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DETERMINATION OF ECOTOXICANTIC SUBSTANCES IN HARD WASTE CAUSED BY HYDROGEN PURIFICATION PROCESS OF PETROLEUM OILS

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The article analyzes the amount of dissolved ecotoxicants in the sample taken from the solid waste obtained during the process of hydrogenation of petroleum oils. Solid waste is the processed or burned waste of AlCoMo and AlCoNi catalysts used during the process. Based on the results obtained, the environmental impact of the solid waste was assessed. The amount of volatile ecotoxicants in the solid waste sample was determined by spectral methods and shown in tabular form. Based on the results obtained, it is possible to assess the environmental impact of solid wastes generated during the technological process at the hydrogen oil treatment plant.

Keywords: petroleum distillates, hydrogen purification, spectral method, ecotoxicants, solid waste, catalyst.

INTRODUCTION

The hydrogen treatment plant for petroleum distillates and other oil distillates at the Heydar Aliyev Oil Refinery is considered to be more environmentally and economically efficient than the old classical technological plants.As it is known, so far in the developed countries of the world's oil industry, complete reduction of emissions has not been achieved during the technological processes of oil refining. That is why conducting environmental research in various areas is one of the most important issues in assessing the environmental impact of each of the many technological processes in the oil refining industry, as one of the main environmental safety requirements of the time [1].

From this point of view, we have programmed an ecological assessment of the environmental impact of the process of hydrogen purification of petroleum oils at the plant №501 of the Heydar Aliyev Oil Refinery. One of the industrial wastes generated during the technological process of this facility is solid waste. The amount of ecotoxicant-metals in the waste sample taken from the tubs in the solid waste storage area of the facility was determined by the mass spectrum method in the laboratory. For the first time, the ecotoxicants contained in the solid wastes formed during the purification of Autol 8 and Autol 15 oil distillates as raw

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materials in the process of hydrogen cleaning mentioned by us were determined spectrally.

As noted in the technical literature, the process of hydrogen purification of petroleum oils has great economic and environmental advantages. Thus, the process of preparation of petroleum distillates as a commodity has been carried out for many years by acid-base, contact methods. Even in the oil refining industry of Azerbaijan, as in many countries, these classic processes are currently used in small quantities, which in turn creates environmental problems. In the process of refining oil and oil distillates by the above-mentioned classical methods, high-quality petroleum oils are produced, which are economically and environmentally effective, despite the fact that they create a very dangerous and harmful environment. In this case, vapors of sulfuric acid, sodium hydroxide and other ecotoxicants are released into the atmosphere along with various harmful hydrocarbons. At the same time, acidic waters containing polycyclic aromatic hydrocarbons and other harmful substances are discharged into water bodies without deep treatment [2].

It is known that in the oil refining industry, as in other industries, it has not yet been possible to carry out completely waste-free technological processes. From this point of view, different types of industrial wastes are formed during the purification processes for the preparation of various brands of petroleum oils, as well as light-colored petroleum distillates as commodities where the process of hydrogen purification of oils is carried out in the unit of the Heydar Aliyev Oil Refinery [3-4].

One of the main directions of our research is the following analysis for the initial assessment of the environmental impact of solid waste generated at the hydrogen oil treatment plant.

EXPERIMENTAL PART

Petroleum oils contain sulfur, nitrogen and oxygen compounds. These compounds have a very negative impact on oil quality. It also reduces the activity of the catalysts used in the purification of oils with hydrogen, and sometimes, conversely, the catalysts become more active due to these compounds. Catalytic systems are used to remove these compounds from the oil. Hydrogen and petroleum oil treatment plants also use AlCoMo and AlCoNi catalysts during the hydrogen cleaning process of oil compounds.In this case, the process of replacing the sulfur, nitrogen and oxygen in the oil fraction with hydrogen takes place due to the chemical reactions that take place in the technological process as a result of purification of oil fractions with catalysts and finally industrial waters and gaseous wastes such as H_2S, NH_3 are formed. As a result of the process, catalysts are obtained in the form of processed or burned solid waste.

Spectral analysis of ecotoxicants in samples taken from solid wastes formed in the process of hydrogen purification of raw materials - Autol 8 and Autol 15 oil distillates with the participation of catalysts was carried out in the above plant.

