FRP in low temperature or cold climate conditions



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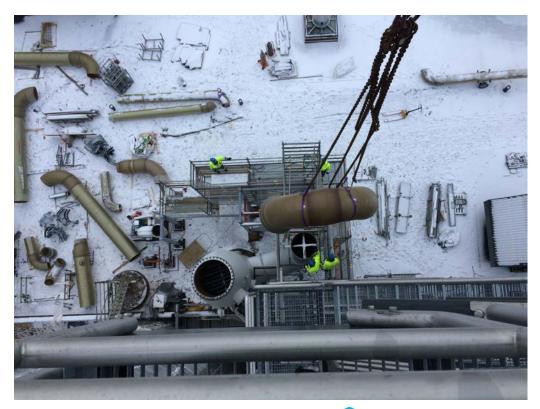
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FRP for broad temperature range

- FRP based on epoxy-modified vinylester resins is a material of choice for temperature range up to 180°C and even higher – as in ducts and chimneys for FGD
- These operational conditions are well accepted and design procedures set up.
- But what if it comes to low temperature such as -50°C?
- Which mechanical properties to expect?
- Do they become britlle as standard PVC, which is not recommended to even transport below 5°C to avoid thermal contraction cracking?



FRP for broad temperature range what we know

- FRP equipment is an accepted material e.g. in aviation for decades and proven material for temperature up to
 -70°C with permanent load changes
- FRP lattice masts can be found all over Scandinavia with temperatures down to -30°C for most time of the year
- Mechanical properties of FRP laminates have been tested for a temperature range down to -50°C/+50°C several times



FRP for broader temperature range

- The use of Fiber-Reinforced Polymer (FRP) in low temperature or cold climate (arctic) conditions is perceived an application, where the physical properties or better the 'retention' of physical properties of FRP, is not enough communicated to develop further innovative applications
- This paper aims to bring to the attention the excellent performance of FRP at this temperature interval, which is representative for many industrial applications











Tests and studies





First studies in 1990s

- Sulphuric acid / Mercury recovery plant planned at a Copper / lead refinery in Kazakhstan
- Design requires low temperature resistance down to -50°C
- Little experience here with FRP/epoxy-vinylester resins
- Minimum winter temperatures of typically -39°C, and lowest ever minimum of -49°C are being used for design / materials selection
- Pipe lines heat traced and insulated in heated buildings once in service
- But: All vessels outdoors



First studies in 1990s

Tests carried out at internal lab and at EPFL-Lausanne What was tested?

- Different FRP laminates based on Vinyl ester resin
- Tensile test, Damage Thresholds, cracking at +23, 0, -50°C
- Flexural properties at +23, 0, -50°C



Results and conclusion

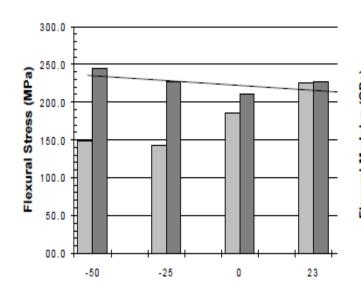
What was the outcome?

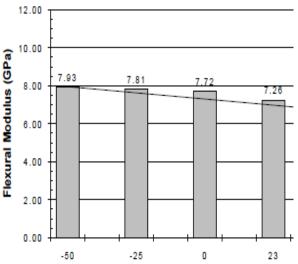
- Results from EPFL-Lausanne showed only slight reduction in damage tolerance properties of specified epoxy-vinyl ester laminates at -50°C compared to room temperature performance
- Full data package (chemical resistance, etc) satisfied customer that full FRP equipment would perform satisfactorily without additional safety factors.

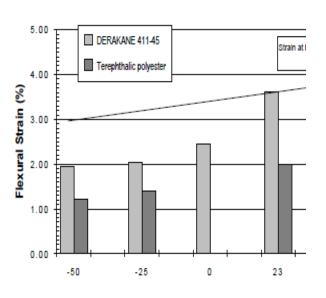


Results and conclusion Laminates

- Comparison of Vinyl ester versus Terephtalic polyester



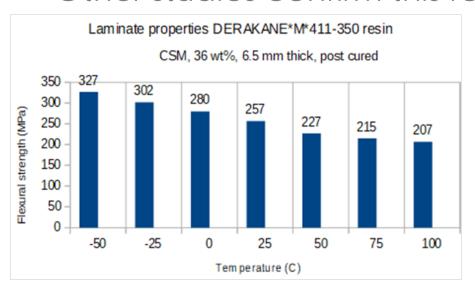


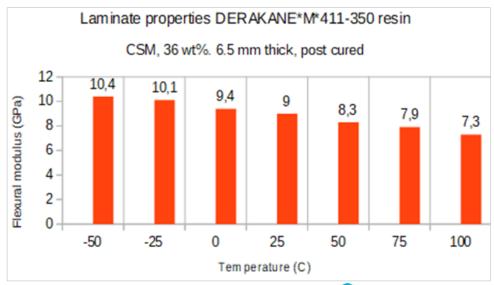




Results and conclusion Laminates

- Current results with vinyl ester resin (CSM) prove increase of material properties such as flexural modulus, strength and strain
- Laminate seems to slightly stiffen at lower temperature
- Other studies confirm this for the shear modulus







