Corrosion control of subsea production control systems: twenty years' experience

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Introduction

The integrity of subsea production control systems can be seriously affected by environmental degradation, primarily corrosion. Many of the components involved are of small size and with otherwise sophisticated design that does not tolerate any corrosion damage. Even a minor leakage may lead to immediate and severe malfunction of the system. Moreover, incipient corrosion that does not jeopardise the integrity of the component involved may still lead to contamination of internal fluids, causing sliding surfaces to seize or small-size nozzles to clog. Many components are exposed to both a corrosive external environment and potentially corrosive internal fluids. Such fluids may not be corrosive during normal operation but may develop corrosivity due to contamination, e.g. the ingress of seawater during subsea operations. Sometimes materials are used in combinations that are not compatible, causing severe galvanic corrosion if measures to control environmental corrosivity have failed.

In most cases, external corrosion of subsea components is efficiently controlled by cathodic protection. However, for cathodic protection to be effective, a reliable connection between anodes and all components to receive cathodic protection must be assured. It is also important to be aware that cathodic protection may have certain detrimental effects which need to be taken into account during design.

During the last 15-20 years, DNV's laboratories at HØvik have carried out a large number of failure analyses related to subsea production systems, many of which concerned the control systems. DNV has also been involved in the design of cathodic protection systems and materials selection for subsea production. There are few papers in the open literature that specifically deal

with corrosion control of subsea production control systems. One such paper was presented by one of the present authors in 1992¹; and another on cathodic protection was given by a colleague in 1996². The purpose of the present paper is to summarise the practical experience gained in the last twenty years from materials selection and corrosion control.

Cathodic protection

For marine floating structures and offshore fixed platform substructures, the role of cathodic protection is primarily to prevent any corrosion damage to structural steel components that could affect the resistance to cyclic loading by waves and sea currents (i.e. fatigue failures), and further to extend the life of coating systems primarily intended to reduce friction. However, for subsea production installations, mostly being installed at depths greater than 100 metres, the environmental forces imposed on structural components are obviously much less severe. In addition, the seawater corrosivity at the seabed is less than in surface waters, the steadystate corrosion rate for C-steel being typically less than 0.1 mm/year. Hence, a C-steel structure for mechanical support and protection would not strictly need any cathodic protection if its objective was only to ensure mechanical integrity (static or accidental loading) for a design life of say 20 years.

The primary objective of the cathodic protection of subsea production installations is rather to safeguard the pressurecontaining piping systems for production and production control. Due to its relatively thin wall and mostly bare steel surface, the production control piping is especially vulnerable to corrosion attack. If fabricated in AISI 316(L) stainless steel, and in the absence of cathodic protection, leakage by either direct penetration of the pipe wall by pitting attack, or more often by crevice corrosion at sealing surfaces of e.g. connectors, can readily be expected within one year of operation. More recently, production control piping in duplex stainless steel in accordance with UNS S31803 has been introduced, taking advantage of the higher yield strength. This material has definitely better resistance to corrosion by seawater; but cathodic protection is still a pre-requisite for safe performance. Certain evenhigher alloyed grades such as a stainless steel or nickel-base alloy in accordance with UNS S31254 or UNS N06625 respectively, or a high-alloyed duplex (ferritic-austenitic) stainless steel in accordance with UNS S32750, should not need any cathodic protection on their own. However, if electrically connected to the cathodic protection system, the associated current demand must still be included in the overall design.

Cathodic protection has largely been quite effective in preventing corrosion damage to components of subsea production control systems. In the early days some failures did occur in components that had not been electrically connected to the cathodic protection system (e.g. hose connectors for hydraulic fluid and electrical connectors). It appears that in most cases the omission of a connection to the cathodic protection system was purely accidental. In some cases, however, AISI 316 stainless steel was actually believed to be intrinsically resistant to corrosion in seawater. With cathodic protection installed, corrosion damage to the control piping in AISI 316 steel is rare. This is due to the electrical continuity to the cathodic protection system being ensured by metallic seals between individual units and by threaded connections at valve blocks and actuators, for instance,

Certain components of the production control system are mounted on the valve tree or manifold units so that their corrosion protection is sustained by the cathodic protection system of these units. However, the cathodic protection design was often performed by a subcontractor for the structural steel framework to which the anodes were to be installed. It appears that in many cases the amount of control piping and other bare steel items associated with the production control system had not been efficiently communicated to the cathodic protection system designer, resulting in insufficient anode capacity being installed. The consequence of this is a higher current load on the anodes than was actually designed for, resulting in premature consumption. On the other hand, there may also be other causes for high anode consumption sometimes observed on subsea production installations. This includes current drain to surface vessels and work-over equipment during downhole completion activities, and to electrically connected stationary items such as adjacent structures and casings, piles and pipelines not included in the overall cathodic protection design.

