

## Corrosive Sulfur, its cause and cure

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**Abstract:** many papers have been written concerning the studies of corrosive sulphur in insulating oils. This paper puts focus on the fact that corrosive sulphur has always been present in transformers but has re-emerged as a problem only the latest years.

**Keywords:** Copper, corrosion, sulphidation, catalysts, Arrhenius, corrosive sulphur

### Historicals. [1]

Chemical knowledge has evolved during centuries and some discoveries and scientists have been more important than others. For the corrosive sulphur problem and transformer chemistry in general four persons have contributed sufficiently to create the knowledge necessary for understanding and solving the problem.

- Oxygen was discovered 1773 by the Swedish chemist Carl Wilhelm Scheele. He called it "fire air". Joseph Priestley discovered deflogistonized air in 1774. Antoine Laurent Lavoisier finally gave the gas its present name (oxygen).
- The phrase catalysis was coined by Jöns Jakob Berzelius who in 1835 was the first to note that certain chemicals speed up reactions.
- Dmitri Mendeleev published the first Periodic Table of the Atomic Elements in 1869 based on properties which appeared with some regularity as he laid out the elements from lightest to heaviest. When Mendeleev proposed his periodic table, he noted gaps in the table, and predicted that as of yet unknown elements existed with properties appropriate to fill those gaps.

The Arrhenius equation is a simple, but remarkably accurate, formula for the temperature dependence of a chemical reaction rate, more correctly, of a rate coefficient, as this coefficient includes all magnitudes that affect reaction rate except for concentration. Svante Arrhenius provided a physical justification and interpretation for it in 1889.

The observations and discoveries of these men were immense and some of them can be summarized as below:

Oxygen and Sulphur are in the same group of elements i.e. having properties very much alike. If sulphur is bad then oxygen is bad and vice versa.

(Another type of elements is the catalytically active elements which comprises several groups of the periodic table of elements. Copper is found among those elements. ) Catalysts lower the energy required for different types of chemical reactions such as reforming and restructuring chemical substances.

### Corrosive Sulphur.

By this it is generally meant (in the transformer community) any form of sulphur that corrodes copper.

The most reactive type is H<sub>2</sub>S (hydrogen sulphide) but there are many compounds which contain sulphur and that are reactive. There are also a number of compound that are relatively stable i.e. not so reactive but eventually sulphur in a hydrocarbon molecule will become corrosive.

Corrosive sulphur obviously became a problem in the 1950's and forced the development of the first analytical methods to determine the corrosiveness of different oil.

By these methods it was possible to deduce how to process crudes to minimize the problem of corrosive sulphur. Eventually ONE of the solutions was to separate copper from the oil phase simply by enamelling the copper and thus avoid contact with the catalytic power of copper.

In **ASTM D 2864** a definition of corrosive sulfur have been entered recently: "elemental sulfur and thermally unstable sulfur compounds in electrical insulating oil that can cause corrosion of certain transformer metals such as copper and silver".

This definition gives the erroneous impression that corrosive sulphur is limited in appearance to electrical insulating oils while in reality corrosive sulphur has been a common source of problem in most industrial activities since oil processing started.

It is not very logical to denominate these compounds as "thermally unstable" as they are most often remaining from the original crude composition and they become unstable because of the presence of a catalyst.

### Copper is catalytically active.

Copper was one of the first catalysts used in the petrochemical business. (started in 1920's).

The catalytic power of copper is thus well documented and has been used to accelerate oil ageing in laboratory testing for many years. One of the earlier tests was ISO 4263 (TOST) (equivalent to BS 4388 - ASTM D 943- DIN 51 587 - JIS K2514) for turbine oils where copper, iron, water and oxygen (air) is reacted at 95° Celsius for an extended period of time (for good oils, several thousand hours).

For cellulose insulated oil-filled equipment additional factors must be considered a part of the problem complex: the cellulose and its content of chemical substances which are often inorganic remnants from the cellulose manufacture and that are known to be aggressive to copper in such a manner that copper surface **etching** occur.

This may increase copper surface area many times over and thus make copper even more active. It is also possible that synergetic catalytic effect appear.

