The Corrosion Chronicle

Fall 2010

In this issue

HETRON™

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FRP: The enlightened choice for bleach storage

The global market for sodium hypochlorite is nearly two billion metric tons (4.4 trillion lbs) on a 100 percent chlorine basis, growing at about two percent annually. North America alone consumes more than 15 trillion pounds (6.8 million metric tons) of sodium hypochlorite (bleach) on a 10 percent chlorine basis. About two thirds of that sum is used in the form of laundry detergent. The remainder goes into disinfectant applications – most notably water and wastewater treatment. Bleach is a rapidly growing alternative to chlorine in water treatment and has increasingly become an essential component in large-scale wastewater treatment and drinking water purification the world over.

Chlorine and bleach have long competed in water purification, paper bleaching and other applications. Legislation for the safe handling of chlorine is strongly influencing users to make the switch to sodium hypochlorite. In the U.S., the practice of shipping chlorine by rail has now come under serious scrutiny by the Department of Homeland Security. Bleach, in contrast, is a common liquid that poses considerably less concern. In fact, the Clorox Company announced recently that it would stop making bleach from shipped chlorine. Instead the company will purchase high-strength bleach (15 percent) and dilute it down to household strength (six percent). Similarly, responding to public concern over the shipping of chlorine, Olin Corporation has now developed a fleet of 300 rail cars specifically designed to carry concentrated bleach as a less hazardous alternative.

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ASHLAND

Bleach storage

continued

The movement away from bulk chlorine rail shipments is causing an upsurge in the regional production, distribution and storage of concentrated sodium hypochlorite. The Clorox announcement alone will affect operations at seven of its nine facilities in the U.S. Clorox is the leading global sodium hypochlorite bleach provider to the household laundry and bleaching sector with 27 bleach plants in 19 countries.

Derek Stone, sales manager with ZCL Composites outlines a similar opportunity with K2 Pure. "With increasing regulations and safety concerns, the transportation of chlorine in any form has become a difficult and dangerous proposition. K2 Pure has approached this hurdle by creating multiple brine to bleach sodium hypochlorite production facilities throughout North America, thus eliminating the need to transport bulk chlorine. ZCL Composites recognized this issue as an opportunity to provide various bulk storage tanks for their process, either in high-temperature chemical processing using dual laminate tanks or in ambient storage of standard industrial 12 percent sodium hypochlorite solution FRP Tanks using premium Ashland Derakane™ epoxy vinyl ester resins. For K2 Pure's California plants we provided four 50,000 U.S. gallons sodium hypochlorite tanks manufactured in our ASME RTP-1 Accredited Xerxes* Anaheim, California facility. These were all designed and built using Derakane 411 epoxy vinyl ester resin with BPO/DMA throughout and a 200 mil corrosion barrier with a double Nexus veil. Since FRP storage tanks were already working perfectly at several other locations there was no reason to look beyond FRP for their material choice."

These production and distribution sites will require hundreds of sodium hypochlorite storage tanks. Few materials of tank construction can withstand the highly aggressive nature of sodium hypochlorite. Improper selection of tank storage construction materials can result in catastrophic failures. As a general rule no metals (with the exception of titanium) should ever be allowed to come into contact with this chemical.

Titanium storage tanks are probably the best choice for storage of sodium hypochlorite. Service life is estimated at 30 years or more. However, the cost of titanium is prohibitive unless there is a requirement for virtually maintenance-free service. Normally titanium tanks are only used for pressure reactors or small process tanks and even then only if time for repairs cannot be tolerated.

Rubber-lined steel tanks have been used successfully for bleach storage using chlorobutyl linings - typically one-quarter inch (6.35 mm) in thickness. These linings require heat curing and a skilled applicator. Unfortunately, depending on the type of rubber and the skill of the applicator the service life is normally only 3 to 6 years, at which time the liner may require total replacement. Furthermore, if liner failure is not recognized in time, the steel tank will be chemically attacked by the sodium hypochlorite, resulting in iron contamination of the product and structural damage to the tank. For these reasons, rubber-line storage tanks are not common in bleach service.

