

Development of New Non-waste Catalytic Technology for Oil Desulfurization as a Method to Reduce the Environmental Pollution

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Abstract

This study is devoted to the development of non-waste technology of oil and petroleum refining. The experimental material of a soft catalytic oxidation of oil sulfurorganic compounds with formation of sulfoxides and sulfacides, having high consumer qualities is presented. Based on the IR-spectral data and mathematical calculations the optimal conditions of the process are defined, the kinetics of the oxidation is investigated and the process mechanism is offered. The results of research and approbation of highsulfurous oils of the Kazakhstan oilfields are presented. These materials are offered for introduction in the application by oil companies, which explore and produce the oil from oilfields of Western region of Republic of Kazakhstan.

Introduction

The republic of Kazakhstan is one of the leading countries in the world by pool hydrocarbon raw materials resources, however, a significant part of extracted oils is sulphurous and highsulfurous.

The production, preparation for transportation and transportation of such oils is accompanied by formation of sulfur-containing wastes, which represent serious danger not only to the state of natural environment possessing of their high aggression, but also render the influence on health of the population because of their high toxicity.

Besides, the presence of sulfurorganic compounds in raw materials promotes the fast corrosion of pipelines. During desulfurization the padding sources of losses of oil and petroleum are created, the level of environmental pollution by hydrocarbons and sulphurous compounds is high; the states of clearing of wastewater are more difficult. The consequent application of such oil in chemical processing results in the destruction of reactive vessels and poisoning of catalysts.

The highsulfurous oil is the oil of Tengiz oilfield, which is of one of the largest in the world. The distinct-

ive peculiarity of Tengiz oil is the high content of volatile mercaptans having odor. Besides, the highsulfurous gas hydrogen sulfide accompanies the production of the oil. Taking into account the high toxicity and corrosion aggression of sulfurcontain compounds the development of new non-waste technology for treatment of oil and petroleum is really actual.

The ways of clearing, existing in the world practice, are limited by hydroclearing, *i.e.* at severe constraints to reduce the organic sulphurous compounds to H₂S, which further by Clause method can be oxidized to free sulfur. The process is characterized by difficult technology and high power consumption. There is a large problem to remove the high-dispersed sulfur [7].

The sulfurorganic compounds of oil are represented basically by sulfides, tiophens, mercaptans *etc.* [2,3]

One of the major reactions of sulphurous compounds is oxidation, which allows the formation of sulfoxides and sulfones, showing significant ability to donor-acceptor interactions with ions of noble metals. So, they can serve as high selective extraction reagents [1,4-6].

It is known, that the Tengiz oilfield is located in a semidesert zone with a sharply continental climate.

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This causes high responsivity of natural environment to negative techniques [7]. So, the introduction of non-waste technology is one of the effective ways to lower the pressure on the environment.

The present work describes the experimental material on catalytic removing of sulfur compounds from oil.

The technology based on a liquid-phase method of soft oxidation, which does not demand difficult instrumentation and superstrong materials and allows utilizing available reagents (HNO_3 or NaNO_3 , H_2SO_4 , H_2O , air).

The current scheme to refine the oil from sulfur on Tengizchevroil (TCO) is the oxidation of mercaptans to disulfides, which are soluble in oil. So, there is a chemical transformation of one sulfur-containing compound to others, not having a smell. So, the aggression of sulfur is not eliminated. Unlike of the process used by TCO, we offer the catalytic system for oxidation of sulfur-organic oil compounds to sulfacides, which are insoluble in oil and remaining in aqueous phase, and, thus, can be extracted from petroleum composition.

Experimental

In order to find the optimal conditions for desulfurization of oil, which prevent the formation of sulfur-containing undesirable waste products we have investigated some inorganic metals sulfides as well as the catalysis of the process. The testing of the process on Karachaganac and Karazhanbas oils was done.

The inorganic sulfides were studied for determination of optimal conditions for sulfurorganic compounds oxidation.

A synthetic bismuth (CC-mark 85%), obtained by sintering of elementary sulfur and metal bismuth, with monitoring of composition by chemical and radiography analysis, was used as a starting material. The measurement of rate was done by volumetric method with absorption of oxygen by the system and reduction of bismuth sulfides amount during the time. The oxidation state of reacting particles in a solution were determined by redox potential measured by a platinum electrode in relation to a calomel half element. The IR-spectra were recorded using Specord, IR-25 and UR-20 spectrophotometers.

The sulfide coating generated during oxidizing dissolution of bismuth was washed by benzene, then again was introduced into the reaction mixture.

The kinetics of soft catalytic oxidation process of sulphurous compounds from Karazhanbas oil fractions is investigated.

The composition of starting and refined fractions of oil was established with the help of elemental analysis and IR-spectroscopy.

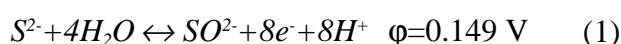
During the study the detection of the factors influencing the oxidation of halkpyrite and pyrite was done, and the opportunity for refining of sulfur-containing oil by a method of homogeneous catalytic soft oxidation using the distillates from Karazhanbas and Karachaganac oil fields was shown.

Results and discussion

Oxidation of metal sulfides

The obtained experimental data indicate, that in the absence of nitrogen oxides the oxidation of bismuth sulfide proceeds slowly ($W_{O_2} < 0.2 \times 10^{-5} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$) owing to the exclusion till a back at interaction by lowest free molecular sulfides orbital. In the presence of NO_x the rate of oxygen absorption by Bi_2S_3 - HNO_2 - MCl_2 - KI - H_2O system increases in 2-3 orders.

The obtained experimental data are summarized in the Table 1. The typical dependencies of oxygen absorption rate (W_{O_2}) as well as the values of redox potential of the system (φ) on amount of oxygen absorbed (Q_{O_2}) are shown in Fig. 1. The analysis of electrode equilibrium, possible in the investigated system is shown below:



Based on the absence of the second saltus on the experimental potentiometric curves one can conclude that it is one-electron process (4); and its redox potential is determined by the following equation:

$$\varphi = 1.09 + \frac{RT}{F} \ln[\text{NO}_2] \cdot \gamma \frac{[\text{H}^+]}{[\text{HNO}_2]} \quad (5)$$

The form of the critical curves $W_{O_2} = f(Q_{O_2})$ defined by two expressed sites: the first is characterized by rather high values of $W_{O_2} > 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ at the stoichiometric ratio with $C_{\text{NO}_2}/Q_{O_2} \sim 2$ and corresponds

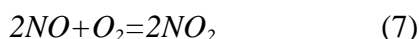
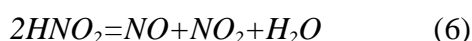
Table 1Bismuth oxidation in $\text{HCl} - \text{MCl}_2 - \text{KI} - \text{NaNO}_2 - \text{H}_2\text{O}$ and $\text{HClO}_4 - \text{MCl}_2 - \text{KI} - \text{NaNO}_2 - \text{H}_2\text{O}$ systems.

