THERMAL LOADING CASES OF HYDROGEN HIGH PRESSURE STORAGE CYLINDERS

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ABSTRACT

Composite cylinders with metal liner are used for the storage of compressed hydrogen in automotive application. These hybrid pressure cylinders are designed for a nominal working pressure of up to 70 MPa. They also have to withstand a temperature range between -40°C and +85°C according GRPE draft [1] and for short periods up to a maximum temperature of 140°C during filling (fast filling) [2]. In order to exploit the material properties efficiently with a high degree of lightweight optimization and a high level of safety on the same time a better understanding of the structural behavior of hybrid designs is necessary. Work on this topic has been carried out in the frame of a work package on safety aspects and regulation (Subproject SAR) of the European IP StorHy (www.storhy.net). The temperature influence on the composite layers is distinctive due to there typical polymer material behavior. The stiffness of the composite layer is a function of temperature which influences global strains and stress levels (residual stresses) in operation. In order to do an accurate fatigue assessment of composite hybrid cylinders a realistic modeling of a representative temperature load is needed. For this, climate data has been evaluated which were collected in Europe over a period of 30 years [3]. Assuming that the temperature follows a Gaussian (normal) distribution within the assessed period of 30 years, it is possible to generate a frequency distribution for different temperature classes for the cold extreme and the hot extreme. Combining these distributions leads to the overall temperature range distribution (frequency over temperature classes). The climatic temperature influence, the filling temperature and the pressure load have to be considered in combination with the operation profile of the storage cylinder to derive a complete load vector for an accurate assessment of the lifetime and safety level.

1.0 NOMENCLATURE

C	[MPa]	Stiffness matrix
C^{-1}	[1/MPa]	Compliance matrix
E	[MPa]	Young's modulus
f(x)	[/]	Probability density function
H	[%]	Frequency of occurrence
sd	[°C]	Standard deviation
T	[°C]	Temperature
u	[/]	Standardized variable
ε	[%]	Strain
μ	[°C]	Mean value of extreme temperature
σ	[MPa]	Stress

Indices:

abs.	Abs. extreme temperature
i	Month
k	Temperature class
1	In fibre direction
2	Perpendicular to fibre
$\bar{\ }$	Mean average
$'$	Time dependency
$''$	Velocity dependency

2.0 INTRODUCTION

The automobile industry is looking for solutions to reduce emissions and the dependency on fossil fuels, for which availability is predicted to decrease over the next decades. For this reason hydrogen as energy source is gaining more and more importance. In automotive applications hydrogen can be used for combustion engines or on the next evolutionary level in fuel cell power trains.

The economical way to store hydrogen for automotive applications with respect to mass production still poses a lot of challenges. In order to achieve a satisfying energy density with compressed gas storage systems the operating pressure has been raised up to 70 MPa. Besides the static and dynamic pressure load the pressure cylinder has to withstand also the temperature load coming from climatic parameters as well as during the filling process where temperature rises up to 140°C (fast filling) [2] due to compression energy. These extreme structural requirements can be achieved in an economical way only with hybrid structures (composite-metal or -plastic combinations). The big advantage of composites is to have the possibility to choose freely the fibre orientation with which an optimal material usage can be achieved. There are basically two design types. The so called type III pressure cylinder is a metal liner with a complete composite wrapping. The liner’s task is to achieve gas tightness and it takes also a minor part of the load. The type IV design has a plastic liner for gas tightness which does not take any structural loads.

In order to address the issues concerning light weight design, safety, economical high-quantity production and reliability under static and dynamic loads of pressure and temperature in hydrogen storage systems for automotive applications the European Union has launched a research program, StorHy (www.storhy.net). Its scope also covers analytical models of hybrid structures for lifetime prediction in order to assess the safety level of high pressure hydrogen cylinders. To achieve a satisfying accuracy and agreement with the test results from the project, existing analytical models had to be enhanced by modules which take into account the specific requirements of high pressure hybrid cylinders.

The influence of temperature on hybrid pressure cylinders gains more and more importance with the increasing degree of lightweight optimization. The alternation of temperature does cause additional structural loads which are a distinctive feature of hybrid composite/metal cylinders. It turns out that temperature effects in hybrid cylinders have a multi-level structure, which has to be solved concurrently.

