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Demetallization and desulfurization of heavy oil residues by adsorbents

Yerdos Ongarbayev[a,b], Shynar Oteuli[a,b], Yerbol Tileuberdi[a,b], Galymzhan Maldybaev[c], and Saule Nurzhanova[c]

[a]Al-Farabi Kazakh National University, Almaty, Kazakhstan; [b]Institute of Combustion Problems, Almaty, Kazakhstan; [c]LLP «Enertek», Almaty, Kazakhstan

ABSTRACT
The purpose of the work is demetallization and desulfurization of heavy oil residues using adsorbents. Optimal parameters of the demetallization and desulfurization processes of heavy vacuum fraction of Pavlodar Petrochemical Plant LLP in the presence of a zeolite adsorbent containing vanadium oxide xerogel were established: temperature 340 °C, pressure 1 atm., bulk feed rate 1 h^{-1}. As a result of the process the extraction degree of vanadium, nickel and iron were 90, 70 and 60%, respectively, and the sulfur content decreased from 1.97 to 1.36%. Composition of the chemical adsorbent for demetallization and desulfurization of heavy vacuum fraction is established, too. Content of vanadium, iron and sulfur increase in composition of the adsorbent after treatment of heavy vacuum fraction, which confirms its high adsorption capacity regarding to metals and sulfur.

KEYWORDS
adsorbents; demetallization; desulfurization; heavy oil residues; heavy vacuum fraction; vanadium oxide; zeolite

1. Introduction

Every year the volume of producing and processing of oil with high content of metals, tar-asphaltene components and heterocompounds increases. Still insurmountable technological barrier for deep and non-residual processing has been associated problems with an increased content of not only metals in oils and oil residues, but also sulfur, which are irreversible poisons for catalysts and corroding equipment. Processing of these residues with the use of catalysts leads to quick coking of the latter, their high consumption and a sharp increase in the cost of processing and, accordingly, finished products.

In a fairly extensive accumulated material on trace elements and the forms of their existence in oils and their fractions, many researchers attach particular importance to vanadium and nickel. It is known that vanadium in most oils is in the form of a vanadyl ion (VO^{2+}), and nickel is completely represented as a divalent ion (Ni^{2+}) (Filby 1975; Ali and Abbas 2006; Wu, Zhu, and Li, 2014).

Nickel and vanadyl ions in oils are part of porphyrin, pseudoporphyrin complexes and non-porphyrin structures. According to the literature data (Fish, Komlenic, and Wines 1984; Pearson and Green 1989) metal porphyrin complexes average 30–80% of vanadium and nickel-containing compounds. The rest of the metal-containing compounds in oils exist as chelates with various ligands, as well as salts of organic acids.

The general direction of development of the processes of demetallization of crude oil is the concentration of metals in the residues using known oil refining processes, in particular secondary

CONTACT Yerdos Ongarbayev Erdos.Ongarbaev@kaznu.kz Al-Farabi Kazakh National University, Al-Farabi Pr., 71, Almaty 050040, Kazakhstan.
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non-catalytic thermodestructive and solvent-adsorption processes or catalytic cracking and hydroconversion processes (Gryglewicz, Rutkowski, and Steininger 1991).

Significantly higher parameters of the yield and quality of distillate products and gas are characteristic of catalytic and hydrocatalytic processes. However, they have significant both capital and operating costs associated with high consumption of catalyst and hydrogen. In addition, they are adapted for processing only a relatively favorable content of sulfur, metals, and coking properties of raw materials; in these processes, it is possible to process heavy oil residues only after preliminary demetallization by solvent, adsorption, and thermal adsorption processes. Solvent processes are characterized by high energy consumption, increased operational and capital costs, they lead to the formation of an even heavier asphalt residue than tars.

