

DE LA RECHERCHE À L'INDUSTRIE



H₂ Composite Pressure Vessel

GTR 13 meeting

stephane.villalonga@cea.fr

5-7/03/2019, PowerTech Lab., Surrey, Canada

PLAN

- French Hydrogen Plan
- H2 Composite Pressure Vessel at CEA
- Burst ratio / HYCOMP project

- French Hydrogen Plan



FRENCH LEVEL

AFNOR

AFHYPAC

CN E29D
CN UF105

H2 Technologies
+ FC



EUROPEAN LEVEL

Standardization Mandate "H2
and power to gas"

CEN / CENELEC

SFEM-WG H2

TC 268

Cryogenic Tank and
Specific Applications
for H2 technologies

WG 5

Specific
Applications for H2
technologies

TC 6

H2 in energetic
systems



INTERNATIONAL LEVEL

JRC

EMPIR

FCH 2 JU
/ RCS SCG

N.ERGHY

EIGA

HYINDOOR

ISO

CEI

TCs 22, 58,
158, 220

SAE

HYSAFE

TC 197

H2
Technologies

TC 105

FC

1st June 2018: French deployment Hydrogen Plan

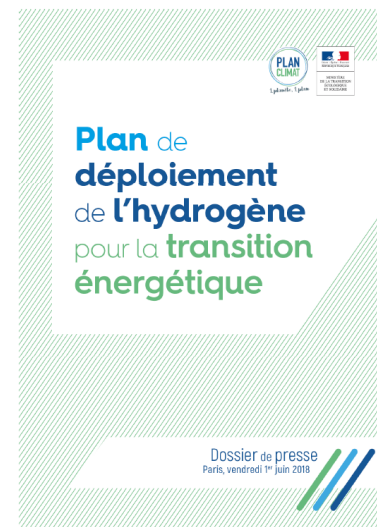
Nicola Hulot

French Minister of Ecological and Solidarity Transition

"...It is in this spirit that I present a plan for hydrogen that will aim to make our country a world leader in this technology.

To do this, I proposed to set a 10% share of hydrogen produced from renewable sources by 2023.

Moreover, because we need innovations, demonstrators and economic champions of storage Electrolysis, I decided to mobilize 100 million euros to support the first deployments of these technologies of production and transport in the territories."



- H2 Composite Pressure Vessel at CEA

CEA is active in 4 main areas



Low-carbon energies
 Defense and security
 Information technology
 Health technologies



CEA is “The World's Most Innovative Research Institution”
 (ranked n°1 by Reuters, 8th of March, 2016)

