The Corrosion Chronicle
Spring 2017

Derakane™ 470HT resin pushes the envelope for high temperature, corrosion-resistant laminates

Derakane epoxy vinyl ester resins long ago established themselves as the "go to" technology when outstanding corrosion resistance in harsh chemical environments was required. From chlor alkali to bleach to hydrochloric acid and beyond, Derakane resins set the standard for corrosion resistance in liquid storage and transport equipment. More recently, however, asset owners have been asking for exemplary corrosion performance in high temperature gaseous environments. To accomplish this, Ashland's Derakane scientists embarked upon a new path, resulting in technology that surpassed the high temperature performance of the workhorse resins of yesterday.

High temperature fiber reinforced plastics (FRP) are commonly used in chimney liners, gas scrubbers and industrial coatings systems where temperatures can reach 430 degrees F (230 C) and beyond. Often these environments not only require outstanding heat resistance, but also resistance to strong acids as well. This is especially true in gas scrubbers where acidic by-products and other pollutants are removed from the flue gas. These hot gases often contain highly corrosive mineral acids such as sulfuric, hydrochloric and hydrofluoric acid. As the gases are being sprayed with water, the containment walls will be exposed to a hot, wet corrosive atmosphere as well as thermal shocks caused by the cooling effect of the water and the heating effect to the flue gases. Derakane resins have been used for many years in such composite applications where resistance to corrosive environments, good mechanical and excellent thermal performance are the major property requirements.

Materials Options

Various construction materials have been evaluated by design engineers for these severe conditions. Rubber linings can often resist the corrosion and thermal shock but the temperatures encountered are too high – leading to degradation of the rubber. Stainless steel and high nickel alloys have also been employed. They are capable of resisting the heat and thermal shock but not the long term hot, wet mineral acid attack – thus resulting in short life expectancies. In fact, it is not unusual to see a

continued on page 2

IN THIS ISSUE

WHERE YOU CAN SEE THE ASHLAND CORROSION TEAM 2017

Pultrusion Conference
Atlanta, GA — April 3-5

AIA
Orlando, FL — April 27-29

COM
Vancouver, Canada — Aug 27-30

SPE ACCE
Novi, MI — Sept 6-8

China Composites
Shanghai, China — Sept 6-8

CAMX
Orlando, FL — Sept 11-14

high nickel alloy showing severe corrosion after only a single year's time. Brick linings are the traditional material of choice as bricks resist acid attack, heat and thermal shock rather well. With brick, however, the difficulty lies in the choice of the mortar system used to adhere the bricks to the vessel wall. The mortar systems are quite susceptible to chemical attack, resulting in bricks falling off the wall and long shut downs as the brick lining is repaired.

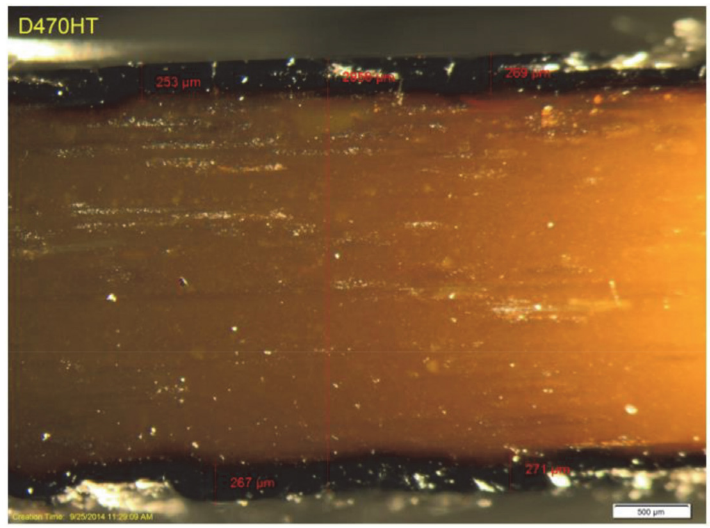
Derakane vinyl ester resins can be produced from a variety of epoxy resin precursors depending on the material science properties that the design engineer desires. For instance, a novolac-based epoxy will give high thermal resistance and tetrabromo-bisphenol A epoxy will greatly improve cured vinyl ester resin fire retardance. Rubber modified epoxy resins, can be used to impart high impact resistance to the laminate. Bisphenol A based epoxies have the best all-around performance, balancing excellent corrosion resistance with outstanding mechanical properties and good thermal resistance.

