DOI: 10.25140/2411-5363-2024-2(36)-215-226
UDC 621.314.212.001:621.315.615.2.004

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CONTROL OF DISSOLVED GAS CONTENT IN FRESH AND OXIDISED TURBINE OILS

The article is a publication of scientific and methodical character. Gas chromatography methods were used to determine the content of dissolved diagnostic gases in mineral turbine oil «Agrinol Tp-46» and in synthetic fire-resistant turbine oils «Fyrquel®L», «Reolube®OMTI», «Reolube®46 RS». The following were studied: the solubility of these gases in mineral oil «Agrinol Tp-46» and in synthetic oil «Reolube®46 RS»; dependence of solubility values for diagnostic gas H_2S on temperature in the system «mineral turbine oil – dissolved gas H_2S»; distribution coefficients of dissolved gases in turbine oils in systems «turbine oil – dissolved gas – gaseous extractant»; dissolved gas content in «Reolube®46 RS» synthetic turbine oils by application method. This will make it possible to determine the content of dissolved gases in wet turbine oils for diagnostics of oil-filled equipment.

Keywords: *gas chromatography; diagnostics; nuclear power; partition coefficient; gas solubility.*
Fig.: 1. Table: 6. References: 21.

Urgency of the research. In thermal mechanical equipment of nuclear power plants (NPPs), turbine oils (TO) are used in the following systems: lubrication and adjustment of steam turbines; lubrication and sealing of generator shafts; lubrication the main circulation pumps and water cooling system pumps; lubrication of condensate electric pumps, pumps for pumping technical water of responsible and non-responsible consumers; lubrication and adjustment of turbine feed pump units and separator pumps [1; 2]. Currently, the thermal mechanical equipment of Ukrainian NPPs uses mineral turbine oils (MTO) of the brands «Tp-22», «Tp-22s», «Tp-22b», «Agrinol Tp-22», «Agrinol Tp-22s», «Agrinol Tp-30», «Agrinol Tp-46», «Azmol Tp-22s» and synthetic fire-resistant turbine oils (SFRTO) of the «Fyrquel®L», «Reolube®OMTI», «Reolube®46 RS» brands [3]. Often, turbine oils contain dissolved water (homogeneous system) and undissolved water as an emulsion (heterogeneous system) [4]. All this requires continuous improvement of diagnostic methods of oil-filled NPP equipment based on the results of monitoring the content of diagnostic components in them, for example, dissolved gases CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2 [5; 6], including in heterogeneous systems of the «oil turbine – dissolved gas – emulsion water» type.

Target setting. Quite often, internal defects in oil-filled thermal-mechanical equipment of nuclear power plants, which contain mineral and/or synthetic fire-resistant turbine oils, arise due to the action of electric, thermal and acoustic fields, as well as the presence of moisture in these turbine oils. At the same time, the development of these defects is influenced by the quality indicators of lubricating turbine oils, including such an indicator as the content of dissolved emulsion form of water in these turbine oils [7]. Currently, the method of diagnosing oil-filled thermal-mechanical equipment based on the results of determining the content of diagnostic dissolved gases in turbine oils during their operation in such equipment is widely used. Reliability of the results of determining the dissolved gases content by gas chromatography methods can be achieved by correctly choosing the range of water concentrations in these turbine oils under study, in which there is no significant influence of water content on the results of gas chromatographic measurements.

Actual scientific researches and issues analysis. In work [8] there is a list of oil-filled electrotechnical equipment, the technical condition of which can be determined by the results of the analysis of insulating oils using gas chromatography methods from this equipment. It is shown that the control of the equipment, which is not included in the above list, can be carried out based on the results of the analysis by gas chromatography methods of insulating oils by the decision of the technical management of the enterprise to obtain additional results of the technical condition of the equipment.

The rate of entry of external contaminants into energy oils, such as wear products of mating friction pairs, atmospheric dust, etc., in the case of a stable operating mode, for example, a turbine unit, and unchangeable external conditions, is considered constant and independent of the operation of the oil system [7; 9]. Degradation of lubricating oil, especially with a high content of emulsion water, often occurs with the release of gases. The presence of these gases, their concentrations and the rate of their increase can be used to diagnose the technical condition of rubbing surfaces, for example, in bearings [10].

