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Composition of Oil and Layer Waters and it's Impact on the Ecology of the Caspian Sea

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ABSTRACT

The article presents a brief analysis in the field of oil chemistry: the study of microelements in oils and formation (layer) waters, as well as environmental problems arising from offshore oil and gas production. The impact of oil and gas production on the ecology of the Caspian is shown; it was noted that from an ecological point of view, the study of the microelement composition of processed oil is very important for identifying sources of environmental pollution by oil, because microelements are present in all oil fractions, starting with gasoline ones, and their amount, as a rule, increases with an increase in the boiling point of the fraction, reaching a maximum in the residues.

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The main problem of pollution of the seas and oceans is the process associated with offshore oil and gas production. Issues of environmental safety are particularly relevant in such areas of the oil and gas industry as drilling and oil production, oil and gas refining, as well as their transportation [1].

These areas of the oil and gas industry in the Caspian region are developing with high intensity. For example: already on March 28, 2023, the support block of the Azeri Central East (ACE) platform was launched in order to support oil production in the Azeri-Chirag-Gunashli (ACG) field block at a level above 400 thousand barrels per day. With ACE at maximum, it is expected that 100 thousand barrels (that is, 5 million tons per year) of oil will be produced. ACG underwater pipelines will be used to transport oil and gas from the platform to the Sangachal terminal. Let us emphasize that this is the world's first remotely controlled platform used by British Petroleum (BP). Naturally, such a pace of oil and gas production will lead to increased problems in protecting the environment of the Caspian region.

The indisputability of environmental control over oil pollution in the Caspian Sea is obvious, especially in the implementation of offshore projects, the operation of oil transportation and storage infrastructure. The role of oil products and oil waste entering the sea has not yet been fully studied, since oil is a mixture of various substances, of which from 50 to 90% (depending on the field) is hydrocarbons, and the rest is heteroatomic compounds containing as carbon and hydrogen, as well as sulfur, nitrogen, oxygen and trace elements. Polyaromatic hydrocarbons (PAHs), which accumulate in marine ecosystems and are cyclic hydrocarbons, consisting mainly of benzene rings with substituted and unsubstituted hydrogen atoms, have a severe impact on the flora and fauna of the Caspian Sea. It is known that almost all PAHs are carcinogenic substances with mutagenic activity, and the most active carcinogenic compound is benzopyrene.

Also, we note the oil-containing field waters, which in their composition contain a high concentration of hydrocarbon compounds, salts and microelements. The general characteristics and composition of commercial waters formed during oil and gas production in the Caspian Sea are shown in [1]. Here we will also show the content of microelements, mainly found in oil-containing commercial waters of the Caspian Sea (in mg/l): Fe (0.1-1100), K (24-4300), Mg (0.9-600), Al (0 .4-410), Mn (0.004-175), Pd (0.008-0.88), Ti (0.01-0.70), etc. Drilling waste also contains such toxic reagents as acrylic polymers, caustic soda, soda ash, polyacrylamide, chromium peak, clay, barite, which have been entering the Caspian for years: they accumulate during the construction of countless wells during large-scale drilling in all sectors of the Caspian countries [1-7].

Note that the presence of microelements (ME) in oil is an important characteristic that carries geological and geochemical information, indicating the age of the oil, the paths and direction of its migration and accumulation. In the near future, due to the trend of depletion of ore deposits, oil may become a raw material for the production of certain mineral elements (vanadium, nickel, copper, chromium, cobalt, etc.). It was previously established that various oils contain more than 60 MEs, and their concentrations vary over a relatively wide range. Using the method of neutron activation analysis, we for the first time measured the concentrations of about 20 metals, as well as bromine and iodine in resinous-asphaltene substances

(RAS) isolated from a number of typical oils of Azerbaijan and their vacuum residues. It was found that the studied RAS contain microelements (heavy metals) in the highest concentrations in order of decreasing concentrations, most often forming the series: Fe > Ni > Cr > V > Co, as well as heavy halogens (iodine and bromine), present mainly in resinous substances [2].
Here we especially emphasize that the waters of oil fields and the reasons for their enrichment with halogens were of interest to many scientists. In formation waters, the concentration of iodine is associated with its accumulation in marine silts and water. In nature, iodine is found in sea water, in the form of minerals and in mineralized waters. Iodine-containing minerals are not of industrial importance due to their rarity and small quantity, and the low content of iodine in sea water is explained by the fact that due to the activity of microorganisms it does not accumulate. Since the waters of oil fields are produced as a by-product, it would be rational to use them as a free raw material for the production of heavy halogens.

Note that with an iodine content of at least 10-18 mg/l, associated waters are already considered promising for iodine extraction [3]. As for bromine, its content in sea water is on average 6 mg/dm3; fluorine has not been found in oils. According to the results of work [3], the iodine content in samples of formation waters of the studied oil fields varies from 7.5 mg/l to 10.5 mg/l. That is, in general, it can be argued that formation waters are a source of iodine and bromine, so they can be used as industrial raw materials for the production of microelements.

It is characteristic that groundwater, due to its ion-salt composition and ME concentration, is of industrial importance and as a hydromineral raw material for the chemical industry. Produced waters contain from 70 to 300 kg/t of metal salts, which could become a long-term source of raw materials for this industry [4]. That is, a detailed study of the microelement composition of oil, formation and groundwater can be a kind of starting point for further studies of the hydrogeochemical conditions of oil fields.

For example, according to the SOCAR Ecology Department (for 2015), as a result of monitoring the water area of the Oil Rocks field at depths from 5 to 50 m, a significant amount of Fe and Zn was found in water samples: 0.140-0.178 mg/l for Fe and 0.128-0.166 mg/l for Zn. This, in our opinion, is primarily explained by the use of metal structures and the active work of drilling equipment.

