Design and maintenance of fibreglass reinforce plastics (FRP) and dual laminate (FRP + thermoplastics) equipment for hydrochloric acid service

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Abstract

Hydrochloric acid is a commonly used substance in the chemical industry. Being so aggressive, it is required to be cautious when choosing the grade of the materials used for manufacturing non metallic components. The substances diluted on the hydrochloric acid must also be considered, since they could increase the chemical attack even at very low amounts.

Vessels and pipelines for hydrochloric acid are needed today at very demanding conditions (pressure and temperature), so it is very important to apply thoroughly a good design code, being EN 13121 [1] and ASME RTP-1 [2] the most advisable for those materials. It is also highly recommended to apply the construction details for secondary bonding shown in document DT-15 Rev. 1 from UIC [3], and the use of other procedures that could increase the structural homogeneity of the material. But not only the design and fabrication procedures are important for these vessels and piping, a well performed quality control is required along the whole fabrication process, in order to obtain a satisfactory and reliable product at the end.

Finally, hydrochloric acid attack will progress very easily through any defect on the corrosion resistant barrier or liner. As a result, performing a good preventive inspection plan (visual inspections, microscope examination of samples, and hydrostatic tests controlled through acoustic emission) in order to diagnose any defect that could appear on the laminate should be compulsory.

Keywords: Hydrochloric acid; FRP; Dual laminate
**Introduction**

Reliability and service lifetime of vessels and piping made of fiberglass reinforced plastic (FRP) and dual laminates (thermoplastic liner + FRP reinforcement) are very important topics to be considered due to safety, environmental and cost effectiveness reasons. During the last forty years there have been some catastrophic accidents on this kind of equipment that has caused irreparable damages, apart from the important economical losses linked to them.

Because of these reasons, it is required to study carefully all the aspects related to the design, manufacturing, quality control, inspection and maintenance, in order to improve the reliability and expected lifetime of vessels and piping used for storage and management of all types of hydrochloric acid (pure or at different percentages of dilution, mixed with other acids or mixed with solvents, etc.). This document analyses all these aspects.

**Composition of the fluid**

First important question is having detailed data about the chemical composition of the hydrochloric acid that is going to be stored or managed. Knowing the weight percentage of the acid, the proportion of other fluids mixed with it and, the maximum and minimum working temperatures is essential for choosing the most suitable thermoset resin and/or thermoplastic liner for the equipment. This choice of materials will lead us to obtain the optimal lifetime for every vessel or piping.

Chlorine-soda plants usually produce synthesis hydrochloric acid that can be perfectly managed with vinyl-ester novolac based resins and with a wide range of thermoplastics, even when the equipment is working within a wide range of temperatures. For high concentrations of hydrochloric acid, it is mandatory using ECR fiberglass to increase the strength against the acid chemical attack. However, having some ppm of chloroform or hydrofluoric acid mixed with the hydrochloric acid, can lead first to an embrittlement of the composite structural matrix and later to a catastrophic failure in a short period of time.

A typical example of why it is important to know the detailed chemical composition of the hydrochloric acid we are going to manage is shown in Figure 1. This figure shows a pipe for handling hydrochloric acid with some ppm of solvents (type ethyl-benzene). This piping was made originally having a polypropylene liner plus an FRP reinforcement layer, and it collapsed several months after its start-up. Next it was replaced by a piping made of straight FRP with vinyl-ester novolac resin, being working with no problems since 2002. Apart from an incorrect choice of materials, failures of adherence between polypropylene liner and FRP increased the problems and lead to a shorter service lifetime.
Figure 1 - Failed pipe made of glassfiber reinforced vinylester lined with polypropylene to handle hydrochloric acid with some ppm of solvent.

Composition of the fluid

Maximum and minimum design temperatures for the equipment are also essential data needed to choose correctly the materials for managing hydrochloric acid. It is very important to follow the recommendations given by the resin’s or thermoplastic’s suppliers and by the codes EN 13121 [1] or ASME RTP-1 [2] to choose the right liners. When applying the design code EN 13121 [1], these recommendations are also very important to calculate correctly the partial safety factor $A_2$.

As a typical example, dual laminates composed by a PVC liner plus FRP give very good results for hydrochloric acid storage at ambient temperature (up to 40 °C), but they are not suitable to be used for outdoors equipment when they are installed at zones with winter temperatures under -30 °C due to embrittlement of PVC at low temperatures.

