Markers of cellulose insulation ageing: calculation of total methanol quantity in the internal insulation of power transformers

L.A. Darian [1,3*] , *R.M.* Obraztsov [1] , *A.V.* Maksimchenko [1] , *D.E.* Verakso [1] , *V.P.* Polishchuk [2] , *V.A.* Logunov [3,4]

[1]JSC "Technical Inspection of UES", Moscow, Russia
[2] United Institute of High Temperatures, Russian Academy of Sciences, Moscow, Russia
[3] Federal State Budgetary Educational Institution of Higher Education "NIU MPEI", Moscow, Russia
[4] FGUP RFNC-VNIITF, Snezhinsk, Russia

Abstract. The methods of calculation of methanol quantity in the internal insulation of power transformers (PT) based on the values of its concentration in transformer oil (TO) are considered. The total methanol quantity formed during the operation of PTs allows estimating the degree of degradation of cellulose insulation. We are considering the models for calculation of the total methanol quantity in PT on the base of:

- literature data characterizing the methanol balance in the cellulose-oil system;
- data on the reduction of methanol concentration after TO replacement during total overhaul.

The errors analysis on the base of the results of calculations using the models showed that their value can reach 30%. Reduction of errors in the calculation results should be based on a deeper study of the kinetics of methanol sorption processes by cellulose and taking into account the structural features of different types of cellulose insulation in the particular PT.

The considered models can be recommended for estimation of total quantity of any dissolved decomposition products of cellulose insulation in TO, which can become an important indicator of technical condition of PT.

1 Introduction

The ageing of the PT internal insulation resulting from various factors, becomes apparent in a gradual deterioration of its characteristics, which can eventually cause an internal short circuit, often leading to a large-scale accident. Analyzing the quantity of the TO ageing markers, i.e. specific chemical compounds formed as a result of the internal insulation ageing, obtain a clear picture of the degree of its degradation.

This paper discusses the measuring results of the methanol concentration in TO conducted over a five-year period. Methanol is formed mainly at lower temperatures as a result of cellulose hydrolysis. The total methanol quantity in the PT internal insulation Q_t is proportional to the change of cellulose polymerization degree [1-3]. It is considered that when the degree of polymerization is less than 250, the service life of PT cellulose insulation has completely expired [3]. The quantity of Q_t allows us to estimate directly the degree of cellulose insulation ageing and, consequently, to estimate PT residual life. During the cellulose insulation aging process, the generated methanol migrates between cellulose and TO. The methanol quantity in the TO Q_o is found from measured methanol concentrations C_o , but the methanol quantity Q_c contained in the cellulose can be a significant part of its total quantity Q_t :

$$Q_t = Q_c + Q_o \tag{1}$$

Currently, there are no available standardized procedure to determine the methanol quantity in cellulose insulation. Therefore, the methanol quantity Q_c can only be determined by calculation methods.

The aim of this work was to develop and analyze non-equilibrium and equilibrium models for calculation of the total methanol quantity in PT and to assess the errors of these methods.

2 Object and methods of research

Measurements of the internal insulation ageing markers concentration were carried out on a three-phase PT of 110 kV voltage class with 80 MVA power, TO mass M_o = 41 tones, its volume V_o =47.8 m^3 . The transformer was put into operation in 1986. The PT was equipped with a diagnostic monitoring system to control the concentration of nine gases dissolved in the TO (carbon oxides, hydrocarbons, hydrogen, oxygen and nitrogen). The monitoring system also recorded hourly the ambient temperature, the temperature of TO upper and lower layers and the PT load current. Based on these data, the temperature of the hottest point of the insulation was calculated in accordance with the methodology [4]. Approximately once a month TO

* Corresponding author: daryan-la@ti-ees.ru

samples were taken to determine the concentration of methanol.

