Stainless Steels in Oil and Gas Production

INTRODUCTION

Although oil is not corrosive in itself, production of this harmless (seen from the corrosion point of view) substance can involve highly corrosive environments because of the simultaneous presence of water and herein dissolved aggressive species such as oxygen, chlorides, carbon dioxide and hydrogen sulphide. To a certain degree oil can in fact act as an inhibitor, though it is somewhat unreliable with regard to stainless steels when only a thin oil film is "isolating" the metal from the corrosive water. Thick films of oil may totally inhibit corrosion.

Initially, mainly carbon steels were used in oil and gas production. However, because of the often increasing amounts of corrosive agents after years of production in old wells and the exploitation of more and more corrosive wells, stainless steels are used increasingly in this industry. Furthermore, environmental considerations have also led to the increased use of stainless steels, since carbon steel demands the addition of vast amounts of various artificial corrosion inhibitors, even under fairly mild corrosive conditions, and most of these inhibitors are more or less hazardous to the environment.

Looking at long term economics, by means of life cycle cost calculations, the use of a stainless steel can often repay the initial extra investment cost, mainly through low maintenance costs and weight savings since stainless steel components do not need to be overdimensioned to compensate for general corrosion as do carbon steel components. Finally, much longer lifetimes can be achieved with stainless steels than with carbon steels.

ENVIRONMENTAL FACTORS

"Sweet" or "Sour" environments

Production fluids and gases in the oil and gas industry are traditionally classified as "sweet" or "sour" environments, depending on whether hydrogen sulphide is absent or present in significant amounts respectively.

Sweet environments are those containing no or negligible amounts of hydrogen sulphide. High amounts of carbon dioxide may be present in sweet environments, causing accelerated corrosion on carbon steel.

Sour environments are those containing significant amounts of hydrogen sulphide. The main concern regarding H_2S is its ability to embrittle metals thereby causing cracking, "sulphide stress cracking (SSC)", under certain conditions.

Hydrogen sulphide

Hydrogen sulphide is one of the main factors to consider, when choosing a material for oil and gas production equipment, because of the risk of sulphide stress cracking.

Sulphides, S^{2-}, HS^- or H_2S adsorbed to the metal surface, catalyse the absorption of hydrogen atoms by the metal, which may subsequently crack due to hydrogen induced cracking (HIC) depending among other factors on the amount of hydrogen absorbed. It is this cracking which is usually termed "sulphide stress cracking", SSC. The full mechanism of hydrogen embrittlement by H_2S is still under debate.

The hydrogen absorption caused by H_2S may work synergistically with the factors involved in chloride stress corrosion cracking, thereby increasing the risk of environmentally induced cracking.

Hydrogen embrittlement seems to be the most active cracking mode at low temperatures, whereas chloride stress corrosion cracking predominates at high temperatures. Consequently, the combined risk of cracking due to H_2S and chlorides tends to be most severe for the non-ferritic stainless grades at intermediate temperatures, approximately in the range 80–100°C.

When H_2S is present, it is generally the risk of cracking that is of concern. However, very small amounts of H_2S should not necessarily be seen as a negative factor since the presence of H_2S guarantees a low redox potential in the environment and thereby lowers the risk of chloride induced localized corrosion, e.g. SCC, pitting and crevice corrosion.

Actual limiting critical values of H_2S partial pressures are difficult to give, due to several other factors–temperature, pH and chloride concentration probably being the dominating ones.

Carbon dioxide

Stainless steels are not susceptible to the general CO_2 corrosion as are carbon steels. For example, pipelines in carbon steel suffering CO_2 corrosion have been replaced with stainless steel and have given very long service lives. However, CO_2 can indirectly affect the performance of stainless steels by dissociation of carbonic acid, which leads to a lowering of pH.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

It is not surprising that a higher hydrogen ion activity will increase the driving force for hydrogen being absorbed into the metal, so that the metal becomes more prone to cracking (SSC). A significant hydrogen uptake is, however, still only possible when H_2S above a certain concentration is present.

It should be borne in mind that most actual systems have natural pH-buffering systems such as from bicarbonate present initially. Therefore the full pH-lowering effect caused by CO_2 may not be felt because of buffering action. So, in many practical situations the system may not be as aggressive as expected from knowledge only of the partial pressures of CO_2 and H_2S.