Spectral analysis is a method of quantitative and qualitative determination of the composition of a substance. It is based on the study of absorption, emission and luminescence spectra. Spectral analysis is divided into several independent methods. These include infrared and ultraviolet spectroscopy, atomic absorption, luminescence and fluorescence analysis, reflection and Raman spectroscopy, spectrophotometry, X-ray spectroscopy and a number of other methods. We used the method of optical emission spectrometry for the analysis of solid waste. The data are shown in Table “Table 1”.

Table 1. Methods for studying the composition of solids

Assigned indicator	Method	MDL	MU
Aluminum (Al)	EPA3051A,EPA 6010D	00mg/kg	5%
Copper (Cu)	EPA3051A,EPA 6010D	40mg/kg	5%
Cobalt (Co)	EPA3051A,EPA 6010D	40mg/kg	5%
Iron (Fe)	EPA3051A,EPA 6010D	50mg/kg	5%
Lead (Pb)	EPA3051A,EPA 6010D	40mg/kg	5%
Manganese (Mn)	EPA3051A,EPA 6010D	25mg/kg	5%
Molybdenum (Mo)	EPA3051A,EPA 6010D	25mg/kg	5%
Nickel (Ni)	EPA3051A,EPA 6010D	40mg/kg	5%
Potassium (K)	EPA3051A,EPA 6010D	50mg/kg	5%
Narium (Na)	EPA3051A,EPA 6010D	50mg/kg	5%
Zinc (Zn)	EPA3051A,EPA 6010D	40mg/kg	5%

MDL – Minimum setting limit
MU – Possible error in measurement

The following are the views of the chromatograms of the spectral analysis of the optical emission spectrometry method used for the analysis of solid wastes:

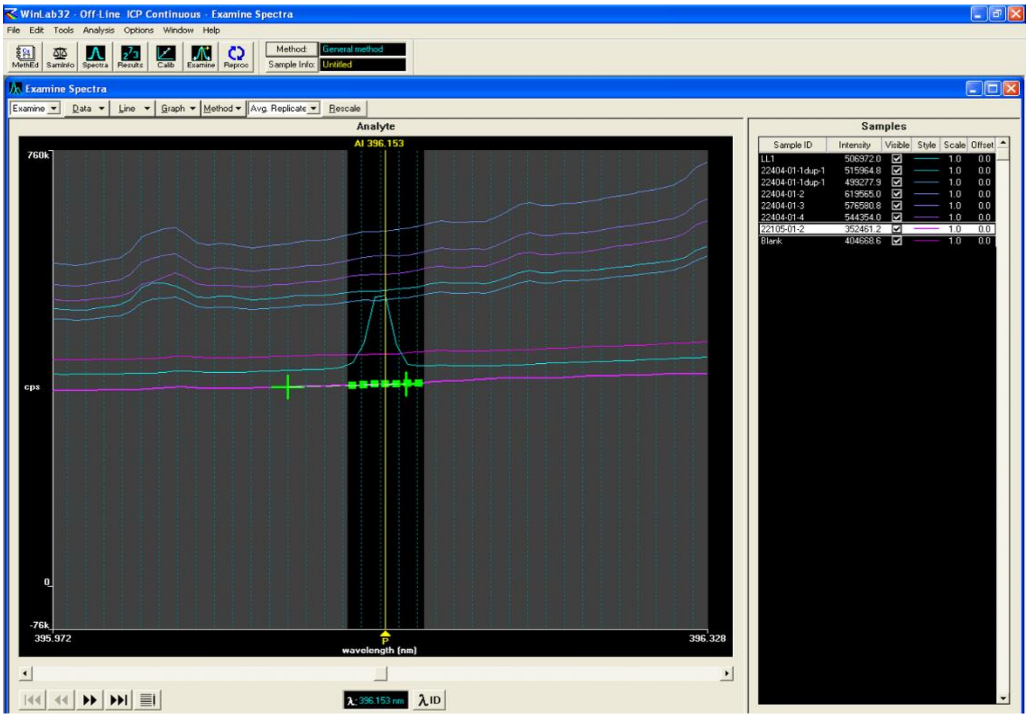


Figure 1. Chromatogram of spectral analysis of aluminum (Al).

