

Absorption of water in silicon gel

Cédric Lesaint, Céline Babault, Knut B. Liland, Lars E. Lundgaard

Electric Power Technology, SINTEF Energy Research

Trondheim, Norway

Cedric.lesaint@sintef.no

Abstract—Water is an important enemy of an electric insulation system. Water vapour can be absorbed by electrical insulation materials (liquids or solid) and migrate in between the materials to achieve the same relative humidity equilibrium everywhere. Water can reduce withstand voltage of the insulation liquid, initiate partial discharges in wet solids and increase dielectric losses in solids like epoxies, gels, PCB cards and produce dielectric heating. In insulation liquid filled system the water content of the liquid should never be allowed to reach saturation. One failure scenario is when typical oil with significant water content is cooled to a temperature where the water content is above the saturation content, and then water will precipitate and may condensate at cold insulating gaps and give breakdown due to electric field enhancement.

Gel samples were investigated in climate chambers in various conditions of humidity and temperature until an equilibrium was reached. Diffusion and absorption of water were measured at different intervals. The aim of the study was to find an appropriate technique/methodology to follow the absorption of moisture in gel as a function of time. Several techniques were tested to determine the moisture content in the gel such as Karl Fischer, weight differences measurement, freeze drying and capacitive relative humidity sensors giving contrasted results. The weight difference method showed "anomaly" indicating bound water, even after equilibrium (measured with the other methods) was reached the weight continued to increase. The use of humidity sensors covered by gel appears to be the most reliable technique.

Keywords—silicon gel, water absorption methodology, electrical insulation

I. INTRODUCTION

This paper concerns the dielectric materials which could be used for subsea converter modules, for oil and gas exploitation. In the specific insulation system considered, electric converters components are covered with silicon gel and surrounded with synthetic esters oil. So, the aim of the work presented herein is to determine if the gel studied has good performances towards water absorption since humidity in insulating materials has a decisive importance on the lifetime of electrical installations. Water reduces the dielectric strength of the insulation, making partial discharges and arching more likely and can cause breakdowns^[1]. There are also several other parameters to evaluate: voltage level, short-circuit current, mechanical stress, chemical influences... However, herein, only the influence of humidity will be tested. In the system considered, insulating material studied is a silicon gel which covers electric components. This installation

is intended to be used for deep-water applications, this implies hard conditions: pressure up to 500 bars, compensated by oil filling, and temperature ranging from -4° C to 150 °C. The compatibility of materials with these conditions is also an essential parameter but will not be presented here. In this kind of system, water transport takes place by diffusion, convection being very low in a gel. To know the performance of a gel, absorption is the other key mechanism. By studying these phenomena, it will be possible to predict the amount of water which can be absorbed by the gel but also how fast this absorption occurs, and so to determine if this particular gel is a good candidate for the envisaged application. Nevertheless the main aim of this study is to determine an effective and reliable technique to know the moisture content in gel for the experiments.

II. EXPERIMENTAL AND THEORY

A. Samples preparation

Water diffusion will be studied for a typical gel used in insulation of some electrical installations: WACKER SilGel® 612 A/B. It is an addition-curing silicon rubber. Silicon is a synthetic compound, a polymer with the chemical formula $[R_2SiO]_n$, where R is an organic group. This gel is used in different applications, as for: encapsulation of electronic components for the automotive and power electronics industries, encapsulation of solar cells, production of damping elements, sealing of clean room filters.

The experiments consisted in putting gel samples in various conditions of humidity and temperature until an equilibrium is reached. A VC4034 climate chamber (Vötsch) was used where it was possible to set the relative humidity (80 %) and the temperature (from 60 to 80 °C).

The relative humidity (RH) quantifies the amount of water vapor compared to water saturation in the gel. It depends both on temperature and pressure conditions. RH is calculated as the ratio of the partial pressure of water vapor to the saturated vapor pressure of water. In practice, in the electrical installations, the gel would be in contact with oil, so the diffusion would take place between these two materials. However, the system studied in the chamber is the uptake of water from the air in gel, Fig. 1. In fact, what is important is to know the performance of the gel towards water. The results would be the same with oil except that the experiments would probably take more time.