### Analytical methods.

There are basically two different groups of analytical methods used in labs:

- *Determination of contents* (concentrations).
- *Determination of effects of chemical processes.*

Example of the first is sulphur content or antioxidant content of oils.

Examples of the latter are: Dissolved Gas Analysis where we observe the chemical changes in oil composition due to catalytic effects of different metals and of cracking effects as the oil is subjected to temperatures where the molecule vibrates to rupture.

These are processes going on in the real transformer and are thus interpretable.

The methods for determining Corrosive Sulfur that have recently come into use again are examples of this latter group. The reason for choosing methods like this is that corrosive sulphur is so dramatically reactive that almost all of it disappears at the same time as it is formed. It corrodes the copper which helped the formation of the corrosive molecule.

This type of reaction is not directly transferable to the real transformer.

The interpretation of this process analysis should be:

### This oil can/cannot be provoked to form corrosive sulphur under the conditions stated for this method.

(The conditions are naked copper available, very high temperature 150° Celsius, extended exposure time of 72 hours and oxygen starvation).

**In reality this means that transformers that operate sufficiently away from these conditions will not form corrosive sulphur at the rate that is experienced in the laboratory method.**

### Arrhenius' equation and catalysts.

This equation  $k = Ae^{-\frac{E_A}{RT}}$  is well known by all chemistry students and professionals.

- $E_A$  is the activation energy, a new concept introduced by Arrhenius.
- $R$  is the universal gas constant.
- $T$  is the absolute temperature (Kelvin).
- $A$  is a statistical parameter symbolising the probability for two molecules to collide with sufficient energy to react with each other.
- $k$  is the reaction rate often written as a differential  $dC/dt$  where  $C$  is the concentration of the reactant and  $t$  is time.

The catalyst decrease  $E_A$  required substantially and thus create favourable conditions for reactions that would not normally appear at those temperatures.

A catalyst also may promote certain reactions while others are suppressed. Catalysts are of vital importance to all hydrocarbons (oils) related chemistry and vast resources are used in catalyst research.

Copper in transformers is not a good catalyst for hydrocarbon reactions. Catalysts in commercial use do their "job" in fractions of a second. The temperature on the transformer winding copper surface is very moderate compared to the temperature in e.g. a catalytic cracker or reformer. This will slow down reaction rates tremendously but the contact time is not fractions of a second; it is YEARS.

The Arrhenius' equation basically tells us:

- *Higher temperature increase reaction rate.*
- *Higher concentration of reactants produces more of the product.*
- *Presence of catalysts increase reaction rate.*

These facts are all we need to know to solve the present "problem" of corrosive sulphur.

## Why has corrosive sulphur re-emerged as a problem NOW?

After corrosive sulphur was identified as a problem in 1950 it “disappeared” until early 1990’s but was not accepted as a problem at that time. It was not until around 2000 it “became” a problem of magnitude. The reason is that it was said to have caused a number of failures.

Literature searches for failure reports have resulted in very little. Discussions with transformer and oil manufacturers have resulted in nothing. Most of the data is apparently kept confidential by those who have access, manufacturers and owners. Therefore few independent assessments about the magnitude of this problem have been made.

We have only to rely on the statements of manufacturers that corrosive sulphur has caused failures and there is no doubt they have. However, there is also no doubt corrosive sulphur has been there all the time. Therefore the interpretations of the actual failures may be wrong; corrosive sulphur may be the symptom of the disease rather than the disease itself.

Since the problem was solved in 1950’s by improved processing and enamelling of copper the oil quality have on the average improved enormously. Sulphur-wise there are now oils that are completely sulphur free and **can** (by definition) **therefore not form corrosive sulphur**.

Some historical and technological events can explain the re-appearance of corrosive sulphur as a problem:

- In 1973 the first energy-“crisis” appeared which forced oil companies to revamp their refineries and cracking of oil was introduced on a very large scale forced by the substantial decrease of fuel oil usage.

An interesting observation is that many transformers manufactured during the late 1970’s today seem to be in bad condition. In Sweden it is mainly those transformers that require Fullers Earth treatment (regeneration of oil) and still after the Fullers Earth treatment the oil is in bad condition due to the high content of un-saturations.