In work [5], using the gas chromatography method, monitoring modes of the physicochemical and thermophysical properties of mineral turbine oil «Tp-30» of the circulating reverse water supply system of evaporative cooling towers of the Rivne NPP were investigated in the process of identifying the causes of bearing failure in an electric pump unit (by detection in this oil dissolved diagnostic gases CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2). The humidity of this turbine oil complies with established standards and does not exceed 0.03% mass [2].

In work [6], the gas chromatography method was used to determine the content of diagnostic dissolved gases CH_4, C_2H_6, C_2H_4, C_2H_2, H_2, CO, CO_2 in samples of operational turbine oil «Tp-22s (grade 1)» from the main oil tank of the circulation supply system of a turbine unit with turbine K-210-130-3 and turbogenerator TGV-200M with hydrogen cooling.

However, the moisture content of turbine oil samples is not indicated. The results obtained make it possible to accumulate statistical data for the development of a diagnostic model for determining the technical condition of a hydrogen-cooled turbogenerator when determining the occurrence of thermal or electrical defects in bearings based on the corresponding diagnostic models used for electrical equipment [8].

The work [11] indicates that the mass fraction of sulfur in fresh mineral turbine olives is: for «Tp-22s (grade 1)» – no more than 0.5% mass; for «Agrinol Tp-30» - no more than 0.8% mass; for «Azmol Tp-22s» – no more than 0.5% mass.

This can be used to identify a thermal defect in oil-filled power equipment in the defect zone at $t = 300$ °C and above, for example, in the contact areas of rubbing surfaces in bearings equipped with a forced circulation system of sulfur-containing mineral turbine oil [5; 14].

At the same time, in [15] it is indicated that the result of determining the H_2S content in liquid media containing water, using the gas chromatography method for gas extraction and using distribution coefficients for H_2S, depends on the pH of liquid media, which in turn affects on the degree of dissociation of H_2S in the proportions of water and on the distribution coefficients for H_2S in equilibrium heterogeneous extraction systems «mineral oil – free water – dissolved dissociated H_2S – gaseous extractant».

In this case, the application of the method of applying H_2S to the analyzed sample of moistened heterogeneous mineral oil can increase the reliability of the results of measuring the content of H_2S in it without using the values of distribution coefficients for H_2S [6].

The work [6] gives the values of the distribution coefficients k_i for dissolved gases in the «Azmol Tp-22s» mineral turbine oil, but the values of the water concentration W in this oil are not indicated.

It is known that for diagnostic gases H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2, O_2, N_2 dissolved in dried electrical insulating mineral oils, a change in temperature in the range of 18–25 °C leads to a change in the distribution coefficients in the «electrical insulating mineral oil – dissolved gas – gaseous extractant» within ± 5% relative [16].

Uninvestigated parts of general matters defining. Despite the presence of a large number of studies of methods for diagnosing electrical and thermal mechanical oil-filled equipment based on the results of analyzing samples of energy oils using gas chromatography methods, the nature of the influence of water content in mineral and synthetic fire-resistant turbine oils on the results of analyzes has not been sufficiently studied.

Thus, in order to diagnose oil-filled equipment of nuclear power plants, there is a need to identify the reliability of the results of studying the content of diagnostic dissolved gases using gas chromatography methods in samples of wet mineral and synthetic fire-resistant turbine oils containing dissolved and emulsified water.

The research objective. The main goal of the article is to ensure the reliability of the results of the study of the content of diagnostic dissolved gases H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2, O_2, N_2 using gas chromatography methods in samples of wet mineral and synthetic flame-resistant turbine oils for further diagnostics of oil-filled NPP equipment.

Research objectives:

1. Improve the mathematical description of the phase equilibrium in the extraction system «wet turbine oil – dissolved gas – gaseous extractant (Ar)».
2. To identify the influence of the concentrations of *i*-dissolved gases in wet turbine oils on the value of distribution coefficients for i-dissolved gases in extraction systems «wet turbine oil – dissolved *i*-th gas – gaseous extractant».
3. Identify the influence of water concentrations in wet turbine oils on the value of distribution coefficients for *i*-dissolved gases in extraction systems «wet turbine oil – dissolved *i*-gas – gaseous extractant».
4. Investigate the solubility of diagnostic gases in dried and wet turbine oils at a temperature of 20 °C.

The statement of basic materials. Tested environments: mixtures of diagnostic components (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2, H_2O, H_2S) in «Agrinol Tp-46» mineral turbine oil; mixtures of the above diagnostic components, except H_2S, in synthetic fire-resistant turbine oils «Fyrquel®L», «Reolube®OMTI», «Reolube®46 RS».

