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The influence of the composition of water on the results of accelerated aging resistance testing of low voltage subsea cables insulation

R Erfurth¹ and O T Gudmestad*

¹ Department of Mechanical and Structural Engineering and Materials Science, University of Stavanger, Norway

* Corresponding author: ove.t.gudmestad@gmail.com

Abstract. The composition of water changes with temperature, for instance, the saturation rate of water in polyurethane membranes is related to the temperature. Thus, it is necessary to evaluate the influence of the composition of water on absorption of water in subsea cable insulation. This paper is suggested to represent a supplement to existing standards regarding “Electrical insulation materials - properties with regard to thermal long-term behaviour.”

1. Introduction

Rahmati et al. [1] reported that the increase in temperature does not have a significant effect on the percent of adsorption of water in polyurethane membranes. This means polyurethane will not adsorb more water at higher temperature, but faster. The Arrhenius approach is based on a constant diffusion according to Ficks’ Law. However, the composition of water changes with temperature, for instance, the saturation rate is related to the temperature. Therefore, it is necessary to evaluate the influence of the composition of water on absorption of water in subsea cable insulation.

In a nutshell, when water is used as a conductor, chemical reactions are induced. These chemical reactions can involve the specimen, the electrodes or the water itself. In literature [2, 3] the dielectric constant (relative static permittivity) and the ion product of water are descriptive parameters of electrochemical behavior. A chemical reaction is hydrolysis. This paper is suggested to represent a supplement to existing standards regarding “Electrical insulation materials - properties with regard to thermal long-term behavior” [4].

To simulate the chemical degradation of the sheath material over time and quantify the insulation properties and application limits of low voltage cable they are artificially aged. The recommended practice to assess insulation properties advises the use of non-destructive measurement of insulation resistance. This approach is based on the Arrhenius behavior for chemical reaction of first order. Most common standards, which are referred to, are: ASTM D3032, VG 95218, NEK 606 and IEEE 1580. [5–8]. Standard test methods which include artificial aging separate aging, so-called pre-treatment and the actual measurement. If cables are artificially aged, then this is done almost exclusively in a heating cabinet in air or in other gas mixtures. Most standards do not define water in more detail, because the water is used exclusively for insulation measurement.



In the present work, the cables were aged at an accelerated rate in artificial seawater and the resistance insulation testing was in situ. The lack of testing guidance along with a wrong theoretical approach result in overly conservative and restrictive design parameters [4]. Hydrolysis is a chemical reaction of an order greater than one and accordingly, adjustments should be made

In this context, improving the validity of insulation resistance testing in combination with artificial aging is the very important. Measurements in water are predominantly of a unique nature and have not yet undergone sufficient assessment. The aim of the present work is to make the measurement results transferable. In previous tests, the electrical insulation resistance was determined according to the known method, Conventional short-term method for characterizing long-term thermal behavior [9, 10]. Great uncertainties have arisen in the process. The aim of the present study is to investigate to what extent the following parameters influence the measurements:

- Dwell time and the exact point in time of the initial/reference measurement,
- The water composition,
- The temperature coefficient and the convertibility of measured results.

Furthermore, the general set-up for the insulation resistance test is examined.

2. Measurements

The method employed in the present study is the point measurement testing, also known as short time measurements, which is the most frequently used method. A test voltage of 500 V is applied for a period of 120 seconds. This method returns a curve as a function of resistance over time.

By comparing periodically determined point measurement with the initial point measurement, it is possible to recognize trends of degradation. In addition to the statements regarding defined limit values that are considered "safe", this allows observations on changes in the condition of the insulation material over time.

Dielectric absorption behavior and polarization provides more information about the condition of the insulating material. However, if these were measured in situ, the mobility of the water molecules would have a misleading effect.

2.1 Initial point measurement

In point measurement the trend is established by comparing the change $R_i(t = 120 \text{ s})/R_{\text{Reference}}$. For the evaluation of long-term characteristic values, a limit value of 0.5, or 50 % relative to the initial value is often used [11] to define the end of service life.