Polyethylene tanks can be of linear or cross-linked polyethylene construction. Usually the tanks are vertical cylindrical construction with flat bottom and domed top. They are very competitively priced. However, these tanks typically have a service life of only 4 to 7 years when placed outdoors and exposed to direct sunlight. If the tanks are painted frequently or located indoors, service life may be extended to 6-9 years. Polyethylene tanks should always be used in a location (inside or outside) where they can easily be replaced upon failure. Mike Covey, vice president business development for Plas-Tanks Industries, a high quality ASME RTP-1 supplier of FRP storage tanks and process vessels to the wastewater treatment industry since 1976, summed it up as follows: "We've replaced dozens of polyethylene tanks that failed prematurely in hypo service – some in as little as five years. Our FRP tanks, on the other hand, last more than twice as long in the very same service."

FRP tanks typically last twice as long as HDPE in Hypo service

The Buffalo (N.Y.) Sewer Authority's Bird Island Wastewater Treatment plant was one of those facilities. Tom Caulfield, administrator of Capital Improvements and Development, relates his experience: "We replaced three 5,000 USG HDPE tanks about two years ago with FRP tanks from Plas-Tanks. The polyethylene tanks showed signs of deterioration after only eight years service with 15 percent sodium hypochlorite. They were leaking badly when we took them out of service. Various metal structures in the storage area were corroding rapidly, and the air was becoming inhospitable. The tanks had become so brittle that we were able to easily cut them up with a Sawzall. The new FRP tanks from Plas-Tanks made with Hetron™ FR992 epoxy vinyl ester resin from Ashland continue to look excellent and are serving us well."

OxyChem reports in their Sodium Hypochlorite Handbook that although some sodium hypochlorite users have had success with polyethylene tanks, many suppliers will not certify their equipment for bleach storage. None of the major U.S. sodium hypochlorite producers or users (OxyChem, K2 Pure, Olin, Clorox and Odyssey Manufacturing) utilizes polyethylene to store bulk sodium hypochlorite in their facilities. All of these producers, however, have a large number of FRP storage tanks. Steve Macy, President of Belco Manufacturing, an RTP-1 accredited fabricator of fiberglass tanks, ducts and piping reports, "Over the years, Belco has supplied hundreds of FRP tanks for sodium hypochlorite storage using Ashland Hetron 922 and 992 epoxy vinyl ester resins. We have many repeat customers because of the long service life of our tanks."

It is interesting to note that in Europe, following a number of environmental stress cracking-induced failures, the most widely used German tank design standard – Merkblatt DVS 2205 – omitted sodium hypochlorite as a suitable application for tanks in polypropylene and HDPE. Moreover, the relatively new and less stringent European Standard BS EN 12573 – 2000 also omits sodium hypochlorite from its listings for polyethylene tanks.

One major source of failure is the mechanical PVC fittings on the tank. Both bulkhead and bolted fittings are flat, which adds stress to the curved sidewall of the tank leading to embrittlement, stress cracking, and failure. Premature tank failure typically occurs on the tank wall near the fittings, especially the larger ones. Over time the fittings also crack, and the tank leaks. Corrosion-resistant titanium bulkhead fittings with titanium bolts should be used below the liquid level with Viton full-faced gaskets between the backing flange and the inside tank wall. These outlet fittings add considerable cost to the polyethylene storage tank, which tends to negate their cost advantage over more durable materials of construction.

There is a perception in the market that FRP storage tanks are more expensive than polyethylene. While initial procurement costs may be less for smaller polyethylene tanks in mild service with standard fittings, this assumption does not hold true for more aggressive service, moderate volumes, user-specified customization, and the ability to maintain equipment for longer periods of time without failures. Diamond Fiberglass specializes in the wastewater treatment market with a variety of products including fiberglass sodium hypochlorite storage tanks. Few companies in this market know this application better. Paul Cohen, vice president of Diamond, put it this way: "FRP can be economically more attractive both at the time of purchase and also in the long run. FRP storage tanks provide greater design flexibility, larger storage capacities, and considerably lower maintenance costs when compared to polyethylene. These benefits, in addition to the competitive pricing of FRP tanks, result in the highest long-term value for our customers, particularly for an aggressive chemical service such as sodium hypochlorite."