When performing research, the following methods are used: a) determination of the humidity of fresh (non-oxidized) turbine oils [2; 17] (coulometric titration); b) determination of the humidity of oxidized turbine oils [2] (calcium hydride; or thermal distillation with a solvent that does not dissolve water); c) gas chromatography determination of: concentrations of dissolved gases in turbine oils, concentrations of gases in gas mixtures, distribution coefficients for dissolved gases in energy oils in the system «turbine oil – dissolved gas – gaseous extractant» [18; 19]; d) titration – to determine the indicator «acid number (AN)» for turbine oils [2; 11]. Before determining the distribution coefficients k_i for dissolved gases, samples of turbine oils were pre-dried at $t = 20$ °C using KSM silica gel granules to a final moisture content of $W \leq 0.005\%$ mass (measurement of W – according to the method [2; 11]).

The conditions for performing research using gas chromatography methods when determining the content of dissolved gases in turbine oils correspond to the requirements specified in the works [18; 19]. When performing measurements, the following were used: a gas chromatograph with gas dispensers, a methanator (to convert CO and CO_2 into CH_4), a thermal conductivity detector (TCD), a flame ionization detector (FID), a flame photometric detector (FPD), liquid evaporators; device for accelerating the achievement of equilibrium with a rotating drum (DAAB) for placing syringes with a volume of 20 sm^3 or 50 sm^3 with analyzed samples of turbine oils and gaseous extractants for establishing phase equilibria in systems «turbine oil – gaseous extractant (Ar)» (duration τ_e of phase equilibrium with a turbine oil volume of 10 sm^3 and a gaseous extractant volume of 10 sm^3, is no less than 1 hour, according to requirements [16]); graduated gaseous mixtures of H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2, C_3H_6, C_3H_8, H_2S, O_2, N_2 in argon; mixtures of turbine oils with distilled water [6].

The measurements were performed at a temperature of t_i = (20±0.5) °C [18]. In the chromatograph, registration of components was performed with the help of: TCD – for H_2, O_2, N_2, and FID – for CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, CO, CO_2 [18]; FPD – for H_2S [4].

When determining: a) the content of dissolved gases in turbine oils, the following were used: a static version of the gas chromatography measurement method using a gaseous extractant and corresponding variants of methods for analyzing the equilibrium gas phase in the systems «turbine oil – dissolved gas – gaseous extract»; b) the content of dissolved gases in gaseous extracts using appropriate gaseous calibration mixtures – the absolute calibration method was used [18; 19]; c) thresholds for determining the concentrations of dissolved gases in turbine oils and distribution coefficients k_i – mixtures of gases H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2, C_3H_6, C_3H_8, H_2S, O_2, N_2 in gaseous argon were used at a concentration of each gas greater than 0.5% volume. Oxidation was carried out: mineral turbine oil – according to the method [2; 11]; synthetic fire-resistant turbine oils – according to method [2; 20]. Water is added to turbine oils using the application method [6].

Table 1 shows the quality indicators of the studied fresh and oxidized turbine oils at a moisture content of W = 0.005% mass (homogeneous liquid) and W = 0.7% mass (heterogeneous liquid).

Table 1 – Quality indicators of the studied turbine oils

Oil condition	Oil condition indicator	*turbine oil*			
		«Agrinol Тп-46»	«Fyrquel®L»	«Reolube®OMTI»	«Reolube®46 RS»
Fresh oil	Moisture contents W = 0.005 % mass or W = 0.7 % mass in oil				
	AN, mg KOH per 1 g of TO	0.45	0.035	0.030	0.032
Oxidized oil	Moisture contents W = 0.7 % mass in oil				
	AN, mg KOH per 1 g of TO	0.65	1.5	1.7	1.6

Source: developed by the authors.

When determining the concentration of Ci, a dissolved gas in turbine oils using the gas chromatography method, a formula was used to calculate the process of a single isothermal extraction [18; 21]:

$$C_{i,0} = \frac{S_k}{K_g}\left(k_i + \frac{V_e}{V_{e0}}\right), \tag{1}$$

where S_k – plane of the gas chromatographic peak for the i-th gas; K_g – calibration coefficient for a gas chromatograph for the i-th gas; k_i – distribution coefficient for i-gas dissolved in turbine oil; V_e – extractant volume; V_{e0} – turbine oil sample volume.

