Effect of Waiting Time on Concentration of Chemical Markers measured on Laboratory Ageing Samples

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Abstract- **Laboratory scale thermal ageing experiments have been used not only to study the degradation of the insulation materials but also to understand the variation of chemical markers in liquid during the ageing process. However, trends obtained from different experiments often disagree with each other due to experimental variations such as material type, material ratio and ageing temperature. In addition to these well-known factors, there are lesser- known factors such as the duration for which samples are left at room temperature after an ageing experiment, which could affect the concentration of chemical markers in liquid. It is known that temperature could affect the partitioning of chemical markers among the liquid, solid and gas phase. Hence the concentration of certain chemical-markers in liquid could vary depending on the duration for which samples are left at room temperature prior to the sampling of oil for the measurements. This paper investigates the effect of this sampling period on the variation of chemical markers including water, methanol and ethanol in liquid after a laboratory scale ageing experiment conducted at 150 °C. Results showed that the concentration of the investigated chemical markers in liquid decrease continuously when the sample is left at room temperature, with water having the highest reduction followed by methanol and ethanol.**

I. INTRODUCTION

Power transformers require monitoring and management to obtain their optimal performance and maximum service life without unplanned outages or failures. Apart from being an insulation and a heat transfer cooling medium the liquid insulation in transformers support management of these assets by allowing the user to monitor the condition through the presence of gases and other chemical-markers which enable the condition of the paper insulation to be monitored. Paper condition is otherwise difficult to establish as it cannot generally be accessed directly for measurements such as tensile strength and degree of polymerization during the service life of a transformer. Water, 2-furfural (2-FAL), carbon oxide gases (CO and CO2), methanol, ethanol and low molecular weight acids are such chemical markers in oil, all of which are related to the ageing of paper insulation [1, 2]. Laboratory ageing experiments conducted at high temperatures are used to understand the variation of these chemical markers measured in liquid during the ageing and to develop models to predict ageing of paper insulation. However, many models often do not agree with each other due

to differences in the experiments such as material types, material ratios, ageing conditions and ageing temperature [3, 4]. In addition to these well-known and controlled parameters, there are other less-controlled parameters such as the time period for which a sample is left at room temperature at the end of an ageing experiment before sampling oil to measure chemical markers; indeed, this waiting time could also affect the relationship between paper ageing and concentration of chemical markers in liquid due to the temperature dependent dynamics in the partitioning of these indicators during the sample cooling period.

Partitioning of chemical markers between oil and paper is a process that has been studied to support interpretation of measurements obtained from transformers-in-service [5, 6]. These studies have identified temperature as one of the main factors which affects the partitioning of chemical markers within the transformer insulation system.

Water content in oil is measured mainly due to its effect on the dielectric properties. In addition, water content in oil is used with attempt to reflect the water content in paper using equilibrium curves as water acts as a catalyst for paper ageing [7]. Partitioning of water between liquid and solid insulation is highly sensitive to temperature [6]. Furthermore, additional factors such as the ageing condition of oil and paper would also affect the solubility and hence the partitioning between them [8].

It has been proposed to use methanol to indicate the early stage of paper ageing; methanol has also been reported to be a better ageing indicator than 2-FAL for insulation systems with thermally upgraded Kraft paper [9]. Experiments have shown that the partitioning of methanol depends on temperature [6] and oil type [10].

Ethanol, which can be measured together with methanol, has been proposed as an indicator to indicate abnormal paper ageing that occurs at very high temperatures [9]. Experiments have shown that partitioning of ethanol is also temperature dependent but the effect is less pronounced than those of water and methanol [6].

2-FAL is another well-known chemical marker which has been used as a paper ageing indicator for more than three decades [4]. Investigations have shown that the effect of temperature on the partitioning of 2-FAL is considerably lower than that of water or the low molecular weight alcohols,

i.e. methanol and ethanol [6]. However, it has shown that other factors such as the water content in paper or the ageing of paper insulation could also affect the partitioning of 2-FAL between liquid and solid insulations [5].

Typically, laboratory ageing experiments are conducted at temperatures above 100 °C to increase the ageing rate and shorten the ageing duration. Once designed ageing period is reached, the aged samples are cooled down at room temperature for certain duration before sampling oil and paper to measure various chemical and physical properties. During this period the sample first undergoes a rapid temperature decrease and stays at room temperature, causing chemical markers to continuously redistribute within the solid, liquid and gas phases of the test cell. Depending on the speed of this process and the amount of migration, the concentration of the chemical markers in each phase will vary with the cooling duration. Therefore, this redistribution needs to be taken into consideration when interpreting the results of any ageing experiment. This paper investigates the effect of waiting time period on the partitioning of chemical markers, with the focus on polar chemical makers such as water, methanol and ethanol.