The metal liner and the composite layers do have different coefficients of expansion. The temperature influence on the metal liner is not as distinctive as on the composite layers due to their typical visco-elastic material behavior. The stiffness of the composite layer is a function of temperature. This generates different global strains in the loaded cylinder, which lead to a variation of stress level in the metal liner. The consequences are residual stresses in the structure.

To improve the lifetime prediction and the assessment of the safety level a realistic modeling of a representative temperature load is needed. Regulation codes such as the GRPE draft [1] just give the numbers of the extreme temperature (-40°C and +85°C) but no information on the quantities of occurrence nor on the level of different temperature classes. For this reason climate data in Europe which was collected over a period of 30 years [3] has been evaluated.

To validate the temperature influence on the structural behavior of the pressure cylinder, static as well as dynamic hydraulic cycling tests under extreme temperature have been conducted at BAM. For this purpose a hydraulic test facility is available with a climate chamber (see Fig. 1). Test can be performed up to a maximum cycling pressure of 120 MPa between -60°C and up to +90°C. For the static test a maximum pressure of 350 MPa is possible. The structural behavior is monitored by strain gauges, acoustic emission sensors and thermocouples.

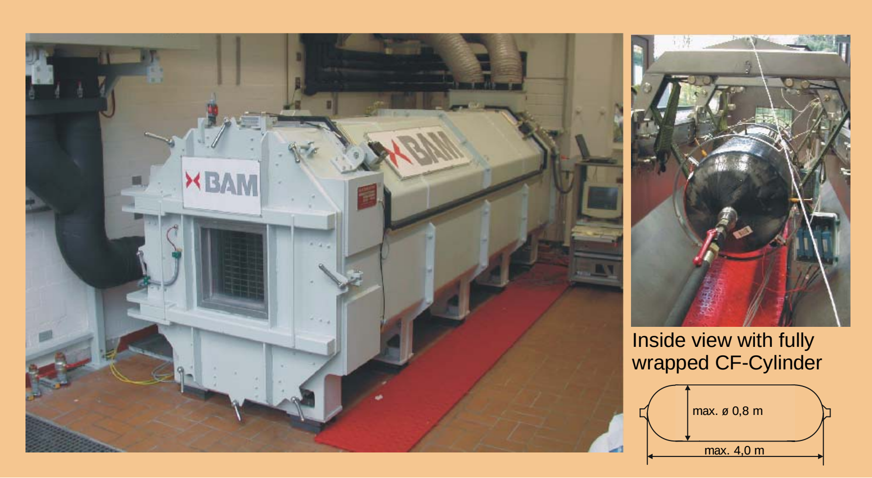

Figure 1. Hydraulic test facility for cycling fatigue and burst tests under extreme temperatures.

3.0 RESIN PROPERTIES

Polymer materials such as epoxy resins which are mostly used for composite cylinders do have material properties distinctively dependent on the actual temperature conditions. The temperature dependency of the composite results mainly from the resin behavior. This has to be considered in the structural model in order to establish an accurate simulation of the structural behavior. Fatigue cycling tests under extreme temperatures showed clearly the influence of temperature on lifetime behavior and underlines the demand for effective simulation models.

To characterize the temperature depending material properties of the resin system, dynamic mechanical thermo analysis (DMTA) and thermo mechanic analysis (TMA) on resin specimens (without fibres) had been conducted.

Following Fig. 2 (left) presents the decreasing Young’s modulus E’(T) with increasing temperature T. Also shown is the damper modulus E’’(T) which indicates with its peak the glass transition temperature. In the glass transition temperature range the epoxy resin loses stiffness dramatically. Temperature does also have an effect on the coefficient of expansion which can be seen in Fig. 2 (right). This nonlinear material property of the Young’s modulus is implemented in the calculation model by a polynomial equation of sixth order.