During the observation period, PT was taken out for repair twice. At the end of spring 2019, an overhaul was carried out which included replacement of the TO, drying of cellulose insulation and revision of the active part. Inspection of the PT inner surface did not reveal any signs of cellulose insulation deterioration and winding clamping. In late spring 2022, the sealing gasket between the PT cover and tank was replaced and the sealing of the welded joints was improved. During this overhaul, methanol concentrations were measured daily.

3 Measurement results

Figure 1 shows the temperature values of the upper and lower layers of the TO; the characteristic difference between these temperatures was ≈10 °C. The ambient temperature differed from the temperature of the lower oil layers by no more than ≈5 °C. During the observation period, the PT load was maintained mainly at the same level (≈25% of the nominal one), so the periodic type of TO temperature dependence was determined by the seasonal change of the ambient temperature. Further, the arithmetic mean value of the temperature of the upper and lower layers of TO is taken as the representative temperature of internal insulation T_i.

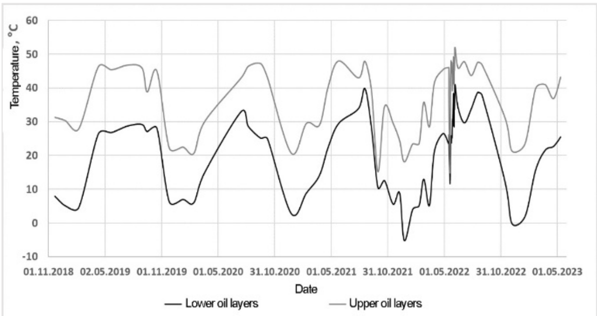

Fig. 1. Temperature of lower and upper oil layers in the PT

Figure 2 shows the values of methanol concentration C_o over the observation time and its average concentration $C_{av}(t)$ after TO replacement, which was calculated using the formula:

$$C_{av}(t) = \frac{1}{t} \times \int_o^t C_o(t')dt' \quad (2)$$

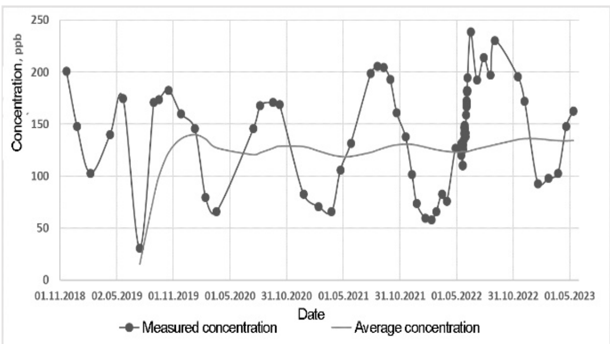

Fig. 2. Methanol concentration over the observation period

The sharp decrease in concentration in summer 2019 is explained by TO replacement during the overhaul. The minimum value of methanol concentration was ≈30 ppb and measured 20 days after TO replacement. "Fresh" TO does not contain methanol, therefore its appearance in samples after TO replacement is explained by desorption from cellulose insulation. In Figure 2 the concentration of points in early summer 2022 is associated with the increased frequency of measurements during the overhaul. The change in methanol concentration during this period is shown in Figure 3 in more detail. This figure also shows the internal insulation temperature T_i .

If we disregard a sharp decrease in methanol concentration due to TO replacement, the periodic time dependence of methanol concentration (Fig. 2) and TO temperature (Fig. 1) are similar at the qualitative level. The value of methanol concentration is established as a result of the competing processes of adsorption and desorption from the cellulose surface. The methanol sorption rate depends exponentially on the cellulosic surface temperature. Thus, it is possible to speak about correlation between extremes of methanol concentration and insulation temperature.

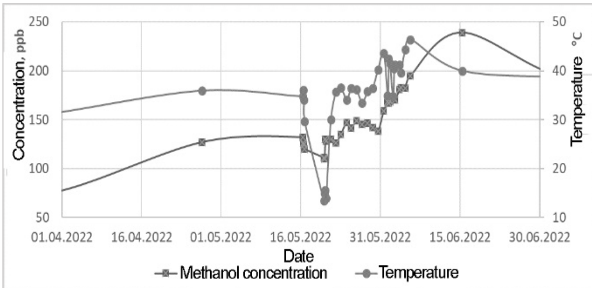

Fig. 3. Methanol concentration and internal insulation temperature T_i in the second quarter of 2022

Figure 4 shows the values of the extremes of methanol concentration and internal insulation temperature during the observation period.