FRP systems utilizing standard Derakane novolac epoxy vinyl ester resins perform admirably when faced with most high temperature corrosive environments and thermal shocks; however even these high performing resins can be challenged by temperatures approaching 430 F (230 C) and beyond. Through modification of the polymer backbone and an adjustment of the resin co-monomer ratio, Ashland scientists have opened a new application window for FRP in high heat applications. Depending upon the post-cure schedule, Derakane 470HT novolac epoxy vinyl ester resin offers an increased Tg into the range of 375 – 430F (190 – 220 C). The polymer structure upgrade also improves the resin's acid resistance which makes it very suitable for use in the corrosive environments commonly found in scrubber gas inlet sections. Moreover, with a 3% tensile elongation value, Derakane 470HT maintains the traditional toughness advantage of vinyl ester resins, considerably outperforming competitive high cross-link resin systems. This feature allows laminates fabricated with the product to more easily withstand the thermal shocks commonly found in scrubber quench applications.

Glass transition temperature (Tg) is not the only determinant of high temperature application suitability, however. Many resins have been introduced to the market over the years with impressively high Tg values. Further study, unfortunately has found that these resins, although high in Tg were not thermally stable and began to decompose when put into service. **Design engineers are wise to look beyond a resin manufacturer's Tg and HDT (heat distortion temperature) data before selecting a high heat resin for this kind of service.**

Heat aging studies conducted with Derakane 470HT show very little impact on mechanical properties up to 355 F (180C) other than a change in color - even after 12 months. If the temperature is raised to 390 F (200 C), however we start to observe slight reductions in Barcol hardness and flexural properties after 9-12 months. At 430 F (220 C), we see a significant loss of weight, Barcol hardness and flexural properties after only 6 months. It should be noted that these observations pertain only to the corrosion barrier portion of the laminate construction. Due to the insulating nature of FRP, the load bearing portion of the laminate (structural layers) is protected by the corrosion barrier from both thermal stresses and corrosion attack.

Sample	Final Laminate Thickness	Estimated Depth of Degradation
D470HT400	2859 µm	253-271 µm



Cross Section of Derakane 470HT coupon exposed to 390 F (200 C) for one year

It is also crucial to balance resin thermal properties with mechanical properties. Often when a resin is designed to deliver very high thermal resistance (HDT and Tg), mechanical properties such as toughness and elongation to break are sacrificed. Previous developments, aiming to reach superior thermal properties at the expense of mechanical properties have generated resins that were incompatible with industrial manufacturing processes. These brittle resins often resulted in heavy delamination during production and/or after short service intervals.

Case Histories

The following are some examples of FRP designs actually in use at high temperatures.