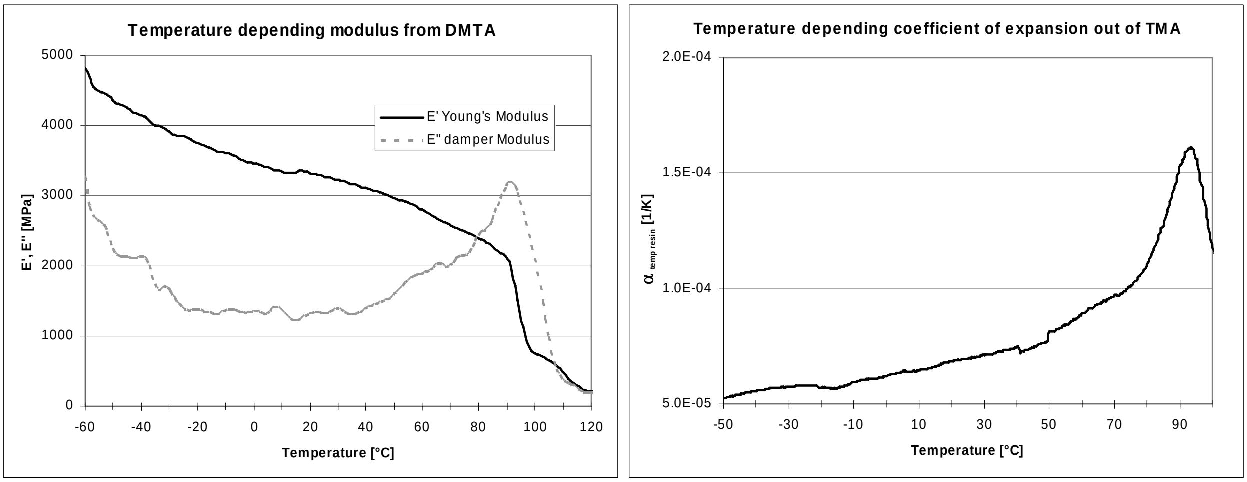

Figure 2. Young's modulus and damper modulus (left) and coefficient of expansion (right) as function of the temperature. DMTA and TMA data on epoxy specimens.

4.0 STRUCTURAL MODEL

An accurate stress analysis is a prerequisite for lifetime calculations. For this purpose an analytical model of a hybrid structure element has been developed which determines the stress conditions in a hybrid pressure cylinder under internal pressure and temperature load. The derived stress level will be used as input for further analytical tools for lifetime and safety level analysis. Starting point for the model is the classical laminate theory (CLT). The CLT is a well established analysis tool for the pre-design of composites. In depth discussion of CLT is provided by the recently published guideline [4] which covers comprehensively almost all aspects concerning the design of composites. The model enhances the CLT by considering the special constraint of hybrid pressure cylinder such as temperature depending material parameters of the resin system and residual stress in the hybrid structure. An overview of the applied model with its enhancements is given in Fig. 3. Further details are presented by the author in [5].

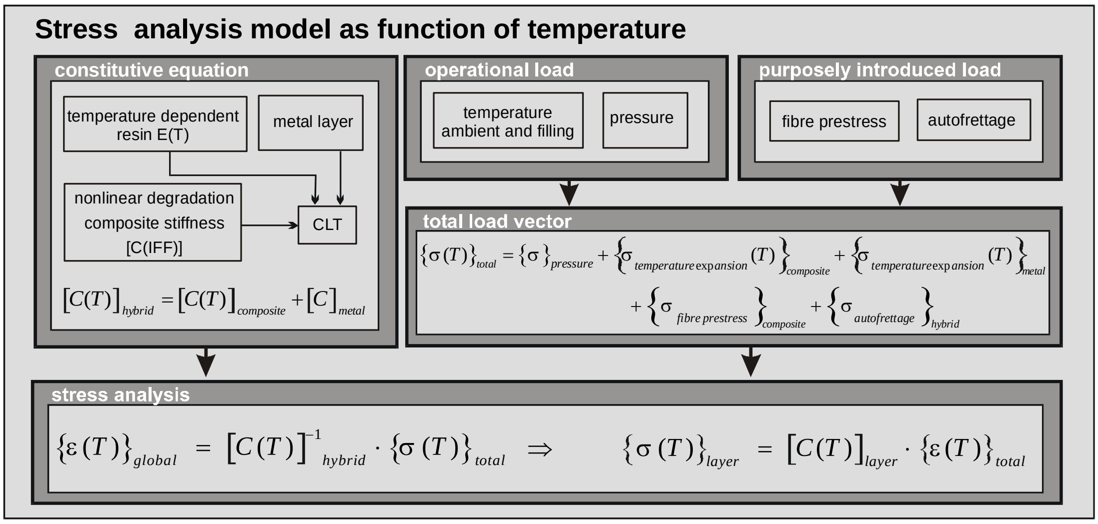

Figure 3: Analytical model for the hybrid element with characteristical enhancements for pressure cylinder with regard of nonlinear structure behaviour due to inter fibre fracture (IFF) according [5].

