Guideline for the use and handling of styrenated resins in cured-in-place-pipe

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This document presents a state-of-the-art guideline for the use and handling of styrene based resins in the CIPP pipeline rehabilitation industry. Following these guidelines does not guarantee that environmental damage, property damage, personal injury, or other damage or injury will not occur at, on, or near a CIPP installation site. CIPP projects and the associated risks vary tremendously and must be evaluated on a case-by-case basis. Some project circumstances may pose environmental risks completely unassociated with styrene. In addition, downstream sewers and receiving waters are variable, not only from place to place but also from time to time, and the discharge of cure water and condensates must be thoroughly evaluated for each installation. This document is not intended as a substitute for professional advice pertaining to the use and handling of styrene based resins, and it is recommended that a professional be consulted for such purposes. NASSCO makes no warranty of any kind whatsoever, whether express or implied, with respect to the guidelines set forth in this document. NASSCO disclaims any and all liability, including but not limited to property damage, personal injury, or any other manner of damage or injury arising out of the use of this document or the use and handling of styrene based resins in the CIPP pipeline rehabilitation industry.

EXECUTIVE SUMMARY

Styrenated resin systems as they are currently used today in cured in place pipe (CIPP) rehabilitation systems produce a safe and environmentally sound solution to the challenges of the need for restoring the nation's failing infrastructure. While current thought by U.S. academics assessing the overall use of styrene is leaning toward the conclusion that one might "reasonably anticipate styrene to be carcinogenic", a similar study carried out by the ECETOC (European Centre for Econtoxicology and Toxicology of Chemicals) concluded that "the carcinogenic potential of styrene, if one exists at all, is rated so low that occupational or environmental exposure to styrene is unlikely to present any carcinogenic hazard to man." Further, the current U.S. study background information states that there is no clear connection for styrene as a carcinogen until you add in the exposure to butadiene and/or benzene; both of which don't exist in the resin systems used by CIPP installers. The risk associated with styrene's use in CIPP is minimal and well within the Clean Water Acts' original intent of keeping the environment as free as is practical of chemical pollutants. CIPP installation sites managed with good housekeeping will present little opportunity for human health risks and/or environmental risks.

Although styrene occurs naturally in many foods such as cinnamon, coffee, and strawberries, styrene derived from petroleum and natural gas by-products have raised many questions about whether its usage in polyester and vinyl ester resin systems commonly used in CIPP to rehabilitate piping systems has the potential to adversely affect human health and/or the environment. While the CIPP process is a potential source of styrene, studies done to date have concluded that these type resin systems do not appear to be a significant source of styrene or any of the other volatile organic compounds (VOCs) that are typically of concern in occupational or air quality studies.

In a study undertaken by the Toronto Works and Emergency Services in 2001, AirZOne, Inc. conducted an investigation of the airborne concentrations of styrene and 24 other VOCs in eight randomly selected residences during the rehabilitation of sewers with CIPP installation. The study also measured ambient air quality, emissions from manholes and occupational exposure from these compounds. Air sampling was executed in three phases, before, during, and after the CIPP's installation. Styrene levels were elevated significantly during the CIPP installation in just two homes where the homes' traps were engineered to be dry in order to simulate a worst case scenario; the levels, although elevated, proved not to be a health concern. Levels measured in these eight homes were 0.1 to 0.2ppm. Styrene emissions from manholes during the CIPP process ranged from 0.16ppm to 3.2ppm. Personal exposure of the installation personnel in the breathing zone ranged from 0.08 to 0.5ppm. Styrene in the breathing zone was well below the industry's voluntary occupational limit of 50ppm for the installation personnel.

Independent, peer reviewed scientific journals have published numerous studies on the fate of styrene and its natural occurrence in the environment. "Biodegradation of Styrene in Samples of Natural Environments" by Min Hong Fu and Martin Alexander of Cornell University, concluded that styrene will be rapidly destroyed by biodegradation in most environments having oxygen; although the rates may be slow at low concentrations in lake waters and in environments at low pH. "Desorption and Biodegradation of Sorbed Styrene in Soil and Aquifer Solids" by Min Hong Fu, Hilary Mayton, and Martin Alexander of Cornell University, concluded that being broken down by microbes is a major fate mechanism by which styrene is destroyed in soils. The "Ecotoxicity Hazard Assessment of Styrene" by J.R. Cushman concluded that styrene was shown to be moderately toxic to fathead minnows, daphnids, and amphipods. It was further shown to be highly toxic to green algae, and slightly toxic to earthworms. There was no indication of a concern for chronic toxicity based on these studies. Styrene's potential impact on aquatic and soil environments, it was concluded, is significantly mitigated by the rapid rate at which it evaporates and biodegrades in the environment. And finally, Martin Alexander, in his "The Environmental Fate of Styrene", concluded that transport of styrene in nature is "very limited" because of its volatility from soils and surface waters, its rapid destruction in air, and its biodegradation in soils and surface and ground waters.