When distilling Azerbaijani oils, iodine and bromine are found in all fractions, with iodine concentrated in low-boiling fractions (80-170°C), and bromine in high-boiling ones (above 350°C). Metals (Cr and Co) are concentrated in the highest molecular weight fractions of oil (in RAS). The presence of lanthanides (La, Eu, Ce, Yb), previously not previously determined experimentally, was also determined in the SAS molecules isolated from Azerbaijani oils [5].

of the majority of microelements contained in oils, the most information is available on Ni and V. This is due to the fact that they are found in relatively high concentrations in oils: Ni is found in fractions after 300°C, and during deasphalting, Ni does not completely transform into RAS. Ni and V are found in oils in the form of porphyrin and non-porphyrin complexes. Porphyrins have a significant effect on the surface-active properties of oils, which is an important factor in oil production. These two elements are of particular interest for isolation from petroleum feedstock. They are almost completely concentrated in petroleum dry active substances, i.e., in fractions that boil away at temperatures above 350°C.

Note that since Azerbaijani oils are low-sulfur, the amount of V in them is inferior to the amount of Ni. When comparing the content of various trace elements in Azerbaijani oils located at different depths, it was found that the concentrations of Ni and Cr decrease with increasing oil depth, and the concentrations of Cd, Mg, Cu, Zn and Mo increase. The concentrations of Mn, Fe and Ca do not depend on the depth of oil occurrence. In general, Azerbaijani oils are characterized by a high content of the iron element, which is mainly concentrated in younger, weakly metamorphosed oils at the initial moment of their formation [5]. This is confirmed by the results of work [6] when studying the microelement composition of oil from the Azeri field: in it, microelements, in order of decreasing concentrations, most often form the series: Na > Fe > K > Ni > Pb > Zn > V > Cu > Mn.

In conclusion, we emphasize that the intensity of development of oil and gas production is typical for all Caspian countries. For example, in Azerbaijan, according to the Ministry of Energy of Azerbaijan (for 2022), 25.2 billion cubic meters of natural gas were produced only at the Shah Deniz gas condensate field, and the proven reserves of Shah Deniz are estimated at 1.2 trillion cubic meters of gas and 240 million tons of condensate. According to SOCAR: confirmed natural gas reserves in Azerbaijan amount to 2.6 trillion cubic meters, and according to forecasts - up to 6 trillion cubic meters).

Thus, since Azerbaijan is currently a reliable pan-European supplier of gas (its intensive production is underway in the Caspian Sea with subsequent supplies of additional volumes to Europe), the environmental safety of the Caspian Sea should be one of the most important and priority areas in the Azerbaijani oil and gas strategy.

Interesting facts (for 2025)

1. On January 27, Kazakhstan sent the first tanker carrying oil from the Kashagan field to Azerbaijan for transportation via the BTC pipeline. According to KazMunaiGas, the Taraz tanker carrying Kashagan oil departed Aktau for Baku, where it will be transported via the BTC pipeline to the Mediterranean Sea (for the development of the Trans-Caspian International Transport Route).
2. As of February 4, the total volume of gas transported via TANAP (a key link in the Southern Gas Corridor) since the start of deliveries reached 75 billion cubic meters. The estimated useful life of the TANAP system is scheduled to extend until 2062.
3. On February 28, Total Energies, SOCAR, and XRG defined the concept for Phase 2 of the Absheron field development, which is based on a subsea production scheme with onshore access. Wells will be drilled at a depth of 500 meters, and their penetration will exceed 7,000 meters, making them among the deepest in the Caspian Sea.
4. On August 2, Azerbaijani gas supplies to Syria began, following the signing of a Memorandum of Understanding between SOCAR and the government of the Syrian Arab Republic in Baku. This is a historic event, as it marks the first time that gas from Azerbaijan will be supplied to the Middle East.
5. By August 25, the volume of Azerbaijani gas supplied to Turkey and Europe via TANAP since the pipeline's launch reached 83 billion cubic meters: 34 billion cubic meters of gas went to Turkey, and 49 billion cubic meters went to Europe.

6. By September 2, TAP had transported 50 billion cubic meters of Azerbaijani gas to Europe since the start of commercial operation (at the end of 2020): over 41.7 billion cubic meters to Italy, over 4.8 billion cubic meters to Greece, and over 3.2 billion cubic meters to Bulgaria.

7. On October 2, SOCAR and Schlumberger signed a document on the redevelopment of the Bakhar and Gum-Deniz fields in the Caspian Sea, which includes the identification of future production zones, the development of comprehensive reservoir modeling, and the design of drilling and well construction programs.
8. On November 4, at the Abu Dhabi International Petroleum Exhibition, Dragon Oil (a subsidiary of Dubai-based Emirates National Oil Co.) signed a Memorandum of Understanding with SOCAR to expand cooperation in the exploration, production, and development of hydrocarbons in the Caspian and other energy regions.

Conclusions

1. From an environmental point of view, studying the microelement's composition of refined oil is very important for identifying sources of environmental pollution with oil, because MEs are present in all petroleum fractions, starting with gasoline, and their amount increases with increasing boiling point of the fraction, reaching a maximum in residues.
2. Formation waters containing significant amounts of heavy halogens (iodine and bromine) can and should be used as a highly promising raw material for their production.
3. Oil and gas companies of the Caspian countries must take into account the need to prepare and implement comprehensive measures to minimize the negative impact on the ecology of the Caspian Sea during the industrial operation of oil facilities.

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