Recently, there is a tendency to develop processes of an intermediate type between thermal and catalytic, so-called hydrothermal processes, such as hydropyrolysis, hydrocoking, hydrovisbreaking, and solvent-donor cracking, but they are limited in depth of conversion, but are not limited in terms of metal content in heavy petroleum residues (Ancheyta 2013; Banerjee 2012). The main drawback is the low quality of the products obtained, and for the processes of thermal cracking and visbreaking, there is also a limited conversion depth.

Thermal adsorption deasphalting and demetallization are among the effective enriching processes. Granular and powdery solid materials are used as adsorbents. In the processes of thermoadsorption refining there is no hardly utilizable asphaltite formed in the process of solvent deasphalting.

Thus, the currently used processes for the processing of heavy oil residues with a high content of metals and sulfur do not have an absolute advantage, since they are rigidly tied to the composition of the raw materials and specific conditions, primarily economic. The complexity of the composition of the source of crude oil affects the choice of a method of demetallization and desulfurization of petroleum and petroleum products, which is one of the main reasons for the difficulty of implementing these processes in enterprises (Dehghan and Anbia 2017; Lee and Valla 2017).

The aim of the study is to develop a method for demetallization and desulfurization of heavy oil residues using chemical modified adsorbents.

2. Experimental

Object of the study is heavy vacuum fraction, which raw material of the delayed coking unit of Pavlodar Petrochemical Plant LLP. Heavy vacuum fraction has following characteristics: appearance—viscous slow-moving liquid, mass fraction of water—up to 0.1 wt.%, vanadium content—200.1 mg/kg, nickel content—64.0 mg/kg, iron content—54.0 mg/kg, mass fraction of sulfur—1.97%, ash content—0.02 wt.% coking ability—14 wt.%, density at 20 °C—981.0 kg/m^3, initial boiling point—380 °C.

Figure 1 shows a flowchart of an integrated laboratory unit for demetallization and desulfurization of heavy oil residues. Demetallization process carried out in short-term contact in a two-section tubular-type reactor at 300–360 °C heating heavy residue with an adsorbent. According to results, contacting the feedstock with the hot adsorbent hydrocarbon vapors are formed, which, in a mixture with water vapor, are transported to the vapor line. During the passage through the first section of the pipe, various transformation reactions occur: easy conversion, demetallization and partial desulfurization.

In the process of demetallization and desulfurization of heavy vacuum fraction in the enlarged laboratory installation, following process conditions were worked out: temperature in the reactor were from 300 to 360 °C, process time was 3 h, raw material consumption was from 2 to 5 l/h, bulk feed rate of the raw material was 1–3 h^{-1}.

In the work, a zeolite carrier of the Novosibirsk Chemical Concentrates Plant used as the basis for manufacture of the tested adsorbent samples, which was modified with a synthesized vanadium-containing gel, contributing to the formation of developed mass structure of the adsorbent,