The exact time at which the reference value is recorded must be identified. According to IEC 60092-350 [12] the first measurement should be made 1 hour after immersion. The pre-treatment taken into account according to DIN VDE 0472-502: "The measurement starts at the very latest 5 minutes after the end of the pre-treatment" [13]. The time of immersion in the water bath is defined as pre-treatment in DIN EN 60216-1: "For determining the initial value of the property [...], these specimens shall be pre-treated by storage for two days (i.e. for 48 hours +/- 6 ours) at the lowest stage of the storage temperature intended for the test [...], in order to achieve a stable value" [14]. Then the initial value is to be measured.

This means that further processing of the data is refined, for example in accordance with DIN VDE 0276-605: "Test report with diagrams showing capacity increases expressed as a percentage of the first day value" [15]. In Figure 1 the percent change compared to the previous measurement is shown, as one can see after 48 hours the variation is sinks significantly to less than 30% change. For more specifics regarding the sheets, see [19]. Note that details of sheet manufacture are confidential. Data points are given in the figure (Figure 1) and lines are shown to connect data points.

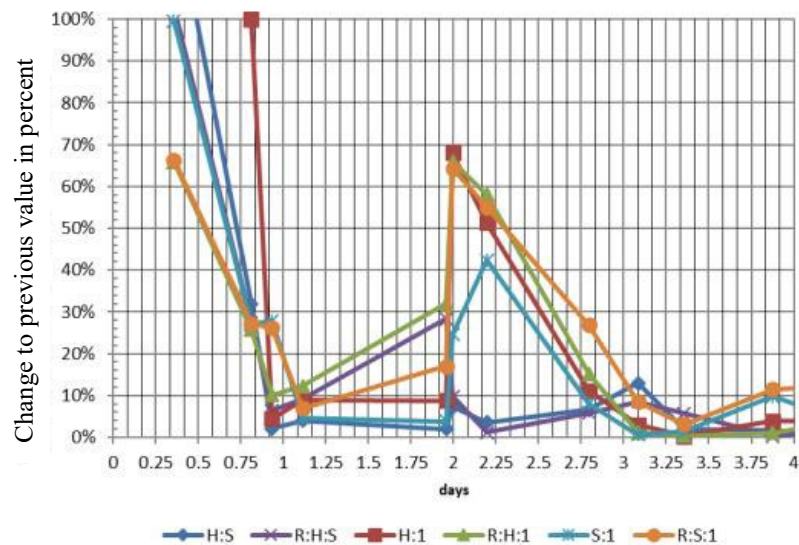
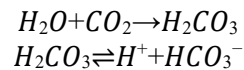


Figure 1. Resistance change in percent to previous readings of various types of cable sheaths.

2.2 Water composition

The electron neutrality condition generally applies for water. The sum of all cation equivalents, respectively concentrations, is equal to the sum of all anion equivalents, respectively concentrations. This means that water behaves electrically neutral. Thus, the pH value provides information about the activity of the hydrogen ion. Pure water (CO_2 free) has a pH value of 7, being neither an acid nor a base. The CO_2 present in the ambient air dissociates to carbonic acid and accordingly reduces the pH value.



Through buffer solutions, as present in real and artificial seawater, the H^+ -ions compound with the OH^- -ions of the calcium hydroxide to form undissociated H_2O . Therefore, pure water (pH 5.6 with dissolved CO_2) is chemically more active, Table 1.

Table 1. Properties of water.

	Ultra-pure water	Pure water	Purified water	Sea water
Resistivity [$\text{M}\Omega\cdot\text{cm}$]	10-18	1-10	1-0,02	~20
Conductivity [$\mu\text{S}/\text{cm}$]	0,1-0.055	1,0-0,1	1-50	~ $4.8 \cdot 10^4$

Gases diffuse from the surrounding air into the water with different saturations points which depend on the type of water, Table 1. Saturation is a factor regarding the transferability of the measurement results, since, for example, passive transport processes such as diffusion, take place until the concentration gradient is balanced, see also Figure 2.

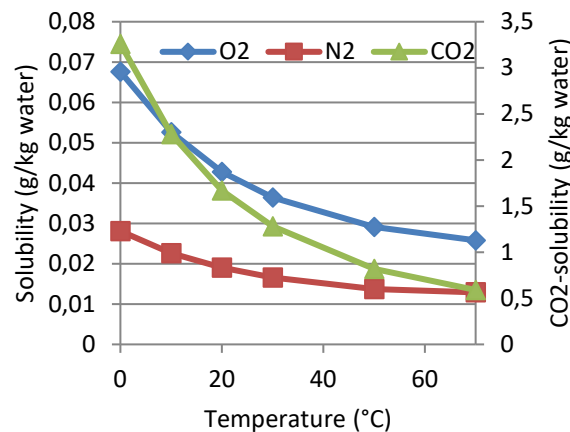


Figure 2. Solubility in water.