Normally designed as a retrievable unit, control pods are mostly provided with a self-sustaining cathodic protection system. Due to the relatively small surface area of a pod, the anodes installed are typically significantly smaller than those on the adjacent valve tree and/or manifold module. This results in a more rapid consumption rate (i.e. in per cent of initial anode mass) which has sometimes raised concerns when a pod was retrieved. However, this effect is unavoidable when anodes with major differences in size are applied for cathodic protection sub-systems that are electrically connected. It is recommended that anodes to be installed on individual units of a subsea production system are chosen to avoid large differences in anode sizes, i.e. unless anode replacement during periodic retrievals is planned for.

Although cathodic protection is the major technique for external corrosion protection of subsea control systems, it may sometimes lead to secondary detrimental effects. One such effect is the build-up of calcareous deposits. These deposits are formed on bare metal components due to the alkalinity produced on cathodically protected surfaces and the fact that seawater is supersaturated with calcium carbonate. The following chemical reactions apply:

$${}^{1}/{}_{2}O_{2(aq)} + H_{2}O + 2e^{-} \rightarrow 2OH^{-}$$
(1)
$$Ca^{2+} + HCO_{3}^{-} + OH^{-} \rightarrow CaCO_{3(s)} + H_{2}O$$
(2)

This results in a thin layer (of the order of 0.1 mm) of calcium carbonate (CaCO_{3(s)}) which is beneficial to the process of marine cathodic protection, reducing the current demand to only a fraction of that required for a truly bare metal surface. In a few cases such deposits have interfered with the intended function of subsea equipment, e.g. the mating of electrical connectors after being exposed to cathodic protection for some time. In one such case, the deposit had to be removed by injecting a small amount of diluted acid using a purposebuilt ROV-operated tool. Another example of such interference examined by DNV was a small spring-loaded relief valve of an actuator, which failed to open due to the accumulation of calcareous deposits on the spring. In general, however, problems associated with calcareous deposits appear to be quite minor. In most cases, any deposits at mating surfaces are readily removed by shearing. However, if such effects are deemed to become a potential problem, the affected surface has to be electrically insulated by means of a non-conductive coating. At the least, temporary corrosion protective grease or drying oil should prevent the formation of calcareous deposits for a relatively short period of time. If coating is not considered practical or reliable, the component must be insulated from the cathodic protection system, which requires the use of materials with intrinsic corrosion resistance.

Another potentially detrimental effect of cathodic protection is hydrogeninduced stress cracking (HISC) related to nascent hydrogen (H.) formed in a cathodic reaction parallel to (1) above: $H_2O + e^- \rightarrow H^+ + OH^-$

Hydrogen atoms may become absorbed in the material, and for those materials susceptible to HISC and subject to high tensile stresses, cracking may occur. The potentially susceptible high-strength materials include quenched and tempered grades of Csteel, low-alloy steel and stainless steel. However, it seems that only very high strength materials are affected in practice. Of the failures related to this mechanism examined by DNV, all materials had a yield strength in excess of 1200 MPa. The DNV design code for cathodic protection (DNV RP B401: 1993) recommends that materials with SMYS larger than 720 MPa shall not in general be used for components to receive cathodic protection. On the other hand, laboratory testing and a few cases of practical experience have confirmed that precipitation hardening nickel-base alloys and, furthermore, duplex stainless steels are susceptible to HISC by cathodic protection if subject to plastic straining in service. The precipitation hardening alloys are, however, mostly used for components which are not likely to receive such straining (e.g. connector housings, springs, etc).

