Corrosive Sulfur Removal from Mineral Insulating Oil by a Novel Modified Catalyst

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***Abstract*— serious failure may occur due to copper sulfide formation on the winding papers of the power transformers. In recent years many researches have been done on mechanism of corrosive sulfur formation and its sources. Metal passivation is one of the major mitigation methods but it doesn't solve the problem completely. Oil change is also a costly alternative choice. Few studies have been done on treatment methods for removing corrosive sulfur. Oil regeneration is a modern method that can reduce corrosive sulfur and Di-Benzyl Di-Sulfide (DBDS). In this study 3 oil samples with corrosive sulfur (4b) and initial DBDS concentration of 175,165 and 160 ppm were subjected to treatment by conventional fuller's earth and also a novel modified catalyst. It was found that after 3 pass of treatment with the catalyst oil is non-corrosive (3a) but in the fuller's earth case is still corrosive (4a). The 91% and 54 % reduction in DBDS was observed for the catalyst and the fuller's earth respectively. The 5 pass treatment with catalyst can reduce DBDS under detectable range while in the fuller's earth case 8 pass is required to make the oil non-corrosive. Other oil specifications like TAN, IFT, Tan δ and oxidation stability also tested and it was found that treated oil with modified catalyst give acceptable results. According to the pilot results an economic study on the oil change and oil reclamation by new modified catalyst is done. This research was done in Rude Shure Power plant (Siemens O&M Company). It seems that treatment with new modified catalyst can be a good alternative for the corrosive sulfur problem both in technical and economical aspect. The researches still is in progress.**

***Keywords*:** Corrosive Sulfur Removal, Fuller's Earth, Di-Benzyl Di-Sulfide (DBDS), Electrical Insulating Oil, Oil Regeneration, novel Modified catalyst, novel modified catalyst

I. Introduction

Power transformers are vital elements of power transmission and distribution. Many parameters are involved in reliable and robust performance of transformers. Among them sulfur and its derivate are well recognized as an oil quality parameter [1][2]. Transformer age and temperature are two important parameters which can affect the contamination rate and conversion of non-corrosive sulfur to corrosive sulfur and Cu_2S formation [3],[4]. Since more than of 89% the corrosive oils have their corrosiveness from DBDS and more than 20 ppm DBDS concentrations make the oil corrosive, DBDS is known as a key parameter in the oil.

The mechanism of failure has been demonstrated to involve conducting particles of copper sulfide, which is formed on the copper conductors and deposited upon the paper insulating tapes, rendering them partially conductive. This gives rise to enhanced dielectric losses within the affected paper tapes, leading to thermal instability and finally to a thermo-electric breakdown of the insulating system [5],[6].

Oil change can be an effective way to the problem, however, the cost may be high in this way, and there is also risk of conversion of non-corrosive sulfur to corrosive after being exposed to elevated temperature on hot metal surfaces and thus produce metal sulfides afterwards[4],[6].

Metal passivation is a well-known method to lower the risk of failure. In most cases this eliminates the formation tendency of copper sulfide [7]. But it cannot solve the problem completely, since the passivation concentration reduces during time, there is always the risk of re-contamination.

Passivation may cause another problem named "passivation induced stray gassing" which may affect transformer condition monitoring by dissolved gas analysis [8].

However, another obvious possibility to reduce the risks is to reduce the amount of the corrosive sulfur compounds in the oil. Oil regeneration or reclamation is another way to eliminate the corrosive sulfur [9]. However it was found that traditional oil reclamation is ineffective and time consuming due to high treatment cycles [10]. Researches have shown that conventional fuller's earth which is used in the oil regeneration systems can reduce corrosive sulfur and DBDS but at least a 8 cycle treatment is required to

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Figure 1: experimental pilot for oil treatment

reach to desirable standards [7],[11],[12].

Amines solutions have been widely used in the refinery industry for sulfur capturing [13]–[15]. Recently some researchers studied the grafting amine to some adsorbent like zeolite to improve the adsorption selectivity and capacity [16], [17]. Manganese oxide also has high affinity for sulfur compound adsorption [18]. It seems that by combining this two reactive sulfur demander with conventional fuller's earth, a new modified catalyst can be produce which may have better performance in the corrosive sulfur treatment.