Bi ₂ S ₃ weight, g	Complex compound, mol/L					Test time, min	Temperat- ure, K	φ, V	Pressure O ₂ , Pa	Start. W _{O₂} , 10 ⁵ mol/L	Oxidation form of bismuthin in solution, mol/L
	HCl	HClO ₄	MeCl ₂	KI, 10 ³	NaNO ₂ , 10 ²						
1	2	3	4	5	6	7	8	9	10	11	12
0.3	1	-	1.5	1	4.8	5	285	0.994	10×10 ⁴	13.6	2.8
0.3	1	-	1.5	1	4.8	20	285	0.998	10×10 ⁴	13.5	3.24
0.3	1	-	1.5	1	4.8	60	285	0.999	10×10 ⁴	13.5	3.50
0.3	1	-	1.5	1	4.8	90	285	1.002	10×10 ⁴	13.52	3.66
0.3	1	-	1.5	1	4.8	180	285	1.010	10×10 ⁴	14.14	3.88
0.3	1	-	1.5	1	4.8	60	303	1.001	10×10 ⁴	21.6	3.68
0.3	1	-	1.5	1	4.8	90	303	1.015	10×10 ⁴	20.6	4.38
0.3	1	-	1.5	1	4.8	5	303	1.0	10×10 ⁴	21.6	3.08
0.3	1	-	1.5	1	4.8	180	303	1.001	10×10 ⁴	21.6	4.30
0.3	1	-	1.5	1	-	3	285	0.572	10×10 ⁴	0.2	0.04
0.3	1	-	1.5	1	-	60	285	0.551	10×10 ⁴	0.4	0.06
0.3	1	-	1.5	1	9.6	3	285	0.987	10×10 ⁴	28.8	3.4
0.3	1	-	1.5	1	9.6	20	285	0.992	10×10 ⁴	27.0	3.5
0.3	1	-	1.5	1	9.6	60	285	0.991	10×10 ⁴	29	3.7
0.3	1	-	1.5	1	9.6	90	285	1.0	10×10 ⁴	27	3.8
0.3	1	-	1.5	1	14.4	3	285	0.982	10×10 ⁴	52	3.4
0.3	1	-	1.5	1	14.4	20	285	0.981	10×10 ⁴	45	3.6
0.3	1	-	1.5	1	14.4	60	285	0.976	10×10 ⁴	55	3.6
0.3	1	-	1.5	1	14.4	90	285	0.979	10×10 ⁴	64	3.7
0.1	1	-	1.5	1	4.8	3	285	0.792	10×10 ⁴	10.2	1.1
0.1	1	-	1.5	1	4.8	20	285	0.992	10×10 ⁴	22	4.0
0.1	1	-	1.5	1	4.8	60	285	0.987	10×10 ⁴	16	4.6
0.5	1	-	1.5	1	4.8	3	285	0.977	10×10 ⁴	14	2.8
0.5	1	-	1.5	1	4.8	20	285	0.984	10×10 ⁴	13	4.2
0.5	1	-	1.5	1	4.8	60	285	0.987	10×10 ⁴	16	4.6
0.3	-	0.5	1.5	1	4.8	3	285	0.966	10×10 ⁴	22	2.1
0.3	-	0.5	1.5	1	4.8	20	285	0.974	10×10 ⁴	19.2	2.4
0.3	-	0.5	1.5	1	4.8	60	285	0.980	10×10 ⁴	10.4	2.5
0.3	-	1	1.5	1	4.8	3	285	0.979	10×10 ⁴	12	2.9
0.3	-	1	1.5	1	4.8	20	285	0.988	10×10 ⁴	9	3.3
0.3	-	1	1.5	1	4.8	60	285	0.986	10×10 ⁴	14	3.8

Table 1
Continued

Bi ₂ S ₃ weight, g	Complex compound, mol/L					Test time, min	Temperat- ure, K	φ, V	Pressure O ₂ , Pa	Start. W _{O₂} , 10 ⁵ mol/L	Oxidation form of bismuthin in solution, mol/L
	HCl	HClO ₄	MeCl ₂	KI, 10 ³	NaNO ₂ , 10 ²						
0.3	-	2	1.5	1	4.8	3	285	0.986	10×10 ⁴	13.2	3.5
0.3	-	2	1.5	1	4.8	20	285	1.001	10×10 ⁴	-	3.8
0.3	-	2	1.5	1	4.8	60	285	1.013	10×10 ⁴	15	4.0
0.3	-	3	1.5	1	4.8	3	285	1.008	10×10 ⁴	14.4	3.5
0.3	-	3	1.5	1	4.8	20	285	1.012	10×10 ⁴	15	3.95
0.3	-	3	1.5	1	4.8	60	285	1.013	10×10 ⁴	15	4.0
0.3	1	-	1.5	-	4.8	3	285	0.978	10×10 ⁴	12	3.1
0.3	1	-	1.5	-	4.8	60	285	0.994	10×10 ⁴	12	4.9
0.3	1	-	1.5	0.6	4.8	3	285	0.982	10×10 ⁴	12.8	2.8
0.3	1	-	1.5	0.6	4.8	20	285	0.988	10×10 ⁴	12	3.6
0.3	1	-	1.5	0.6	4.8	60	285	0.986	10×10 ⁴	13	4.3
0.3	1	-	1.5	0.6	4.8	90	285	0.991	10×10 ⁴	12	4.4
0.3	1	-	1.5	2.0	4.8	3	285	0.987	10×10 ⁴	14	2.1
0.3	1	-	1.5	2.0	4.8	20	285	0.984	10×10 ⁴	13.2	2.9
0.3	1	-	1.5	2.0	4.8	60	285	0.991	10×10 ⁴	14.6	3.6
0.3	1	-	1.5	2.0	4.8	90	285	0.990	10×10 ⁴	15.2	3.6
0.3	1	-	1.5	1.0	4.8	60	285	1.043	3.3×10 ⁴	8	0.63
0.3	1	-	1.5	1.0	4.8	60	285	1.042	5.3×10 ⁴	12	0.94
0.3	1	-	1.5	1.0	4.8	60	285	1.043	8.0×10 ⁴	14	1.35
0.3	1	-	1.5	1.0	4.8	60	285	0.893	10×10 ⁴	12.2	1.23

to the following reactions (6) and (7):



The second site, which affects the catalytic processes, is connected with the dissolution of bismuth. The kinetics of HNO₂ disproportion is investigated. The rate of direct reaction is defined by the following expression:

$$W_I = k_3[\text{HNO}_2]^2, \text{ at } 25^\circ\text{C}, k_3 = 5.8 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$$

For reverse reaction the kinetic equation is the following:

$$W_I = k_4[\text{NO}][\text{NO}_2], \text{ at } 25^\circ\text{C}, k_4 = 2.1 \times 10^7 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$$

In the presence of oxygen the disproportion of HNO₂ is shifted to the right with formation of NO₂. The comparison of redox potentials for HNO₂ (HNO₂ + e⁻ + H⁺ > NO + H₂O φ=0.9 V) and for NO₂ (NO₂ + H + e⁻ > HNO₂ φ=1.09 V), and also the kinetic results of the Table 2, specify the fact, that as a result of reactions (6) and (7) in the solution stronger is formed as contrasted to HNO₂ an oxidizer - NO₂.

Separately we investigated the kinetics of HNO₂ oxidation by oxygen in HCl - MCl₂ - KI - H₂O solution in conditions identical to oxidizing dissolution of bismuth. The kinetic results are presented in the coordinates W_{O₂} - Q_{O₂} in Fig. 1b. The dependence of absorption rate of oxygen in the solution HNO₂ - MCl₂ - KI - H₂O (W_{O₂} at τ > 0) on starting concentration of

