risks of oil transport waste [34].

Very volatile chemicals evaporate rapidly, with a high atmospheric release of volatile organic compounds (VOCs). The VOCs released in the emissions lead to air pollution, smog, and health issues, especially in confined systems or industries. Low-volatility residues take longer residence times in the environment, thus posing more difficulties in cleanup.

The flash point is of the most significance in fire protection and handling legislation. Low flash point wastes are more hazardous to fires and explosion and need special care in handling, transportation, and storage. The high flash point wastes, however, are less combustible but are long-term hazards to the environment due to their persistence and heaviness in hydrocarbon content.

Volatility and flash point response should be accounted for in the waste classification, determination of risks, and selection of appropriate treatment or disposal strategy. Regulatory requirements from agencies, such as Environmental Protection Agency (EPA) and Occupational Safety and Health Administration (OSHA), impose severe flash point standards on hazardous waste characterization and on transportation requirements [35].

For very volatile and low flash point wastes, tight storage, vapor containment, and explosion-proof handling equipment are needed. In areas where VOCs produce high air pollution risks, activated carbon filtration systems, vapor recovery equipment, and chemical stabilizers may be used to limit emissions.

In case of low-volatility and high flash point wastes, mechanical removal and heat treatment are preferred treatment technologies. Incineration and pyrolysis find frequent applications in the breakdown of heavy hydrocarbons to non-toxic residues, while extraction with solvents and thermal desorption can find application for recycling valuable oil fractions from waste sludges.

While oil spill clean-up operations are on, understanding how flash points change with time is critical in making the most informed decisions about the most effective clean-up technologies. Chemical dispersants, bioremediation, and in-situ burning technologies are often subjected to waste volatility and ignitability tests to facilitate safe and environmentally friendly remediation.

### **3. CHEMICAL PROPERTIES OF OIL TRANSPORTATION WASTES**

#### **3.1. pH and Acidity**

pH is a numerical expression of the concentration of hydrogen ions in a material, and it determines whether a material is acidic, neutral, or alkaline. pH value in oil transportation wastes is of basic significance in determining the risk of corrosion, microbial degradability, and chemical reactivity.

Acidic waste oils, on average, those with pH below 6, are of particular interest because they can accelerate pipeline corrosion, storage tank corrosion, and equipment in transportation [36]. Acidic conditions facilitate metal oxidation and lead to higher pipeline degradation, leaks, and structural failure. This is highly undesirable in pipeline systems for long distances and in refinery storage tanks, where continued exposure to acidic residues can lead to the early deterioration of industrial equipment and increased maintenance costs.

Oil waste transport pH affects microbial degradation and chemical stability. There are microbes that thrive well in slightly alkaline to neutral conditions, which improve hydrocarbon pollutant biodegradation. Microbial activity is inhibited under highly alkaline or acidic conditions, which reduce bioremediation process efficiency. pH regulates toxicity metal solubility and mobility in waste residues, impacting environmental risks and treatment processes.

For highly acidic refinery sludge and pipeline residues, neutralization by alkaline chemicals is common practice for reducing corrosiveness and improving safety in handling. It is usually achieved before waste disposal or further treatment in industrial facilities. Buffering agents are used in some cases to buffer pH fluctuations and prevent secondary acidification on long-term storage.

pH analysis and chemical treatment are required for ballast water and marine oil waste residues to comply with discharge standards set by maritime environmental authorities [37]. Microbial bioremediation and alkaline treatment processes are widely used for pH stabilization and oil degradation induction before discharge.

### **3.2. Hydrocarbon Composition**

Their toxicity, environmental persistence, and treatability are mostly a function of the hydrocarbon content of the oil waste. Oil wastes contain a blend of alkanes, cycloalkanes, aromatics, resins, and asphaltenes, and each influences the physical characteristics, degradability, and environmental impact of the waste [38].

Saturated hydrocarbons, a bulk fraction of waste oil, are largely chemically inactive but yield significant contributions to high viscosity and resistance to processing. Aromatic hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX), are very harmful, environment-borne persistent pollutants of considerable extremity in hazard to human health [39]. The inclusions of resins and asphaltenes have additional effects on waste characteristics, such as introducing stability, emulsifiability, and anti-degradation capability.

Knowledge of hydrocarbon composition is important for the design of successful treatment, determination of environmental risks, and regulatory compliance. Hydrocarbons have diverse degradation patterns; lighter fractions evaporate or biodegrade immediately, while heavier fractions persist for decades, accumulating in sediments and causing long-term ecological risk.

