MODEL TO OPTIMIZE THE DESIGN OF FIBERGLASS REINFORCED PLASTIC IN CHLORINE DIOXIDE SERVICE

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ABSTRACT

Fiberglass reinforced plastic (FRP) is used for tanks and pipe to contain a wide range of corrosive vapors and liquids – in many cases with superior performance and lower cost compared to stainless steels. Conventional practice for FRP specifies the same construction of layers nearest the process-side of the FRP. This approach does not usually consider individual corrosion processes, thus producing uniform equipment for non-uniform service conditions. Further, ordinary practice defines these inner layers as the only component that is important for its fitness for service. FRP experiences a number of simultaneous damage mechanisms that affect its structural capacity. Based on extensive inspection history in similar services, this paper presents a model for design of FRP in chlorine dioxide service to optimize the life and maintenance of FRP assets.

INTRODUCTION

Fiberglass reinforced plastic is both a structural material and a corrosion resistant material. FRP is used successfully in a diverse range of industries for storage tanks, process vessels, tank linings and piping. Similar to stainless steel, FRP equipment provides corrosion resistance to the contents and environment while providing structural support for the stresses from containment.

FRP is used in several applications in the pulp bleaching process, as well as for handling and storage of other chemicals used throughout papermaking. Applications in this discussion involve handling solutions containing chlorine dioxide including bleach filtrates, chlorine dioxide, and stock.

Engineering education normally emphasizes metals and concrete as structural materials. Formal education in design of fiber reinforced composites, especially for corrosion applications generally only occurs at the introductory level. To address this and meet industrial needs for this knowledge, several standards and codes have been developed to provide guidance primarily for the structural elements of FRP design. These standards have improved the reliability of FRP equipment and have served to educate engineers. These standards include ASME RTP-1, ASTM D3299, ASME Boiler & Pressure Vessel Code Section X, among others.

Along with their clear benefits for structural design of FRP, these standards also identify standardized construction of FRP for pipe and containers made for corrosion service. Figure 1 illustrates this standardized construction as a cross-sectional view with the process side of the FRP (in contact with the fluid contained) on the left side and the non-process surface on the right.

From the inside, there is a thin layer using a tissue (veil) of glass or polyester with 90% resin by weight. This is followed by several layers of randomly oriented, short, glass fibers (CSM) that are saturated with resin to 70% by weight. These high-resin layers form what is termed as the “Corrosion Barrier” (CB), which is intended to protect the structural layers of FRP from the contents of the pipe or vessel, primarily through the high resin content. It is conventional practice to exclude any of the real contribution to structural capacity by the corrosion barrier from the design.

The CB specified for most FRP process equipment is between 0.25mm to 5mm thick. Normally, CB thickness of 2.5mm, with one or two veils and two CSM layers, is recommended in most practices and standards.
The use of the standards listed above has significantly increased the overall reliability of FRP for most applications.

Worldwide, corrosion applications of FRP include a wide range of services and chemical exposures. A typical list includes humid chlorine, chlorine dioxide, brines, seawater, hydrochloric acid, weak sulphuric acid, sulphur dioxide and more. Of all the FRP assets in one comprehensive database, oxidizing chlorine compounds, including chlorine dioxide and chlorine, comprise only about 3% of the FRP process equipment in use. Special considerations for service with these chemicals is not identified in any standards.

This paper will discuss a new approach to optimize the lifecycle cost of FRP for use with chlorine dioxide.

FRP FAILURE MODES AND DAMAGE MECHANISMS
A failure mode is the way in which FRP fails so that it is not suitable for use. Normally a failure mode is visible to the naked eye and can include cracks, fractures and holes.

Damage mechanisms or degradation mechanisms, are the changes that take place that can lead to failure. Examples of damage mechanisms are corrosion and abrasion.

In FRP, three basic damage mechanisms can occur. They are; damage to the resin, damage to the reinforcement fibers and damage to the bond (interface) between the resin and reinforcement. This damage can be caused by chemical attack, corrosion and mechanical action.

The most common failure that occurs for all FRP equipment is cracking of flanges, generally due to improper mating and bolting. These cracks appear first on the outer surface of the flange as a result of overloading. An example is shown in Figure 2.

The crack shown in Figure 2 cannot be repaired. Replacement of flanges that are cracked in this manner is the only repair option.
Figure 2 – Typical flange failure

TAPPI provides guidance for monitoring some damage mechanisms in its best practice document, TIP 0402-28 “Best practice for inspecting used fiber-reinforced plastic (FRP) equipment” (TAPPI, 2007). This document provides thorough guidance on what is involved in an inspection and states that the condition of the corrosion barrier defines when repairs should be made. The document does not appear to provide guidance on criteria to be used to assess the condition of the corrosion barrier.

