

THE ANALYSIS OF THE DISSOCIATION PRODUCTS OF SF₆ FORMED BY THE ELECTRICAL DISCHARGE.

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ABSTRACT

This work parses the present of the particular dissociation products of sulphur hexafluoride formed by the action of electrical discharge. The products under the consideration are quantitatively analysed on the laboratory gas chromatograph CHROM 5 together with the recorder TZ 4210.

1 INTRODUCTION

Sulphur hexafluoride, used in the instruments and the transformers HV a EHV, allows more effective construction of the equipment specially in the hard conditions, which means conditions on the development and industrial centers and in the extreme operating conditions in the area of the transmission and the distribution of electricity.

For using in the electrotechnics it has its benefits (compared to solid and liquid insulators):

- high specific dielectric strength (in usual conditions just about 2,5 times more than air) and smaller volume at the elevated pressure
- regenerative capability (the dielectric strength is recovered after the breakdown to its initial value)
- small pressure rise while by the extinction of the electric breakdown or arc (it increases by warming up and later goes back to starting value). [1]

2 BASIC CHARACTERISTICS

This synthetic gas of the inert nature is colorless, odorless, fire-resistant and insoluble in the water. It is one of the heaviest gases. In the liquid state exists only at pressure higher than atmospheric, at the normal pressure is in the gaseous state, which by heat of sublimation – 63,8 °C goes straight into solid state. It is appurtenant to the electronegative gases. In other words, it is able to trap the free electrons. [2]

2.1 CHARACTERISTIC OF THE DISSOCIATION PRODUCTS

At electrical spark discharge or arc discharge, sulphur hexafluoride dissociates at the temperature (1500-2500) K, at temperature higher than 3000 K the dissociation is complete. Most of the decomposition products recombine quickly to beginning gas, part of it still stays dissociated and it reacts with the impurity and the ambient material. This includes the waste products in the gaseous state, and also the solid one, specially the fluoride of the metal.

SOF₂ - fluoride of sulfurous acid (sulfur oxide-difluoride) – in the normal conditions is steady, toxic, what is obvious at concentrations from 100 to 500 ppm. SOF₂ rises by reaction with a oxygen absorbed in contact W/Cu or W/Ni/Cu used ordinarily as the materials for contacts, where rises the arch. The copper electrodes or the electrodes from the stainless steel essentially limit the rise of SOF₂.

SO₂F₂ - fluoride of the sulfuric acid (sulfur dioxide-difluoride) – in normal conditions is steady, toxic (it causes convulsions of the respiratory system), it is formed in smaller amount than SOF₂ and is dangerous at concentrations from 2000 to 4000 ppm. It occurs always together with SOF₂, so is easily identifiable. It rises by reaction of oxygen with the activity of the arc.

SOF₄ a SF₄ - fluoride of fluorosulphuric acid and sulphurous fluoride (sulphur ofide-tetrafluoride and sulphur tetrafluoride). They have similar effects as SOF₂. They are less stable and they dissociate in the present of water.

S₂F₂ - sulphur fluoride – is odoriferous toxic gas. While the discharges it reacts with hydrogen, this caused a rise of H₂S a H₂F₂. By reaction with the oxygen rises SO₂.

CF₄ - tetrafluormethane - rises by the reaction with the materials of the contact metals and surrounded insulators. It cannot be absorbed by filters.

HF - hydrogen fluoride – is aggressive and unsteady. It reacts with the surrounding metals and insulators. It can not be captured by filters.

WF₆ a SiF₄ - tungstic fluoride and silicic fluoride – they rise by reactions as CF₄. They dissociate in the presence of the water vapor under formation of the solid waste products.

H₂SO₄ - sulfuric acid – is formed by the reaction with the water.

SO₂ - sulfur dioxide - it is formed at corona discharge. [3,4]

Following components have been analyzed during the influence of sparks: CF₄, CO₂, SF₆, SO₂F₂, SOF₂ a H₂O+H₂S.

