Environmental Aspects of the Use of Oil and Oil Components

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Abstract The article discusses the environmental aspects of the use of oil and oil components. It is shown that for the most complete solution of applied problems in oil and gas production, taking into account the preservation of ecological biodiversity (meaning a decrease in anthropogenic environmental pollution), it is important to know the qualitative composition of the used hydrocarbon raw materials.

Keywords: high molecular weight compounds of oils, resins and asphaltenes, inhibiting properties, microelements, catalytic poisons, waste production.

Rezumat: Articolul discută utilizarea petrolului și a componentelor petrolului în relație cu mediul. Se arată că pentru cea mai completă soluție a problemelor aplicate în producția de petrol și gaze, și pentru a ține seama de conservarea biodiversității ecologice (ceea ce înseamnă o scădere a poluării antropogene a mediului), este important să se cunoască compoziția calitativă a materiilor prime de hidrocarburi.

Cuvinte cheie: compuși cu greutate moleculară ridicată a petrolului, rășinilor și asfalturilor, proprietăți inhibitoare, microelemente, otrăvuri catalitice, producerea deșeurilor.

Introduction

The article shows that the problem of chemical processing and rational use of heavy oil residues is currently acute. Resinous-Asphaltene Substances (RAS), which make up a significant proportion (up to 40%) in oils and even more in oil components, are the main reserve for deepening oil refining and increasing the degree of qualified use of petroleum raw materials. Scientific information on the chemical composition of the RAS will contribute to the qualitative identification of sources of environmental pollution, especially if we consider the effect of oil properties on the pollution of the atmosphere, soil and water surface in the region of deposits.

Main part

The oil industry of Azerbaijan is one of the main sources of pollution of the environment with toxic substances, and the air is polluted not only by various gas emissions generated in the process of oil refining, but also by gaseous oil products. If we consider oil in three aspects - as a natural resource, a product of production and an environmental pollutant,

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then it is obvious that it is necessary to organize a comprehensive analysis of the impact of the properties of oil and its components on the environment. The solution to this issue is extremely important in the context of the future ecologinizing of oil producing industries.

At oil refineries, which are today industrial complexes with a high degree of mechanization and automation of production processes, raw materials are not fully used, by-products are formed, and so far not completely captured. This reduces the technological performance of production processes and sharply degrades the environment. A significant part of oil and gas emissions (carbon oxides, sulfur, nitrogen, hydrocarbon vapors, metal oxides, carcinogenic substances, dust) are highly toxic. When the atmosphere is polluted, there is an accelerated destruction of metal and reinforced concrete structures, ancient monuments, soil acidification, poisoning and death of flora and fauna, and also a negative impact on human health.

Therefore, the technological perfection of oil processing methods must be assessed not only by production and economic indicators, but also by their environmental friendliness. Sources of gaseous hydrocarbons (natural and associated petroleum gases, some synthetic gases obtained during thermal and thermocatalytic processing of oil and oil products) make a certain "contribution" to the pollution of the external environment, including the air basin.

At present, a lot of attention is paid to the complex study of High Molecular Weight compounds (HMW), since they contain significant amounts of heteroatomic compounds that adversely affect the catalytic processes of oil refining and petro chemistry. The main part of all microelements is concentrated in the highest boiling fractions of oils (resins and asphaltenes), which allows us to consider them as the main catalytic poisons of many oil refining processes.

For example, the presence of asphaltenes in the feed reduces the hydrogenation rate by $2 \div 4$ times and increases the rate of catalyst deactivation by several times. The RAS, which remained in the oil products, have an extremely negative effect on their operational properties[2],[3].

Since there is a continuous exchange of microelements between oil, rocks, formation waters, oilfield and refinery equipment, the RAS can be a link through which the relationship between the oil system and the environment is carried out.

We have found that the highest concentrations in the RAS of Azerbaijani oils contain elements of the iron group and heavy halogens, especially iodine[4]. For example, it was found that the highest concentration of iodine among the oils of Azerbaijan belongs to the oil of the Gunashli field. And halogens in all cases are concentrated mainly in the resinous components of oils.

The chemical nature of the halogenated components of oils has not yet been finally established and the relatively high content of bromine and iodine in Azerbaijani oils indicates that these oils, especially the oil from the Gunashli field, are promising objects for scientific research. Interest in petroleum microelements increased significantly when it was discovered that the amount of certain metals (in particular, vanadium and nickel) could be comparable to their content in ores. It is characteristic that the study of metals in oils was previously mainly by geochemists, but after it became known about the harmful effects of metals on the processing technology and operational properties of fuels, they began to be dealt with by chemists-technologists and ecologists. From an

[2] Мир-Бабаев М.Ф., 1998. Высокомолекулярные соединения нефтей Азербайджана // Химия и технология топлив и масел, №5, с.44-45.

