

Understanding and Mitigating Corrosive Sulfur Risks in Oil-Filled Transformers

Lessons Learned from Laboratory Work and the First Field Trial

1022573

Understanding and Mitigating Corrosive Sulfur Risks in Oil-Filled Transformers

Lessons Learned from Laboratory Work and the First Field Trial

1022573

Technical Update, March 2011

EPRI Project Manager

B. Rodriguez

ELECTRIC POWER RESEARCH INSTITUTE 3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA 800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

REFERENCE HEREIN TO ANY SPECIFIC COMMERCIAL PRODUCT, PROCESS, OR SERVICE BY ITS TRADE NAME, TRADEMARK, MANUFACTURER, OR OTHERWISE, DOES NOT NECESSARILY CONSTITUTE OR IMPLY ITS ENDORSEMENT, RECOMMENDATION, OR FAVORING BY EPRI.

THE FOLLOWING ORGANIZATIONS, PREPARED THIS REPORT:

Electric Power Research Institute Powertech Labs Inc.

This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute, EPRI, and TOGETHER...SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2011 Electric Power Research Institute, Inc. All rights reserved.

ACKNOWLEDGMENTS

The following organizations prepared this report:

Electric Power Research Institute (EPRI) 1300 West W.T. Harris Blvd. Charlotte, NC 28262

Principal Investigator B. Rodriguez

Powertech Labs Inc. 12388 88th Avenue Surrey, BC V3W-7R7

Principal Investigator S. Kovacevic

This report describes research sponsored by EPRI.

EPRI acknowledges the support of the following organizations:

Detroit Edison Co. ENEL SpA. Lower Colorado River Authority National Grid UK, Ltd. New York Power Authority

This publication is a corporate document that should be cited in the literature in the following manner:

Understanding and Mitigating Corrosive Sulfur Risks in Oil-Filled Transformers: Lessons Learned from Laboratory Work and the First Field Trial. EPRI, Palo Alto, CA: 2011. 1022573.

ABSTRACT

In recent years, there have been an increasing number of documented cases of transformer failures attributed to corrosive sulfur in oil. Reports to date include failures in generator step-up (GSU) transformers, high-voltage direct current (HVDC) transformers, and shunt reactors from various designs and manufacturers with different oil sources. Most utilities see this as a serious concern because failures have occurred without prior warning and failures can not be predicted by traditional tests (for example, dissolved gas analysis). Even though oil refiners are by now well aware of the problem, it is interesting to note that several oils are still testing positive or borderline for corrosive sulfur.

In an effort to further the understanding and mitigation of corrosive sulfur risks in oil-filled transformers, the Electric Power Research Institute (EPRI) has a project that aims to answer questions such as the following:

- What are the sources of corrosive sulfur in transformers?
- What can be done to mitigate corrosive sulfur attacks?
- What measures can be taken to prevent future attacks?
- Can corrosive sulfur be removed on-line?

As part of this project, a process for removal of corrosive sulfur from oil containing dibenzyl disulfide (DBDS) was developed and evaluated. Laboratory tests have demonstrated that DBDS is the most dominant corrosive sulfur compound. However, although DBDS plays a major role in the corrosiveness of oils, it is not the only corrosive sulfur compound present. In an effort to demonstrate the feasibility of removing corrosive sulfur compounds from DBDS-free oils, a transformer was selected to perform a field test.

The objective was to attempt to demonstrate the corrosive sulfur removal capabilities from oils free of DBDS (that tested corrosive). At this stage, the preliminary results of the field test of the on-line corrosive sulfur removal unit show the oil as borderline corrosive, with ASTM 1275B confirming that progress has been made in removing unknown corrosive sulfur from this oil.

Although good progress has been made so far, there still remain many unresolved issues—in particular, the identification of specific corrosive sulfur compounds and their correlation to corrosive sulfur qualitative and quantitative testing as well as the development of noninvasive techniques to detect the presence of copper sulfide deposits in operational transformers.

Keywords

Corrosive sulfur On-line removal Dibenzyl disulfide HVDC transformers GSU transformers Shunt reactors

CONTENTS

1 INTRODUCTION1-	-1
Background1-	-1
Project Objectives1-	-2
2 LESSONS LEARNED FROM LABORATORY WORK2-	-1
Source and Identity of Potentially Corrosive Sulfur Compounds2-	-1
Corrosive Sulfur Tests—Efficiency and Reliability2-	-3
Removal of Corrosive Sulfur from Oil2-	-4
Preliminary Work2-	-4
Analysis of in Service Oils from US Utilities2-	-5
Removal of Corrosive Sulfur from Oils that Contain DBDS2-	-6
Removal of Corrosive Sulfur from Oils that Do Not Contain DBDS	-8
3 FIRST FIELD TRIAL: LESSSONS LEARNED	-1
Transformer Chosen for First Field Trial3-	-1
Results Obtained During First Field Trial3-	-2
4 CONCLUDING REMARKS4-	-1
Lessons Learned from Laboratory Work4-	-1
Lessons Learned from On-going Field Trial4-	-1
Ongoing Work4-	-2
Future Work4-	-2
5 REFERENCES	-1

