Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Composite storage systems for compressed hydrogen - systematic improvement of regulations for more attractive storage units

G.W. Mair [a,*], B. Becker [b], S. John [a], E. Duffner [a]

[a] Bundesanstalt für Materialforschung und -prüfung BAM (Federal Institute for Materials Research and Testing), Unter Den Eichen 44-46 12203 Berlin, Germany

[b] H2 Mobility Deutschland GmbH & Co.KG, EUREF-Campus 10-11, 10829 Berlin, Germany

ARTICLE INFO

Article history:
Received 24 November 2017
Received in revised form
15 March 2018
Accepted 6 April 2018
Available online 26 April 2018

Keywords:
Probabilistic
Monte-Carlo
Regulations
Composite cylinder
Hydrogen vehicles
Transport of dangerous goods

ABSTRACT

Hydrogen is an attractive energy carrier that requires high effort for safe storage. For ensuring safety, they must undergo a challenging approval process. Relevant standards and regulations for composite cylinders used for the transport of hydrogen and for its on-board storage are currently based on deterministic (e.g. ISO 11119-3) or semi-probabilistic (UN GTR No. 13) criteria. This paper analysis the properties of such methods with respect to the evaluation of load cycle strength. Their characteristics are compared with the probabilistic approach of the BAM. Based on Monte-Carlo simulations, the available design range (mean value and scatter of strength criteria) of current concepts was exemplarily estimated. The aspect of small sample sizes is analysed and discussed with respect to the evaluation procedures.

Introduction

Hydrogen is an attractive energy carrier that needs to be compressed (CGH_2) or liquefied (LH_2) for storage and transport. The high storage pressure bares a risk of rupture with high consequences. Therefore, H_2-storage systems must undergo an extensive approval process. Relevant assessment criteria for approval and definition of retest periods of composite cylinders are intended to ensure a safe use over its entire service life. The overall aim is to avoid a critical failure during service. The risk of such a failure can never eliminated but must be reduced to a broadly accepted level. In this case the residual risk is accepted as a function of consequence.

The usual methods for the approval of composite cylinders for compressed hydrogen are based on determined minimum performance criteria. They follow the concept of a deterministic approach, i.e. the proof of minimum values concerning burst pressure and load cycle strength.

The approval of composite cylinder for CGH_2 storage systems for vehicles needs to follow the criteria from the Global Technical Regulation No. 13 of the United Nations (WP.29), so called UN GTR 13 [1]. Regarding burst pressure, this GTR 13 is

* Corresponding author.
E-mail addresses: georg.mair@BAM.de (G.W. Mair), becker-ben@freenet.de (B. Becker), sebastian.john@BAM.de (S. John), eric.duffner@BAM.de (E. Duffner).

https://doi.org/10.1016/j.ijhydene.2018.04.068

based on an extended semi-probabilistic approach. This means, there is a specific minimum burst pressure as usual. In addition to that the maximum scatter of the single burst test results is also limited. Regarding load cycle strength, it is required to demonstrate a minimum number of load cycles (e.g. 11,000) without failure by testing just three specimens resisting.

BAM (Bundesanstalt für Materialforschung-und prüfung) has developed a probabilistic approach (PA) that could be developed to an alternative to the GTR 13. The BAM-PA [2,3], is based on sample testing and statistical assessment in combination with reliability criteria. Sample means here always a group of nominally identically manufactured and used composite cylinders. The approach is currently used by the BAM to determine retest periods for composite cylinders according to ADR/RID P200 (9) [4] and for service life tests for UN composite cylinders according to section 6.2.2.1.1 of IMDG Code [5] and ADR/RID.

The comparison of these different assessment methods leads to the question: Which level of safety do they ensure and how much potential do they offer for further optimization of composite cylinders?

Concerning burst pressure, this has been already investigated in Ref. [6] by using a theoretical analysis without a Monte-Carlo simulation and in Ref. [7] by using Monte-Carlo simulation. In the following, the Monte-Carlo simulation is extended to the statistical analysis of test results created by cycle testing with respect to the GTR 13 and the BAM-PA. This is done on the basic analysis of LC-requirements in Refs. [8,9].

Monte-Carlo simulation

The concept of a Monte-Carlo simulation [10] bases on a high number of computer-generated values. These values represent physical properties or test results taken out from a basic population. This basic population follows an assumed distribution function with defined mean value and scatter. For simulating the evaluation of sample testing (in the meaning of a sampled group of specimens), even the generated values can be grouped into samples with a determined sample size n. Due to the limited sample size, mean value and scatter of a single sample deviate from the true characteristics of the original basic population.