2.3 Temperature

Conductivity is temperature-dependent, and the change is described by temperature coefficients. In most insulation-resistance measurements, the range of temperature differences is in a relatively small interval and changes of material properties are neglected. At limits within which the material properties change little, a linear change in the temperature difference is assumed. However, the rate of change in a chemical system depends exponentially on temperature. Based on this relation, the resistance is derived:

$$R_T = R_{T_0} \cdot e^{-b\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

Where

R_T	Resistance at temperature T
R_{T_0}	Resistance at reference temperature
b	Correction of insulation resistance

For a NaCl solution, in a small temperature interval, change in conductivity as a function of temperature can be assumed to be linear, Figure 3.

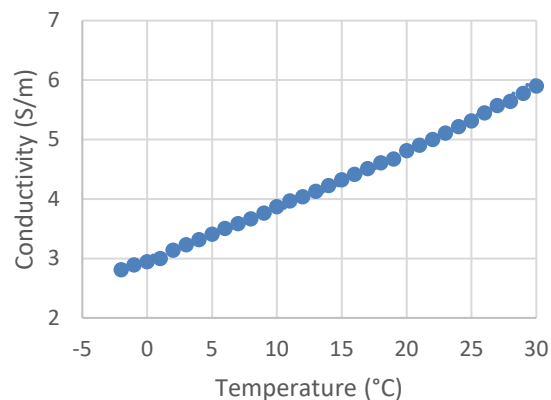


Figure 3. Conductivity of a NaCl solution (35%) as a function of temperature.

However, if a trend-line is derived from a temperature interval of 30°, i.e. Figure 3, the following coefficient of determination is obtained:

Linear	$y = 0.0959x + 2.9204$	$R^2 = 0.998$
Exponential	$y = 3.0186e^{0.023x}$	$R^2 = 0.996$

In a paper by Ellison [15], the conductivity of seawater was measured. (Here we should note the differentiation between seawater and artificial seawater: According to investigations by Riley and Skirrow in 1965 [16], the density of the organic content of seawater is in the range of $1.50\text{--}3.00\text{ g/m}^3$, which applies to most seawater areas. The particle sizes ranged from $1 \cdot 10^{-6}\text{ m}$ to $50 \cdot 10^{-6}\text{ m}$. It was estimated that 14% of particulate suspensions were of organic origin. Organic particles included bacteria, fungi, phytoplankton, zooplankton and detritus. The inorganic suspensions consisted of different types of mineral particles. Trace elements of various complexes of metals, mercury, cadmium etc. were also detected. The dielectric constant measured in the study showed minimal deviations. However, these were in the range of the measuring error of 1 %.

The relation between salinity and conductivity is shown in Figure 4 at four different temperatures. Within a temperature interval of 30°C and a relatively small salinity-range a linear model of conductivity is reasonable. It is assumed that there is a direct proportional increase of the conductivity with the number of free ions dissolved in the water. Ellison summarizes that there is no significant difference between natural seawater and synthetic seawater, prepared according to the standard recipe [17]. However, he clarified that there is a significant difference in the conductivity and permittivity between natural seawater and an aqueous NaCl solution of the same salinity, [16].

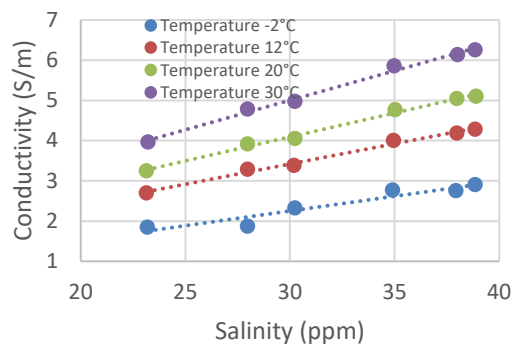


Figure 4. Conductivity as function of salinity at four temperatures with values taken from [16].