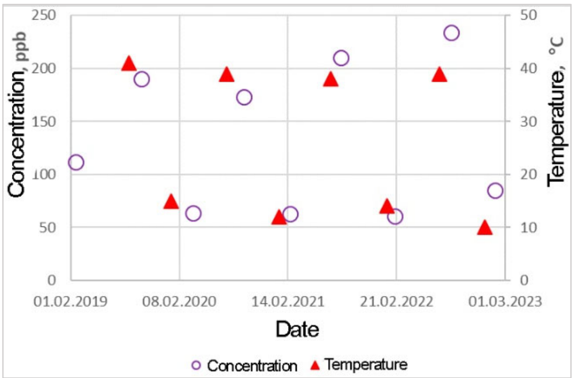

Fig. 4. Extremes of methanol concentration and internal insulation temperature

It can be seen that concentration extremes were preceded by temperature extremes, the time lag between these extremes ranged from 25 to 75 days [5]. Concentration maxima were recorded in late summer or early autumn, and concentration minima were recorded in the second half of winter or early spring. The maximum concentration of $C_{o.r.}$ =175 ppb (22.05.2019) and the minimum concentration of 30 ppb (15.07.2019) are not shown in Figure 4 because these extremes are explained by TO replacement.

Table 1 summarizes the values of methanol concentration extremes $C_{o.i}$, where i is the extremum number. The estimate of the maximum concentration and representative values of methanol concentration $C_o(90)$ at temperature 90 °C in 2018 have been added to Table 1, and the calculation methods are explained below.

Table 1. Extremes of methanol concentration

№	Extremum type	Extreme date	$C_{o.i}$, ppb	$C_o(90)$, ppb
1	Max	≈*01.10.2018*	≈*240*	≈*1334*
2	Min	17.02.2019	112	1995
3	Max	01.10.2019	190	1056
4	Min	27.03.2020	64	1082
5	Max	17.09.2020	173	913
6	Min	21.02.2021	63	1134
7	Max	16.08.2021	210	1098
8	Min	17.02.2022	61	1090
9	Max	29.08.2022	234	1203
10	Min	25.01.2023	85	1366

The data in Figure 2, Figure 4, and Table 1 provides an estimate of the maximum methanol concentration in 2018. In Figure 2, the earliest methanol concentration value measured on 21.11.2018 was 201 ppb. This value was obtained shortly after the autumn maximum. Figure 2 shows that by 21.11.2018 the methanol concentration should have decreased by ≈20%, meaning that the maximum concentration in 2018 could presumably have been ≈240 ppb. Approximately the same maximum methanol concentration could have been recorded in 2019 if the TO had not been replaced. This follows from the extrapolation of the concentration value of 175 ppb measured on 22.05.2019, three to four months before the autumn maximum. Thus, the maximum methanol concentration of $C_{o.3}$ =190 ppb recorded on 01.10.2019 turned out to be ≈50 ppb less than it would have been without the TO replacement. The methanol concentration in the second minimum (64 ppb) decreased by about the same amount compared to the first (112 ppb).

From the data in Table 1 it can be concluded that in 2021-2023 the methanol concentration in the extremes owing to cellulose aging increased at a rate of ≈20 ppb/yr. Figure 2 shows that from 2021-2023 the average methanol concentration in the TO increased at a rate of ≈5 ppb/yr. Note that over the 32 years of PT operation the average rate of increase of methanol concentration in TO was ≈7 ppb/year. Taking into account the obtained spread of values, the most reasonable value for the average rate of methanol concentration increase is ≈10 ppb/year.