In this study, performance of modified catalyst was compared with traditional fuller's earth in a pilot (in Rude Shure Power plant, Siemens O&M Company shown in Figure 1) . Other oil specifications also monitored in order to evaluate the novel catalyst as an alternative for corrosive sulfur treatment and also oil regeneration simultaneously.

II. Experimental

A. Material and Methods

Oil samples with corrosive sulfur and high DBDS level were obtained from 3 contaminated transformers by the help of some laboratories. The samples were all corrosive and their initial DBDS concentrations were 175,165 and 160 ppm which are named OS1, OS2 and OS3 respectively. Conventional fuller's earth which is used in the industrial oil regeneration systems was purchased from the market. All other chemicals for modification of adsorbents were procured from the Merck (purity >99%) and were used without further purification.

B. Fuller's Earth Modification

Conventional fuller's earth sample which is used in the transformer oil regeneration systems is named as the F1. In order to improve the sulfur reduction characteristic of F1 first it was washed with methanol to wipe out any organic compound in it. Then it was dried in a vacuum oven at 120 °C and 1 bar pressure for 12 hours.

F1 sample was soaked in 1 molar NaOH for 12 hours and another 12 hours in 3% (w/w) Dopamine aqua solution. Active manganese oxide was prepared as [19] and added to this solution with a 1:10 ratio. The mixture then stirred in 45 °C for 1 hour and washed with distilled water.

In order to activate the catalyst, it was treated at 450°C in furnace for 30 min. After cooling down the modified fuller's earth which is named F2 was stored for further application.

C. Oil Treatment

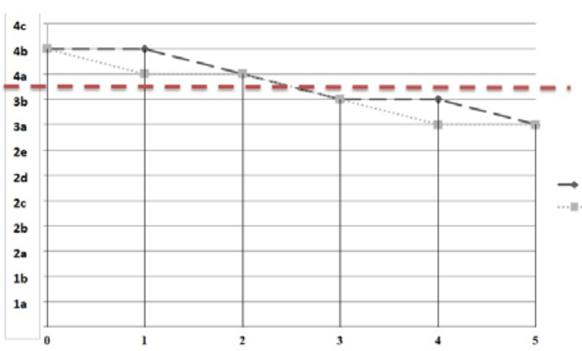

Figure 2: Effect of treatment cycle on reduction of corrosive sulfur for modified catalyst.

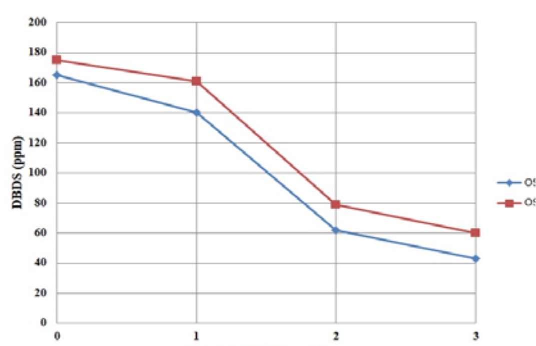

Figure 4: Reduction of DBDS VS. Treatment cycles for the conventional fuller's earth

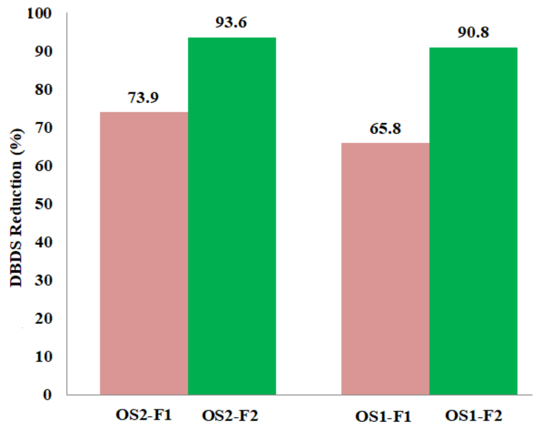

Figure 6: comparison of performance of F1 and F2 for OS1 and OS2 oil samples in DBDS reduction

In order to treat the oil samples, a pilot set up was made. Fig 1 shows this set up. The set up consist of a feed tank , an indirect heater with paraffin bath, a 1 m lengths column of fuller's earth, a trap , a 5 micron filter, treated oil tank and a vacuum pump as the driving force for moving the oil thorough the catalyst bed. Before each test the set up was disassembled and washed carefully with acetone and 1
Feed tank was filled with 2 liters of each oil sample and the paraffin bath was set on 55 °C, velocity of the oil in the catalyst bed was controlled by means of a needle valve on the vacuum pump.
In the case of multiple cycles, the column was emptied and filled again with fresh catalyst for the next oil pass.