Measurement should be carried out in similar temperature conditions. If it is not possible, the results can be compared by conversion to a reference temperature. However, as shown in Figures 4 and 5, temperature and salinity are identified factors, which have a direct effect on the measurement result, a standardized measurement method is essential in order to achieve the best possible comparability.

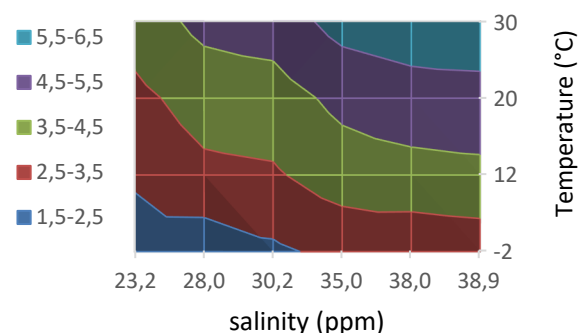


Figure 5. Conductivity as function of salinity and temperature.

2.4 Temperature coefficient

"The long-term thermal behavior of an electrical insulation material always applies only to a fixed property and a certain limit value," [14]. Since different properties change at different rates, a material may have different temperature indices. For materials with non-negligible changes in material properties

within the temperature interval, the resistance value varies quasi exponentially. In order to determine a dominating temperature coefficient for the specimen, a ramp test is carried out. The water temperature is successively increased until the defined apex is reached and then temperature is gradually reduced to the initial temperature in the same way. The insulation resistance is measured during this procedure in four hour intervals. In Figure 6, the averaged curve of insulation resistance versus time must be described by an exponential function (Too few data points are available to suggest formula at the moment).

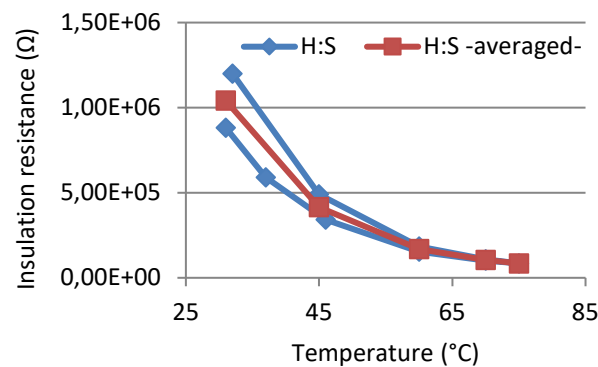


Figure 6. Ramp to determine the temperature function.

The arrangement of the cables is mentioned for the sake of completeness, as the standards do not provide any general recommendations. The geometry and position relative to the electrode in the water tank etc. have no significant influences. However, the attachment point of the guard terminal is noteworthy. To exclude the surface leakage current from the measurement a guard terminal must be attached to the cable.

3. Results and discussion

The total resistance is the sum of the internal resistance of the conductor, the insulation resistance in the cable and the resistance of the artificial seawater. The artificial seawater contributes to the total resistance due to the measurement of the specimen, taking place in situ. When a current is applied, the water turns into an electrolyte. Figure 7 shows the fluctuation of voltage right after an insulation resistance measurement with 500V over 2 minutes. The potential then decreases for about an hour and a half. The measured insulation resistance between two stainless steel electrodes, which were 15 cm apart, drops to a value of 4 mega ohm within an hour. The noise in the measured signal can be attributed to the formation of bubbles at the electrodes caused by water electrolysis.

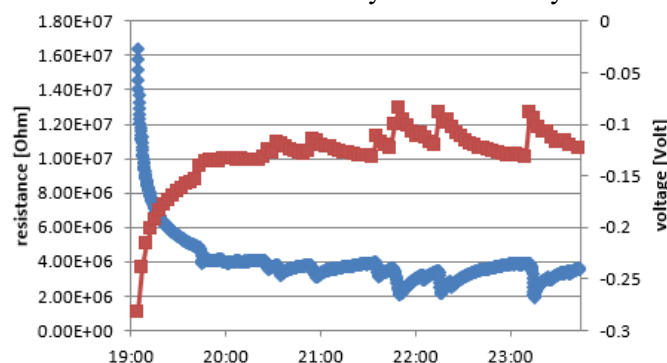


Figure 7. Resistance versus voltage fluctuation caused by electrolysis over of time.