1 INTRODUCTION

Background

A multitude of sulfur containing compounds is always present in crude oil. Some of the compounds are reactive while others are stable. Elemental sulfur, mercaptans and sulfides will react with the copper in the transformer system and produce copper sulfide. Disulfides are believed to be stable and non reactive although DBDS (dibenzyl disulfide) proved to be very corrosive. Thiophenes are very stable and can be beneficial as they improve the oxidation stability of the transformer oil. Generally speaking, the refining of crude oil is undertaken to remove or transform reactive sulfur compounds and to preserve the beneficial ones. Unfortunately this is not always easily achieved since the most suitable crudes used for production of insulating oils are depleted.

In recent years, there have been an increasing number of documented cases of transformer failures [1-7] attributed to corrosive sulfur in oil. Reports to date include failures in step-up transformers, HVDC transformers and shunt reactors from various designs and manufacturers with different oil sources. Most utilities see this as a serious concern since failures have occurred without prior warning and failures cannot be predicted by traditional tests (DGA and others).

The introduction of hydrotreating in the refining process around 1990 resulted in a dramatic reduction of the total sulfur content of insulating oils. The average total sulfur content dropped from approximately 3000 ppm to less than 1000 ppm [8], and in some cases even less than 100 ppm, yet at the same time the number of transformer oils testing positive for corrosive sulfur increased [9]. This also coincides with the increase in the number of transformer failures attributed to corrosive sulfur. The link between the increased amount of corrosive sulfur in newer oils and increased transformer failures is of great concern as the trend implies a continued risk for transformer failures. To complicate matters, the problem is not restricted to one source or type of oil. More than 100 large transformers and reactors have failed worldwide since 2000 due to corrosive sulfur in oil, with no advance warning.

The failure mechanism is believed to be that corrosive sulfur from the oil attacks copper components to form copper sulfides not only on the copper surface but also on and within the paper insulation, compromising the paper's dielectric integrity and eventually causing equipment failure.

Even though utilities and oil refiners are by now well aware of the problem, it is interesting to note that a number of oils introduced to the North American market are still testing positive or borderline for corrosive sulfur by ASTM D1275 B, and will likely test corrosive by either CIGRE/Siemens (now IEC 62535) or CCD-ABB teats. This indicates that oil distributors and utilities have to be very diligent before they consider buying new oil. The picture below shows the results of the new oil offered for sale in Canada that did not pass IEC 62535 corrosive sulfur test and was found to be borderline corrosive by the ASTM 1275B.



Figure 1-1

Test results from ASTM 1275B (at left) showing a borderline corrosiveness and IEC 62535 corrosive sulfur test (at right) showing corrosiveness both on the copper and on the paper for a new oil offered at the beginning of 2009.

Project Objectives

The objectives of this project are:

- Perform laboratory work that will provide the necessary information about oil(s) from selected in-service transformers and the expected efficiency of a corrosive sulfur removal process.
- DBDS is the only corrosive sulfur compound identified in most oils, and usually present in the highest amounts compared to other sulfur containing compounds. This work will try to identify any other corrosive sulfur compounds that may originate from new or used oil.
- Build prototype units and carry out field trials in order to investigate the effective removal of corrosive sulfur compounds from transformers filled with oil that has tested positive for corrosive compounds and to prove that it can be done without power outage and any interruption to the transformer operation.
- Develop an analytical technique capable of detecting and measuring sulfur compounds in oil at the oil ppm level. This fingerprinting technique could be used to monitor the progress of the removal of corrosive sulfur compounds or any changes to the sulfur fingerprint that may result from chemical transformation of non-corrosive to corrosive sulfur or contamination from other components in contact with the oil.

2 LESSONS LEARNED FROM LABORATORY WORK

Source and Identity of Potentially Corrosive Sulfur Compounds

Sulfur compounds are indigenous to oils of petroleum origin. Their amount and type in insulating oils is dependent on the type of refining process used. Typically only some organosulfur compounds are expected to remain in the processed oil. Many of them are natural oxidation inhibitors and are beneficial to oil aging; others are corrosive and detrimental to transformer internal components [3,4]. Total sulfur content is not sufficient to assess the potential towards corrosion, as many sulfur compounds are inert.