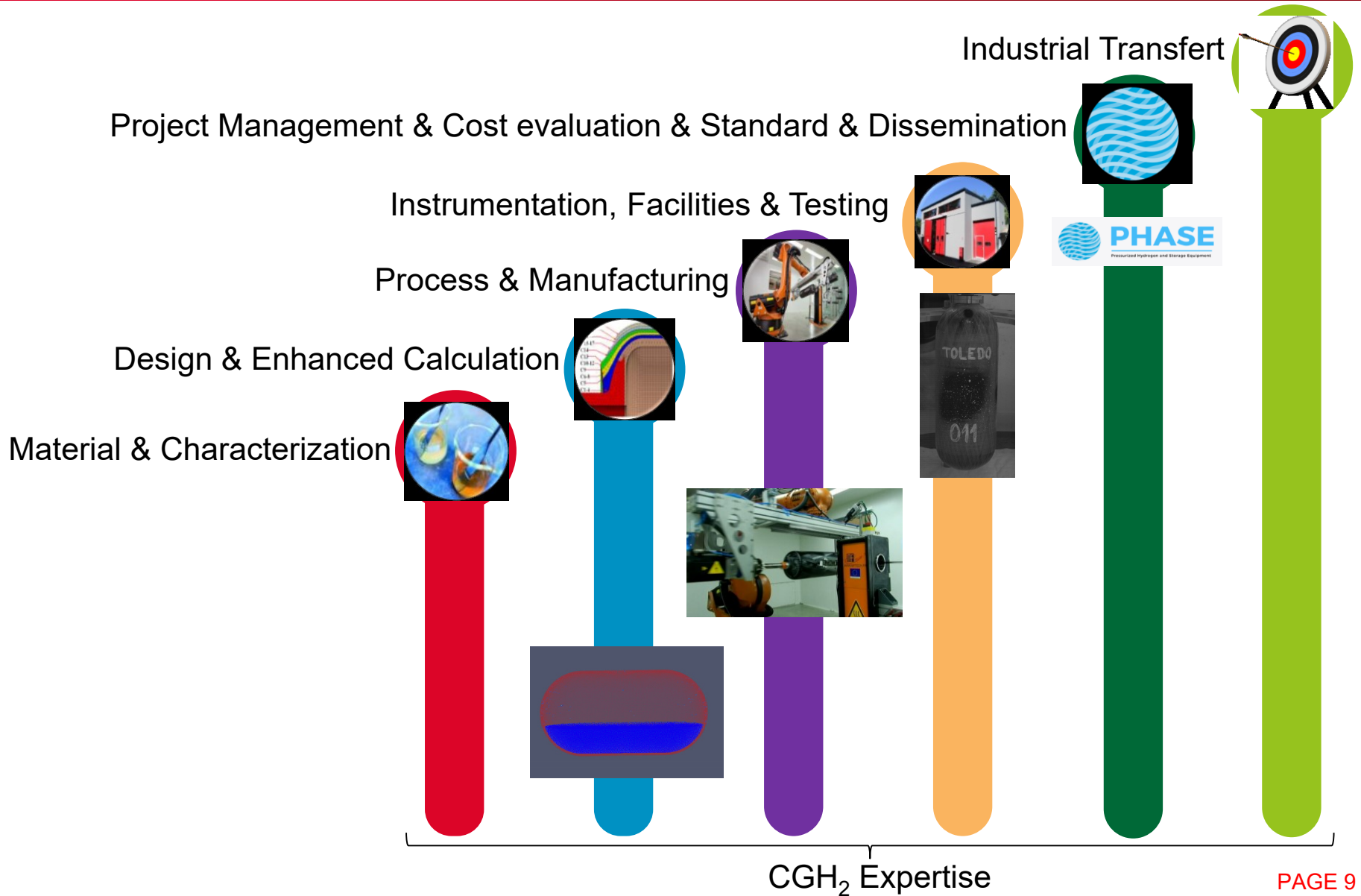
CEA CPV platform = Lavoisier Platform



- ❖ CEA Le Ripault: Lavoisier Facility (Tours): dedicated to H₂ application (storage, EMA, Bipolar plates) and batteries (1000 m² lab + Cycling Facility + TER experimental testing center + CEA CESTA Bordeaux



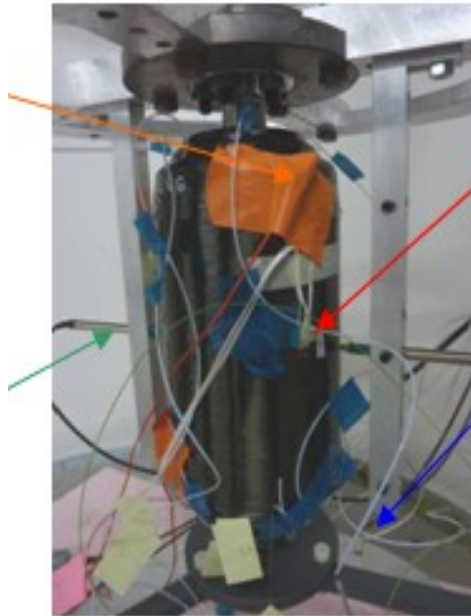
CEA CGH₂ storage Value Chain



Multi-instrumented test (pressure, temperature, optical fibers, strain gauges, acoustic emission, LVDT, fast camera, 3D digital image correlation)