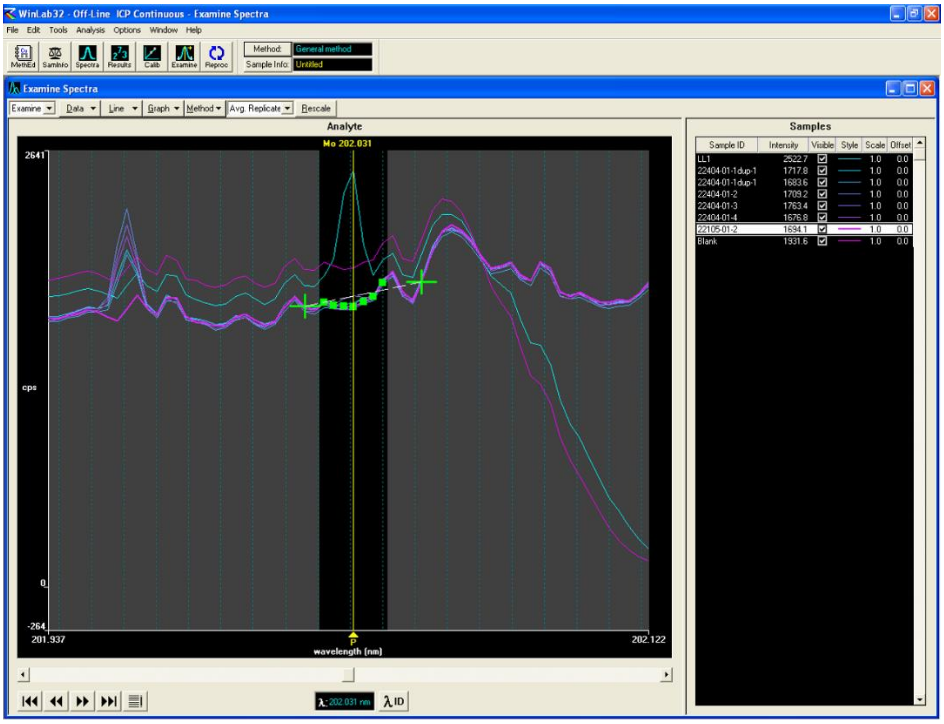


Figure 2. Chromatogram of spectral analysis ofmolybdenum (Mo).