Distribution coefficients k_i for dissolved gases were determined by gas chromatography by sequential double isothermal extraction of dissolved gas from a sample of turbine oil with equal volumes of pure gaseous extractant and using the calculation formula [21]:

$$k_i = \frac{S_i}{S_2 - S_1}\cdot\frac{V_e}{V_{e0}}, \tag{2}$$

where S_1, S_2 are the areas of gas chromatographic peaks for the i-th gas after its first and second gas extraction with argon.

Determination of the content of dissolved gases in turbine oils using the application method includes the following operations: 1) a known volume of a gaseous pure extractant that does not contain a component is added to a sample of turbine oil with a known volume; 2) perform gas extraction of the i-th dissolved gas from the volume of turbine oil into the volume of the gaseous extractant; 3) using the gas chromatography method, the content of the i-th dissolved gas in the volume of the gaseous extractant is determined; 4) to a sample of turbine oil with a known volume, add a known volume of a gaseous extractant containing the *i*-th dissolved gas with a known content; 5) perform gas extraction of the *i*-th dissolved gas from the volume of turbine oil into the volume of the gaseous extractant; 6) using the gas chromatography method, the content of the *i*-th dissolved gas in the volume of the gaseous extractant is determined; 7) calculate the concentration of the contents of the *i*-th component in the volume of turbine oil according to formula (1).

The mathematical description of phase equilibria in the process of gas extraction of the *i*-th dissolved gas consists in the use of known relationships [21]:

$$C_{i,0}\cdot V_{e0} = C_{i,e0,1}\cdot V_{eo} + C_{i,1,e}\cdot V_e; \tag{3}$$

$$C_{i,0}\cdot V_{e0} + C_{i,\partial}\, V_e = C_{i,eo,2}\cdot V_{eo} + C_{i,2,e}\cdot V_e, \tag{4}$$

where $C_{i,0}$ is the concentration of the *i*-th dissolved gas in the volume of turbine oil; V_{eo} is the volume of this turbine oil; $C_{i,e0,1}$ is the concentration of the *i*-th dissolved gas in the volume of turbine oil after gas extraction with a pure extractant that does not contain the ith dissolved gas; V_e – volume of added pure extractant; $C_{i,1,\mathrm{e}}$ is the content of the *i*-th dissolved gas in the volume of the gaseous extractant after gas extraction; $C_{i,\partial}$ is the concentration of the *i*-th dissolved gas in the volume of the gaseous extractant added to the turbine oil sample; $C_{i,2,e}$ is the concentration of the *i*-th dissolved gas in the volume of turbine oil after gas extraction with an extractant containing the *i*-th dissolved gas with a known content; $C_{i,2,e}$ is the content of the *i*-th dissolved gas in the volume of the gaseous extractant after gas extraction.

The formula for calculating the content of the *i*-th dissolved gas $C_{i,0}$ in the volume of turbine oil, obtained from equations (3) and (4), has the form:

$$C_{i,0} = \frac{V_e}{V_{e0}} \cdot \frac{C_{i,1,e} \cdot C_{i,d}}{C_{i,2,e} - C_{i,1,e}}. \tag{5}$$

The application method does not require determining the distribution coefficients k_i for the *i*-th dissolved gases.

Experimentally obtained threshold values for determining the concentrations of dissolved gases in turbine oils when performing measurements using gas chromatography methods [18]: 2 ppm – for H_2, O_2, N_2, H_2S; 1 ppm – for CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8; 0.5 ppm – for C_2H_2; 5 ppm – for CO, CO_2. The values of the limit of permissible relative error δ_i (% relative for determining the concentrations of dissolved gases C_i based on the results of the analysis of turbine oils using gas chromatography methods meet the requirements of [18] depending on the range of concentrations of dissolved gases.

Table 2 shows the distribution coefficients k_i for dissolved gases in turbine oils at t = 20 °C in equilibrium systems «turbine oil – dissolved ith gas – gaseous extractant».