Acoustic emission

LVDT



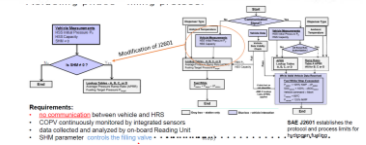
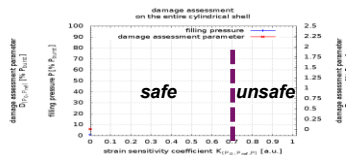
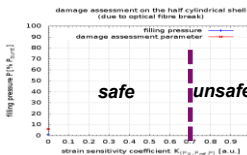
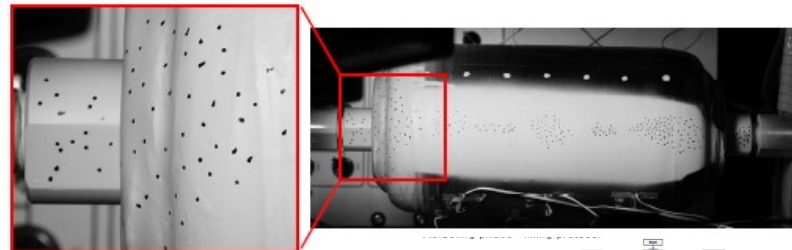
Strain gauges

Optical fibers

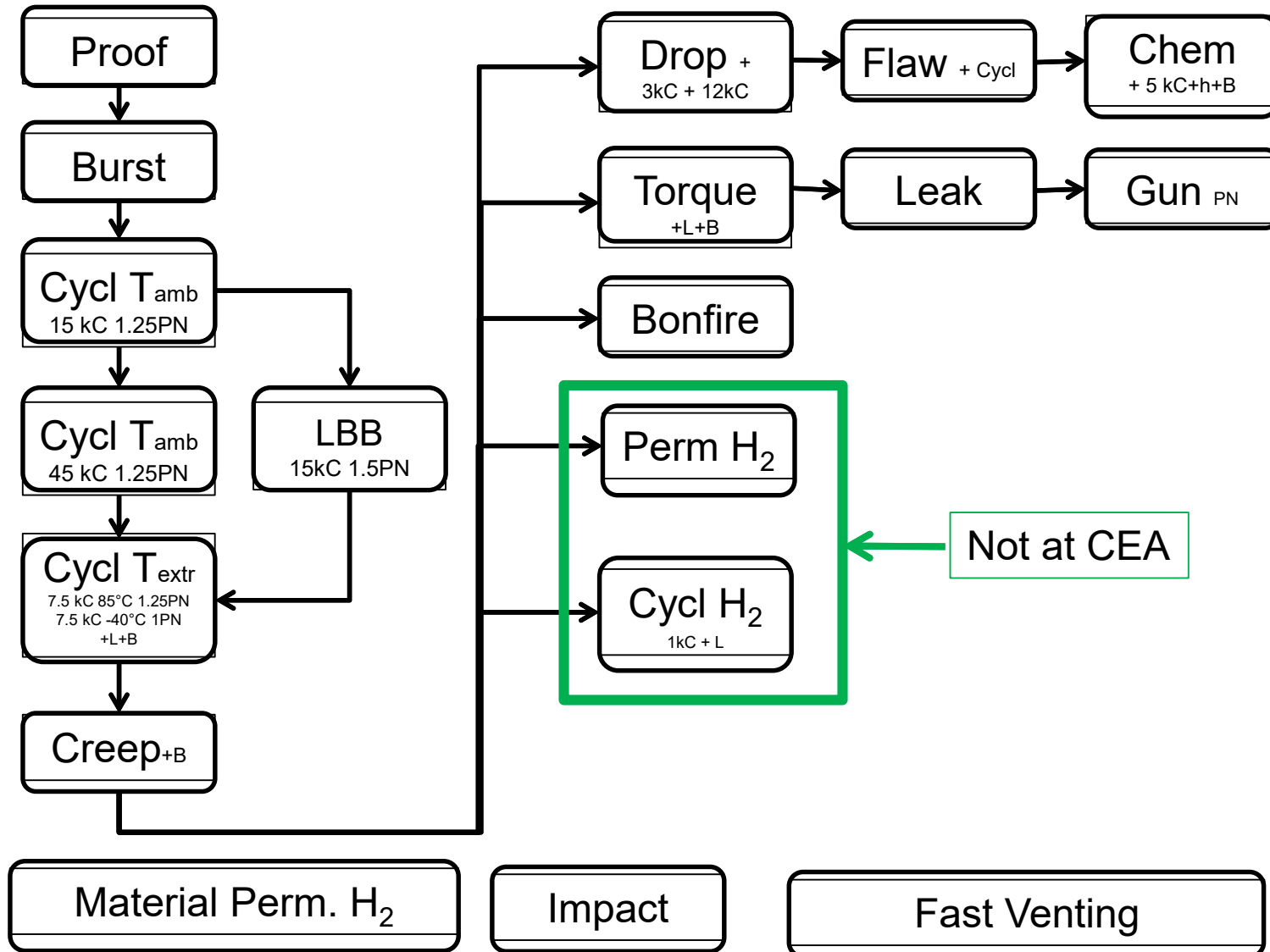
Fast camera



3D DIC

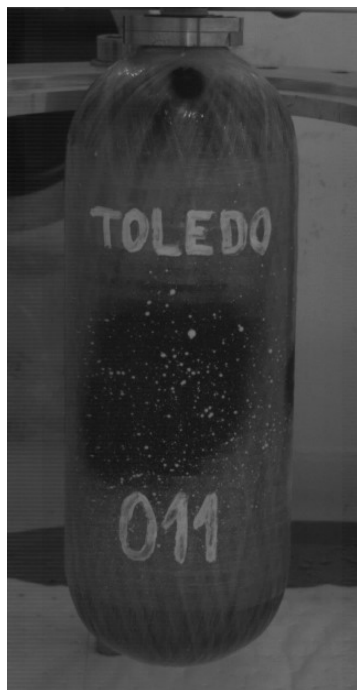


CEA Testing: EC79 + other tests (R134...)



- Performances & safety assesment

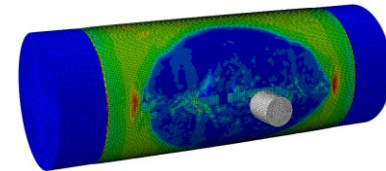
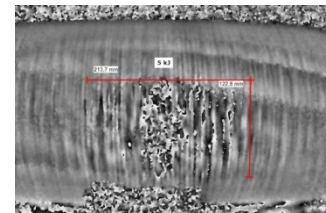
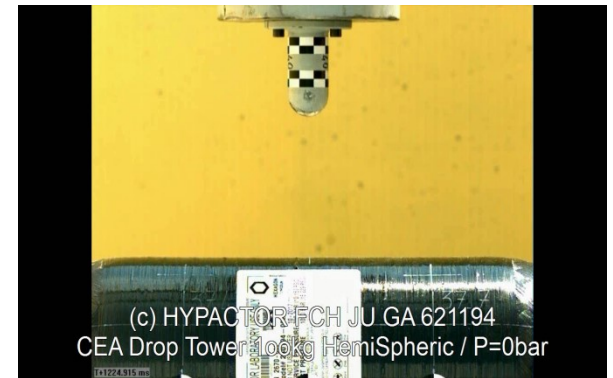
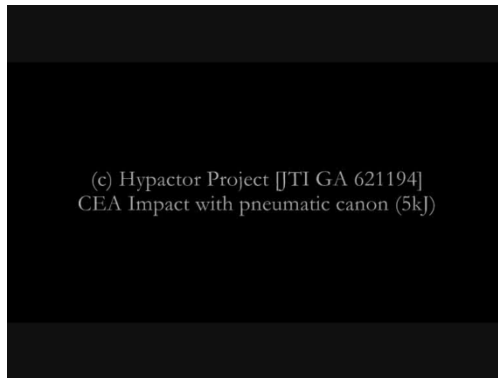
Compliance to standard testing (EC79, R134)



- **Performances & safety assessment**

- with Hexagon and Air Liquide
- Resistance to abusive testing (e.g. impact, pressure overload/creep...)
- Provide recommendations for Regulation Codes + Standards (RCS)

HYPACTOR





Main characteristics:

- at Ambient Temperature
- for vessels with damage (flaws, impacts, chemical exposure...)
- at **Extreme Temperatures** (-40°C, +85°C) extended to (-60°C to +100°C)
- for Leak before burst
- for Accelerated stress rupture test : Pressure Constant Load at given extreme temperature and hygrometry
- Cycles from **5 bar to 1100 bar**
- Max Volume Expansion at 1050 bar : 46L
- Frequence: 5 cycle/min for 300L
- Maximal Vessel Volume : **300L**
- Hygrometry: $0 < RHH < 100\%$
- 2 cells compatible with 300L/1100 bar