Case History from 1981 (reported '93) HCl Storage Tanks in Northern Canada

- Several Hydrochloric acid (25-30% by weight) storage tanks (approx 15 feet in diameter, 20 feet high)
- Tanks are not insulated and have no internal heaters
- Outside of the tanks see ambient temperatures of -40C to +30C
- Inside of the tanks: acid at -20C to 25C (acid pumped into the tanks is 25C).
- The tanks are now 12 years old and have suffered no ill effects from the cold temperatures.
- There are numerous other vessels and piping which are partially insulated, but again will have the outside surface of the pipe seeing ambient conditions and the inside of the pipe above 0C.

Standards and guidelines





FRP in extreme conditions and the standards?

 VGB Standard "Anwendung, Konstruktion und Güteüberwachung von faserverstärkten Kunststoffen im Kraftwerksbau"

1.2 Grundlagen

Die Bauteile müssen den zu erwartenden Beanspruchungen und Einwirkungen für die vorgesehene Nutzungsdauer, falls nicht anderes vereinbart 25 Jahre, sicher widerstehen. Sie müssen standsicher, formstabil und gebrauchstauglich sein. Es muss gegenüber mechanischen (Lasten, Verschleiß), physikalischen (Temperatur, Diffusion) und chemischen (Medien) Angriffen eine hinreichende Beständigkeit gegeben sein.

Es ist nachzuweisen, dass der Schubmodul, gemessen bei der vorgegebenen Betriebstemperatur, gegen den Schubmodul, gemessen bei 23°C, um nicht mehr als 30 % abfällt. Außerdem muss die Glasübergangstemperatur nach Torsionsschwingversuch (DIN 53445) mindestens 30 K oberhalb der Betriebstemperatur liegen.



FRP in extreme conditions and the standards?

- British Standard BS 4994,
- The maximum allowable design strain for corrosion resistant GRP equipment designed to the British Standard B.S.4994 is 0.2%.
- Based on results of beforehand mentioned studies:
- No special considerations or safety factors should be necessary for equipment to perform satisfactorily even under such extreme temperature conditions.



FRP in extreme conditions and the standards?

- EN 13121-3 Design and Workmanship
- "...gives requirements for the design, fabrication, inspection, testing and verification of GRP tanks and vessels with or without thermoplastics lining for storage or processing of fluids, factory made or site built, nonpressurized or pressurized up to 10 bar, for use above ground. "
- "This part of EN 13121 covers vessels and tanks subject to temperatures between – 40 °C and 120 °C."
- The EN 13121-3 Norm refers to the fact that information on 'any extreme temperature' (Ref.: 5.2 b1) [15] needs to be obtained by the manufacturer



EN 13121-2

Laminate of type of polyester resin	CSM	Mixed lam. WR	Wound laminate		
				laminate umference	±65°
Polyester resin	0,30 %	0,25 %	0,20 %	0,27 %	0,27 %
Bisphenol-Vinyl resin	0,35 %	0,30 %	0,23 %	0,30 %	0,30 %
Novolak-Vinyl resin	0,30 %	0,25 %	0,20 %	0,27 %	0,27 %
Furane resin	0,20 %	0,15 %	0,15 %	0,20 %	0,15 %

- In addition the EN 13121-3 specify, that the limit strains for laminate with various reinforcement types meets certain minimum requirements
- FRP based on Bisphenol-epoxy vinyl ester resin and Novolac-epoxy vinyl ester resin has an actual strain significant greater than the specified min. requirements.
- Studies confirmed that the safety factors, covered by the overall design factor, K (acc. to EN 13121-3 Chapter 7.9.5.1) and the partial factor for material properties, γm of 1.40 for all laminates (Chapter 7.9.5.7), enclose the safety factors for low temperatures.



Applications





Lattice masts used in airports all over the world

- Safety Support Structures
- Frangible masts and towers for lightening and weather observation
- Structures and airport fencing
- Weather proof and located far north
- E.g. in Middle Finland: Average annual minimum -1°C, with peaks up to -20°C





Airport approach masts and antenna radome

Unique combination of needed fragile behaviour as well as rigidity (stiffness) while delivering a right transparency to electromagnetic signals and minimum maintenance.









