

Sulphur corrosion in transformer insulating oils: its effects, detection methods, and mitigation strategies

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ABSTRACT

Oil-immersed transformers are subjected to electrical, thermal, and mechanical stresses over time, which inevitably affect the insulating oil and paper insulation. The presence of sulphur corrosion also degrades the insulating oil and paper insulation. Sulphur corrosion in insulating oils has been a prevalent problem for many years, as it culminates in the failure of oil-immersed transformers. The longevity of oil-immersed transformers is dependent on the integrity of the insulating oil and paper insulation, which can deteriorate owing to sulphur corrosion. The occurrence and accumulation of copper sulphide (Cu_2S) can result in transformer malfunctions, which is a significant issue for transformer manufacturers and operators. This paper provides a concise overview of the effects of sulphur corrosion, its detection methods, as well as its mitigation strategies. It is believed that this paper will enhance the understanding of sulphur corrosion in insulating oils, provide the best practices for sulphur corrosion management, and serve as guidance on enhancing transformer reliability and performance.

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1. INTRODUCTION

In general, there are two types of transformers: oil-immersed transformers and dry-type transformers. The parameters of these transformers are determined by their applications [1]. Oil-immersed transformers are used to transmit and supply electricity to electrical substations [1]–[3]. The insulating oil transfers heat from the cores and windings to the transformer's naturally or artificially cooled exterior surfaces, making it more efficient as a cooling medium than air [4]. The insulation system has two parts: primary insulation and minor insulation. The primary insulation is located between the core and low-voltage windings, between the low-voltage and high-voltage windings, and between the top and bottom of the windings. Minor insulation covers the conductors, turns, layers, laminations, joints, and connectors. Kraft paper is used to insulate these components [5], [6].

Oil-immersed transformers are severely damaged by the presence and accumulation of corrosive sulphur [7], [8]. Sulphur corrosion in insulating oil creates a low-resistance path through the paper insulation, leading to potential transformer breakdowns. Dissolved copper increases dielectric losses in the insulating oil, while copper deposition can significantly increase the conductivity of the paper insulation. To ensure the

insulating oil in large transformers and electrical equipment remains suitable for use, the electrical and chemical properties of the insulating oil are evaluated on a periodic basis. Filtration and treatment can sometimes improve the condition of the insulating oil. Corrosion-induced insulation failure can severely impact the safe and stable operation of oil-immersed transformers. Figure 1 shows the photographs of copper winding failures due to sulphur corrosion. Various factors may influence the progression of sulphur corrosion, such as the elemental sulphur concentration and ageing period [9]. Surface resistivity measurements have been conducted to investigate the effects of corrosion factors on the surface resistivity of the kraft paper, which is used to assess the occurrence of sulphur corrosion in insulating oils [10], [11].

The sulphur content of transformer mineral oils (TMOs) falls within a range of 0.001-0.500%. Sulphur is intentionally incorporated into TMOs as an antioxidant, namely dibenzyl disulphide (DBDS), to enhance the thermal stability of the TMOs [12]–[14]. Oxidation and copper dissolution are positively correlated because dissolved metal cations are potent oil oxidation catalysts. The sulphur corrosion issue was extensively debated in 1958. This is demonstrated from experiments in which the copper concentration in spontaneously oxidizing oils is measured over time [15]–[18]. In addition, various methodologies have been devised to detect sulphur corrosion in TMOs. Assessing the effects of sulphur corrosion is crucial to identifying the fundamental causes of corrosion and developing effective treatments. The development of sulphur corrosion detection techniques is essential as early detection can reduce severe damage and prolong the operational lifetime of oil-immersed transformers.



