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The Use of FRP (Fiberglass-reinforced Plastic) in Phosphate Fertilizer and Sulfuric Acid Processes

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ABSTRACT

The demand for corrosion resistant composite equipment increased significantly starting mid 2000 when nickel prices raised very rapidly. With a 50-year reputation for low maintenance and relatively stable cost, Fiberglass-reinforced Plastic (FRP) made with Epoxy Vinyl Ester Resins provides process engineers with a reliable, cost effective construction material that can be employed in numerous applications that are corrosive to stainless steel, and at a much lower cost than high alloy clad steel. Although some other materials may be cost competitive with FRP, their use typically results in higher life cycle costs due to maintenance.

The purpose of this paper is to compare FRP made with Epoxy Vinyl Ester Resins with high nickel alloy in "wet process" phosphoric acid and sulfuric acid environments. Comparison of relative cost and corrosion data are presented to provide the information necessary for process engineers to facilitate future decisions concerning material of construction. Examples of equipment will be shown to demonstrate that it is an ideal product for the fertilizer industry.

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

INTRODUCTION

Amongst the commercial fertilizers the phosphate fertilizers represent the major group. Phosphate fertilizers are commonly obtained by extraction from minerals containing the anion PO_4^{3-}. Most often soluble salts are produced by chemical treatment of phosphate minerals. The most popular phosphate containing minerals are referred to as phosphate rock (phosphorite), which are mined in various parts of the world e.g. deposits of igneous ore in South Africa and Brazil or sedimentary ore found in Morocco, Algeria etc.

The main minerals are fluorapatite $Ca_5(PO_4)_3F$ (CFA) and hydroxyapatite $Ca_5(PO_4)_3OH$. These minerals are converted to water-soluble phosphate salts by treatment with sulfuric- or phosphoric acids. There are various manufacturing routes to produce the phosphoric acid (H_3PO_4) from the phosphate rock and sulfuric acid (H_2SO_4), using a wet process, such as the Dihydrate- (DH) and Hemihydrate- (HH) process.

The reaction also forms calcium sulfate (CaSO4), commonly referred to as gypsum. The insoluble gypsum is separated from the reaction solution by filtration.

The operating conditions are generally selected so that the calcium sulfate will be precipitated in either the dihydrate or the hemihydrate form, thus producing 26-32 % P_2O_5 at 70-80 °C for dihydrate precipitation and 40-52 % P_2O_5 at 90-110 °C for hemihydrate precipitation. The concentration of phosphoric acid is normally expressed as % P_2O_5 (percent phosphoric anhydride) rather than % H_3PO_4 (percent phosphoric acid).

In all these processes typically high concentrated acids as well as high chloride- and fluoride levels are present, which demand good corrosive resistant construction materials to meet the necessary life time expectation.

Since phosphate fertilizer production plant capacity is expected to increase by at least 15% over the next years, there will be a significant need for new corrosion resistant equipment in these plants. The cost of new equipment depends greatly on the materials of construction. Materials such as high nickel alloy will be very expensive, and will create a demand for less expensive materials such as Fiberglass Reinforced Plastic (FRP) that have proven performance in phosphate fertilizer processes.

FRP has a long history of success in a number of phosphate fertilizer processes including the sulfuric acid process. Typical applications include phosphate- and sulfuric acid reaction vessels, scrubber systems for both fertilizer and sulfuric acid processes and pipes for phosphoric acid and gypsum transport. Fertilizer process equipment made from FRP is relatively inexpensive and has case histories dating back to 1973 to prove its successful use in fertilizer systems.

Alternative materials, besides high nickel alloy, include rubber-lined carbon steel, acid brick-lined carbon steel and resin coated carbon steel, which can be used in 'wet process' phosphoric and sulfuric acid environments. However, these materials do not all have the same service life expectancy nor do they have the same cost.

In this paper, FRP will be used as a reference material and compared to other materials for service life and cost in phosphate fertilizer production.