In principle, there is no possibility to demonstrate that an assumed distribution of parameters describe the production of a certain design type. But [3] and [8] show a lot of test results and explains a lot of interactions with respect to measured data from new and even from aged composite cylinders of several design types. Thus [3], demonstrates that the used parameters are realistic in principle and are worth to be studied with respect to their evaluation by regulations.

A Monte-Carlo simulation allows analysing complex technical systems under consideration of statistical deviations of their properties.

This concept can be adopted to burst pressure and load cycle strength of composite cylinders. Corresponding studies on the statistical distribution of both performance parameters are presented in Refs. [11,12].

The burst pressure p_B of composite cylinders (composite pressure vessels) follows usually a normal distribution that can be (roughly) described by a mean value and standard deviation. Following example bases on the related burst pressure Ω_B. Ω_B represent a burst pressure in relation to the test pressure (PH) as the maximum accepted load level. The related mean value Ω_μ and related standard deviation Ω_σ of a normal distributed basic population existing of N cylinder can be calculated as shown in equations (1) and (2).

$$\Omega_\mu = \frac{1}{N} \cdot \sum_{i=1}^{N} p_{Bi}/PH \tag{1}$$

$$\Omega_\sigma = \sqrt{\frac{1}{N-1} \cdot \sum_{i=1}^{N} \left(p_{Bi}/PH - \Omega_\mu \right)^2} \tag{2}$$

The generation of virtual burst pressures Ω_B out of Ω_μ and Ω_σ requires a random number generator for uniformly distributed numbers in the interval of [−1... 1]. These random numbers can be converted into a normal distribution with the parameters Ω_μ and Ω_σ by the polar method as shown in equations (3)–(5).

u, v = random points in [−1...1]

$$q = u^2 + v^2 < 1 \tag{3}$$

$$x = u \cdot \sqrt{\frac{-2 \cdot \ln q}{q}} \tag{4}$$

$$\Omega_B = \Omega_\mu + x \cdot \Omega_\sigma \tag{5}$$

Fig. 1 shows for example the variety of sample properties from burst tests according to GTR 13. Mean value and scatter of the samples scatter around the true (but unknown) characteristics of the basic population. Each individual point in Fig. 1 was generated using the Monte-Carlo simulation and represents burst values of a sample of n = 3 cylinders. The comparatively small sample size of n = 3 creates a wide range of possible sample properties out of the same basic population. The challenge of an approval requirement is to identify potentially unsafe design types despite the high variability of the test results.

Fig. 1 uses the sample performance chart (SPC) developed and applied by the BAM since 2012. The combined representation of mean value and scatter in relation to the test pressure PH enables the display of both properties relevant for a safety assessment. The shown scatter of sample properties results from the basic population with a mean burst pressure $\Omega_{50\%}$ of 260% PH and a scatter Ω_s of 10% of PH.

When these generated samples get combined with an assessment criterion, they can be divided into two groups: Samples that meet the criterion (black) and those, which do not meet it (red). Fig. 1 bases on the criterion according to GTR 13. Each of the three burst pressure values within a sample must exceed the test pressure PH by 1.5 times, i.e. the nominal working pressure (NWP) by 2.25 times. Additionally, each burst pressure needs to be within a range of ±10% of the mean value $\Omega_{50\%}$.

As shown in Fig. 1, around 93% of the generated samples include adequate test results and fulfil the burst criterion of the GTR 13. That means that the underlying basic population of composite cylinders would be accepted with a probability