Chlorides

Chlorides are very often present in high concentrations in water associated with oil and gas formations. Localized corrosion on stainless steels induced by chlorides is well known. However, the oxygen content of these fluids is mostly extremely low and significantly higher chloride levels are therefore acceptable than under oxygen saturated conditions. The main cathodic reaction in these systems is the reduction of hydrogen ions.

Temperature

As is well known, normally the higher the temperature the more aggressive the environment with regard to localized corrosion induced by chlorides. However, as mentioned above, non-ferritic stainless steels seem to show their greatest sensitivity towards SSC at around 80–100°C in terms of critical partial pressure of H_2S. This effect is most pronounced in the duplex stainless steels and lower alloyed austenitic stainless steels. This phenomenon is thought to be explained by the reverse temperature dependency of sulphide induced SSC and chloride induced SCC.

Sulphur

The presence of elemental sulphur has shown to be highly deleterious for stainless steels and may reduce the critical partial pressure of H_2S appreciably. One possible explanation for the deleterious effect of elemental sulphur is that it can be reduced by hydrogen ions to form H_2S. However, elemental sulphur does not seem to be present in most wells.

Galvanic effects

Creating a galvanic contact between stainless steels and carbon steels will often result in full cathodic protection of the stainless steel with regard to chloride induced localized corrosion. However, ferritic and duplex stainless steels may during long periods of exposure develop hydrogen embrittlement from the increase in the cathodic reaction (hydrogen ion reduction) on the stainless steel surface. Obviously this effect is most pronounced at low pH.

Artificial environments

In many cases the limiting environment with regard to corrosion may not be the gases or formation waters present in the well. A number of chemicals are frequently added to the well in order to optimize the productivity or as part of the initial drilling and setup procedures.

Stimulation acids are widely used to increase formation permeability. These acids are most often inhibited, however many of these inhibitors have been developed for carbon steel, and there is no guarantee that the inhibition is effective on stainless steels without prior testing.

In general, the use of organic acids is recommended. Excessively large injections should be avoided. This will minimize the risk of creating an unnecessarily aggressive local environment with low pH. It should be recognised that even though the pH is lowered during acidizing the concentration of dissolved sulphides is also lowered by general dilution in the near vicinity of the metal.

Completion fluids are sometimes used to counterbalance the formation pressure. These fluids may contain high concentrations of chlorides or bromides which inherently introduce an enhanced risk of chloride (halide) induced localized corrosion.

Injected waters to help secondary recovery may be seawater in the case of offshore production, or produced water in either onshore or offshore production. These waters can be treated in various ways which influence their corrosivity–like deaeration (less aggressive) or chlorination (more aggressive).

Seawater (Offshore production only)

Topside equipment may be exposed to seawater internally in the case of seawater being used as a cooling liquid or used for the production of freshwater. External exposure of topside equipment to seawater is caused by the unavoidable splashing from the marine environment.

In these cases, the selection of a stainless steel grade should be based on the maximum temperature and the condition (aerated and untreated, chlorinated, deaerated, etc.) of the seawater. In the case of splashing from the marine environment, possible evaporative conditions should be considered.

The superaustenitic 6Mo stainless steel grade 254 SMO has shown excellent performance in many seawater environments.

Submerged pipelines are another example where the outside environment is sometimes potentially more aggressive than that on the inside.

METALLURGICAL FACTORS

It is generally accepted that the sensitivity towards hydrogen embrittlement increases with increasing strength. This has led to the practice of specifying a maximum hardness of the material when used in sour service, as in NACE standard MR0175, which is discussed below.

It should be recognised that the traditional correlation between strength, hardness and SSC sensitivity was based on industry experience with carbon steels. The application of this rule is not as straightforward for stainless steels, where the strength in the annealed condition can vary greatly depending on a number of different metallurgical factors. For example, a high nitrogen content in the fully austenitic stainless steel 254 SMO or in the superduplex stainless steel SAF 2507^{TM} introduces a high strength in the annealed condition, but these steel grades are in general less sensitive towards SSC compared to the similar stainless steels containing lower amounts of nitrogen and having lower annealed strength.

Certain stainless steels do, however, become more susceptible to SSC, when they have been cold worked.

DUPLEX IS A /FERRITIC STEEL

Ferritic and martensitic stainless steels

Ferritic stainless steels are fairly susceptible to SSC, especially in the cold worked condition. For common ferritic grades the resistance to chloride induced pitting and crevice corrosion is also limited. Ferritic stainless steels have therefore found limited use in sour production environments.