It is also interesting to note that transformers manufactured in the late 1960’s seem to be in better condition than the 1970’s models.

Cracked oils contain un-saturations (double bonds) that are subjected to catalyst activity and thus cracked oils are more prone for reactions than straight-run (i.e. saturated) oils. The saturation processes used when manufacturing base oils involves hydrogen, which is an expensive material and the processes are therefore almost

never driven to full saturation. A certain portion of the bonds remain unsaturated and reactive. In its natural state, no double bonds exist in crude oils except in the aromatic molecules.

For long time use, cracked products that are not fully saturated (i.e. do not contain olefins) shall never be allowed. This aspect is not covered in any national or international oil standards.

DBDS (Di-Benzene-Di-Sulfide) is a known chemical substance used in catalytic operations and has been found in many oils in operation. It has also been found to be corrosive.

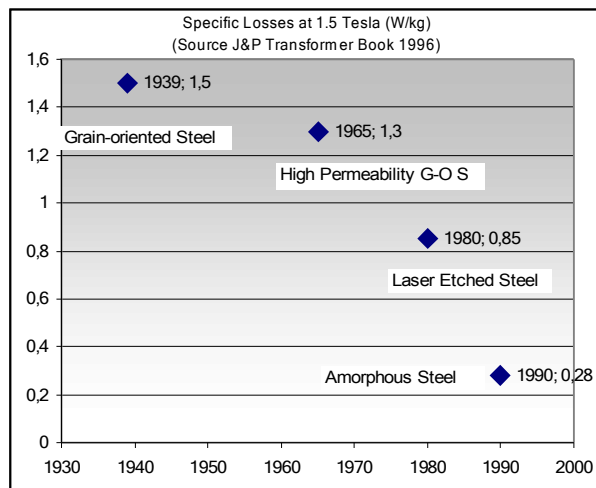
Today’s oils are very low in sulphur. The removal of sulphur is performed by reforming sulphur containing compounds so that e.g. H<sub>2</sub>S is formed and removed. The hydrogen is then recovered from H<sub>2</sub>S for re-use in the process.

We have seen samples of new oils manufactured to meet IEC-specification that have 10 times more un-saturates than the average sample. So far we have found ONE oil that has un-saturation below the detection limit for the method we use.

This is however not the real reason for the re-emergence of the problem. It is stated only to show what every chemist knows; *oil is a “fragile” product and should be treated accordingly.*

Instead **the reason is that the oils chemical environment has by time become harder**. This is being created by the electrical design engineers because they have very little knowledge about chemical aspects and restrictions and thus do not make provisions for them.

- On the core material side there has been a continuous development since the beginning of transformer design and in 1939 the grain-oriented silicon steels were introduced. The losses of these steels were then continuously decreased by improved purity of the product.



In 1965 a technological leap was made in the transformer core materials losses when new core

materials (grain oriented high permeability) were introduced and core losses decreased substantially. Since then several new processes have been introduced a resulted in even lower losses.

The transformers total losses are the sum of core and conductor losses. If the core losses decrease, the conductor losses can be allowed to increase and still the sum of losses can be less than before the improved material was introduced.

Less copper also means higher copper losses and thus higher copper temperatures which makes the copper more active as catalyst.

#### This is the major source to the problem.

Higher copper temperatures also lead to higher oil temperatures. This problem was easily dealt with by simply increasing the cooling capacity (a solution that does not dramatically decrease the temperatures on the copper surfaces).

It is also very likely that the strong electrical fields around conductors will enhance reactions. / 1/

- In the beginning of the 1970's a second technological leap was made: introduction of the computer as design aid.
- A contributing reason for the problems is also the situation in many of the standards committees.

This is a question which involves both chemistry and physics. Corrosive sulphur is caused by high copper temperatures and lacking catalyst passivation but do the designers who allow these harsh chemical environments know about the consequences of it?

#### **Defining the Problem.**

Formation of corrosive sulphur takes place on catalytically active copper surfaces. When the corrosive sulphur species is formed, the major portion of it reacts with the copper surface and forms copper sulphide. By time part of the copper sulphide starts migrating through the cellulose insulation and impregnates the insulation so that it becomes a semi-conductor.