Table 2 – Partition coefficients ki for dissolved gases in turbine oils in systems «turbine oil – dissolved gas – gaseous extractant»

Dissolved gases											
CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_3H_8	H_2	CO	CO_2	O_2	N_2	H_2S
1	2	3	4	5	6	7	8	9	10	11	12
Distribution coefficients k_i at t = 20 °C											
MTO «Agrinol Тп-46»», *W* = 0.005 % mass, AN = 0.45 mg KOH per 1 g of fresh MTO											
0.44	2.76	1.80	1.30	8.30	8.80	0.053	0.12	1.18	0.17	0.09	15.2
MTO «Agrinol Тп-46», *W* = 0.7 % mass, AN = 0.65 mg KOH per 1 g of oxidized MTO											
0.42	2.72	1.88	1.40	8.30	8.75	0.05	0.11	1.19	0.17	0.1	15.4
SFRTO «Fyrquel®L», *W* =0.005 % mass, AN = 0.0355 mg KOH per 1 g of fresh SFRTO											
0,43	2.60	1.76	1.35	8.20	8.90	0.05	0.12	1.06	0.16	0.10	abs.
SFRTO «Fyrquel®L», *W* =0.7 % mass, AN =1.5 mg KOH per 1 g of oxidized SFRTO											
0,45	2.65	1.70	1.30	8.20	8.70	0.05	0.11	1.18	0.16	0.10	abs.

End of the table 2

1	2	3	4	5	6	7	8	9	10	11	12
SFRTO «Reolube$^{®}$OMTI», *W* =0.005 % mass, AN = 0.030 mg KOH per 1 g of fresh SFRTO											
0.43	2.74	1.75	1.25	8.25	8.75	0.05	0.12	1.18	0.17	0.09	abs.
SFRTO «Reolube$^{®}$OMTI», *W* =0.7 % маси, AN = 1.7 mg KOH per 1 g of oxidized SFRTO											
0.42	2.65	1.75	1.25	8.20	8.60	0.05	0.11	1.17	0.16	0.09	abs.
SFRTO «Reolube$^{®}$46 RS», *W* =0.005 % mass, AN = 0.032 mg KOH per 1 g of fresh SFRTO											
0.50	2.70	1.85	1.40	8.40	8.90	0.05	0.11	1.20	0.18	0.10	abs.
SFRTO «Reolube$^{®}$46 RS», *W* =0.7 % mass, AN = 1.6 mg KOH per 1 g of oxidized SFRTO											
0.5	2.65	1.80	1.35	8.35	8.80	0,05	0,12	1.2	0.17	0.10	abs.
Water *[21]											
0.0367	0.0514	0.128	1.108	0.216	0.0424	0.0194	0.0249	0.937	0.0334	0.0169	2.792
Notes: abs. – absent; * – values for comparison											

Source: developed by the authors.

From the table 2 it follows that the values of the distribution coefficients k_i for the corresponding dissolved *i*-gases in the studied turbine oils practically do not depend on: the nature of these oils (mineral or fire-resistant synthetic turbine oil) or the water content in them in the range of its concentrations 0.005–0.7% mass; the «acid number» indicator in its range is 0.032–1.7 mg KOH per 1 g of turbine oil.

Table 3 shows the results of a study of the nature of the effect of temperature on the value of distribution coefficients k_i for H_2S in the system «turbine oil «Agrinol Tp-46» – dissolved gas H_2S - gaseous extractant (Ar)» on the gas extraction temperature in the temperature range 15–80 °C.

Table 3 – Dependence of distribution coefficients k_i *for* H_2S *in the system «turbine oil Agrinol Tп-46 – dissolved gas* H_2S *– extractant» on gas extraction temperature*

t_i, ˚C	15	20	25	30	40	50	60	70	80
T_i, K	288	293	298	303	313	323	333	343	353
k_i	16.1	15.0	14.0	13.1	11.6	10.3	9.2	8.3	7.5
γ_i, % rel.	7.3	0	- 6.7	- 12.7	- 22.7	- 31.3	- 38.7	- 44.7	- 50.0
Note: γ_i – relative deviations of the values of coefficients k_i (% rel.) at measured temperatures t_i from the value γ_i = 0 obtained at t = 20 ˚C.									

Source: developed by the authors.

From the table 3 it follows that in the temperature range t_i = 15–25 °C changes in k_i values do not exceed 7.3% relative, which is acceptable for technical calculations, and gas extraction of H_2S from turbine oil «Agrinol Tp-46» with argon gas is recommended to be performed at t = 20 ± 2) °C.

In the temperature range t_i = 15–80 °C, the values of the distribution coefficients k_i for H_2S in the system «turbine oil «Agrinol Tп-46» – dissolved gas H_2S – gaseous extractant», depending on the gas extraction temperature, can be calculated using the empirical formula:

$$\lg k_i = 1184 \cdot T^{-1} - 1.35\,, \tag{6}$$

where k_i is the distribution coefficient for H_2S; T_i is the gas extraction temperature, K.