Figure 3 shows a chart of damage mechanisms and failure modes. The chart also shows these relative to the corrosion barrier and structural layers.
In chlorine dioxide service, as well as humid chlorine and other strong oxidizing environments, the dominant damage mechanisms are usually oxidation of the resin in the CB, also leading to diffusion of the species through the damaged resin of the barrier. The oxidation products often appear as “butter” which has no structural value. This oxidation serves to reduce the thickness of the FRP by constantly removing resin.

The rate of resin loss depends on the resin chemistry. In general, oxidation rates vary with the degree of cure and the density of cross-linking in the resin. For some resins, the rate of thickness loss can be predicted with some reliability.

Stress in the structural layers will reduce the elastic modulus over a period of time. This is known as creep. For thermoplastics that can be melted, such as PVC, polypropylene and polyethylene, creep will result in some permanent deformation. For cured FRP resins, creep does not result in permanent deformation, but it shows as reduced stiffness. When the stiffness is reduced, the deflection, or strain, in the FRP will increase for the same applied load.

Figure 4 shows typical performance of FRP when loaded and no corrosion or thickness loss occurs. The curve in Figure 4 can also be used to characterize changes in the flexural modulus as identified in Figure 3. Note from Figure 4 that the normal design range for FRP is below the curve. When the effects of corrosion or chemical attack are incorporated, the flexural modulus will often decline at a faster rate and to lower values. Although the general shape of the curve is known, it is not usually possible to predict the rate of change until the FRP has been under load for some time and the original values for the FRP are known. Any reduction in FRP thickness while in service will increase the rate of change.
Consider Figure 4 and flange failure as noted above. Note that flange failure shown in Figure 2 may not occur immediately at installation, but will often occur after some time in service. In the context of creep, it makes sense that the bending in the flange will increase as creep occurs, and when the strain reaches the failure point of the resin, cracks will appear.

![Figure 4 – Typical FRP Creep](image)

A study of more than 300 FRP vessels worldwide has found that normal design practices for applied stress can result in lifetime of more than 40 years for FRP vessels under the following conditions:

- The FRP manufacturer produces FRP that meets the design modulus and strength requirements.
- Loads applied to items such as flanges remain within the design values.
- Corrosion barrier thickness remains constant.
- The resin used and corrosion barrier provides good resistance to the chemicals contained.
- Workmanship meets the criteria of suitable design standards.

In many cases, this lifetime is achieved without any significant repairs.

To summarize, FRP equipment in chlorine dioxide service will experience two dominant damage mechanisms; thickness loss of the FRP and creep.

**CURRENT PRACTICE**

Current practice for FRP vessels in pulp bleach plants is to design and build equipment according to standards such as ASME RTP-1 (American Society of Mechanical Engineers, 2015) or ASTM D-3299 (ASTM, 2010).

After the vessels are put into service, periodic inspections are made to monitor the damage to the corrosion barrier and repairs are completed as required by inspector judgement. The condition of the corrosion barrier is the primary consideration for determining repairs, with each inspector generally using his/her own criteria. TAPPI TIP 0402 (TAPPI, 2007) describes conventional inspection methods. Following TIP 0402, any inspection to evaluate the corrosion barrier surface requires confined space entry.

When the corrosion barrier is considered to be no longer effective, the most common repair is to replace it during a pulp mill outage. The replacement process consists of removing the remaining corrosion barrier materials, often by abrasive grit blasting, and placing a new corrosion barrier on the inner surface.

There are several features of this repair process that should be noted:
• These repairs commonly have no float time in a pulp mill shutdown schedule, making them critical path items. This usually limits the amount of replacement thickness that can be applied. There is also risk that the resin in the repair will not have sufficient time to be fully cured.
• Any chlorine dioxide that is present on the surface will affect the bond and will present a workplace hazard because when chlorine reacts with styrene, a chemical similar to tear gas is formed in the confined space.
• Relining often does not repair the inner surface of small nozzles in a vessel, leading to the possibility that failures could still occur on nozzle walls and nozzle to flange face transitions. An example is shown in Figure 5. This practice also can allow accelerated exposure of the structural layers as the nozzle wall deteriorates.