1.1 CONSTRUCTION MATERIALS

As construction material for applications as pipes, tanks, ducts etc. a variaty of materials can be considered, which cover amongst alloy steel, brick lining and Fibreglass Reinforced Plastic (FRP). High nickel alloys were in the past often used for the ‘wet process’ even though these environments often contain high chloride and fluoride levels that are highly corrosive to stainless steel. Rubber-lined carbon steel is used to some extend and also glass flake coated carbon steel but these proved to have drawbacks in maintenance costs. As shown, in Table 1, the available materials do not all have the same service life expectancy in an aggressive chemical environment, nor do they have the same investment cost.

Comparative cost for the various constructions materials, as FRP, 2205 stainless steel and Alloy C-276 clad carbon steel, is given in Table 2. (Source: Major FRP manufacturer in North America).

1.2 NICKEL PRICE DEVELOPMENT

The nickel price development over the recent years triggered a great demand for alternative and less expensive materials with adequate corrosion resistance. The development of the nickel price (stainless steel follows this trend) over the time span 2005 to 2015 is illustrated in Fig. 1 (Source: MEPS International).

Prior to 2006, high nickel alloy was often the material of choice for wet process environments and used in applications with high concentrated sulfuric acid. However, as the cost of new equipment depends greatly upon the materials of construction, it is obvious that drastically increasing raw material pricing for construction materials makes design engineering for ‘fixed contracts costs’ difficult or impossible.

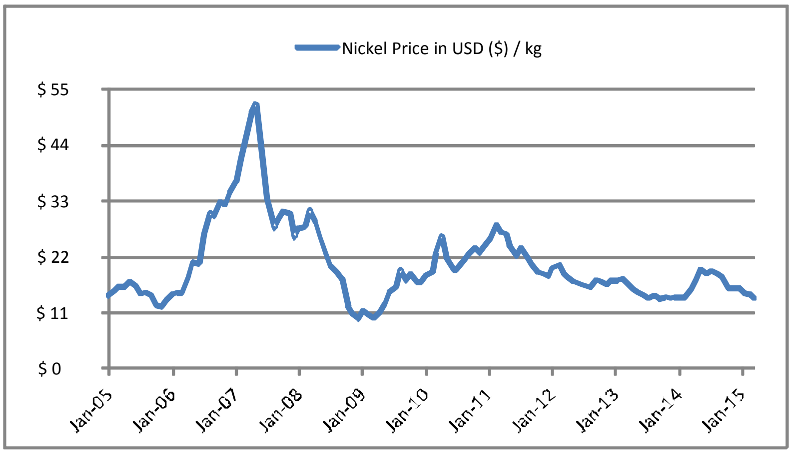

Figure 1. Nickel price development 2005 – 2015
Source: MEPS International, London Metal Exchange, and Bureau of Labour Statistics.

1.3 COMPARATIVE CHEMICAL RESISTANCE OF VARIOUS CONSTRUCTION MATERIALS

The chemical resistance of a material is a key parameter to estimate a potential life time of a construction material and so an important factor in decision making for service life expectations and anticipated maintenance costs.

Compared to metals, see Tab. 1, Fibreglass Reinforced Plastic (FRP) when manufactured from a chemical resistant Epoxy Vinyl Ester Resin proved to have a good or better resistance then Alloy C-276 and 2205 Stainless Steel.

Table 1. Comparative chemical resistance of FRP, 2205 SS and Alloy C-276

Materials	Corrosive Environment		
	Sulfuric Acid	Hydrochloric Acid	Acid Chloride Salts
FRP made with Epoxy Vinyl Ester Resin	100°C to 50%	80°C to 15%	100ºC all concentrations
2205 Stainless Steel	30°C to 30%	60°C to 1%	65ºC to 2000 ppm @ low pH
Alloy C-276	80°C to 30%	80°C to 15%	65º to 50,000 ppm @ low pH

FRP proved to deliver the adequate resistance to chloride and better chemical resistance compared to alloys in high chloride environment. Beyond the available data base of chemical resistant performance of FRP composites additional studies (sulfuric acid at elevated temperature) by e.g. by an independent institute as Swera KIMAB, Sweden are ongoing to compile further expertice [9].
Based on more then 50 years of experience and use in industrial enviroment, FRP made from Epoxy Vinyl Ester Resin proved to meet the chemical resistance necessary for long-term service life.