[3] Плотникова И.Н., 2012. Элементный состав нефти и рассеянного органического вещества; методы их изучения. - Казань: Казанский университет, 163 с.

[4] Алёшин Г.Н., Самедова Ф.И., Мир-Бабаев М.Ф., 1990. Микроэлементный состав высокомолекулярных компонентов нефтей и нефтяных остатков // Нефтехимия, т.30, №2, с.175-183.

environmental point of view, the study of the microelement composition of refined oils is important in order to identify sources of environmental pollution with oil.

The presence of halogen-containing compounds in low-boiling oil fractions is apparently associated with the decomposition of high-molecular halogen-containing components during the distillation process, which leads to increased corrosion of oil refining equipment. That is, the purpose of the ongoing research of petroleum metal-containing compounds is not only the rational extraction of microelements from petroleum feedstock, but also the fight against corrosion[5],[6].

So, when burning boiler fuel containing increased amounts of heavy metals, intensive destruction of refractory masonry occurs in furnaces, with vanadium being the most aggressive component. Vanadium pentoxide and vanadium salts present in the ash are low melting compounds. Together with sulfur-containing substances, they form dense deposits that cause metal corrosion. The amount of vanadium pentoxide emitted annually with the smoke of modern power plants is measured in hundreds and even thousands of kilograms. Organic vanadium compounds have a negative effect on the performance of petroleum products, and vanadyl porphyrins present in oils are effective stabilizers of petroleum emulsions that impede their destruction. Vanadium in oils, which is a part of non-porphyrin complexes, is also associated with sulfur, which leads to atmospheric pollution and sulfur oxides.

It is known that ashes of heating oil are rich sources of valuable metals (vanadium and nickel etc.), which can be effectively leached under weakly acidic reducing conditions. With the help of synchrotron radiation, arsenic in the form of pentoxide was detected in oil fly ash emitted into the atmosphere, in addition to vanadium and nickel[7].

When using fuel oil (which is to some extent a concentrate of petroleum RAS), and, therefore, microelements) as boiler fuels, the environment is polluted with significant amounts of metal oxides. According to calculations[8],[9], during the combustion of 1 ton of liquid fuel in power plants and industrial facilities, $1kg \div 2kg$ of metal oxides, mainly iron and vanadium, enter the atmosphere.

Knowing the microelement's composition of oils, it is possible to identify the sources of oil pollution of the environment, since trace elements are present in all oil fractions, starting with gasoline, and their amount, as a rule, increases with increasing boiling point of the fraction, reaching a maximum in the residues[10].

For the qualitative extraction of metals from oils and petroleum components, we used neutron-activation analysis, which is universal in relation to a very large number of elements and does not require preliminary preparation of samples (ashing)[11],[12]. The application of this analysis made it possible to establish about 20 different microelements in characteristic oils of Azerbaijan, including lanthanides, which were not determined

[5] Мир-Бабаев М.Ф., 1996. Нефтяные смолисто-асфальтеновые вещества // Химия и технология топлив и масел, №6, с.43-46.Мир-Бабаев М.Ф., 1997. Микроэлементный состав нефтей по данным нейтронно-активационного анализа // Химия и технология топлив и масел, №5, с.46-47.

[6] Мир-Бабаев М.Ф., 1997. Микроэлементный состав нефтей по данным нейтронно-активационного анализа // Химия и технология топлив и масел, №5, с.46-47.

[7] Silk J.E., Hansen L.D., Eatough D.J., 1989. Chemical characterization of vanadium, nickel and arsenic in oil fly-ash samples using EXAFS and XANES spectroscopy // Physica, v.158, №1, p.247.

[8] Штраус В., Мэйнуорринг С., 1989. Контроль загрязнения воздушного бассейна. - Москва: Стройиздат, 144 с.

[9] Мир-Бабаев М.Ф., Халилова А.А., 2009. Экологические проблемы в некоторых отраслях промышленности // Учёные записки, АзТУ, №4, с.69-71.

[10] Колодяжный А. В., Ковальчук Т. Н., Коровин Ю. В., 2006. Определение микроэлементного состава нефтей и нефтепродуктов. Обзор. // Методы и объекты химического анализа, т. 1, № 2, с. 90-104.