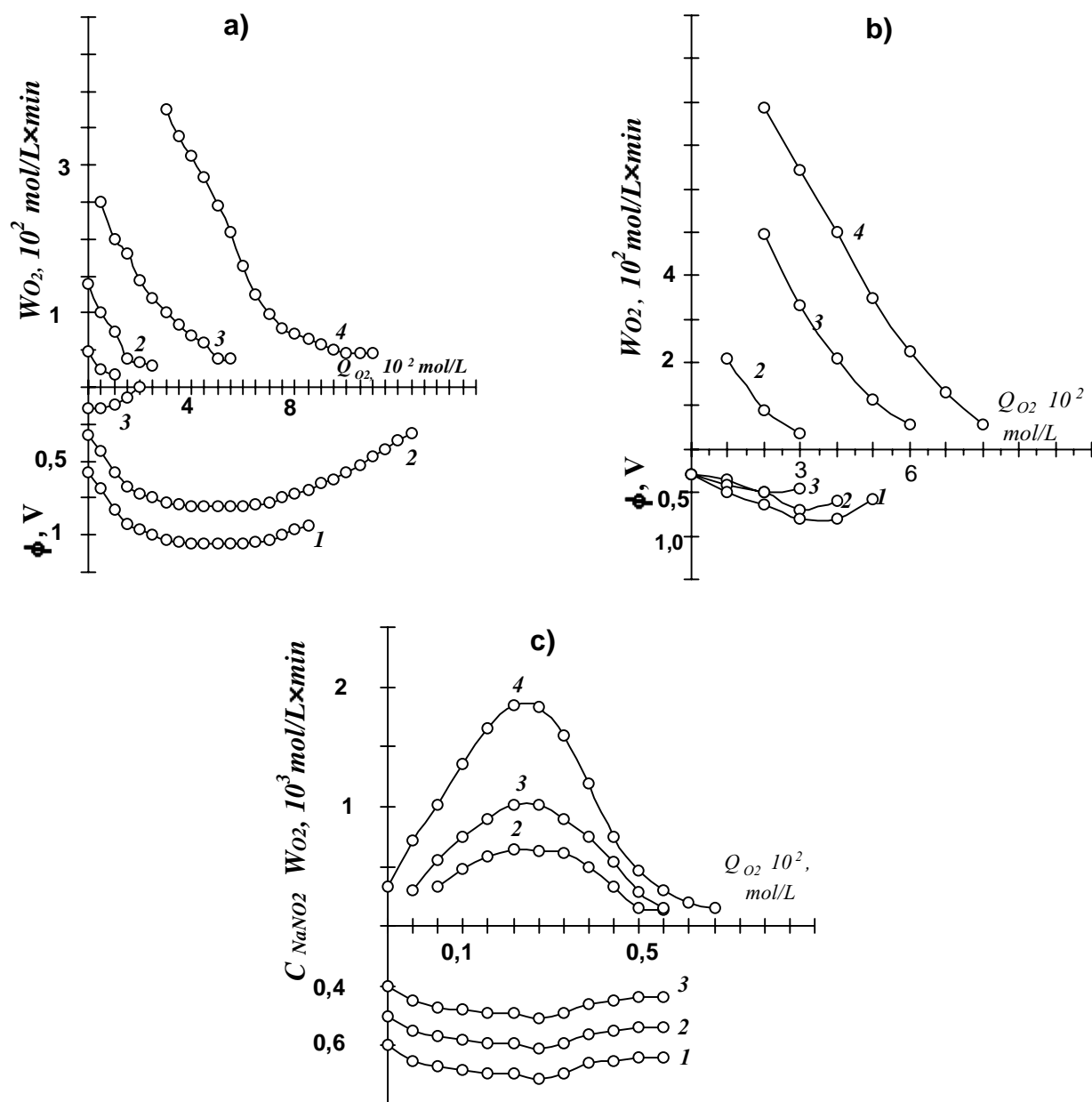


Fig. 1. Oxidation of bismuth sulfide by oxygen in the presence of nitrogen oxides.

a, b, c $C_{\text{MCl}_2}=1.5$, $C_{\text{HCl}}=1.0 \text{ mol}\times\text{L}^{-1}$ C_{NaNO_2} : 1- 0.46, 2-0.92, 3-1 $\text{mol}\times\text{L}^{-1}$ a, c) $\text{Bi}_2\text{S}_3=0.3 \text{ g}$, b) $\text{Bi}_2\text{S}_3=0 \text{ g}$

Table 2

Probable kinetic equation in HNO_2 - KI - H_2O - MCl_2 - H_2O - Bi_2S_3 system.

Reaction	Kinetic equation
$4\text{HNO}_2 + \text{HI} > \text{I} + \text{NO} + \text{H}_2\text{O}$	$k_5 = 3 \times 10^4 \text{ M}^{-2}, \text{ s}^{-1}$ $[\text{HNO}_2][\text{HI}][\text{H}^+]$
$\text{NO}_2 + \text{HI} > \text{I} + \text{HNO}_2$	$k_6 = 3 \times 10^6 \text{ M}^{-2}, \text{ s}^{-1}$ $[\text{HI}][\text{NO}_2]$
$\text{NO}_2 + \text{H}_2\text{S} > \text{HNO}_2 + \text{HS}$	$k_7 = 7.24 \times 10^6 \text{ M}^{-2}, \text{ s}^{-1}$ $[\text{H}_2\text{S}][\text{NO}_2]$

nitrite is described by the equation:

$$W_{O_2} = k_8 [\text{NaNO}_2]^2, \text{ at } 22^\circ\text{C}, k_8 = 9.13 \times 10^{-2} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$$

These results were used for determination of oxidizing dissolution rate of bismuth by a subtraction from common absorption rate of oxygen in Bi_2S_3 - MCl_2 - KI - HCl - H_2O system W_{O_2} , concerning with the oxidation of nitrite to NO_2 only. The obtained, thus, kinetic regularities are summarized in Fig. 1.

The curves had an extreme nature (Fig. 1c) in coordinates $W_{O_2} = F(\alpha)$. In the beginning of the reaction the rate is small, then it increases, passes through a maximum and decreases practically to a zero, or to the values, which are distinct from zero, feebly time-

dependent. Such character of the curves frequently meets the kinetics of topochemical behavior reaction in the systems, which are powering up even one solid reagent and a solid product of the reaction. So, the solid products can be and on its basis polysulfides. The inclination of sulfur atoms to formation of polysulfides phases, is probably conditioned by aspiration of sulfur atoms to acquisition of energetically steady electronic configurations, that is possible as a result of acquisition by one atom of sulfur s^2p^6 , and another sp^3 ($s^2p^4 + s^2p^4 > s^2p^6 + sp^3$) with continuous interchanging by configurations between these atoms and realization of bond between them by pair of electrons crossing from atom to atom. The presence of elementary sulfur and of polysulfides phases formed during disincalining on a surface of bismuth, is tested by IR - spectra of benzene extracts from the cover of disincalining samples (Fig. 2).

The absorption band in the field of 470 cm^{-1} belongs to the valence vibrations of S-S group. Upon contact of gas with starting solid (Bi_2S_3) the reaction rate is small. As the nucleuses (kernel), and phase of solid product of the reaction are formed, there is an interface of solid phases. The value of this interface increases in the process of sulfides oxidation and the reaction rate increases.

The further increasing of nucleuses of the phase of solid product begin to merge. The formation of new nucleuses practically does not occurred because the absence of a free surface and the reaction rate is decreased. The kinetic curves of topochemical reactions contain a special point, the maximum of reaction rate. According to the independent growth of nucleuses of the phase of the solid product the maximal rate should be observed at the moment of a contingency of growing nucleuses. So, the value of specific rate can be defined from the following equation:

$$W_{yg} = \frac{2W \max}{\pi \cdot g \cdot S_g}$$

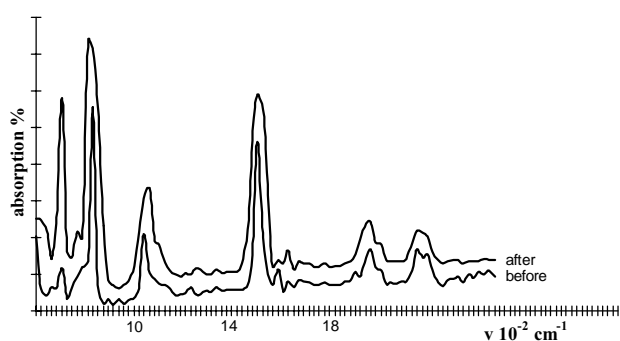


Fig. 2. IR- spectra of benzene extract.

g- weight, S_g - specific cover of the sample.