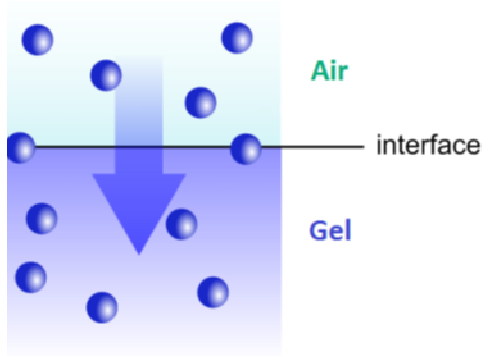


Fig. 1. Absorption of water in gel.

The gel was prepared by mixing WACKER SilGel® 612 A and WACKER SilGel® 612 B in the same quantities, with the same volume using syringes. After stirring, the mixture was put under vacuum in a *V1000S* chamber (KLM GmbH) for a few minutes to eliminate potential air bubbles. Approximately 0.5 mL of gel was then introduced in some aluminum trays (10 mm x 20 mm), which is equivalent to 2.5 mm of gel thickness. Aluminum prevented the absorption of water both on the sides and at the bottom of the samples. In this way water got into the gel only from one direction. The samples were then put in an oven at 70 °C overnight for curing.

The gel studied is very viscous and sticky. So the convection can be ignored, water is transported by diffusion only. This phenomenon is characterized by the Fick's law (for a one-dimensional diffusion):

$$j = D \cdot \frac{\partial n}{\partial x}$$

where j is the diffusion flux ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), n is the concentration of water ($\text{mol} \cdot \text{m}^{-3}$) and x is the position (m). So, during the experiment, water is absorbed in the gel. Water content increases, leading to the drop of the derivative, because the difference between the concentration inside and outside the gel is reduced. Consequently, the amount of water in gel increases less and less with time: the curve of the moisture content of the gel versus time should approach equilibrium. Moreover, at the equilibrium, the relative humidity in the gel is the same as in the air. This equality is obtained starting from Henry's law, valid at the equilibrium

$$C = S P_i$$

where C is the concentration of water in gel ($\text{mol} \cdot \text{L}^{-1}$), S the solubility coefficient ($\text{mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$) and P_i the vapor pressure (atm). By dividing it by the same expression in condition of 100% of relative humidity, the previous equality is found.

B. Techniques

The amount of water absorbed in the samples as a function of time was measured using different methods. Some were destructive such as Karl Fischer or freeze drying, and some were not, such as gravimetric analysis.

1) Karl Fischer

Two different instruments using the Karl Fischer titration methods were used. The first device is a Karl Fischer with a sample exchanger and an oven. Each sample is heated in the oven to desorb water which pulled along by a gas flow in the titration cell. The device used was a 756 KF Coulometer (with a sensibility of 10 μg) with a 774 Oven Sample Processor from Metrohm, controlled by Tiamo software. The titrant was a solution of HYDRANAL – Coulomat AG Oven. The second device is a Karl Fischer instrument with manual injection. The principle is the same as previously described, except that the sample has to be liquid because it is directly injected in the titration cell. The entire sample was mixed with dry methanol to extract water and before each injection, it was stirred and a well-known volume was then introduced in the Karl Fischer using a dry syringe. The same procedure was realized with methanol only to determine the amount of water present in the solvent as a blank value. The device used was a 737 KF Coulometer from Metrohm and the titrant was a solution of HYDRANAL - Coulomat AG-H.

