Cryogenic spill protection and passive fire protection in the LNG industry
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Abstract

Liquefied Natural Gas (LNG) is a sector of the energy industry that is growing rapidly and brings with it new challenges for owners, designers and suppliers alike. While fire protection has long been established in the oil and gas processing industry, the combination of fire protection and LNG spill protection (variously known as cold spill or cryogenic spill protection - CSP) is relatively new for epoxy passive fire protection products. Codes such as EN 1473 and NFPA 59A require that the LNG support structure be resistant to, or protected from, cryogenic exposure and the latter can now be achieved with epoxy based products that provide cryogenic spill protection, passive fire protection and ‘life of asset’ durability. This paper discusses epoxy syntactic foam insulation and epoxy passive fire protection products and the testing of these relevant to LNG spills.

Keywords: coatings, fire protection

Introduction

Low temperature grades of steel and other special alloys with low temperature resistance may be used in specific areas of the LNG industry but common structural grades of steel such as EN 10025 S355 are still widely used. Codes such as EN 1473 and NFPA 59A require that the LNG support structure be resistant to, or protected from, cryogenic exposure.

Normal structural grade steel undergoes ductile to brittle transition at temperatures in the range -20 °C to -40 °C and hence for LNG spillage (-162 °C) protection of the steel may be required. The period of time for CSP will be determined from the risk analysis of the particular process and will vary from project to project. In addition to cold induced brittle fracture, spilled LNG will vapourise and present a potential fire hazard leading to the need for passive fire protection, the extent of which should be determined by the risk analysis process.

Epoxy passive fire protection (EPFP) products have been used for many years for the fire protection of carbon steel structures and equipment and the accepted durability of these products has led to their almost universal use in the offshore environment.

Epoxy syntactic foam insulation products can be used to provide simple to install, cost effective protection for cryogenic spill that is both durable and compatible with EPFP.

Still air provides effective insulation and indeed most commercially available insulation products rely on trapped air. Epoxy syntactic foam insulation uses a range of different diameter hollow ‘microspheres’ containing air or other inert gas. These spheres are dispersed within an epoxy resin at very high concentration to provide a thick coating that has inherent

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insulating properties and can be wet applied to a substrate in a joint-free continuous layer (see figure 1).

![Figure 1 - Optical microscope image showing glass spheres in epoxy resin](image)

Unfortunately there are as yet no national or international test standards available for cryogenic spill followed by hydrocarbon fire but there are some project specific and meaningful ad hoc tests available. Such testing has proven the effectiveness of epoxy syntactic foam in protecting carbon steel against cryogenic cracking as well as providing hydrocarbon fire protection as a composite system with EPFP.

This paper will examine the use of epoxy syntactic foam products for cryogenic spill protection in conjunction with EPFP products designed to meet specific needs of the LNG processing industry.

**Methodology**

LNG facilities are predominantly situated either onshore in coastal locations or offshore, in either case product durability is desirable or essential. To evaluate the durability of epoxy syntactic insulation materials they have been subjected to various tests including; salt spray (BS3900-F4), marine environment (BS3900-F6) and fresh and salt water immersion (BS EN ISO 2812-2).

The epoxy syntactic materials were applied at (10 – 20) mm onto blast cleaned (Sa 2½ - ISO 8501-1/SSPC SP 10) steel panels which were primed using an epoxy phenolic primer (Epigrip M251). All test panels featured a ‘holiday’ (a deliberate defect to expose a portion of the steel substrate). Once testing was completed 2 cuts were made through the insulation material perpendicular to the plane of the substrate intersecting at 30° at the centre of the holiday. To
assess if any corrosion undercutting had occurred attempts were made to remove the coatings, beginning at the holiday.

Physical and thermal testing was also carried out to determine the characteristics of epoxy syntactic insulation materials. Thermal conductivity (ISO8301) was measured along with compressive strength (ASTM D695), tensile strength (ISO 527) and flexural modulus (ASTM D790).

There are as yet, no international or national standards for the testing of epoxy syntactic insulation products against LNG spill. However, there is at least one project test method that has been used by more than one manufacturer and has some relevance as it exposes a candidate product to simulated LNG spill followed by hydrocarbon fire testing. This test method was devised for the South Hook (1) project in the UK and has become colloquially known as “the South Hook test”. The test requires the insulation and fire protection specification to be applied to a square hollow tubular steel section, see figure 2a. The steel has thermocouples attached and these are used to monitor the steel temperature during both the cryogenic immersion and hydrocarbon fire exposure periods.