5.0 THERMAL LOAD VECTOR

For a realistic modeling of a representative temperature load, climate data in Europe which was collected over a period of 30 years [3] has been statistically evaluated.

Depending on the geographic position rather big differences of temperature distributions occur. To represent the temperature range found in Europe two geographical spots each representing an extreme temperature distribution had been chosen. Therefore climate data of the meteorological station of Jokkmokk (Sweden) representing extremely cold and Athens representing extremely hot temperatures were selected.

By processing climatic data it’s possible to generate a frequency distribution of different temperature classes for the cold extreme (Jokkmokk) and the hot extreme (Athens). Combining these distributions leads to the overall temperature range distribution (frequency over temperature classes). The climatic temperature influence, the filling temperature and the pressure load have to be considered in combination with the operation profile of the storage cylinder to derive a complete load vector. This is an important input for an accurate assessment of lifetime and safety level of high pressure hybrid cylinders.

Fig. 4 shows two different temperature distributions depending on the geographic position. Jokkmokk shows a typical distribution of extremely cold temperatures. The maximum amplitude between winter and summer is 76.5 °C with minimum temperature of -42.0°C. Investigating the other side of the temperature load with extreme hot temperature distribution, data of the meteorological station of Athens were assessed. The maximum amplitude here is 48.3°C with a maximum temperature of 42.6°C.

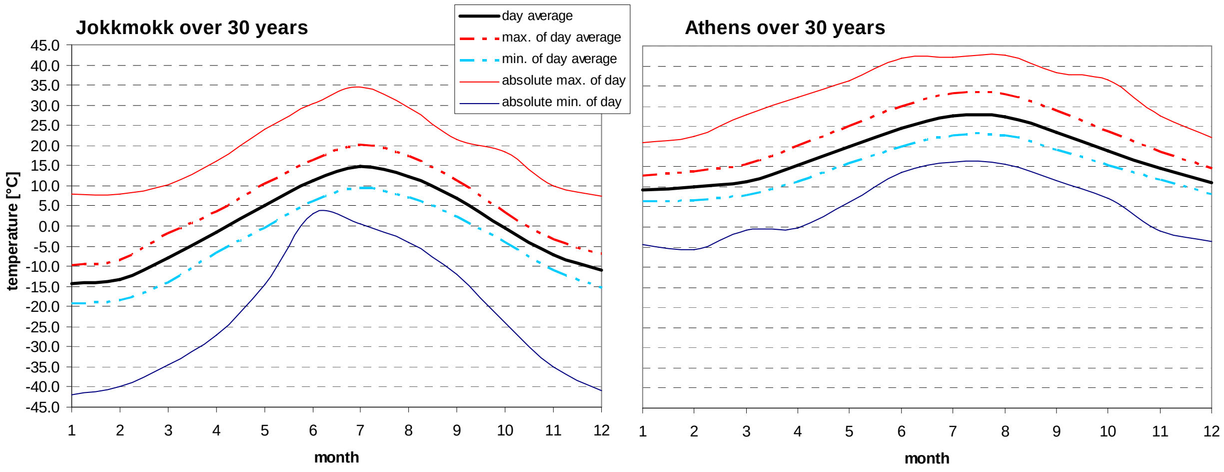

Figure 4. Temperature variation over the year as average number for each month over the period of 30 years.

The objective is to derive out of the above described data two thermal load spectra, one for the cold extreme (Jokkmokk) and one for the hot extreme (Athens). These will be further combined to an overall thermal load spectrum in the frequency domain.

To generate a temperature distribution by statistical means, the following values from the climatic tables are needed:

- Mean value of the minimum temperature μ_{T_min} and
- Absolute minimum temperature $T_{abs.\ min}$.