On the other hand, working temperatures above ambient temperature will increase the acid permeability and diffusion on the laminate, so the expected service lifetime of the equipment will be reduced. A typical example is shown in Figure 2, where blisters on a fiberglass reinforced vinyl-ester resin tank after being in service for 5 years in HCl solution at 80°C can be seen.
Figure 2 - Blisters on a liner made of Derakane 470 resin (vinyl-ester novolac). Tank for HCl at 80 ºC after 5 years of service.

Design conditions: Pressure, maximum vacuum wind, snow and seismic loads

Being obvious that all these loads must be considered for the design, it is convenient to remind that, if they are not correctly considered in the calculation stage, they can lead to structural failures and even to catastrophic accidents.

Hydrostatic head and/or internal pressure are the most obvious loads applied for vessels and piping calculation, but vacuum or external pressure must never be forgotten because it is one of the most problematic loads that can be applied to the equipment. Vacuum could appear for example when direct escape of hydrochloric acid gases to the atmosphere is controlled. Several accidents have happened due to a wrong design or maintenance of the “hydraulic guards” or more sophisticated systems used to control those gas escapes as shown in Figure 3.

Figure 3 - Catastrophic failure caused by a wrong maintenance of the “hydraulic guard” on an HCl dual laminate tank (PVC + FRP) after 10 years of service.
Wind, seismic and snow loads must be correctly determined according to Eurocode [4] [5] [6], ASCE 7 [7] or applicable local rules. The application of these loads usually requires increasing the structural thicknesses to avoid failures that could even destroy completely the equipment. As an example about the importance of considering these loads, we have studied two cases where hydrochloric acid tanks installed on different places have collapsed after being exposed to a strong storm.

Manufacturing and quality control

It is well known that fiberglass composites can work properly only when the corrosion resistant barrier withstands correctly the chemical attack of the fluid. As a result, corrosion resistant barrier (made of FRP or thermoplastic liner) is the most important and critical factor for having a good strength against the hydrochloric acid attack, so it is essential having the best quality on this part of the equipment.

Once the material and the thickness for the corrosion resistant barrier have been correctly chosen, it will just remain to perform a good manufacturing process and a strict quality control. Apart from following the recommendations of the design codes detailed before (ASME RTP-1 [2] and EN 13121 [1]), it is a very good practice to apply the recommendations of the DT-15 Rev. 1 of the U.I.C. [3] for butt and wrap joints and set-in branches (nozzles, tees, etc.). This French document has very well explained execution details for those elements (which usually are the weakest parts of FRP vessels and piping), giving as a result better quality equipment for corrosive service and a longer service lifetime. Figure 4 shows how a wrong design can lead to cracking of the corrosion layer reducing the strength of the laminate against the acid chemical attack.

Figure 4 – Cracks on flat bottom of an hydrochloric acid storage tank having 4000 mm inside diameter. Among other design and manufacturing defects, the lack of a knuckle on the joint cylinder-flat bottom, made six tanks to fail during its start-up.
Hand lay up and filament winding (whether orthogonal or classical filament winding) are the most typical manufacturing procedures used for FRP vessels and piping. FRP corrosion resistant layers must be always made through hand lay up procedure. Structural layers can be made by any of both procedures but technical and economical advantages of filament winding procedure are clear nowadays. One of these advantages is that filament winding constructions are safer than hand lay up constructions because the risk of unexpected catastrophic failures is reduced.

A case where a 33 % hydrochloric acid storage tank failed after 4 service years is studied to show this safety advantage. Fortunately its failure was detected before becoming catastrophic. This tank had a hand lay up FRP corrosion layer with 2,5 mm thickness made of bisphenolic vinyl-ester resin. The structural layer of the tank was made by filament winding procedure using the same type of resin. Due to the diffusion of the hydrochloric acid through the laminate, the low thickness of the corrosion layer and some defects on its laminate (porosity), the acid went through the whole corrosion layer in quite a short time (only 4 years). Once the hydrochloric acid had reached the structural layer, where the content of resin is lower, the acid could go through it very fast, reaching the external side of the tank as shown in Figure 5. When the acid came to the atmosphere, it evaporated so the operators saw the tank surrounded by those hydrochloric acid vapours, so they activated the alarm on the plant. Next the tank was emptied and replaced by a new one, avoiding an unexpected catastrophic failure.

*Figure 5 – Attack and diffusion of HCl after 4 years of service. The tank was put out of service since it was not suitable for repairing.*

The acid has passed through the corrosion-resistant barrier, and some parts already attacked can be seen due to its different color (light green).
If the structural layer had been made by hand lay up (using alternate layers of chopped strand mat and woven roving tissue) as it was usual some years ago, the hydrochloric acid would have gone through this structural layer more slowly, weakening and destroying layer by layer the tank wall. As a result of this slow progress of the acid through the structural layer, the risk of a catastrophic failure would have been very high.