Figure 1. Failure of copper windings in oil-immersed transformers due to sulphur corrosion [9]

2. METHODS USED TO DETECT SULPHUR CORROSION IN TRANSFORMER MINERAL OILS

In the absence of overload or overheating in in-service transformers, the sulphur compounds present in the TMO can function as antioxidants. According to the IEC 60296 standard, the maximum permissible concentration of sulphur compounds in insulating oils is 5 ppm. Corrosion arises when sulphur molecules undergo a chemical reaction with the copper wires, resulting in the formation of copper sulphide (Cu_2S). The Cu_2S penetrates and degrades the paper insulation, reducing its efficacy. This eventually leads to deterioration of the coil insulation over time [19]–[21]. TMO manufacturers perform initial detection of corrosive sulphur to ensure compliance with industrial standards. The task is executed by the operators of the transformer system, who are in charge of continuously monitoring the quality of the TMO [22], [23].

Accelerated ageing tests are conducted in conjunction with adsorption treatment to determine the presence of sulphur corrosion, as shown in Figure 2. Yang *et al.* [24] investigated the effects of DBDS in insulating oil and the level of corrosion on copper after adsorption treatment. Activated alumina, molecular sieve, and silica gel effectively inhibited the degradation of the insulating oil. Figure 2(a) shows the changes in the DBDS concentration in the insulating oil after adsorption treatment. The DBDS concentration significantly decreases as the adsorption period increases, particularly for the adsorption treatment using silica gel. Silica gel reduces the DBDS concentration from 24 to 200 ppm in ~48 h. This suggests that adsorption treatment can be used to detect sulphur corrosion in insulating oil. The results indicate that the DBDS activity decreases after adsorption treatment.

According to Samarasinghe *et al.* [25], on-load tap changers (OLTCs) are a vital component used to regulate the output voltage of the transformer. The formation of silver sulphide on the OLTC tap selector is influenced by several factors, including the presence of elemental sulphur, moisture levels, and oxygen concentration in the insulating oil. Even at low concentrations, elemental sulphur is highly corrosive to silver, and the risk of corrosion increases with higher moisture content [26], [27]. The OLTC can fail due to the build-up of silver sulphide. Corrosive sulphur compounds such as elemental sulphur, mercaptans, and disulphides react with the silver coating on the surface of the OLTC tap selector. Figure 2(b) shows the silver

atomic percentage for sample A (indicating only silver) and sample C (indicating both silver and copper). Based on the results, it can be deduced that the rate of silver sulphide deposition increases in the presence of copper. Scanning electron microscopy-energy-dispersive x-ray (SEM–EDX) spectroscopy reveals the formation of silver sulphide, as shown in Figures 3, where copper sulphide on copper surfaces is shown in Figure 3(a), silver sulphide (clump formation) is shown in Figure 3(b), silver sulphide (dendrite formation) is shown in Figure 3(c), and flakes of silver sulphide is shown in Figure 3(d). During the OLTC operation, the silver sulphide layer is exposed to compressive and frictional forces, causing flakes to detach and mix with the insulating oil.

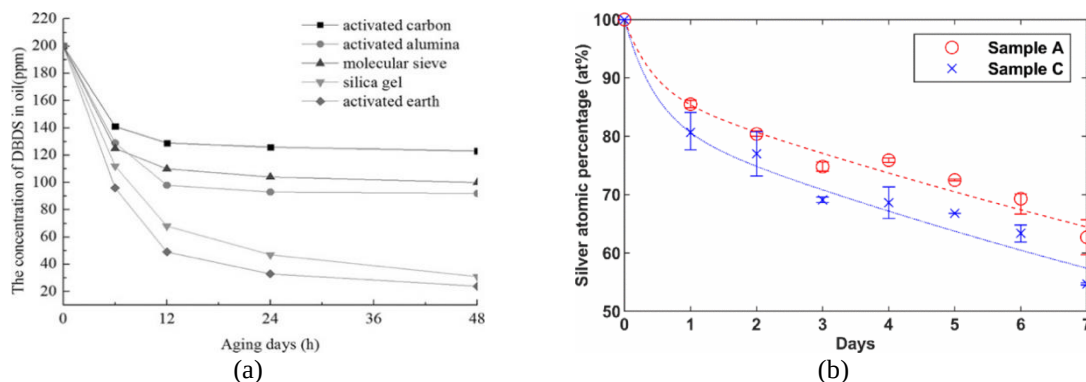


Figure 2. Tracking corrosion activity in transformer oil of (a) concentrations of DBDS in the insulating oil after adsorption treatment [24] and (b) atomic percentage of silver-on-silver metal strips obtained from SEM–EDX spectroscopy [25]