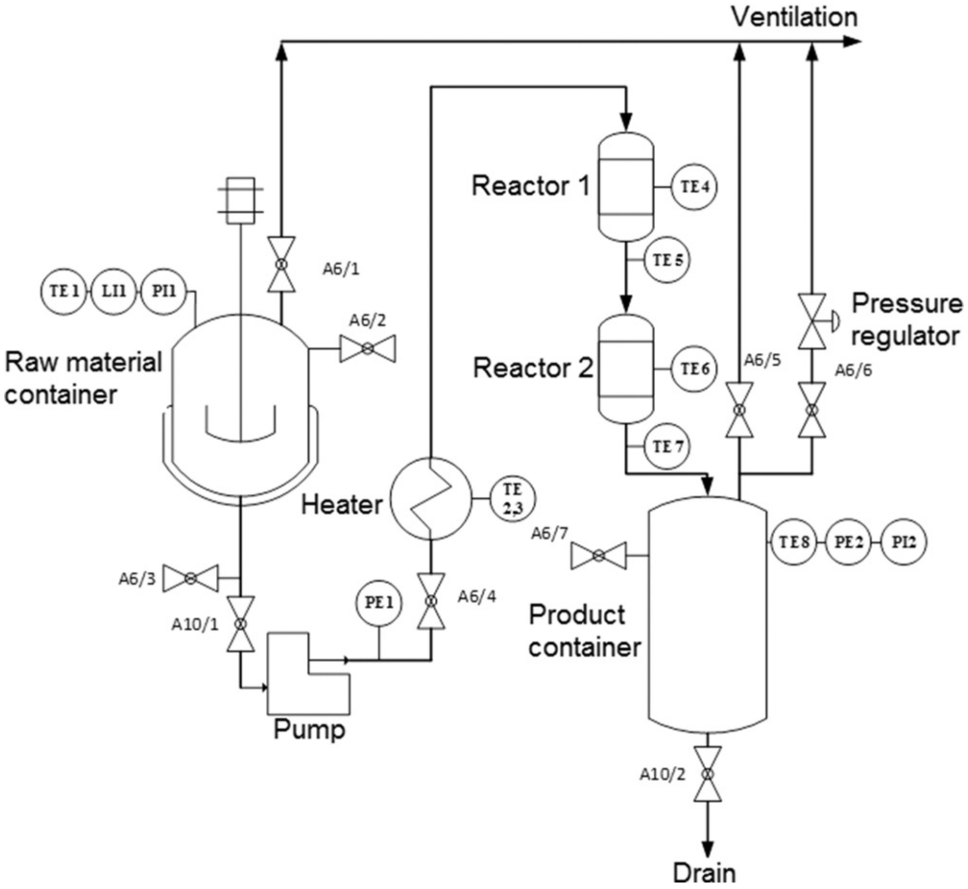


Figure 1. Technological scheme of the installation of demetallization and desulfurization of heavy oil residues.

i.e. increase pores. Vanadium pentoxide, used for the synthesis of vanadium gel, has a complex crystalline structure and is a combination of large number of individual agglomerates.

The content of metals in the heavy vacuum fraction was determined by the atomic absorption method and mass spectrometry with inductively coupled plasma (ICP-MS). The elemental composition of adsorbent samples were determined using an Inca Energy energy dispersive spectrometer (Oxford Instruments, England) mounted on a Superprobe 733 electron probe microanalyzer with an accelerating voltage of 25 kV and a probe current of 25 nA. Fractional composition of heavy vacuum fraction and products of its processing were determined on the chromatograph "Crystal Lux."

3. Results and its discussion

The process of demetallization and desulfurization was carried out in the presence of zeolite adsorbent containing xerogel vanadium pentoxide, obtained by sol-gel synthesis. In accordance with the scheme of the general structure of the oil dispersion system and mutual transition of resinous-asphaltene components to each other, it can be assumed in the processes of thermal deasphalting and demetallization in oil, meanwhile the supramolecular structures (metal, sulfur-containing oil complexes) are destroyed and their subsequent adsorption on chemical adsorbents.

To establish the optimal technological parameters of the process, the initial heavy vacuum fraction and its products were analyzed for the content of metals and sulfur.

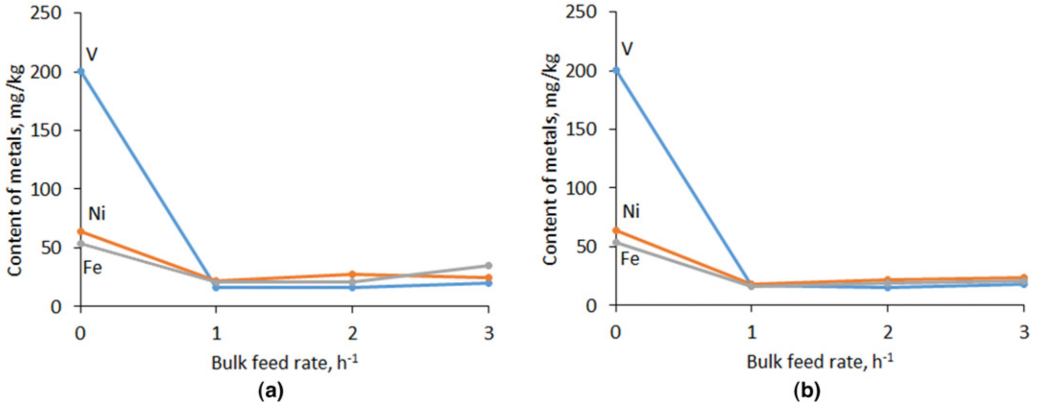


Figure 2. Dependence of the content of metals in the heavy vacuum fraction on the bulk feed rate: (a) $T = 300\,^\circ C$; (b) $T = 340\,^\circ C$.