To address the above concerns, several suspect oils from different manufacturers and from inservice equipment were acquired for detailed analysis for sulfur compounds. Given that sulfur compounds are typically in the parts per million ranges and in the presence of hundreds of potentially interfering hydrocarbon compounds, traditional analytical methods were deemed inadequate for this purpose. To assist in overcoming these hurdles, research was focused on other analytical techniques, including:

- Analysis for total sulfur by inductively coupled plasma spectroscopy (ICP)
- High resolution gas chromatography equipped with an Atomic Emission Detector (GC-AED) specific for sulfur and
- Gas chromatography-mass spectrometry for compound identification

Mineral insulating oils are a complex mixture of thousands of hydrocarbon compounds not readily distinguished from each other. Interdispersed among them is a host of complex organosulfur compounds, making their identification very difficult. Figures 2-1 and 2-2 show chromatograms of insulating oils analyzed by GC-AED with the detector tuned to the sulfur wavelength. Although in this mode the instrument is highly selective for organosulfur compounds, it cannot positively identify them. This is better accomplished by GC-MS. However, as evident from Figure 2-1 this oil contains only small amounts of sulfur compounds that are inseparable from the hydrocarbons, making it difficult to identify them even by this technique.

A sample of oil from a reactor that had failed the ASTM D1275B corrosive sulfur test was subjected to a selective extraction process to concentrate the sulfur compounds. The extract was analyzed by GC-MS and the major sulfur compound as indicated in Figure 2-1 was tentatively identified as dibenzyl disulfide (DBDS) and confirmed by comparison to the MS spectrum of an authentic standard. The identity of this compound has also been confirmed by other researchers [10].





Testing oils with and without its presence confirmed the corrosive nature of dibenzyl disulfide. In laboratory tests, non-corrosive oil without a passivator was deliberately spiked with low levels of dibenzyl disulfide and tested for corrosive sulfur in accordance to ASTM D1275 Method B. In this case, the spiked oil failed the test.

Figure 2-2 shows a GC-AED chromatogram in sulfur mode, of old stock oil with a high sulfur content (~2000ppm of total sulfur), but with no detectable presence of DBDS. This oil originally passed the ASTM 1275 corrosive sulfur test.



Figure 2-2

GC-AED Chromatogram in Sulfur Mode of Mineral Insulating Oil with High Sulfur Content, Old Stock. No Detectable Presence of DBDS in this Oil.

From Figures 2-1 and 2-2 it can be concluded that total sulfur content alone is not a good indicator of potentially corrosive sulfur compounds as many sulfur compounds are inert or

beneficial [1,2,4,11-14]. Only certain sulfur compounds (these that contain reactive sulfur) are responsible for oil corrosiveness, which can be detrimental to transformer internal components [15].

Corrosive Sulfur Tests—Efficiency and Reliability

There are several industry standards used to measure the presence of corrosive sulfur in oil. For example, ASTM 1275B expose the oil to a copper strip at 150°C for 48h. IEC follows DIN 51353 in which the oil is exposed to a silver strip at 100°C for 18h. Both of these tests measure the extent of darkening on the metal strips. However, their reliability has been in question as there have been reports of cases where copper sulfide deposits were detected in transformers in which the oil had tested non-corrosive.

To address this issue, ABB developed the Covered Conductor Deposition (CCD) test that measures the presence of copper sulfide deposits both on the copper and the paper [1]. This test was designed to study the effects of corrosive sulfur at simulated transformer operating conditions. One version of this test exposed the oil to the paper covered copper strip at 140°C for 96 hours with restricted access to oxygen through a capillary tube inserted through the cap of a vial. Additionally, Siemens developed a similar test that also exposes oil to a paper covered copper conductor in a hermetically sealed vial, at 150°C for 72 hours.

After evaluating three proposed tests (ABB, Siemens and one identical to ASTM 1275B) through an international round robin test, CIGRE [4] decide to recommend the Siemens test to be adopted in Europe as an official standard. This recommendation came after the conclusion that both the copper conductor and paper need to be examined for the presence of copper sulfide to minimize the number of false negative results, since all these test are qualitative and subjective in nature.

In our review of these tests, it was also noticed that the metal passivator was consumed to a much greater degree when the test was carried out in the presence of oxygen. What is clear from the various tests (see Figure 2-3), is that classifying oils as corrosive or non-corrosive depends on the time and temperature of the test. Thus oils may be corrosive with one test but non-corrosive in another [15].

This is particularly the case when the metal passivator is added to the oil. These tests rely on the degree of discoloration of the metal surface or the paper color as an indication of corrosivity. This makes it difficult to establish accurate values and criteria for acceptance specifications and maintenance guides.