3 EXPERIMENTAL PART

The reaction chamber: the vessel has been made from the PVC. Its capacity was 3,1 x 10⁻³ m³.

Used samples: experiment proceeded at the samples of the composite materials based on the epoxy resin. The company ABB Brno, a.s. uses this material for the production of the rods of the high-tension switch. Delivered rods by company Orgrez, a. s. have the dimensions 10 x 260 x 31 mm. It was necessary to cut cable into smaller pieces - with regard to proportions of the reaction chamber filled by SF₆. In this case was the cable cut into for pieces, three of them were used for the measurements. A three-electrode system was fabricated on them using the conductive graphite lacquer SIB 643.

Exposition time of the electric discharge on the samples: the sample No. 1 was exposed for 1380 minutes, the sample No. 2 for 1020 minutes, and both experiments were terminated because the resistivity R_V dropped almost to zero to values below the measuring range of the IM6. The sample No. 3 was sparkled for 1500 minutes and it was ended because the spark plug electrodes were damaged by erosion.

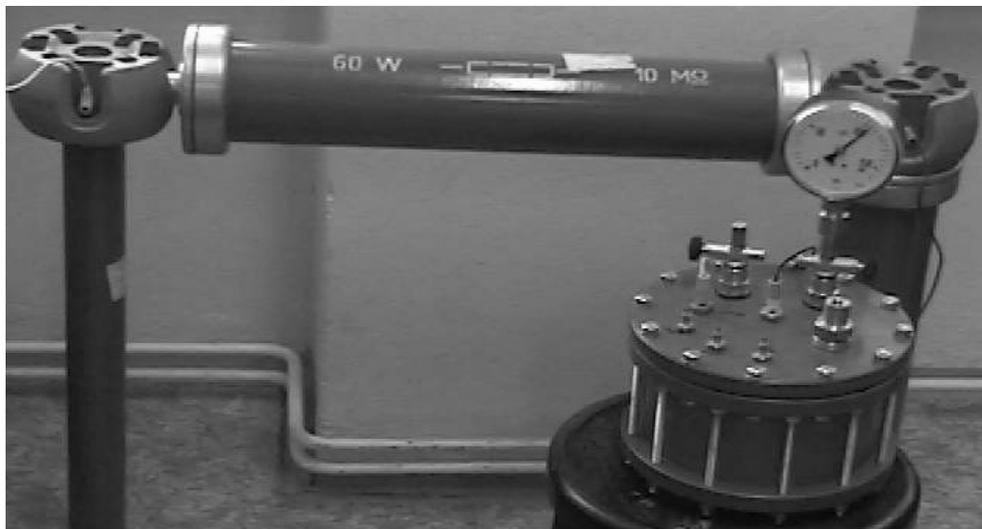


Fig. 1: The reaction chamber plugged into the sparking perimeter

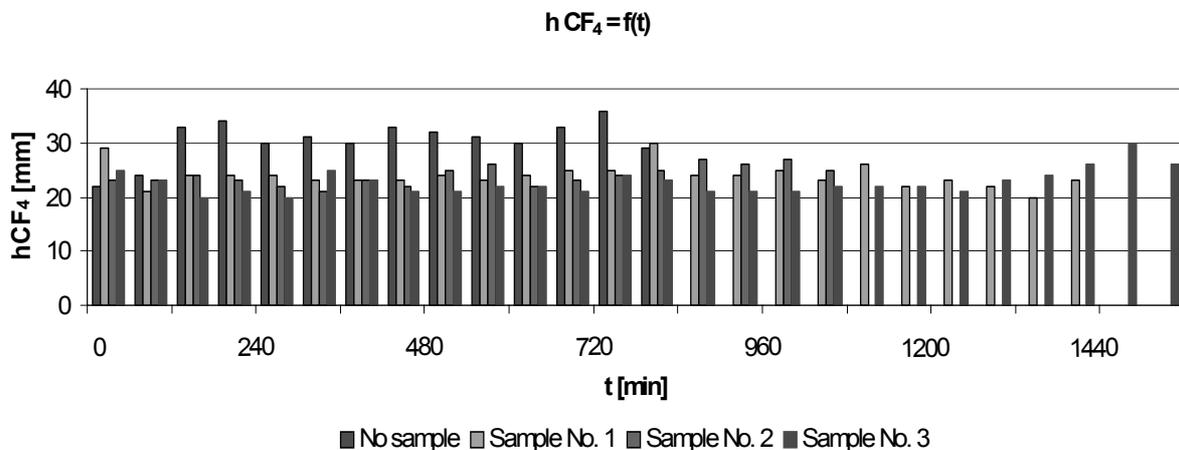
3.1 EXPERIMENTAL PROCEDURE