Although duplex stainless steels are widely used subsea with cathodic protection, only three failures associated with HISC and related to cathodic protection are known to DNV. One of these³ concerned two 6-inch nibs on forged hubs of a subsea manifold. The cracking developed in the vicinity of welded flowline connections and it was concluded that this had been caused by high local stresses (>0.5% strain), a highly susceptible microstructure in the same area and high hydrogen charging due to the absence of any coating. A second failure in the late 1990s concerned a production flowline where cracking developed in a tie-in spool. The crack had initiated in the base material, but close to the welded connection of an anode insert. No coating had been applied in the affected area and it was said that there had been excessive straining by thermal cycling during operation. The third failure occurred in 1999 when a production control manifold started to leak during pressure testing due to cracking in a weld. The manifold did not have any coating. No details regarding mechanical loading are known to DNV, but it may be suspected that local plastic straining was also involved.

A third potentially detrimental effect of cathodic protection is cathodic disbonding leading to blistering of paint coatings. Such blisters do not necessarily ruin the primary function of coatings subsea. However, if a subsea unit with blistered coating is retrieved to the surface, rapid degradation of the coating may occur due to cracking of the blisters and subsequent rusting. The susceptibility to cathodic disbonding is enhanced by poor surface preparation and low coating thickness. Zinc-containing primers are also considered to increase susceptibility to cathodic disbonding.

Coatings

For subsea production systems, external paint coatings are applied with the following objectives: corrosion protection during handling and storage in marine atmosphere; reduction in current

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demand for cathodic protection; and improvement of visibility subsea.

Liquid epoxy type coatings are the most widely used and in general the experience is satisfactory. However, excessive disbondment and flaking are common when coating has been applied on stainless steel components without proper surface treatment (i.e. blasting). Hence, coating has often been applied directly on to machined or as-delivered stainless steel surfaces lacking a proper anchor pattern for coating adhesion. As mentioned above, marginal coating thickness may lead to cathodic disbondment and associated blistering on Csteel even with proper surface treatment. Thermal setting resins are sometimes applied for special components of relatively small size. According to DNV's experience, such coatings have in general performed quite well for subsea applications.

Electroless nickel coatings have sometimes been used for production control valve components. The objective of such coating may be either corrosion protection or hard facing, sometimes in combination. For components exposed to water-based hydraulic fluid that has become contaminated with seawater, electroless nickel applied on Csteel has in some cases developed deep pitting attacks, probably due to galvanic interaction at pores or other defects in the coating.

Materials selection

The selection of materials for components of subsea production control systems must take into account all environments that may be encountered after installation. These may include one or more of the following:

- □ Marine atmosphere.
- □ Seawater, with or without cathodic protection.
- Hydraulic fluid based on water/glycol or oil.
- 🗇 Methanol.
- Corrosion and scale inhibitors.
- Dielectric fluid.

□ Produced fluid or annulus (completion) fluid.

With the exception of dielectric fluid, all the above-mentioned environments should be considered as potentially corrosive to C-steel materials. Hydraulic fluid, even if non-corrosive as-delivered, may become contaminated by raw seawater rendering the fluid corrosive. Even if the residual corrosivity is too low to cause any actual damage to components, corrosion products may cause detrimental effects by seizing of sliding surfaces or clogging of valve nozzles.

Pure methanol as used for hydrate prevention is virtually non-corrosive. However, due to its low vapour pressure, this fluid is highly sensitive to cavitation and some cases of damage to production control components have been examined by DNV. It is important to realise that cavitation damage is not sufficiently controlled by materials selection. Hard and brittle materials as used for abrasion resistance (e.g. sintered tungsten carbide) are rather more susceptible to damage than ductile materials. Hence cavitation damage in methanol systems must be prevented by design.

AISI 316 stainless steel is the most widely used material for production control piping, valves and containers. In most cases this material performs well in marine atmospheres, although a few cases when accumulation of sea salts leads to corrosion damage have been experienced. It appears, however, that other factors such as improper surface treatment may have contributed to the damage. This material is otherwise fully resistant to produced fluid and annulus fluid, concentrated inhibitor solutions and hydraulic fluid. To our knowledge, contamination of water/glycol based hydraulic fluid by seawater has not yet caused any damage to such piping, although susceptibility must be expected. Martensitic and precipitation hardening stainless steels with about 17Cr, e.g. AISI 430 (UNS S43000) and type 17-4PH (UNS S17400) are used for components for which high strength and hardness are required, sometimes in combination with ferromagnetic properties. These materials readily suffer staining by corrosion in marine atmosphere and the resistance to hydraulic fluid contaminated by seawater is marginal.