- Burst ratio / HYCOMP project

HYCOMP project: Safety Factor definition



Analysis of existing design requirements

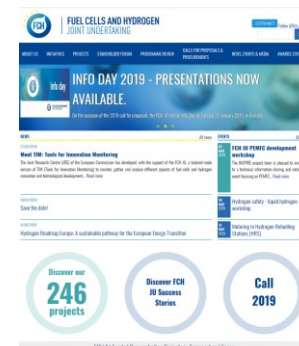
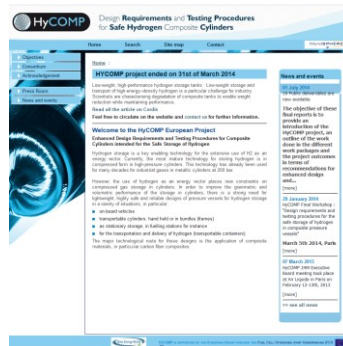
HYCOMP : European FCH-JU project

“Enhanced Design Requirements and Testing Procedures for Composite Cylinders intended for the Safe Storage of Hydrogen”

HyCOMP is a Pre-Normative Research
January 2011 to March 2014 (39 months)
Budget: 3 802 542 €

www.hycomp.eu
<https://fch.europa.eu/>

public information available

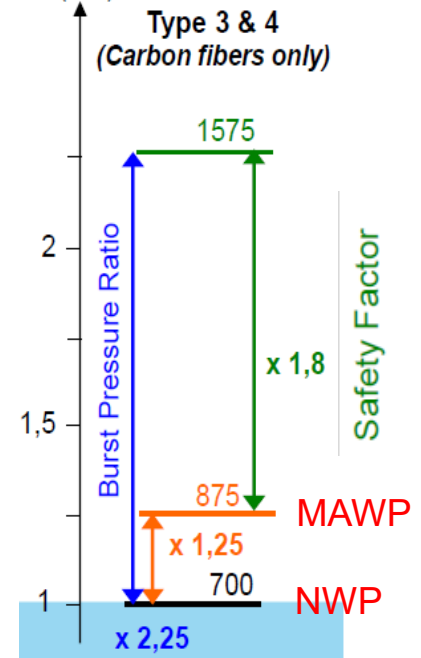


$$SF = \frac{\text{MinimalBurstPressure}}{\text{DesignPressure}}$$

ON-BOARD APPL.

(79/2009/EC and EU 406/2010 - GTR No 13)

Pressure related to NWP (bar)

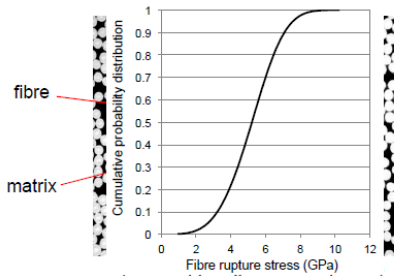


NWP=Nominal Working Pressure, MAWP=Maximum Allowable Working Pressure, Design Pressure=MAWP

Carbon Epoxy Composite Damage Process



Unidirectional carbon-epoxy composites



Carbon fibres:

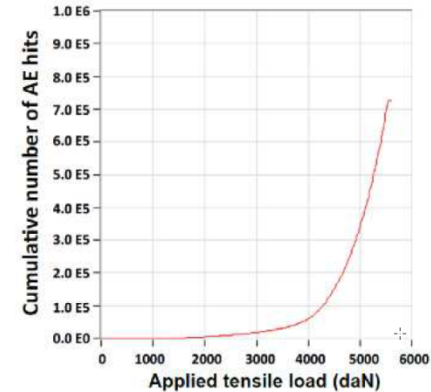
- have high tensile strength and modulus properties,
- have *variable tensile rupture strength*, influencing tensile damage process of the composite,
- and carry 99% of unidirectional composite strength

Epoxy matrix:

- is important for *load-transfer process*.
- is accounting for long-term damage process in the composites.