4 Models for calculating total methanol quantity

When calculating the volume of methanol contained in TO, it can apparently be assumed that due to diffusion and convective currents it is distributed uniformly over the volume of TO, therefore:

$$Q_o = C_o \times V_o \quad (3)$$

To analyze the methanol quantity in the cellulose, we can formally introduce an integral distribution coefficient K_{in}, determined from the correlation:

$$K_{in} = Q_c / Q_o \quad (4)$$

The total methanol quantity in the internal insulation is:

$$Q_t = Q_o \times (1 + K_{in}) \quad (5)$$

Equilibrium and non-equilibrium models of methanol distribution in the oil-cellulose system can be used to calculate the total quantity of methanol Q_t. Note that at equilibrium distribution extremes of methanol concentration should coincide with extremes of insulation temperature T_i, but the data in Figure 4 clearly show that this condition of existence of equilibrium is not fulfilled.

4.1 Non-equilibrium model

In the absence of equilibrium, some additional information is needed to estimate the methanol quantity of cellulose insulation Q_c. Such information can be the change in the methanol concentration in the inner insulation during TO replacement. Since the generation rate of methanol in the inner insulation is relatively low, the values of its total quantity Q_t during the first and second concentration maxima (≈01.10.2018 and 01.10.2019) differ by the methanol quantity $Q_{o.r.} = V_o \times C_{o.r.}$ ($C_{o.r.}$ =175 ppb) that was removed during the overhaul:

$$Q_{o.1} \times (1 + K_{in.1}) \cong Q_{o.3} \times (1 + K_{in.3}) + Q_{o.r.}\ , \quad (6)$$

where $K_{in.1}$ and $K_{in.3}$ are integral distribution coefficients during the first and second maxima.

The above data show that $Q_{o.1}$ ≈*11*.5 mL (≈*01*.10.2018, $C_{o.1}$ ≈240 ppb) and $Q_{o.3}$ =9.1 mL (01.10.2019, $C_{o.3}$ =190 ppb). The thermograms of the internal insulation of the PT in autumn 2018 and 2019 were similar, so there is reason to believe that:

$$K_{in.1} \cong K_{in.3}. \quad (7)$$

From formulas (6) and (7), we can derive a correlation for the integral distribution coefficient ($K_{in} = K_{in.1}$):

$$K_{in} \cong (C_{o.3} - C_{o.1} + C_{o.r})/(C_{o.1} - C_{o.3}) \quad (8)$$

Substituting the above concentration values into this correlation, we obtain K_{in} =2.5. Accordingly, the value of the total methanol concentration in the internal insulation of the PT was ≈40.3 ml before overhaul, and ≈31.8 ml after. The values of the integral coefficient K_{in} and the volume of methanol concentration, are probably slightly underestimated due to incomplete accounting of the volume of methanol released from the internal insulation during the overhaul, because the calculation does not take into account the methanol which was removed during the drying of cellulose insulation.

4.2 Equilibrium models

If the distribution of methanol in the cellulose-oil system is close to equilibrium, the Q_t value can be estimated by two different methods based on the available literature data.

The first method is based on the use of the temperature coefficient $K_{c.f}$, which is the ratio of methanol concentrations in TO at the reference temperature of 20 °C and at the insulation temperature T_i [3, 6]:

$$K_{c.f}(T_i) = C_o(20)/C_o(T_i) \quad (9)$$

In [6], the temperature coefficient for methanol was measured on the PT model up to a temperature of ≈ 100 °C. At high temperature intensive desorption of methanol occurs, so that at temperature ≈90 °C it practically ceases to be absorbed by cellulose [6]. Accordingly, at 90 °C it can be assumed that $Q_t = Q_o$. The experimental results [6] are well described by the correlation:

$$K_{c.f}(T_i) = a \times exp(b/(T_i + 273)), \quad (10)$$

where a and b are empirical constants (b = 3720 K).

