20 years of experience with FRP at desulfurization plants

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A characterization of the Paper:

This paper is primarily about blistering in FRP components operated with water-vapor saturated media. Several theoretical publications from the 1980's have been confirmed by the operational experiences of the last 20 years. As a result of these experiences, details about better methods of manufacturing for FRP components are given in hopes of moving the industries' standards forward.

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Experiences and new developments with industrially used glass fiber reinforced plastics

Abstract:

Components made of FRP have been in use successfully for many years in several applications. A large number of applications are vessels, ductwork and piping in the chemical industry as well as at desulfurization units inside power plants.

The range of possible applications has grown larger with regards to higher operating temperatures. In the past years many FRP-components, which have been operated at temperatures above 50°C (122°F) and in a water-vapor atmosphere, have seen blistering occur. The blisters were mainly in the corrosion barrier layers.

Are these blisters only a visual problem or do they have a performance impact on the stability and durability of the components? To answer this question, many samples were analyzed to check the blister's effect on the mechanical values and chemical resistance [1], [2], [4], [9].

The theoretical estimates regarding blistering made in 1987 by Prof. Nonhoff, Mr. Wagner [1] and Mr. Nordberg [2] were confirmed.

As a result of technical expertise, new methods of manufacturing laminates were developed to make blistering nearly impossible. The following description of this new type of laminate construction and the testing of these FRP-components is based on actual results from several facilities.

1. Practical examples with extended operational experience

Examples for the successful use of FRP in Power applications:

- flue gas ductwork 19’-8” - 29’-6”∅ behind a flue gas scrubber in brown coal and hard coal plants (table 1.1)
- FRP Liners for industrial chimneys [7]
- flue gas stacks (ex. for incinerators)
- circulating water piping [8]
- vessels, slurry piping and many other applications

Some references for these projects are listed in a publication dating back to 1997 [3]. In the decade since then many other applications have followed.

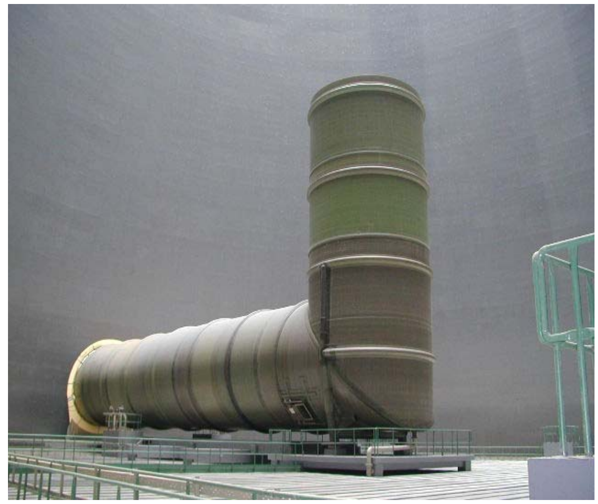

Image 1.1: Flue gas duct (23’-0”∅) in a brown coal plant at Florina (inside of cooling tower)

Image 1.2: Flue gas duct (21’-4”∅) at Schwarze Pumpe

Plant Site	Owner	Diameter [ft]	Length [ft]	Operating temp. [°F]	Operational year	Manufacturing method
KW Weisweiler	RWE Power, Essen	16’-5”	525	149 - 158	1987	Using a typical Corrosion Barrier - fully cured before winding
KW Weisweiler	RWE Power, Essen	23’-4”	1,050	149 - 158	1987	
KW Neurath	RWE Power, Essen	16’-5”	1,180	149 - 158	1987	
KW Neurath	RWE Power, Essen	21’-4”	1,050	149 - 158	1987	
KW Frimmersdorf	RWE Power, Essen	16’-5”	790	113 - 122	1988	
KW Weiher III	Saarberg Werke	16’-5”	495	113 - 122	1989	
HKM Völklingen	Saarberg Werke	13’-2”	400	113 - 122	1989	
KW Staudinger	Preussen Elektra	21’-4”	235	113 - 122	1993	
KW Jänschwalde Außenkanäle	VEAG Berlin	19’-8”	3,935	158	1995	
KW Rostock	Preussen Elektra	21’-4”	235	113 - 122	1995	
KW Jaworzno	Stadt Jaworzno	21’-4”	425	149 - 158	1996	
KW Jänschwalde EK	VEAG Berlin	19’-8”	1,970	158	1995	Using the “wet in wet” method of fabrication
KW Schwarze Pumpe	VEAG Berlin	21’-4”	2,300	158	1996	
KW Florina	PPC, Griechenland	23’-0”	375	158	2002	
KW Niederaußem	RWE Power, Essen	23’-0”	785	149 - 158	2002	