The useful information is presented by IR - spectra of the gas phase (Fig. 3).

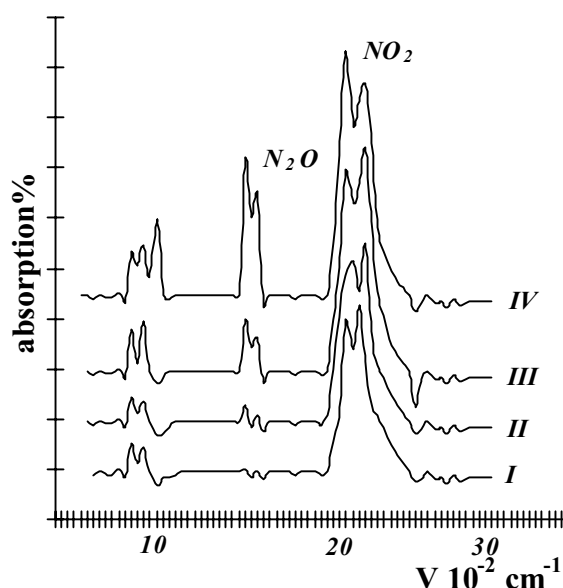
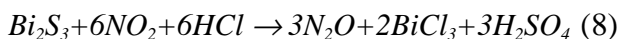
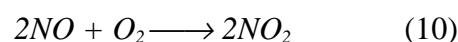
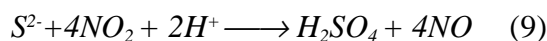


Fig. 3. IR- spectra of the gas phase. $C_{\text{HCl}}=1.0$, $C_{\text{MCl}_2}=1.5$, $C_{\text{NaNO}_2}=0.456\text{ mol}\cdot\text{L}^{-1}$, $\text{Bi}_2\text{S}_3=0.3\text{ g}$, τ : I- 3 min; II- 20 min; III- 60 min, IV- 90 min.

In the spectra of the sample selected from the reactor, containing aqueous solution $\text{HCl} - \text{MCl}_2 - \text{NaNO}_2 - \text{KI} - \text{H}_2\text{O}$ through 3, 20, 60, 90 minutes after experiment was started there are bands with frequencies of vibrations of nitrogen dioxide (1318 cm^{-1}), (749 cm^{-1}) and (1617 cm^{-1}) and N_2O ($1200\text{--}1300\text{ cm}^{-1}$) with maximum at 1250 and 1270 cm^{-1} , NO ($500\text{--}600\text{ cm}^{-1}$) with peak 588 cm^{-1} and NO ($2150\text{--}2240\text{ cm}^{-1}$) with peaks 2190 and 2220 cm^{-1} . The absence of absorption bands, characteristic for N_2O without of bismuth sulfides gives foundation to believe, that N_2O is the product of more deep reduction of NO_2 by bismuth by the reaction:



And the amount of N_2O as increased as higher the weight of Bi_2S_3 and higher the acidity of the solution. The redox potential for N_2O ($\text{N}_2\text{O} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{N}_2$) is 1.59 V and the nitrous oxide does not oxidate by oxygen. According to it, the part of nitrogen oxides irrevocably disappears from a catalytic cycle, which includes the following reaction:



Using the IR-spectra of N₂O (vol.%) and IR-spectra of samples selected during experiment (Fig. 2) it was possible to calculate the amount of N₂O formed and accordingly amount of sodium nitrite leaving from a catalytic cycle in each case. For further accounting of the rate constants value of maximal rate on the curve $W_{O_2}=f(Q_{O_2})$ and value, accordingly to NaNO₂ concentration were used.

The dependence of the process rate on the sodium nitrite concentration is described by the equation of the first order:

$$W_{max} = k_1 \times C_{NaNO_2}, \text{ at } 22^\circ C, k_1'' = 2.5 \times 10^4 \text{ s}^{-1}$$

The increase of the weight of bismuth is a result of increase in the process rate.

The dependence of k_1'' on the amount (g) of Bi₂S₃ is described by the expression:

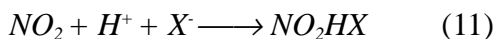
$$k_1 = k_2 \times g^{2/3}, k_2'' = 3.2 \times 10^4 \text{ g}^{-1} \cdot \text{s}^{-1}$$

At $P_{O_2} > 0.6 \times 10^5$ Pa practically there is no influence of a partial pressure of the oxygen in the mixture on the rate of O₂ absorption in the system. In gases enriched by oxygen the formal regularities are observed, and on the contrary, at $P_{O_2} < 0.5 \times 10^5$ Pa, the following equation is realized:

$$W_{O_2} = k' \times P_{O_2}$$

The order of reaction on bismuth is lowered and the order of reaction on concentration of sodium nitrite is increased, *i.e.* the conditions are created, when the stage with oxygen participation is limiting.

At $P_{O_2} = 1.01 \times 10^5$ Pa the influence of solution acidity on oxidation rate of bismuth in HCl - MgCl₂ - KI - NaNO₂ - H₂O solution is investigated. The increasing of acidity in the interval of C_{HClO_4} from 0 up to 1 mol/L positively has the effect on the reaction kinetics (3). The increasing of activity of the solution in this interval C_{HClO_4} is a result of the accumulation of NO₂HCl and NO₂HI particles in solution by the following equilibrium (8):



As a result of the oxidation the salts of sulfuric acid are formed. It is the important moment, because it determines the opportunity for extraction of heavy metals as soluble forms in the liquid phase from petroleum composition, and, generating, the acid accelerates process and extraction of a vanadium and nickel from the oil of Tengiz oil field becomes possible.

The quantum characteristics for NO₂, NO₂HCl, NO₂HI were calculated, and are presented in the following table:

	Atom's charge		Structure of LVMO	E _{LVMO} , ε V
	N	X		
NO ₂	0.289	-0.198	-0.83P _y (NO)-0.39P _y (O)	-3027
NO ₂ HCl	0.236	-0.029	-0.78 P _z (Cl)	-7061
NO ₂ HI	0.205	0.039	-0.86 P _z (I)	-7.0

For NO₂ the lowest vacant molecular orbital (LVMO) is basically presented by P_y-orbital of nitrogen, also there is a composition P_z-orbital of halogen, and at transferring from NO₂HCl to NO₂HI in it's the contribution of this orbital increases. The values of E_{LVMO} show that the acceptor properties of NO₂HX are higher, than that of NO₂.

Upon the increase of $C_{HClO_4} > 1$ mol/L the character of the kinetic curves varies, the maxima decreases, the sharp decrease of the rate is observed during the oxidation of bismuth. In IR - spectra of the gas phase in these solutions there are some absorption bands in the field of 500-600 cm⁻¹, 1500-1650 cm⁻¹, 1700-1820 cm⁻¹ with maximum at 595-1580 cm⁻¹, 1798 and 1802 cm⁻¹, concerning with the NO in NOX (X-Cl, I), that specifies the realization in data states of equilibrium (12), (13):



The particles of NOX are reduced by bismuth sulfide to the N₂O and so the concentration of sodium nitrite from 4.56×10^{-1} mol/L (C_{NaNO_2}) to 0.16 mol/L is originated.

The increase of temperature in the interval from 22 to 40°C results in the fact that the maximum on the curve becomes brightly expressed and it is displaced to the side of smaller time.

The values of maximal rate calculated on the foundation, that the value of activation energy of the bismuth sulfide oxidation by oxygen in the presence of NO_x equal to 10.205 kcal/mole and is decreased up to 7 kcal/mole at $Q_{O_2} = 2.5 \times 10^{-2}$ mol/L (after a maximum).

The above mentioned fact indicates the diffusive stopping of the reaction after reaching maximal rate, that results in the sample covering by the polysulfide coating.