From formulas (10) and (11) it follows that the concentration of methanol in the TO at a temperature of 90 °C is calculated by the formula:

$$C_o(90) = C_0(T_i) \times \exp(b \times (1/(T_i + 273) - 1/363)) \quad (11)$$

The total volume of methanol in the inner insulation is found from correlation (3):

$$Q_t \cong C_o(90) \times V_o \quad (12)$$

Calculations according to formula (12) are reasonable for concentration extremes, since in these modes the rate of change of methanol quantity in TO is minimal, so the error of using the equilibrium approximation should be the smallest. Calculated values of concentration $C_o(90)$ are given in Table 1. To simplify the calculation, the correlation of the internal insulation temperature in the calculation of $C_o(90)$ was described (interpolated) by a harmonic function.

It is interesting to note that when the time lag is taken into account, the ratio of $C_o(90)$ concentrations in the neighboring extremes (maximum-minimum) differs by no more than 25%, which indicates that the accuracy of methanol quantity determination in the internal insulation of PTs is high enough for practical calculations.

From the correlation (12) follows, that the total volume of methanol during the first maximum concentration after overhaul (01.10.2019) is 44.9 ml. It should be noted that the calculation takes into account the time lag between the temperature of the internal insulation and the concentration of methanol [5], i.e. as a representative temperature of the internal insulation was taken the temperature of its previous maximum (41 °C, 24.08.2019) Under this condition, the concentration $C_o(90)$ = 940 ppb.

The second method to estimate the total methanol quantity is based on use in formula (5) to calculate the integral factor K_{in} the equilibrium distribution coefficient K_e (T_i), which is the ratio of methanol concentrations in cellulosic insulation and TO. The integral coefficient K_{in} is calculated by the formula:

$$K_{in} = K_e(T_i) \times \rho_o \times M_c/(\rho_c \times M_o), \quad (13)$$

where M_c is the mass of cellulosic pulp; ρ_c is its density; ρ_o is the density of TO.

The error in calculation of the distribution coefficient K_{in} with formula (13) can be large, and it is not easy to estimate it correctly. Firstly, it is explained by the fact that the equilibrium distribution of methanol in the internal insulation of PTs in operation is apparently unattainable. Secondly, quite often, as, for example, in the researched PT, the mass of cellulose insulation M_c remains unknown.

The time it takes to achieve the equilibrium concentration of methanol at temperature change T_i is determined mainly by the time of equalization of its concentration in cellulose owing to diffusion. The diffusion coefficient in cellulose materials depends on their porosity and increases with the temperature rise. Two types of cellulosic materials are used in PT: cable paper and electric-grade cardboard with densities of ≈ 750 and ≈ 950 kg/m^3 respectively [7]. The temperature of cable paper is higher than that of electric-grade cardboard since it is used as turn insulation. The typical thickness of turn insulation is ≈*0*.5 mm; electric-grade cardboard has a thickness of ≈1-3 mm and mainly used in barrier insulation. Therefore, the methanol quantity of cable paper may be closer to the equilibrium methanol quantity than in electric-grade cardboard, however, it makes up only *≈10%* of the total cellulosic pulp mass [3]. This may mean that the amount of adsorbed and desorbed methanol depends not only on the mass of cellulose insulation, but also on paper grades and their operational conditions in PT.

Taking into account this uncertainty, the calculation using formula (13) is mainly of methodological interest. In accordance with the survey data [3], the calculation was carried out for two ratios M_c/M_o: ≈0.07 and 0.1. For the calculation of the distribution coefficient K_{in} we used values of the equilibrium coefficient K_e *(*T_i), which was measured in experiments with 0.5 mm thick kraft paper [8]. The calculation was performed for the second maximum of methanol concentration ($C_{o.3}$ =190 ppb), which was recorded on 01.10.2019. The temperature of its previous maximum (41 °C, 24.08.2019) was taken as the representative temperature of the internal insulation. At this temperature, the coefficient K_e *(*T_i) is 59.4 [8], consequently, the integral distribution coefficient K_{in} from (13) is 3.8, and the total methanol quantity Q_t, determined from (5), with M_c/M_o =0.07 and M_c/M_o =0.1, is 43.9 mL and 58.5 mL respectively. Thus, the ratio of the cellulose insulation mass to the oil mass has a significant effect on the result of calculating the total methanol quantity in the internal insulation of the PT.