Table 4 shows the results of a study of the nature of the effect of temperature on the solubility of X_i for H_2S in the system «turbine oil «Agrinol Tp-46» – dissolved gas H_2S» in the temperature range 15–80 °C. Solubility X_i for H_2S is defined as the amount of dissolved volume of H_2S in one volume of «Agrinol Tp-46» turbine oil.

Table 4 – Dependence of solubility values for H_2S *on temperature in the system «turbine oil Agrinol Tp-46 – dissolved gas* H_2S*»*

t_i, ˚C	15	20	25	30	40	50	60	70	80
T_i, K	288	293	298	303	313	323	333	343	353
X_i,% vol.	4.36	4.06	3.79	3.54	3.14	2.79	2.49	2.25	2.03

Source: developed by the authors.

From the table 4 it follows that in the temperature range t_i = 15–25 °C, an increase in temperature reduces the solubility of H_2S in the «Agrinol Tp-46» mineral turbine oil. In the temperature range t_i = 15–80 °C, the solubility values X_i for H_2S in the system «mineral turbine oil «Agrinol Tп-46» – dissolved gas H_2S», depending on temperature, can be calculated using the empirical formula:

$$\lg X_i = 1190 \cdot T_i^{-1} - 2.69, \qquad (7)$$

where X_i is the content of H_2S in turbine oil, the volume of H_2S in one volume of mineral turbine oil; T_i – temperature, K.

Table 5 shows the results of a study of the solubility of gases (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2) at t = 25 °C in «Agrinol Tp-46» turbine oils with a moisture content of W = 0.005 mass and «Reolube®46 RS» with moisture content W = 0.005% mass.

Table 5 – Solubility of gases in energy oils

Solubility of gases in energy oils, % volume, при t = 25 ˚C										
CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_3H_8	H_2	CO	CO_2	O_2	N_2
MTO «Agrinol Tп-46», W =0.005 % mass										
28	270	265	430	1250	2000	6.5	8.5	115	15	9.0
SFRTO «Reolube®46 RS», W =0.005 % mass										
35	290	290	450	1300	2100	7	9	120	17	10

Source: developed by the authors.

From the table 5 it follows that: the solubility of gases CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2 in turbine oils «Agrinol Tп-46» and «Reolube®46 RS» practically do not depend on the nature of these oils at t = 25 °C. The study of the constancy of the values of distribution coefficients k_i in a given range of concentrations of i-th diagnostic gases dissolved in turbine oils was carried out using the method of sequential multiple gas extraction of i-th gases from turbine oils, which makes it possible to construct a linear dependence $\lg C_{i,e} = f(n)$, where $C_{i,e}$ is the concentration of the i-th gas in the gas extractant above the turbine oil after the n-th sequential gas extraction.

In this case, the value of k_i for the i-th dissolved gas is calculated according to the formula [21] taking into account the concentrations of dissolved gas in the gas extract above the turbine oil after the first (C_1) and after the n-th (C_n) extraction of dissolved gas from the turbine oil at t = 20 °C:

$$k_i = \frac{V_e}{V_{e0}} \cdot \frac{(C_n)^{n^{-1}}}{(C_1)^{n^{-1}} - (C_n)^{n^{-1}}}, \qquad (8)$$

Figure shows a generalized graph of the results of determining the constancy of the distribution coefficients k_i for dissolved gases in a sample of synthetic fire-resistant turbine oil «Reolube®46 RS» at its humidity W = 0.005% mass (homogeneous liquid).

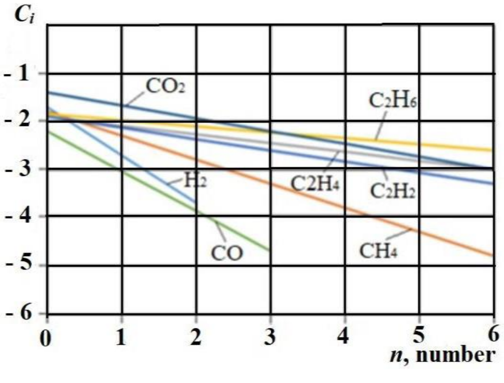

Fig. Graph of the results of determining the constancy of the distribution coefficients for dissolved gases in the «Reolube®46 RS» turbine oil: $C_i = \lg C_{g,i}$; $C_{g,i}$ concentration of the i-th gas in the gaseous extractant above the surface of the energy oil, % volume; n is the number of successive gas extractions after replacing the extractant with its pure portion of the original volume

Similar results were obtained when determining the constancy of the distribution coefficients k_i for dissolved gases in other studied turbine oils at their humidity $W = 0.005\%$ mass. The graph practically repeats the results obtained in [6] for the system «mineral transformer oil - dissolved gas - gaseous extractant».

