MATERIALS FOR CORROSIVE APPLICATIONS USED AT VALVES

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1. Types of corrosion

1.1 Uniform corrosion

Uniform corrosion is considered an even attack across the surface of a material and is the most common type of corrosion. It is also the most benign as the extent of the attack is relatively easily judged, and the resulting impact on material performance is easily evaluated due to an ability to consistently reproduce and test the phenomenon. This type of corrosion typically occurs over relatively large areas of a material's surface.

1.2 Pitting corrosion

Pitting is one of the most destructive types of corrosion, as it can be hard to predict, detect and characterize. Pitting is a localized form of corrosion, in which either a local anodic point, or more commonly a cathodic point, forms a small corrosion cell with the surrounding normal surface. Once a pit has initiated, it grows into a "hole" or "cavity" that takes on one of a variety of different shapes. Pits typically penetrate from the surface downward in a vertical direction. Pitting corrosion can be caused by a local break or damage to the protective oxide film or a protective coating; it can also be caused by non-uniformities in the metal structure itself. Pitting is dangerous because it can lead to failure of the structure with a relatively low overall loss of metal.

1.3 Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal. Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents re-passivation. As a stagnant solution builds, pH shifts away from neutral. This growing imbalance between the crevice (microenvironment) and the external surface (bulk environment) contributes to higher rates of corrosion. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

1.4 Intergranular corrosion

An examination of the microstructure of a metal reveals the grains that form during solidification of the alloy, as well as the grain boundaries between them. Intergranular corrosion can be caused by impurities present at these grain boundaries or by the depletion or enrichment of an alloying element at the grain boundaries. Intergranular corrosion occurs along or adjacent to these grains, seriously affecting the mechanical properties of the metal while the bulk of the metal remain intact.

An example of intergranular corrosion is carbide precipitation, a chemical reaction that can occur when a metal is subjected to very high temperatures (e.g., 800°F - 1650°F) and/or localized hot work such as welding. In stainless steels, during these reactions, carbon “consumes” the chromium, forming carbides and causing the level of chromium remaining in the alloy to drop below the 11% needed to sustain the spontaneously forming passive oxide layer.

1.5 Stress corrosion cracking

Stress corrosion cracking (SCC) is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes. It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. In stress corrosion, most of the surface usually remains intact; however, fine cracks appear in the microstructure, making the corrosion hard to detect. The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress. Selecting proper materials for a given environment (including temperature and management of external loads) can mitigate the potential for catastrophic failure due to SCC.

1.6 Galvanic corrosion

Galvanic corrosion is the degradation of one metal near a joint or juncture that occurs when two electrochemically dissimilar metals are in electrical contact in an electrolytic environment; for example, when copper is in contact with steel in a saltwater environment. However, even when these three conditions are satisfied, there are many other factors that affect the potential for, and the amount of, corrosion, such as temperature and surface finish of the metals. Large engineered systems employing many types of metal in their construction, including various fastener types and materials, are susceptible to galvanic corrosion if care is not exercised during the design phase. Choosing metals that are as close together as practicable on the galvanic series helps reduce the risk of galvanic corrosion.

2. Corrosion resistant materials

2.1 Low alloy steels

S41001 (A182 F6a) (1.4006) (X12Cr13)
This material is a martensitic stainless steel that combines good mechanical properties and good corrosion resistance in moderately aggressive media. In order to achieve optimal corrosion resistance of this chrome steel, a smoothed (industry-polished) and residue-free surface is required. It is used in construction parts in water and steam, in the petroleum industry, in mechanical engineering, in the pump industry as well as in areas of the food industry and can be used up to 400°C. It is easy to machine and very easy to weld.

S42000 (A276 420) (1.4021) (X20Cr13)
This type of steel has a medium hardness among chrome steels and good corrosion resistance in (non-chlorine-containing) water, steam and moderately aggressive chemicals. With a share of more than 12%, chrome makes the steel material corrosion resistant. It shows good corrosion resistance only in tempered (+ QT) and ground-polished (+ SL) condition. This corrosion resistance is no longer present in the annealed and naturally hard state. All martensitic stainless steels are not resistant to sea water. When it is used in sea water, pitting corrosion occurs. It has good corrosion properties in non-chlorine-containing media with moderate aggressiveness, e.g. water, water vapor, air humidity, soaps, solvents, organic acids and alkalis. Corrosion resistance in oxidizing media is up to approx. 600 ° C.