Because the styrene odor can be detected at such low concentrations (0.4 to 0.75ppm, depending on one's ability to detect odors), styrene's odor can be considered a nuisance to those not used to working around it. Some people are offended by this odor and are fearful of it; even though the concentrations they smell present no harm to them. To minimize odor problems during the installation of CIPP, residents should be advised to ensure that their sewer traps are in a proper state of repair. In cases of damaged, dry, or non-existent traps, the areas or rooms where floor drains or access to traps are located should be ventilated, if possible, by leaving doors or windows open to the outside during the CIPP installation process.

The CIPP installation contractor should practice good housekeeping and protect the project site such that any accidental resin spillage can be cleaned up and properly disposed of by the contractor. Given the nature of these resin systems to resist movement once placed in the tube's fiber matrix only very small quantities should be anticipated; excepting in the case of over-the-hole saturation installations.

The impact of styrene concentrations in the process water when discharged directly into a sewer collection system is insignificant. An eight inch pipeline 650 linear feet in length will discharge approximately 1700 gallons of water to the receiving sewer. At a typical concentration of 20ppm, the resultant discharge would be less than 0.3 pounds of styrene. A 48-inch pipeline 650 linear feet in length will discharge approximately 61,300 gallons of water to the collection system; which, again, amounts to approximately 10.2 pounds of styrene at a concentration level of 20ppm. With the assimilative capabilities of the downstream flows, no harm is thus anticipated to the wastewater treatment works and/or the POTW's discharge requirements.

Based upon the above given discharge quantities of typical CIPP installations, a CIPP installation contractor discharging these same quantities of process water to a ditch or other waterway is expected to meet the requirements of the EPA's small quantity generator exemption. In fact, due to the nomadic nature of the installer's discharges, a case could be made that the discharges fall under the category of non-point source contributions. However, the installation contractor is still advised to consider the negative impacts of the temperature of the water at discharge if the receiving drainage conveyance contains aquatic organisms that can be harmed by the possible sudden drop in available oxygen due to the large temperature difference between the process water and the receiving water body's temperature.

Any time an environmental release of a hazardous substance exceeds its reportable quantity as defined in 40 CFR Part 302, the contractor shall report this release immediately to the National Response Center (NRC). The reportable quantity for styrene per 40 CFR § 302.4 is 1000 pounds (or 2500 pounds of resin). Quantities below this amount are to be handled by the contractor in an expeditious manner; but do not require reporting.

INTRODUCTION

Styrene is the ideal monomer used for cross-linking polyester and vinyl ester resins. Although alternative monomers have been extensively investigated, none of those monomers have matched the overall performance of styrene. Over the last 30 years the increasing awareness of the need to limit the effects of styrene exposure have lead the polyester resin processing industry to pursue strategies to reduce exposure in the manufacturing and processing plant environment. Most, if not close to all, of the studies undertaken to date have centered on these producers and users environments which are dramatically different than the work environment of the CIPP installation contractor. Given the desire to address the rehabilitation industry's need for standards in the proper safe use and handling of styrenated resins for CIPP, NASSCO created a styrene task force to review the technical information available from these studies and current CIPP installation practices to produce this CIPP specific guideline. In addition to this guideline, NASSCO has prepared an Inspector Training Course to properly equip the owner and the project engineer with the necessary knowledge to ensure that a proper installation is achieved which will minimize the potential for release of styrene to the environment.

Polyester and vinyl ester resin systems have been used for more than 35 years in CIPP. During this timeframe there have been no noted serious consequences to their usage in CIPP. However, as no definitive document for these resin systems as used in this specific application existed, the unknown has given rise to speculation as to their safety with respect to the work force involved, the general public when the odors enter the structures connected to the piping under rehabilitation, and to the greater downstream environment from where the work is taking place.

Styrene is a common chemical compound found where we live and work. Indoor sources of styrene emissions include off-gassing of building materials and consumer products and tobacco smoke. Styrene is emitted from glued carpet, floor waxes and polishes, paints, adhesives, putty, etc.; and infiltration of gasoline-related VOCs from attached garages is well documented.