	Tensile modulus	Failure strength	Failure strain
T700 carbon fibres	230 GPa	4.9 GPa	2.1%
General epoxy polymer	3 GPa	0.07 GPa	3.0%

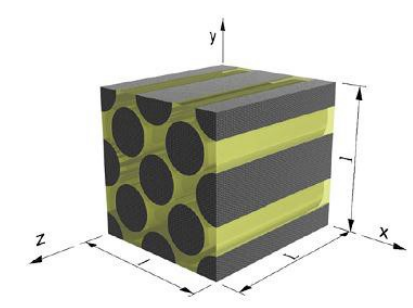
Figure shows that a rapid increase in volumetric density of fibre breaks was found as the applied tensile stress increased beyond 80% of its tensile failure strength.



The failure of UD composites are dependent on clustering process of fibre breaks.

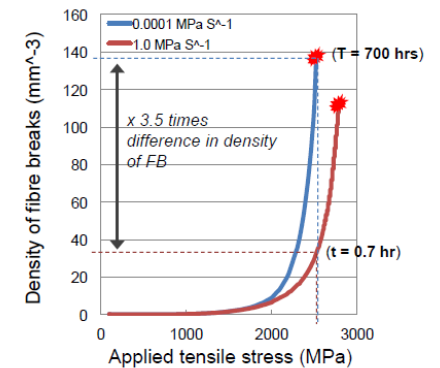
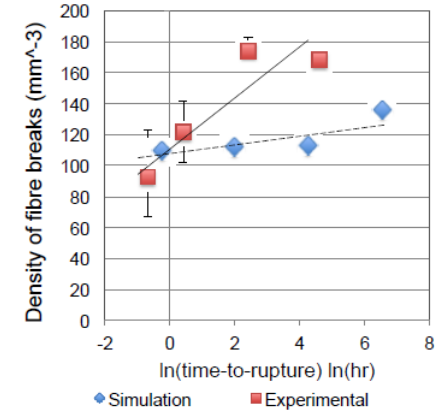
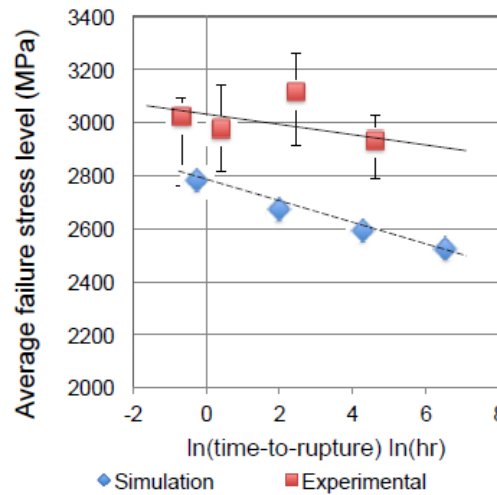
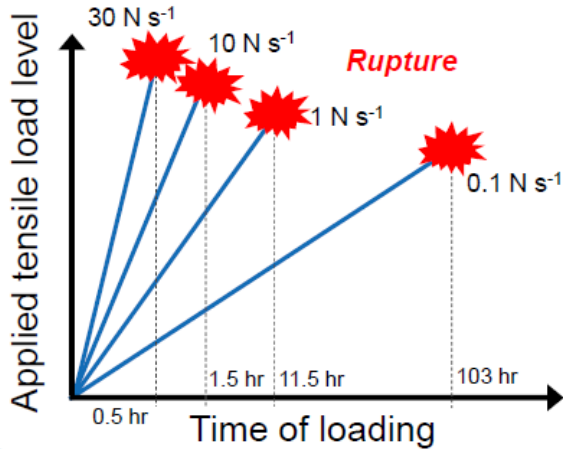
- Two different fiber/matrix systems studied:

		Plate specimens CAQ's & Faber's cylinders (Reference system)	Hexagon's cylinders (Specific system)
Carbon fiber		T700 (E = 230 GPa, ϵ = 2,1%, UTS = 4,9 GPa)	
Epoxy resin	Commercial reference	Huntsman resin	Hexagon proprietary
	Glass transition temperature T_g	Measured around 115°C	110°C





Effect of the applied loading rate on fibre damage process



Methodology for Intrinsic Safety Factor analysis: iSF



General methods for iSF analysis

Step 1: Determine the average failure stress of the UD composites.