These values are documented for each month i in Table 1.

Table 1. Climate data of the meteorological station of Jokkmokk. Mean cold temperatures and absolute cold temperature of each month according to [3].

Jokkmokk	**January**	**February**	**March**	**April**	**May**	**June**
μ_{T_min} [°C]	-19.1	-18.3	-14.1	-6.6	-0.4	6.1
$T_{abs.\ min}$ [°C]	-42.0	-40.0	-34.5	-27.0	-14.5	3.0
Jokkmokk	**July**	**August**	**September**	**October**	**November**	**December**
μ_{T_min} [°C]	9.4	7.1	2.3	-4.1	-10.9	-15.3
$T_{abs.\ min}$ [°C]	0.5	-4.0	-12.0	-24.0	35.0	-41.0

For each month a probability density distribution is fitted to the data in Table 1. To derive the density distribution the following two assumptions are made:

- The temperature will follow a Gaussian (normal) distribution within the assessed period of 30 years. This is valid according to Hartung [6] for a sufficiently large sample of a single attribute.

- Each absolute minimum temperature $T_{abs.\,min}$ will occur once within the period of 30 years within a 30 day months. This means that this value occurs once in the total number of 30 • 30 = 900 days which leads to a relative frequency of:

$$H(T_{abs.\min,i}) = \frac{1}{900} = 0.00\bar{1} \tag{1}$$

Every normally distributed variable can be transformed to the standard normal variable u(x) by the following relationship:

$$u(x) = \frac{x-\mu}{sd} \tag{2}$$

Where x is the non-transformed value of the random variable, μ its mean and sd its standard deviation. The quantiles of the standard normal variable, i.e. its values at a certain cumulative frequency, are tabulated or available through computer programs like EXCEL or MATHEMATICA. For a frequency of 0.001 the approximate value of the standard normal variable u(x) is -3.059. By substituting this into equation 2 together with the data from Table 1 ($\mu_{T\_min,i}$ for μ and the $T_{abs.\,min,I}$ for x) we can calculate the standard deviation of the temperature distribution, sd_i, for every month:

$$sd_i = \frac{T_{abs.\min,i} - \mu_{T\_\min,i}}{-3.059} \tag{3}$$

With the two parameters $\mu_{T\_min,i}$ and sd_i, the normal probability density function (PDF), say *f*(x), is completely determined:

$$f_i(x) = \frac{1}{\sqrt{2\cdot\pi}\cdot sd_i}\cdot e^{-\frac{(x-\mu_{T\_\min,i})^2}{2\cdot sd_i^2}} \tag{4}$$

In the next step temperature classes are set at increments of ΔT = 5°C. The frequency of one class, H_k, is determined by equation (5), by calculating the area underneath the normal PDF within the corresponding limiting temperatures of that class. The integrals are numerically solved.

$$H_{k,i}(\Delta(T_k, T_{k+1})) = \int_{-\infty}^{T_{k+1}} f(x)\,dx - \int_{-\infty}^{T_k} f(x)\,dx \;; with\ T_{k+1} > T_k \tag{5}$$

Fig. 5 visualizes this integration of the normal PDF for the month April and the temperature class between -15 and -10 °C.