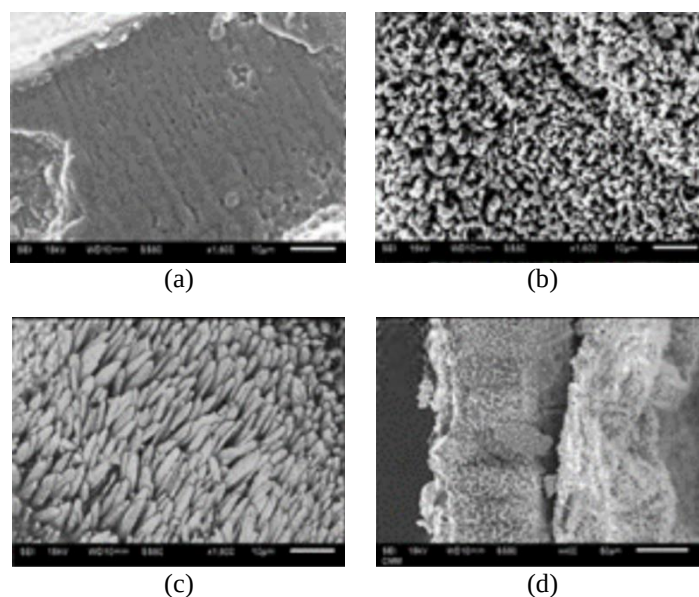


Figure 3. Analyzing corrosion on OLTC by using SEM–EDX spectroscopy of (a) Cu_2S on copper surfaces, (b) silver sulphide (clump formation), (c) silver sulphide (dendrite formation), and (d) flakes of silver sulphide [25]

3. EXPERIMENTAL STUDIES ON SULPHUR CORROSION IN TRANSFORMER MINERAL OILS

Many experimental studies have been carried out regarding sulphur corrosion in oil-immersed transformers [28], [29]. These studies collectively focus on the effects of sulphur compounds on transformer components, such as copper corrosion, insulation degradation, and formation of corrosive by-products, as shown in Figure 4. The role of environmental factors (such as temperature), interactions between different additives, and efficiency of various detection and prevention techniques were also explored. Based on the

study by Jaber *et al.* [30], qualitative measurements were conducted according to the IEC 62535 standard, and quantitative measurements were performed using liquid–liquid extraction pre-treatment and gas chromatography–high-performance liquid chromatography (GC/HPLC) to investigate the effects of using antioxidants 2,6-Di-tert-butyl-p-cresol (DBPC) and 2,6-Di-tert-butyl phenol (DBP) combined with a metal passivator benzotriazole (BTA) and corrosive sulphur DBDS [31]. The results were compared with those of the new TMO according to the IEC 60296 standard. The samples were aged at 150 °C over a period of 5 days. For each accelerated ageing interval, the liquid-liquid extraction process appeared to remove any additives that remain in the TMO, and it is sensitive to fractions as low as 1 mg/L [31], [32]. Figure 4(a) shows the concentration of dissolved copper with respect to the heating time over a period of 500 h. It is evident that the concentration of dissolved copper in the additive-free insulating oil (without metal passivator) shows a marked increase with respect to the heating time.

Studies have also explored the use of highly selective adsorbents (HSA) to remove elemental sulphur [33]. A kinetic model was used to explore the sorption mechanism and potential rate-controlling steps such as mass transport and chemical reaction processes [34]. The process involves modifying the raw material by combining it with HSA. This includes impregnating the raw material with silver ions on a silicon dioxide substrate, using an aqueous solution containing ammonia as a complexing agent [35]. The experimental results showed that the adsorbent could significantly reduce the presence of elemental sulphur and corrosive sulphur compounds (including DBDS) from the insulating oil. This ensures the oil retains its desirable qualities after treatment, making it suitable for reuse in power transformers. The purpose is to verify the efficiency of HSA in removing elemental sulphur from the insulating oil, better simulate on-site conditions, and assess the overall performance.