Most failures of subsea control systems examined by DNV and caused by internal corrosion have been related to the use of so-called free-machining (i.e. re-sulphurised) stainless steels like AISI 303 (UNS S30300) and AISI 416 (UNS S41600). The high S-content of these materials (typically about 0.2%) added to improve machinability render them extremely sensitive to corrosion attack. As a matter of fact, components in these materials are typically more severely attacked by corrosion than Csteel. In some cases the corrosion products from the re-sulphurised grade had initiated the corrosion attack on ordinary AISI 316 stainless steel. In most cases the use of free-machining grades had not been specified in the materials list of the equipment affected. Typically *"stainless steel"* had been specified without any further specification of grade designation.

Duplex stainless steel of type 25Cr7Ni4Mo (primarily UNS S32750) has become a standard grade for umbilicals for subsea production control systems, taking advantage of its high strength compared to that of AISI 316 stainless steel (SMYS of 550 MPa and 200 MPa respectively). One major supplier has further introduced duplex stainless steel for hydraulic and other small-bore piping on production/injection valve trees and manifolds. Considering that such pipes contain high residual stresses from cold bending and that they are used without any coating, there should obviously be concerns regarding HISC induced by cathodic protection. However, although this material has been used for this application for ten years and tens of thousands of meters have been installed, no failures have occurred. Laboratory testing carried out by DNV under conditions of severe hydrogen charging and loading above yield did not induce any cracking. Hence it appears that conditions of progressive plastic straining are required to induce this type of cracking. Apparently production control piping does not experience such straining.

Austenitic stainless steel and nickelbased alloys with 18 to 20Cr and minimum 6Mo may be considered immune to corrosion in ambient temperature seawater, i.e. provided heat treatment, surface treatment and welding are adequate. The same applies to duplex stainless steel of type 25Cr7Ni4Mo. These materials are thus applicable to components for which cathodic protection is not practicable. It should be realised, however, that to ensure "nominal" corrosion resistance and mechanical properties, stringent quality control is essential during any manufacturing or fabrication affecting the microstructure and surface state.

Conclusions and recommendations

Type AISI 316 stainless steel has adequate corrosion resistance in marine atmosphere of ambient temperature and to most internal fluids encountered by subsea production control systems. However, cathodic protection is

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required for seawater exposure exceeding some weeks.

Martensitic and precipitation hardening stainless steel with about 17Cr and \Box 1Mo are marginally resistant to marine atmosphere and to hydraulic fluid severely contaminated by seawater ingress.

Austenitic stainless steel and Ni-base alloys with □18Cr and □6Mo and duplex (i.e. ferritic-austenitic) stainless steels of type 25Cr7Ni4Mo are applicable for components requiring immunity to corrosion in ambient temperature seawater. However, these materials, and the duplex grades in particular, are dependent on stringent control of manufacturing and fabrication procedures affecting the microstructure. Hence quality control is essential.

Laboratory testing has demonstrated that duplex stainless steels are susceptible to hydrogen-induced stress cracking (HISC) during conditions of hydrogen charging by cathodic protection and plastic straining in service. The same applies to precipitation hardened Nibase alloys. Bare duplex stainless steel hydraulic and other small-bore piping has been used extensively for subsea production control systems, but only one operational failure is known by DNV. It appears that high residual stresses from welding or cold-bending, or static external stresses are not sufficient to initiate such cracking but that conditions of progressive plastic straining are required. Austenitic grades (stainless steels and Ni-base) are in practice immune to HISC. For other materials such as low-alloy and stainless steel quenched and tempered grades a maximum SMYS of 720 MPa is suitable as a conservative approach.

Free-machining steels should not be used for any applications of subsea production control systems (although dielectric fluid should not actually cause any corrosion). It is recommended that material lists are carefully reviewed and that special attention is given to any machined components specified to be in "stainless steel".

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C-steel and low-alloy steel. Electroless nickel coatings have marginal resistance to hydraulic water-based fluid contaminated by seawater.

Cathodic protection is highly efficient in preventing corrosion damage of components installed subsea; this applies also to crevice corrosion of stainless alloys and galvanic interactions between dissimilar materials. However, the provision of electrical continuity to anodes by welded or threaded connections, mechanical seals or special bonding straps is a pre-requisite.

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