- I. For comparison, the sulfur hexafluoride was exposed to the sparks without any sample in the chamber. Gas chromatograph was used for determination of the amounts of the products formed by dissociation of the SF₆ caused by the spark discharge. The gas was sampled by samples of volume 0,5 ml from the reaction chamber and analyzed after each 60 minutes cycle. The sparking of the gas in the chamber without the sample took 780 minutes.
- II. Before every insertion of the sample to the reaction chamber it was necessary to clean all the interior of the chamber from the dirt and the waste products made by previous sparking. After it was inserted the sample, the chamber was closed. Then, the air was removed by a vacuum pump and then the chamber was filled by the SF₆ on demanded pressure 100 kPa.
- III. The sparking of the sulphuric fluoride together with the inserted sample proceeded in the 60 minutes cycles. The composition of the gas in the chamber was analyzed after each sparking cycle using a chromatograph. Its sensitivity was adjusted so that all components exhibited a measurable peak.

3.2 EVALUATION

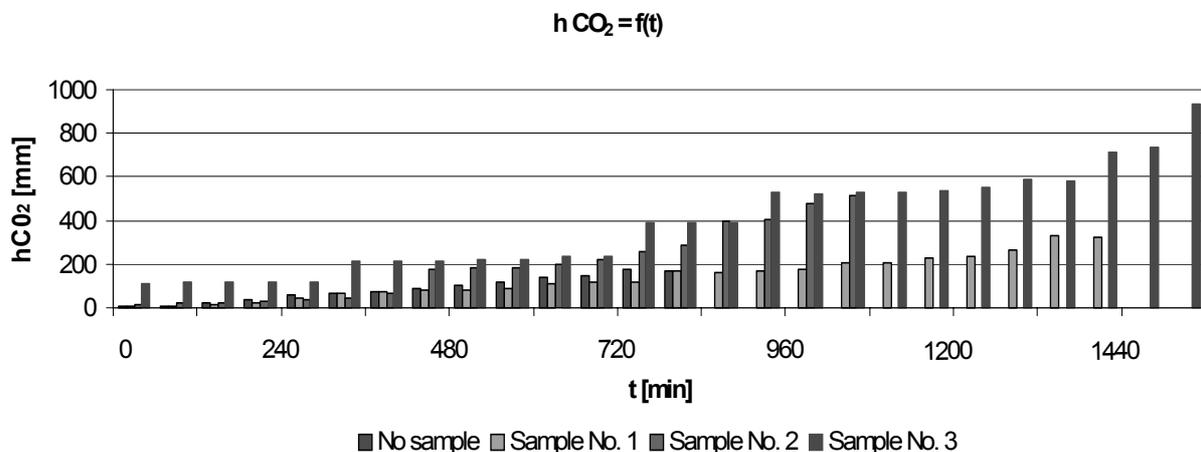
The calibration of the chromatograph on CF₄, CO₂, SOF₂ has been done using standard gas mixtures delivered by the company Orgrez.

- I. Tetrafluormethane CF_4 : its concentration reached the limit $1,670 \mu\text{l}$ after 720 minutes of the sparking without the inserted sample. If the sample was inserted, the highest value on the sample No.3 $1,392 \mu\text{l}$ after 1440 minutes was measured. Lower amount of CF_4 was found almost in all cases if the sample was inserted in the chamber.