In order to remove the sulfides coating, the generating during oxidizing dissolution a sample was washed by benzene, then again reverted to the reaction

mixture. The increase of oxidation rate of bismuth sulfide testifies the dissolution of a sulfur coating. This fact is confirmed by the IR-spectrum of a benzene extract from washed bismuth surfaces. The absorption band at 470 cm^{-1} corresponds to the frequency vibrations of the S-S band (Fig. 4).

This experiment has a practical importance for originating of bismuth oxidizing dissolution in mixed solvent.

The obtained results have allowed offering the following mechanism of the oxidation of bismuth sulfide by oxygen in the presence of nitrogen oxides:

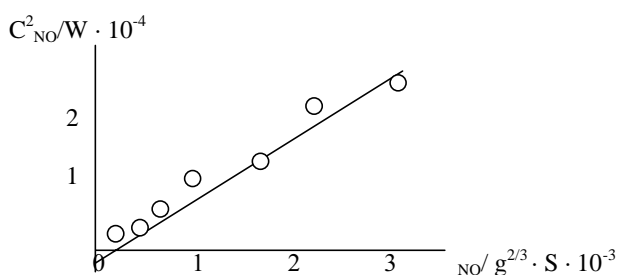
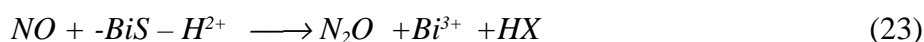
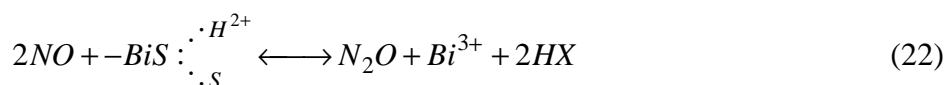
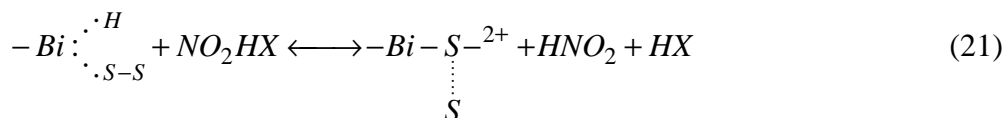
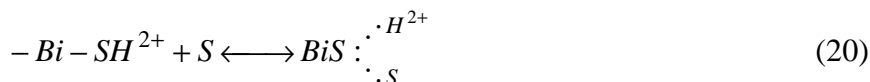
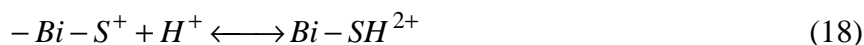
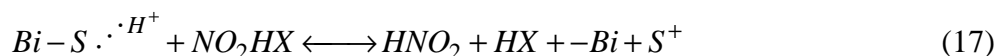


Fig. 4. Oxidation of bismuth sulfides by oxygen in a solution Bi_2S_3 - HCl - MCl_2 - NaNO_2 - H_2O .

According to the reactions (14,15) the NO_2 and more reactive forms of NO_2HX are formed. In limiting stages (17) and (21) the NO_2HX attacks coordinated sulfide or polysulfide with transferring of one electron and formation of HNO_2 . As a result of the reaction (22) the concentration of the catalyst NO_x is decreased. According to the offered scheme and the theory of topochemical reactions as well as the method of sta-

tionary concentrations the obtained rate law describing the experimental results in kinetic conditions are described by the equation (24).

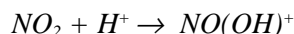
$$W_{\text{O}_2} = \frac{k' \cdot C_{\text{NO}_x} \cdot C_{\text{O}_2} \cdot k'' \cdot g^{2/3} \cdot C_{\text{NO}_x}}{k' \cdot C_{\text{NO}} \cdot C_{\text{O}_2} + k'' \cdot g^{2/3}} \quad (24)$$

The equation (24) describes satisfactorily the obtained experimental results. The experimental points are stacked on straight lines in coordinates $[\text{NO}]^2/W \times 10^4 = [\text{NO}]/g^{2/3} \times S \times 10^{-3}$ (Fig. 4).

In investigated interval of C_{HClO_4} the value of k' practically does not depend on the acidity of the solution. The influence of C_{HClO_4} on k'' is described by the equation:

$$k_1'' = \frac{k_2'' \cdot \gamma \cdot a_{\text{H}_3\text{O}^+}}{1 + \gamma \cdot a_{\text{H}_3\text{O}^+}} \quad (25)$$

where γ - equilibrium constant:



The solution of the equation (25) by the least squares method has allowed defining the parameters of the equation (25), which are the following:

$$k_1'' = 4 \cdot 10^{-1} \text{ g}^{-2/3} \cdot \text{s}^{-1} \quad \text{and} \quad \gamma = 7.8 \times 10^{-2}$$

The segment of the axis ordinate, cutting off by straight line gave us the value of the constant of oxidation rates of the sodium nitrite by oxygen (k') in

the investigated conditions. The tangent of inclination corner allows determining the rate constant of interaction of NO_2 or him of the protons forms with bismuth in (k''). The results presented in the Table 3 testify that the k' and the k'' do not depend on starting nitrite concentration in the system and on the weight of bismuth sulfides. The values of k' are in accordance with the literature data. The obtained data prove the proposed mechanism.

Table 3

Kinetic characteristics of bismuth sulfides oxidation by oxygen in HCl - MCl_2 - KI - NaNO_2 - H_2O system $T=295\text{K}$, $C_{\text{MCl}_2} = 1.5 \text{ mol/L}$.

C_{NaNO_2} , mol/L	Bi_2S_3 , g	CHClO_4 , mol/L	k , $\text{mol}^2 \times \text{L}^2 \times \text{s}^{-1}$	k'' , $\text{g}^{-2/3} \times \text{s}^{-1}$
4.8×10^{-2}	0.3	1.0	2.25	0.93×10^{-1}
3.6×10^{-2}	0.3	1.0	2.20	0.90×10^{-1}
14.4×10^{-2}	0.3	1.0	2.3	0.91×10^{-1}
4.8×10^{-2}	0.1	1.0	1.87	0.7×10^{-1}
4.8×10^{-2}	0.5	1.0	2.1	0.6×10^{-1}
4.8×10^{-2}	0.3	1.5	2.2	1.1×10^{-1}
4.8×10^{-2}	0.3	2.0	2.15	1.47×10^{-1}
4.8×10^{-2}	0.3	3.0	2.18	3.3×10^{-1}

Oxidation of sulfur compounds of oil

The method of homogeneous soft catalytic oxidation was investigated on the sulfur-containing oil fractions. The sample from Karachaganac oil field (№ 126 well) was taken for the study. According to the data obtained in our study the common sulfur is 1.28% by weight. The weight fraction of mercaptanous and hydrosulfurous sulfur compounds is 0.21%.

The experimental data of regular study of the sample of oil and catalizate by the method of homogeneous soft catalytic oxidation is shown in the Tables 4-9 and Figures 5-11.

The potential contents of fractions in starting oil and catalizate were determined by the method of rectifying distillation on the ROD-2.

According to the diagram of samples distillation the initial boiling temperature moving almost to 40°C , the weight fraction of 10-grades of fractions varies. At temperature higher than 150°C , for oil boils away 28.39% of total weight, and for catalizate only 18.22% (Table 4, Figs. 5,6). It is possible to approve, that the

hydrocarbon composition of catalyst significantly "is weighted" as contrasted with starting sample of oil. The pressure of 10-grades of fractions also significantly varies.