Step 2: Determine time-to-rupture properties of UD composites.

Steps 3 - 5: Statistically analyze the obtained time-to-rupture results and determine the time-to-rupture as a function of the applied creep stress level for the failure probability of p .

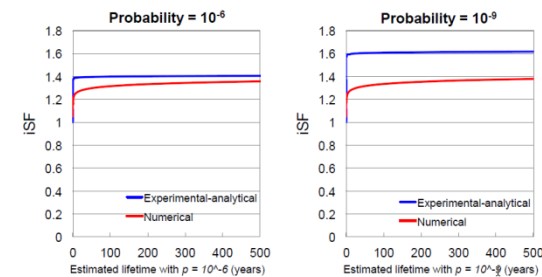
Step 6 - 7: Calculate iSF for the composites.



$$iSF = \frac{\text{Average material strength}}{\text{Design load level}}$$

Results of iSF analysis

The iSF values were calculated for various lifetime and failure probability:



	Numerical		Experimental-Analytical	
	15 years	150 years	15 years	150 years
$P = 10^{-6}$	1.28	1.32	1.39	1.40
$P = 10^{-9}$	1.29	1.34	1.60	1.61

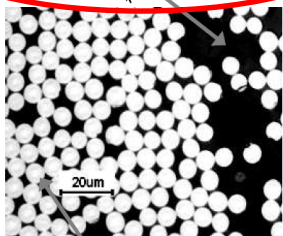
- A quasi-asymptotic behavior of iSF value with respect to the lifetime was observed.
- Based on specimen results ONLY, A “science based” minimum SF has been defined (hypothesis = Under a constant load and 10^{-6} probability of failure or 10^{-9}) a minimum iSF value of 1.4 or 1.6 must be applied to guarantee specimen lifetime ≥ 15 years under a constant load, with a probability of failure (10^{-6} or 10^{-9})

Effect of environmental temperature on fibre damage process

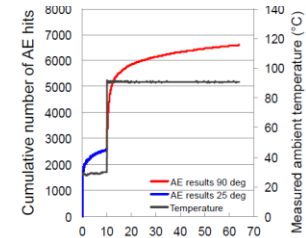
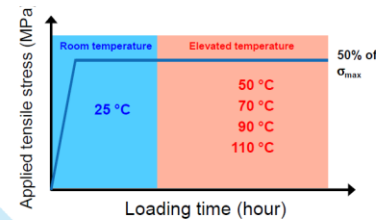
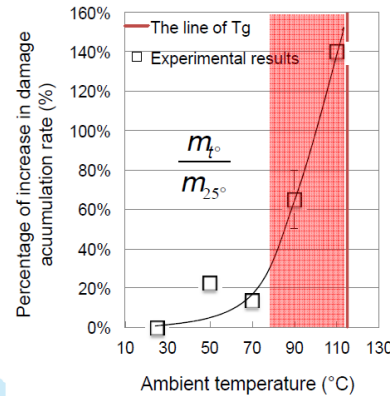
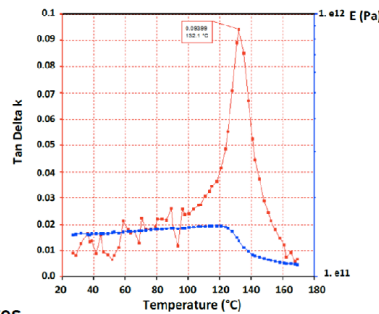


Effect of environmental temperature on fibre damage process

Mechanical properties of epoxy polymer are **HIGHLY** dependent on the temperature



Mechanical properties of carbon fibres are **NOT** dependent on the temperature.



- Increase in damage accumulation rate was found as the temperature increased, in particular when approaching to the T_g .
- These behavior are due to thermal expansion of the material and augmentation of stress relaxation process of the composites.
- The rise in damage rate could further increase when the composites are subjected to higher creep stress level (now is 50% of σ_{max}).
- The T_g of the composites could vary depending on the type of polymer used and composite curing condition.