For PAH- and asphaltene-rich wastes, treatment processes prefer mechanical and thermal treatments [40]. Incineration, pyrolysis, and solvent extraction are commonly used to degrade or recover hydrocarbons in heavy sludge [41]. Bioremediation processes are also under investigation, but because PAHs and asphaltenes are low in biodegradability, microbial treatment tends to be very lengthy in process time and in need of specialized conditions.

In the case of environmental pollution and oil spills, understanding hydrocarbon composition helps to decide the most effective cleanup method. Light crude spills are regularly cleaned up using dispersants and bioremediation, while mechanical recovery, in-situ burning, and sediment dredging are preferred for heavy oil residues.

### **3.3. Oxidation and Stability**

Oxidation is a chemical process in which oil transportation residues react with oxygen, light, and the ambient environment to form a change in their composition, stability, and degradability potential [42]. Oxidation plays a critical role in influencing oil waste durability, environmental persistence, and storage and disposal safety.

The oxidation of hydrocarbons leads to the formation of new chemical substances, including ketones, aldehydes, carboxylic acids, and peroxides, which alter the physical



and chemical properties of the waste. Oxidized oil residues thicken, becoming therefore more difficult to transport and process. In some cases, oxidation may lead to spontaneous polymerization, which leads to the formation of very stable emulsions and sludge deposits resistant to traditional treatment processes.

Oxidation affects the oil residue flammability and toxicity. Some oxidized hydrocarbons, being heavy in sulfur compounds and aromatics, can form toxic gases or auto-ignite under certain conditions, thus contributing to greater fire and explosion risk. The extent of oxidation is a function of temperature, time of exposure, intensity of light, and chemical composition.

Understanding oxidation behavior is mandatory in determining the optimum treatment, handling, and disposal practices. Through the control of oxidation rates with chemical inhibitors, controlled storage environments, and protective coatings, industries can minimize the formation of long-lasting sludge and improve waste management effectiveness [41].

For raw oil residues, prevention of oxidation by sealed storage, nitrogen blanketing, or antioxidant additives can preserve fuel quality and save waste treatment costs. Proper handling and controlled storage conditions prevent premature oxidation, allowing more efficient hydrocarbon recovery and reprocessing.

### **3.4. Heavy Metal Content**

Heavy metals are toxic, persistent environmental contaminants with long-term ecological and health risks as a result of their capacity to bioaccumulate in living organisms and persist in the environment. Heavy metals in oil transport wastes are of concern due to their potential to leach in the soil and water and cause widespread contamination.

Heavy metals come into oil transport wastes mainly due to natural crude composition, refining operations, and corrosion of pipelines. Heavy metals usually present in oil wastes include lead (Pb), nickel (Ni), vanadium (V), cadmium (Cd), mercury (Hg), and arsenic (As), each with its own toxicological and environmental hazards.

Because they are non-degradable, the heavy metals accumulate in soils and aquatic sediments, with a strong possibility of groundwater contamination and poisonous transfer to aquatic and terrestrial organisms. Chronic lead, mercury, and cadmium exposure has been linked to neurological damage, renal impairment, and developmental disabilities in human beings, while nickel and vanadium compounds are involved in causing respiratory disease and carcinogenic characteristics.

The presence of heavy metals in oil transport wastes complicates the treatment and disposal of wastes because they cannot be neutralized or removed by usual processes of biodegradation and oxidation [41]. Physical and chemical stabilization treatments are instead required to immobilize the metals so that they cannot leach into the environment. Regulatory limits on concentrations of heavy metals in industrial wastes are very strict in most countries, and this forces industries to adopt sophisticated treatment processes before disposal or reuse.

Heavy metals are a chronic challenge to oil waste management that requires constant monitoring, advanced treatment technology, and stringent controls by regulation.

## CONCLUSION

Physicochemical characteristics of oil transportation wastes determine their impact on the environment, treatment sufficiency, and disposal. The wastes are found in pipeline carriage, tanker operation, and refining processes and possess diverse characteristics based on hydrocarbon content, water content, solids burden, oxidation level, and heavy metals contamination. Understanding these properties is the foundation of developing competent waste management practice and compliance regulation in the petroleum and natural gas sector.

Physical properties such as density, viscosity, and volatility influence the behavior of oil wastes during storage, transport, and in environmental conditions. Low-density, highly volatile light residues pose airborne contamination risks, while high-viscosity, low-volatility heavy oil sludges settle in sediments and soil and cause long-term contamination. Water-in-oil emulsions and the presence of sediments contribute to waste management complexity by increasing stability, reducing biodegradability, and necessitating advanced separation technology.