When the insulation is sufficiently conductive a flash-over from one winding turn to another can appear and the failure is a reality. *Winding turn to turn flash over is thus the expected failure mode for conductive insulation.*

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One conclusion is that finding copper in the transformer oil is a serious indicator that copper corrosion is a reality. The copper compound is generated at the winding surface and concentration and thermal gradients forces it to travel through cellulose into oil.

In Sweden we find that the majority of transformers have copper in the oil in measurable amounts but still failures are very rare. >50 % of the transformers of a well known make has >0.1 mg Cu per kg oil (ppm) and ~2% have >1 ppm. This copper can only originate from corrosion.

It is a simple but expensive operation to remove the copper and that action does not cure the disease; it is merely a cosmetic improvement on the symptoms.

Few laboratory analytical programs have copper content determinations as standard method for transformer condition assessment.

The experience is that transformers seem to operate well despite the fact that the cellulose insulation apparently is more or less soaked in copper-sulphur compounds rendering the insulation semi-conductive. Possible interpretations of this fact are:

- The transformer insulation system is over-dimensioned (or.)
- The transformer operates substantially below design load.

As transformers that have failed also seldom (as far as we have found) are reported to contain copper in the oil while large amounts are found in the cellulose indicate that the diffusion rate (migration) through the cellulose is much slower than the formation rate at the cellulose-copper conductor inter-phase.

Despite this obvious fact, corrosive sulphur is blamed, and not the fact that favourable reaction conditions for the formation of corrosive sulphur (i.e. transformer design criteria) is the cause.

We observe a pronounced effect of the copper in oil on oil oxidation (ageing) (and therefore also on cellulose ageing). If the transformer is open i.e. has access to oxygen and there is copper present in oil there will be strong ageing. It is a well established fact that many analytical process methods rely on.

On the other hand we have diagnosed the condition of some large transformers with aluminium windings. The hottest part of these transformers are made by aluminium and we find that their conditions are as new despite the fact they are open and >30 years of age! Aluminium is a metal with no catalytic power at all.

The advice to counter sulfidation by allowing air into transformers is therefore not very wise as it will kill the transformer by oxidation instead. The idea is that oxidation will replace the sulfidation reactions. This is not a fact as the reactions will have synergetic effects and boost each other instead. (Good for manufacturers but not for owners).

Iceland is a country where virtually ALL transformers of all sizes are sealed (due to presence of corrosive sulphur in the air from geothermal sources). They do not have a higher incidence of transformer failures than other countries and their transformers are on the average in much better health than the Scandinavian transformers.

Increasing oxygen will not have a pronounced affect on the amount of oxygen present adjacent to the conductor. That amount is governed by the diffusion rate of oxygen through the cellulose (material transportation rate) and the rate of consumption on the copper surface. This latter parameter is determined largely by the copper temperature.

### **Problem Solution Assembly. Cures.**

The formation of corrosive sulphur is dependent on available copper surface, copper surface temperature and availability of chemical compounds containing sulphur.

In the drive for cheaper transformers and maximizing manufacturer's profits it is quite obvious that the use of expensive materials like copper is preferred to as small as possible while still meeting the transformer specifications/requirements.

The main reason behind the problem is the international design norms that allow very high copper temperatures (winding hot spot). An increase from 55° Celsius to 65° Celsius temperature rise will decrease copper usage but will increase the degradation reaction rates very substantially.

It must be noted that chemistry is not related to temperature rise; instead it is the ABSOLUTE temperature that is of interest.

- When **specifying new transformers** it is necessary to take the chemical working conditions into account. High temperatures can be allowed if there is no copper surface available i.e. the *copper winding shall ALWAYS be enamelled*. Furthermore the oil specified shall ALWAYS be *inhibited (antioxidants have a profound effect on formation of corrosive sulphur) and be sulphur-free and saturated (no reactive molecules due to cracking)*.

Work should be initiated to create at least one international oil standard that prevents corrosive sulphur formation to the maximum extent.