Anyway, even considering that filament winding construction gave a clear safety advantage, there were some design and manufacturing defects on this tank that must be highlighted:

1. Wrong choice of the resin used on the corrosion-resistant layer. Using a novolac vinyl-ester resin instead of a bisphenolic vinyl-ester resin would have delayed the diffusion of the hydrochloric acid. As a result, the liner would have withstood the acid diffusion for a longer time, probably between 7 and 8 years.

2. Wrong thickness of the corrosion-resistant barrier. A tank for storage of 33 % hydrochloric acid requires, at least, a 4 mm thickness liner according EN 13121 [1] design code. Some resin suppliers recommend using 5 mm minimum thickness for this layer. Finally, the DT-15 Rev 1 of U.I.C [3] recommends using 6.3 mm for this layer, therefore the corrosion resistant barrier was not thick enough.

3. Wrong quality control during manufacturing. After inspecting the corrosion-resistant barrier of the tank, it was discovered that it had a high level of porosity, much higher than the maximum level allowed by the design codes. This porosity increased considerably the diffusion rate of the acid through the liner laminate.

Apart from the previous considerations, as it is required for metallic tanks, it is also compulsory to work always with qualified workshops which have qualified lamination procedures and laminators, in order to reach the required quality for managing corrosive fluids. Another important factor is the implementation of postcuring process during the tank manufacturing, since this treatment will improve the chemical and mechanical properties of the laminate. As a result, the service lifetime and reliability of the equipment will be enhanced.

Finally, it is also required to follow the erection recommendations given by the design codes. It is quite frequent to have damages on the tank (mainly on the corrosion resistant layer or liner) due to a wrong erection process, so problems will appear sooner than expected.

**Inspection and preventive maintenance**

The design failures and manufacturing defects described on the previous examples could have been easily avoided. A good technical advice during the design stage and a good quality control during the manufacturing process could have avoided the failure during operation. For these reasons, inspection and preventive maintenance have become a very important topic for chemical industries which have to deal with chemical attack on FRP equipment.

The best practice for final users and engineering companies is to strictly follow the specifications given in the international standards ASME RTP-1 [2] and EN13121 [1].

Considering that hydrochloric acid is a very aggressive chemical, it is mandatory performing a rigorous inspection of the equipment not only during the manufacturing process on the
workshop, but also after the transport and after the onsite erection. It is quite frequent to discover damages due to a wrong handling/transport or a wrong erection of the equipment, so a good practice followed by some end users of this kind of equipment is requesting the tank manufacturer to perform this inspection after transport and erection.

It is recommended that the inspection program includes two essential parts:

1. Routine inspection to detect cracks, blisters and any other defects, plus measurement of hydrochloric acid diffusion through the corrosion-resistant layer or liner. This latest control will allow on straight FRP equipment, knowing when it is required to repair the corrosion-resistant layer, avoiding catastrophic failures caused by high degrees of diffusion of the acid through the laminate. Figure 6 shows how the chemical attack has been increased due to a crack on the surface of the liner. Figure 7 shows how the diffusion rate can be measured through the Barcol hardness measurement on a laminate sample.

2. Full control of the equipment structure using acoustic emission tests. This non-destructive test is a powerful tool that allows detecting structural failures in FRP equipment, so it will be possible repairing these failures or if required, putting the vessel or piping out of service before having a high risk of catastrophic failure. Unfortunately, the application of acoustic emission tests in the field is not always possible.

Figure 6 – Increase of the chemical attack of HCl due to a crack on the liner’s surface.
Conclusions

The next conclusions can be obtained from this paper:

1. It is essential knowing the concentration of the hydrochloric acid, the percentage of other solvents or chemical products mixed, and the maximum and minimum working temperature to choose correctly the most suitable material (FRP or and thermoplastic) and the thickness of the corrosion resistant barrier required for managing the acid.

2. Once the working and operation conditions have been determined, the application of the international design codes EN 13121 [1] or ASME RTP-1 [3] will allow calculating correctly the structural thicknesses required, according to the expected lifetime established for the equipment.

3. The two previous questions are the essential tools that will allow end users and engineering companies choosing the most suitable bid of the FRP equipment for hydrochloric acid according to their needs. The choice must be made considering not only economical factors, but also the technical criteria obtained from those tools.

4. Once the equipment is erected, an inspection and preventive maintenance program must be established. This program has to include the objective criteria for diagnosing the state of the equipment, repairing it if required by the inspection results, and putting it out of service before having a high risk of catastrophic failure. These considerations will allow us to increase the service lifetime, reliability and safety of the equipment.
References

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