Chemical properties such as pH, hydrocarbon composition, oxidation properties, and heavy metal content influence oil transport wastes' toxicity, persistence, and the requirement for remediation. Sulfur oxidation products' inclusion in acidic residues favors corrosion of storage tanks and pipelines, enhancing maintenance and environmental risks. Hydrocarbon composition identifies flammability, biodegradation potential, and treatment efficacy, with aromatic hydrocarbons (PAHs and BTEX) constituting primary toxicity threats due to their carcinogenic and persistence features. Oxidation reactions alter stability of waste, forming hard-to-remove sludges and stable emulsions, and heavy metal contamination risks long-term harm to soil, water, and biological systems through bioaccumulation and toxicity concerns.

Implications for waste treatment and management emphasize multi-stage, waste-specific processes. Highly viscous sludges require thermal treatment, solvent extraction, or mechanical separation to enhance flow properties and recover usable hydrocarbons. Very oxidized and weathered residues require chemical stabilizers, surfactants, or pyrolysis-based technologies to break down refractory fractions. Heavy metal wastes need solidification, precipitation, and leachability control processes to prevent groundwater contamination. Additionally, regulatory regulations necessitate the strict control of VOC emissions, metal, and hydrocarbon discharge, which must be monitored and complied with on a regular basis and according to international safety standards.

Overall, effective description and management of oil transportation wastes are essential for the control of environmental risk, the optimization of waste recovery, and industrial sustainability. By applying advanced waste treatment technologies and adherence to regulations, the petroleum and natural gas sector can minimize pollution impacts and transition towards cleaner waste management.

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## ASSESSMENT OF THE ECO-CHEMICAL SITUATION OF OKCHU RIVER (AZERBAIJAN) ACCORDING TO THE RESULTS OF THE AUGUST 2023 MONITORING

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**Abstract:** Compared to other layers, the migration of pollutants in the hydrosphere, especially in running waters, occurs very rapidly. That is, the spread of chemical pollutants through water bodies occurs rapidly, making their continuous study essential. In this context, special attention should be given to transboundary rivers. From an ecological safety perspective, it is important to conduct chemical monitoring of transboundary rivers. The Okchu River is being studied, because it is a transboundary river. The eco-chemical research of the territories liberated from occupation must be conducted constantly, the object was taken from the Karabakh region. The physicochemical parameters of water were examined on water samples. Were used, for this, devices such as an oximeter, conductometer, pH-meter and autotitrator. Since the physical and chemical parameters of water impact the biota of the ecosystem, these indicators were analyzed first. We used, for this purpose, spectrometer, atomic absorption spectrometer, and optical emission spectrometer devices. For the protection of water resources, both anions and cations were also studied. Their dependence on time (i.e., on the volume of water) was examined. It was found that the concentrations of elements such as iron, magnesium, and molybdenum exceeded the standard by 1.9 times, 1.25 times, and 1.04 times, respectively. The variation in concentration depending on the water volume in the river during the summer month of August was also investigated. The simultaneous high presence of cations such as magnesium and iron is evidence of anthropogenic impact on the ecosystem. It was found that they exceeded the permissible concentration limits several times in the upper reaches, and decreased in the lower reaches due to the self-cleaning of the river and its transition to bottom sediments.

**Keywords:** manganese, iron, hardness, Okchu river, ecology, ecological risk, ecological monitoring, biota, anion, cation.

## INTRODUCTION

Eco-chemical monitoring of transboundary rivers must be carried out continuously. This is because the spread or long-distance migration of chemical pollutants in aquatic environments occurs much more easily compared to the lithosphere. Parameters such as water volume, pH, and hardness in rivers influence the migration of chemical pollutants [1–5]. Among transboundary rivers, the Oxchu River is classified as a polluted river according to the literature. As noted, the river has been subjected to chemical pollution over an extended period. Mining and metallurgical plants in Meghri, Kajaran, Kapan, and Dastakert have discharged hundreds of thousands of tons of highly acidic water, heavy metal salts, and other wastes into the Oxchu river, causing severe pollution. At various times, the copper concentration in the water exceeded MPC standards by 25–50 times, while phenol levels regularly surpassed the limit by 6–15 times. The river also contains pollutants such as aluminum, zinc,

manganese, titanium, and bismuth [6,7]. For this reason, we selected the heavily polluted Oxchu river as the object of our research. Considering that rivers have a natural self-purification ability, three water samples were taken and analyzed within a one-month period. The samples were collected from the sections of the river located within the territory of Azerbaijan.

