Abstract

Metallic corrosion is a serious problem affecting electrical industry. Corrosion is the deterioration of the material by chemical interaction with their environment. There are many consequences of corrosion and the effects of corrosion by-products on the safety, reliability and efficient operation of the electrical equipment are often very challenging.

Power industry uses different Power apparatus like Power and distribution transformers and shunt reactors which use mineral insulating oil for electrical insulation as well as to cool the apparatus and prevent the core and the winding from direct exposure to atmosphere. The mineral insulating oil present in transformers basically performs the two functions. It acts primarily as an electrical insulator and performs the role of a coolant to maintain the temperature of the transformer as a whole, within reasonable limits.

Transformers have a very long service life and hence the mineral oil used in them is required to sustain its properties over long periods, not allowing any chemical reactions to take place in the insulation system. Oxidation and copper corrosion are the major problems in transformer oil insulation which may results in deterioration of transformer insulation which ultimately leads to breakdown of transformers. The chemistry of transformer oil is very complex since they are driven by electro-chemical processes.

In typical transformer insulation, oxidation of mineral oil can be easily controlled by the addition of antioxidants whereas diagnosis and mitigation of copper corrosion is a challenging task for both chemists and Power engineers.

Power transformers are very important assets of Power transmission companies. Any adverse effect on transformer causes huge economic losses to the company and inconvenience to the society. Hence maintenance of transformers and extension of their useful life of beyond their normal life is very important to the Power utilities. Repairing or replacing the transformer matters both in terms of cost and time. Hence great care is exercised in maintaining the health of transformer insulation. Paper-oil insulation is the heart of transformers and there are many factors which affect the life of insulation. These
include oxidation, moisture, ageing due to thermal and electrical stresses etc., in addition to formation of copper sulphide due to corrosive sulphur compounds in oil.

In the last decade, a number of failures of power transformers and reactors have taken place due to formation of copper sulfide on conductors and insulating materials. A number of transformers have been affected by corrosive sulphur mainly due to the presence of Dibenzyl-disulfide (DBDS), which is basically added to improve the oxidation stability. The conductive copper sulfide reduces the electrical strength of the insulation system. Therefore the problem of copper corrosion due to sulphur is of significance and there is a need to understand the processes leading sulphur corrosion of copper and then attempt to successfully control corrosion by understanding the chemistry of copper sulphide formation. This has to be followed with development and deployment of sensitive methods for detection of sulphur compounds. In the majority of transformer failures reported, the identified mechanism for failure was arcing between adjacent disks of conductors of winding due to formation of deposits of copper-containing materials on cellulosic insulating paper. Copper corrosion in oil is a highly complex phenomenon which is not yet fully understood. It has been suggested that the certain organic sulphur compounds in oil cause copper corrosion.

The primary effect of the corrosive sulphur species in mineral oil is the formation of copper sulfide on the surface of copper conductors and its subsequent migration through many layers of insulating paper, both of which lead to electrical faults. The former may produce conductive particles of copper sulfide which detach from the conductor surface to become the focal point for electrical discharge and gas generation. The latter causes the progressive degradation of the dielectric properties of the insulating paper, leading to short circuit failures. Hence early detection of sulphur compounds and development of techniques to mitigate their formation is very crucial for safe working of transformers.

To understand in depth the basics of the problems of copper corrosion in electrical apparatus which use mineral insulating oils, an exhaustive survey of literature was carried out to understand the fundamental processes involved and to identify the gaps in the understanding of mechanism of copper corrosion. It was also intended to
study the various mitigation techniques and analyse their merits and limitation so that alternative techniques can be evolved.

A critical survey of literature revealed that Corrosion of copper conductors is one of the major problems affecting the performance of power transformers. Reaction of sulphur compounds from oil on copper conductors in transformers leads to the formation of copper sulphide which degrades both the oil and paper insulation. Dibenzyl disulphide (DBDS) is observed to be a major sulphur source in oil which undergoes thermal degradation finally leading to copper corrosion. Literature survey reveals that:

- Temperature is the main factor leading to the formation of copper sulphide
- Among chemical methods, determination of total sulphur, mercaptan sulphur, DBDS and oil acidity are promising methods for understanding the chemistry of the processes involved.
- Copper corrosion phenomenon is predominantly observed at temperatures of 90 to 150°C
- Liquid-liquid extraction is observed to be promising method for the removal of sulphur compounds from mineral insulating oil.