Styrene, with its low vapor pressure, is expected to exist solely as a vapor in the ambient atmosphere (Hazardous Substances Data Bank 2008). In its vapor phase it is expected to react rapidly with hydroxyl radicals and with ozone. Half-lives based on these reactions have been estimated to range from 0.5 to 17.0 hours (Luderer et al. 2005). Atmospheric washout (the removal from the atmosphere of gases and sometimes particles by their solution in or attachment to raindrops as they fall) is not expected to be an important process because of these rapid reaction rates and styrene's relatively high Henry's law constant (the extent to which a gas dissolves into a liquid is proportional to its vapor pressure). Outdoor air monitoring by the EPA for 259 monitoring sites involving some 8,072 observations in 2007 showed that the mean concentrations for these sites ranged from 0.028 to 5.74 ppb. The primary sources of styrene in outdoor air include emissions from industrial processes involving styrene and its polymers and copolymers, vehicle emissions, and other combustion processes.

Volatilization and biodegradation are expected to be the major fate and transformation processes in water. Again, based on its Henry's law constant, styrene is expected to volatilize rapidly from environmental waters; the extent of volatilization depends on the water depth and turbulence with low volatilization occurring in stagnant, deep water. The estimated volatilization half-life of styrene in a river three feet deep with a current of three feet per second and wind velocity of 9.5 feet per second is roughly three hours. Half-lives have been estimated from one hour for a shallow body of water to 13 days in a lake. Some biological oxygen demand studies have shown styrene to be biodegradable. Cohen et al. 2002 found that styrene generally does not persist in water because of it biodegradability and volatility.

MATERIAL FACTS

Styrene Monomer

Property	Value
Auto-ignition Temperature (in air)	914°F
Boiling Point:	
14.7 psi	293°F
1.9 psi	180°F
0.6 psi	130°F
Color	Colorless
Corrosivity	Non-corrosive to metals except copper and alloys of copper
Density (in air):	
32°F	7.71 lbs/US Gallon
68°F	7.55 lbs/US Gallon
122°F	7.33 lbs/US Gallon
Solubility: Styrene in Water	
32°F	0.018 gms/100 gms$H_2$0
104°F	0.040 gms/100 gms$H_2$0
176°F	0.062 gms/100 gms$H_2$0
Solubility: Water in Styrene	
32°F	0.020 gms/100 gms styrene
104°F	0.100 gms/100 gms styrene
176°F	0.180 gms/100 gms styrene
Vol. Shrinkage upon Polymerization, typ.	17%

RECEIVING AND STORING CIPP RESINS AND INITIATION CHEMICALS

Resins should be received and stored in controlled conditions. Today's state of the art facilities for tube saturation (wet out) consist of temperature controlled storage tanks mounted outside in a spill prevention area with interconnecting piping to the static mixing (and resin system disbursement) unit inside the saturation shop. This minimizes the typical styrene concentration in the work area to less than 0.5ppm, well below the industry's voluntary standard of 50ppm (for an 8-hour work period). The remainder of the facilities in use varies from working with resin stored in totes to resin stored in drums; and catalyzed by combining the initiators, typically Perkadox and Trigonox, with the resin directly in the drums or in a vat (batch mixing) using a mixing blade. These latter methodologies can, without proper ventilation create styrene concentrations around 2-3ppm in the work area. A well ventilated work area is recommended if mixing is to be done in this fashion.

Based on studies to date, worker exposure to concentrations between 20 and 50ppm have been shown to produce no negative health effects. At concentrations above 50ppm, reversible effects on the central nervous system have been observed. With increasing exposure levels, e.g. levels of 200ppm, a distinct irritation of mucous membranes can result. Such effects are reversible and similar in character to exposure to solvents without adequate ventilation or after excessive intake of alcohol. According to a study carried out by the ECETOC (European Centre for Econ-toxicology and Toxicology of Chemicals), the carcinogenic potential of styrene, if one exists at all, is rated so low that occupational or environmental exposure to styrene is unlikely to present any carcinogenic hazard to man.

Drums and Totes

Drums and totes of resin should not be allowed to stand in the sun for more than a few hours. As soon as possible after being received, drums and totes should be moved to a cool, shaded area. In hot weather they can be cooled with a water spray. It is advisable that inventories utilizing these two storage methods be kept to a minimum during summer months and that the resin be stored no longer than is necessary. Having the resin manufacturer acknowledge your usage rates and tailoring any additional inhibitor needs to compensate for the storage environment is strongly recommended.