1. **Turow, Poland / Power Plant Chimney liner and Ducting system**
   The FGD (Flue gas desulfurization) unit operates at a temperature of 160 F (70C) under normal conditions. However, during the construction period, two of the four units were not operative and ran in the bypass mode. During the by-pass operation one of the units ran for two years at temperatures up to 320F (160 C). The previous chimney liners were made out of borosilicate blocks which needed to be replaced due to the wet circumstances and the huge swings in temperature 70 – 320 F (20 – 160 C). Each of the four units consisted of a chimney liner 17 feet (5.3 m) in dia and 395 feet (120 m) tall. In addition, there was a total of 1100 feet (330 m) of ductwork with the same diameter. FRP fabricated with Derakane 470HT was selected for this project due to its chemical resistance to the wet flue gas and its ability to manage the huge swings in temperature up to and beyond 320F (160 C).
2. **Heidelberg, Germany / Municipal Waste Incinerator**
   The original quench section of this scrubber was made in Hastelloy™ C (>70% Nickel). After only 6000 hours service, holes began to appear in the walls of the vessel. When the piece was taken out of service, the wall thickness was found to have been reduced from 5 mm to 2 mm – far under the required structural strength and stiffness for a safe design with the actual mechanical loading. An FRP solution based on Derakane 470HT replaced the damaged Hastelloy construction. After 30 months of service at an operating temperature of 430F (220 C), it was inspected and found to still be structurally sound without any holes. Another year later it was inspected again and reported to be in excellent condition.
3. **Alkamar, The Netherlands / Municipal Waste Incinerator**
   The quench section in this incinerator has a design temperature of 445 F (230 C) and normally operates between 390 – 430F (200 – 220 C). An FRP part based on Derakane 470HT with many spray and instrumentation nozzles was first placed into service in 1995. Due to the positioning of the spray nozzles, an abnormal degree of thermal shock was induced during service and by mid-1995 some delamination was encountered. Protective thermal shields were designed using a carbon/graphite in the FRP and an insulating air gap. The new design resulted in very good performance.
4. **Terragona, Spain / Industrial Waste Incinerator**
   This chimney was designed for 300 – 390F (150 – 200 C) normal operating temperatures and an upset temperature of 430 F (220C) which occurs in combination with a rapid temperature change during the heat up and cool down cycle. The liner is 5 feet (1.6 m) in diameter and greater than 200 feet (60 m) in height. Originally the chimney liner was fabricated with a competitive high temperature resin which blistered badly on post cure and had to be removed. A new chimney liner made with Derakane 470HT was put in place and tested with a series of severe thermal cycles to represent normal upset conditions. The new chimney liner performed admirably and has remained in service since 1998. It was inspected recently (after 16 years of service) and found to still be in good condition.

In Conclusion

Derakane 470HT is a novolac epoxy vinyl ester type resin with corrosion resistance similar to the proven performance of Derakane 470 but with increased acid resistance. It also demonstrates very good thermal stability both in the lab and in the field. It is quite capable of withstanding the temperatures and corrosive environments found in scrubber gas inlets and chimney liners. Experience has shown that the use of FRP in advanced applications up to 430 F (230 C), should not be undertaken lightly. Careful consideration should be given to laminate design, including use of heat-conducting additives in the inner liner section, inclusion of an air insulating gap and the standard resin structural component all need to be considered for top performance in these aggressive conditions. The fabricator, design engineer and asset owner should all be involved as early as possible in the project.

Ashland Corrosion Science Center
Trusted support for FRP applications in corrosive environments.
Contact Kevin Lambrych / krlambrych@ashland.com
Ashland™ always solving

FRP triumphs over rubber lined carbon steel (RLCS)

Rubber lined carbon steel (RLCS) is often chosen as a means to manage corrosion and abrasion in challenging environments. It can commonly be found in chemical service and slurry piping. Durability is affected by the degree of severity of the chemical environment. In slurry systems, performance is also tempered by variables such as particle size and morphology, slurry concentration and flow rate. Properly designed and installed, RLCS can deliver up to a decade of uninterrupted service to the asset owner. Unfortunately, RLCS is not without its issues and is far from a panacea for corrosion control.

The problem with rubber lined piping systems is that the rubber can be permeated by a wide variety of corrosive media. Once permeated, the corrosive media is able to freely attack the substrate behind the rubber lining (typically steel) and corrode it significantly. Ultimately, the rubber liner loses adhesion to the steel substrate and breaks away to plug filters, nozzles and pumps which lie downstream from the lined equipment. Expensive, unplanned outages are the result.

Chemical attack behind a rubber lined carbon steel pipe

FRP systems conversely, are much more resilient to chemical attack than RLCS. Moreover, with the addition of a hard filler (e.g. silicon carbide), FRP systems can also be very resistant to erosion corrosion from slurry environments. In the end result, properly designed and installed FRP equipment (e.g. piping and scrubbers) can deliver 20 or more years of uninterrupted service. Incorporation of smooth flow fittings and long radius elbows can extend service in piping systems even further.