### **What can be done to transformers already in service?**

First the owner has to determine if the transformer has enamelled copper windings or not.

1. If they are enamelled no operational restrictions need to be applied.

2. If they are *not* enamelled the transformer should be condition diagnosed.

If the diagnosing results in suspected there is one alternative that is not attractive to owners but simple to introduce: **de-rating**. This will decrease winding hot spot temperature and thus slow down reaction rates.

Diagnosing the oil using the provisional CIGRÉ method may result in the conclusion that the oil can be provoked into forming corrosive sulphur. If the conductors are enamelled corrosive sulphur is only a theoretical problem.

Using *copper passivator* is a method of "enamelling" in-situ which has major disadvantages. The copper passivator (is a benzo-tri-azol derivate which) chemically adheres to the catalytic copper surface to form a molecular mono-layer that hinders oil from direct contact to the catalytic surface.

Instead the benzo-tri-azol is in contact with copper and subjected to chemical stresses which lead to the decomposition of copper passivators into gases interfering with the DGA<sup>1</sup>-interpretation. In reality mostly H<sub>2</sub> seem to be formed but we have also detected tendencies of oxygen starvation i.e. the consumption of large quantities of oxygen by the copper passivators.

Needless to say, this decreases the possibility to use DGA for early fault detection. Faults need to become large before they can be detected accurately.

It is recommendable to use **antioxidants**<sup>2</sup> in transformers with this problem. In lab tests strong positive effects can be detected.

### **Conclusions:**

- The corrosive sulphur problem is easy to explain by classical chemistry and its existence is not surprising.
- Interpretation of the new corrosive sulphur determination methods is wrong in the aspect that, just because the oil can form corrosive sulfur when provoked it will do it. Aspects to be considered are: is there any naked copper surface present at elevated temperatures? Is the operating temperature high? etc.
- Corrosive sulphur formation in winding cellulose can be avoided by enamelling the copper conductor i.e. incapacitate the catalytic surface.

<sup>1</sup> Dissolved Gas Analysis.

<sup>2</sup> Hindered phenols (e.g. BHT)

- Sulphur free oil has been possible to produce for great many years. (The production methods have been known for >75 years.)
- Sealed transformers are less prone to fail due to conductive cellulose than open transformers are because oxidation and sulfidation are partly synergetic.
- The cause is that copper's catalytic activity has been neglected by designers so that the catalytic surfaces are free for exposure to unstable chemical substances.
- The high copper prices have aggravated the problem as it has forced a drive for less copper usage and thus higher copper temperatures.
- Use of antioxidants will diminish the problem.
- Use of copper passivators of benzo-tri-azol type will cause generation of gases which may be misinterpreted as faults. When evaluating DGA's it is of vital importance to have the information about copper passivator's presence.
- Few failure reports in this matter are available for independent evaluations. For some reason all are kept confidential. This leads to the possibility to blame corrosive sulphur for failures that cannot be explained (where the true reason is not found).
- Temperature rise over ambient should not be used when thermally dimensioning transformers. Instead absolute temperatures should be applied.

### Summary.

Corrosive sulphur has been present in transformers since the combination of cellulose and (sulphur containing) oil was applied for insulation systems.

Corrosive sulphur is not a problem if designs are kept within the limits of what the chemistry close to the copper conductor can accept.

Copper is a catalyst for creation of corrosive sulphur and is also attacked by it and corrodes. It is very likely that synergetic effects with cellulose impurities play a role in the complex chemistry that results in the formation of corrosive sulphur.

In order to solve the problem it is essential to change focus from the products of the process to the process conditions itself. Bad process conditions are large and catalytically active copper surfaces, high ABSOLUTE temperatures (design criteria and international norms), relaxed oil specifications.

The chemical requirements for cellulose have up to now been more or less completely ignored and there is a need for improved cellulose specifications.

The transformer OWNERS need:

- Lower copper conductor surface temperatures or surfaces that have no catalytic activity. This means lower maximum temperatures or passivated (e.g. enamelled) warm copper surfaces.
- User oriented Oil specs forcing production of good oils.
- User oriented Cellulose specifications.

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