Inhibitors are customarily added to resin systems to prevent polymer formation and oxidative degradation during shipment and storage. Inhibitors prevent polymerization in two ways; (1) they can react with and deactivate the free radicals in a growing polymer chain and (2) they can act as an antioxidant and prevent polymerization by reacting with oxidation products in the styrene monomer. Sufficient oxygen must be present for this inhibition to be realized. In the absence of oxygen, polymerization will take place as if no inhibitor were present. The rate of the inhibitor's depletion is dependent on the set of environmental conditions seen in the storage environment. Heat, water, and air can greatly accelerate the depletion of the inhibitor; with heat being the most influential. The table below illustrates the effects of temperature and oxygen levels on the storage time of styrenated resin systems.

Temperature	12ppm Inhibitor		50ppm Inhibitor Saturated w/ Air
	Saturated w/ Air	Less than 3ppm O_2	
60°F	6 months	10 to 15 days	1 year
85°F	3 months	4 to 5 days	6 months
110°F	8 to 12 days	Less than 24 hours	Less than 30 days

The safe storage and use of resins in non-bulk packaging is described in the National Fire Protection Association's (NFPA) code 30, chapter 4. Although each state can enforce other fire codes, such as the UFC and BOCA, the NFPA codes serve as a good initial planning document. It is strongly recommended that contractors engaged in their own saturating their tubes consult this book if they intend to store resins in non-bulk packaging.

Bulk Storage Tanks

In designing bulk storage facilities, certain basic factors must be considered. Resins containing the styrene monomer can be stored for relatively long periods of time if simple, but carefully prescribed conditions are met. In addition to the usual precautions taken with flammable liquids against fire and explosion hazards, precautions must also be taken against conditions that would promote the formation of polymer and oxidation products. To accomplish this, the design and construction of a satisfactory bulk storage system for styrenated resin systems requires careful consideration to eliminate excessive temperatures and to prevent contamination of the resin from infrequently used lines and other equipment.

Vertical storage tanks are commonly used for large volume storage. Horizontal storage tanks are equally satisfactory for resin storage; but are used for smaller volumes such as are typical of CIPP saturation facilities. The inlet and outlet piping is normally located near the bottom. To facilitate mixing where external refrigeration or heating are employed, it is recommended that either the inlet or outlet line operate through a floating swing-pipe adjusted so that the resin is always either withdrawn or discharged a few inches below the surface. Warm resin is withdrawn from the top, circulated through the chiller, and discharged to the bottom of the tank; cooling the tank from the bottom up.

A self-supporting-type dome roof is recommended for vertical storage tanks. This type of construction simplifies the installation of tank linings and permits the rapid drainage of uninhibited condensed vapors back into the liquid resin, thus reducing the polymer and stalactite problem. Roof and sidewall openings above the normal liquid levels in the tank should be of large diameter and the number kept to as few as practical. Large diameter openings are easily lined and can also be used for dual service features.

Insulation and temperature control equipment are key elements of a well done bulk storage system. The resin should be kept around 65°F (between 60°F and 75°F is acceptable) to facilitate the saturation process and allow for proper maintenance of the calibration of the resin mixing system.

The working capacity of the storage tanks should be, within reason, based upon the installer's resin usage. A general rule of thumb is that a bulk tank system should be of a size to allow for the turning of the resin inventory every 45 days. Given that a full truckload shipment is approximately 4,500 gallons, a typical system would have a minimum storage volume of 5,500 to 6,000 gallons to ensure that the system does not completely empty prior to receiving another resin shipment.

Requirements of diking, tank spacing, and other features of safety are detailed in guidelines set by the National Fire protection Association (see NFPA 30, Chapter 2). These, as well as local building codes and governmental regulations, should be consulted since some requirements vary with the size and configuration of the installation.

