PARAMETERS AFFECTING THE FORMATION OF CORROSIVE SULPHIDE DEPOSITION ON COPPER CONDUCTORS

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Abstract: It is widely accepted that the problem of copper sulphide deposition is source of corrosive sulphur, time, oxygen access and temperature dependent. Which of these factors has the most influential impact on copper sulphide deposition? To address this concern, a quantitative laboratory investigation was performed. In this contribution, a series of experiments have been performed according to ASTM D 1275 B. To simulate the impact of different parameters (oxygen, temperature and time) on our samples of copper, various scenarios were considered. First of all, the impact of each parameter was individually simulated. In the second approach, the combined impact of these parameters was simulated when partnered. The results obtained from the measurements show that the process is accelerated when time and aggressiveness of oxygen are partnered.

1 INTRODUCTION

Power transformers are critical, highly loaded and expensive part of the electricity generation and distribution network. The potential consequences of transformer failure can be quite damaging [1-2]. In recent years, several failures of transformers and reactors due to copper sulphide formation in the cellulose insulation have been reported worldwide. The most common reason for such failures is arcing between adjacent disks or conductors of winding, due to the formation of copper sulphide deposition on the cellulosic insulating paper. This is an important concern for transformer owners, given the consequences it generates. The replacement of corroded materials is for the industry, a very high financial concern that must be added the shortfall related to the halt, time needed for repairs. Many test methods have been developed to study the problem. Recent experience has shown that the present standard methods are not accurate enough in detecting corrosive sulphur. These methods mainly provide information on the qualitative aspect of sulphur deposition on the conductors. Indeed, these undesirable sulphur compounds can be detected by observing the effect of insulating oil on copper surfaces. This is a qualitative criterion comparing the color of the copper strip with color standards, described in a table indicating what is corrosive or non corrosive. This qualitative method cannot truly inform about the corrosion of copper since the total amount of sulphur that is allowed in most of electrical grades of copper used in electrical equipment is 15 ppm or less [3]. Knowledge of the permissible value of sulphur on copper conductor is very important. This paper documents a series of experiments, determining the total sulphur content on copper conductors. The influence of oxygen, time and temperature) is also emphasized and discussed.

2 BACKGROUND AND LITERATURE REVIEW

Scientifically, corrosive sulphur is defined as elemental sulphur and thermally unstable compounds in electrical insulating oil that can cause corrosion of certain metals such as copper and silver [4]. Sulphur is commonly found in crude oil. There are five basic groups of sulphur and sulphur compounds found in crude oil such as [3]: elemental sulphur (S), mercaptans (R-SH), sulphides (R-S-R'), disulfides (R-S●S-R) and thiophenes. Corrosive sulphur is not unique to transformer mineral oils. Materials used in electric apparatus or to fill electric apparatus with oil may contain sulphur compounds, some of which may be corrosive. This includes the gaskets, some water-based glues, copper and paper insulation [5]. Sulphur can also be introduced into the transformer through accidental means such as through the use of incompatible hoses [3]. According to [6], the following reaction sequences lead to the formation of copper sulphide:

- oil dissolves the copper oxide;
- dissolved copper reacts with the mercaptans to form soluble copper mercaptide in oil;
- mercaptides copper are transported by the oil and decompose (under favorable conditions) to form Cu_2S and a residual organic soluble in oil.

The main reactions can be represented as follows:

$$Cu_2O + 2\,RSH \rightarrow 2\,CuSR + H_2O$$

$$2\,CuSR \rightarrow Cu_2S + RSR$$

where RSH is a mercaptan and R any alkyl or other hydrocarbon radical.
Corrosive sulphur affects not only adversely the conductor material and other metal surfaces but may have also drastic effects on paper insulation. Copper sulphide reduces electrical strength of conductor insulation. Copper sulphide deposits produce a low resistance path across and through the cellulose insulation and can lead to internal discharges and flashover. Several techniques are used to address the problem. Mostly used in north America is: ASTM D 1275 B for bare copper effects, Covered Conductor Deposition (CCD) for propensity to form deposits in paper (with sealed and air breathing tubes), and Dibenzyl Disulfide (DBDS) a compound which is considered as a potential contributor to corrosive sulphur failures.

3 EXPERIMENTAL INVESTIGATIONS

The investigations were performed using a 250 ml narrow-mouth glass, a copper foil (99 + % pure, 0.127 to 0.254 mm in thickness), a polishing material consisting of 240-grit silicon carbide paper. The experimental procedure defined in ASTM Test Method D 1275 B was used. 250 ml of non-filtered oil is added to a flask with glass stopper with an abraded and polished copper strip (6 mm x 25 mm). Before adding in flask, copper strip is previously bent in V. The oil is sparged with dry nitrogen for 1 minute, sealed and aged for 48 hours at 150°C. Figure 1 shows the sample ready to be put in the oven.