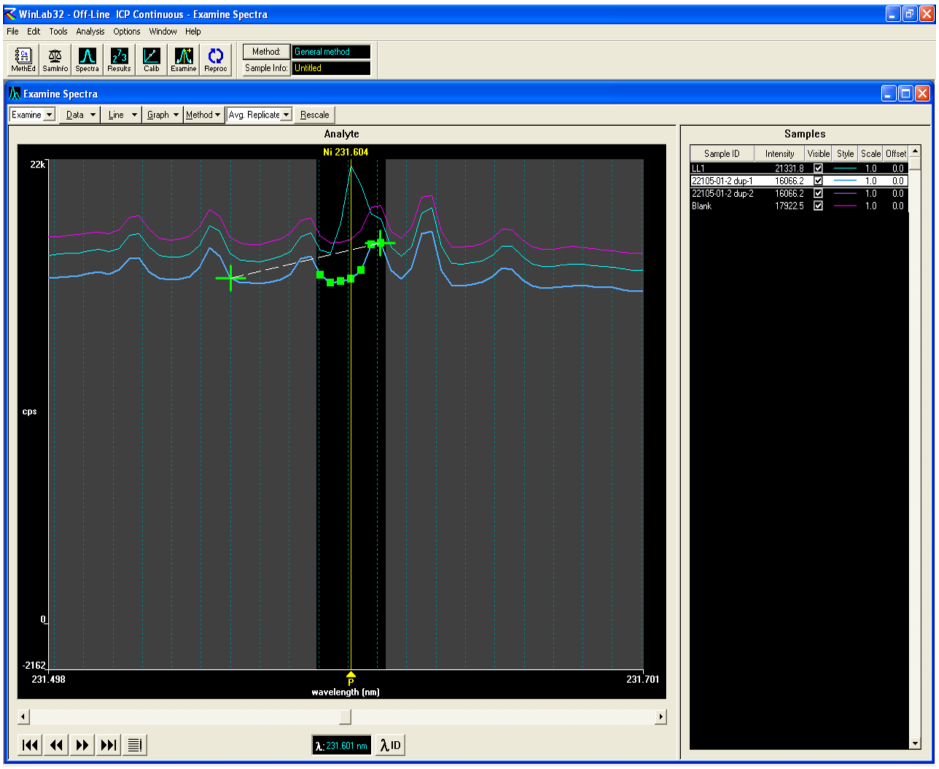
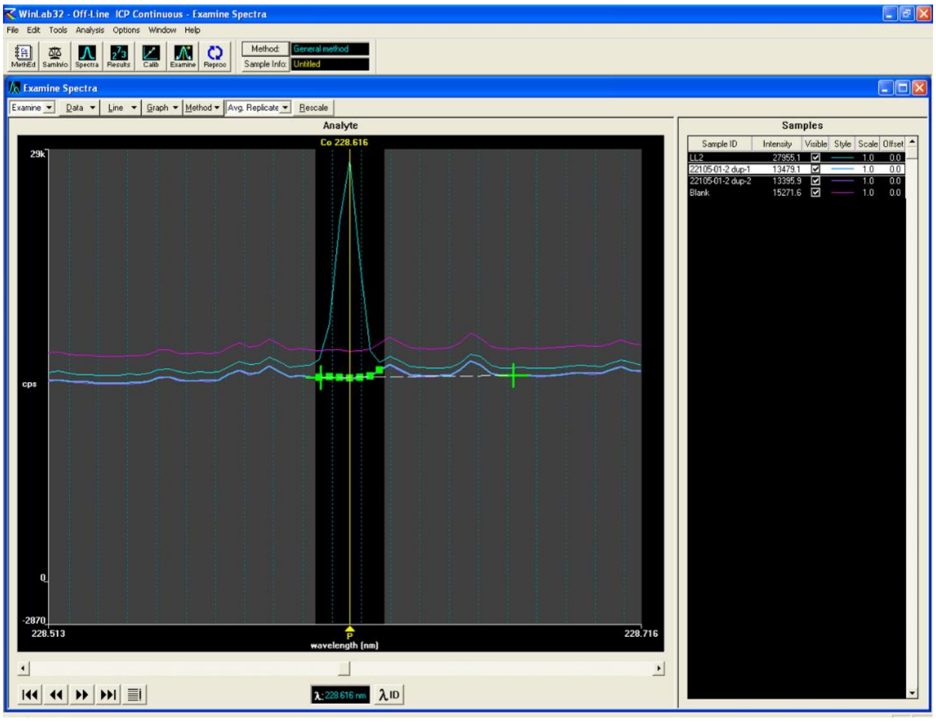


Figure 3. Chromatogram of spectral analysis ofnickel (Ni).



Figue 4. Chromatogram of spectral analysis ofcobalt (Co) .