1.4. FRP COSTS VERSUS OTHER CONSTRUCTION MATERIALS

As result of the rising cost of nickel, FRP has become a very competive construction material. Depending on the site of manufacturing and whether shop- or field-fabricated FRP is applied, the installed cost of FRP typically ranges from 1000 to 1500 $/m2 in the USA and Europe, Tab. 2 (Source: USA / Europe fabricator data). This implies it is less expensive compared to 2205 Stainless Steel and significantly less expensive than Alloy C-276 clad carbon steel.

Table 2. Comparative costs of various construction materials
Based on Feb. 2015 Ashland North America internal data

Construction Material	Cost Ratio
Shop Fabricated FRP (total installed cost)	1.0
Field Fabricated FRP (total installed cost)	1.4
2205 Stainless Steel	1.9
Hastelloy C 276	2.9

1.5. TYPICAL FRP COMPOSITE DESIGN

For Chemical Resistance (CR) applications commonly Epoxy Vinyl Ester Resins are used, of which the main property characteristics- and handling- characteristics can be summarised as quoted in Fig. 2.

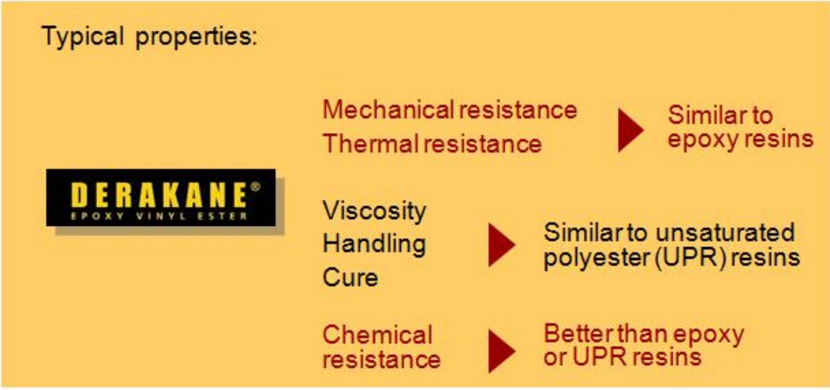

Figure 2. Characteristics of chemical resistant Epoxy Vinyl Ester Resins

To verify whether a specific resin and laminate design can meet these requirements, dedicated lab tests (lab screening) are made, in accordance with the representative industry norms e.g. ASTM C-581, whereby the changes of laminate properties are studied versus time and control parameters over a test period up to 12 months. For a screening of the performance properties, the change of laminate characteristics are investigated (e.g. sample weight, hardness, appearance, mechanical properties). The final decision whether a specific resin and laminate design can meet the chemical environment is decided on basis of the lab results and backed up by industrial data.

The FRP design has in correlation to a typical metal design a similar safety concept. Instead of a ‘corrosion allowance’ as for metal, a ‘chemical resistant layer’ is applied. The chemical resistant layer typically contains a high resin content (low glass content) to reach optimum resistance to the chemical environment and the structural laminate contains a high glass content (low resin content) to reach optimum strength and stiffness.

The chemical resistant layer is typically made with 1 or 2 chemical suitable veils (e.g. C- or E-CR-glass) and the structural laminate may contain high-acid resistant E-CR glass when required for the environment. In addition, a special ‘wet-in-wet’ process, may be applied for the transition of ‘chemical resistant layer’ and ‘structural laminate’, to obtain a best possible design and long-term service life.