Case Histories

1. Soutern United States / FGD Plant

In 1996 an electric utility in the southern US added pollution control equipment to an existing 2000 MW coal fired boiler to remove sulfur dioxide from the boiler flue gases. Wet limestone flue gas desulfurization (FGD) scrubbers were added downstream of the boilers. Flue gases enter the tower and as they rise to the top, limestone slurry is sprayed counter current to the gases. The SO2 in the flue gases is absorbed by the limestone slurry scrubbing liquor. The slurry is then recycled from a sump in the bottom of the tower and pumped through external recycle slurry pipes back to the top of the absorber.

The FGD plant for this 2000 MW station included 10 absorber towers with 6 spray levels in each absorber. The limestone slurry reagent is both abrasive and corrosive. The original recycle slurry piping as supplied with the FGD plant was rubber lined carbon steel. The plant was experiencing significant problems with the RLCS pipe within only a few years of start-up. Permeation of the slurry reagent through the rubber lining was causing corrosion of the steel pipe and leaks through the pipe wall. Moreover, the rubber lining was blistering and in some locations peeling completely away from the pipe wall. This rubber would then become lodged in spray nozzles inside the absorber tower.

After several years of significant maintenance cost associated with repairing and relining the RLCS pipe, the plant operators and engineers evaluated their options for replacement of the RLCS pipe. Alloy pipe, RLCS steel pipe and FRP with an erosion resistant liner were all considered. Based on decades of proven performance in erosion resistant pipe systems, RPS Composites Inc's abrasion resistant FRP pipe was chosen as the preferred replacement material. RPS pipe was constructed using Ashland Hetron™ FR 992 fire retardant vinyl ester resin and a proprietary reinforced erosion resistant liner. This liner has a proven track record in over 150 FGD plant installations dating back to 1970. The fittings were fabricated with Derakane™ 510C epoxy vinyl ester resin.

Ultimately all 10 FGD units were retrofitted with RPS piping. The first two have now been in service for more than fourteen years. Based on installed experience it is expected this recycle pipe will provide more than twenty years of maintenance free service providing the plant owners with an excellent return on their investment.

FRP chosen to replace RLCS in FGD Operation

2. **Belgium / Leach Tanks**

In 2012, Plasticon Composites engaged Nystar Belgium to replace several rubber-lined steel and stainless steel **tanks from their hot leaching process**. The vessels were 21 feet (6.5 m) in diameter and 20 feet (6 m) tall. In this leaching process a range of metals (zinc, lead and copper) are leached from an ore slurry at 185 – 200 F (85 – 95 C). The original tanks had a life expectancy of 12 years but with significant ongoing maintenance costs. The new vessels were fabricated with Derakane 441 epoxy vinyl ester resin. Plasticon has thus far replaced five of the original 12 rubber lined steel vessels for Nystar. An inspection conducted in 2016 showed them all to be in very good condition. The client plans to replace the remaining 7 vessels later this year.

Ultra large FRP vessels becoming commonplace

At one time it was thought that FRP vessels could not be fabricated larger than 12 feet (3.5 m) in diameter. Many asset owners and design engineers were certain that FRP technology could not be made structurally sound beyond those diameters. Moreover, it would be far too difficult to transport tanks beyond these dimensions on public roadways. Today we know different. Tanks fabricated to 50 feet (15 m) in diameter are commonly seen. Some vessels are over 100 feet (30 m) in diameter. Similarly, these fabricated structures can be over 50 feet (15 m) tall. In fact, if we include chimney liners in this discussion, FRP structures have been constructed which are more than 900 feet (274 m) tall.

Ultra large FRP vessels are being specified for projects around the world. There seems to be no limit to the size to which these structures can be designed. With the advent of modern field winding technology, transportation to the construction site is no longer a limitation. World class fabricators can now build these vessels right in place. And if on site field winding is not an option, fabricators can construct the tanks elsewhere, oblate them prior to shipment and bring them to the job site for final erection.