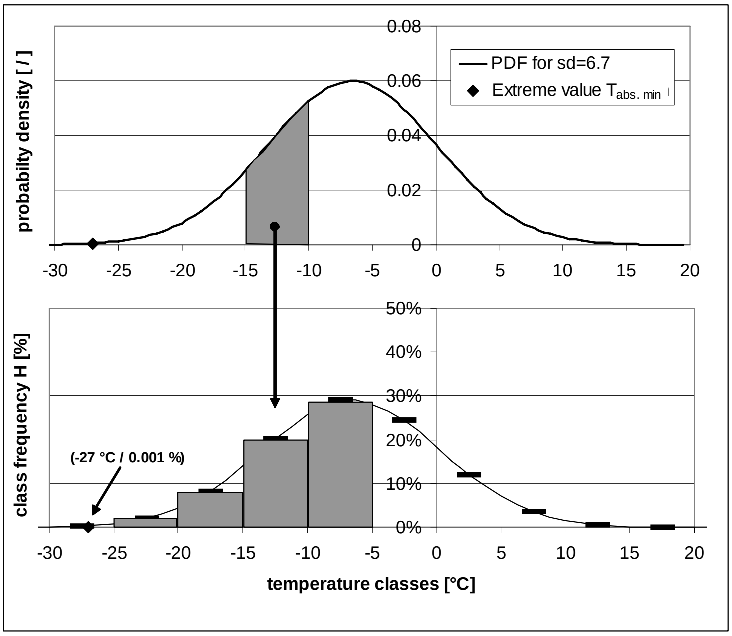

Figure 5. Procedure how to derive out of PDF the class frequency H_k for the month April with mean value of the minimum temperature μ_{T_min} = -6.6°C, absolute minimum temperature $T_{abs. min.}$= -27°C and standard deviation sd_{April} = 6.7 °C.

This procedure has to be carried out for all 12 calendar months, i, and all temperature classes k. In order to derive for Jokkmokk the frequency $\overline{H_k}$ of temperature classes for the whole year the arithmetic mean value for each temperature class over the 12 calendar months is determined:

$$\overline{H_k} = \frac{1}{12}\sum_{i=1}^{12} H_{k,i} \tag{6}$$

To derive the year’s class frequency of the hot temperature distribution (Athens) the same procedure is being applied. Only the input data are different as the values of the absolute highest temperature $T_{abs. max}$ and the mean value of the hot temperatures $\mu_{T\,max}$ (see Table 2).

Table 2. Climate data of the meteorological station of Athens. Mean hot temperatures and absolute hot temperature for each month according to [3].

Athens	**January**	**February**	**March**	**April**	**May**	**June**
μ_{T_max} [°C]	12.9	13.9	15.5	20.2	25.0	29.9
$T_{abs. max}$ [°C]	20.9	22.5	27.8	32.2	36.2	41.9
Athens	**July**	**August**	**September**	**October**	**November**	**December**
μ_{T_max} [°C]	33.2	33.1	29.0	23.8	18.6	14.6
$T_{abs. max}$ [°C]	42.3	42.6	38.4	36.5	27.7	22.2

The resulting class frequency for the cold (Jokkmokk) and hot (Athens) temperature distribution are presented in Fig. 6. It shows with which portion the different temperature classes occur.

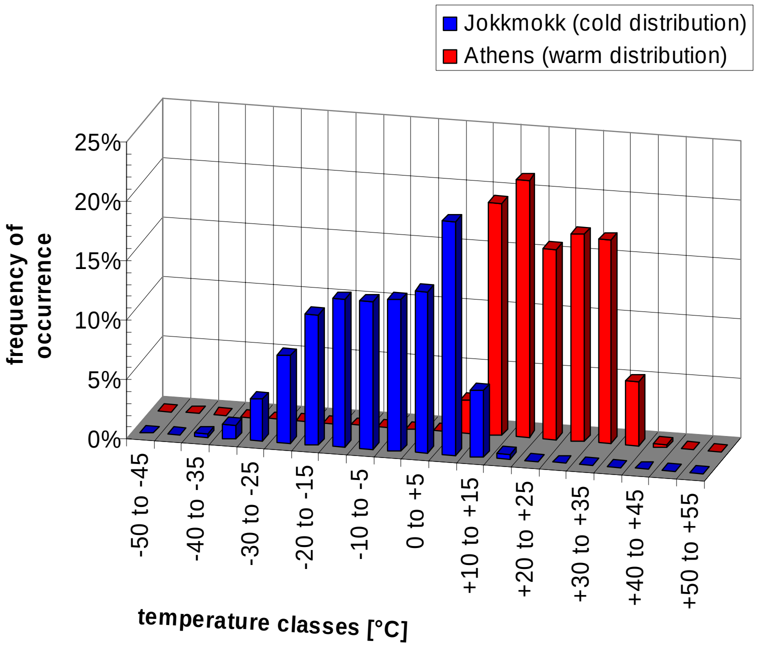

Figure 6. Frequency of temperature classes.