## EXPERIMENTAL PART

In order to carry out the research work, analyzes were carried out in the parts of the river passing through the villages of Burunlu, Jahangirbeyli and Shayifli. Their GPS coordinates were determined using a Garmin Etrex-10 Handheld GPS device. At the same time, the analyzes of water samples were analyzed on the spot for possible parameters, others were stored according to the preservation method of the samples and analyzed the next day. Initially, water samples were taken in Burunlu village and analyzed (7000 Shimadzu), AAS spectrometer (Specord 205), conductometer (Biobase d-950), oximeter (Ox 4100 H) and pH meter (PHS-25CW) were used [8-12].

## RESULTS AND DISCUSSION

First, the physical parameters of the water were checked. Then, other indicators, namely metals, were examined. The results of the analyzes are given in table 1.

Table 1

Analytical results of water samples taken from Okchu River in August in Burunlu village

№	Name of component	Measurement	Amount of component			MPC
			Okchu River-Zengilan district			
			Burunlu village 02-04.08.2023	Burunlu village 1012.08.2023	Burunlu village 22- 23.08.2023	
1	Hydrogen indicator, Ph	—	8.1	7.6	8.0	6.5-8.5
2	Dissolved oxygen	mgO <sub>2</sub> /l %	5.0 62.0	5.1 61.0	5.2 62.0	≥4.0
3	Electrical conductivity	μSm/sm	854	916	1268	—
4	Hardness	mg-ekv/l	7.2	7.76	8.3	7.0
5	Chloride ion, Cl <sup>-</sup>	mg/l	10.3	19.5	23.0	350
6	Sulfate ion, SO <sub>4</sub> <sup>2-</sup>	mg/l	207.8	224.9	253.0	500
7	Ammonium ion, NH <sub>4</sub> <sup>+</sup>	mg/l	0.15	0	0	0.5
8	Nitrite ion, NO <sub>2</sub> <sup>-</sup>	mg/l	0.04	0.32	0.09	3.3
9	Nitrate ion, NO <sub>3</sub> <sup>-</sup>	mg/l	7.3	5.4	6.0	45.0
10	Copper, Cu	mkg/l	47.9	6.29	5.58	1000
11	Iron, Fe	mkg/l	577.0	35.2	63.5	300
12	Manganese, Mn	mkg/l	125.0	22.6	41.2	100
13	Lead, Pb	mkg/l	1.733	1.817	<LOD	30
14	Zinc, Zn	mkg/l	58.8	0.829	64.3	1000
15	Nickel, Ni	mkg/l	<LOD	<LOD	<LOD	100
16	Molybdenun, Mo	mkg/l	210.0	259	249	250

As can be seen from this table, the hardness has exceeded the norm within the parametric month. It exceeded the norm by 1.02 times at the beginning of the month, 1.07 times in the second decade, and 1.18 times in the third decade. Although iron was 1.92 times more in the beginning of the first decade, it was within the norm in the following months. At the same time, manganese ion was 1.25 times higher, and on other days it was within the norm. Molybdenum gradually increased during the month, and then decreased within the norm. Molybdenum is an element that directly affects biocenosis [13-21].

In order to analyze this change, at the same time, analyzes were conducted in the village of Shayifli. The results are given in table 2.

Table 2

Analytical results of water samples taken from Okchu River in the area of Shayifli village during the month of August

№	Name of component	Measur ement	Amount of component			MPC
			Okchu River-Zengilan district			
			Shayifli village 02- 04.08.2023	Shayifli village 10- 12.08.2023	Shayifli village 22- 23.08.2023	
1	Hydrogen indicator, pH	—	8.1	7.7	7.9	6.5-8.5
2	Dissolved oxygen	mgO <sub>2</sub> /l %	4.7 61.0	5.1 61.0	5.1 61.0	≥4.0
3	Electrical conductivity	μSm/sm	858	916	1267	—
4	Hardness	mg-ekv/l	7.3	7.76	8.3	7.0
5	Chloride ion, Cl <sup>-</sup>	mg/l	17.9	19.6	22.9	350
6	Sulfate ion, SO <sub>4</sub> <sup>2-</sup>	mg/l	213.1	225.0	253.2	500
7	Ammonium ion, NH <sub>4</sub> <sup>+</sup>	mg/l	0.03	0.17	0	0.5
8	Nitrite ion, NO <sub>2</sub> <sup>-</sup>	mg/l	0.06	0.4	0.1	3.3
9	Nitrate ion, NO <sub>3</sub> <sup>-</sup>	mg/l	5.7	5.3	5.2	45.0
10	Copper, Cu	mkg/l	46.6	10.9	2.749	1000
11	Iron, Fe	mkg/l	564.0	34.1	58.9	300
12	Manganese, Mn	mkg/l	125.0	19.8	34.8	100
13	Lead, Pb	mkg/l	1.579	1.06	1.594	30
14	Zinc, Zn	mkg/l	48.5	1.5	43.7	1000
15	Nickel, Ni	mkg/l	1.77	<LOD	<LOD	100
16	Molybdenun, Mo	mkg/l	221.0	248	237	250