There are numerous examples of ultra large FRP vessels and ducting. One such example are the hydrochloric acid tanks fabricated by Plasticos Industriales de Tampico (PITSA) for the Goro Nickel project in New Caledonia. The tanks ranged in diameter from 30-45 feet (10 - 14 m) in diameter and 25 – 60 feet (8 – 18 m) tall. "We had to use the best materials available," said Engineer Francisco Sainz Inguanzo, general manager – PITSA, "including Derakane™ epoxy vinyl ester resins from Ashland." A few years later, Ershigs won a project to fabricate a number of ultra large hydrochloric acid tanks for the Vale Nickel project in Newfoundland. Three vessels measuring 44 feet in diameter (13 m) and heights up to 51 feet (16 m) were called for. Initially, Vale was unconvinced that such large vessels could be made from FRP. In the end, however, Ershigs was able to persuade Vale that it was indeed feasible to fabricate and transport vessels of this size. Part of that persuasive argument was to visit flue gas desulfurization (FGD) projects in the power industry where Ershigs and Augusta Fiberglass had each built even larger FRP structures. In fact, the current record for large diameter FRP structures is the six 119-foot diameter Jet Bubbling Reactors (JBR) located in major Power Generation Plants in the Southeast US. Once Vale toured one of these air pollution control facilities and inspected the enormous JBR scrubber, feasibility was no longer in doubt.

The FGD market is home to another ultra large structure. That being the absorber hoods used in Southern Company's Plant Scherer air pollution control unit. Each FRP hood was approximately 128 feet (39 m) in length, 34 feet (10 m) wide and 32 feet (10 m) high, weighing about 270,000 pounds (122 MT). In all, a total of four FRP hoods were installed on Scherer units, saving a total of about $16.9 million vs construction in Hastelloy C. In Brazil, Techniplas has fabricated a 3 million cubic meter fire water storage tank for Vale Fertilizer. That's nearly 800 million gallons! The vessel was 50 feet (15 m) in diameter.

These a but a few of the ultra large FRP vessels that reside at industrial sites around the world. Contact a member of the Ashland Derakane team to learn where you might see one such engineering marvel near you.

Derakane Momentum™ 640 – a resin for rough edges

Derakane Momentum 640-900 meets the requirements of **demanding pultrusion applications** where premium mechanical properties are required along with rapid line-speeds and outstanding corrosion resistance. Such demands typically exclude the use of UPR resins as well as anhydride-cured epoxies. DM 640-900 can produce demanding profile geometries with sharp edges, undercuts etc. and superior surface quality. In addition, its low styrene content lowers workplace emissions, thus making a positive contribution to the environment.

High strength and thermal resistance with impressive toughness round out the performance properties of DM 640, making it a preferred resin for structural applications. Profiles fabricated with this resin also deliver very good fatigue and creep resistance.

Case Histories

1. **Transport Trailer**
   A light-weight all composite transport trailer was developed to minimize trailer weight and consequently increase its net payload. Pultruded structural beams made with DM 640 resin provide high strength and stiffness into the trailer chassis. It also incorporates unique sandwich panels made with three-dimensional stitched composite technology for the floor and side walls. DM 640 Resin met the project's demanding mechanical property requirements and need for excellent corrosion resistance. The resin also delivered the fatigue and creep resistance these large trailers require when used rough environments. Comprehensive road tests showed that the 'all composite trailer' had a far better 'road grip' compared to standard trailers. The full composite chassis and superstructure design on this innovative trailer is clearly is a door opener for further light weighting applications in automotive and industrial markets.

Pultruded profiles and panels for cooling tower in corrosive environment

2. **Ma'aden, Saudi Arabia / Cooling Towers**
   The Ras Al Zour fertilizer complex in Ma'aden, Saudi Arabia includes a total of 16 large, draft-cell type cooling towers developed by Hamon Thermal Europe. Structural profiles and wall panels for the towers were fabricated with pultruded glass-reinforced plastic (GRP) and DM 640 Resin. Derakane resin was critical to achieve superior corrosion resistance to the aggressive chemical environment. A long lifetime without maintenance is projected and so fulfills the requirements of the owner.

CSSI's 118 foot communications tower built with Derakane Momentum 640-900

3. **Massachusetts USA / Communications Tower**
   Dr. Clement Hiel, founder of Composite Support & Solutions (CSSI), recently won a prestigious Tibbett's award from the Small Business Administration for a 118-foot (36 m) communications tower installed by the Air Force at Hanscom AFB in Massachusetts. The tower was fabricated using Ashland Derakane™ 640 resin designed for pultrusion.