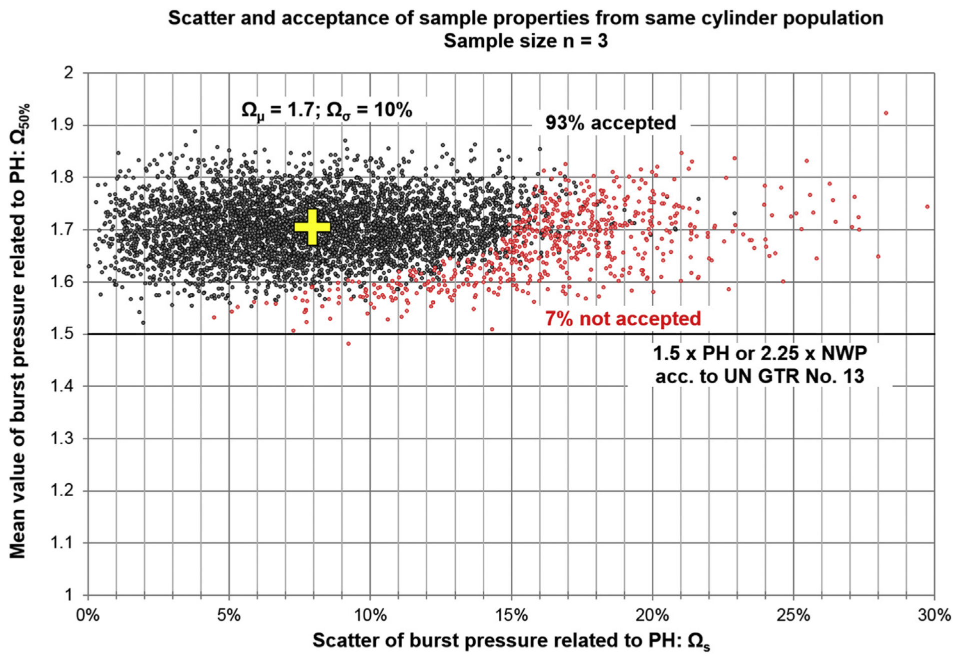

Fig. 1 – Monte-Carlo simulation of sample properties for a cylinder population $\Omega_\mu = 1.7$; $\Omega_\sigma = 10\%$, assessed by UN GTR No. 13.

93%. This probability is called Acceptance Rate (AR). Conversely, the basic population would not meet the criterion with a probability of about 7%.

The example shows that the evaluation of a small sample with n = 3 leads to considerable uncertainties. These uncertainties are always present but usually covered by appropriate safety margins and additional tests. However, the decisive point of an assessment criterion should be the risk that an unsafe design type could be accepted - or even not.

To evaluate this, it is necessary to define clearly the term "unsafe" respectively "safe".

In the case of burst pressure, "safe" can be defined by the reliability or survival rate (SR) against a sudden rupture at a certain pressure [3,4,11]. A comparable criterion for load cycle strength could be based on the reliability against a leakage or sudden rupture after N[1] further additional load cycles. In case of a composite cylinder at its end of service life N corresponds to just one (the very last) residual load cycle.

Evaluation OF UN GTR 13

The adoption of Monte-Carlo simulation to generate load cycle values requires a suitable assumption of the distribution function for the load cycle strength of composite cylinders.

The average load cycle strength $N_{50\%}$ and scatter N_s are obtained by a combination of Log-Normal and Weibull distribution [8]. Fig. 2 shows the adopted sample performance chart for load cycle values and the Monte-Carlo Simulation of samples (n = 3) derived from a basic population with the properties of $N_{50\%} = 15{,}000$ LC; $N_s = 1.2$. These samples are evaluated according to the determined load cycle acceptance criteria in GTR 13. Each number of load cycles of a sample shall be higher or equal than 11,000 LC. For the given example, 80% of the derived samples fulfil this requirement.

[1] Due to common practise, "N" is used here for the size of a basic population as well as for the number of tested load cycles. The meaning becomes always clear within the context.

Each sample of load cycle values is described by its mean load cycle strength $N_{50\%}$ and its scatter value N_s. These two parameters result from the residual load cycle strength N_i of n individual test results by using a Log-Normal distribution, as shown in equations (6)–(9).

$$m_{log} = \frac{1}{n}\sum_{i=1}^{n}\log_{10}(N_i) \tag{6}$$

$$s_{log} = \sqrt{\frac{1}{n\text{-}1}\sum_{i=1}^{n}\left(\log_{10}(N_i)\text{-}m_{log}\right)^2} \tag{7}$$

$$N_{50\%} = 10^{m_{log}} \tag{8}$$

$$N_s = 10^{s_{log}} \tag{9}$$

With respect to load cycle strength, the BAM-PA is based on a Weibull distribution, since the approach aims on a sufficient safety at end of service life. The Weibull distribution is a conservative assumption for residual load cycle properties of composite cylinders. A Weibull distribution is described by the parameters characteristic lifetime T and form parameter b, equation (10).

$$SR(N) = e^{-\left(\frac{N}{T}\right)^b} \tag{10}$$

In combination with the SPC the Weibull parameters can be transformed to parameters of a Log-Normal distribution according to [13].