Table 2 shows the values of the total methanol quantity Q_t, which were calculated above on the base of different models. As can be seen, the "non-equilibrium" value of methanol volume (31.9 ml) was noticeably smaller than that obtained by "equilibrium" calculations. This was to be expected, since at equilibrium there is no methanol concentration gradient inside the cellulose insulation, which in reality always exists. At the same time, it has already been noted that the "non-equilibrium" calculation seems to have slightly underestimated value of Q_t.

In view of the above, it can be concluded that after the overhaul the value of the total methanol quantity Q_t was in the range from 35 to 40 ml. Accordingly, it can be assumed that the error of calculation of the total quantity of methanol on the base of equilibrium models for the researched PT was *≈30%*. The value of the error of the "equilibrium" calculation can be specified after analyzing the kinetics of the processes of methanol sorption-desorption by the cellulose surface taking into account the diffusion transfer of absorbed methanol. At present, apparently, there is no necessary set of experimental and theoretical data to carry out such an analysis.

Table 2. Total methanol quantity in PT as of 01.10.2019.

№	Calculation model	Q_t , ml
1	Non-equilibrium model, data on methanol quantity decrease with TO replacement are used, integral distribution coefficient K_{in} is calculated by formula (8)	≈32
2	Equilibrium model, calculation by formula (12) using data on temperature coefficient from [6]	≈45
3	Equilibrium model, integral distribution coefficient K_{in} calculated by formula (13) using data on the equilibrium distribution coefficient from [8]	≈44 (M_c/M_o = 0.07) ≈58 (M_c/M_o = 0.10)

The error of equilibrium models for the calculation of methanol distribution in the PT can be relatively small at low temperature change rate for the internal insulation on account of changes in ambient temperature and PT load.

5 Conclusion

1. We considered non-equilibrium and equilibrium models for calculating the total methanol quantity in PT internal insulation on the base of methanol reduction data obtained during overhaul and literature data on the effect of temperature on methanol distribution in the oil-cellulose system.
2. Data on the change in methanol concentration in transformer oil after replacement may allow estimation of the total methanol quantity of PT internal insulation. However, these data may be underestimated due to the difficulty in accounting for methanol losses from cellulose insulation during the insulation drying process.
3. A significant influence of "oil-to-paper" mass ratios on the results of calculation of the total methanol quantity is shown. To reduce the error of methanol quantity calculation in the internal insulation of the PT, it is necessary to take into account structural features.

References

1. E.M. Rodriguez-Celis, S. Duchesne, J. Jalbert and M. Ryadi. Cellulose, 22, pp. 3225–3236, (2015)
2. E.M. Rodriguez-Celis, J. Jalbert, S. Duchesne, B. Noirhomme, and M-C. Lessard. CIGRE-083, CIGRE Canada Conference (2012)
3. CIGRE TB 779. WG A2/D1-46. (2019)
4. IEC 60076-7:2018 Power transformers. Part 7. Loading guide for the loading of oil-filled power transformers (2018)
5. L. Darian, R. Obraztsov, A. Maksimchenko, V. Polistchook, S. Asoskov. Seasonal changes in the concentrations of cellulose aging markers in transformer oil, RSES 2023, E3S Web of Conferences 461, 01017 (2023)
6. J. Jalbert, M.-C. Lessard, and M. Ryadi. IEEE Trans. Dielectr. Electr. Insul. 20(6), pp. 2287-2291 (2013)
7. Reference book on electrical insulating materials, Part I. M.: Energia (1986)
8. H. Zheng, K. Shi, Y. Zhang, C. Zhang, E. Zhang, C. Zhang, Effect of Temperature on Methanol Equilibrium in Oil-paper Insulation System of Power Transformers (Inter. Conf. on High Voltage Engineering and Application, ICHVE, 6-10 Sept., 2020)