   The pultruded composite tower was erected using fastener-less joining technology where individual components, such as the lattice cross members, "snap" together without the need for metallic bolts. CSSI selected Derakane because of its mechanical properties and its outstanding corrosion resistance.

   "CSSI's snap-join approach is an enabling technology for the fabrication of modular composites. There is great interest these days in lightweight, easy-to-assemble, easy-to-disassemble materials. This award-winning technology should spur widespread interest in the automotive, aerospace, and construction industries." said Joe Fox of Ashland. The CSSI tower is the first of a new generation of composite towers with the distinct advantage of significantly reducing long-term maintenance costs and dramatically shortened construction times.

ASME primed to release new non-metallic piping standards

Nonmetallic piping design standards, including FRP and thermoplastics, have long challenged plant owners and engineers alike. The industry today contains a myriad of guides and reference standards, many of which are not very comprehensive or consistent in their direction. Generally, most piping codes and standards are recognized as being deficient in both detail and direction when it comes to nonmetallic piping. There are a number of ASTM product standards that provide guidance on product design and testing. AWWA also has a guide which provides design guidance for aboveground and buried piping. And there are still many other national and international standards to wade through. Depending on the source, guidance and critical factors may vary. Plant owners and design engineers needing to specify / design nonmetallic piping must have a thorough knowledge and understanding of a great many standards in order not to be confused or conflicted by the guidance therein.

In 2011, ASME commissioned its Nonmetallic Pressure Piping Standards (NPPS) Committee to develop comprehensive standards for nonmetallic piping, covering Fiberglass Reinforced Plastic (FRP/GRP), thermoplastics, lined steel and multi-layer composite piping. Representatives of Maverick Applied Science, Inc. including its Director of Engineering and Technology – Jeff Eisenman - have been involved with the development of FRP piping standards since the early days of this effort. ASME is now in the final stages of review and publication of these groundbreaking standards. They should become available to the public in July of this year. These standards will represent the culmination of literally thousands of volunteer hours by a multitude of Subject Matter Experts and practitioners from the piping and materials community, all under the guidance of ASME.

These will be world-class standards and are expected to be recognized and adopted internationally. Jeff Eisenman put it best when he said, "Plant Owners and Engineers have asked for better FRP standards for many years. We believe these standards will be impactful and will provide the needed guidance that will create an increased confidence in FRP piping systems." After a tremendous effort by many, it is quite exciting to see this work come to fruition with the publication of these comprehensive nonmetallic piping standards.

Keep an eye out for these new ASME standards from ASME later this Summer.

We want to hear from you!

Do you have a technical question about using an Ashland resin? Want to know what resin is suitable for a given application? Send your inquiries to derakane@ashland.com. We're also looking for interesting news stories and welcome your ideas. Simply send in your question or idea — we'll be in touch soon!

North America — Dublin, OH USA
Tel: +1 614 790 3361

Europe — Barcelona, Spain
Tel: +34 93 206 5120

India — Navi Mumbai
Tel: +1 800 209 2475

Asia Pacific —Shanghai, P.R. China
Tel: +86 21 2402 4888

Latin America — Araçariguama, Brazil
Tel: +55 11 4136 6477

derakane.com

® Registered trademark, Ashland or its subsidiaries, registered in various countries
™ Trademark, Ashland or its subsidiaries, registered in various countries
© 2017, Ashland / PC-13829

The information contained in this brochure and the various products described are intended for use only by persons having technical skill and at their own discretion and risk after they have performed necessary technical investigations, tests and evaluations of the products and their uses. Certain end uses of these products may be regulated pursuant to rules or regulations governing medical devices, drug uses, or pesticidal or antimicrobial uses. It is the end user's responsibility to determine the applicability of such regulations to its products.

All statements, information, and data presented herein are believed to be accurate and reliable, but are not to be taken as a guarantee of fitness for a particular purpose, or representation, express or implied, for which seller assumes legal responsibility. No freedom to use any patent owned by Ashland, its subsidiaries, or its suppliers is to be inferred.

Ashland™
always solving