II. Experimental Description

A laboratory ageing experiment was conducted with inhibited mineral oil (NYTRO 10XN from Nynas), thermally upgraded Kraft paper, non-thermally upgraded pressboard, copper and core steel materials to generate chemical markers in the test cell. Table I shows the amount of each material used for the ageing experiment.

TABLE I
MATERIALS USED FOR THE AGEING EXPERIMENT

Material	Amount
Thermally upgraded Kraft paper	102 cm^3
Non-thermally upgraded pressboard	10.6 cm^3
Inhibited mineral oil	1800 cm^3
Copper sheet	95 cm^2
Core steel sheet	95 cm^2

Paper and pressboard samples were first dried at 105 °C under vacuum of less than 500 Pa for 72 hours. Next the temperature of the vacuum oven was reduced to 60 °C and oil was added into the chamber under vacuum. Samples were left inside the vacuum oven for 48 hours to allow the impregnation of paper and pressboard. The oil impregnated paper and pressboard had water content less than 0.5% (w/w). Finally, the test samples were prepared by mixing oil, oil-impregnated paper, pressboard and other materials in a 2-litre stainless-steel cell. Fig. 1 shows a sketch of the test cell. Test cell consists of a pressure-relief valve set at 68.9 kPa (10 psi) and two pipes; one connected to the headspace of the cell and the other connected into the oil. The two pipes were used to purge the cell with nitrogen and to sample oil at the end of the experiment without opening the cell. Prior to the ageing experiment test cell was purged with nitrogen and the initial pressure was set at 13.8 kPa (2 psi). Two test cells prepared according to the above procedure were aged at 150 ℃ for up to 138 days.

At the end of the experiment, cells were taken out of the oven and 30 ml of oil was sampled immediately into glass syringes from both cells before leaving them at room temperature for 336 hours (14 days). During this period oil was sampled intermittently from one cell (Cell No. 1) and at the end of 336 hours, oil was sampled from both cells. Oil was sampled from the tubing connected into the oil while pressurizing the headspace with nitrogen through the tubing connected to the headspace. It was noted that the oil temperature decreased to room temperature within the first 24 hours of the sampling period.
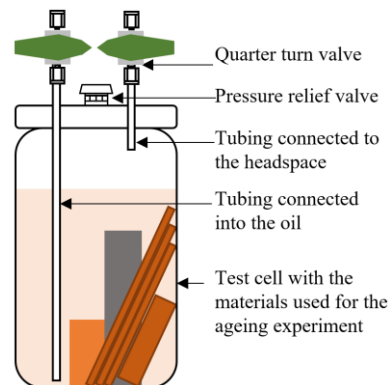

Fig. 1. Sketch of the test cell used for the ageing experiment

Water, methanol and ethanol concentrations were measured in all the oil samples obtained from the test cells. At the end of the 336-hour waiting time period, both test cells were opened and additional measurement of acidity in oil and the degree of polymerization (DP) of the paper were conducted to compare the ageing condition of the cells. Table II shows the standards / procedures used to measure the parameters of oil and paper insulation. Each chemical parameter was measured twice and the average is plotted with the error bars showing high and low values.

TABLE II
PARAMETERS MEASURED AND THE MEASUREMENT TECHNIQUE

Measurement	Standard / procedure
Water content	Evaporative stripping method according to IEC 60814
Methanol/ ethanol content	In-house method using a headspace extractor combined with a gas chromatography and a mass spectrometry unit
Acidity in oil	Potentiometric titration according to IEC 62021-1
DP of paper	Viscometric method according to IEC 60450

Table III shows the acidity in oil and the DP of paper measured in both test cells. It can be seen that paper in both cells have aged considerably compared to the oil.

TABLE III
ACIDITY IN OIL AND DEGREE OF POLYMERISATION OF PAPER

Cell number	Acidity (mg KOH/g)	Degree of polymerization
Cell 1	0.04	253
Cell 2	0.05	310

III. Experimental Results and Discussions

A. *Variation of the water content in oil*

Fig. 2 shows the variation of water content in oil over the 336-hour waiting time period. Water content in oil reduces rapidly as the sample cools down. At the end of the 336 hours, water content in oil reduced from 191 ppm to 10.5 ppm; a

reduction of more than 95%, with about 83% of the reduction occurring in the first 24 hours.
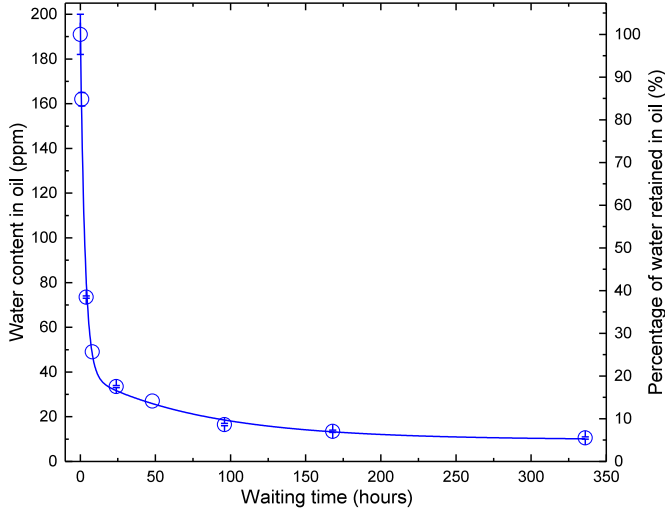