Pipes and Tanks installed in Sweden

- Installation of tanks at -15°C
- Connection of 2 tanks including flange and laminate connection
- Tanks to be insulated afterwards







Vessels on Nickel Mine Field in Finland

- Talvivaara nickel mine largest mine in Finland
- VE storage and process tanks and equipment







Source: Sulmu

Titanium Dioxide Plant

- Ducts and chimney at Venator (earlier Huntsman pigments) in Pori, Finland
- Pori has a capacity of 130,000 metric tons, which represents approximately 10% of total European titanium dioxide demand
- Factory burned in January 2017. Again the material of choice is FRP based on epoxy-vinyl ester resin



Polyvinyl Chloride Complex in Russia



Source: Plasticon



Polyvinyl Chloride Complex in Russia

- Location: Kstovo, Nizhniy Novgorod Oblast, Russia
- Project executed: 2015
- Technical specification:
- Pressure: 10 bar and Full Vacuum
- Geometry: 25 700 mm Diameter
- Medium: HCI, NaOH, Brine
- Temperature: -40 till +95 °C



Source: Plasticon



Field Guidance



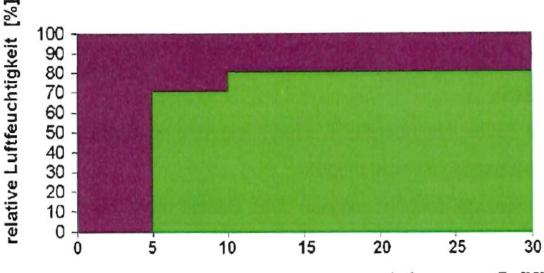


Low temperature in practice What about lamination at low temperature?

- Avoid laminate connections by choosing flange connections where possible
- Ashland position: special experience required for lamination below 15°C and for considering humidity

 Acc. To state of the art (VGB) lamination below and at 5°C should not be considered without special measures,

such as:



Low temperature in practice What about lamination at low temperature?

- Weather protection
- Heating housing or tent for the work space
- Heat the part to be laminated
- Adjust curing recipe
- Check proper cure on the finished part (Barcol or bonding)
- Post cure if necessary / possible
- Document relevant parameter





Low temperature in practice What about filling for start-up and standstill?

- Give guidance for filling after standstill time at temperature below 0°C
- During standstill the equipment is empty and cools down to surrounding environent
- Recommendation: start with room temperature water (max. 30°C) until FRP surface temperature above 0°C
- Flush all connected pipes and equipment
- Repeat until FRP reaches room temperature
- Increase temperature stepwise to operational temperature



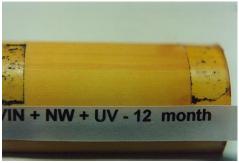
Low temperature in practice What else?

- For a new factory in North Scandinavia UV radiation is said to be a problem
- UV absorber or topcoat for the external layer required
- Ashland experience: Good cure and a resin rich layer minimize degradation











Source: Sulmu

Failure due to wrong assumptions

When transferring a plant design from e.g. South Europe to North Europe?

- Consider climate conditions for design
- Consider thermal expansion within design especially with thermoplastic lining
- Cover specific requirements such as thermal shock by design (glass content, conductive filler)
- Provide instructions and guidance for transport, handling and installation
- Also consider storage at low temperature (dead load, deflection, occuring loads on internals)



Conclusion

- Fiberglass Reinforced Polymer (FRP) proved an ideal material of construction for a broad temperature interval from 'desert climate' to 'arctic climate' (ca. -50 C to 50 C)
- Polyester resin is more susceptible to cracking and will therefore prove less durable in practice
- Design standards such as EN 13121 for corrosion resistant
 GRP equipment cover extreme temperature conditions
- Proven performance for over 30 years (Ref. Case histories)

The industrial experience, backed up by a significant number of FRP case histories for a broad range of media and applications, represents a positive outlook for future composites applications in this environment.



References

- [1] Jaeger M. et al. Experience with epoxy vinyl ester resins in chemically resistant FRP-piping systems, TÜV SÜD Conference, Oct. 2001
- [2] Report of National Institute of Standards and Technology (NIST) 1993 / Ashland lab data on thermal shock with cryogenic environment, 2013 (None public data).
- [3] Williams D., Decentralized energy in a cold climate: Alaska report on lessons learned, Jan. 2018
- [4] Nonhoff G., Garbe S None public correspondence on safety factors at low temperatures, Oct. 2017
- [5] Spörl G., Applications of fiber reinforced plastics in Cryogenics, air conditioning and refrigeration techniques, TÜV Süd Conference, Oct. 2001
- [6] Ashland Performance Materials, CR Chronicle High Temperature Resins, 2017
- [7] Ashland Performance Materials, Chemical Resistance Guide DERAKANE resins, 2015
- [8] Special Metals Corporation,: Publication number SMC-026, High Performance Alloys for Resistance to Aqueous Corrosion, 2010
- [9] Low Temperature Steel, Indemat 2003
- [10] Youd S., DERAKANE Epoxy Vinyl Ester Resins from the first 25 years to the 21st century, Johannesburg, SA, Aug. 1994
- [11] SPI Composites, USA, Jan. 1997
- [12] Kappenstein et al. Effects of temperature excursions in flue gas on FRP, FRP Unlimited, March 2013
- [13] Hexagon Lincoln, public literature
- [14] van Buren A., Garbe S. Composite solutions as innovative problem solver in industrial chimneys and cooling towers. FRP Unlimited, Feb. 2015
- [15] DIN EN 13121-3 European standard for: GRP tanks and vessels for above ground Part 3 Design and workmanship. CEN/TC 210
- [16] Low-temperature and freeze-thaw durability of thick composites, Piyush K. Dutta and David Hui, 1996 Elsevier Science Limited



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