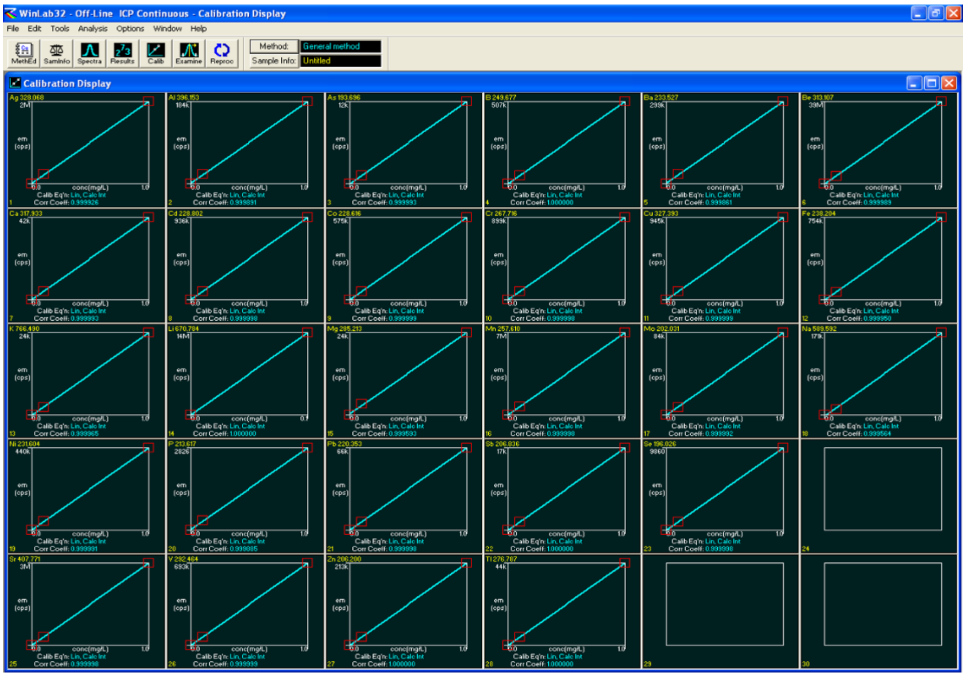
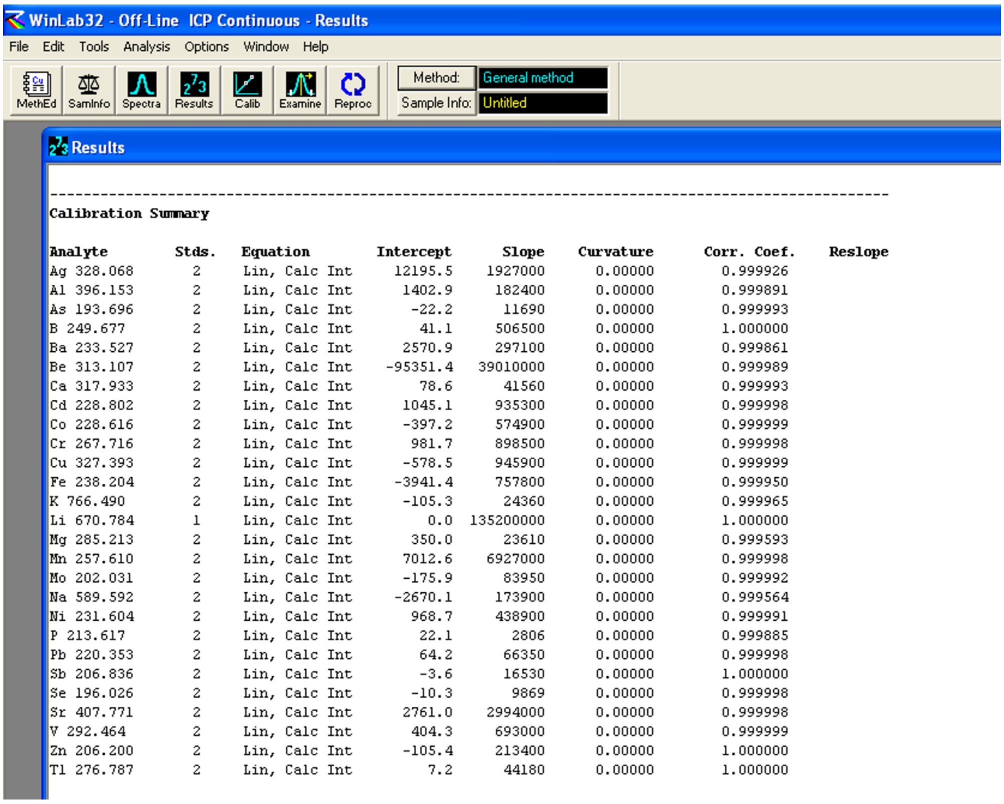


Figure 5. Chromatograms of spectral analyzes of other metals.