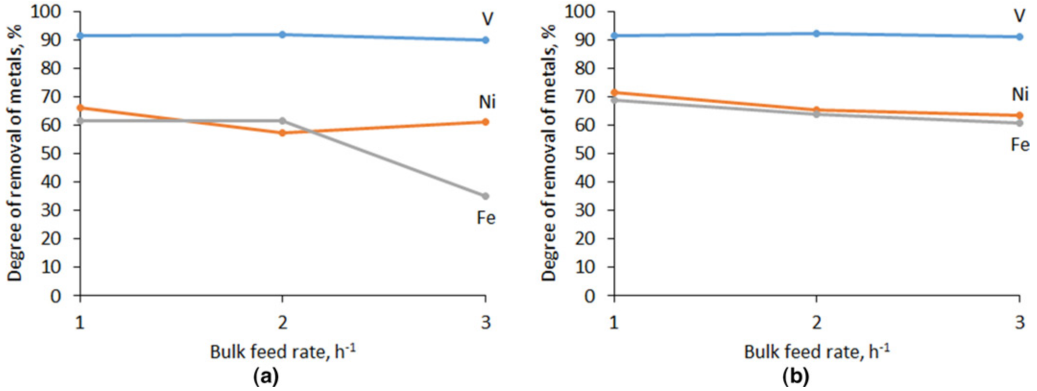


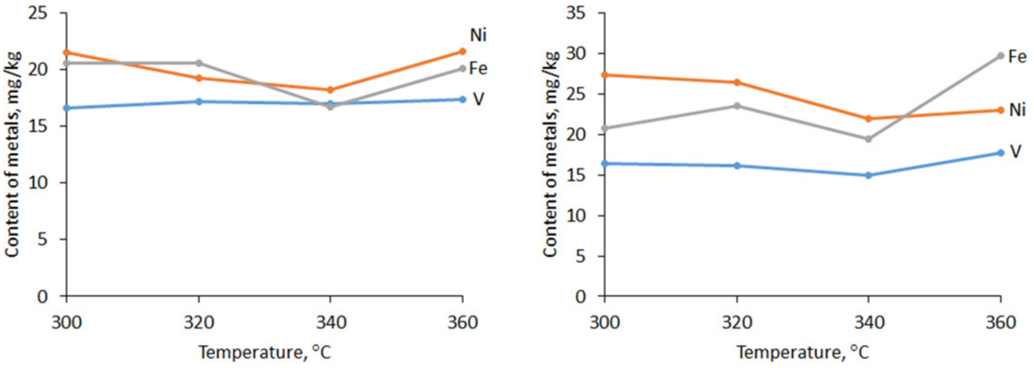
Figure 3. Dependence of the removal degree of metals on the bulk feed rate: (a) $T = 300\,^\circ C$; (b) $T = 340\,^\circ C$.

Figure 2 shows the dependences of the metal content in heavy vacuum fraction on the bulk feed rate at various temperatures. As can be seen from Figure 2, at all tested process temperatures there is a decrease in the content of metals in the composition of the raw materials, while there is a sharp decrease in the content of vanadium. The increase in the bulk feed rate from 1 to $3\,h^{-1}$ leads to a slight increase the residual content of metals in the heavy vacuum fraction after processing.