Figure 1: Copper strip in oil.

3.1 Simulation of parameter impacts

To simulate the impact of different parameters (oxygen, temperature and time) on our samples of copper, various scenarios were considered. First of all, the impact of each parameter was individually simulated. In the second approach, the combined impact of these parameters was simulated when partnered.

3.1.1 The impact of each parameter

- Impact of dissolved oxygen

Three oils (of the same brand) conditioned with 4259 ppm, 17169 ppm and 45018 ppm of oxygen content were used. These oxygen contents were obtained by degassing the oil sample. Determination of oxygen content was performed with the gas chromatograph (GC-2014) manufactured by Shimadzu. The values of oxygen content were selected bearing in mind that the content of dissolved oxygen in an oil sample, taken from the tank of a freely breathing transformer, shows values between 5,000 and 40,000 ppm [7]. Samples of copper were aged during a period of 48 hours at 150°C.

- Impact of time

Only service-aged oil having 4259 ppm of oxygen was used. Samples of copper were aged at different durations (48 h, 96 h, 168 h), at 150°C.

- Impact of temperature

Samples of copper were aged at different temperatures (70°C, 115°C, 150°C) during 48 h. Service-aged oil sample with 4259 ppm of oxygen was used.

3.1.2 The combined impact of parameters

- Combined impact of oxygen and time

Samples of copper were aged at different aging times (48 h, 96 h, 168 h), at 150°C. Oil with 45018 ppm of oxygen is used.

- Combined impact of time and temperature

Oil with 45,018 ppm of oxygen is used. Samples of copper were aged at different durations and temperatures:

$$(48\text{ h}, 96\text{ h}, 168\text{ h}) \otimes (70°\text{C}, 115°\text{C}, 150°\text{C})$$

This crossing means that for each aging time, sample of copper was aged at different temperatures (70°C, 115°C, 150°C).

- Combined impact of oxygen and temperature

Samples of copper were aged at different temperatures (70°C, 115°C, 150°C) during 48 h. Oil with 45,018 ppm of oxygen was used.

3.2 Determination of sulphur on the conductors

Total sulphur analysis is performed with the EMIA-220V induction furnace (Figure 2) from HORIBA which uses the high-frequency furnace method, based on infrared light absorption during combustion in an oxygen flow. The sample is mixed with accelerators (Fe, Sn, W) and put into a porcelain crucible which is heated in the induction furnace. The sample reacts with the oxygen flow, causing carbon to transform into CO_2 and CO and sulphur into SO_2. During analysis, water can be released (H_2O or H_2) and, since it is considered a contaminant, is eliminated by dehydratation with magnesium perchlorate ($Mg(ClO_4)_2$). The oxygen flow is then regularized and passes through an infrared detector. The sulphur concentration is measured with CO, CO_2 and SO_2 detector. Figure 3 shows the operating diagram.

Figure 2: Model EMIA 220 V induction furnace

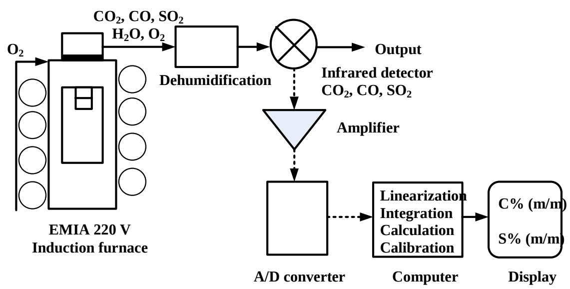


Figure 3: EMIA 220 V operating diagram.

4 RESULTS AND DISCUSSIONS

4.1 Qualitative Analysis

Figure 4 shows the ASTM copper strip corrosion standard used to evaluate the corrosion of copper conductor.

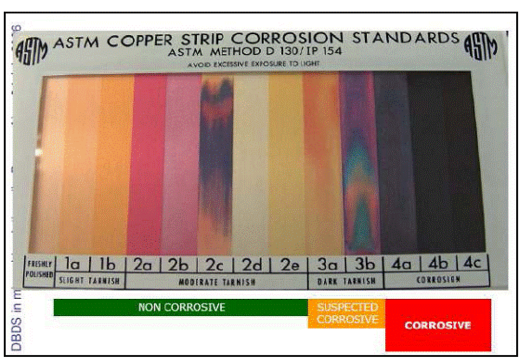
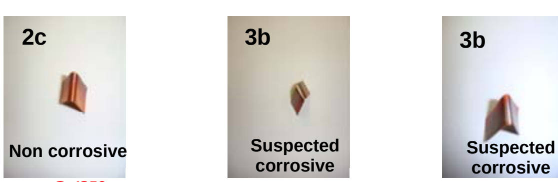


Figure 4: ASTM Copper strip corrosion standard [8].