Martensitic stainless steels are used mainly when high strength is needed in sweet environments, where they have shown to be cost effective in replacing carbon steel suffering from CO_2-corrosion. Martensitic stainless steels have a fairly limited chloride induced localized corrosion resistance, and they show a high susceptibility to SSC.

Austenitic stainless steels

Low-alloyed austenitic stainless steels, types 304 and 316, are being used for a large number of components. These alloys are far less prone to SSC than ferritic and martensitic alloys as long as they are in the annealed condition. However, heavy cold work of these alloys does increase their susceptibility to SSC even at ambient temperature. Stainless steel type 304 cold worked 30% exhibits susceptibility to SSC even at very low chloride concentrations (1).

The superaustenitic 6Mo stainless steel grade 254 SMO has shown excellent resistance to SSC and SCC. Even after cold work up to 80% and coupled to carbon steel, 254 SMO is highly resistant to SSC. The carbon steel coupling increases the driving force for hydrogen induced cracking as discussed above. Laboratory results documenting the high SSC resistance of 254 SMO are shown in Table 1.

TABLE 1

SSC test of 254 SMO at ambient temperature, $pH_2S = 1$ atm, $pH \approx 3$, (NACE solution), stress: 90% of $R_{p0.2}$ (4-point bend test)

Cold worked condition	NaCl conc.	A	B	Coupled to carbon steel A	B
40%	5%	0	2	0	2
50%	5%	0	2	0	2
60%	5%	0	2	0	2

A = number of failed specimens;
B = number of tested specimens.

At high temperatures the high chloride induced SCC resistance is a further argument for the widespread use of 254 SMO in oil and gas production.

Duplex stainless steels

The high strength of duplex stainless steels together with their high resistance to chloride induced localized corrosion are important reasons for their popularity in oil and gas production.

However, it is necessary to observe some restrictions on their use in severe sour environments, since laboratory investigations have indicated moderate SSC susceptibility. It should be borne in mind that pH and stresses in practical applications are often less severe than in accelerated laboratory tests. This is clearly illustrated by a number of successful applications of duplex steels at far higher partial pressures of H_2S than a number of laboratory investigations have indicated should be possible.

NACE MR0175

NACE standard MR0175 presents material requirements for resistance to sulphide stress cracking (SSC) in oil and gas production equipment and related equipment. The document is a broadly written document. Certainly not all materials listed in MR0175 are satisfactory for all practical sour service applications. However, MR0175 is frequently used as a minimum requirement for selection of materials for sour service.

In this standard a sour gas environment is defined as one containing water as a liquid and hydrogen sulphide in the gas at a partial pressure exceeding 3 mbar (0.05 psi), and with total pressures greater than 4.5 bar (65 psi).

In the case of multiphase systems (gas/"oil"/water) MR0175-92 defines sour environments as systems with H_2S partial pressure exceeding 3 mbar (0.05 psi) at a total pressure above 18.3 bar (265 psi). At total pressures below 18.3 bar, the partial pressure of H_2S above 0.7 bar (10 psi) or more than 15% H_2S also defines a sour environment. Sour multiphase systems which have operated satisfactorily with standard equipment are outside the scope of MR0175.

MR0175 lists a wide range of metallic materials and product forms that under certain conditions are found to be acceptable for use in sour service. In general the main restriction put on the materials is a maximum hardness level. Requirements for welds are generally the same as for the annealed wrought material with regard to the maximum hardness level.

Table 2 gives some examples of stainless steels accepted for sour service by MR0175.

TABLE 2

Some stainless steels mentioned as acceptable for sour service in MR0175.

Steel design.	UNS No.	Max. hardness HRC	Comments
304 316/316 HighMo 317L	S30400 S31600 S31703	22 22 22	No cold work designed to enhance mechanical properties allowed
Sanicro28 254 SMO®	N08028 S31254	33 35	–
2205	S31803	36	max. pH_2S=20 mbar (0.3 psi)
SAF 2507™	S32750	34	max. pH_2S=100 mbar (1.5 psi)

It should be remembered that MR0175- only addresses SSC in the context of the H_2S partial pressure, whereas effects of pH and chloride induced localized corrosion are not taken into account.