The optimal bulk feed rate can be set on the basis dependences of the removal degree of metals on the specified parameter. As can be seen from Figure 3, with an increase in the bulk feed rate of raw materials from 1 to $3\,h^{-1}$, a decrease the removal degree of metals are observed. In case of demetallization from vanadium, its content in heavy vacuum fraction processing products is almost independent to the bulk feed rate. In fact for the nickel and iron, the optimal bulk feed rate is $1\,h^{-1}$.

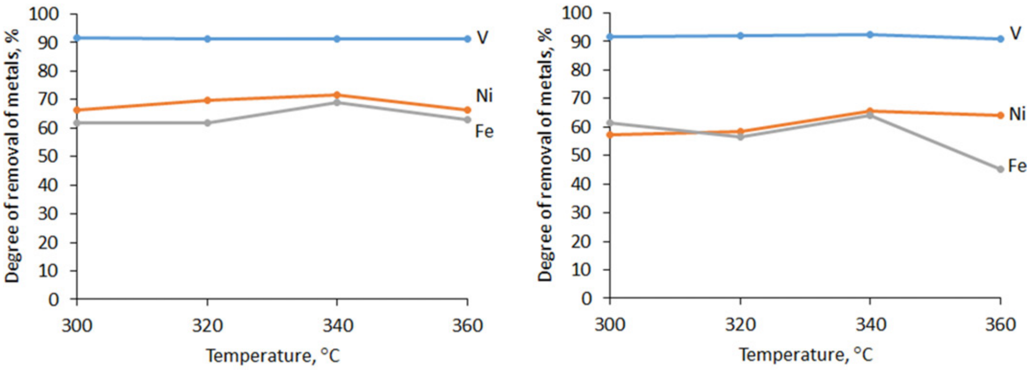
Figure 4 shows the dependence of the metals content in the heavy vacuum fraction on the process temperature of demetallization and desulfurization at different volumes of the feed rate of raw material. Curves of changes in the content of metals pass through a minimum. As can be seen from the graphs, the minimum metal content is observed at a process temperature of 340 °C. As noted earlier, the change in the content of vanadium is not as dramatic as in case of nickel and iron.

The dependence of removal degree of metals on the process temperature (Figure 5) is confirmed by data on the metals content after the process of demetallization of heavy vacuum fraction. The degree of vanadium removal from tar is almost independent of the process temperature. The degree of removal of nickel and iron, depending on the temperature of



(a) **(b)**

Figure 4. Dependence of the content of metals in the heavy vacuum fraction on the process temperature: (a) bulk feed rate 1 h^{-1}; (b) bulk feed rate 2 h^{-1}.



(a) **(b)**

Figure 5. Dependence of the removal degree of metals on the process temperature: (a) bulk feed rate 1 h^{-1}; (b) bulk feed rate 2 h^{-1}.

demetallization pass through the maxima, which allows to determine the optimum temperature of the process. As the curves show, the optimal process temperature is 340 °C, at which the removal degree of metals has maximum values.

Figure 6 shows the dependence of the sulfur content in the heavy vacuum fraction on the bulk feed rate and the process temperature. As can be seen from the figure, as a results of the desulfurization process of heavy vacuum fraction, the sulfur content was decreases. As in case of the demetallization process, the optimal bulk feed rate is 1 h^{-1}, the optimum process temperature is 340 °C, at which the minimum sulfur content in heavy vacuum fraction is observed.

Table 1 shows the results of chemical analysis of the content of metals and sulfur in the composition of the initial heavy vacuum fraction and after its processing. As can be seen from the tabular data, the degree of extraction of vanadium is 90–92%. Unlike vanadium, the degree of nickel and iron removal varies over a wide range—for nickel from 57.2 to 71.6%, for iron—from 35.2 to 69.1%. The maximum degree of extraction of metals is observed at a temperature of 340 °C and a bulk feed rate of 1 h^{-1}. The sulfur content in heavy vacuum fraction composition after desulfurization decreases from 1.97 to 1.36%, which also occurs at a temperature of 340 °C. In general, the results of the analysis of heavy vacuum fraction after demetallization and desulfurization in the presence of a zeolite adsorbent containing vanadium pentoxide at different values of temperature and bulk feed rate showed that the degree of extraction of vanadium, nickel and iron are on average 90, 70, and 60%, respectively. Whereas the sulfur content decreased from 1.97 to 1.36%.