Organic Peroxides

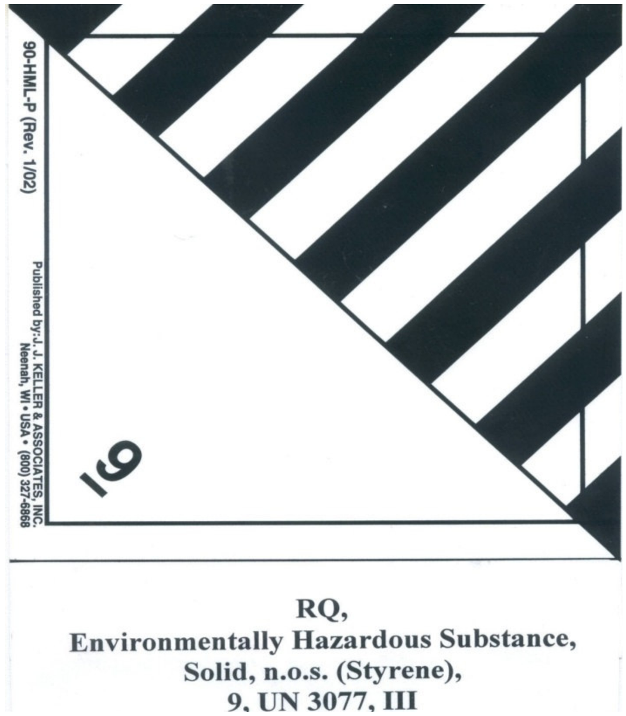
All peroxides are heat sensitive to some degree and require a controlled temperature for storage. Storage temperatures should be kept at, or below, 59°F for longer shelf life and stability. Prolonged storage at temperatures greater than 68°F is not recommended. Perkadox 16 will degrade if stored at elevated temperatures leading to gassing and potential container rupture which can result in a fire and/or explosion. Prolonged storage of Trigonox above 80°F is not recommended. All storage should be done in the peroxides' original containers away from flammables and all sources of heat, sparks, or flames; out of direct sunlight; and away from cobalt naphthenate, other promoters, accelerators, oxidizing or reducing agents, and strong acids or bases.

HANDLING CIPP RESINS AND INITIATION CHEMICALS

Styrene based polyester resins are sensitive to contact with both heavy metals and red metals. Interaction with these metals is not predictable as in some cases they will inhibit the cure; and in others they will accelerate it. Common metals to avoid are; copper, brass, beryllium, chromium, lead and galvanized metal. The recommended metals or plastics to be used for storage and piping are carbon steel, stainless steel, aluminum, polyethylene, polypropylene, and Teflon. Resin transfer hoses must be chemically resistant and approved for use with styrene.

TRANSPORTATION OF RESIN-SATURATED TUBES

Per previous correspondence with the Federal Highway Transportation Agency, the resin-saturated tube is considered an acceptable “container” for shipment to the project site from the saturation shop. Currently, each tube is to be identified on its end with a class 9 placard and a description of its contents as shown in the figure to the right. If any one tube being transported in the truck exceeds 1000 pounds of styrene (approximately 2500 pounds of resin), then the truck itself must be placarded with the class 9 placard bearing the UN 3077 designation.



The transporting truck should be equipped with provisions to keep the saturated tubes out of direct sunlight and at or below 40°F. The floor should be insulated well enough to keep any heat from the roadway generating heat in the stored liners.

Depending upon the number of tubes being shipped and/or the residence time in the truck, styrene concentration levels in the air space of the storage box can reach approximately 90ppm. While this level can be irritating to the eyes, it will not produce any harm to the workers (NIOSH allowable concentration for work areas is 215ppm STEL, or short term exposure limit) and dissipates quite rapidly once the doors are opened.

CIPP INSTALLATION PRACTICES

All CIPP resin systems require that good housekeeping be practiced by the installation team on the project site. Provisions must be made by the contractor in advance for containing any accidental spillage of the resin on the work area. Further, if more than 2500 pounds of resin (1000 pounds of styrene) is spilled, the spill must be reported to the appropriate local pollution control authorities. Spills less than this “reportable quantity” are to be handled in a responsible manner by the contractor. Absorption with an inert material and placing in an appropriate waste disposal container is the industry standard for handling small spills on the ground. Some absorbing agents, such as untreated clays and micas, will cause an exothermic reaction which might ignite the styrene monomer. For this reason, absorbing agents should always be tested for their effect on the polymerization of the monomer before they are used on larger spills. Claymax®, a loose “vermiculite-like” material has been found to be an effective absorbent. Oil dry, kitty litter and sand will also work well. If the spill occurs on a hard surface, the area should be scrubbed with soap and water after the bulk of the spill has been cleaned up by the absorbent material. If the spill gets into a waterway, the spill must be contained using a floating dike similar to those used for oil spills. The resin can then be picked up by vacuuming the resin into a vacuum truck and subsequently placed in an appropriate waste disposal container.