Table 1.1: Examples for FRP-flue gas ductwork manufactured by Vanck / Christen & Laudon, Staffelstein

2. Origin of blisters

Blistering is generally induced or influenced by a number of different parameters; however the operation of the plant, the respective internal and external temperatures and external influences remain the most important factors. Some of the most important influences are:

- diffusion of water vapor
- moisture expansion
- differences in heat expansion of the layers of laminate ($\alpha CB \geq 55 \cdot 10^{6}$ /K) vs. ($\alpha Lam \geq 10 - 25 \cdot 10^{6}$ /K)
- thermal gradient variances (inside: warm, outside: cold)
- single layers of laminate may have a locally bad bond; mostly between the corrosion barrier and the structural laminate
- locally bad bonding between fibers and the resin matrix
- osmosis and the osmotic pressure resulting from osmosis

Experience shows blistering to appear mostly in parts:

- that have significantly less glass fibers in the corrosion barrier layer than in the structural laminate
- where application of the structural laminate is put on hold until after the corrosion barrier is allowed to fully exotherm and cool down.

Mainly this applies to FRP parts that are manufactured utilizing filament winding overtop of a contact molded corrosion barrier. (See Image 2.4) In parts manufactured completely using the hand laminate method of construction the differences between the structural laminate and the corrosion barrier are not such great as to induce blisters. Also, the “wet in wet” process is used for most typical hand layup parts; therefore blisters between the corrosion barrier and the structural laminate is rarely found in parts resulting from hand laminate construction.

Examples of blistering

Image 2.1: Small blisters in a flue gas duct

Image 2.2: Blisters in a storage container

Additional details on the creation of blisters have been mentioned in [1]. In cooperation with the main lab of the RWE [4] several laminates have been tested. These tests confirmed the criteria for the creation of blisters as mentioned in [1]. It became evident, that diffusion equilibrium takes place between the blister liquid and the medium in the duct or vessel. Yet there are no relevant amounts of osmotic pressure, as the analysis of the blister liquid confirms. Testing by imagery showed that there was no reduction or attack of the glass fibers made from E-CR glass or the laminate matrix itself [4]. (see Image 2.7)

Image 2.3: Bigger blisters in a flue gas duct

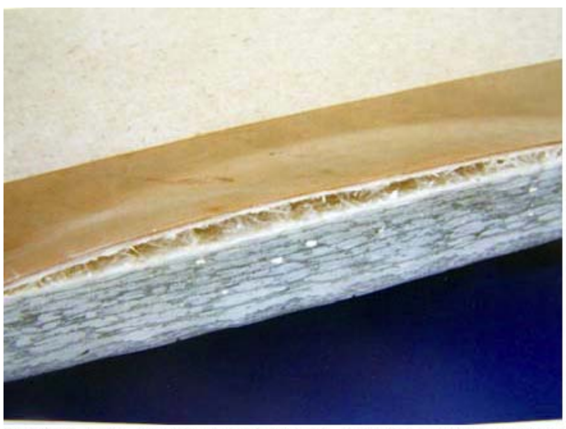

Image 2.4: cross section of a blister (from Image 2.3)

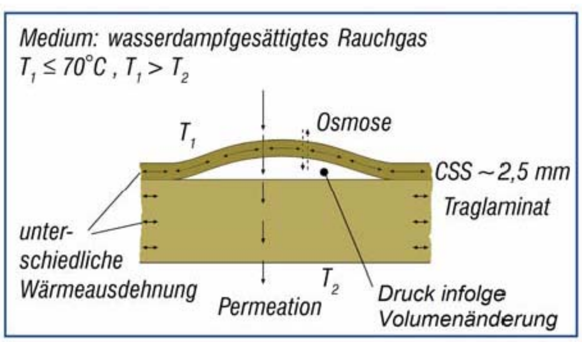

Image. 2.5: Mechanism of blistering in FRP-parts [3]