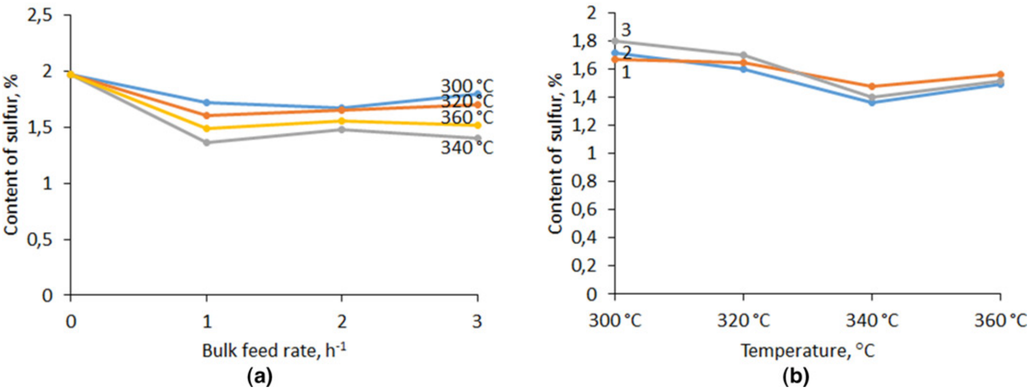


Figure 6. Dependence of the sulfur content in the heavy vacuum fraction on the bulk feed rate of the raw material (a) and process temperature (b).

Table 1. Content of metals and sulfur in the heavy vacuum fraction before and after the process of demetallization and desulfurization

	Metal content, mg/kg				Degree of removal of metals, %		
Bulk feed rate, h^{-1}	V	Ni	Fe	Sulfur content, %	V	Ni	Fe
Heavy vacuum fraction	200.1	64.0	54.0	1.97	–	–	–
T = 300 °C							
1	16.62	21.5	20.6	1.72	91.7	66.4	61.8
2	16.46	27.4	20.8	1.67	91.8	57.2	61.5
3	20.2	24.7	35.0	1.8	90.0	61.4	35.2
T = 320 °C							
1	17.2	19.3	20.6	1.6	91.4	69.8	61.8
2	16.1	26.5	23.5	1.65	92.0	58.6	56.5
3	18.3	24.3	21.1	1.7	90.8	62.0	60.9
T = 340 °C							
1	17.0	18.2	16.7	1.36	91.5	71.6	69.1
2	14.9	22.0	19.4	1.48	92.5	65.6	64.1
3	17.69	23.4	21.1	1.4	91.1	63.4	60.9
T = 360 °C							
1	17.4	21.6	20.1	1.49	91.3	66.2	62.8
2	17.7	23.0	29.7	1.56	91.1	64.1	45.0
3	20.3	26.6	29.6	1.52	89.8	58.4	45.2

Table 2 presents the elemental composition of the chemical adsorbent before and after the process of demetallization and desulfurization of heavy vacuum fraction. As can be seen from Table 2, the content of the adsorbent after treatment of heavy vacuum fraction increases the content of vanadium from 0.59 to 1.07%, iron from 0.13 to 0.20% and sulfur from 0.01 to 0.51%, which confirms it high adsorption capacity with respect to metals and sulfur.

Table 3 is presenting the material balance and fractional composition of heavy vacuum fraction after the process of demetallization and desulfurization at different temperatures. As can be seen from the tabular data, during demetallization by adsorbent, the gas yield increases from 8.0 to 12.1%, the coke yield decreases from 10.5 to 6.7%, the yield of liquid distillate remains at the same level as without adsorbent, about 81 mass%. At the same time, after demetallization and desulfurization at a temperature of 340 °C in the composition of heavy vacuum fraction, the yield of the fraction boiling up to 180 °C rises from 5 to 22.5%. The results obtained confirm the beneficial effect of the action of the adsorbent on qualitative fractional composition of the liquid distillate.

