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Preventing pitting and crevice corrosion of offshore stainless steel tubing

Tubing corrosion can lead to perforations and escape of highly flammable chemicals.

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Stainless steel tubing on oil and gas platforms is used in process instrumentation and sensing, as well as chemical inhibition, hydraulic lines, impulse lines and utility applications, over a wide range of temperature, flow and pressure conditions. Unfortunately, all over the globe, including the Gulf of Mexico (GOM), the North Sea, the China Sea and so on, corrosion of 316 stainless steel tubing has been observed.

The two prevalent forms of localized corrosion are pitting corrosion, which is often readily recognizable, and crevice corrosion, which can be more difficult to observe. The selection of inadequate tubing alloy and suboptimal installation practices can lead to deterioration of tubing surfaces in a matter of months. Today's minimally alloyed 316 stainless steel tubing, with close to 10.0% nickel, 2.0% molybdenum and 16.0% chromium, may experience corrosion more readily than the more generously alloyed 316 tubing products produced decades ago.

Contamination is another leading cause for surface degradation. Such contamination may be caused by iron particles from welding and grinding operations; surface deposits from handling, drilling and blasting; and from sulfur-rich diesel exhaust. Periodic testing of seawater deluge systems, especially in combination with insufficient freshwater cleansing, may also leave undesirable chloride-laden deposits behind.

PITTING AND CREVICE CORROSION

In most cases, pitting corrosion of tubing can be readily recognized. Individual shallow pits, and in later stages, deep and sometimes connected pits, can be observed by visual inspection with the unaided eye, Fig. 1. Pitting corrosion starts when the chromium-rich passive oxide film on 316 tubing breaks down in a chloride-rich environment. Higher chloride concentrations and elevated temperatures increase the likelihood for breakdown of this passive film. Once the passive film has been breached, an electrochemical cell becomes active. Iron goes into solution in the more anodic bottom of the pit, diffuses toward the top and oxidizes to iron oxide, or rust. The iron chloride solution concentration in a pit can increase as the pit gets deeper. The consequence is accelerated pitting, perforation of tubing walls and leaks. Pitting can penetrate deep into the tubing walls, creating a situation where tubing could fail.

Crevices are very difficult, or even impossible, to avoid in tubing installations. They exist between tubing and tube supports, in tubing clamps, between adjacent tubing runs and underneath contamination and deposits that may have accumulated on tubing surfaces. Tight crevices pose the greatest danger for crevice corrosion. General tubing corrosion in a tight crevice causes the oxygen concentration in the fluid contained within a crevice to drop. A lower oxygen concentration increases the likelihood for breakdown of the passive surface oxide film, resulting in the formation of a shallow pit. Unlike in pitting corrosion described above, pit formation on tubing that is surrounded by a crevice will lead to an increase in Fe^{++} concentration in the fluid in the gap. Because of the strong interaction of Fe^{++} ions with OH^- hydroxyl ions, the pH value drops. Chloride ions will also diffuse into the gap, being attracted by Fe^{++} ions, resulting in an acidic ferric chloride solution that can lead to accelerated corrosion of tubing within the crevice.

Ideally, tubing should resist all forms of corrosion, including general, localized (pitting and crevice), galvanic, microbiological, chloride-induced stress corrosion cracking and sour gas cracking. The tubing should also have adequate mechanical properties especially when fluid pressures are high. Erosion resistance comes into play when fluids contain potentially erosive particles. The environmental impact of the tubing should also be of concern: Aquatic life can be harmed by small concentrations of copper ions that can be readily released by copper-zinc alloys.

An alloy's resistance to localized tubing corrosion can be estimated by calculating from its chemical composition the alloy's Pitting Resistance Equivalent Number (PREN). The most frequently used relationship is:

$$\text{PREN} = \%\text{Cr} + 3.3\cdot\%\text{Mo} + 16\cdot\%\text{N}$$

The higher the PREN value of an alloy, the higher its resistance to localized corrosion, i.e., the higher its Critical Pitting Temperature (CPT) and critical Crevice Corrosion Temperature (CCT). These critical temperatures can be experimentally determined following common testing procedures such as ASTM G48 and ASTM G150.

Fig. 1. Pitting corrosion of 316 stainless steel tubing.