Based on normal CB thickness and observed thickness loss rate, relining of new vessels, when the resin in the CB is cured to at least 90% of full cure, is often expected at 5 to 10 years. If the cure is less than that, thickness loss will be accelerated. In the case of relined vessels, it is common to see faster deterioration.
Several owners have advised that the cost to reline a FRP vessel is about 50% to 75% of the replacement cost of the vessel.

This paper focuses on FRP vessels.

A NEW PRACTICE

Since the dominant damage mechanisms in chlorine dioxide service are understood, it makes sense to design FRP equipment to suit them, departing from conventional standards, if necessary.

Corrosion Barrier

Consider first oxidation of the CB. As noted above, FRP equipment could be expected to last for 40 years without significant repairs. For chlorine dioxide, this is only possible if the combination of corrosion barrier and structural support can survive for this period. There are two methods proposed here to extend the life of the corrosion barrier:

1. Make the corrosion barrier thicker to minimize the risk of relining.
   For a 20 year lifetime, a corrosion barrier should be as thick as 20mm. This additional thickness should also be applied inside nozzles, and the seal bonds must also include this thickness. One way to do this is illustrated in Figure 5.

Figure 5 – Proposed construction at small bore nozzles

Figure 5 includes several features:
- A corrosion barrier of 10mm thick is illustrated for a 4 inch nozzle.
- Conventional straight nozzles are replaced by engineered nozzles that also use lap-joint (Vanstone) flanges. These flanges usually solve the flange failures noted above.
- The flare in the nozzle at the tank shell will improve the ability of the manufacturer to seal the nozzle to the inner surface.

Some benefits of this approach are that longer service life will be realized from 2 sources. The first will be that the corrosion barrier is thicker. The second source is that the resin cure through the CB can be maximized by the manufacturer with few time constraints.
Some drawbacks are that a thicker CB will increase the cost of the vessel, usually in proportion to the additional weight of CB materials added. The engineered nozzles may also cause some cost increase.

2. Use a corrosion barrier of polyvinyl chloride (PVC)

PVC offers good protection against oxidation. The major damage mechanism that occurs in this environment is loss to flexibility as plasticizing compounds are leached from the polymer. The other damage mechanism to monitor is leakage at welds that may occur.

When a thermoplastic lining is used as a corrosion barrier, sheets of polymer are formed onto the mold and welded together. After the welds are determined to be leak tight, FRP is applied to the outer surfaces to provide structural support. When nozzles are inserted, the FRP is also formed over a thermoplastic nozzle. When inserted, the thermoplastic is welded together and FRP is applied on the outer surface for structural support.

The FRP support structure for PVC is relatively stiff. When the PVC is bonded to the FRP, loss of stiffness is not a significant issue.

Longer service life will be realized from the improved performance of PVC as a CB material. FRP vessels with a thermoplastic lining are known as “Dual Laminate” vessels. The cost of these vessels is greater than the cost of FRP vessels and the additional cost is largely related to the cost of the thermoplastic used. PVC-lined chlorine dioxide storage tanks have

Flanges

Now consider flange failures. As noted from Figure 5, lap-joint flanges will significantly reduce flange failures.

Benefits to this approach are:

- Lower bolt loads are usually required to seal the flanged joint.
- The steel ring applies even pressure to the FRP.
- The flanges can be mated to raised face valves.
- The steel backing ring carries the stresses that normally cause FRP flange failure.

Drawbacks are:

- Cost is slightly higher.
- If mating to flat face FRP, an engineered spacer ring is required.
- Backing ring can damage the FRP during shipping if it is not properly secured.

CONDITION MONITORING

The condition of these modified vessels should still be monitored while they are in service, similar to existing vessels. Questions that should be answered from condition monitoring are:

1. Is the vessel fit for continued service? This includes determining that the vessel has sufficient mechanical integrity to meet its process requirements in addition to any regulatory requirements. In this case, it is recommended that the vessel nameplate and drawing should include key information that any inspector and engineer can use when making mechanical integrity decisions. Information such as minimum structural capacity and total thickness and “as supplied” FRP composition and thickness.

2. What is the rate of change of key factors in the vessel? These key factors should include both corrosion barrier condition and thickness and structural capacity. This will allow future replacement or repair decisions to be planned based on objective information.

In this case, non-destructive condition monitoring that does not require confined space entry can be used. Using an advanced ultrasonic technique, the thickness of the corrosion barrier can be monitored at the same time as the total structural capacity. These values can be used to provide ongoing evaluations.
OPTIMIZATION

Using the methods outlined above, the repair and replacement of FRP vessels in pulp mills can be optimized using knowledge gained from decades of mill experience combined with up-to-date technologies.

References