For the electrolyte, one assumes an exponential temperature coefficient. Measured resistance from 19.5 °C to 80 °C result in a graph shown in Figure 8, approximated as a function:

$$R(T) = 227.05\Omega \cdot e^{-(T/71.42)}$$

Taking diffusion and hydrolysis into account, the composition of materials and water changes at elevated temperatures of 70 °C and more, resulting in a temperature coefficient that changes over time. This leads to an error, which is increasing over time. The ramp tests of the insulation resistance leads to a temperature-dependent function of the insulation resistance as shown in Figure 9.

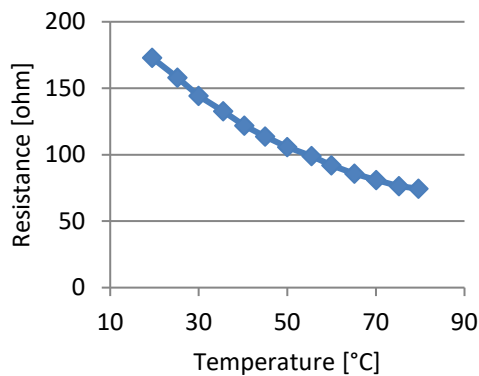


Figure 8. Resistance of water versus temperature (19.5 °C - 80 °C).

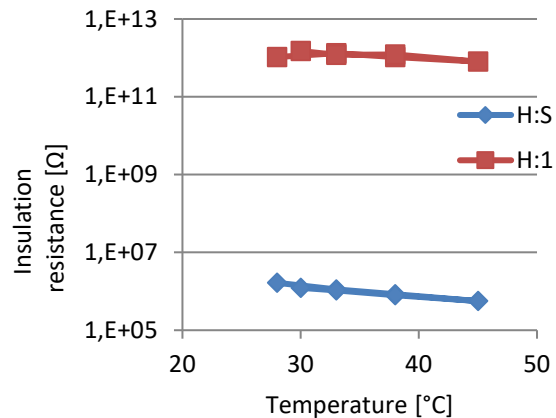


Figure 9. Dependence of insulation resistance as function of temperature.

$$R_{sheat}(T) = 8M\Omega \cdot e^{-(T/16.67)}$$

$$R_{core}(T) = 3T\Omega \cdot e^{-(T/41.67)}$$

In our experiments, the gradient of the exponential temperature coefficient was decreasing over 320 days by 13%. Rudorf [18] proposed a calculation method to compare the measured values from the short-term bearings with those of the base curve. The measured values of the time to failure to be regarded as provisional are to be corrected by comparing the calculated values with the values from the long-term storage - the basic characteristic:

$$t_N = t_R + R^k \cdot t_E$$

- t_N Service life at normal temperature
- t_R Period of time at normal temperature. Conditions
- t_E Period of time at elevated temp conditions
- R Extension factor
- k Temp-coefficient with $k = \frac{T_{elevated} - T_{normal}}{10}$

The extension factor was originally assumed to be 2. By the changes of the temperature coefficient function over time presented before, the constant R should be adapted to the exponent dependent on time.

$$R = \frac{-0.13}{320} \cdot t_E + 2$$

As shown in Rudorf [18], this makes it possible to evaluate the measured values and to predict the estimated service life more precisely.

4. Conclusions

The resistance of water is several orders of magnitude lower than the resistance of the insulation material and can be neglected. However, the type of water dictates the extent of hydrolysis and chemical by-products. The complexity of the salinity/ temperature/conductivity ratio is enhanced by a further dimension caused by the ions dissolved during hydrolysis. This limits the comparability of test results despite materials with identical compositions and additives have been tested. Furthermore, the degree of chemical activity of the water will directly influence the process of artificial ageing.

The temperature at which the water is set up for testing differs among studies, or is unspecified. In conclusion, it can be said that the reference temperature of the insulation test is different among the reviewed standards. It is recommended to measure the reference value at an elevated temperature. Artificial seawater containing inorganic salts according to ASTM-D 1141 [17] is the recommended practice for use for in laboratory testing where reproducible simulation seawater is required.

A ramp test at the beginning and at the end of artificial aging can determine the temperature function of the material and the change of the gradient over time. The subsequent modification of the extension factor of Rudolf's adjustment function [18] increases the accuracy of the prognosis.

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