Calibration Summary

Analyte	Stds.	Equation	Intercept	Slope	Curvature	Corr. Coef.	Reslope
Ag 328.068	2	Lin, Calc Int	12195.5	1927000	0.00000	0.999926	
Al 396.153	2	Lin, Calc Int	1402.9	182400	0.00000	0.999891	
As 193.696	2	Lin, Calc Int	-22.2	11690	0.00000	0.999993	
B 249.677	2	Lin, Calc Int	41.1	506500	0.00000	1.000000	
Ba 233.527	2	Lin, Calc Int	2570.9	297100	0.00000	0.999861	
Be 313.107	2	Lin, Calc Int	-95351.4	39010000	0.00000	0.999989	
Ca 317.933	2	Lin, Calc Int	78.6	41560	0.00000	0.999993	
Cd 228.802	2	Lin, Calc Int	1045.1	935300	0.00000	0.999998	
Co 228.616	2	Lin, Calc Int	-397.2	574900	0.00000	0.999999	
Cr 267.716	2	Lin, Calc Int	981.7	898500	0.00000	0.999998	
Cu 327.393	2	Lin, Calc Int	-578.5	945900	0.00000	0.999999	
Fe 238.204	2	Lin, Calc Int	-3941.4	757800	0.00000	0.999950	
K 766.490	2	Lin, Calc Int	-105.3	24360	0.00000	0.999965	
Li 670.784	1	Lin, Calc Int	0.0	135200000	0.00000	1.000000	
Mg 285.213	2	Lin, Calc Int	350.0	23610	0.00000	0.999593	
Mn 257.610	2	Lin, Calc Int	7012.6	6927000	0.00000	0.999998	
Mo 202.031	2	Lin, Calc Int	-175.9	83950	0.00000	0.999992	
Na 589.592	2	Lin, Calc Int	-2670.1	173900	0.00000	0.999564	
Ni 231.604	2	Lin, Calc Int	968.7	438900	0.00000	0.999991	
P 213.617	2	Lin, Calc Int	22.1	2806	0.00000	0.999885	
Pb 220.353	2	Lin, Calc Int	64.2	66350	0.00000	0.999998	
Sb 206.836	2	Lin, Calc Int	-3.6	16530	0.00000	1.000000	
Se 196.026	2	Lin, Calc Int	-10.3	9869	0.00000	0.999998	
Sr 407.771	2	Lin, Calc Int	2761.0	2994000	0.00000	0.999998	
V 292.464	2	Lin, Calc Int	404.3	693000	0.00000	0.999999	
Zn 206.200	2	Lin, Calc Int	-105.4	213400	0.00000	1.000000	
Tl 276.787	2	Lin, Calc Int	7.2	44180	0.00000	1.000000	

Figure 6. Calibration summary.

The results obtained during the laboratory analysis of the solid waste of the facility are shown below “Table 2”.

Table2. Results of solid waste analysis.

Assigned indicators	Used catalyst
Silver Ag, mg / kg	<0.1
Cobalt Co, mq / kg	15290
Copper Cu, mg / kg	<0.4
Iron Fe, mg / kg	1718
Potassium K, mg / kg	34
Manganese Mn, mg / kg	89.3
Molybdenum Mo, mq / kg	18240
Sodium Na, mg / kg	406
Nickel Ni, mg / kg	3290
Lead Pb, mg / kg	<0.4
Zinc Zn, mg / kg	30

As can be seen from the results obtained from the tables, the reasons for the formation of each of the ecotoxicant substances in the solid waste sample taken from the refinery's water treatment plant can be explained as follows:

- Volatile ecotoxicants are formed during the purification of sulfur, nitrogen and oxygen in the distillates Autol 8 and Autol 15 with hydrogen gas. The cause of toxicants is the presence of organic compounds, mixtures of hydrocarbons and metal salts of various structures, and chemical transformations that occur during the technological process under the influence of catalysts, pressure and temperature up to 280-310^{0}C.

- Catalysts in the reactors of the plant sometimes burn and become unusable in accidents caused by a sharp rise in temperature. As a result, waste metals are formed in the processed, burned catalysts.

As can be seen from the table, the amount of metals such as Co, Fe, Ni, Mo is many times higher than normal and this is due to the chemical composition of the alumocobaltmolibdenum and alumonicelmolybdenum catalysts. The presence of dissolved ecotoxicants in the solid waste sample of the plant is mainly due to the content of sulfur, nitrogen, oxygen, metals, etc. in the raw materials distillates Autol 8 and Autol 15, as well as the content of petroleum acids, alumocobaltmolybdenum and aluminosilicolmolibenum used in the purification process.

Thus, the following explanations can be given briefly about the technological process of hydrotreating of petroleum distillates and the reactions that take place during this process.

The hydrotreating process is carried out in a hydrogen environment in the presence of aluminocobaltmolybdenum and almonikelmolybdenum catalysts at high temperatures - 350-430^{0}C, 30-70 atmospheres, circulating hydrogen gas in the ratio of 100-600 m^3 of raw material and 60-95% hydrogen. Reactions such as hydro-desulfurization, hydrocracking, hydrogenation of unsaturated hydrocarbons, isomerization of paraffin and naphthenic hydrocarbons occur during this process [5-9].

During the hydrogenation process, different types of waste are formed depending on the nature of each compound in the oil distillate. Phenols, ketones, alcohols in the resin formed in the technological process are easily reduced by hydrogen. The mixture of these resins is saturated with hydrogen and broken down to form hydrocarbons, hydrogen sulfide, ammonia and the above-mentioned ecotoxicant compounds. Solid wastes containing a mixture of dissolved ecotoxicants are separated from the technological process.