2) Gravimetric analysis

The amount of water absorbed can be determined by weight difference. Moisture content in gel, expressed in ppm, is the ratio of the weight of water and the weight of wet gel. So it is expressed as

$$M_t = \frac{w_t - w_0}{w_t - w_{alu}} \cdot 10^6$$

where M_t is the moisture content at the time t (ppm), w_t the weight of the sample at t (mg), w_0 the weight at $t=0$ (mg) and w_{alu} the weight of the aluminum container (mg). To measure such small weight differences, a *UMX2* micro weighing scale (Mettler Toledo), with a sensibility of 0,1 μg , was used.

3) Freeze drying

Water content can be determined by pressure difference. The principle has been described elsewhere [2]. First, the device is put under vacuum to remove any trace of air. It has to be perfectly airtight to have a good measurement. The sample is heated at 60 °C for one hour in order to desorb water from the gel. Desorbed water, in vapor form, is then gradually deposited by an ice trap. To determine the amount of water, heating is stopped and ice is removed. Then, water returns to gaseous state and creates a pressure difference, which can be directly read. The height change is calibrated: for the device used, 1 mm corresponds to 3.2 μg of water.

4) Relative humidity sensors

The limit of the previous techniques is that there is no possibility to determine if the water is adsorbed or absorbed by the gel. To determine water absorption, SHT71 capacitive sensors from the company Sensirion were used. In the sensor, a thin polymer layer absorbs water from the air until equilibrium is reached. This equilibrium is fast and reversible. The water content in the polymer is proportional to its capacitance. Each sensor was connected to a multiplexer, which had four ports and was connected to a computer. The multiplexer box displayed both the temperature and the relative humidity values. The values recorded by the sensors

only give information on the time needed to reach the equilibrium, but not on the amount of water in the samples. Indeed, only relative humidity was displayed and not absolute humidity. Samples were prepared by putting sensors at the bottom of aluminum trays (10 cm x 10 cm) and by covering them with approximately 4mm of gel. The trays were placed in the climate chamber with a controlled temperature and relative humidity (80 %). For each experiment, a sensor without gel was also put in the chamber to control the temperature and the humidity of the air.

III. RESULTS AND DISCUSSION

1) Karl Fischer and freeze drying

The results obtained by both Karl Fischer techniques and with the freeze drying technique did not provide reliable results. For the Karl Fischer with a sample exchanger and an oven and for the freeze drying, the results obtained showed no coherence and no repeatability (not shown). For the Karl Fischer with the manual injection, the gel samples kept taking more and more water, even after more than eight days. No stabilization could be observed, Fig. 2.

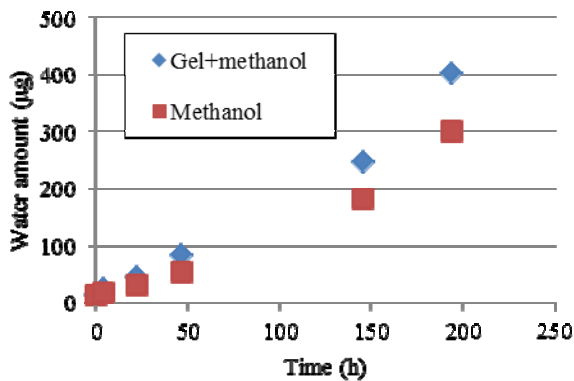


Fig. 2. Water uptake on a silicon gel determined by Karl Fischer with manual injection ($T = 60\text{ }^{\circ}\text{C}$, $\text{RH} = 80\%$).

Other tests were done with a higher temperature (not too high to not damage the gel), but the results obtained were not better.

2) Gravimetric analysis

The first series of gravimetric experiments were carried out at 60, 70 and 80 °C, Fig. 3. For all temperatures studied, the weight of sample increased to finally reach a plateau after approximately 200 hours. One can also notice that temperature does not seem to have an effect since all three curves obtained are very similar. Nevertheless a second series of experiments gave result slightly different, Fig. 4. It seems that at 70 and 80 °C (phenomenon not observed at 60 °C), the amount of water that the sample can absorb that does not reach the same plateau as previously observed. That could be explained by the formation of bounds inside the gel between water and silicon molecules leading to a continuous increase of weight of the sample. Besides, as far as methodology is concerned, these results seem to indicate that weight measurement is not an appropriate method because of the poor repeatability. Many experiments were performed giving very different results.