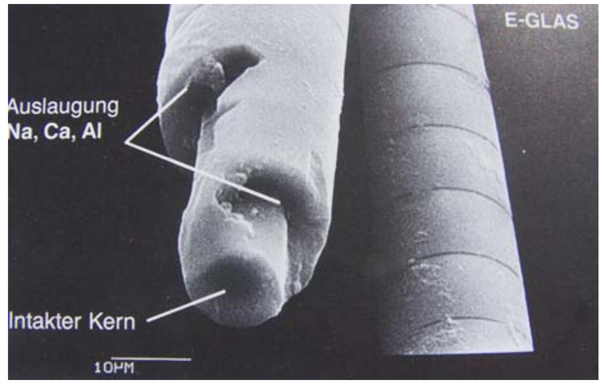

Image 2.6: Damaged E-glass fibers after being stored in acid (REM-Image) [5]

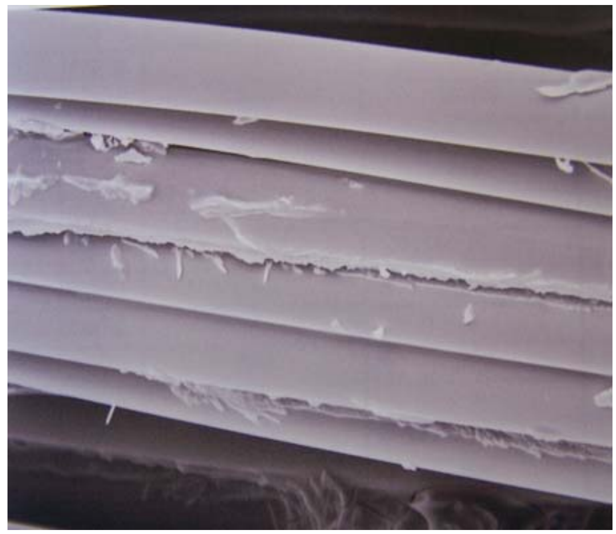

Image 2.7: Intact E-CR-glass fibers from the inside of a blister (REM-Image) [4]

The main reason for blistering lies in the mechanical side of laminate construction. Huge pressure expansions resulting from $\Delta\alpha$ and ΔT, and from moisture expansion due to the inclusion of diffusing fluids, lead to instabilities, flaking and blistering, when there is not enough adhesion between the layers.

In the case of separation, one or more layers flake off (see Image 2.4) and create a hollow space. With time this space will fill up with liquids included within the flowing medium. As a result of the small molecule size, water diffuses easily into these hollow spaces. Operational changes in temperature leads to pressure inside the hollow space (contraction of the flaked layers), which expands the edges of the blister. The void space grows until a balance is found between the edge strength and the adhesion to the base material. The thicker the flaking layer is, the bigger the resulting blister will become.

Often it's enough to have moisture expansion pressure to get blisters. That process is evident in bathtubs, boats and in containers used for the storage of drinking water.

3. Influence of the blisters on the mechanical properties of the structural laminate

In an effort to examine the blisters' influence on the mechanical properties many samples have been taken out of the flue gas ductwork from the RWE power plant in the Rhenish Brown Coal Region and from the ductwork in Jänschwalde and Boxberg. Testing took place at RWE's main lab, the IMA in Dresden and at the Institute for fiber-reinforced composites of the University FH Aachen. The following table illustrates only some of the results, since the full documentation would extend the scope.

When comparing the results shown in table 1.2 with those from different operational time spans, one finds that:

- the E-modules from the three point bending test showed no results beyond the usual diffusion spectrum
- the tendency to creep (kn), measured at room temperature and pressurized with 20% of the short-term bending load, is very low and remains within the usual spectrum
- the bending properties showed only a small decline in results

The decline of the bending property can be traced back to an "embrittlement" of the layers of outer fibers due to temperature and medium influences. This means that the outer fibers form small cracks when expanded, thus reducing the bending point in term of breaking elongation. The tests show a drop of breaking elongation in the outer fibers of about 1.8 % versus the expected values of 1.2%-1.4%.

Parameters for 60,000h (checked without corrosion barrier) have been determined with samples, where only the flaked layer of CB has been worn out. During all bending tests, the pressurized layer was situated within the tensile area.

These results and the results from the scanning electron microscope lead to the conclusion that the flaking of protective layers or the creation of blisters has no relevant influence on the stability, reliability and operating safety of the components. It is important though, as was the case with all of the tested parts, that the raw materials used in the laminate matrix including the resin and the reinforcing fibers are resistant to the attacking fluids and that the operating temperatures are far enough below the laminate's Heat Distortion Temperature. Several vinyl ester resins have proven to be very usable matrix materials, as has E-CR glass for the reinforcement layers. The reinforcement in the resin-rich layer facing the medium should not include synthetic non-woven materials, since these are not as resistant against hydrolysis. C-glass material or an E-CR glass veil material is preferred.