![Figure 2a – Test specimen ready to be immersed in LN2 as part of the “South Hook” test](image)

For reasons of safety liquid nitrogen (LN$_2$) is used rather than LNG. LN$_2$ has a boiling point of -196 °C where LNG has a boiling point of -162 °C and thus immersion in LN$_2$ is more severe meaning the results of such testing would be conservative. The South Hook test calls for the test specimen to be immersed in LN$_2$ for a period of 15 minutes, see figure 2b. During the LN$_2$ immersion the average steel temperature must not fall below -30 °C which was selected as a typical temperature at which structural grade steel passes through the ductile to brittle transition.
Following immersion the test requires the sample to be immediately transferred to a test furnace running the UL1709 fire test curve. According to the standard, transfer from immersion to furnace and start of fire test must occur within 10 minutes. The fire test is then run for a period of 60 minutes. At the end of the fire test, see figure 4c, the average steel temperature shall not be greater than 400 °C. This temperature is regularly used as the critical failure temperature in hydrocarbon fire testing and represents a recognised point at which typical structural grades of steel retain the majority of their structural strength.

The South Hook test is a relatively large scale test that requires both cryogenic immersion and hydrocarbon fire exposure of a 1 m long steel test piece. The test provides only for a cryogenic immersion of 15 minutes and other projects may have different spill durations depending on the process risk analysis. In addition not all projects have a fire resistance requirement.
As the cryogenic spill protection requirements will depend on the project specific risk analysis, then the tested insulation thickness may not be the most cost effective for the project. Thermal calculations can be used to ‘fine tune’ the thickness of insulation required but these may not be accurate enough to ensure the steel in a cryogenic spill situation is adequately protected. Ideally there will be a suitable test that facilitates verification of the insulation thickness for a given cryogenic spill case.

To ensure the optimum thickness of syntactic insulation Leighs Paints have designed a low cost yet effective method as follows:

Steel plates are coated with various thickness of epoxy syntactic insulation on one side with thermocouples attached to the rear face. Using additional syntactic product to form a boundary we are able to maintain a pool of LN$_2$ and monitor rear face temperature over time, figure 3.

![Figure 3 – Duplex system of epoxy syntactic insulant and EPFP after exposure to LN$_2$](image)

**Results and discussion**

It is well established that epoxy coatings have excellent adhesion to steel and that they can provide excellent corrosion protection. Testing of epoxy syntactic foam insulation materials has also shown them to have excellent performance; Table 1 shows durability results for one such material.
Table 1 – Durability testing of epoxy syntactic foam insulation

<table>
<thead>
<tr>
<th>Test Environment</th>
<th>Test Duration</th>
<th>Coating Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Water Immersion</td>
<td>10 Years</td>
<td>No Defects</td>
</tr>
<tr>
<td>Salt water Immersion</td>
<td>10 Years</td>
<td>No Defects</td>
</tr>
<tr>
<td>Marine Environment</td>
<td>10 Years</td>
<td>No Defects</td>
</tr>
<tr>
<td>Salt Spray</td>
<td>4000 Hours</td>
<td>No Defects</td>
</tr>
</tbody>
</table>

Examination of the test panels showed no breakdown of the coatings, as would be expected when subjecting a (10 – 20) mm thickness of epoxy coating to such exposure conditions. Careful examination of the area around the holiday showed no corrosion undercutting of the coatings. Corrosion under insulation (CUI) is a well documented phenomenon but by using a wet applied epoxy syntactic foam product the potential for CUI can be eliminated.

Thermal conductivity \((k) \text{ Wm}^{-1}\text{K}^{-1}\) is a key value used in determining the required thickness of insulation and materials with lower \(k\) are more effective insulators. Table 2 shows typical values of some common materials. It can be seen that both mineral wool and cellular glass insulation have lower thermal conductivity than epoxy syntactic foam but it should be noted that mineral wool has to be dry to achieve this rating.

Table 2 - Thermal conductivity \((k)\) values of some common materials

<table>
<thead>
<tr>
<th>Material</th>
<th>(k)-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td>50.2</td>
</tr>
<tr>
<td>Concrete</td>
<td>0.8</td>
</tr>
<tr>
<td>Epoxy (unfilled)</td>
<td>0.12 - 0.18</td>
</tr>
<tr>
<td>Cellular Glass</td>
<td>0.04</td>
</tr>
<tr>
<td>Mineral Wool Insulation</td>
<td>0.04</td>
</tr>
<tr>
<td>Epoxy Syntactic Insulation</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 3 shows the \(k\) values for an epoxy syntactic material applied by airless spray and trowel. Despite the high pressures associated with airless spray application, when the latest generation epoxy syntactic foam is spray applied there is no significant loss of thermal efficiency. Tests have been carried out at up to 13.8 MPa (2000 psi) pump pressure.
Table 3 - Thermal conductivity values for different application methods

<table>
<thead>
<tr>
<th>Application method</th>
<th>k value @ 20 °C Wm⁻¹K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Syntactic Foam - Trowel applied</td>
<td>0.088</td>
</tr>
<tr>
<td>Epoxy Syntactic Foam - Spray applied</td>
<td>0.094</td>
</tr>
</tbody>
</table>

Putting syntactic foams under high pressure will rupture a proportion of the microspheres. The testing carried out on this material show that it may be applied by airless spray with minimal affect on the k value. When using such materials it is important to ensure that the k value used for thickness calculations has been determined for product applied using the appropriate method.