The results of chromatographic study are presented in Table 5. These data confirm and supplement the

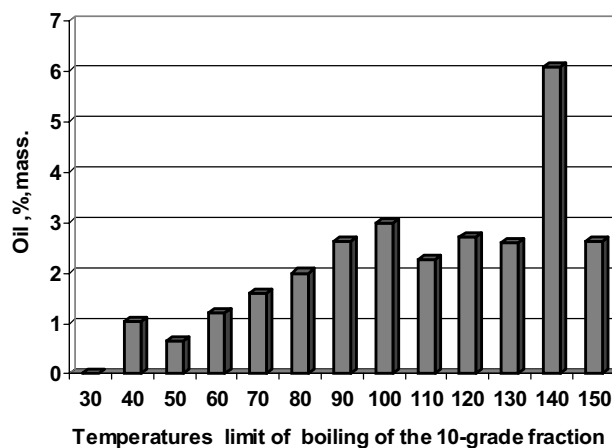


Fig. 5. Diagram of oil distillation of the Karachaganac oil field from № 126 well.

Table 4

Pressure of 10-grades fractions of samples of oil and of catalizate from № 126 well.

Boiling temperature of fractions, °C	Oil		Catalizate	
	% mass.	ρ , kg/m ³	% mass.	ρ , kg/m ³
33.6-40	1.04	638.6	-	-
40-50	0.64	649.2	-	-
50-60	1.22	659.7	-	-
60-70	1.6	671.2	-	-
70-80	2.00	685.4	0.78	721.8
80-90	2.63	709.8	1.39	733.9
90-100	2.99	724.7	2.19	723.1
100-110	2.27	736.6	2.03	735.7
110-120	2.72	742.7	2.57	740.9
120-130	2.60	751.8	3.37	753.3
130-140	6.06	757.4	3.38	764.3
140-150	2.62	765.2	2.51	764.0
fractions total	28.39		18.22	

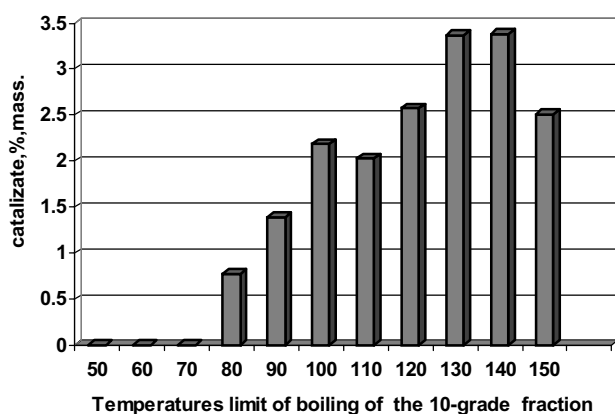


Fig. 6. Diagram of catalizate distillation.

results of distillation.

The most significant result of the study is the fact, that the catalyst does not contain even traces of mercaptanous and hydrosulfurous sulfur after originating the homogeneous catalytic oxidation of raw oil. The sulfur containing organic compounds are absent in all fractions.

The addition of nitrogen oxides to the solution of the acid, or their addition to oxidizer promotes the increase of oxidation rate. The oxides of nitrogen are easily deleted from oil at temperature of the reaction (80-90°C) and are dissolved in sour water solution, in which they are collected as a result of sulfoxides and sulfacides oxidation.

Table 5

Chromatographic analysis (component composition) 10-grades of fractions of oil and catalizate from № 126 well.

Boiling temperature of fractions, °C	Oil	catalizate
	Hydrocarbons, % mass.	Hydrocarbons, % mass.
33.6-40	C ₆ – 12%	–
40-50	C ₆ – 17%	–
50-60	C ₆ – 29.6%	–
60-70	C ₆ – 16.2% C ₇ – 3.0%	–
70-80	C ₆ – 2.4% C ₇ – 3.0%	C ₆ – 18.4% C ₇ – 3.0%
80-90	C ₆ – 5.2% C ₇ – 4.7%	C ₆ – 10.5% C ₇ – 16.6%
90-100	C ₆ – 1.0%	C ₆ – 3.3% C ₇ – 17.3%
100-110	C ₈ – 12.9% C ₉ – 1.3%	C ₆ – 0.94% C ₇ – 8.0% C ₈ – 13.2% C ₉ – 0.47%
110-120	C ₈ – 21% C ₉ – 6.7%	C ₈ – 3.0% C ₉ – 6.0%
120-130	C ₈ – 21% C ₉ – 19.2%	C ₈ – 14% C ₉ – 24%
130-140	C ₈ – 10.3% C ₉ – 23.0%	C ₈ – 3.0% C ₉ – 29.3%
140-150	C ₈ – 7% C ₉ – 12.3% C ₁₀ – 1.9%	C ₈ – 2.4% C ₉ – 8.6% C ₁₀ – 1.2%

The aqueous solution can be utilized multiply up to concentration of sulfacides - 70%. The obtained by abovementioned procedure solution, represents acid contact obtained in the industry at the suffocation of oil. It has surface-active properties and can be utilized as marketable products for preparation of washing-up liquids, flotators, *etc.*

At present time the industry and transport of Republic of Kazakhstan consumptions are increased and great money are required. According to the

tearing up of economic links with the countries of CIS the Kazakhstan oil begin to play an increasing role. Not the last place among them belongs to the oil of Karazhanbas, Tengiz and Karachaganac oil fields.

Based on the consideration of physical-chemical characteristics of the Karazhanbas oil one can say that it contains the large portion of paraffin, resins and asphaltens, and can be processed with high part of light fractions (Table 6).

Table 6
Physical-chemical properties of Karazhanbas oil.

Concentration at 293 K	940 kg/m ³ (State standard 3900-85)
Dynamic viscosity at 293 K	1000 (State standard 33-82)
Dynamic viscosity at 423 K	150 (State standard 33-82)
Weight fraction of water	up to 1% (2477-65)
Concentration of chloride salts	30-300 mg/dm ³
Weight fraction of mechanical impurities	0.01-0.03%
Weight fraction of sulfur	up to 1.8% (State standard 1437-7)
Weight fraction of paraffin	1.4-17% (State standard 11851-85)
Weight fraction of resins	14-17% (State standard 1185 -86)
Weight fraction of asphaltens and porphyrins	6-14% (State standard 11011 -85)

The results of distillation under vacuum (266.6 Pa and 1066 Pa) (Table 7) show, that the percentage of light fractions is more than 30%. The total percentage of oil boiling up to 673 K is 30.61%.

As a result of distillation at atmospheric pressure (Tables 8,9) in the temperature interval from 273 K up to 593 K it is possible to obtain the light fractions up to 87%. Probably, such variance of distillation under vacuum and at atmospheric pressure is due to the fact that the Karazhanbas oil contains big amounts of asphaltenes and porphyrins contains, which are internal catalysts of cracking of oil.

All this information testifies that the Karazhanbas oil is a favorable source for the process. However, the presence of big amount of sulphurous compounds in the oil makes difficulties in its processing, because it promotes fast corrosion of pipelines, and next use of its fraction at chemical processing or as fuel results in destruction of reactors. Besides it leads to the poisoning of catalysts and negative ecological influence

on the environment.

So, the problem of highsulphurous oils refining is very actual.

Table 7
Physical-chemical properties of Tengiz oil.

Concentration at 293 K	To 800.6 kg/m ³
Viscosity at 293 K	To 2.51
Weight fraction of water	1.4%
Concentration of chloride salts	26%
Weight fraction of mechanical impurities	0.002%
Weight fraction of sulfur	2%
Weight fraction of paraffin	9.8%
Weight fraction of resins	2.3%
Weight fraction of asphaltens and porphyrins	0.36%

Table 8

Data of distillation of hallmark of Karazhanbas oil.