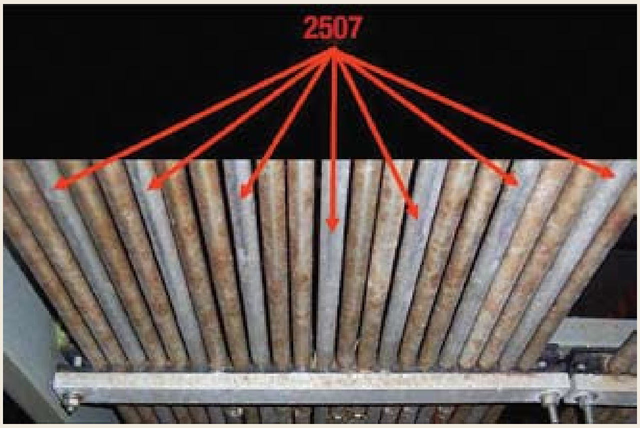
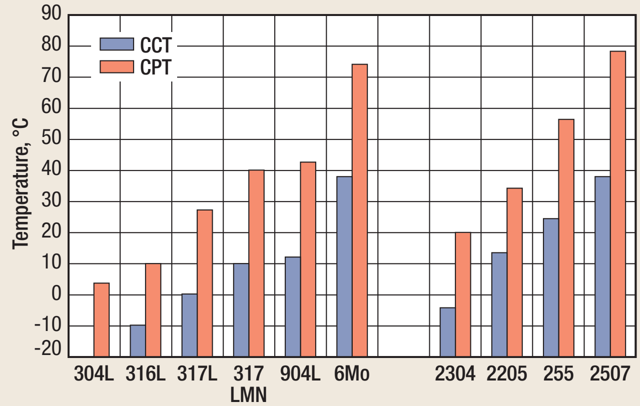


Fig. 2. Image shows 316 stainless steel and alloy 2507 superduplex tubing installed side by side, with the 316 tubing showing extensive corrosion and the superduplex tubing showing none.



Source: Practical Guidelines for the Fabrication of Duplex Stainless Steels, Int. Molybdenum Assoc., 2001.

Fig. 3. Bar chart shows critical pitting temperature and critical crevice corrosion temperatures of austenitic and duplex stainless steels. Measured by ASTM G48 in 10% ferric chloride.

ALLOY SELECTION

The importance of selecting the optimal alloy for an installation is demonstrated in Fig. 2. When installed side by side, austenitic 316 stainless steel tubing experienced heavy corrosion, while no signs of corrosion were detected on alloy 2507 superduplex tubing. In a GOM installation of alloy 2507 tubing, only a very small number of cases of external chloride crevice corrosion damage were identified. Perforations leading to the loss of system fluid containment were not observed. The only crevice corrosion damage involved plastic support strips and neoprene gaskets.

Numerous alloys are candidates for use in installations that require resistance to seawater corrosion. The most frequently used alloys have been the 300-series austenitic stainless steels, mainly 316 and in some cases 317. Alloys with at least 6% molybdenum, the so-called "6-moly" alloys, have performed well in offshore systems. Typical 6-moly alloys include 254SMO, AL6XN and 25-6Mo. More recently, alloys with slightly more than 6% molybdenum have been introduced: 654SMO, AL6XN Plus, 27-7Mo and 31. The published properties of these alloys suggest that they would perform well in chloride environments. Nickel alloys such as 825, 625 and C-276 are more frequently used for their performance in sour gas applications. Of these alloys, 625 and C-276 have demonstrated excellent resistance to localized corrosion. Ferritic alloys like Sea-Cure and AL29-4C are resistant to attack by aqueous chloride solutions and are primarily used as heat exchanger tubing. Tungum is a copper-zinc alloy that has been used because of its relative ease of installation. However, it carries disadvantages: Lack of hardness indicates susceptibility to erosive wear; low yield strength restricts its use to low pressures or requires high wall thickness; and corrosion liberates copper ions that can be detrimental to sea life.

The growing number of duplex alloys reflects the increasing use of this promising class of materials. The 2205 duplex alloy was introduced decades ago. Now there is superduplex alloy 2507, which has performed very well in recent years in more demanding applications that require PREN values of 40 and above. More recently, the hyperduplex alloy 3207 was introduced with an even higher PREN value. At the low end of alloy content, several lean duplex alloys such as 2101, 2304 and 2003 present themselves as candidates for less demanding applications.