FRP storage tanks for sodium hypochlorite are common and when designed properly can be one of the best choices for product storage. The success or failure of this type of tank in bleach service depends upon a large number of variables including resin type, reinforcement type, fabrication technique, storage temperature, and the characteristics of the solution. A well-designed and properly-constructed FRP tank can last for 20 years or more with only routine inspection and minor repair of the corrosion barrier as required. While FRP tanks are the industry standard for bleach storage, it is still advisable to deal exclusively with fabricators having experience with sodium hypochlorite. Cohen continues: "Qualifying fabricators is critical for purchasers of sodium hypochlorite tanks: buyer's should visit multiple fabrication shops, review their quality assurance programs, understand the procedures for properly fabricating bleach tanks (which are different from most tanks) and then review a list of reference projects that demonstrate the fabricator's capabilities. Competent fabricators will have no objection to this level of qualification."

Odyssey Manufacturing reports that FRP tanker trucks are very successful for hauling sodium hypochlorite when the entire container is made of FRP with the correct construction methods. The industry trend in Canada and the United States has been the replacement of steel-lined tankers with FRP tankers over the past 10 years due to the long life of the FRP tanker. The FRP trailer has over 30 years of use, and it has been proven to be the best choice for sodium hypochlorite if constructed correctly.

As confirmed by a 2004 Dow Chemical company industry survey, FRP based on premium epoxy vinyl ester resin is the most common material of construction for bulk sodium hypochlorite storage and transport, backed up with case histories of more than 20 years service life. Well-specified and properly-constructed FRP tanks were found to last 20 to 30 years or more with only routine corrosion barrier inspections (typically every two years) and minor repairs as required. Ashland Performance Materials has conducted exhaustive research over the past several decades to determine the best FRP solutions for sodium hypochlorite service. This research culminates with the most recent paper given at the WEFTEC 2010 Conference in New Orleans, "Best Available Technology for sodium hypochlorite Storage Tanks," by Michael Stevens and Paul Cohen.

Based upon ASTM C-581 laboratory corrosion testing, FRP coupon testing in the field and a portfolio of case histories, Ashland has determined that storage tanks and equipment exposed to 9 percent or higher sodium hypochlorite solutions should utilize a corrosion liner fabricated with Derakane 510A-40 epoxy vinyl ester resin or Hetron FR992 epoxy vinyl ester resin. Maximum durability will be obtained with a BPO/DMA cure system. No cobalt should be present in the corrosion liner. Cobalt/MEKP cure systems can, however be used in the structural portion of the equipment. The corrosion liner should contain a minimum of one layer of C-glass veil, (two layers are preferred), backed by five millimeters of chopped strand boron-free glass reinforcement. Service life will be maximized if the corrosion barrier is post-cured. A properly designed and fabricated FRP tank can be expected to last over 20 years, even in this aggressive environment.

Service life on any sodium hypochlorite tank can be further extended by keeping the product stabilized. The stability of sodium hypochlorite solutions is adversely affected by heat, light, pH and metal contamination. The GE Water Purification Handbook reports that the rate of decomposition of 10 percent and 15 percent bleach solutions doubles with every 10 degree F rise in the storage temperature. Sunlight reduces the half-life of a 10 percent to 15 percent hypochlorite solution by a factor of three to five. If the pH of a stored solution drops below 11, decomposition is even more rapid. As little as 0.5 ppm of iron causes rapid deterioration of 10 percent to 15 percent solutions. Care should be taken to avoid all of these conditions in order to maximize storage stability and storage tank service life.