The constancy of the distribution coefficient values in the studied range of measured concentrations of gases dissolved in turbine oils, depending on the number of extractions performed, indicates the possibility of using gas extraction equations (1) and (2) in the studied range of measured concentrations of dissolved gases, as well as the reproduction of phase equilibrium conditions in DAAB.

Table 6 shows the results of a study of the content of dissolved gases in model synthetic fire-resistant turbine oils «Reolube®46 RS» using the application method at t = 20 °C.

Table 6 – Results of a study of the content of i- th dissolved gases in model synthetic fire-resistant turbine oils «Reolube®46 RS» using the application method

Concentration of dissolved gases $C_{i,0}$, % volume										
CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_3H_8	H_2	CO	CO_2	O_2	N_2
SFRTO «Reolube®46 RS», W =0.005 % mass										
0.1	0.1	0.1	0.1	0.3	0.3	0.2	0.2	1.0	2.0	5.9
SFRTO «Reolube®46 RS», W =0.7 % mass										
0.11	0.09	0.11	0.12	0.33	0.28	0.2	0.2	1.1	2.0	5.9
Relative deviation γ_i, % relative										
+10	–10	+10	+12	+10	–7.6	0	0	+10	0	0
Note: γ_i – relative deviations (% rel.) of $C_{i,0}$ values at moisture content W =0.7% mass (heterogeneous liquid) from $C_{i,0}$ values at humidity W =0.005% mass (homogeneous liquid) for SFRTO										

From the table 6, it follows that the relative deviations of γ and the values of $C_{i,0}$ at a moisture content of W =0.7% mass (heterogeneous liquid) in the turbine oil «Reolube®46 RS» from the values of $C_{i,0}$ at a moisture content of W =0.005% mass (homogeneous liquid) in the turbine oil oils do not exceed the value of 12% relative, which is permissible for performing technical calculations when determining the content of diagnostic dissolved gases in this turbine oil with its humidity in the range of 0.005–0.7% mass.

Conclusions.

1. The mathematical description of the phase equilibrium in the extraction system «moistened turbine oil – dissolved *i*-th diagnostic gas – gaseous extractant (argon)» has been improved for dissolved diagnostic gases CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2.

2. It has been established that: a) the values of the distribution coefficients k_i for the corresponding dissolved diagnostic gases in the studied turbine oils are practically independent of the nature of the turbine oils (mineral or fire-resistant synthetic turbine oils), or the water content in them in the range of its concentrations of 0.005–0.7% mass; b) at $t = 25$ °C, the solubility of diagnostic gases in energy oils such as mineral transformer oil and in turbine oils «Agrinol Тп-46» and «Reolube®46 RS» practically does not depend on the nature of these energy oils; c) the constancy of the values of the distribution coefficients k_i in the studied range of measured concentrations of gases dissolved in turbine oils, depending on the number of gas extractions performed, indicates the possibility of using the known gas extraction equation (1) in the studied range of measured concentrations of gases dissolved in turbine oils.

3. The following were studied: a) the nature of the effect of temperature on the value of distribution coefficients k_i for H_2S in the system «mineral turbine oil «Agrinol Tp-46» – dissolved gas H_2S – extractant (argon)» in the temperature range 15–80 °C, and it was found that an increase in temperature leads to a decrease in the distribution coefficients k_i for H_2S.

A similar result was obtained when studying the nature of the dependence of H_2S solubility values on temperature in the system «mineral turbine oil «Agrinol Tp-46» – dissolved H_2S gas»; b) The content of *i*-dissolved gases in the model synthetic fire-resistant turbine oil

«Reolube®46 RS» according to the application method at t = 20 °C, and it is shown that the relative deviations of γ and $C_{i,0}$ values at moisture content W = 0.7% mass (heterogeneous liquid) in turbine oil «Reolube®46 RS» from the values of $C_{i,0}$ with a moisture content in W = 0.005% mass (homogeneous liquid) turbine oil, do not exceed the value of 12% relative, which is acceptable for performing technical calculations when determining the content of diagnostic dissolved gases in this oil with its humidity in the range of 0.005–0.7% mass.