III. RESULTS AND DISCUSSIONS

A. *Corrosive Sulfur Reduction*

Corrosive sulfur in the oil samples were measured as per ASTM D1275-b[20]. All samples have initial corrosive sulfur 4b. Conventional fuller's earth (F1) was used for treatment of OS1 and OS2. After 3 cycles of treatment for both oil samples the sulfur reduced but was still corrosive and stood at the 4a scale. OS1 after 8 cycles of treatment with and OS2 after 7 passes became none-corrosive and 3b scale. For the corrosively scale, ASTM D130 standard is used [21]. Fig 2 represents these results. Maina et al also reported at least 8 passes of treatment with fuller's earth to achieve a none-corrosive scale[5].

For the modified fuller's earth (F2), OS1 and OS3 samples used for treatment. As can be seen in Fig 3, results showed that after 3 treatment cycles, the initial corrosive sulfur of 4b reduced to non-corrosive level of 3b. It was found that after 5 passes of purification, the corrosivity of the oil reduced to 3a which is a far more better results

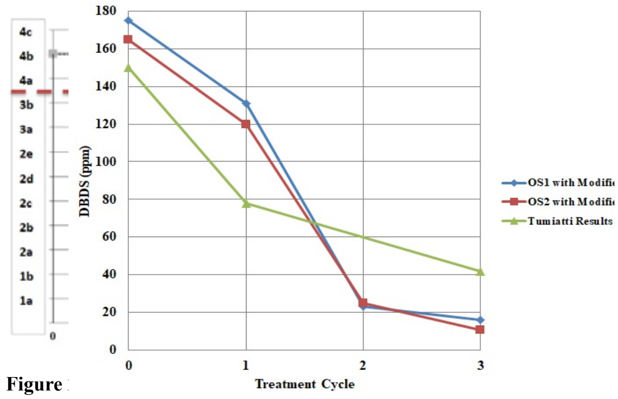

Figure
sulfur for conventional fuller's earth
Figure 5: comparison of DBDS reduction VS treatment

comparing with conventional fuller's earth. This ability in reducing the corrosive sulfur may be interpreted with manganese oxide groups on the catalyst which have high affinity for adsorption of sulfur compounds.

B. *DBDS Removal*

DBDS was measured according to IEC 62697 method. Performance of Conventional fuller's earth and modified catalyst in DBDS removal was investigated same as previous section but just in 3 cycles. Two insulating oils of OS1 and OS2 with initial DBDS concentration of 175 and 165 ppm passed from the F1. Results showed that after 3 passes DBDS is reduced to 59 and 43 ppm for OS1 and OS2 respectively. This is far from 5 ppm DBDS limit in the transformer oil[5]. Tumiatti et al found that a 10 cycle treatment with conventional fuller's earth systems is required to reduce DBDS from 150 ppm down to acceptable amounts [11]. Werle et al also reported 8 cycle treatment to reduce 60 ppm DBDS down to 5 ppm [7]. DBDS reduction trend for F1 is presented in Fig 4.
Modified catalyst showed more reasonable results. While conventional fuller's earth F1 and also reference [11] fuller's earth can finally reduce the DBDS to 40ppm in 3 cycles, the F2 catalyst reach the DBDS down to 16 ppm and 10.6 ppm for the OS1 and OS2 samples respectively. Modified catalyst and commercial fuller's earth results for DBDS reduction can be found in Fig 5. The amine grafted groups on the catalyst may have an important role in this large amount of DBDS reduction.
Performance of modified catalyst versus conventional fuller's earth for two oil samples is shown in Fig 6. As can be seen F2 catalyst has 93.6% DBDS reduction VS. 73.9 % of F1 for OS2 sample. In case of OS1 with higher initial DBDS also the F2 catalyst performance is still more than 90% while the F1 lost its performance below 66%.
Further purification cycles take place for OS1 sample with modified catalyst and it was found that after 5

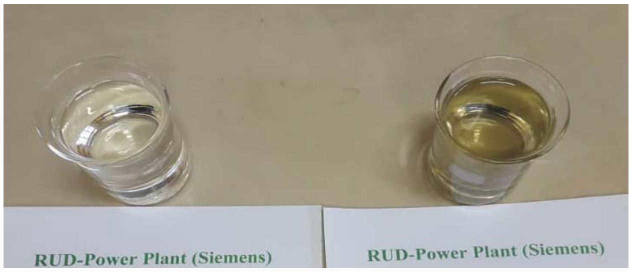

Figure 7: Right: OS3 sample with corrosive sulfur and 160 ppm DBDS Left: OS3 after treatment with modified catalyst, none corrosive and <5 ppm DBDS

passes of purification DBDS eliminated to none detectable range (<5 ppm).