Buffalo Sewer Authority Hypo tanks made with Hetron FR992 epoxy vinyl ester resin

ATEA Environmental builds scrubber for pharmaceutical technology company

One of the world's leading producers of pharmaceutical products recently invested $175 million to build a new plant in Changshu, China, for the production of intermediates for Active Pharmaceutical Ingredients (APIs). The plant was put in operation in 2009.

The production of API's often leads to hazardous waste gas, which must to be treated in waste gas treatment units. Organic waste gas is typically combusted at high temperatures. The resulting flue gas at 300 degrees C, containing HCl, Cl_2 and CO_2, is then cooled in a quench tower and ultimately treated in a counter-current scrubber before discharge to the atmosphere.

ATEA Environmental Ltd., along with its subsidiary ATEA Composite Co., Ltd (Shanghai), specializes in the design, consultancy and construction of composite equipment and composite piping for use in a variety of industries. The team is comprised of highly knowledgeable engineers and technicians, most of whom have extensive experience in industrial applications. ATEA Environmental Ltd. (Shanghai) secured the flue gas treatment unit for this project and started the engineering in 2008.

The challenge of this project was the high temperature flue gas leaving the heat recovery unit after the combustion process. Industrial quench towers and scrubbers require careful material selection and design consideration due to a combination of high heat and corrosive chemical attack. Heat resistant materials such as steel alloys are often not suitable for these chemical environments whereas FRP materials have superior resistance against chemical attacks but relatively weak mechanical properties under thermal exposure.

ATEA decided to build the quench tower and scrubber in FRP. In order to protect the equipment against elevated temperatures, a water film was applied onto the inner quench-wall surface, acting as a heat barrier. ATEA selected Derakane 470-300 epoxy vinyl ester resin, a heat resistant Novolac*-based resin from Ashland, to maximize resistance of the quench tower and scrubber to the hot flue gases inherent in this process. They also increased the thickness of the corrosion barrier to further protect the FRP structure against corrosive chemical attack.

ATEA Scrubber made with Derakane 470- epoxy vinyl ester resin

Quench Tower
Diameter: 1,200mm
Height: 11,300mm

Scrubber
Diameter: 2,000mm
Height: 11,700mm

Outotec chooses LEPSA and Derakane for sulphuric acid plant

Votorantim Metais, one of the 10 largest zinc metal producers in the world and the largest zinc producer in Latin America recently invested $500 million in their Cajamarquilla Refinery in order to increase production of refined zinc from 160 thousand to 320 thousand tons per year. The investment will also allow Votorantim to increase production of metallic Indium, a high value-added metal, to 72 tons annually. The Cajamarquilla mineral processing facility is located in the Lurigancho-Chosica district near Lima, Peru.

Outotec's Peruvian office was placed in charge of design, development and procurement for the Cajamarquilla project, which included a sulphuric acid plant and acid plant scrubbers. LEPSA S.A. was chosen by Outotec to construct and install an extensive amount of FRP tanks, scrubbers, piping and ducting required for this large project. With more than 15 years of experience in the Peruvian market, LEPSA specializes in engineering development, design, manufacture and installation of FRP equipment for major projects in applications with high levels of corrosion.

Outotec further specified Derakane Momentum™ 411-350 epoxy vinyl ester resin for all of the FRP equipment shown below due to its wide range of chemical resistance to acids, bases and organic compounds. According to Jeffrey Gonzales Herrera, Project Engineer at LEPSA, "We selected Derakane Momentum 411-350 and Derakane Momentum 510C-350 resins for this project based on Ashland's recommendations for the type and composition of the corrosive gases in the process. We also went back to our successful experiences with the DOE RUN project where we used the same Derakane resins for the same process environment, concentration and temperature."