Fig. 2. Variation of the water content in oil during the cooling period

Table IV shows the water content in both cells measured at the beginning and at the end of the waiting period. There is a substantial reduction in the water content in both cells. At the beginning of the waiting time period two cells had water content of 191 ppm and 171.5 ppm, respectively. Even though the values appear to be very high, it is still justifiable considering the temperature dependency of the water solubility in mineral oil. Based on the solubility curve given in the mineral oil maintenance guide [11] water solubility of new mineral oil at 150 °C could be about 2400 ppm. Therefore, the relative water saturation level of oil in the two cells will be between 7% and 8%. However, the water solubility of oil decreases with the decrease in oil temperature resulting in an increase in the relative saturation level, which drives the water into the solid insulation. As shown in Table IV water content in all both cells has reduced by more than 86% during the waiting period. The results further confirm that water content in oil is highly dependent on the waiting time for sampling after ageing experiment ceased.

TABLE IV
WATER CONTENT IN OIL MEASURED AT THE BEGINNING AND AT THE END OF THE SAMPLING PERIOD

Cell Number	Water content in oil (ppm)		Percentage reduction (%)
	0 hours	336 hours	
Cell 1	191	10.5	94.5
Cell 2	171.5	22.5	86.9

B. Variation of methanol content in oil

Fig. 3 shows the variation of methanol content in oil against the waiting time period for sampling. Methanol content in oil reduced from 3.44 ppm to 0.99 ppm after 336 hours, a more than 70% reduction from the initial concentration. However, in contrast to water only about 13% of reduction occurred within the first 24 hours which is lower than the percentage reduction of water during the same period. This indicates that methanol migrates more slowly from oil to paper/pressboard compared with water and takes a longer time to reach equilibrium, which is in line with previous research in [10]

which claimed that methanol took more than 50 days to reach equilibrium at room temperature.
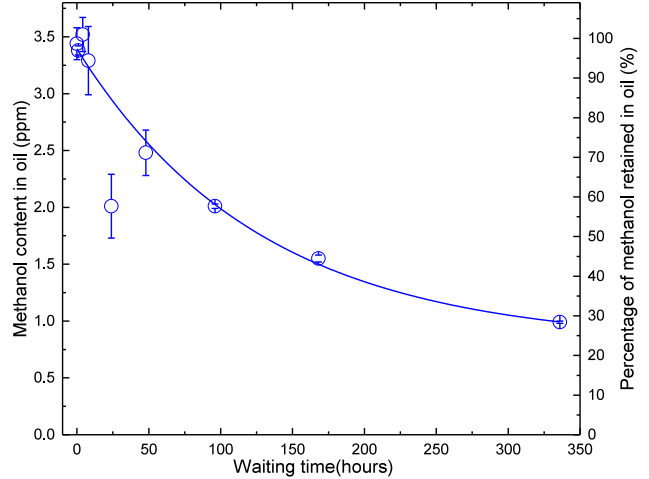

Fig. 3. Variation of the methanol content in oil during the cooling period

Table V compares the methanol content in oil measured of both test cells at the beginning and end of the waiting time period for sampling. After the 336-hour period methanol content in cell 1 and cell 2 has reduced by 71.2% and 58.7%, respectively. However, it is unlikely for methanol to reach equilibrium even after this period of time, as can be seen in Fig. 3.

TABLE V
METHANOL CONTENT IN OIL MEASURED AT THE BEGINNING AND AT THE END OF SAMPLING PERIOD

Cell Number	Methanol content in oil (ppm)		Percentage reduction (%)
	0 hours	336 hours	
Cell 1	3.44	0.99	71.2
Cell 2	2.76	1.14	58.7

