**Proven Solutions for Phosphoric and Sulfuric Acid Service**

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**ABSTRACT**

A variety of material solutions are available today to construct vessels, piping, ducts and scrubbers for the demanding environments found in phosphoric and sulfuric acid plants. Many have been time tested over decades of service. One in particular, however, has risen above all others in terms of reliability, performance and economy. This presentation will outline how FRP outperforms alloys and rubber lined steel in phosphoric and sulfuric acid service. In particular, it will illustrate how to design, assemble and maintain an FRP system so as to deliver its best performance and avoid costly mistakes. Case histories will confirm material selection and design criteria in real world environments.

Keywords: corrosion, epoxy vinyl ester resin, fertilizer, fiberglass-reinforced, high nickel alloy, plastic, phosphate, phosphoric acid, reinforced thermoset plastic, dual laminate, sulfuric, vinyl ester resin

**INTRODUCTION**

Phosphoric acid (H3PO4) and Sulfuric acid (H2SO4) are the top two inorganic acids manufactured and consumed globally. Sulfuric acid is used in a wide variety of industrial processes but more than half of all volume finds its way into the production of phosphoric acid. The vast majority (>80%) of phosphoric acid goes into the manufacture of phosphate fertilizers.
Nearly all phosphoric acid is derived from phosphate rock with some 200 million tons of phosphate rock being mined each year. The International Fertilizer Industry Association (IFA) forecasts that global phosphoric acid demand will continue to grow at a rate of 2% annually between 2012 and 2017. Phosphate rock is converted into Phosphoric acid through one of two industrial routes. The first is known as the wet process whereby phosphate rock is acidulated with a strong inorganic acid, typically sulfuric. The second route is the furnace process, where phosphorus pentoxide (P2O5) is liberated from phosphate rock thermally and then dissolved in water. The wet process is the predominate source of phosphorous used to produce fertilizers and animal feeds. Sulfuric acid is preferred in the wet process due to its favorable economics over alternative inorganic acids, the relative ease of end product isolation and because of severe corrosion problems which typically occur with other acids.

The acidulation of phosphate rock in the wet process is typically carried out at elevated temperatures; 74°C - 85°C (165°F - 185°F) in the dihydrate process or 98°C - 102°C (210°F and 215°F) in the hemihydrates process with the level of free sulfuric acid held below 3% in order to improve gypsum crystal formation. These conditions are quite corrosive and hence mandate great care in the selection of durable materials of construction for piping, process vessels, scrubbers and storage tanks.

With world population growing at just over 1% annually and arable land per capita decreasing there is little doubt that phosphate fertilizer production will continue to rise for the foreseeable future. This will create a continuing need for new corrosion resistant equipment in these plants. In the last millennium, stainless steel, high nickel alloys and rubber lined steel were the preferred materials of construction for many “wet process” phosphoric acid and sulfuric acid environments.

Fiber Reinforced Plastic (FRP) has been used to build highly durable corrosion-resistant chemical processing equipment for more than 60 years. FRP has a long history of success in both wet process phosphoric and sulfuric acid production facilities. The use of fiberglass reinforced plastics based on epoxy vinyl ester resins for the construction of storage & process vessels, scrubber systems, transfer piping and ducting offers both durable and cost-saving solutions for these applications. Today, more and more design engineers are specifying FRP composites for equipment used in these demanding chemical processes.

FRP CHEMICAL RESISTANCE VERSUS METALS

Chemical resistance is a key predictor of service life in phosphoric and sulfuric acid processes. Compared to metals (Table 1), FRP made from epoxy vinyl ester resin has as good or better chemical resistance than Alloy C-276 and is superior to 2205 and 316 stainless steels. FRP has unusual resistance to chlorides and is superior to alloys in high chloride environments. Based on more than 30 years of experience and testing in “wet process” fertilizer systems, FRP made from epoxy vinyl ester resin has the chemical resistance necessary for long-term service life.

When process engineers are seeking to design piping or vessels for even higher chemical resistance, they often rely on thermoplastic lined FRP laminates or “Dual Laminates”. These
specialized materials of construction surpass the chemical resistance of even FRP based on epoxy vinyl esters to deliver durable long-lasting equipment. Depending on the particular corrosion environment and temperature, various types of thermoplastics can be used in the construction of Dual Laminate: (PVDF, PVC, CPVC, PP, ECTFE, FEP, PFA).