Removal of Corrosive Sulfur from Oil

Preliminary Work

This work was focused on developing methods to selectively remove corrosive sulfur compounds from oil. The first graph in Figure 2-4 shows the GC-AED chromatogram for sulfur in the corrosive oil before it was treated. There is one dominant sulfur compound (DBDS) and several minor ones. On the right side of Figure 2-4 the graph shows the GC-AED chromatogram for sulfur of the same oil following corrosive sulfur removal treatment. This treatment was capable of removing most of the dominant sulfur compound (DBDS) and the treated oil passed the corrosive sulfur test.

The treated and untreated oils were tested for corrosive sulfur using the test method proposed by Siemens/CIGRE. We can see from the picture in Figure 2-4 (right) that the treated oil shows no signs of corrosion on the copper strip or the paper whereas the untreated oil shows Cu_2S deposits on both the copper and the paper Figure 2-4, left image.

After proving that corrosive sulfur from the oil could be successfully removed, the project expanded to the evaluation of oils from US utilities. Ten in service oils from US utilities were chosen for evaluation as a part of the project.



Figure 2-4

GC_AED Chromatogram of Oil Prior to Corrosive Sulfur Removal with Images of the Copper and Paper Strips of the Siemens Corrosive Sulfur Test Before and After Corrosive Sulfur Removal.

Analysis of in Service Oils from US Utilities

Oils from ten different power equipments from US utilities were analyzed for the presence of corrosive sulfur (DBDS), presence of additives and for the relevant oil quality parameters to establish a baseline. The results of the analysis are shown in Tables 2-1 and 2-2.

Table 2-1

Oil #	Sample Name	DBDS by GC-AED (ppm)	DBDS by GC-ECD (ppm)	Total S by ICP (ppm)	Passivator (ppm)	DBPC (%)
1	NI-RM7	<3.8	<3.8	280	<1	0.073
2	CE-R2N1	165.6	156.4	438	<1	0.285
3	CE-R2N2	187.9	181.0	577	<1	0.284
4	CE-SLL	182.9	196.7	728	108	0.006
5	CE-TU	22.3	6.1	264	38	0.075
6	CE-EBG	161.7	159.1	434	<1	0.029
7	BN-T2	<3.8	<3.8	126	<1	0.091
8	G-T1	<3.8	<3.8	215	<1	0.344
9	SS-T3	<3.8	<3.8	151	<1	0.254
10	SW-T1	<3.8	<3.8	662	<1	0.315

Sulfur, Metal Passivator, and Oxidation Inhibitor Content in Oils from Ten Different Power Equipment from US Utilities (Laboratory Test Results).

From Table 2-1 it can be noted that half of the oils contain some amount of DBDS, though the amount of DBDS in oil #5 is not significant. The total sulfur content varies between 126 and 728 ppm, which is typical for newer, more refined oils. Only oils #4 and 5 are passivated. The amount of passivator in oil #4 is close to the common amount that can be found in passivated oils, while the amount of passivator in oil #5 is about half of what can be considered the typical passivator content in passivated oils. Oils # 2, 3, 8, 9, and 10 are inhibited, while the rest of the oil samples contain trace amounts of DBPC.

All of these oils were also tested for oil corrosiveness using ASTM 1275B and CCD test method. The test results are shown in Table 2-2.

Oil #	Sample Name	ASTM 1275B (150°C/48hrs)	CCD-ABB (140°C/96hrs)
1	NI-RM7	Non-Corrosive	Corrosive
2	CE-R2N1	Corrosive	Corrosive
3	CE-R2N2	Corrosive	Corrosive
4	CE-SLL	Non-Corrosive	Non-Corrosive
5	CE-TU	Non-Corrosive	Non-Corrosive
6	CE-EBG	Corrosive	Corrosive
7	BN-T2	Corrosive	Corrosive
8	G-T1	Corrosive	Corrosive
9	SS-T3	Corrosive	Corrosive
10	SW-T1	Borderline	Corrosive

Table 2-2Test Results for Oil Corrosiveness from ASTM 1275B and CCD-ABB.

Except in the case of oils #1 and #10 both of the test methods were in agreement. The ASTM test for oil #10 did not display an undoubtedly positive corrosive result while the CCD-ABB test did. Also, even though oil #10 on average has more than three times the total sulfur than any other oil, the severity of the corrosiveness on both tests was somewhat lower than that for all the other oils. These results indicate that the total amount of sulfur in the oil cannot be directly related to the corrosiveness of the oil.

Removal of Corrosive Sulfur from Oils that Contain DBDS

Since DBDS was identified as the major compound responsible for numerous transformer failures worldwide, the focus of this research first aimed to test oils that contained DBDS under laboratory conditions for their suitability for corrosive sulfur removal process.