That is why every gas, liquid, solid waste formed during the process of hydrogen purification of petroleum distillates in the oil refining industry has a negative impact on the environment in various ways.

One of the main directions of our scientific research is the ecological assessment of the environmental impact of solid wastes formed in the process of hydrogen purification of petroleum distillates.

RESULTS AND DISCUSSIONS

The following explanations can be given about the results of the research:

- The degree of content of ecotoxicants in the main solid waste sample formed in the technological process of hydrogen purification of petroleum distillates was determined by environmental analysis by spectral method.

- The reasons for the production of many metal compounds in the solid waste of the hydrotreating process and our initial classification are given.

Each of the ecotoxicant metals in the catalyst sample developed during the study, based on the information provided in the technological literature on environmental and sanitary permissible concentration limits, can cause environmental pollution. Therefore, the storage and disposal of these wastes must be carried out in accordance with the rules that meet modern environmental safety requirements.

As it is known, even in the developed countries of the world, such negative impact on the environment is inevitable as a result of methods such as treatment, transportation and burial of solid waste generated in the oil refining industry.

Thus, given the extensive information in the technical literature on the effects of each identified ecotoxicant on human health and the ecosphere and biosphere in general, and their allowable concentrations, additional explanations of the effects of these substances on the environment are no needed.

The assessment of the ecological impact of technological processes on the environment, depending on the composition of raw materials, based on the identification of ecotoxicants in the various types of waste generated in this facility, can be considered scientifically based.

CONCLUSIONS

According to the results of the research, it can be noted that the solid wastes generated in the hydrogen treatment plant of oil refineries have a composition that will damage of the soil structure.Therefore, we consider it reasonable to send the waste to the company that sells the catalyst for disposal at the required level and arrange for its regeneration there. Because it is very likely that the company that produces the catalyst has every opportunity.

When refining petroleum oils with hydrogen, waste generation and environmental impact are inevitable.Until today, in order to prevent this, these wastes are buried in the ground and neutralized.This causes the soil to become petrified, its pores filled, its structure disturbed and it becomes unusable.In our opinion, these catalysts can be used as a construction material by adding them to concrete instead of stone and gravel.Considering the hardness, radiation safety and molybdenum content of catalysts, their use in concrete preparation is suggested as an environmentally friendly idea.

REFERENCES

[1] Davydova, S .L.; Teplyakov, V.V. D13. Environmental problems of oil refining, Proc. Allowance, M.: RUDN University, 2010, pp. 54-67.
[2] Sukhanov, V.P. Oil refining. Uçebnik. Vyssha school, 1974, pp.211.
[3] Ajamov, K.Y.; Bagirova, N.N.; Mammadkhanova, S.A.; Huseynova, E.A. Catalyst and adsorbent preparation technology, Baku, 2011, pp. 181-182.
[4] Shperber, E.R. Some kinds of wastes of oil refineries and their classification. Environ. Prot. Oil-And-Gas Indus, 2011, pp. 27–32.
[5] Bellussi, G.; Rispoli, G.; Landoni, A.; Millini, R.; Molinari, D.; Montanari, E. Hydroconversion of heavy residues in slurry reactors: Developments and perspectives. Journal of Catalysis, 2013, pp. 189-200, DOI: 10.1016/j.jcat.2013.07.002
[6] Ching Thian Tye. Catalysts for hydroprocessing of heavy oils and petroleum residues, 2019, pp. 12, DOI: 10.5772/intechopen.89451
[7] Rana, M. S.; Sámano, V.; Ancheyta, J.; Diaz, J. AI.. A review of recent advances on process technologies for upgrading of heavy oils and residua, Fuel. 214, 2007, pp. 1216-1231, DOI: 10.1016/j.fuel.2006.08.004
[8] Rodríguez, E.; Félix, G.; Ancheyta, J.; Trejo, F. Modeling of hydrotreating catalyst deactivation for heavy oil hydrocarbons. Fuel.225, 2018, pp.118-133, DOI: 10.1016/j.fuel.2018.02.085

[9] Sahu, R.; Song, BJ.; Im, JS.; Jeon, Y-P.; Lee, CW. A review of recent advances in catalytic hydrocracking of heavy residues, Journal of Industrial and Engineering Chemistry, 2015, pp.12-24, DOI: 10.1016/j.jiec.2015.01.011