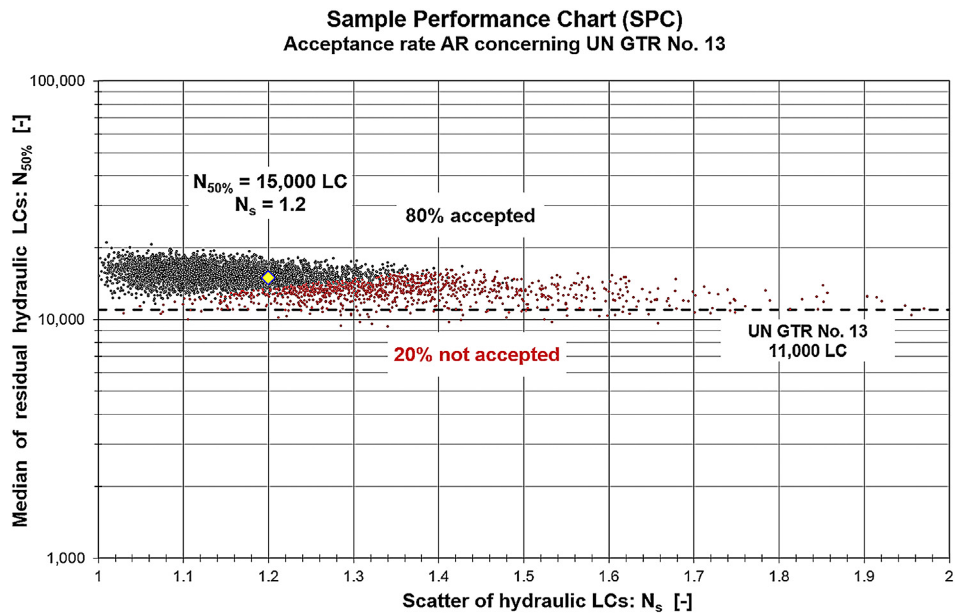

Fig. 2 – Monte-Carlo simulation of sample properties for a cylinder population $N_{50\%} = 15{,}000$ LC; $N_s = 1.2$, assessed by UN GTR No. 13.

$$T = N_{50\%} \cdot N_s^{0.48416} \tag{11}$$

$$b = 1.02743/(2 \cdot \log_{10}(N_s)) \tag{12}$$

The equations (11) and (12) allow a simplified representation of a Weibull distribution by parameters of a Log-Normal distribution.

A high number of Monte-Carlo simulations for different combinations of $N_{50\%}$ and N_s allows to calculate acceptance rates (AR) over the entire range of the SPC. Points from basic populations (N_s; $N_{50\%}$) with same AR are linked together to isolines of a constant acceptance rate, called "AR-isoasfalia".

Fig. 3 shows the distribution of AR for the load cycle criterion of GTR 13. For a better understanding: if the properties of a basic population of composite cylinders are located e.g. on the isoasfalia AR = 50%, there will be a probability of 50% that this basic population meets the requirement of GTR 13. Fig. 2 combines the calculated isoasfalia for AR with the safety criterion of a reliability of $1\text{-}10^{-6}$ (99.9999%) against failure at the next load cycle (red line).

Two main questions arise in this context:

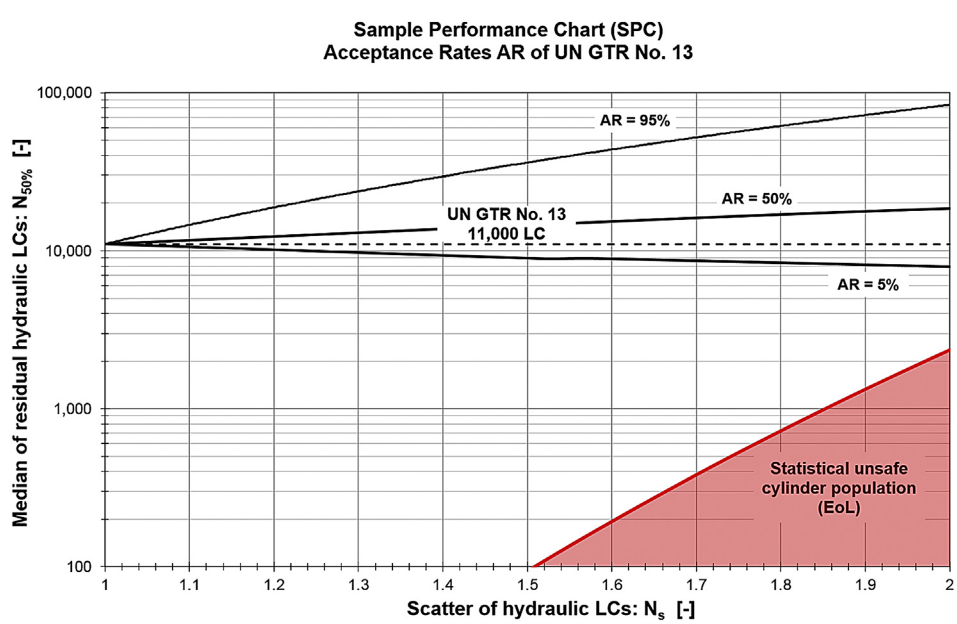

Fig. 3 – AR-isoasfalia for GTR 13 in comparison to statistically unsafe cylinder populations.