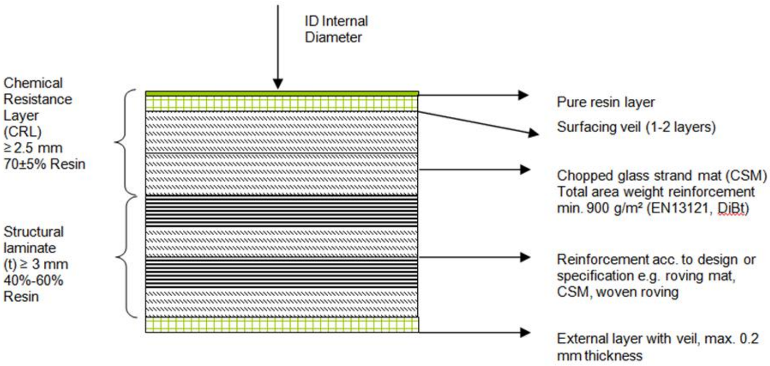

Figure 3. Typical Cross section through a FRP composite design

For most ‘wet’ applications, the maximum operating temperature is ca. 100 ºC (212 °F) with excursions up to 120 ºC (248 °F). Dry environments can operate at ca. 175 °C (347 °F) with excursions up to ca. 200 °C (392 °F). Because not all resins are suitable for processes that have thermal cycling or high temperature excursions, it is important to consult the resin manufacturer when choosing a resin for these types of applications.

2. PHOSPHATE FERTILIZER CASE HISTORIES

Morocco possesses 75 per cent of the world's known phosphate reserves. To transform the phosphate rock from nearby mines to more commercially valuable products, like fertilizer, sulfuric acid or phosphoric acid, FRP equipment were used for plenty of applications. Some examples of use of FRP in Morocco, but also around the globe are shown below. Case histories of Fibreglass Reinforced Plastic (FRP) in phosphate fertilizer production include storage tanks, 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, so close to 50 years of experience with this material. More recently, FRP pipe based on Epoxy Vinyl Ester Resin pipe have been successfully in numerous plant sites with an abrasion-resistant liner for abrasive slurry.

2.1. Tanks, storage tanks, process vessels:

The corrosion resistance properties of FRP and the fact that you can more easily inspect a FRP equipment made it the material of choice for the replacement of two rubber lined steel tanks used to process phosphoric acid. The 7.2 m (24') high x 9.0 m (30') diameter FRP tanks, were fabricated using Epoxy Vinyl Ester Resin. The tanks, operating between 60-71 °C (140 – 160 °F), 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. The FRP solution reduced the maintenance costs, as it drastically reduced the potential for problems with regular visual inspections and tests made with the acoustic emission technique.

FRP tanks were also used for outdoor storage tanks of sulfuric acid (22.5% concentration) or phosphoric acid (35% and 80% concentration) – see Fig 4 and 5. Some tanks were also used for the phosphoric acid recovery system at 25 – 80°C (75°F – 175°F) and were found in good conditions after 18 years of service.

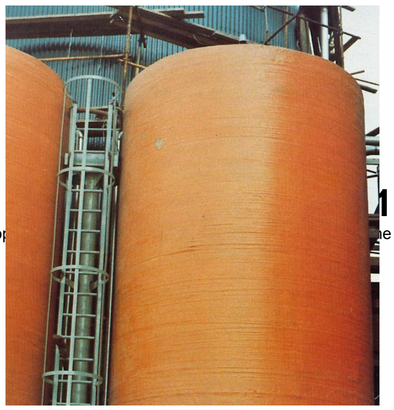

Figure 4: Storage tank of phosphoric acid at 75% concentration with an outside temperature from -25°C up to + 40°C in Finland, 50 m3 volume

Figure 5: Storage tank for phosphoric acid (max 30%) sulfuric acid (40g/L), and some hydrofluoric acid (2%) 7.8 m diameter, 10.7 m height, in perfect condition after 9 years of service in Spain.

2.2. Scrubbers, stacks

A gas scrubbing system (Fig.6) at a fertilizer plant was made of FRP based on Epoxy Vinyl Ester Resin to resist attack from aggressive flue gases consisting of phosphorus pentoxide, hydrofluoric acid, phosphate dust, water vapor up to 110°C (230 ºF). Stainless steel could not withstand the highly corrosive mixture of acid and dust, which is formed in the scrubbers.