The treated oils were analyzed by GC-AED and GC-ECD chromatography for the presence of DBDS, and tested for corrosiveness by ASTM 1275B and CCD-ABB tests. The oil quality of these oils (IFT, PF, KV, etc.), before and after the treatment, were also analyzed and compared. The test results of the oils before and after treatment for corrosive sulfur removal are presented in Table 2-3.

Table 2-3Before and After Results for Relevant Oil quality Parameters for Oils that Contained DBDS(Laboratory Test Results).

Oil #	IFT (Dynes/c m)	PF (%)	KV (kV)	Acid Number (mgKOH /g)	Color	DBP C (%)	S from DBD S (ppm)	ASTM 1275B	CCD-ABB	Oxidation Stability (min)
2	31.9	0.84	68	< 0.01	<1	0.285	43	Corrosive	Corrosive	200
2*	40.6	0.05	70	< 0.01	0.5	0.27	<1	Noncorrosive	Noncorrosive	226
3	32.1	0.18	75	< 0.01	0.5	0.291	47	Corrosive	Corrosive	216
3*	41.9	0.03	67	< 0.01	0.0	0.244	<1	Noncorrosive	Noncorrosive	225
4	37	0.03	75	0.028	0.0	0.065	51	Noncorrosive	Noncorrosive	66
4*	41.8	0.01	66	< 0.01	0.0	0.005	<1	Noncorrosive	Noncorrosive	64
5	35.6	0.85	61	< 0.01	0.5	0.082	1.6	Noncorrosive	Corrosive	175
5*	42.5	0.08	70	< 0.01	0.5	0.081	<1	Noncorrosive	Noncorrosive	171
6	24.4	0.45	58		<1	0.03	42	Corrosive	Corrosive	147
6*	41.6	0.06	66		0.5	0.03	<1	Noncorrosive	Noncorrosive	143

*Treated oil, DBDS removed

Figures 2-5 and 2-6 show an example of the changes in the GC-AED (amount of DBDS) for the oils before and after the treatment.



Figure 2-5 GC-AED Chromatogram in Sulfur Mode of Oil #2 Before Treatment.



Figure 2-6 GC-AED Chromatogram in Sulfur Mode of Oil #2 After Treatment. The DBDS was Removed to Less than 3.8ppm.

After treatment, the oils tested non-corrosive under both the ASTM 1275B and the CCD-ABB test methods. Figure 2-7 presents an example of the results obtained.



Figure 2-7

Test Results from the ASTM 1275B (left) and CCD-ABB Corrosive Sulfur Tests (Right) of Oil #2 After Treatment.

The results of the laboratory work for oils that tested corrosive and contained DBDS demonstrated:

- Potential for corrosive sulfur removal by the on-line process developed by Powertech
- After corrosive sulfur removal all the relevant oil parameters remain at the same level or better.
- Oils had similar oxidation stability before and after corrosive sulfur removal

Removal of Corrosive Sulfur from Oils that Do Not Contain DBDS

Since DBDS was identified as the major compound responsible for numerous transformer failures worldwide, oil manufacturers changed their refining and formulating process so that newer oils on the market came free of DBDS. Unfortunately some of these oils are still testing corrosive. At the same time, broad research into transformer failure caused by copper sulfide buildup on and in the paper insulation discovered that corrosive sulfur related failures were still happening in transformers filled with DBDS free oil [1]. This oil later tested corrosive by newer corrosive sulfur test methods. This discovery introduced new challenges in regards to the quantitative determination of corrosive sulfur presence in oil, and to the feasibility of removing

unknown corrosive sulfur compounds from oil. Therefore, after proving that corrosive sulfur from oils containing DBDS can be successfully removed, the work was expanded the work to other oils that were free of DBDS, but tested corrosive.

The treated oils were analyzed by GC-AED and GC-ECD chromatography for the presence of DBDS, and tested for corrosiveness by ASTM 1275B and CCD-ABB tests. The oil quality of these oils (IFT, PF, KV, etc), before and after the treatment, were also analyzed and compared. The test results of the oils before and after treatment for corrosive sulfur removal are presented in Table 2-4.

Table 2-4

Before and After Results for Relevant Oil quality Parameters for Oils that Do Not Contained DBDS (Laboratory Test Results).