1. What is the acceptance rate for a potentially unsafe population of composite cylinders?
2. Which range of $N_{50\%}$ and N_s can be used for designing composite cylinders acc. to GTR?

Concerning the first question, Fig. 3 shows at very high scatter values of $N_s = 2$ the general possibility to accept a basic population with a mean load cycle strength of $N_{50\%} < 8000$ LC. The probability to accept a potentially unsafe cylinder population below the red line is less than 5% and consequently practically irrelevant.

For the second question, it can be assumed that an acceptance rate of above AR = 50% should be relevant in practice. Otherwise a design type would be conspicuous due to too many rejected batch tests and becomes therefore uneconomical. Acceptance rate of AR = 95% appears to be realistic from experience.

The range between the line of AR = 95% and the red line of minimum reliability can be considered as a range of permissible reduction in load cycle strength during service life.

This example shows, that even in case of a deterministic criterion, the scatter of a tested properties has a significant impact on an approval process.

Evaluation of BAM-PA

A similar application of the Monte-Carlo simulation to the BAM-PA for the probabilistic assessment of load cycle strength is shown in Fig. 4.

The BAM-PA is based on statistical assessment in combination with reliability criteria depending on failure consequences. The method is not bound to a fixed sample size.

A cylinder population with a reliability of less than $1\text{-}10^{-6}$ against failure (red line, compare [3,6,12]) is regarded as unsafe for further use. A reliability of $1\text{-}10^{-6}$ is related to failure consequences of a sudden rupture. The required reliability level can be reduced to $1\text{-}10^{-4}$ in case of a cylinder design with proven leak-before-break behaviour.

The already explained uncertainty of sample testing is covered in the PA by operating a confidence level of 95%. Therefore, a sample needs to demonstrate at least an average strength for load cycles and a scatter value above the dotted line. Aim of this approach is to ensure that the acceptance rate of a potentially unsafe cylinder population is not significantly higher than 5%. The shown example is based on a sample size of n = 5 test results.

Fig. 4 shows that in case of a cylinder population which is located on the line of the minimum requirement, a sample would be accepted by slightly more than 50%.

The isoasfalia of AR = 95% limits the range of the de facto required properties for a cylinder population as otherwise the requirement would not be fulfilled very often.

There is an interesting other approach in the literature described in Refs. [14,15] that should be mentioned at this point. Unfortunately, the approach does not consider the importance of the influence of scatter properties.

GTR 13 compared WITH BAM-PA

Regarding the acceptance of potentially unsafe cylinder populations, Fig. 5 shows the acceptance rates of a cylinder population with a marginal reliability of SR = $1\text{-}10^{-6}$ against failure depending on scatter N_s.

As already explained, the BAM-PA results into a constant level of acceptance of around 5%. The corresponding line for the GTR 13 are separately shown for the minimum requirement of 11,000 LC. The GTR 13 criterion shows a sharp increase in the acceptance rate at a scatter level of $N_s > 2$. For

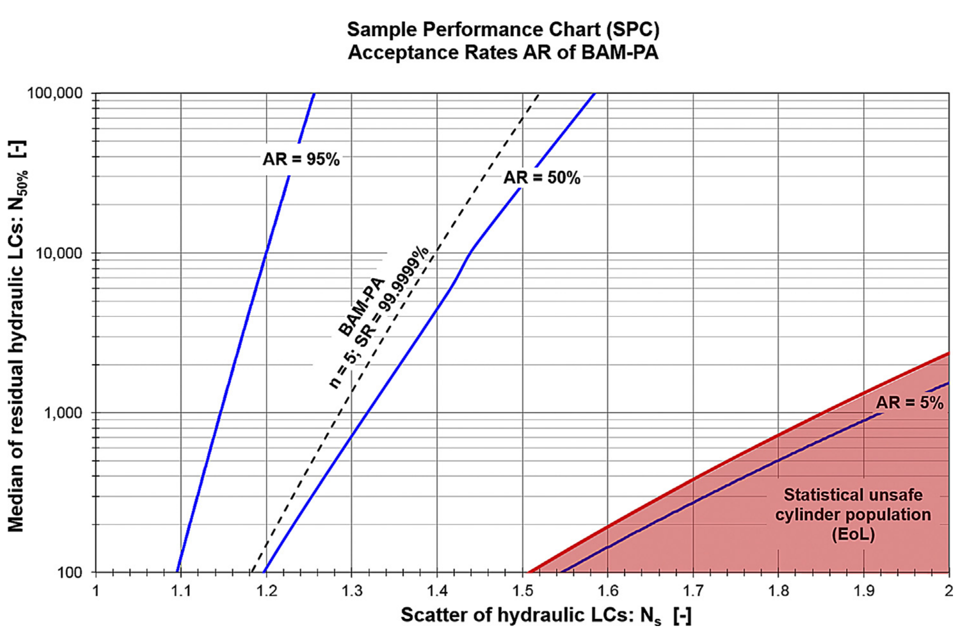

Fig. 4 – AR-isoasfalia for BAM-PA in comparison with statistically unsafe cylinder populations.