Derakane resins were used in this facility for the following:

- Gas Cooling Tower
- SO_2 Stripping Tower
- Settling Tank
- Wet ESP Flushing Tank
- Sodium Silicate Tank
- Strainer
- Droplet Separator
- Start Stack
- Process Water Tank

Cajamarquilla Acid Plant

Corrosion barrier design

Michael Jaeger and Don Kelley

The corrosion barrier is a critical component of fiberglass-reinforced plastic (FRP) designed for service in chemical environments. It is a sacrificial layer, so its thickness can often be directly related to the service life of the FRP part. A number of standards have been written to specify the minimum requirements for the thickness and composition of a corrosion barrier for service in liquid chemical environments. The purpose of this article is to present an overview of existing standards and how they impact the number of layers of chopped strand mat that are required to meet these standards.

The following table summarizes the most common current and historical standards for corrosion resistant FRP around the world:

Standard	Minimum Thickness	Minimum Layers	Comments
ASME RTP-1-2005	100 mils (2.5 mm)	Veil between 10 and 20 mils (0.25 and 0.5 mm), 2 layers of total 3 oz/ft^2 (900 g/m^2), CSM or chopped/sprayed	Minimum thickness of 2.5 mm / 100 mils is specified. This has priority over the number of layers to reach the required thickness. This standard specifies the veil layer.
EN 13121-2 2003	2.5 mm (100 mils)	1 or 2 Veils, 1 or 2 layer(s) of total 900 g/m2 (3 oz/ft^2) CSM, 25 % to 35 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. This has priority over the number of layers to reach the required thickness. This standard specifies the veil layers and the glass content.
NF T 57900 1987	2.5 mm (100 mils)	Veil of minimum 0.25 mm, 2 layers of 300 g/m2 (1.0 oz/ft^2) CSM	Minimum thickness of 2.5 mm / 100 mils is specified. This has priority over the number of layers to reach the required thickness. This standard severely overestimates the thickness obtained with 2 CSM of 300 g/m^2
BS 4994 1973	Not specified	Veil between 0.25 and 0.5 mm, 1200 g/m2 (4.5 oz/ft^2) CSM, 25 % to 33 % glass content, by weight	Minimum thickness is not specified. The total weight of the CSM layers is considered sufficient to reach the required thickness of 2.5 mm / 100 mils. This standard specifies the veil layers and the glass content.
BS 6464 1984	Not specified	Veil between 0.25 and 1.0 mm, 900 g/m^2 (3 oz/ft^2) CSM, 25 % to 33 % glass content, by weight	Minimum thickness is not specified. The total weight of the CSM layers is not considered sufficient to reach the required thickness of 2.5 mm / 100 mils. This standard specifies the veil layers and the glass content.
DIN 18820-3 : 1991	2.5 mm (100 mils)	V/CSM, max. 30 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. The number of CSM layers is not specified. This standard specifies the veil layers and the glass content.
DIN 16965-4, Pipe Type D	2.5 mm (100 mils)	V/CSM, 25 - 30 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. The number of CSM layers is not specified. This standard specifies the veil layers and the glass content.
DIN 16965-5, Pipe Type E	2.5 mm (100 mils)	V/CSM, 25 - 35 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. The number of CSM layers is not specified. This standard specifies the veil layers and the glass content.
AS 2634 1983	2.5 mm (100 mils)	V/CSM, 20 - 30 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. The number of CSM layers is not specified (E-Glass is specified, 6-900 g/m2 considered sufficient). This standard specifies the veil layers and the glass content.
NBS PS15-69	2.5 mm (100 mils)	V/CSM, 20 - 30 % glass content, by weight	Minimum thickness of 2.5 mm / 100 mils is specified. The number of CSM layers is not specified. This standard specifies the veil layers and the glass content.

As can be seen in the table above, all the standards except for two require a minimum corrosion barrier thickness of at least 2.5mm (100 mils). If the veil layer is 0.25 mm (10 mils) thick, the chopped glass fiber stand layer must be at least 2.25 mm (90 mils) thick. If chopped strand mat is being used, the total thickness of the mats must be at least 2.25 mm (90 mils) thick.

When using chopped strand mat, the thickness can vary depending on the supplier. Therefore, it is important to measure the actual thickness of the corrosion barrier after the resin has cured. This can be done by measuring cutouts of the finished product using a micrometer or similar device. The surface of the cutout needs to be sanded until smooth and polished so that accurate measurements can be taken.