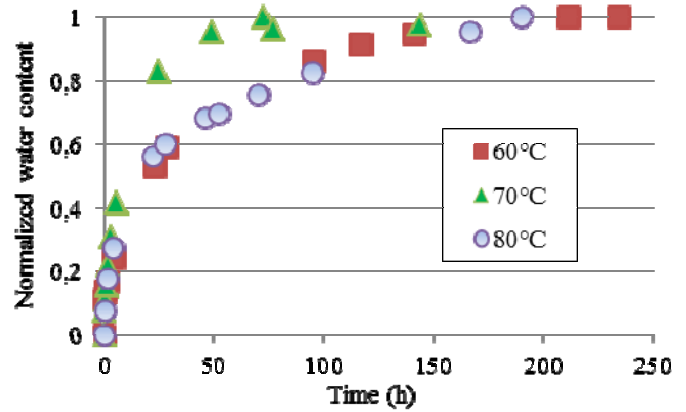


Fig. 3. Gravimetric measurements on silicon gels as a function of time and temperature ($\text{RH} = 80\%$) – Series 1.

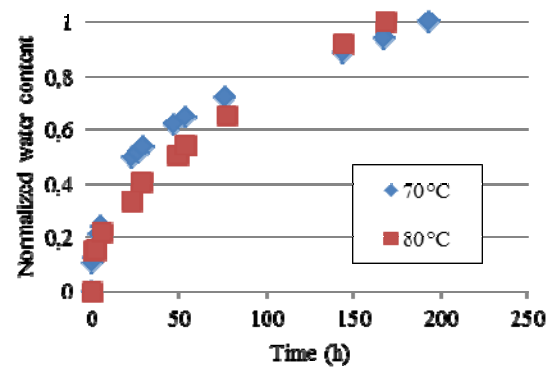


Fig. 4. Gravimetric measurements on silicon gels as a function of time and temperature ($\text{RH} = 80\%$) – Series 2.

3) Relative humidity sensors

The use of capacitive relative humidity sensors seems to be an effective method to observe the absorption of water in gel. In fact, for all the experiments carried out with these sensors, the increase of the amount of water seems to stabilize. Moreover, for samples with the same thickness of gel, the responses of the sensors are very similar, Fig. 5. Since the sensors are located at the bottom of the samples, it is obvious that water is not only adsorbed (at the surface) but also absorbed into the gel.

The influence of the thickness of the gel has also been investigated at 80 °C, Fig. 6. The first parameter is the time necessary for water to reach the sensor, the bottom of the samples. For the thin layer of gel, 5 mm, about 7.5min were necessary to observe an increase of humidity whereas for a thicker layer, 9 mm, it was about 33.5min. The second parameter is the time necessary to reach the equilibrium. It took about 4 hours with the low thickness of gel and 11 hours with the thicker layer of gel. However, this equilibrium is reached much more rapidly with this technique. For example, at 60°C, around 6 hours were required to reach it for a gel with a thickness of 4 mm whereas it took about 150 hours with gravimetric measurements (with a gel thickness of 2.5 mm for these samples).

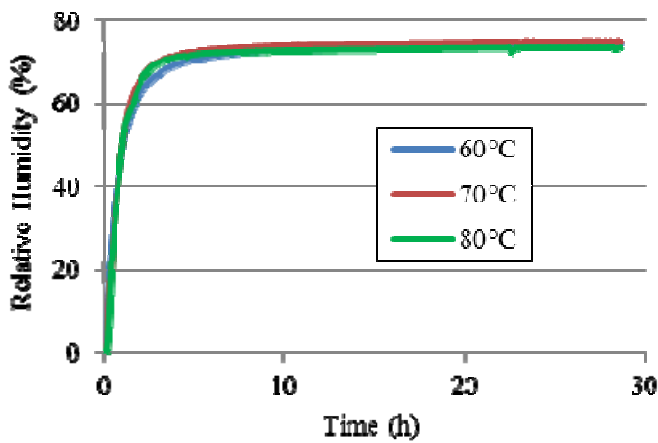


Fig. 5. Relative humidity measurements on silicon gels as a function of time and temperature determined with capacitive relative humidity sensors (RH climate chamber = 80 %).