In 2012, an abnormal dielectric loss (110 kV) occurred successively [36], [37]. The sulphur corrosion experiments were performed on a bushing model at 130 °C for different DBDS concentrations over a period of 40 days [38]. The aim of this study was to replicate a real-life bushing model by tightly winding a copper rod with five layers of paper insulation and one layer of aluminium foil. To secure the windings, the copper rod was wrapped with two layers of aluminium foil and secured with a cotton thread. The experiments involved three sequential steps. First, the paper insulation and TMO were dried at 90 °C and 50 Pa for 48 h. Second, DBDS was added into the TMO at different concentrations, the TMO and paper insulation were mixed and placed in containers at 40 °C and 50 Pa for 24 h. Finally, the containers were hermetically sealed and placed in a vacuum chamber at 130 °C and 50 Pa for 7–40 days.

Dissolved oxygen and copper play a critical role in the formation of Cu_2S . Since Cu_2S is produced from the reaction between copper and DBDS, a higher oxygen content can accelerate its deposition on transformer components [20], [39]. Figure 4(b) shows the effects of atmospheric conditions on copper deposition in the insulating oil. No changes were observed during the accelerated thermal ageing test at 140 °C. The model consisted of two coil windings, each with a length, thickness, and width of 16, 0.2, and 1.4 cm, respectively. The coil winding was divided into three sections, where the first section was a straight piece measuring 10 cm, and the second section was a 3 cm bent portion, forming an angle of 30° with respect to the horizontal [40].

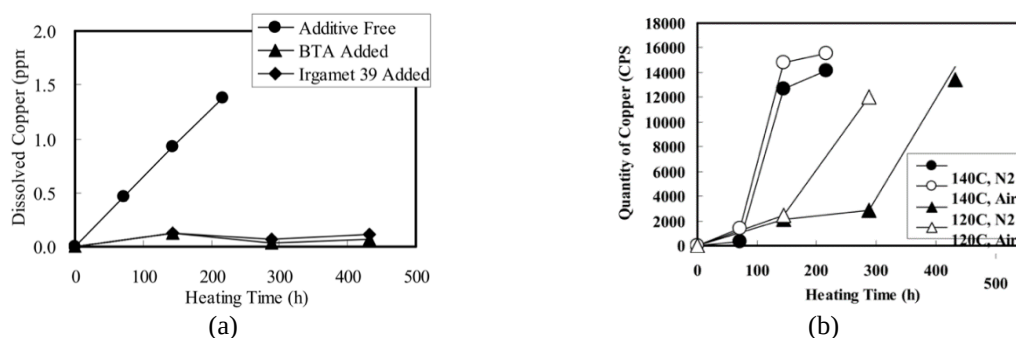


Figure 4. Monitoring corrosion activity in transformer oil of (a) progression of dissolved copper levels in response to air exposure [32] and (b) effects of atmospheric conditions on the Cu_2S deposition [39]

4. SUPPRESSION OF SULPHUR CORROSION USING METAL PASSIVATOR

The implementation of best practices is known to effectively mitigate sulphur corrosion; however, it is imperative to optimise the associated costs while ensuring that the reliability of transformers remains high [41]–[43]. Metal passivator serves as a sulphur corrosion inhibitor, where the metal passivator forms a protective film on the metal surface and protects it from sulphur corrosion. Although metal passivators are

used to protect metal components from corrosive environments, they do not remove corrosive sulphur compounds already present in the insulating oil. The use of metal passivators facilitates decelerating the progression of sulphur corrosion. However, metal passivators do not stop sulphur corrosion entirely. The amount of metal passivator in the insulating oil decreases over time as it reacts with copper surfaces and degrades due to heat and oxygen [44], [45]. Table 1 summarizes the types of metal passivators used by other researchers and their effectiveness in inhibiting sulfur corrosion.