6.0 TEMPERATURE INFLUENCE ON STRESS VALUES

A worst case for thermal amplitudes would be fast filling (maximum hot temperature) in Jokkmokk (minimum cold temperature). The maximum amplitude would be from the temperature class '-40°C to -35°C' up to filling temperature of 140°C which represents the absolute maximum temperature for a short period of time. This temperature range $\Delta T = 175°C/180°C$ would occur with a frequency of 0.27 % according to the derived frequencies in Fig. 6.

To determine the effects of temperature a stress analysis of a hybrid element was performed. The element consists of one aluminum layer and eight carbon fiber layers (0° and 90° orientation). No further loads besides the thermal load were applied. In the calculation for the following Fig. 7 and Fig. 8 the effects of inter fiber fracture (IFF) on the structure behavior have not been included. It presents exclusively the thermal effects taking into account the nonlinear material behavior of the resin system due to temperature load and the residual stresses due to different coefficients of expansion of the metal layer and the composite layers.

Under cyclic loading the most common failure mode is leakage due to fatigue cracks in the cylindrical part of the liner. Therefore the stress level of the liner is of interest for lifetime calculations. The tensile stresses of the internal pressure load are superposed on the thermal stresses. Fig. 7 shows that thermal stresses of the liner do have a sufficient distance to the yield strength of 290 MPa of the used liner material. Nevertheless they do effect lifetime calculations. Fig. 7 also shows the maximum frequency and maximum stress amplitude for the two geographical spots.

In Fig. 8 the distinctively decreasing Young's modulus of the resin can be recognized by the decreasing stress values σ_2 with rising temperature. In this direction the resin material properties are dominating the structural behavior of the composite layer. At a temperature of about 100°C the glass transition temperature is being reached and the composite stiffness in perpendicular direction to the fiber drops to a value close to zero. Therefore the stresses drop as well.

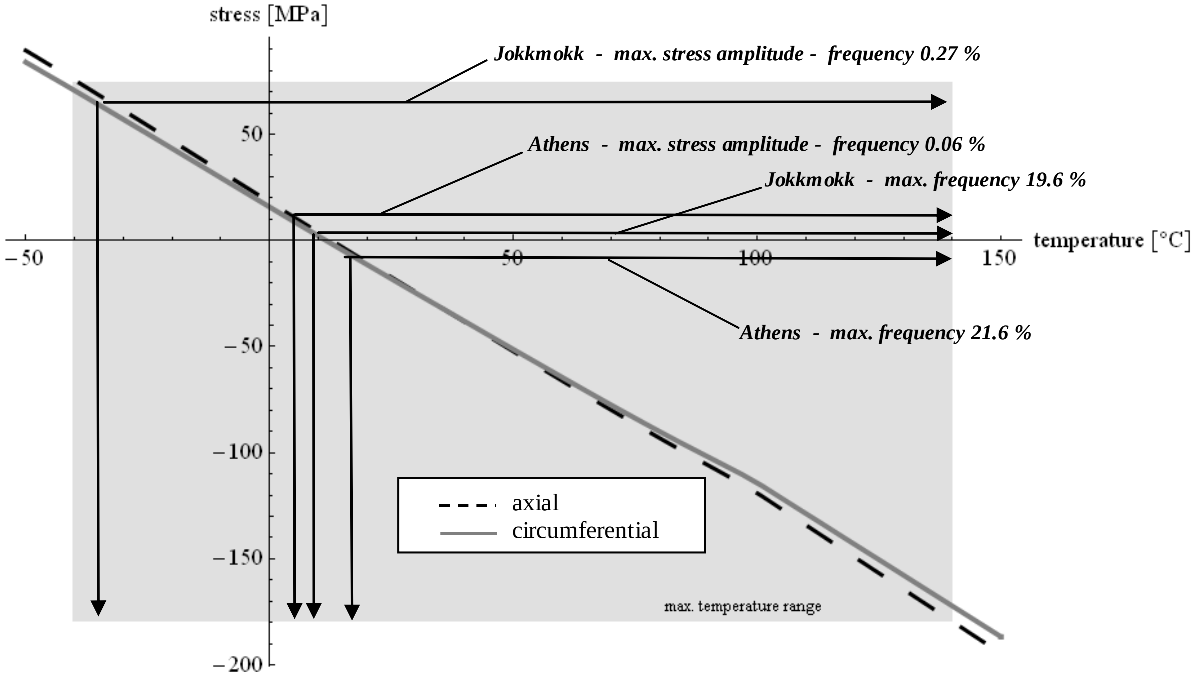

Figure 7. Occurring stresses in the aluminum liner due to changes of temperature.