Operating time [h]	0	6000+	25000+	21000*	33000**	60000++
N/mm²	with CB					
E_{ub}	12,400	≥ 13,700	≥ 11,200	≥ 11,900	≥ 14,290	≥ 11,770
E_{lb}	7,800	≥ 7,500	≥ 7,700	≥ 7,913	≥ 8,210	≥ 8,400
E_{lz}	12,400	-	-	≥ 12,500	-	≥ 11,555
σ_{ub}	300	≥ 320	≥ 297	≥ 335	≥ 345	≥ 303
σ_{lb}	134	≥ 115	≥ 140	≥ 113	≥ 110	≥ 108
kn,u [%]	2.0	2.8	2.4	2.5	2.7	0.8
kn,l [%]	3.5	6.1	5.0	4.2	4.3	1.3
	without CB					
E_{ub}	16900	-	≥ 18,800	≥ 17,900	≥ 18,500	≥ 15,580
E_{lb}	10900	-	≥ 12,090	≥ 11,500	≥ 10,720	≥ 10,130
σ_{ub}	470	-	-	≥ 357	≥ 443	-
σ_{lb}	190	-	-	≥ 120	≥ 112	-
b= bending, z = pull u=circumferential direction l= axial direction		+ = Weisweiler Block G ++=Weisweiler Block F			* = Neurath Block C ** =Neurath Block A	

Table 1.2: Mechanical variables after different periods of operation

4. Prevention of blisters

Even if, as seen above, blistering and flaking have no real influence on the mechanical properties of the structural laminate, they must still be regarded as critical, because they can appear in areas, where they would be dangerous to the system itself. This is especially the case with blisters below secondary bonded laminates. Ever since the mid-eighties, when first blisters appeared in flue gas ducts behind brown coal combustion plants, Christen & Laudon (formerly known as Theodor Vanck GmbH) has been developing and building laminates that prevent blistering under the circumstances mentioned above. Since blisters typically take a long time to appear during operating conditions, it's a long process to develop a new manufacturing method for these laminates.

At first it was assumed that the main problem lay with the curing between the corrosion barrier and the structural laminate, and not with the corrosion barrier layer itself. Therefore the production process was as follows:

Production of a veil reinforced pure resin layer

↓

Completed curing stage

↓

Application of layers of randomly oriented fibers within the corrosion barrier layer followed immediately with the layers of the structural laminate wound "wet-in-wet"

The laminates produced with this technique looked very good; however they increased the risk of blistering when put into practical use. The possible reasons for this were hinted at in section 1. The laminar boundary layer created between the hardened veil layer and the following layers is very thin and can be bypassed easily by diffusion. A balance is created between the flaking layer and the rim of the bubble, so that in the end many little blisters occurred.

During the second attempt to eliminate the blistering issue, parts were produced using the "wet in wet" process only and without any breaks in production. The first of these parts were industrially produced in 1991 and put into use in 1995. They remain blister-free today. Due to the production process the fibers are more visible on the inside than in typical corrosion barriers produced according to current DIN and ASTM standards.

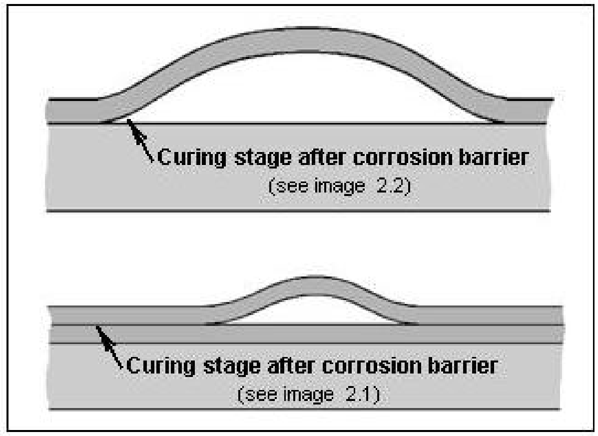

Image 4.1: Typical .100" corrosion barrier after water vapor applied

The results of these tests have been included in the media list of the German Institute for Structural Engineering. Therefore a unique type of corrosion barrier was created, which must be used under media temperatures of 80°C.

So far no blisters have been found in the secondary bond connections of these components. So why don't blisters appear in the area beneath the secondary bonds of these laminates, since there is a cured base layer as well? Don't the hand laminated secondary bonds have a lower percentage of glass than the wound duct below them? The most plausible explanation is that any secondary bond laminate connection takes place in a limited space only, and this space is able to expand laterally. When the secondary laminate is applied broadly or a whole duct is re-lined internally, there is no chance for expansion, and thus blisters will occur.