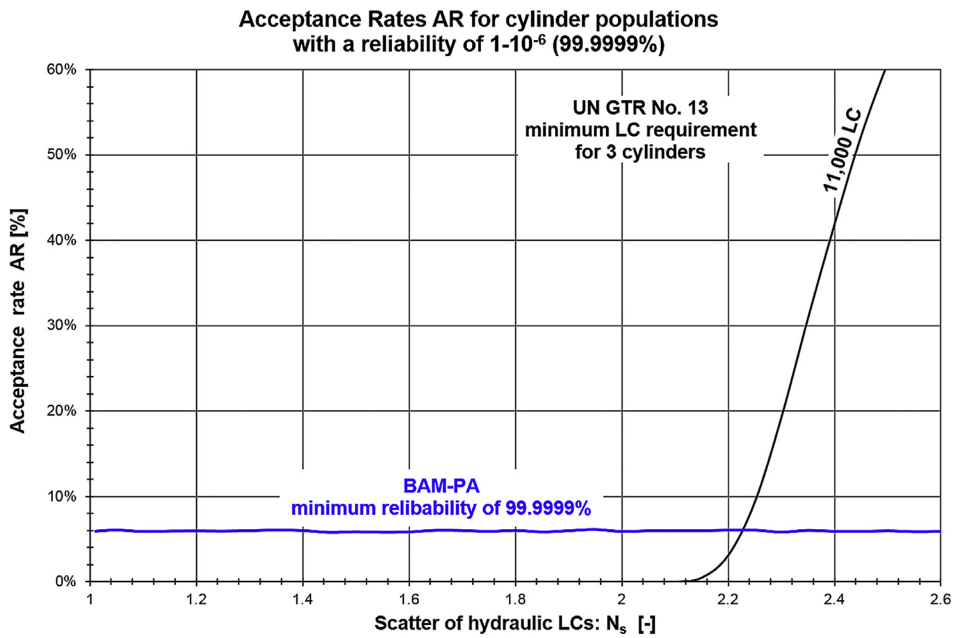

Fig. 5 – Acceptance rates of cylinder population with a critical reliability of 99.9999.

$N_s < 2$, the acceptance rate is close to zero. The GTR 13 exclude the acceptance of cylinder population with critical reliability against failure only up to a scatter level of around $N_s = 2$. This method is in most cases sufficient, but cannot detect potentially unsafe cylinder designs with a very high scatter of load cycle strength.

Fig. 6 shows the AR isoasfalia for the GTR 13 and the BAM-PA. For the BAM-PA with n = 5 the scatter N_s of a cylinder population should be lower than 1.25 for reaching an acceptance rate of AR = 95%. In comparison, the GTR 13 allows to accept cylinder populations with a much higher scatter value. On the other hand, the BAM-PA allows accepting cylinder populations with very low mean load cycle strength in case of a scatter $N_s < 1.2$. A low scatter value of load cycle strength leads to an increased reliability against failure. This is considered in the BAM-PA and demonstrates the general potential of weight and cost savings by probabilistic assessment criteria. A high production quality ensures a high reliability against failure even at lower mean load cycle strength.

Even if the isoasfalia AR = 95% of the BAM-PA seems to reduce the scatter to a relatively small range this requirement is far less limiting the freedom for design in practical terms. In contrast to the GTR 13 and other standards based on deterministic requirements, a probabilistic assessment does not