Oil #	IFT (Dynes/cm)	PF (%)	KV (kV)	Acid Number (mgKOH /g)	Color	DBPC (%)	S from DBDS (ppm)	ASTM 1275B	CCD-ABB	Oxidation Stability (min)
7	33.1	0.264	60	0.01	1.0	0.091	<1	Corrosive	Corrosive	197
7*	40.4	0.035	53	< 0.01	0.5	0.069	<1	Noncorrosive	Noncorrosive	195
8	32.1	0.201	68	< 0.01	1.0	0.344	<1	Corrosive	Corrosive	288
8*	40.5	0.030	67	< 0.01	0.5	0.283	<1	Noncorrosive	Noncorrosive	276
9	34.7	0.138	53	< 0.01	1.0	0.254	<1	Corrosive	Corrosive	289
9*	41.3	0.037	50	< 0.01	1.0	0.224	<1	Noncorrosive	Noncorrosive	258
10	33.5	1.21	32	< 0.01	1.0	0.315	<1	Borderline	Corrosive	211
10*	41.7	0.021	42	< 0.01	0.5	0.280	<1	Noncorrosive	Noncorrosive	269

*Treated oil, DBDS removed

Figures 2-8 and 2-9 show an example of the changes in the GC-AED (even though they did not contained DBDS only corrosive sulfur compound that have been positively identified in oils that tested corrosive) for the oils before and after the treatment. From these chromatographs it is apparent that some sulfur compounds in the treated oil are removed while the amounts of others are reduced to various degrees. The sulfur compounds that were completely removed seem to be responsible for oil corrosiveness, since this oil tested non-corrosive after treatment. Efforts have been made to identify the compounds that were removed, unfortunately no characterization have been possible at this time.



Figure 2-8 GC-AED Chromatogram in Sulfur Mode of Oil #7 Before Treatment.



Figure 2-9 GC-AED Chromatogram in Sulfur Mode of Oil #7 After Treatment.

After treatment, the oils tested non-corrosive under both the ASTM 1275B and the CCD-ABB test methods. Figure 2-10 presents an example of the results obtained.





Test Results from the ASTM 1275B (left) and CCD-ABB Corrosive Sulfur Tests (Right) of Oil #7 After Treatment.

The results of the laboratory work for oils that tested corrosive and were free of DBDS demonstrated:

- Potential for corrosive sulfur removal by the on-line process developed by Powertech.
- After corrosive sulfur removal all the relevant oil parameters remain at the same level or better.
- Oils had similar oxidation stability before and after corrosive sulfur removal.

In addition extensive laboratory work was performed in an attempt to identify any of corrosive sulfur compounds in these oils, but up to now without tangible success. Since the transformer oil matrix is very complex and the amounts of corrosive sulfur may be at trace levels it was expected that the identification of any corrosive sulfur compound (apart from DBDS) would be difficult. In the future more efforts will be geared towards finding a way to identify corrosive sulfur compounds that cause these oils to test corrosive.

3 FIRST FIELD TRIAL: LESSSONS LEARNED

As previously reported [15, 16], a process for removal of corrosive sulfur from oil that contained DBDS has been developed and evaluated in the laboratory and in the field. Powertech's proprietary process for on-line removal of corrosive sulfur from transformers/reactors that are at risk proved that it is capable of removing DBDS from corrosive oil. The advantages of on-line removal of corrosive sulfur include: no power interruption, no wasted oil, and no negative impact on the environment.

Transformer Chosen for First Field Trial

After laboratory testing of the oils presented in the previous section, oil #10 was selected for a field trial. The on-line corrosive sulfur removal unit was installed on a Three-Phase, 30MVA, 138kV transformer manufactured in 1999. The transformer contains 5,515 gallons of oil. This oil presented a challenge not only from the corrosive sulfur removal aspect (oil free from DBDS), but also because of the high power factor, which had been a problem since this oil was new.

The objective of this field trial was an attempt to prove the corrosive sulfur removal capabilities from oils free of DBDS (that tested corrosive). The unit has been running continuously on the energized transformer without any disturbance to the transformer operation and it is likely that at the end of this trial the treated oil will test noncorrosive. The corrosive sulfur removal unit can be observed in Figure 3-1.





Results Obtained During First Field Trial

The results of this ongoing field trial are documented in Table 3-1. Based on these results the prototype corrosive sulfur removal unit has shown the following;

- All relevant oil properties were brought to the level of new oil after only two sets of columns being exhausted. Power factor improved from 1.3% to 0.07%, which had been a problem for this oil.
- The result from May 2010 by ASTM 1275B method shows that the oil as non-corrosive.
- At this stage the oil is showing as borderline corrosive by ASTM 1275B confirming that progress have been made in removing un-known corrosive sulfur from this oil.