The critical pitting temperature and critical crevice temperature of several alloys are shown in Fig. 3. The increase in chromium, molybdenum and nitrogen clearly leads to an increase in the CPT and CCT values of austenitic and duplex stainless steels. Also, despite their overall lower content of costly constituents nickel and molybdenum, they offer a similar performance to that of highly alloyed austenitic stainless steels.

Duplex alloys offer satisfactory resistance to localized corrosion and have high mechanical properties, which make them prime candidates for high-pressure applications. Alloy 2507 has a yield strength more than three times that of 316L.

JACKETED TUBING

For applications in seawater environments, a tubing alloy that is highly resistant to localized corrosion is not the only option. Alternatively, a less resistant alloy may be used if it is shielded, Fig. 4a. A thermoplastic polyurethane jacket offers adequate protection that can be cost-effectively extruded onto continuous tubing. The jacket must offer reliable protection from corrosive fluids and fulfill a series of additional requirements. The jacket must be durable, i.e., resist impact, abrasion and degradation by UV radiation. It must allow for tubing bending and cost-effective tubing installation, i.e., jacket removal and tubing connections makeup. Once made up, the connections typically have to be protected from the environment using shrink tubing or tape. Without this type of protection, seawater access could cause pitting corrosion of exposed tubing or crevice corrosion in the gap between the tubing and the jacket.

Appropriate tubing clamps must be selected and care taken to prevent clamps from cutting into jackets and sacrificing their protective character, Fig. 4b. An added advantage of jacketed tubing is the possibility to insulate, or heat and insulate, tubing when system fluids must be kept above ambient temperature.

Polyurethane-jacketed 316 stainless steel tubing was installed on a platform in the Gulf of Guinea in early 2006. No problems or incidences of malfunction or corrosion had been reported by late 2008.

TUBING SUPPORTS AND CLAMPS

Many different types of tubing supports and clamps have been used. Some of these designs have led to significant crevice corrosion, especially when tight crevices with large surface areas result in oxygen depletion so the alloy cannot reform the passive oxide layer. In particular, plastic tubing clamps have

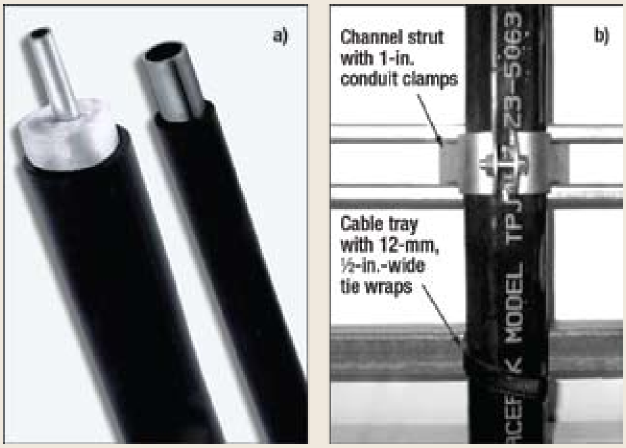


Fig. 4. a) Insulated jacketed tubing and jacketed tubing. b) Installed bundled jacketed tubing, with two appropriate clamping options.

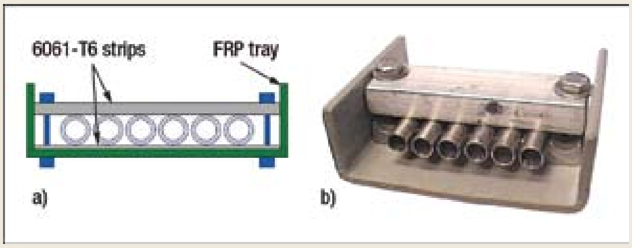


Fig. 5. Schematic (a) and photograph (b) of tubing supports that utilize aluminum alloys.

Fig. 6. Installation using 2507 superduplex tubing in the Gulf of Mexico. These tubing supports are based on half-round thermoplastic support rods.

been prone to inducing crevice corrosion because the plastic deforms around the tubing and creates tighter crevices that limit oxygen ingress.

One of the early approaches to preventing or mitigating crevice corrosion has been the use of marine aluminum alloys in tubing supports and clamps. In the schematic in Fig. 5a, the tubing rests on a thin strip of aluminum alloy that is contained within a fiber-reinforced plastic tray. The tubing is held in place with an aluminum alloy bar. Figure 5b shows an implementation of this design, with the difference that the tubing now rests on corrugated aluminum alloy in sections.