Scrubbing towers in a phosphate fertilizer process have been in service since 1998. Operating at 70°C (160ºF), gas temperature. The scrubber treats the ammonia containing gas with an acidic solution of phosphoric acid and sulfuric acid. On Fig. 7, a scrubber followed directly by a chimney on top of it. It can handle waste gases from the fertilizer production with droplet of phosphoric acid, sulfuric acid and traces of fluorine at 60-80°C (140 -180°F).

Figure 6: FRP Gas Scrubbing System in Tunisia, 7.5 m height, 2.5 m diameter.

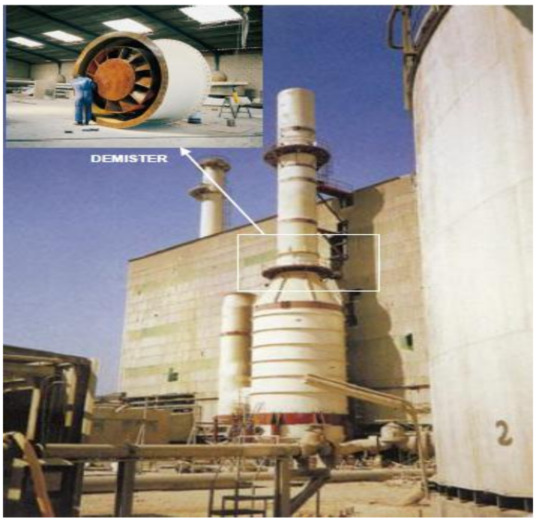

Figure 7: FRP scrubber system with duct, exchangeable demister due to high abrasion. In service for 20 years in Spain.

2.3. Process equipment with various shapes

All kind of shape or equipment could be made in FRP. A large FRP fan (Fig. 8), designed to handle P_2O_5 fumes from the reaction of phosphate rock and H_2SO_4 at 80 ºC (176 ºF) was installed in 1993 and was still fine after 12 years of service. On fig. 9, the equipment is a digester. It is used in contact with sulfur dioxide, phosphorus pentoxide and hydrofluoric acid, water and dust.

Figure 8: FRP Phosphate Fertilizer Process Fan for 80°C (182º) P2O5 Fumes in Spain

Figure 9: Acid Digester Fume Outlet Fabricated in various shapes with stiffening structures, Morocco.

The advantage of the light weight of the FRP compared to metal combined with excellent mechanical and chemical resistant properties were also used here for making a reactor tank roo(see Fig 10).

Figure 10: Reactor roof in contact with acidic fumes containing phosphorous acid and fluorine at 80°C (180°F), Morocco

Pipes and ducts, fittings:

Connecting all equipment together is done with pipes and fittings made from full FRP (see fig. 11, 12). They are made by filament winding, and could be also abrasion resistant if needed. FRP pipe can be used for the transport of phosphoric acid through production, as to and from storage tanks. Some lines have to carry a suspension of abrasive gypsum away for disposal. They can be kilometers long.

Figure 11: FRP Pipes and fittings for phosphoric acid (46- 54% concentration) at 80°C (180°F) in India

Figure 12: Effluents water and gypsum sludge pipes and fittings for phosphoric acid at 95°C (203°F) in Jordan

CONCLUSION AND OUTLOOK

Fibreglass Reinforced Plastic (FRP) is an ideal material of construction for phosphate fertilizer reaction vessels, ductwork, absorber towers, stacks and gypsum slurry piping with the following advantages:

- Proven performance for close to 30 years (Ref. Case histories) all over the world
- Significantly lower installed cost compared to Alloy C-276 clad carbon steel
- Less maintenance compared to other materials, and inspections that could be done more easily than for other materials
- Possibility of creating all kind of shapes in full FRP with excellent mechanical and corrosion resistant properties.
- Typical low weight construction compared to metal based designs

FRP did prevent price excursions for equipment during a period of unpredictable drastic nickel price development. The industrial experience, backed up by a significant number of case histories, in the phosphate fertilizer and sulfuric acid processes, with FRP based on DERAKANE™ Epoxy Vinyl Ester Resin actually represents a positive outlook for future composites applications in this process.

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