Date	Oil Sample	IFT (Dynes/cm)	PF (%)	DBPC (%)	Oxidation Stability (min)	Oil Corrosivene ss (ASTM 1275B)
3-Dec-08	M _{in} 1	36.6	1.289	0.348	211	Corrosive
3-Dec-08	M _{out} 1	45.3	0.023	-	-	-
23-Dec-08	M _{out} 1*	43.7	0.1382	0.359	-	-
23-Dec-08	M _{in} 2	40.3	1.05	-	-	-
23-Dec-08	M _{out} 2	44.9	0.067	-	262	-
21-Jan-09	M _{in} 3	42.8	0.269	0.354	-	-
21-Jan-09	M _{out} 3	43.8	0.05	0.365	-	-
29-Jan-09	M _{in} 4	42.5	0.19	-	-	-
29-Jan-09	M _{out} 4	43.9	0.045	-	-	-
14-Apr-09	M _{in} 6	41.9	0.066	-	-	-
14-Apr-09	M _{out} 6	41.3	0.037	-	-	-
14-Apr-09	M _{in} 7	42.2	0.05	-	-	-
14-Apr-09	M _{out} 7	42.5	0.03	-	-	
23-Jul-09	M _{in} 8	42.1	0.05	-	-	Corrosive*
23-Jul-09	M _{out} 8	42.3	0.02	-	-	Noncorrosive
23-Jul-09	M _{in} 9	-	-	-	-	Corrosive*
23-Jul-09	M _{out} 9	-	-	-	-	Corrosive*
9-Aug-09	M _{in} 10	-	-	-	-	Corrosive*
9-Aug-09	M _{out} 10	-	-	-	-	Noncorrosive
22-Oct-2009	M _{in} 12	-	-	-	-	Corrosive*
22-Oct-2009	M _{out} 12	-	-	-	-	Noncorrosive
6-Nov-2009	M _{in} 15	43	-	0.334	-	Corrosive*
6-Nov-2009	M _{out} 15	42.5	-	0.339	-	Noncorrosive
28-Jan-2010	M _{in} 16	-	-	-	-	Corrosive*
28-Jan-2010	M _{out} 16	-	-	-	-	-
29-Jan-2010	M _{in} 17	-	-	-	-	Borderline
29-Jan-2010	M _{out} 17	-	-	-	-	-
4-May-2010	M _{in} 18	-	-	-	-	Noncorrosive
4-May-2010	M _{out} 18	-	-	-	-	Noncorrosive
20-Sep-2010	M _{in} 20	-	-	-	-	Borderline
20-Sep-2010	M _{out} 20	-	-	-	-	Borderline
6-Oct-2010	M _{in} 21	-	-	-	-	Corrosive
6-Oct-2010	M _{out} 21	-	-	-	-	Noncorrosive

Table 3-1Test Results of Oil from 300 MVA Transformer During the Field Trial.

4 CONCLUDING REMARKS

The work described on this technical update is part of an on-going EPRI effort to improve the understanding and mitigation of corrosive sulfur in oil filled transformers/reactors.

Lessons Learned from Laboratory Work

Work to date in the laboratory has demonstrated the following:

- DBDS (the most dominant corrosive sulfur compound) can be removed from oils.
- While DBDS plays a major role in the corrosiveness of oils, it is not the only corrosive sulfur compound present.
- The removal of other corrosive sulfur compounds from DBDS-free oils that test corrosive is also feasible and will produce oils that will test non-corrosive.
- Oil quality parameters (PF, IFT, KV, etc.) of all oils after corrosive sulfur removal treatment showed improvement.
- Oil oxidation stability of treated oils was practically unchanged.

Lessons Learned from On-going Field Trial

The initial field test results of a new on-line corrosive sulfur removal unit that has been installed and is operating smoothly on 300 MVA transformer have confirmed that all relevant oil properties (oil quality parameters) were brought to the level of new oil.

Field evaluation which is underway is designed to remove unknown corrosive sulfur compounds so that at the end of the treatment the oil will test non corrosive. However, it has not been easy to determine the exact progress of the corrosive sulfur removal process because of

- The fact that the corrosive sulfur compounds removed are unknown.
- The accuracy and reproducibility of the inductively coupled plasma spectrometry (ISP) method for total sulfur content in the oil is close to the amount of the unknown corrosive sulfur compound in the oil.
- Since we do not know which sulfur containing compound(s) are corrosive (in oil that doesn't contain DBDS) and the accuracy and reproducibility of the ISP method for total sulfur content in the oil is close to the amount of the unknown corrosive sulfur compound, it is not easy to determine the exact progress of the corrosive sulfur removal. Efforts are needed to improve the method accuracy and we are looking for other available options. At present, the only exact way to determine oil corrosiveness is the ASTM 1275B method or IEC 62535.

The result from May 2010 by ASTM 1275B method showed the oil as non-corrosive. However, this does not mean that the oil is free of corrosive sulfur. At this stage the oil is testing as borderline corrosive by ASTM 1275B confirming that progress have been made in removing

unknown corrosive sulfur from this oil. This confirms the progress in removing un-known corrosive sulfur from this oil. Further testing of subsequent oil samples is underway and will help verify this result.