Tubing support structures that utilize aluminum alloys are in use today and appear to be performing well. Galvanic corrosion between aluminum alloy and stainless steel may occur, but the aluminum alloy is more anodic than stainless steel, which means aluminum will corrode preferentially. Once sufficient corrosion has taken place over a number of years, affected aluminum supports and clamps can be replaced while the stainless steel tubing remains in place.

An alternative design has more recently been adopted for the installation of stainless steel tubing. In Fig. 6, tubing is sandwiched between two half-round rods of a thermoplastic material. With the round tubing running perpendicular to the round support rod surface, the crevice contact area is minimized. Theoretically, there should be only one point of contact; however, some plastic deformation of the support rod takes place that results in a finite contact (crevice) area. A benefit of this design is that the supports/clamps allow for differential expansion of tubing and support structure.

INDUSTRY STANDARDS

The recently published industry standard NACE SP0108-2008, "Corrosion control of offshore structures by protective coatings," provides guidance for using more effective corrosion protection for offshore structures. The standard covers coating materials and generic protective coating systems, fastener coatings and corrosion control of flanges, pipe supports and stainless steel tubing. It allows for the use of extruded thermoplastic coatings, corrosion resistant alloys and/or cathodic protection. Flexible polyurethane thermoplastic coating is only allowed if it contains carbon black pigment for UV resistance, is of a fire-retardant grade, has a coating thickness of 1–3 mm and avoids crevices at the splices. This standard specifically states that plastic clamps and clips shall not be used offshore. It mentions the use of marine-grade aluminum alloy support trays. Thin film coatings on 316 stainless steel tubing are described as not being reliable.

Another industry standard, API RP 552, "Transmission systems," contains a section on installation practices. The described practices in the standard do not address the avoidance of crevice corrosion. Hence, the recommendations of this standard should be carefully reviewed for installations where a possibility of crevice corrosion exists.

CONCLUSIONS

Localized corrosion of stainless steel tubing on offshore platforms can have serious and adverse consequences. Hence, the selection of proper materials and the use of robust design and safe construction practices are mandatory.

An increase in topside 316/316L stainless steel tubing failure incident rates has been observed globally. The predominant cause of failure has been external pitting and crevice corrosion caused by chloride ion attack. Hence, unprotected 316/316L tubing appears to lack the necessary long-term resistance to localized corrosion in marine environments. Among several factors that may have contributed to the observed incidents, clamping systems made of polymer tubing support strips and stress bars with neoprene strip gaskets presented the most severe crevice conditions.

Tubing alloys are available that offer a combination of attractive properties for even unique sets of requirements that may exist for global construction projects. It is good practice to select an alloy with a critical pitting temperature above operating temperature. Depending on the application, it may be just as important to select an alloy with a critical crevice corrosion temperature above operating temperature.

Performance of even highly corrosion-resistant tubing can be sacrificed when tubing surfaces are not kept clean. If possible, tubing should be installed following heavy construction activities that would otherwise allow weld splatter and grinding debris to accumulate on tubing. Where adjustments of construction sequences are not possible, tubing should be shielded from becoming contaminated, and if contaminated, should be thoroughly cleaned.

Tight crevices between tubing, supports and clamps are difficult to avoid, and hence must be managed. Plastic tubing clamps that lead to large crevice contact areas should not be used. Support and clamping designs that are based on marine aluminum alloys appear to have a good track record in mitigating tubing corrosion. A new support and clamping method for tubing has more recently emerged. In this design, the round surfaces of semi-round thermoplastic rods come into contact with perpendicularly oriented tubing, and the crevice area at the rod/tubing interface is minimized. Recent installations in the Gulf of Mexico have combined this clamping concept with the use of superduplex tubing (Fig. 6) and will generate valuable performance data in the future.

An alternative approach involves the use of jacketed tubing. The extrusion of a thermoplastic coating onto tubing represents an economically attractive solution. Tubing is typically 316 or 317 stainless steel, and the preferred coating is polyurethane. Limited installations that have utilized urethane-jacketed 316 tubing have reported satisfactory results. **WO**

THE AUTHORS

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