Laminate matrix composition of a corrosion barrier produced using the "wet in wet" process

The composition of an FRP corrosion barrier layer is defined by the resin-glass ratio of materials in the matrix. Commonly produced corrosion barrier laminates today have a glass content of 25% – 30%.

The corrosion barriers of parts produced "wet-in-wet" have a higher glass content of roughly 45%. So one question is valid: Do concerns about chemical resistance apply to a corrosion barrier that has been produced "wet-in-wet"?

Usually, the chemical resistance is accepted, when all reinforcement layers use an acid resistant E-CR type glass. The engineer must check if the diffusing medium can lead to an attack on the glass, and then optimize the structure of the laminates accordingly (ex. by using carbon fiber products).

5. Manufacturing method “wet in wet”

In order to produce wound laminates “wet in wet” the manufacturer has to be very experienced. Also, the right equipment (Image 5.1) is needed for manufacturing a successful part.

During the winding process the rovings, which have been soaked in resin, are applied to a turning mandrel. The winding rovings thus build up a tension that spreads out onto the mandrel as well. During the “wet in wet” production process without a cured corrosion barrier this thread tension can extend into the mandrel and lead to damage, if it is not specifically designed to accept these forces. This problem is lessened a bit in the case of a cured corrosion barrier, because the hardened layer can absorb most of this thread tension. Another important factor is the choice of a curing system of the resin and the respective adjustment of the promotion system used during the winding process.

The following parameters must be kept in mind during manufacturing:

- the complete matrix structure of laminate

- the width and strand tension of the roving layers

- the adjustment of the resin viscosity

- finding a suitable curing system for the resin

Image. 5.1: Production "wet in wet"

Notes on specifications using “wet-in-wet” winding

With regards to the laminate construction of wound FRP-components which have to endure high steam diffusion – like FRP flue gas ducts and chimneys liners used in flue gas desulfurization plants – the following specification changes are recommended:

- On the media side (inside) a layer of pure resin, followed by a veil reinforced layer, is to be used. (Note: Do not use synthetic veil)
- The veil layer should have a pure resin final layer applied of approximately 0.010”.
- The following layers should consist of a mixture of randomly oriented chopped fibers, Uni-directional fabric and wound roving band layers.
- All layers of the corrosion barrier and the structural laminate must be produced without breaks and without a curing stage.
- Corrosion barrier laminate glass content should be 40% on average and the glass content should increase steadily through wall up to the glass content of the final structural laminate.
- The reinforcing materials of the corrosion barrier layer must be made of E-CR glass, unless the diffusing medium does not require this.
- When the size of a component (ex. flue gas ducts greater than 35’Ø) makes it necessary to interrupt the production, this interruption may only take place after at least .4” of the structural laminate has been applied.

Note:

In order to produce “wet-in-wet” laminates, special equipment and experienced FRP workers are needed. Since important parts of the corrosion barrier are made using wound rovings or uni-directional fabrics and layers of randomly oriented glass fibers, one has to ensure that these materials are applied in a consistent manner as well.

6. Examples of use

Some recently erected power plants don't use re-heating in order to remove the water vapor from the flue gases. Older power plants, especially the chimneys, are being retooled similarly to accommodate this. With these plants it is important to minimize the amount of condensate. Corrosion resistant materials are required. Therefore the following technical recommendations should be taken in order to ensure a successful project:

- Utilizing the "wet in wet" – fabrication method to avoid blistering
- insulation of the FRP ducts along with a corrosion resistant FRP outer skin in order to reduce the creation of condensate on the inside wall
- installing proper liquid collecting systems for the condensate inside the components carrying flue gas

Image 6.1: Insulated 17'ø flue gas duct section

Image 6.2: Pre-assembly of a 17'ø mitered elbow

As an example we have chosen pictures from a recent power plant project (Maasvlakte Power Station in the Netherlands), where all these precautions were utilized to provide a successful project.

Image 6.3: Insulated 17'ø flue gas duct section, connected to 10'x30' breeching

Image 6.4: Assembled FRP flue gas duct with the breeching connection to chimney

7. Summary

The results show, that the past theories and difficulties with blistering and bubble sizes are proven out by actual cases over and over again. The most important lesson learned from this: Without correctly manufacturing parts using the "wet in wet" production method, blistering cannot be avoided.

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