C. Variation of ethanol content in oil

Fig. 4 shows the variation of ethanol content in oil against the waiting time for sampling. During this 336-hour period ethanol content in oil decreased from 0.51 ppm to 0.4 ppm with nearly 20% reduction, which is much lower compared with the reduction of water and methanol content in oil.
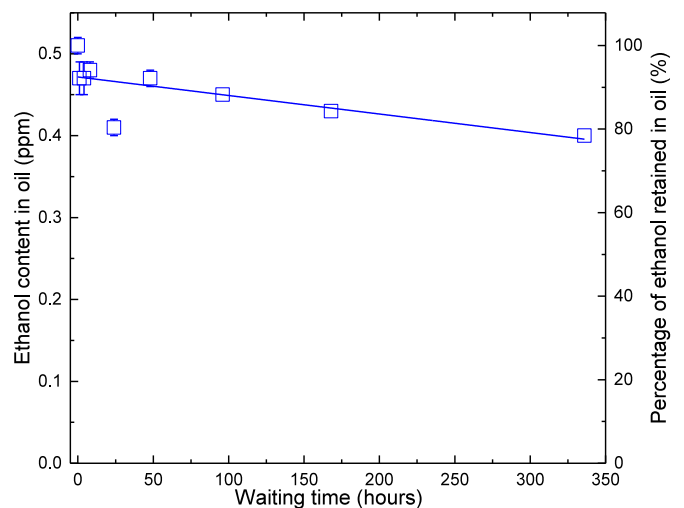

Fig. 4. Variation of ethanol content in oil during the cooling period

Table VI shows the ethanol content measured in both test cells at the beginning and at the end of the sampling period. It should be noted that these concentrations are much higher than the detection limit of 0.01 ppm. Hence, it is confident to say that the ethanol content in both test cells has reduced by about 0.1 ppm resulting in percentage reduction of 21.6% and 12.8% respectively. These results confirm that out of the investigated chemical markers partitioning of ethanol has the lowest temperature dependency.

TABLE VI
ETHANOL CONTENT IN OIL MEASURED AT THE BEGINNING AND AT THE END OF SAMPLING PERIOD

Cell Number	Ethanol content in oil (ppm)		Percentage reduction (%)
	0 hours	336 hours	
Cell 1	0.51	0.4	21.6
Cell 2	0.86	0.75	12.8

D.   Comparison between the percentage reduction of chemical marker concentration in oil during the waiting time for sampling

Fig. 5 shows the average percentage reduction of the chemical marker concentration in oil obtained from both test cells during the 336-hour waiting time period. Water content in oil, with about 91% reduction, has shown the largest percentage reduction followed by methanol (65% reduction) and ethanol (17% reduction).

Even though both samples were prepared and aged under similar conditions, it can be seen that there is still a difference in terms of both absolute and percentage reduction in the chemical marker concentration values between the two cells. Apart from the difference between their initial chemical marker concentrations, variations in the oil to paper ratio during the sampling period could have also contributed to the difference between two test cells. It should be noted that due to oil sampling, oil amount in both cells was less than the initial amount of 1800 ml. However due to the continuous oil sampling process, oil in cell 1 was nearly 210 ml lower than that in cell 2, which cause the oil to paper ratio of cell 1 to be different from that of cell 2.
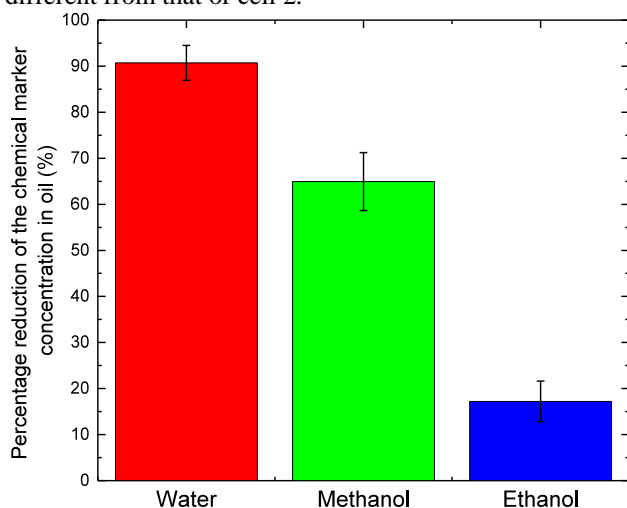

Fig. 5. Percentage reduction of the chemical marker concentration in oil at the end of 336-hour waiting period

IV. Conclusion

This paper investigates the effect of waiting time for sampling on the concentration of chemical markers in oil measured after laboratory ageing experiments of transformer oil and paper insulations. Test cells with solid and liquid insulation, after ageing experiments at a high temperature; were left at room temperature while the concentrations of the chemical markers were monitored. Results showed that the concentration of chemical markers reduces during this period of waiting time due to their temperature and time dependent partitioning within the insulation system. Water content in oil showed the largest percentage of reduction followed by methanol and ethanol. Results confirm that waiting time for sampling is an important factor which contributes to the variations in the ageing experiment results published in research literature and 'when to sample' needs to be addressed for the laboratory ageing experiments.

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