The principal goal of this research investigation is to understand the mechanism of formation of copper sulphide in presence of sulphur compounds like DBDS and 2MBT and to evolve mitigation techniques using metal passivators. Hence, studies were carried out on the mechanism of action of sulphur compounds like dibenzyl disulphide and mercaptan sulphur on copper corrosion to quantify the same in terms of their thermal degradation over a temperature range of 100 to 150 °C.

Further, the study involved understanding of the effect of initial concentrations of sulphur compounds and implications of duration of thermal ageing and the influence of the surrounding environment like air and sealed conditions during thermal ageing. These methods carried at investigation of the effects of DBDS and mercaptan sulphur in quantifiable terms on the dielectric and chemical properties of oil.

The investigation also proposes to Study, analyze and understand the mechanism of action of metal passivators or metal deactivators namely Irgamet 39 and BTA and
estimate their thermal depletion over a range of temperatures. It is also intended to understand the depletion rate of metal passivators in presence of sulphur compounds like DBDS and 2MBT, against which they are expected to protect copper conductors.

The study aims to explore the use of solvent extraction as a possible mitigation technique for copper corrosion, as a viable alternative to the use of metal deactivators or passivators. Objective of this investigation also includes the study moisture dynamics in paper oil insulation in presence of MS and DBDS since moisture is an important cellulose ageing parameter and its accumulation will be a serious threat to the life of insulation.

Mineral oil samples containing DBDS and 2MBT are thermally aged in presence of pigtail sample representing a transformer winding at different temperatures. Effects of environment on degradation of sulphur compounds are investigated. Concentration of mercaptan sulphur, DBDS and total sulphur are monitored throughout the ageing duration. Mercaptan sulphur is determined using potentiometric titrator whereas DBDS analysis is carried out using Gas chromatography- Mass Spectrometry and total sulphur is estimated using Wavelength Dispersive X-ray Fluorescence (WDXRF). Apart from these, different parameters of mineral oil such as, acid number, IFT, moisture content, dissolved copper, break down voltage, flash point are determined in the case of oil recovered from solvent extraction. The analysis of concentration passivators are analyzed using HPLC.

EDAX was used for surface analysis of copper and paper and frequency domain spectroscopy was used for studying moisture dynamics. Atomic absorption spectroscopy is used for analyzing the dissolved copper and UV-visible spectroscopy is also made used in determining oil impurities.

For better correlation of laboratory results, analysis of in-service transformers was carried out. Laboratory results are compared with the results of in-service transformers wherever possible to arrive at practical solution. This has led to the strong conclusion that role of sulphur compounds in mineral oil of transformers is very complex and it mainly depends on temperature. Degradation of DBDS is also influenced by its cleavage and reformation. These mechanisms are mainly related to temperature of thermal ageing and mineral oil characteristics. Variations in total sulphur are divergent and it is difficult
to correlate it to copper corrosion. Kinetic studies of the reaction rates involved in thermal degradation of DBDS is very complex because of many parameters involved in the process like thermal degradation of DBDS, degradation of DBDS in presence of copper which is a function of time, recombination of radicals to form DBDS which is again a time dependent parameter, formation of DBDS-Cu complex, release of copper ions in oil and formation of Cu$_2$S and its release from copper surface. However, passivation and solvent extractions are the promising techniques to prevent copper corrosion. Studies on in service transformers showed that problem of copper corrosion due to the presence of mercaptan sulphur and DBDS is not present in Indian scenario due to the use of conventional design of transformers and use of paraffinic mineral oil in preference to naphthenic oil. However, presence of DBDS in oil and compact design of higher rating transformers can lead to the formation of copper sulphide in transformers.