T, to vacuum	T, at normal conditions	m, g	of %, weight	D, kg/m ³
1066 Pa				
313-347	432-472	1.30	0.21	-
347-377	472-512	15.99	2.60	828.1
377-409	512-552	36.40	5.92	836.1
266.6 Pa				
384-415	552-592	26.42	4.30	861.2
415-448	592-632	50.30	8.18	875.3
448-485	632-673	57.82	9.40	896.2

Table 9

The data of distillation of hallmark of Karazhanbas oil at atmospheric pressure.

T, To	Contents of fractions, %	Contents of S in a fraction, %
273-443	53.9	0.34
443-593	32.93	1.065
> 593	13.7	2.54

In order to determine the optimal composition of the catalyst and optimal state of a catalytic oxidation of the sulfurous sulfur, the mechanism of reaction as well as the kinetics of soft catalytic oxidation processes of sulphurous compounds from fractions of Karazhanbas oil was investigated in details. The characteristic spectra of the oils are presented in Figs. 7,8,9. The absorption bands corresponding to sulphurous compounds have the maxima in the area 460, 580, 620, 680, 700, 1070, 1330, 1450 cm⁻¹, which are characteristic for sulfidous and mercaptanous sulfur.

The data of IR - spectra have shown predominance of absorbed structures as CH, CH₂ and CH₃ (absorption bands in the field of 3000-2800, 1470, 1380 cm⁻¹) and group CH₂ of long paraffin links, included in the composition (absorption band 730 cm⁻¹), weakly expressed [1,8-10]. For all samples the presence of aromatic structures of different types of substitution (900-750 cm⁻¹) (one -, di -, three-substituted derivatives of benzene is typical). The absorption band at 815 cm⁻¹ together with absorption band at 1610 cm⁻¹ can be attributed to the presence of para-substituted benzene ring [1,8-10]

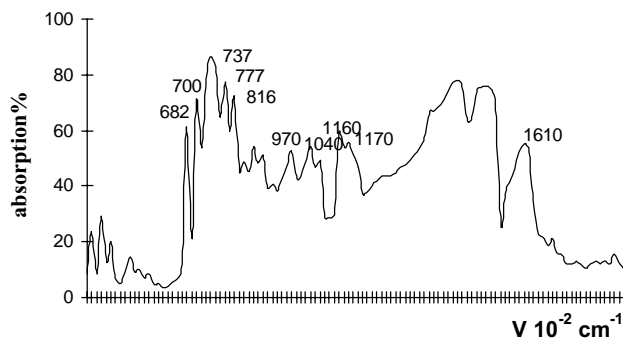


Fig. 7. IR-spectra of the petrol fraction.

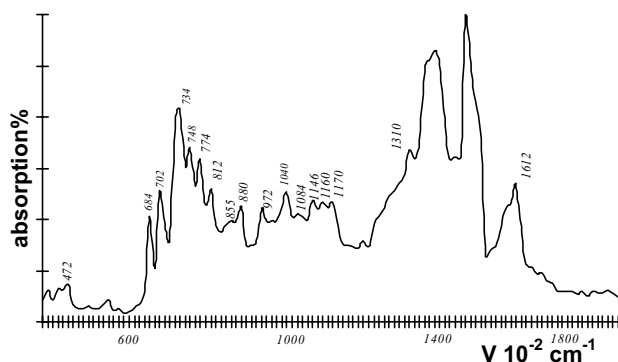


Fig. 8. IR-spectra of diesel fraction.

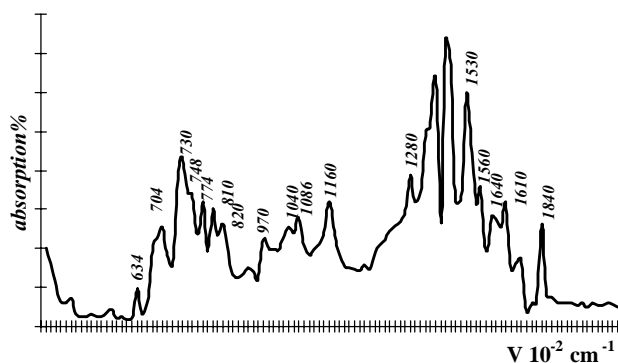


Fig. 9. IR-spectra of cleaned petrol.

The kinetic regularities of the catalytic oxidation in the temperature interval 293-323 K were investigated depending on the concentration of all reagents making up the catalytic system, partial pressure of oxygen and temperature of experiment.

The typical conversion curves of the catalytic oxidation of oil sulfides by oxygen in system FeSO₄ × 7H₂O - Kt - H₂SO₄ - oil fraction - H₂O, where Kt-water soluble P-oxide being the with - catalyst of the given process of activation of oxygen are presented in Figs. 10,11.

In the absence of Kt and compounds of iron the rate of oxygen absorption, as for petrol, and for diesel fractions is small and also does not exceed the

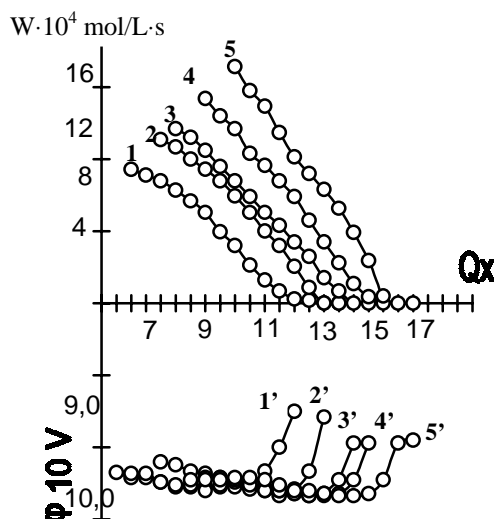


Fig. 10. Oxidation of oil sulfides of petrol fraction.

$T=303\text{ K}$, $P_{O_2}=1.05 \cdot 10^5\text{ Pa}$, $C_{Kt}=2 \cdot 10^{-1}\text{ mol/L}$, $CH_2SO_4=1.75\text{ mol/L}$,

C_{Fe} : 1 – $5.0 \cdot 10^{-2}\text{ mol/L}$; 2 – $1.0 \cdot 10^{-1}\text{ mol/L}$, 3 – $1.5 \cdot 10^{-1}\text{ mol/L}$, 4 – $2.0 \cdot 10^{-1}\text{ mol/L}$, 5 – $2.5 \cdot 10^{-1}\text{ mol/L}$.

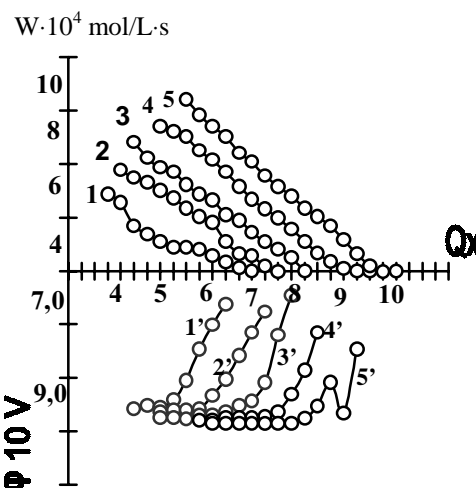


Fig. 11. Oxidation of oil sulfides of diesel fraction.

error of experiment. As for petrol, and for diesel fractions the dependence of initial velocity of process (W_{O_2} at $\tau > 0$) on starting concentration of compounds of iron in the system is described by the equation of the first order:

$$W = k \times C_{FeSO_4} \quad (26)$$

At $T=303\text{ K}$ the rate constant for petrol and diesel fractions is equal to 1.32 s^{-1} and $8.7 \times 10^{-1}\text{ s}^{-1}$ accordingly.

It is necessary to note, that the activity of sulfides of the petrol fraction is higher, than the activity of sulfides of the diesel fraction.