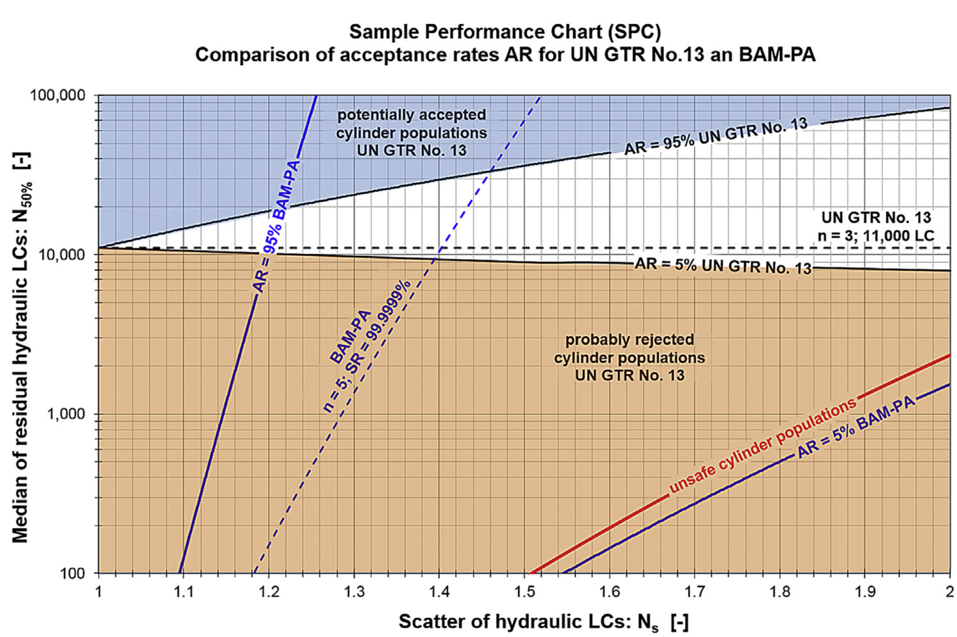

Fig. 6 – Requirements and of areas of acceptance for GTR 13 and BAM-PA.

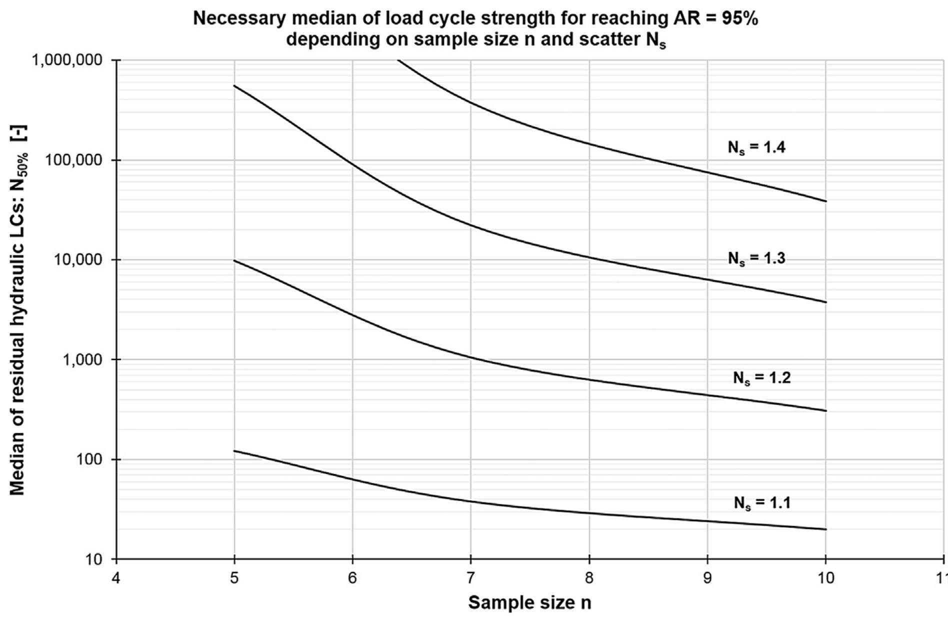

Fig. 7 – Required load cycle strength for BAM-PA to achieve an acceptance rate of 95% for specific scatter values of basic populations.

require fixed minimum values. It is important to look at the characteristics of the entire sample.

Therefore, it is possible within the BAM-PA to increase the sample size if necessary. This offers additional and more accurate information about a cylinder population. In practical use of the BAM-PA, an increased sample size often proves that the minimum requirement for the sample is met despite a critical first impression.

An increased sample size reduces the statistical uncertainty. Regarding Fig. 4, this means that the dotted black line and corresponding lines for AR moves further right and allows higher scatter values.

The isoasfalia for AR = 95% and a sample size of n = 5 follows an exponential function as shown in equation (13).

$$N_{50\%;AR=95\%;n=5} = N_s^{50.4} \tag{13}$$

An increase of sample size to n = 7 and n = 10 reduced the exponent of N_s as follows:

$$N_{50\%;AR=95\%;n=7} = N_s^{38.1} \tag{14}$$

$$N_{50\%;\ AR=95\%;\ n=10} = N_s^{31.4} \tag{15}$$

The resulting dependencies between sample size n, scatter N_s and mean load cycle strength $N_{50\%}$ are shown in Fig. 7 for an acceptance rate of AR = 95%.