The above recommendation also applies to corrosion barriers made with chopped roving. To make sure that the minimum thickness has been applied, it is recommended that the corrosion barrier thickness is measured as described above.

Conclusion

Current standards require corrosion barriers with a minimum thickness of 2.5 mm (100 mils). Prior to 1999, two layers of 450 g/m2 (1.5 oz/ft2) CSM was usually sufficient to meet the requirement. This is not necessarily the case today. The only way to insure that these standards are being met is to measure the corrosion barrier thickness on a finished part.

Standards evaluated

- ASME/ANSI RTP-1-2005, Reinforced Thermoset Plastic Corrosion Resistant Equipment, American Society of Mechanical Engineers
- EN 13121-2: 2003, GRP tanks and vessels for use above ground - Part 2: Composite materials - Chemical resistance, European Committee for Standardization
- NFT 57 900: 1987, Réservoirs et appareils en matières plastiques renforcées, Association Française de Normalisation
- BS 4994: 1973, Specification for Vessels and Tanks in Reinforced Plastics, British Standards Institution
- BS 6464: 1984, British Standard Specification for Reinforced Plastic Pipes, Fittings and Joints for Process Plants, British Standards Institution
- DIN 18820: 1991, Part 3, Glass Fibre Reinforced Unsaturated Polyester (GF-UP) and Phenacrylic (GF-PHA) Resin Structural Composites; Protection of Structural Layer, Deutsches Institut für Normung e.V.
- DIN 16965-4, Rohre aus Glasfaserverstaerkten Polyesterharzen (UP-GF), gewickelt, Rohrtyp D; Masse, DIN Deutsches Institut für Normung e.V.
- DIN 16965-5, Rohre aus Glasfaserverstaerkten Polyesterharzen (UP-GF), gewickelt, Rohrtyp E; Masse, DIN Deutsches Institut für Normung e.V.
- AS 2634-1983, Chemical Plant Equipment made from Glass-Fibre Reinforced Plastics (GRP) based on Thermosetting Resins, Standards Association of Australia
- NBS PS15-69 Voluntary Product Standard, Custom Contact-Moulded Reinforced-Polyester Chemical-Resistant Process Equipment, National Bureau of Standards

Corrosion Person of the Year

Nominations 2010

The Corrosion Chronicle will be recognizing the "Corrosion Person of the Year" in its next issue. We are currently collecting nominations for this award. Candidates should have a rich history of accomplishments in the design and use of FRP composites for corrosion applications. Please send your nominations to Thom Johnson at tljohnson@ashland.com for consideration.

Where you can see the Ashland corrosion team

MS&T Conference	Houston, Texas U.S.A Oct. 17 – 21, 2010
Feiplar	São Paulo, Brazil Nov. 10 – 12, 2010
Jornadas de Compuestos	Barcelona, Spain Nov. 23 – 24, 2010
TueV Sued, Schwerer Korrosionschutz	Munich, Germany Nov. 24 – 25, 2010
UNCM	Moscow, Russia Nov. 25, 2010
Composites 2011	Fort Lauderdale, Florida U.S.A. Feb. 2 – 4, 2011
SME	Denver, Colorado U.S.A Feb. 27 – Mar 2, 2011
NACE	Houston, Texas U.S.A. March 13 – 17, 2011
JEC	Paris, France March 29 – 31, 2011

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!

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Corrosion Chronicle is published by Ashland Inc. and reports the many ways professional fabricators tell us they are using Derakane epoxy vinyl ester resins to manufacture corrosion resistant reinforced plastic (fiberglass) applications. For additional technical product information on Derakane resins, visit www.derakane.com or send an email to Derakane@Ashland.com. You can also contact your Ashland representative at Ashland Composite Polymers, P.O. Box 2219, Columbus, OH 43216, 614.790.4059. Address all news items to: Corrosion Chronicle Editor, Ashland Communications, P.O. Box 2219, Columbus, OH 43216.