4. The promise of the research results obtained lies in the possibility of their further use to determine the influence of moisture, temperature, thermal, electric and acoustic fields on the degradation of turbine oils for further improvement of the elements of the system for ensuring the reliability of operation of oil-filled equipment of nuclear power plants.

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Отримано 19.06.2024

УДК 621.314.212.001:621.315.615.2.004

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КОНТРОЛЬ ВМІСТУ РОЗЧИНЕНИХ ГАЗІВ У СВІЖИХ ТА ОКИСНЕНИХ ТУРБІННИХ ОЛИВАХ

Стаття є публікацією науково-методичного характеру.

Застосування сучасних методів контролю стану оливонаповненого тепломеханічного обладнання АЕС потребує безперервного удосконалення методів діагностування такого обладнання, в тому числі за результатами контролю вмісту розчинених діагностичних газів, таких як CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8, H_2, CO, CO_2, O_2, N_2, *в мінеральних та синтетичних вогнестійких турбінних оливах, у тому числі в гетерогенних системах типу «турбіна олива – розчинений газ – емульсійна вода».*

Добитися достовірності результатів визначення вмісту діагностичних розчинених газів в турбінних оливах за методами газової хроматографії можна при правильному виборі діапазону концентрацій води в цих досліджуваних турбінних оливах, в якому відсутній значний вплив вмісту води на результати газохроматографічних вимірювань.

Аналіз досліджень і публікацій з питань досліджень методів діагностування електротехнічного та тепломеханічного оливонаповненого обладнання за результатами аналізів проб енергетичних олив методами газової хроматографії показав, що питанням сталого підвищення достовірності результатів визначення вмісту діагностичних розчинених газів у турбінних оливах за методами газової хроматографії на сьогодні приділено мало уваги в науковій літературі.

Виявлення характеру впливу вмісту розчиненої та емульсійної води в мінеральних та синтетичних вогнестійких турбінних оливах на результати газохроматографічних аналізів на сьогодні приділено мало уваги в науковій літературі.

Метою статті є забезпечення достовірності результатів дослідження вмісту діагностичних розчинених газів H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2, O_2, N_2, *за методами газової хроматографії в пробах вологих мінеральних та синтетичних вогнестійких турбінних оливах для подальшого діагностування оливонаповненого обладнання АЕС.*

На підставі існуючих методів досліджень, було: удосконалено математичний опис фазової рівноваги в екстракційній системі «волога турбінна олива – розчинений і-й газ – газоподібний екстрагент» для досліджуваних турбінних олив «Агрінол Тп-46», «Fyrquel®L», «Reolube®OMTI», «Reolube®46 RS». За методами газової хроматографії: виявлено *вплив концентрацій і-х розчинених газів у вологих турбінних оливах на значення коефіцієнтів розподілу для і-х розчинених газів в екстракційних системах «волога турбінна олива – розчинений і-й газ – газоподібний екстрагент»; виявлено вплив концентрацій води у вологих турбінних оливах на значення коефіцієнтів розподілу для і-х розчинених газів в екстракційних системах «волога турбінна олива – розчинений і-й газ – газоподібний екстрагент»; досліджено розчинність діагностичних газів в осушених та вологих турбінних оливах при температурі 20 ^{0}С.*

У роботі досліджено: розчинність цих газів в мінеральній турбінній оливі «Агрінол Тп-46» та в синтетичній вогнестійкій турбінній оливі «Reolube®46 RS» із вмістом в них вологи в інтервалі 0,005 –0,7 % маси при температурі 25 ^{0}С; залежність величин розчинності для H_2S від температури в системі «мінеральна турбінна олива – розчинений газ H_2S» в інтервалі температур 15–80 ^{0}С; коефіцієнти розподілу розчинених газів в досліджених турбінних оливах при температурі 20 ^{0}С в системах «турбінна олива – розчинений газ – газоподібний екстрагент»; вміст розчинених газів в модельних синтетичних вогнестійких турбінних оливах «Reolube®46 RS» за методом додатку. Це дозволить визначати вміст розчинених газів у вологих турбінних оливах для подальшого діагностування оливонаповненого обладнання.

Ключові слова: *газова хроматографія; діагностика; ядерна енергетика; коефіцієнт розподілу; розчинність газу.*

Табл.: 6. Рис.: 1. Бібл.: 21.

Zaitsev, S., Kishnevsky, V., Tikhenko, V. (2024). Control of dissolved gas content in fresh and oxidised turbine oils. *Technical sciences and technologies*, (2(36)), 215-226.