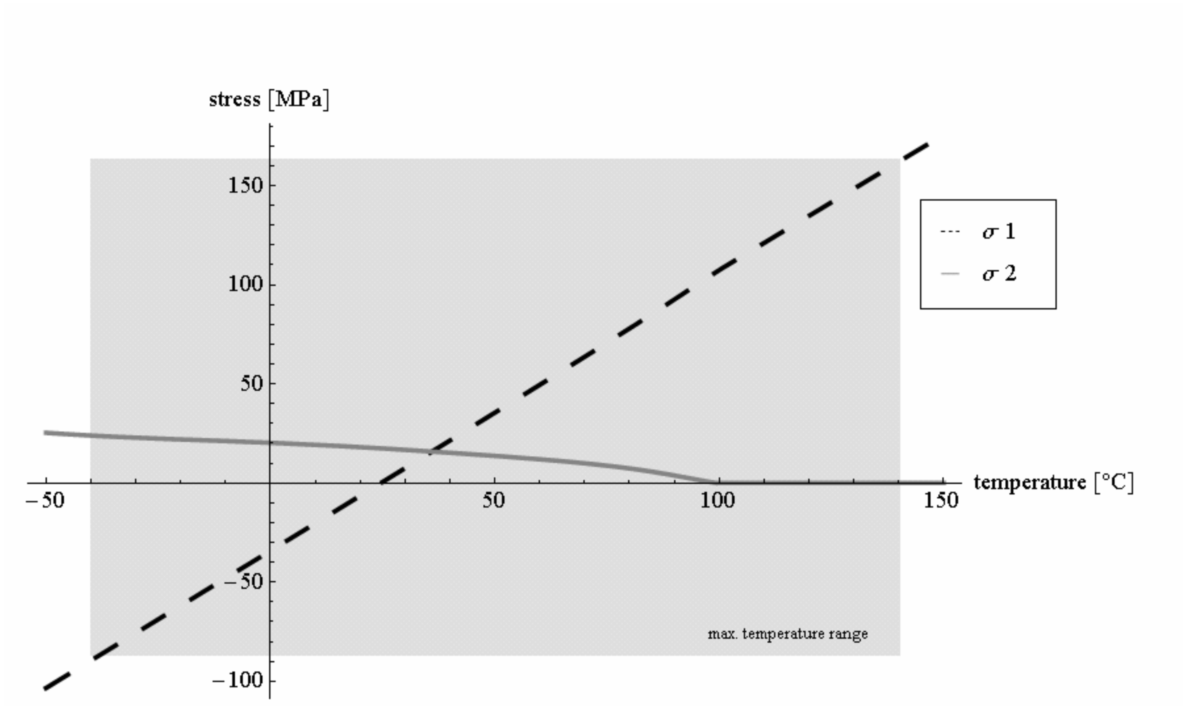

Figure 8. Occurring stresses in a unidirectional carbon fibre layer due to changes of temperature.

7.0 CONCLUSIONS

The presented statistical procedure is one step towards a more realistic simulation of the structural behavior of a high pressure storage cylinder. The knowledge of the occurring frequency of occurrence, time, and range of temperatures in the life of a pressure cylinder is especially important for composite cylinders with their typical temperature depending material behavior.

For lifetime calculations the presented statistical procedure gives two important pieces of information. First the temperature range as a thermal cycle form minimum to maximum values to evaluate numbers of load cycles. Secondly, it gives the frequency of occurrence or the time of how long one temperature is applied to the cylinder. This is input data for the sustained load calculations (creep simulation). Both phenomena will have to be regarded and combined in future assessments.

First simulations showed that the temperature changes from -40°C up to +140°C, which had been derived from the statistical assessment of climate data, generate non-negligible stresses in the liner and composite layers. This effect on the material must therefore be taken into consideration in further lifetime and safety assessments of composite pressure composite cylinders (type III and type IV).

8.0 ACKNOWLEDGEMENTS

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