Oxygen @ 4259 ppm
Time @ 48 h
Temperature @ 150 °C

Oxygen @ 17169 ppm
Time @ 48 h
Temperature @ 150 °C

Oxygen @ 45018 ppm
Time @ 48 h
Temperature @ 150 °C

Figure 5: Impact of oxygen.

Oxygen @ 4259 ppm
Time @ 48 h
Temperature @ 150 °C

Oxygen @ 4259 ppm
Time @ 96 h
Temperature @ 150 °C

Oxygen @ 4259 ppm
Time @ 168 h
Temperature @ 150 °C

Figure 6: Impact of time.

Oxygen @ 4259 ppm
Time @ 48 h
Temperature @ 70 °C

Oxygen @ 4259 ppm
Time @ 48 h
Temperature @ 115 °C

Oxygen @ 4259 ppm
Time @ 48 h
Temperature @ 150 °C

Figure 7: Impact of temperature.

Figures 5, 6 and 7 show the quality of copper strip for different impacts by using ASTM Copper Strip Corrosion Standard. Out these Figures, it can be seen that only sample of copper were corroded with the impact of time and temperature. No corrosion of copper is found in the impact of temperature.

4.2 Quantitative Analysis

The sulphur content determined for the new copper by the EMIA 220 V is 2.3 ppm. Figures 8, 9 and 10 show the sulphur content for different impacts. They can be accommodated in the same graph (Figure 11) for a better comparison.
Analyses of these results (Figures 8 to 11), indicate the increase of sulphur content. Sulphur content increases with oxygen content indicating the harmful character of oxygen in power transformer. At low temperatures (<115°C) (Figure 10) sulphur content deposited on the copper conductor is not a reason for concern since their amount does not exceed the acceptable limit sulphur in copper (≈ 15 ppm). She becomes to be significant from 150°C. Experience has shown that non-corrosive sulphur can becomes corrosive after being exposed to elevated temperatures [3]. High sulphur contents are observed for the impact of time and that of oxygen. It is noted for oxygen @ 4,259 ppm (Figure 8), an amount sulphur equal to 30.3 ppm is about two times the amount of sulphur that is allowed in most the electrical grades of copper. At this value is non-corrosive sulphur detected by the qualitative method (Figure 6). This information clearly demonstrates that the qualitative method is insufficient in detecting corrosive sulphur. It can accept that there is a risk of corrosion of copper at this value of sulphur content. The results obtained for small amount of oxygen (<5,000 ppm) show that even in low oxygen environment such as that available in transformers conservator (gas blanketed, sealed

conservators), there is formation of copper sulphide. This result is in agreement with those reported in the literature [3]. The qualitative method is not accurate enough to diagnose it. In the case of the impact of time, the maximum sulphur content reached was 147.8 ppm; this is approximately 65 times higher than the value initial of sulphur.

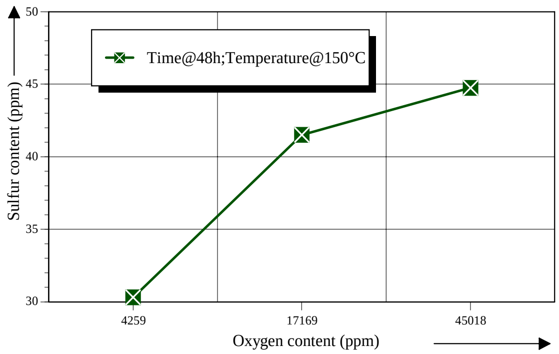


Figure 8: Sulphur content in copper: impact of oxygen.

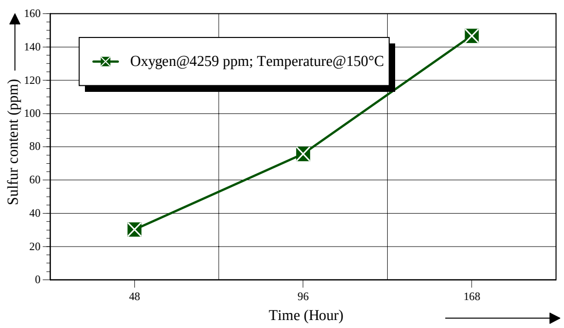


Figure 9: Sulphur content in copper: impact of time.

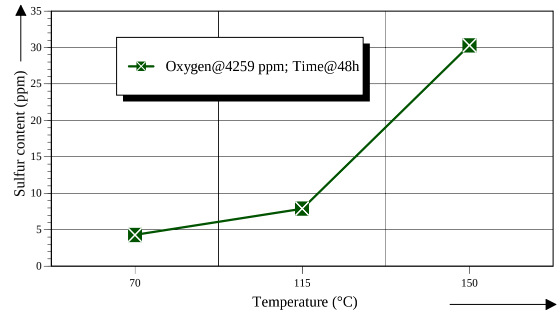


Figure 10: Sulphur content in copper: impact of temperature.