The good results of the demetallization process of heavy oil residues are associated, first of all, by modifying the zeolite with vanadium pentoxide, which increases its basic properties, as well as

Table 2. Elemental composition of adsorbents before and after demetallization and desulfurization of heavy vacuum fraction

	Content of elements, %							
Sample	C	O	Al	Si	S	Ca	V	Fe
Initial adsorbent	–	47.49	7.37	43.16	0.01	0.13	0.59	0.13
Adsorbent after process	11.43	48.04	6.89	32.37	0.51	–	1.07	0.20

Table 3. Material balance of the process and the fractional composition of heavy vacuum fraction before and after demetallization and desulfurization

		Yield, wt.%						
					Fractions of liquid distillate, °C			
Samples	т, °C	Gas	Coke	Liquid distillate	<180	200–350	350–500	>500
Heavy vacuum fraction	350	8.0	10.5	81.5	5.0	28.0	29.5	19.0
Heavy vacuum fraction after demetallization	300	11.0	7.5	81.5	13.5	27.5	32.2	8.3
	320	10.5	6.7	82.8	17.5	27.4	31.3	6.6
	340	10.1	8.5	81.4	22.5	24.8	18.2	15.9
	360	12.1	8.1	79.8	20.6	25.6	19.7	13.9

the isomerizing and cracking activity of the modified zeolite. Zeolite media containing vanadium makes it possible to more effectively convert high-molecular compounds as resins and asphaltenes into more practically important low-molecular compounds as oils. The addition of vanadium pentoxide to zeolite leads to intensification of the splitting process of high-molecular-weight hydrocarbons, while the rate of polycondensation reaction leading to coking is slowed down.

It is known that thermal processes of decomposition and condensation of hydrocarbons have a radical-chain character. At high temperatures in the zeolite-catalytic system, which modified by nanoparticles, organic-mineral radicals are formed (stable radicals VO^{2+} nanopowder interact, which account for over 50% of all radical centers). These radicals have a significant reactivity and bind organometallic—vanadium porphyrin compounds of oil according to the principle of "similarity," that is, they attract their own kind, forming heteroframe structures, and then adsorb to surface of the adsorbent. As a result of complex chemical interactions of oil components with the organomineral structure of the zeolite mass, the degree of demetallization reaches to 90%. On the other hand, high demetallizing ability is associated with a sharp increase in concentration of Lewis acid sites, which include the modifying metals, in particular vanadium in the modified adsorbent.

By the mechanism of demetallization of heavy oil residues, it can be assumed that resin-asphaltenic substances, organometallic, sulfur and nitrogen-containing tar compounds are transformed into isomeric homologs, lower molecular weight compounds and frame structures (as a result of cracking reactions) are destroyed with subsequent adsorption on the surface zeolite.

In addition, the unique properties of zeolite modified by rare metal nanocompounds promote selectivity to certain ions and molecules during purification of oil residues by sorption. It means due to the presence of ion-exchange functional groups and the geometric parameters of the crystal lattice.

4. Conclusion

Thus, optimum technological parameters of the process of demetallization and desulfurization of heavy vacuum fraction of Pavlodar Petrochemical Plant LLP in the presence of zeolite adsorbent containing vanadium xerogel are established: process temperature—340 °C, pressure—1 atm, volumetric feed rate—$1\,h^{-1}$. As a result of the process, the degree of extraction of vanadium, nickel and iron were 90, 70, and 60%, respectively. At the same time sulfur content decreased from 1.97 to 1.36%. Composition of the chemical adsorbent for demetallization and desulfurization of heavy vacuum fraction is established, too. Content of vanadium, iron and sulfur increase in composition of the adsorbent after treatment of heavy vacuum fraction, which confirms its high adsorption capacity regarding to metals and sulfur.

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