**TABLE 1**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sulfuric Acid</th>
<th>Phosphoric Acid</th>
<th>Acid Chloride Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L Stainless Steel</td>
<td>30°C to 5%</td>
<td>100°C to 5%</td>
<td>Not Recommended</td>
</tr>
<tr>
<td>2205 Stainless Steel</td>
<td>30°C to 30%</td>
<td>100°C to 50%</td>
<td>65°C to 2000 ppm @ low pH</td>
</tr>
<tr>
<td>Alloy C-276</td>
<td>100°C to 30%</td>
<td>100°C to 85%</td>
<td>65°C to 50M ppm @ low pH</td>
</tr>
<tr>
<td>FRP made with epoxy vinyl ester resin</td>
<td>100°C to 30%</td>
<td>100°C to 115%</td>
<td>100°C All conc.</td>
</tr>
<tr>
<td>FRP Dual Laminate*</td>
<td>120°C All conc.</td>
<td>120°C All conc.</td>
<td>120°C All conc.</td>
</tr>
</tbody>
</table>

*150°C with PFA based Dual Laminate (all concentrations)

**FIBERGLASS-REINFORCED PLASTIC (FRP)**

FRP most commonly consists of glass fibers that are bonded together with a thermoset resin to form a composite structure. In corrosive chemical environments, FRP structural layers must be combined with a corrosion barrier to protect the structural layers from chemical attack. The composition of the corrosion barrier takes into account the chemicals present, their concentration, and the operating temperature of the equipment.

The composition of a standard corrosion resistant laminate is shown in Figure 1. From left to right, the figure shows a corrosion barrier consisting of a veil followed by at least two layers of chopped strand mat. The purpose of the corrosion barrier is to provide a resin rich layer of glass to protect the structural layers from chemical attack. The veil layer contains about 90% resin and comes into direct contact with the chemical environment. The chopped strand mat layers back up the veil and contain about 75% resin. The total thickness of the corrosion barrier is normally 100 mils, but the corrosion barrier may be much thicker for very aggressive chemical environments. It is very important to have a properly designed corrosion barrier based on the chemical environment. This information is available from resin suppliers, and they should be contacted for resin and corrosion barrier recommendations.
Resin selection is the first critical step in the design of FRP for chemical service. Not all resins are suitable for chemical resistant applications, so the resin must be carefully selected based on three critical pieces of information: (1) the generic identity of the chemical(s) service, (2) the concentration of each chemical, and (3) the operating temperature of the chemical or chemicals that comprise the chemical environment.

When additional corrosion protection or temperature resistance requirements surpass that of FRP, a properly designed Dual Laminate construction can be employed. Proper selection of the thermoplastic corrosion liner is key to optimum performance of the Dual Laminate. Criteria for the design and fabrication of a Dual Laminate is covered in ASME RTP-1 appendix M12 as well as in various European DIN Standards. An example of a Dual Laminate pipe is shown in Figure 2.

FIGURE 1. Typical Corrosion Resistant FRP Laminate Construction
Thermoset resins come in a variety of compositions that greatly affect the chemical resistance of FRP. Corrosion resistant FRP made from epoxy vinyl ester resin has excellent chemical resistance to acids, bases, salts, and many types of solvents. FRP made from epoxy vinyl ester additionally is characterized by unusually good toughness and resistance to cracking commonly caused by mechanical impact and thermal cycling.

In most metal extraction processes, engineering companies will typically specify FRP equipment made from Bisphenol A epoxy vinyl ester resin or epoxy novolac vinyl ester resin. The resin choice will depend on the temperature and concentration of the acid employed in the metal extraction process. FRP made with novolac epoxy vinyl ester resin generally can be used at higher acid concentrations and/or temperatures as well as in solvents. For example, FRP made with Bisphenol A epoxy vinyl ester resin is suitable for 75% sulfuric acid up to a maximum temperature of 38°C (100°F), whereas novolac epoxy vinyl resin is suitable up to 82°C (180°F). Therefore, when choosing a resin, it is imperative to consult the resin selection guide of a knowledgeable resin manufacturer or contact them directly for a suitable resin recommendation.

**OPERATING TEMPERATURE AND PRESSURE LIMITATIONS**

Operating temperature limitations are often dictated by the chemical type and concentration. For epoxy vinyl ester resins, most liquids are limited to 100°C (212°F) no matter what the chemical concentration. Gases can be handled as high as 177°C (350°F). The pressure limitation for tanks is 15 psig and 150 psig for pipe. Higher pressures require special fabrication standards and procedures. It is important to consult the resin manufacturer when choosing a resin for these types of applications. Dual laminate systems, however, can go to higher temperatures.
Depending on the choice of the thermoplastic liner, these materials can withstand liquid temperatures up to 120°-150°C (248°-302°F).

FRP COST VERSUS OTHER MATERIALS OF CONSTRUCTION

FRP has become a very competitive material of construction in demanding corrosion service environments. The total installed cost for FRP equipment is typically much less than higher nickel alloys depending upon the complexity of the design and the geographical region of installation. It is commonly less expensive than 2205 stainless steel (Table 2) and much less expensive than C-276 alloy clad carbon steel yet it has a considerably longer service life in high chloride and fluoride applications.