Graph 1: The comparison of the peaks size of the dissociated products CF_4 during the sparking with and without the inserted samples No. 1, 2, 3. ($10\text{mm} \cong 0,464 \mu\text{l}$).

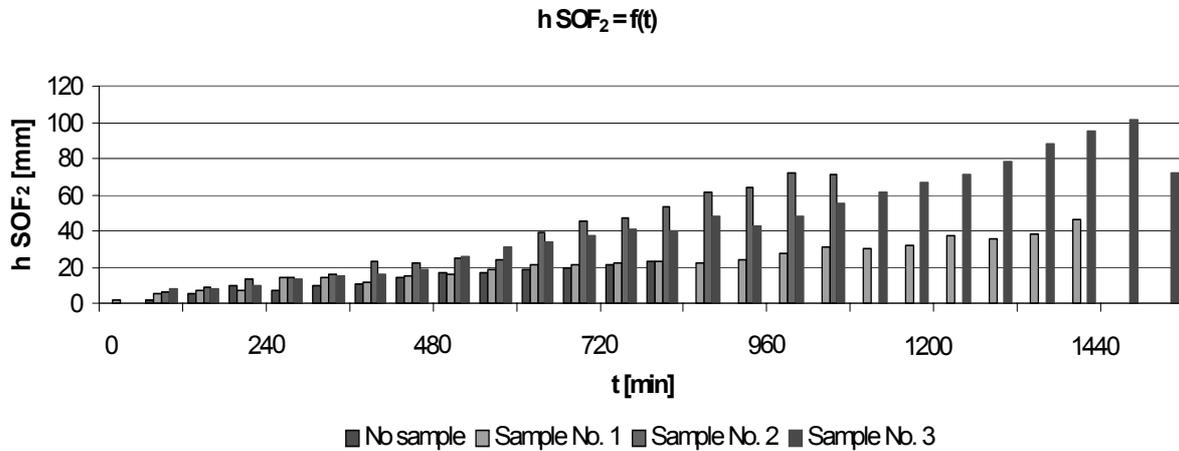
- II. CO_2 reached the ceiling during the sparking without the inserted sample after 720 minutes ($52,096 \mu\text{l}$), in the case with the inserted sample it was at sample No. 3 $277,056 \mu\text{l}$, and its concentration exhibited a permanent rise (with the inserted samples).



Graph 2: The comparing of the peaks size of the dissociated products CO_2 during the sparking with and without the inserted samples No. 1, 2, 3. ($200\text{mm} \cong 6,36 \mu\text{l}$).

- III. Fluoride of the sulphuric acid SO_2F_2 : its concentration was the same with and without the sample till the time 540 minutes. However, from that time a permanent rise occurred. Till that time the gas probably did not cause any reaction. Quantitative calibration was impossible due to absence of calibration gas.

- IV. The next component which could be evaluated quantitatively is fluoride of the sulphurous acid SOF_2 . Its concentration reached the equivalent of $0,530 \mu\text{l}$ without the composite material after 780 minutes, in opposite case after 1440 minutes of the sparking $2,329 \mu\text{l}$.



Graph 3: The comparing of the peaks size of the dissociated products SOF_2 during the sparking with and without the inserted samples No. 1, 2, 3. ($100\text{mm} \cong 2,31 \mu\text{l}$).

- V. The peaks corresponding to H_2S and water H_2O overlap in a common one. It has not been affected by the inserted sample and by the discharge either.

4 CONCLUSION

Its very important to deliver the constant energy, which is not easy thanks several factors such as leakage currents on the surface of any insulator in the chamber, burning of the contacts of the spark gap and other similar phenomena. That makes the reproducibility of the measurements worse.

Next work should be concentrated on the analysis of another composite materials and the possibility of their the surface treatment of this materials designed for the use in the atmosphere SF_6 and about the way of the identification of the damaged rod while the normal activity.

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