In the first ten days, the level exceeded the norm by 1.04 times, in the second ten days by 1.1 times, and by 1.18 times in the third ten days. Iron and manganese exceeded the permissible concentration by 1.88 times and 1.25 times, respectively. Results were lower in the midstream compared to the upstream. Reanalyses were also investigated downstream. The results are given in table 3.

The water hardness in the water sample taken from Jahangirbeyli area exceeded the norm by 1.03 times, and by 1.12 times in the second decade, and by 1.18 times in the last decade. Although the iron ion exceeded the norm in the first ten days by 1.91 times, it was lower in the other ten days, that is, it did not exceed the permissible hardness limit. Manganese exceeded the norm by 1.23 times in the first decade.

Despite the low flow, even if the water level of the river affects it, the self-cleaning ability has decreased, but it still exceeded the permissible concentration limit. Iron and manganese compounds also gradually decreased from the upstream to downstream of the river.

Table 3

Analytical results of water samples taken from Okchu River in August in Jahangirbeyli village

№	Name of component	Measur ement	Amount of component			MPC
			Okchu River-Zengilan district			
			Jahangirbey li village 02- 04.08.2023	Jahangirbey li village 10- 12.08.2023	Jahangirbeyli village 22- 23.08.2023	
1	Hydrogen indicator, pH	—	8.1	7.7	7.9	6.5-8.5
2	Dissolved oxygen	mgO <sub>2</sub> /l %	5.0 62.0	5.3 63.0	5.0 60.0	≥4.0
3	Electrical conductivity	μSm/sm	856	926	1266	—
4	Hardness	mg-ekv/l	7.25	7.84	8.3	7.0
5	Chloride ion, Cl <sup>-</sup>	mg/l	18.4	19.9	22.7	350
6	Sulfate ion, SO <sub>4</sub> <sup>2-</sup>	mg/l	212.0	229.0	251.0	500
7	Ammonium ion, NH <sub>4</sub> <sup>+</sup>	mg/l	0.02	0.1	0	0.5
8	Nitrite ion, NO <sub>2</sub> <sup>-</sup>	mg/l	0.06	0.02	0.07	3.3
9	Nitrate ion, NO <sub>3</sub> <sup>-</sup>	mg/l	6.2	6.1	5.4	45.0
10	Copper, Cu	mkg/l	47.2	6.89	3.11	1000
11	Iron, Fe	mkg/l	574.0	28.9	13.0	300
12	Manganese, Mn	mkg/l	123.0	14.2	26.6	100
13	Lead, Pb	mkg/l	1.669	1.21	<LOD	30
14	Zinc, Zn	mkg/l	63.6	1.26	21.0	1000
15	Nickel, Ni	mkg/l	0.461	<LOD	<LOD	100
16	Molybdenun, Mo	mkg/l	238.0	227.0	235	250

Taking into account that the river is a self-regulating system, we can say that the amount of chemical pollutants gradually decreases from the upper reaches of the water. A decrease in the amount of these pollutants remains its indicator. Too much pollution in aquatic ecosystems creates difficulties for the organisms living in this aquatic environment and at the same time limits their further habitat. An excess of parameters such as turbidity in water greatly damages the microbiota, and at the same time has a negative effect on the organisms living there [22-28]. In addition, the amount of iron ions begins to decrease slightly towards the permissible concentration limit in the lower streams.

It is true that even in the downstream Jahangirbeyli, the permissible concentration cannot be lowered, and the permissible concentration is still too high. But since self-cleaning of rivers is taken into account, both of the above indicators decrease from top to bottom. Manganese is an element that negatively affects the formation of the ecosystem [29-32]. Thus, it can affect the embryos and stop their

formation from the initial stages. This is a very serious problem. In biocenosis, the destruction of living things takes place.

## CONCLUSION

Thus, taking into account that water performs important functions for the metabolism of substances and energy, we can say that water must be constantly monitored. Given all this, it concluded that the parameters that led to the destruction of biochemistry creatures in August were higher than the density limit allowed in the water.

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