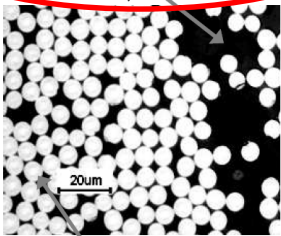
- The long-term damage processes of composites, which are time-dependent, are governed by the viscoelasticity properties of epoxy polymer.
- The effect of the temperature on damage process of the composites is relatively small when the increase in ambient temperature is 30°C below the T_g .
- The efficiency of load transfer mechanism at the interface of fibre and matrix declined and the effect of the existing fibre breakage on the neighbouring fibres was enlarged.

Effect of environmental temperature on fibre damage process

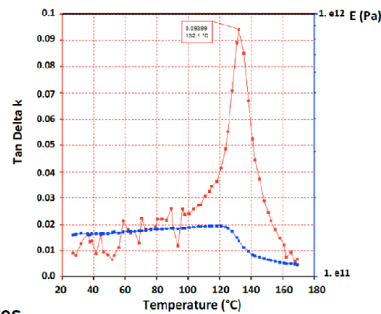


Effect of environmental temperature on fibre damage process

Mechanical properties of epoxy polymers are **HIGHLY** dependent on the temperature



Mechanical properties of carbon fibres are **NOT** dependent on the temperature.



WP4 - Task 4.2 / Conclusions

- Improper curing has shown important effects on cyclic test with Type 3 cylinders and on the scatter of the test results for Type 4 cylinders. It has been confirmed that the curing quality is of high importance to ensure good properties of the composite structure, as indicated also by the WP2 investigations. This suggests the need to introduce a control of this characteristic by additional tests (such as a Barcol test on each cylinder) to verify the optimum curing of the resin mix.

- It was calculated that the lifetime for the composites subjected to creep test **at 70% of the average failure stress** decreased from 2E27 years to 0.2 year when the ambient temperature changed from the room temperature to 90 °C.
- Since the rise in the temperature level could influence the lifetime of the composites, the temperature effect must be taken into account in the safety factor analysis, which can be determined in the future analysis.



WP conclusions

- Synthesis of recommendations:
 1. Reduce the Design Pressure to the **Maximum Developed Pressure** at the maximum temperature
 2. Reduce Safety Factor to a **fixed value in between 1,4 and 2** (to be decided), e.g. 1,8
 3. Add specifications on T_g
 4. Make statistical assessment
 5. Perform tests at the new Design Pressure
 6. Tests at elevated temperature should be performed at **5°C above T_{max}** defined for the application
 7. Add test to verify the good curing of the resin (e.g. Barcol test)
 8. Control each manufactured cylinders to detect any deviation from a reference batch, for example by using Acoustic Emission
 9. Continue to **develop Non-Destructive Techniques** to carry out periodic inspection of composites pressure vessels.

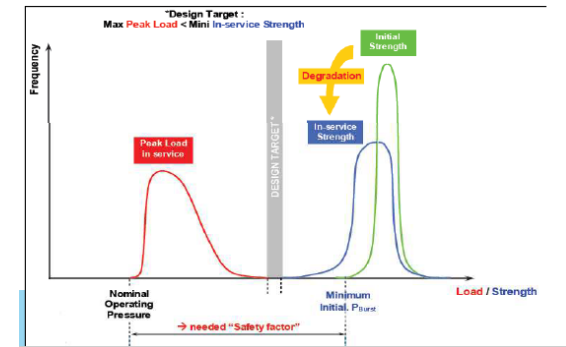
Decreasing Burst Ratio!

- Burst ratio

Decreasing burst ratio from 2,25 to 2

=> Decreasing Hycomp safety factor from 1,8 to 1,6

=> No margin with the Intrinsic Safety Factor (1,6) without taking into account temperature and humidity effects



nominal pressure	filling pressure	burst ratio	burst pressure	Hycomp safety Factor
700	875	2,25	1575	1,8
700	875	2	1400	1,6

- Specification on Composite Tg

Example of ISO 19881 where a new specification on Tg has been added (chapter 6.6: $T_g > T_{max} + 20^\circ\text{C} = 105^\circ\text{C}$; $T_{max} = 85^\circ\text{C}$)

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LE RIPAUT

Thank you
for your attention

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