Water inversions require that consideration be given to the temperature of the process water and any styrene content it may have after the CIPP installation has been completed. Depending on the volume of water used in the processing and the receiving environment (sanitary sewer, drainage ditch, waterway, etc), the water may require transportation and/or treatment prior to its final disposition. As stated in the introduction of this guideline, styrene readily dissipates through volatilization and degradation. In order to ensure that the cured liner remains tight fitting and dimensionally stable with the release of the cure water, the standard in the industry is to require that the cool down be continued until the temperature of the liner (and the surrounding ground) is no more than 100°F. During the cool down process a small hole is made in the downstream end to release hot water as cold water is introduced at the boiler truck to facilitate this effort. Process water once the liner temperature reads 100°F will probably have a temperature around 90°F or less which has been observed to have a styrene concentration in the range of 20 to 25ppm. The releasing of the process water directly to the sewer is not a problem due to the benefits of dilution in the downstream wastewater.

Process water released directly to a surface water course such as a drainage ditch or waterway must consider the allowable styrene concentration with respect to the receiving environment and the possible oxygen depleting capabilities of the process water's elevated temperature. Based upon the exhaustive literature review of the quick volatilization of the styrene and its potential to result in any long-term harm to plant and animal life, discharges of process water having the normal concentration levels of styrene and temperature at cool-down directly to a dry waterway should pose no harm. Further, while the common practice of many CIPP installers is to transport the process water to the nearest wastewater treatment facility, releases of process waters to ditches and/or waterways containing water and/or aquatic life containing no more than a concentration of 25ppm styrene and a temperature approximately equal to that of the receiving waterway should not create any environmental harm (see note below). For projects requiring large quantities of process water to be directly discharged to the environment, it is recommended that an engineering analysis be undertaken to determine the assimilative capacity of the receiving stream with respect to the temperatures and styrene concentrations anticipated.

Note: A typical 24-inch diameter culvert 100 linear feet in length will require around 2400 gallons of water to process. If released at 25ppm, the amount of styrene anticipated in its release is approximately 0.45 pounds.

Air inversion of the resin-saturated tube and curing the liner by the introduction of steam into the pressurized air flow greatly reduces the amount of styrene that will potentially be released into the environment. This is because the very quick cross-linking of the resin effectively binds up the styrene to a much higher degree using this method for curing. Most of the styrene released in this method of curing will be in the vapor form and requires little or no action on the contractor's part so long as the discharge point is maintained 6-inches above ground. The condensate generated in the pipeline being processed should be minimized by maximizing the flow of air for the site-specific conditions. The small volume of condensate produced during processing should be detained in a temporary impoundment if the quantity is expected to be discharged to a ditch or waterway containing water and/or aquatic life. Measurements made to date have shown that the condensate will probably have a concentration of around 30ppm. Depending upon the assimilative capacity of the receiving waterway, the condensate may be released once it has cooled to near ambient temperature (which will also result in a drop in the styrene concentration due to volatilization); or it can be retrieved into the steam generation system's water storage tank for later use in the production of steam during curing of the next CIPP.

It is imperative that the processing of the liner, whichever method of curing is used, is properly completed. Properly cured liners release little or no styrene to the environment. Thermocouples placed strategically in the liner-host pipe interface are a must. A written curing schedule developed for a CIPP system acknowledging the conditions present in the curing environment and the resin system proposed will lead to a proper cure and a long CIPP life; and no environmental impact.

SUMMARY

Proper curing and handling of CIPP systems should be done using the following guidelines:

Water Curing

Sanitary Sewers

1. Cure resin system per written curing schedule
2. Release process water to the sewer after per industry standards during/after cool-down.

Storm Sewers and Culverts

1. Cure resin systems per written curing schedule
2. Based upon receiving waterway's assimilate capabilities

    a. Discharge water once at ambient air temperature
    b. Discharge water once styrene concentration is confirmed to be at or below 25ppm; or
    c. Transport process water to nearest wastewater treatment facility

Steam Curing

Sanitary Sewers

1. Cure resin system per written curing schedule
2. Release condensate water directly to receiving sewer while processing

Storm Sewers and Culverts

1. Cure resin system per written curing schedule
2. Based upon receiving waterway's assimilative capabilities
    a. Detain condensate in a lined holding pond until it cools to ambient
    b. Discharge water once styrene concentration is confirmed to be less than 25ppm; or
    c. Retrieve condensate by pumping it into the steam generation truck's reservoir; or
    d. Transport condensate to nearest wastewater treatment facility.

Any residual styrene concentrations from a properly cured resin system that are taken into the runoff water from storm events will typically be short-lived, in the range of less than 1.0ppm and therefore pose no significant environmental threat.

APPENDIX

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* indicates the paper was peer reviewed prior to publication.