Ongoing Work

A second on-line corrosive sulfur removal unit field test is underway in a shunt reactor. The objectives in this case are to demonstrate the corrosive sulfur removal from oil containing DBDS and the development of a methodology to quantify the progress made in the removal process. The corrosive sulfur removal unit can be observed in Figure 4-1.



Figure 4-1

On-line Corrosive Sulfur Removal Prototype Unit Installed on a Shunt Reactor.

Future Work

Although good progress has been made so far, there still remain many unresolved issues that could be of further focus for this project:

- The identification of specific corrosive sulfur compounds.
- Further development is needed towards a quantitative method to determine the progress made on the removal of corrosive sulfur compounds. For example, after several filter changes, one should be able to calculate with certain degree of confidence, the time (or filter changes) required to eliminate corrosive sulfur compounds from the oil.
- Understanding of the correlation of sulfur compounds to corrosive sulfur qualitative and quantitative testing.
- The development of non-invasive techniques to detect the presence of copper sulfide deposits in operational transformers.

5 REFERENCES

- 1. J. Hajek, M. Dahlund, L. Paterson, "Quality of Oil Makes the Difference, ABB Discovers the Solution to Transformer Breakdowns", ABB Review, No 3-2004.
- 2. L. Lewand, "The Role of Corrosive Sulfur in Transformers and Transformer Oil", Proceedings of the 69thnd International Conference of Doble Clients, Boston, MA, 2002.
- 3. L. Lewand, "Investigating Copper Sulfide Contamination in a Failed Large GSU Transformer", Proceedings of the 72nd International Conference of Doble Clients, Boston, MA, 2005.
- 4. C. Bengtsson et al., "Oil Corrosion and Cu₂S Deposition in Power Transformers", CIGRE Moscow Symposium, 2005.
- 5. L. Lewand, "The Evolving Problem of Corrosive Sulfur In Transformer Oil". Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN.
- 6. ABINEE, Workshop on Corrosive Sulfur in Oil, June 2005, Sao Paulo Brazil, presentations by ABB, Toshiba, Doble, Nynas, Siemens, Terna and Areva.
- 7. Hjortsberg and Jose-CarlosMendes, "Oil Corrosion & Cu₂S Deposition, ABB Testing, Passivation and Diagnostics".
- 8. V. Tumiatti, "Condition Monitoring by Oil Chemical Analysis", presented at the CIGRE General Meeting, Paris, 2000.
- 9. V. Tumiatti, et al. "Corrosive Sulphur in Mineral Oil: Its Detection and Correlated Transformer Failures", IEEE International Symposium on Electrical Insulation, 2006, p. 400.
- 10. C Bengtsson, et al. "Oil Corrosion and Conducing Cu2S Deposition in Power Transformer Windings", CIGRE 2006 Paris Meeting.
- 11. F. Scatiggio "Corrosive Sulphur", Proceedings of IEC TC 10 Plenary meeting, Cape Town, 2005.
- 12. C. Clairborne, "Specification & Testing of Transformer Oils with Respect to Corrosion". Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN.
- M. Eklund and K. Sundkvist, "Transformer Oils-An Orientation About Sulphur and its Characteristics and Effects", Proceedings of the 72nd International Conference of Doble Clients, Boston, MA, 2005.
- 14. T.V. Oommen, "Corrosive and Non-corrosive Sulfur in Transformer Oils" Proc. Electrical/Electronic Insulation Conference, Chicago, IL, Oct. 4-7, 1993, pp. 309-311.

- 15. Stevo Kovacevic, Nick Dominelli, Ed Hall, & Mike Lau, "Corrosive Sulfur in Transformers: Its Presence, Fate and Removal", 74th International Conference of Doble Clients, Boston, April 25-28, 2007.
- 16. Stevo Kovacevic, Nick Dominelli, Ed Hall, Salim Hassanali and Bhavin Desai, "Understanding the Impact of Corrosive Sulfur on Transformers", EPRI Substation Equipment Maintenance Optimization and Diagnostics Conference XV, 2008.

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute Inc., (EPRI, www.epri.com) conducts research and development relating to the generation, delivery and use of electricity for the benefit of the public. An independent, nonprofit organization, EPRI brings together its scientists and engineers as well as experts from academia and industry to help electricity. address challenges in including reliability, efficiency, health, safety and the environment. EPRI also provides technology, policy and economic analyses to drive long-range research and development planning, and supports research in emerging technologies. EPRI's members represent more than 90 percent of the electricity generated and delivered in the United States, and international participation extends to 40 countries. EPRI's principal offices and laboratories are located in Palo Alto, Calif.; Charlotte, N.C.; Knoxville, Tenn.; and Lenox, Mass.

Together...Shaping the Future of Electricity

© 2011 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute, EPRI, and TOGETHER...SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

1022573