Table 1. Studies on the effectiveness of metal passivators in inhibiting sulphur corrosion

Type of metal passivator	Concentration	Findings
BTA	20-100 ppm	The effects of BTA were studied, where accelerated thermal ageing was conducted on the oil–paper insulation with and without BTA at a temperature of 130 °C [46]. The BTA concentration in the insulating oil was 100 ppm; however, a BTA concentration of 50 ppm ensures the safety of the oil-immersed transformer. The weights of the BTA to produce a BTA concentration of 100 and 200 ppm were measured to be 0.0885 and 0.177 g, respectively. One litre of TMO was used for the samples with and without BTA in order to perform comparative experiments [32], [47], [48].
Irgamet 39	100 ppm	Experiments were conducted to investigate the effects of adding 100 ppm of Irgamet 39 on the mitigation of sulphur corrosion [41], [49], [50]. The paper insulation and copper conductors were mixed with the insulating oil with and without a metal passivator, and the samples were exposed to a temperature of 140 °C for 1,400 h. The main purpose of these studies was to determine the maximum acceptable quantities of DBDS and mercaptans in the insulating oil before the insulating oil was used in in-service transformers.
Irgamet 30	100-300 ppm	A new additive (Irgamet 30) was discovered in recent years, which has a similar structure to Irgamet 39. The efficacy of Irgamet 30 on the oxidation stability and sulphur corrosion of insulating oil was investigated, and the results were compared with those obtained using Irgamet 39. The following conclusions were drawn. Irgamet 30 functions as a metal deactivator in the insulating oil, which prevents the oil from oxidising and improves the oxidation stability of the insulating oil. However, unlike Irgamet 39, Irgamet 30 did not provide any protection for copper surfaces. Due to its inability to function as a metal passivator in insulating oil, this undisclosed substance cannot generate protective layers on copper surfaces [51].
Extreme pressure additives (RC 8210, RC 4220)	0-1.0 wt.%	Extreme pressure additives form protective layers over surfaces when there is high friction. The additives include chlorine, sulphur, and phosphorous compounds that react tribochemically with metal surfaces throughout mechanical interactions. The sulphur in the extreme pressure additives reacts with the metal, forming a tribofilm that improves the wear and friction behaviour of the metal component [52], [53]. The solubility of sulphur present in the TMO is limited due to the addition of extreme pressure additives, where the additive concentration should be kept within a range of 0.25-1 wt.%. Even at the lowest concentration (0.25 wt.%), the copper strip showed discolouration, with different levels of tarnish [54]. Further experiments were carried out by adding corrosion inhibitors at different concentrations, ranging from 25 to 200 ppm. The results revealed that the Irgamet 39 and RC 8210 were effective at a concentration of 25 ppm.

5. CONCLUSION

To date, sulphur corrosion is the well-known cause of transformer insulation system failures. The rapid progression of sulphur corrosion in oil-immersed transformers needs to be examined. In this paper, a brief overview is provided on the methods used to detect sulphur corrosion, experimental studies related to sulphur corrosion in TMOs, and the use of metal passivators in inhibiting sulphur corrosion in TMOs. The findings provide insight into the major impact of sulphur corrosion on the performance of TMOs as well as the feasibility of various metal passivators in mitigating sulphur corrosion.

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AUTHOR CONTRIBUTIONS STATEMENT

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Name of Author	C	M	So	Va	Fo	I	R	D	O	E	Vi	Su	P	Fu
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C : Conceptualization

M : Methodology

So : Software

Va : Validation

Fo : Formal analysis

I : Investigation

R : Resources

D : Data Curation

O : Writing - Original Draft

E : Writing - Review & Editing

Vi : Visualization

Su : Supervision

P : Project administration

Fu : Funding acquisition

CONFLICT OF INTEREST STATEMENT

Authors state no conflict of interest.

DATA AVAILABILITY

Data availability is not applicable to this paper as no new data were created or analyzed in this study.

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