C. Other Oil Specifications

In order to ensure the specification of purified oils and studying any possible negative effect due to the new modified catalyst, other oil properties were investigated. As can be seen in table 1, the most important among them Dielectric Dissipation Factor including tan δ, Resistivity and permeability, TAN, IFT and oxidation stability. It was found that the modified catalyst have more enhancement on the tan δ and resistivity than permeability. Both oil samples OS1 and OS2 after treatment with F2 gain better results in these two items while permeability stayed without significant change.

Table 1: comparison of vital oil specifications after treatment with modified catalyst and conventional fuller's earth

Results showed that oil acidity reduction doesn't have any difference in both F1 and F2 cases. This may confirm different nature of molecules which cause the oil acidity and others which stand for corrosive sulfur and the role of modification which was done on the DBDS and corrosive sulfur reduction.

OS3 sample which had an initial 160 ppm DBDS concentration was subjected to treatment with modified catalyst in order to study the effect of catalyst on oxidation stability of the oil after treatment. Fig 7 shows OS3 sample before and after treatment with the modified catalyst. These two samples were subjected to oxidation stability test as per IEC 61125 C (164 hrs.) standard [22]. After oxidation 3 parameter of TAN, tan δ and sludge were measured.

Results are shown in the table 2. Treated oil with modified catalyst produce about 59% less sludge. Its acidity increase was also 15% lower and also a 61% lower increase in tan δ after oxidation was observed comparing with the OS1 before treatment. It was found that oxidation stability of the treated oil was improved. As the OS3 was uninhibited oil, these results confirm that oil regeneration by modified catalyst can simultaneously solve the corrosive problem and enhance oil specification and also life time by removing contamination and decay products in the oil.

Table 2: Effect of treatment with modified catalyst on oxidation stability of OS1 sample.

	Oil	tan δ	Resistivity	Permeability	IFT	TAN
	type		GΩ.m		mN/m	mgKOH/g
Modified Catalyst	**OS1**	**0.0023**	**144**	**2.12**	**38.1**	**0.01**
	OS2	**0.0013**	**153**	**2.11**	**38.2**	**0.01**
Conventional Fuller's Earth	**OS1**	**0.0042**	**78**	**2.14**	**33.7**	**0.01**
	OS2	**0.0040**	**91**	**2.14**	**37.1**	**0.01**

Oxidation Stability Test

	Oil	tan δ	TAN	Sludge
	type		mg KOH/g	%
OS1 Before Treatment	**Corrosive**	**0.0501**	**0.45**	**0.133**
After treatment with Modified Catalyst	**Non-Corrosive**	**0.0195**	**0.38**	**0.054**

IV. CONCLUSION

Corrosive sulfur can cause major failures in the power transformers. Different methods like oil change, metal passivation and oil regeneration can be used as a solution. Among them oil regeneration can be a cost effective and reliable alternative but suffer from too many treatment cycle which is required to eliminate DBDS and corrosive sulfur to the acceptable standard levels [2], [11], [12], [18], [23], [24].in this study a new modified catalyst is synthesized based on grafting amine and manganese oxide groups to the commercial fuller's earth which have more affinity to the corrosive sulfur compounds. This means the modified catalyst can reduce the DBDS to safe concentration limits.

The modified catalyst could reduce DBDS by 92% while conventional fuller's earth reduced DBDS by 69 % averagely. Comparing with other researches [5], [11], [12] these results suggests that oil regeneration by new modified catalyst can be a cost effective and time saving method against commercial fuller's earth and an alternative method for solving the corrosive sulfur problem beside improving other oil specifications like TAN, dissipation factor, IFT, oxidation stability and other properties.

It is suggested that more research take place on the modification of the catalyst and make it capable to reduce the DBDS and corrosive sulfur even in lower treatment cycles.

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