TABLE 2
COST COMPARISON OF CONSTRUCTION MATERIALS*
(6000 Gal Atmospheric Storage Tank)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/S</td>
<td>$20,000</td>
</tr>
<tr>
<td>304L SS</td>
<td>$40,000</td>
</tr>
<tr>
<td>FRP</td>
<td>$60,000</td>
</tr>
<tr>
<td>316 SS</td>
<td>$80,000</td>
</tr>
<tr>
<td>2205 SS</td>
<td>$100,000</td>
</tr>
<tr>
<td>C22</td>
<td>$120,000</td>
</tr>
<tr>
<td>C276</td>
<td>$140,000</td>
</tr>
</tbody>
</table>

2013 Ashland Engineering Survey

CASE HISTORIES

Case histories of FRP in phosphoric and sulfuric acid environments include reaction vessels, absorber towers, slurry piping, ductwork, and stacks. The use of FRP in phosphate fertilizer environments dates back to the early 1970s and includes absorber towers, ductwork, and chimneys. Dual laminate vessels have been in service nearly as long (Figure 3). More recently, FRP pipe based on epoxy vinyl ester resin is commonly used for abrasive slurry. With an abrasion-resistant liner, FRP pipe based on epoxy vinyl ester resin has been successful in numerous plant sites.
The corrosion resistance properties of fiber-reinforced plastic made it the material of choice for the replacement of two rubber-lined steel tanks used to process phosphoric acid (Figure 4). These 24'-high x 30'-diameter tanks operating at temperatures between 60°-71°C (140°-160°F) were used to process 42% phosphoric acid solution for granular fertilizer production. After the phosphoric acid has settled in the tanks, the solution is agitated to remove gypsum solids.
A gas scrubbing system (Figure 5) at a fertilizer plant was made of FRP based on vinyl ester resin to resist attack from aggressive flue gases consisting of hydrochloric acid, hydrofluoric acid, and phosphate dust at 60°C (140°F). Stainless steel could not withstand the highly corrosive mixture of acid and dust formed in the scrubbers.

The service life of the FRP components in this process was considered to be 50 years. Three pairs of scrubbers in series wash flue gases from a rotary drying unit. Another pair of scrubbers performs a similar function at the output of the cooling. Cleaned outlet air from the scrubbers collects in a manifold and is released into the atmosphere through a chimney.

Figure 5. Gas Scrubbing System

Figure 6. Dual Laminate Tanks
In another pollution control process (Figure 7), 120ºC (250ºF) gas containing fluorides and ammonia was transported through FRP ducts to a scrubbing tower and is then reacted with sulfuric acid at 68ºC (155ºF).

Figure 7. FRP Scrubber in Diammonium Phosphate Process

Waste gases from phosphate fertilizer production, containing droplets of phosphoric acid and traces of fluorine at 60-70ºC (140ºF-158ºF) are handled by a FRP scrubber and chimney pollution control system (Figure 8) installed in 1974.

Figure 8. Scrubber Including Chimney for Fertilizer Process Waste Gases
Another scrubbing tower in a phosphate fertilizer process has been in service since 1973. Operating at 100°C (212º), the scrubber handles a combination of 40% phosphoric acid (H3PO4), ammonia, air, water and fertilizer dust (Figure 9).

Figure 9. Phosphate Fertilizer Process Scrubber for 100°C (212º) Dust Laden Fumes

In a separate installation, a large FRP fan (Figure 11), designed to handle P2O5 fumes from the reaction of phosphate rock and H2SO4 at 80ºC was installed in 1993.

Figure 10. Dual Laminate Tanks
Figure 11. Phosphate Fertilizer Process Fan for 80°C (182º) P2O5 Fumes

On the western edge of the Sahara, Morocco possesses some 75 per cent of the world's known phosphate reserves. To upgrade phosphate rock from nearby mines to more commercially valuable phosphoric acid, a vast refining plant in Jorf Lasfar uses an abrasion resistant FRP piping system to transport phosphoric acid and gypsum slurry.

The plant, built in 1986, is believed to be one of the largest phosphoric acid facilities in the world with a capacity of 1.3 million tons annually. The complex also includes one of the world's largest plants for producing the sulfuric acid that is used to extract phosphoric acid from phosphate rock.

Filament wound abrasion resistant FRP pipe (Figure 12) transports phosphoric acid through production, as well as to and from storage tanks. Two 1.5 meter (5 feet) diameter lines, each 6.5 km (4 miles) long, also carry a suspension of abrasive gypsum away for disposal.

Figure 8. Abrasion Resistant FRP Pipe for Phosphate Fertilizer Process Slurry
As seen previously, FRP can be used extensively for pollution control in phosphate fertilizer processes. It can also be used to recover acid that would be otherwise lost as fumes. The unit pictured below (Figure 9) condenses phosphoric acid at 85% concentration out of waste air. Average process temperature is 85°C, rising to a maximum of 95°C.

Figure 9. FRP Separator Recovers Phosphoric Acid from Waste Fumes

Venturi scrubbers (Figure 10) can also be made from FRP for cleaning phosphate fertilizer fumes containing ammonia and hydrogen sulfide at 65–90°C (150°F-195°F)

Figure 10. Venturi Scrubber for Ammonia and Hydrogen Sulfide

CONCLUSION

Sulfuric and phosphoric acid processes are very demanding environments from a corrosion standpoint. Few materials of construction can stand up to these conditions for any length of time. FRP and dual laminates made with epoxy vinyl ester resin are ideal materials, however, for the fabrication of vessels, piping, ducts and scrubbers employed in these corrosive
processes. Moreover, FRP solutions are generally less expensive to procure, install and maintain than rubber-lined equipment or higher nickel alloys.

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