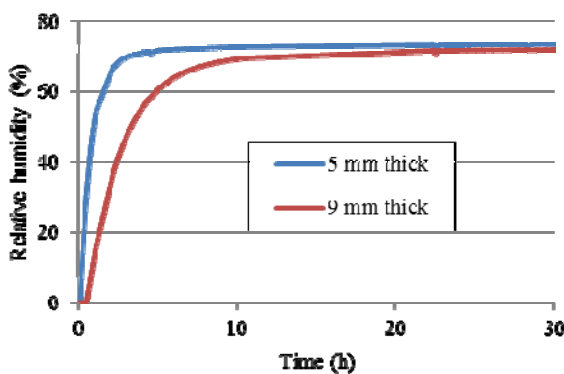


Fig. 6. Relative humidity measurements on silicon gels as a function of time and gel thickness at 80 °C determined with capacitive relative humidity sensors (RH climate chamber = 80 %).

Moreover, one should notice that at the equilibrium, the relative humidity should reach 80 %, or 78 % recorded by the sensor in the climate chamber for the experiment at 80 °C. Nevertheless, the sensors displayed between 72 % and 73.5 % of relative humidity after 30 hours. When the experiment was left running longer, the humidity continued to increase, but very slowly. Then, after almost 200 hours, it was measured to be between 73 % and 74.5 %. This very slow increase may be due to desorption of water which offset the absorption in the gel or to a reaction between water and the silicon gel as described previously.

IV. CONCLUSION

The performances of dielectric insulating materials are an important issue during the lifetime of all electrical apparatus.

One of the very important aspects is water absorption, as it accelerates ageing and reduces breakdown voltages. Two topics were investigated: First, finding a suitable technique to follow the absorption of water in a silicone gel. Second, investigate the kinetics of this absorption.

Several methods were tested to determine the moisture content in a silicone gel as a function of time and of relative humidity. The two Karl Fischer devices tested and the freeze drying device did not provide reliable results, the weight measurement technique showed problems of repeatability. On the other hand, the use of capacitive humidity sensors seems to be reliable, even if they do not give access to the absolute amount of water in the gel. Nevertheless, more experiments remain to be done with these sensors and with different thicknesses of gel.

In spite of the difficulties to find and implement relevant analysis method, results showed that water is not only adsorbed (in surface) but also absorbed (in bulk) by the gel. The results obtained with the weight difference method; meaning an increase of weight with no equilibrium indicates the formation of bonds inside the gel between water and silicone molecules. The same trend was observed by the authors with silicon oil ^[1b].

Moreover, another interesting result is that the time required to reach saturation was very short for every technique tested. One has to keep in mind that the insulating material is intended to be used in electrical installations which should work for years and a saturation of the gel in water was observed after only a few days. A possible solution could be to use desiccants or water traps in the installations to eliminate water prior to any contamination.

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REFERENCES

- [1] a) K. B. Liland, K. Eidnes, K. Bjorneklett, S. Hvidsten and Ieee in *Measurement of solubility and water content of insulating oils for HV XLPE cable terminations*, Vol. Ieee, New York, **2008**, pp. 7-10; b) J.-P. Crine, H. Garbay, R. Grob and J. Casanovas, *IEEE Transactions on Electrical Insulation* **1986**, EI-21.
- [2] E. Ildstad in *Water Migration and Water Treeing in Cross-Linked Polyethylene Cables*, Vol. PhD thesis The Norwegian institute of technology, Trondheim, **1982**.