As a result of catalytic process the data of IR-spectra have shown the absence of absorption bands in the hydrocarbon stratum, characteristic for sulphurous compounds. It is the fact that the complete absence of sulfur in the organic stratum. According to Fig. 9 the absorption band in the area $460, 580, 620, 680, 700\text{ cm}^{-1}$ have vanished. These data are confirmed by the results of elemental analysis.

The potentiometric results and analysis of literature data on catalysis by compounds of iron on oxidation of different substratum by oxygen have shown, that the most limiting stage of the process is connected with regeneration of three-valence iron by oxygen. So, the catalyst (Kt) in the system was selected. The concentration of Kt was changed in the interval: $5 \times 10^{-2} - 2.5 \times 10^{-1}\text{ mol/L}$ the concentration of other components is remained consternated and were: $P_{O_2}=1.05 \times 10^5\text{ Pa}$, $C_{FeSO_4}=1.0 \times 10^{-1}\text{ mol/L}$, $C_{H_2SO_4}=1.75\text{ mol/L}$.

The rectilinear dependence of initial rate of the oxidation on starting concentration of the catalyst (Kt) in the system, as for petrol, and for diesel fraction is observed:

$$W = k_1 \times C_{Kt} \quad (27)$$

At 303 K the value k_1 for petrol and diesel fractions is equal accordingly: $9.0 \times 10^{-1}\text{ s}^{-1}$; $4.6 \times 10^{-1}\text{ s}^{-1}$.

The comparison of k_1 values for petrol and diesel fractions specifies the large activity of sulfides of petrol fraction to the oxidation as contrasted to diesel.

The sulfuric acid was selected as the proton-donating agent, which concentration in the system was varied from $1.75-7.0\text{ mol/L}$, at constant concentrations of the other components of the system, which were: $C_{Fe}=1.0 \times 10^{-1}\text{ mol/L}$, $C_{Kt}=2.0 \times 10^{-1}\text{ mol/L}$, $P_{O_2}=1.05 \times 10^5\text{ Pa}$.

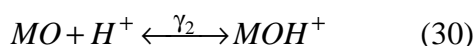
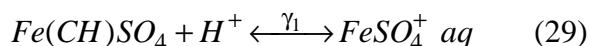
When the concentration of the acid in the investigated interval was increased the character of the conversion curves was not varied. The starting potential according to the increase of concentration of the acid is increased on $0.1-0.15\text{ V}$. When the acid concentration is increased, the character of movement of potential varies at the end of the reaction up to the concentration of the acid equal to 3.5 mol/L (at the end of experiment). All this specifies the influence of acidity of environment on the oxidizing ability of the system, activation rate of oxygen in a sluggish stage.

The dependence of initial rate of oxygen absorption, as for petrol, and for a diesel fraction from concentration of the acid is described by the follow-

ing equation:

$$W = \frac{k_1 \cdot \gamma_1 \cdot a_{H_3O^+} + k_2 \cdot \gamma_1 \cdot \gamma_2 \cdot a_{H_3O^+}^2}{1 + \gamma_1 \cdot a_{H_3O^+} + \gamma_1 \cdot \gamma_2 \cdot a_{H_3O^+}} \quad (28)$$

where 1 and 2 constants following protolitic equilibriums (29), (30):



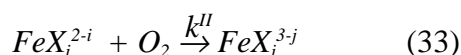
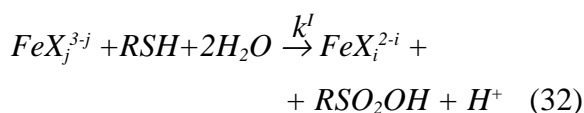
The solution of the equation (28) by the least squares method has allowed defining the partial rate constants k_1 and k_2 and value of the equilibrium constant

The absence of sulfur as the product of the reaction, and the quality detection of sulfoacides in water solution after reaction, allow to assume, that the oxidation of sulfides of petrol and diesel fractions origins up to water-soluble sulfoacides in the studied conditions.

The completely exceeded kinetic results are described by the equation (31):

$$W_{O_2} = \frac{k^I \cdot C_{Fe} \cdot C_k \cdot k^{II} \cdot C_{O_2}}{k^I \cdot C_{Fe} \cdot k^{II} \cdot C_K \cdot C_{O_2}} \quad (31)$$

The indicated mechanism of the oxidation of oil sulfides in our conditions includes two slow stages (32), (33):



Selection of the equipment now is made, the designer account of installation is picked up by productivity 20 t/day of raw oil and tested apparatus ensuring intensive of mass transfer a gas - fluid during oxidizing desulfurization of oils.

The review of the literature of last years has shown, that the apparatus which is carrying out gas liquid agitating in a turbulent state is the most suitable for this purpose. The most widespread device of a rotational type is the scrubber of Venture, which main body of it for purposes of lowering harmful hydraulic losses is executed as the pipe of Venturi having smooth lowering on the input of gas (conphuzor) and smooth expansion on its exit (diffuser). There is the great of constructions of scrubbers of Venture dis-

tinguished by a way the intake of the trickle fluid, section and length of a neck, by arrangement etc. It is usual intake of the fluid is carried out immediately in the neck at right angle to a stream of gases, and precipitation of drops in the device of the centrifugal operation. The fluid (in this case catalyst) is brought to confessor on some distance from the neck with the help of nozzles allowing to inspect the sputtering. As the liquid trap after the pipe is established the straight-flow a cyclone. The mathematical accounts of pipe of Venture made on the basis of filtration model.

Conclusion

At the condition of development of oil industry in our republic expedient and necessary the introduction of non-waste technologies is made. The soft catalytic desulfuration of oil allows to solve not only the task of improvement of state of environment of region arranging of the plant, but also will open new ways of deriving of quality fuel, and defined after sulfurtreatment of oil and the gas, probably, will let off for the prices appropriate to high-quality fuel raw material in the world market. The degree of desulfuration of the given technology is great enough (92%), and it allows to recommend it to introduction on TCO oil company.

References

1. G.R. Bolshakov, Sulfuroorganic compounds of oil. Science, 1986, p. 248
2. E.N. Karaulova, L.R. Barikina, G.D. Galpern Etc. -In: 14 scientific. Ses. On chemistry both technique of organic compounds of sulfur and sulphurous oils: Articles. Riga: Zinatne, 1976, p. 70
3. R.D. Obolencev, U. E. Nicitin. - In: chemistry of sulfurorganic compounds contained in oils and petroleum., M.: High School., 1968, p.163-170
4. R.D.Obolencev, N.K. Phaizulina, V.G. Buharov. In "The Chemistry of sulfur- and nitrogenorganic of compounds contained in oil and petroleum". Ufa: BF SA USSR, 1960, v. 3, pp. 67-73
5. N.K. Lyapina, V.S. Shmatov, M.A. Parvernov, L.I. Zinchenko, Individual composition of mercaptans and disulfides of Zhanazhol oil a deposit, Journal "Oilchemistry", 1989, №2, p.128
6. D.A. Vyahireva, L.E. Reshetnikova, G.Y. Malkova, etc., In "Chemistry of sulfur-containing compounds contained in oils and petroleum",

- Moscow, High School, 1972, pp. 376-379
7. Sulphurous compounds of Tengiz oil. – J.-Oil and gas, №2, 1999, A., pp. 65-78
 8. E.M. Davidova, U.M. Shecochihina, A.B. Mashkina, Kinetics and catalysis, 1970, v.20, pp. 978-983
 9. K.R. Shayahmetova. Oxidation of sulfur dioxide by oxygen and oxides of nitrogen in the presence of ferric complexes. – A.: Abstract dissertation, 1993, p.32
 10. E.A.Glebovskaya. Application infra-red of oil geochemistry. - L. Nedra., 1971, p.140
 11. Cacanisi To. Infra-red spectra and structure of organic compounds. - M.: Mir, 1965, p. 216

Received 8 May 2001.