[11] *Idem.*

[12] Самедова Ф.И., Мир-Бабаев М.Ф., 1992. Высокомолекулярные гетероатомные соединения нефтей. - Баку: Нефис, 135 с.

earlier (La, Eu, Yb, Ce). The type of elements contained in all Azerbaijani (low-sulfur) oils, or in the overwhelming majority of them, are Fe, Ni, Cr, V, Co, Zn, Au, Sb, Se, I, Br. These microelements (in particular, Ni, V, Cr, and Co) isolated from crude oil can be used for micro alloying steels, which is very important.

Some words about the practical application of oil components[13],[14].

Petroleum RAS are natural inhibitors; they exhibit a certain inhibitory activity in reactions with a free radical chain mechanism. The total concentration of natural inhibitors in asphaltenes can reach 0.28 mol / kg of oil. They are present in high effective concentrations $(0.66 \div 0.79) mol/kg$ in RAS extracted from oil of the Banka Darwin field. Natural inhibitors contained in the RAS of characteristic (low-sulfur) oils of Azerbaijan are in most cases not inferior to synthetic antioxidants in their inhibitory effect, and resins from Gunashli oilfield are comparable in "strength" of action with the most effective synthetic antioxidants: naphthol and topanol[15].

The concentration and activity of inhibiting centers in the RAS naturally depend on the chemical type and the degree of metamorphic transformation of oil, which in turn determines the role of RAS as preservatives that stabilize the reservoir oil system and thereby ensure the preservation of oil in the bowels during geological time.

Oil residues (high-boiling oil fractions) are one of the raw material sources for the production of oil stabilizer concentrates. In particular, tar deasphalting asphalt, containing active antioxidants, is comparable in its inhibitory effect with common synthetic phenolic and naphthylamine antioxidants. The simplicity and low production cost, as well as the relatively high antioxidant properties of petroleum concentrates, consisting mainly of RAS, contribute to a more rational use of petroleum feedstock (in particular, production waste).

Various substances that have valuable practical applications in industry can be obtained from petroleum RAS by chemical modification using sulfonating, amination, chloromethylation, condensation, phosphorylation, and thermolysis reactions. The introduction of a significant number of active functional groups into molecules of RAS leads to the production of materials with anion and cation exchange properties.

We found[16], that the concentration and activity of inhibiting centers in low-sulfur Azerbaijani oils decrease with an increase in the depth of the deposits, that is, catagenic transformations lead to a decrease, and hypergene transformations lead to an increase in the inhibitory ability of oil components, in particular resins and asphaltenes. Inhibitors, concentrated mainly in RAS, are represented by heteroatomic compounds, and up to 10% of inhibitors are also contained in heavy residual products of oil refining (asphaltenes, tar and pitches). Therefore, it is of interest to use the residual products of oil refining as an inhibitor of the oxidation of fuels and oils instead of expensive additives. This will effectively solve the problem of maximum use of secondary resources.

The practical use of petroleum CAS as stabilizers for various polymeric materials is also conditioned by their inhibiting properties.

For example, chloromethylated asphaltites are accelerators in the chemical curing of epoxy resins and reagents for sulfurless vulcanization of rubbers. When rubber mixtures are filled with asphalt, more elastic rubber is obtained than when filled with soot. Asphalting concentrates increase the thermal-oxidative stability of epoxy compositions, and petroleum asphaltenes are emulsion stabilizers: their small additives (up to 1%) reduce

[13] Мир-Бабаев М.Ф., Самедова Ф.И., Алекперова Н.Г., 1993. Отход процесса деасфальтизации гудрона как антиоксидант топлива // Азербайджанское нефтяное хозяйство, №10, с. 28-32.

[14] Самедова Ф.И., 2011. Нефти Азербайджана. – Баку: Элм, 412 с.

[15] Мир-Бабаев М.Ф., Самедова Ф.И., Алекперова Н.Г., 1993. Отход процесса деасфальтизации гудрона как антиоксидант топлива // Азербайджанское нефтяное хозяйство, №10, с. 28-32.

[16] Мир-Бабаев М.Ф., 1997. Микроэлементный состав нефтей по данным нейтронно-активационного анализа // Химия и технология топлив и масел, №5, с.46-47.

the hydraulic resistance during the movement of oils in wells by $20\% \div 40\%$. Asphaltene concentrates are also used as antifriction fillers for lubricating compositions instead of graphite.