Table 4 gives a number of results for the physical characteristics of an epoxy syntactic insulation material.

Table 4 – Physical and thermal test data for epoxy syntactic foam insulation

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength</td>
<td>4.3 MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2.4 MPa</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>81.5 MPa</td>
</tr>
<tr>
<td>Density</td>
<td>0.46 gcm⁻³</td>
</tr>
</tbody>
</table>

The density of the material is such that it can be considered as an insulation material for use on weight critical projects, including off shore facilities such as floating LNG (FLNG) projects. The physical properties of epoxy syntactic foam insulation materials are sufficiently resilient to allow application to deck surfaces which will be subject to light traffic.

Figure 4 shows the temperature data for a duplex system of epoxy syntactic insulant and EPFP being subjected to the South Hook test. The test piece was immersed in LN2 from time = 0 minutes to time = 15 minutes, it was then placed in the furnace and at time = 18 minutes the fire test started. This shows a transfer time of 3 minutes where the maximum allowed transfer time is 10 minutes. The minimum steel temperature of -21 °C was reached at time = 22 minutes, 9 °C within the limit of -30 °C, and at time = 78 minutes the mean steel temperature reached 295 °C which is 105 °C below the 400 °C failure temperature.
A combined or duplex system of around 10 mm of epoxy syntactic foam and 10 mm of EPFP satisfies the performance requirements of this test. The surface of the EPFP material was cracked by exposure to the LN$_2$ but these cracks do not result in any detachment of the protection materials or any reduction in the fire resistance performance.

Using a series of panels with various thicknesses of epoxy syntactic insulation, the data in figure 5 was generated. The back face temperatures were recorded for 60 minutes whilst the upper face was kept flooded with LN$_2$. The resulting data was analysed to produce an insulation thickness against temperature graph for various time periods.

It was found that at an intermediate thickness of insulation the steel substrate temperature could be prevented from falling below -30 °C after 60 minutes cryogenic spill exposure.
Figure 5 – Substrate back face temperature against epoxy syntactic insulation thickness at various cryogenic contact time periods

Data is available for a range of epoxy syntactic insulation product thicknesses and time durations up to 60 minutes cryogenic contact time.

A combination of data from these tests will allow estimation of the optimum solution for cryogenic spill and fire protection requirements.

Conclusions

With the increasing need to handle and transport LNG the risk of accidental release is growing. Interest in cryogenic spill protection from those involved in the LNG industry has prompted Leighs Paints to develop CSP solutions.

It has been shown through extensive testing that epoxy syntactic insulation materials, in conjunction with epoxy passive fire protection products, can offer an effective solution to the cryogenic spill hazard.

LNG facilities are typically situated in coastal or offshore locations which are normally associated with the highest levels of corrosion. Accelerated weathering tests alongside long term actual exposure evidence has shown that epoxy syntactic materials can provide excellent corrosion protection to the underlying steel structure.
‘Dry fit’ forms of insulation can allow corrosion under insulation problems. Epoxy syntactic materials, which are ‘wet’ applied, bond effectively to the substrate and hence prevent CUI from occurring.

The latest generation of epoxy syntactic insulation materials, as discussed in this paper, have been designed to allow application by airless spray. This facilitates rapid and cost effective application to the substrate. The first generation of such products suffered significant degradation of the insulation provided (increase in thermal conductivity k) when applied by spray. Development work, specifically focussing on the selection of microspheres and optimising the binder system, has improved the resilience of the material allowing airless spray application with minimal affect on the k value.

There are not, at this time, any international or national standards for evaluating cryogenic spill protection followed by hydrocarbon fire. Project specific test methods and ad hoc tests have been developed and used as reported in this paper. These tests have shown that epoxy syntactic materials with EPFP can provide an effective and versatile solution to the challenges of cryogenic spill, with or without a subsequent hydrocarbon fire, in the LNG industry.

**Bibliography**

(1) South Hook LNG project, UK. Client Quatargas 2 of which a partner is ExxonMobil with design by CB&I Paddington, London. Details of the test protocol jointly developed by EM, CBI and Leiggs Paints.