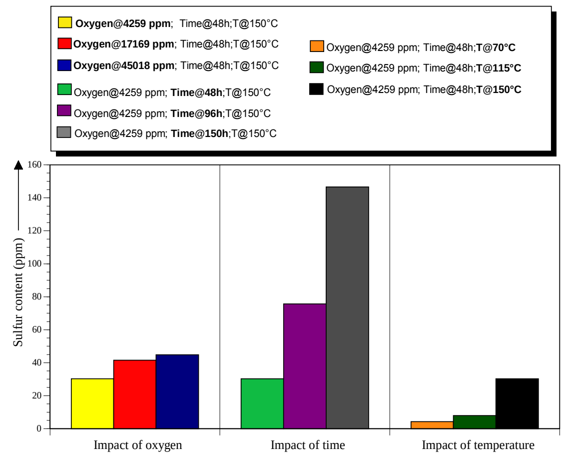


Figure 11: Comparative summary of different impacts.

Figure 12 shows a comparative summary of the combined impacts. Out this Figure, it can be seen that the sulphur deposition increases. The maximum value reached is 187.5 ppm which is about 82 times the initial value contrary to 65 times the initial value when impact is alone.

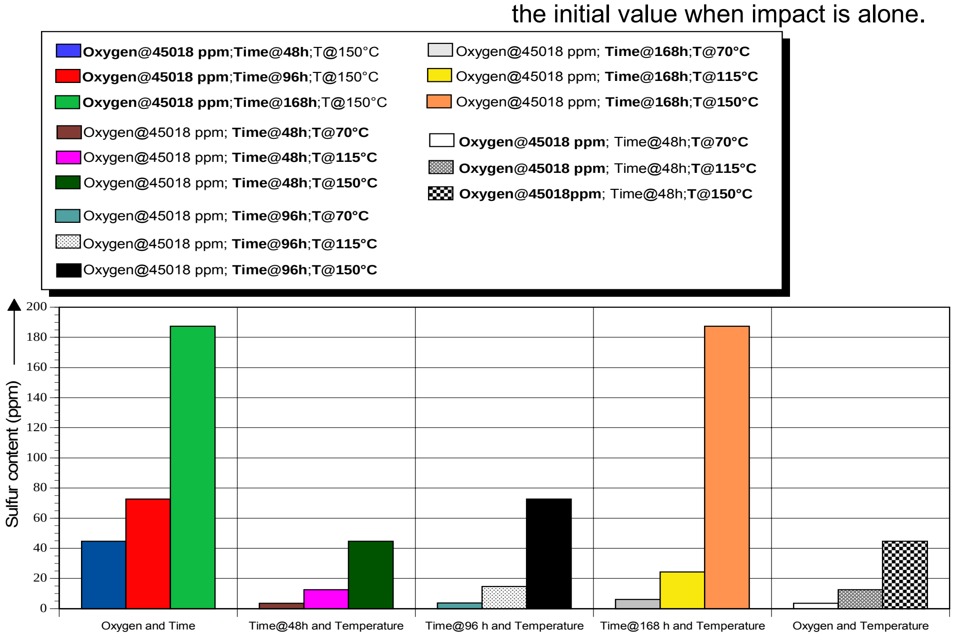


Figure 12: Comparative summary of combined impacts.

Oxygen and sulphur are in the same group of elements, i.e. having very much similar properties.

The effect of oxygen on corrosive sulphur deposition has been reason for concern these last decades. In the past, a low oxygen content of oil was considered to promote the deposition of sulphur [9]. The reason might be related to the fact that very few failures were reported in free breathing transformers.

This result indicates that the combination of impacts depicts higher contribution in the production of the corrosive sulphur on the copper conductor. For a given amount of sulphur content in oil, the combined impact of time and aggressiveness oxygen is more destructive. It is the same for impact of time and temperature, but only at high temperatures (from 150°C). At low temperatures (70°C) small amount of sulphur are produced indicating that copper is still usable. Impact of oxygen and temperature seems to be less harmful. The maximum sulphur value of sulphur deposition for this combination is 44.75 ppm, approximately 19 times the initial value.

5 CONCLUSION

Copper is a catalyst for the formation of corrosive sulphur and is also attached by it and corrodes it. Synergetic effects with temperature, time and oxygen, were recognized to play a role in the complex chemistry that results in the formation of corrosive sulphur. A study to evaluate the parameters affecting the formation of corrosive sulphide deposition on copper conductors has therefore been undertaken. A series of experiments were studied according to ASTM D1275-B. A quantitative laboratory technique was used to evaluate sulphur content on copper. Even under low oxygen content, corrosive sulphur may be formed. It is also shown that, at a given temperature, the process is accelerated when time and aggressiveness of oxygen are partnered.

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