The main carriers of the biological activity of Azerbaijani oils from the Balakhani, Naftalan and Surakhani fields are naphthenic hydrocarbons with high cyclicity and optical activity; they are associated with the structures of biologically active compounds - the most important relict hydrocarbons related to steranes and triterpanes. Due to their clear association with biological products, these hydrocarbons are called biological tags. The concentration of steranic and triterpanic hydrocarbons in Azerbaijani oils does not exceed $0.3\% \div 0.5\%$. The predominant amount of steranes and triterpanes is contained in oil from the Balakhani field, which determines the use of high-boiling fractions of this oil for the production of medical and perfume oils[17].

The main carriers of the optical activity of Azerbaijani oils are also naphthenic hydrocarbons (their highly annular representatives). The most optically active oils and their fractions were discovered from the Azeri, Balakhani and Jafarli fields. Optical activity is an important property of oils and their components, as it makes it possible to solve the problem of the genesis of oil and determine its age.

At present, the use of luminophores based on petroleum fractions (components) is widely developed. Among the studied samples of Azerbaijani oils from the Oil Rocks and the Banka Darwin fields, aromatic hydrocarbons isolated from the residues (fractions above 350 degrees Celsius), which have an intense yellow glow, are of greatest interest. This creates a good opportunity to use these aromatic hydrocarbons in capillary luminescent flaw detection as a luminescent component of an indicator liquid.

Conclusion

The presented brief review on the environmental aspects of the use of oil and oil components has shown the practical value of these substances. The range of application of petroleum components is very wide, and their potentialities are far from being exhausted, since only the chemical transformations of RAS already make it possible to obtain a number of compounds with valuable properties necessary for solving the problem of developing a technology for the non-residual use of oil. When planning the rational use of oil and its components in the future, it is possible to identify sources of oil (anthropogenic) pollution of the environment and thereby significantly reduce emissions of pollution into the atmosphere, which will generally contribute to an improvement in the environmental situation. And this is one of the measures to conserve global biodiversity.

Bibliography

[1] Мир-Бабаев М.Ф., 1998. Высокомолекулярные соединения нефтей Азербайджана // Химия и технология топлив и масел, №5, с.44-45.

[2] Плотникова И.Н., 2012. Элементный состав нефти и рассеянного органического вещества; методы их изучения. - Казань: Казанский университет, 163 с.

[3] Алёшин Г.Н., Самедова Ф.И., Мир-Бабаев М.Ф., 1990. Микроэлементный состав высокомолекулярных компонентов нефтей и нефтяных остатков // Нефтехимия, т.30, №2, с.175-183.

[17] Самедова Ф.И., 2011. Нефти Азербайджана. – Баку: Элм, 412 с.

[4] Мир-Бабаев М.Ф., 1996. Нефтяные смолисто-асфальтеновые вещества // Химия и технология топлив и масел, №6, с.43-46.

[5] Мир-Бабаев М.Ф., 1997. Микроэлементный состав нефтей по данным нейтронно-активационного анализа // Химия и технология топлив и масел, №5, с.46-47.

[6] Silk J.E., Hansen L.D., Eatough D.J., 1989. Chemical characterization of vanadium, nickel and arsenic in oil fly-ash samples using EXAFS and XANES spectroscopy // Physica, v.158, №1, p.247.

[7] Штраус В., Мэйнуорринг С., 1989. Контроль загрязнения воздушного бассейна. - Москва: Стройиздат, 144 с.

[8] Мир-Бабаев М.Ф., Халилова А.А., 2009. Экологические проблемы в некоторых отраслях промышленности // Учёные записки, АзТУ, №4, с.69-71.

[9] Колодяжный А. В., Ковальчук Т. Н., Коровин Ю. В., 2006. Определение микроэлементного состава нефтей и нефтепродуктов. Обзор. // Методы и объекты химического анализа, т. 1, № 2, с.90-104.

[10] Самедова Ф.И., Мир-Бабаев М.Ф., 1992. Высокомолекулярные гетероатомные соединения нефтей. - Баку: Нефис, 135 с.

[11] Мир-Бабаев М.Ф., Самедова Ф.И., Алекперова Н.Г., 1993. Отход процесса деасфальтизации гудрона как антиоксидант топлива // Азербайджанское нефтяное хозяйство, №10, с.28-32.

[12] Самедова Ф.И., 2011. Нефти Азербайджана. – Баку: Элм, 412 с.