The required load cycle strength which ensures a minimum reliability against failure for a sample scatter of $N_s = 1.2$ is reduced from 10,000 LC (n = 5) to 300 LC (n = 10). This effect is directly related to reduced statistical uncertainties in case of a sample size of 10 test specimens versus a sample size of only 5 test specimens with otherwise equivalent properties. The consideration of additional test results leads to an improved knowledge about the true properties of a cylinder design.

Additional tests to increase the sample size for a statistical assessment cannot be compared with the very questionable praxis of retesting individual results in deterministic procedures. In case of a statistical assessment all previous test results are still part of the sample. In contrast, retests procedures for deterministic requirements are ignoring previous test results.

Conclusions

It is shown that deterministic and probabilistic requirements result in very different safety evaluation and thereby in differences concerning the acceptance of test results. This difference is obvious at high scatter values and therefor at potentially unsafe cylinder populations.

The used method of operating the Monte-Carlo simulation offers detailed analyses of approval criteria. Monte-Carlo simulation can be used to identify under which conditions minimum requirements could be reduced without critical safety losses; or need to be improved.

Especially probabilistic approval requirements allow considerable improvements regarding the avoidance of critical cylinder populations. A probabilistic safety assessment offers a high potential for future optimization of cylinders design and production. The consideration of scatter values provides additional information about production quality and reliability. Additionally, an optional increase of sample size allows immediate reactions on uncertainties in demonstration of safety.

Acknowledgements

Particularly with regard to the complexity of the issue, we thank to lot of scientists, who have given hints on certain effects and on deficits during the last years concerning their interpretation and understanding.

This work did not receive any specific grant and has been financed by the BAM Bundesanstalt für Materialforschung und -prüfung.

Nevertheless, the experience accumulated in many projects are the basis. These projects were “StorHy” (EU-frame work program FP 6), “INGAS” (FP 7), “HyComp” (FP7), “HyCube” (KIC: knowledge and innovation communities) on European level and German projects like “Long-term behaviour” (BMVI: German ministry for transport) and “Cryo-Code” (NOW: national organization hydrogen).

REFERENCES

[1] UN GTR No. 13. Global technical regulation concerning the hydrogen and fuel cell vehicles. 2013.

[2] BAM. Official publications: dangerous goods containments – composite pressure receptacles, Berlin, Germany. 2016. http://www.tes.bam.de/en/regelwerke/amtliche_mitteilungen/index.htm.

[3] Mair GW. Safety assessment of composite cylinders for gas storage by statistical methods. Springer International; 2017.

[4] ADR/RID. Technical annexes to the European agreements concerning the international carriage of dangerous goods. 2017.

[5] International Maritime Code for Dangerous Goods (IMDG Code). Amendment 37–14. London, UK: International Maritime Organization; 2014.

[6] Becker B, Mair GW. Statistical analysis of burst requirements from regulations for composite cylinders in hydrogen transport. Mater Test Mar. 2017;59:226–32.

[7] Mair GW, Hoffmann M, Scherer F. Type approval of composite gas cylinders – probabilistic analysis of RC&S concerning minimum burst pressure. Int J Hydrogen Energy 2015;40(15):5359–66.

[8] Mair GW, Becker B, Scholz I. Assessment of the type of statistical distribution concerning strength properties of composite cylinders. In: Proceeding of 20th International Conference on Composite Materials, Copenhagen; 2015.

[9] Mair GW, Becker B, Duffner E, Saul H, Schoppa A. Composite gas cylinders - probabilistic analysis of minimum load cycle requirements. Int J Hydrogen Energy 2017;42(2017):7474–84.

[10] Zio E. The Monte Carlo simulation method for system reliability and risk analysis, London, 2013. 2013.

[11] Becker B, Mair GW, Scherer F. Burst strength of composite cylinders – assessment of the type of statistical distribution. Mater Tes Sep. 2014;56:642–8.

[12] Becker B, Mair GW. Risks and safety level of composite cylinders. In: Proceedings of WHEC 2016; 2016. p. 34–5. Saragossa.

[13] Haibach E. Betriebsfestigkeit: verfahren und Daten zur Bauteilberechnung. Düsseldorf: VDI-Verlag; 1989.

[14] Kaspar Lasn K, Echtermeyer AT. Safety approach for composite pressure vessels for road transport of hydrogen. Part 1: Acceptable probability of failure and hydrogen mass. Int J Hydrogen Energy 2014;39(2014):14132–41. https://doi.org/10.1016/j.ijhydene.2014.06.116.

[15] Echtermeyer AT, Lasn K. Safety approach for composite pressure vessels for road transport of hydrogen. Part 2: safety factors and test requirements. Int J Hydrogen Energy 2014;39(2014):14142–52. https://doi.org/10.1016/j.ijhydene.2014.06.016.