S42000 (AISI 420) (1.4031) (S39Cr13)
This material presents a good corrosion resistance in moderately aggressive, non-chlorine media such as soaps, solvents and organic acids. The best corrosion resistance is in the hardened state with a polished surface. In terms of corrosion properties, it shows a somewhat improved resistance as result from the slightly higher chromium. This can somewhat compensate for the chromium depletion caused by the increased carbon content.

2.2 Stainless steels

S30400 (AISI 304) (1.4301) (X5CrNi18-10)
As a high chrome alloy, it has good corrosion resistance. It is also ductile which facilitates several manufacturing processes. The low carbon content is beneficial for welding and it is widely used for food and medical applications.

S31600 (AISI 316) (1.4401) (X5CrNiMo17-12-2)
This has improved corrosion resistance and better creep strength at high temperatures than S30400. It is the standard material and can be used with a wide range of chemicals. It is easily welded.
Neither S30400 nor S31600 is suitable for applications where there is a high chloride content and they are susceptible to pitting corrosion in seawater environments.
This material is used almost universally and can be found in many chemical, food and pharmaceutical applications.

S31603 (AISI 316L) (1.4435) (X2CrNiMo18-14-3)
This material is a derivation of S31600 which has superior resistance to intergranular corrosion following welding or stress relieving. It may therefore be selected in preference to other grades for certain manufacturing processes.

S31635 (316Ti) (1.4571) (X10CrNiMoTi18-10)
This is a further derivation of S31600 which is stabilized by the addition of titanium.
It can be used to reduce intergranular corrosion and ensure good mechanical properties at room and elevated temperature.

S32100 (AISI 321) (1.4541) (X6CrNiTi18-10)
It is a development of AISI 304 with some Ti content which helps prevent chromium carbide precipitation resulting from welding or elevated temperatures. It also has good resistance to scaling and vibration fatigue. It is therefore a useful material for high temperature process equipment and gas turbines.

S34700 (AISI 347) (1.4550) (X6CrNiNb18-10)
An alternative option for metal gaskets selected for good heat resistance a resistance to intergranular corrosion.

2.3 Nickel alloys

N10276 (Alloy 276) (2.4810) (G-NiMo30)

One of the most widely used nickel alloys and is likely to be referred to as HASTELLOY C276^{R}. It is suitable for use in seawater, brine and many acids. It is readily welded and retains good properties in the welding zone. Widely used in high temperature or corrosive applications. It can be used as a spring material.

N07718 (Alloy 718) (2.4668) (NiCr19FeNbMo)

It is a high nickel, chrome alloy with some iron content that has excellent corrosion resistance and high temperature properties that is readily heat treated to obtain the required characteristics.
It is used in hot hydrocarbon service.

N06600 (Alloy 600) (2.4816) (NiCr15Fe)

This material is familiarly known as Inconel 600^{R}. It is a nickel-chromium alloy with good oxidation resistance at high temperatures and resistance to chloride-ion, stress-corrosion cracking, corrosion by high purity water, and caustic corrosion. It is used for the manufacture of metal O-rings.

N07750 (Alloy X750) (2.4669) (NiCr15Fe7TiAl)

This is a nickel-chromium alloy similar N06600 also known as Inconel X750^{R}.
The addition of aluminum and titanium make it precipitation hardenable. It has good resistance to corrosion and oxidation with high tensile and creep-rupture properties up to 700°C. Its excellent relaxation resistance is useful for high temperature springs and bolts and it is used for the manufacture of high temperature C section metal seals.

N04400 (Alloy 400) (2.4360) (NiCu30Fe)

This material is also often known familiarly as Monel^{R}, but again it is one of several alloys available under that trade name. It is a copper-nickel alloy that has particularly good corrosion resistance against sulphuric and hydrochloric acid, alkalis and seawater. It is also not liable to stress corrosion cracking and is often the material of choice for seawater applications and in hydrofluoric acid.

N05500 (Alloy K-500) (2.4375) (NiCu30Al)

A further material of the Monel^{R} family which has higher strength and is used where this may be required as set screws and fasteners.

2.4 Chromium alloys (DUPLEX / SUPERDUPLEX)

S31803 (A182 F51) (1.4462) (X2CrNiMoN22-5-3)
This is a duplex stainless steel which has up to twice the yield strength of S31600 and much improved corrosion resistance. It is used where the improved corrosion resistance is required. The higher strength may also be an advantage in some cases.

S32760 (A182 F55) (1.4501) (X2CrNiMoCuWN25-7-4)
This is a super duplex stainless steel with 25% Cr, a high resistance to pitting corrosion and high strength. The high resistance to stress corrosion cracking and crevice corrosion makes it a suitable material for components in oil exploration, refining, seawater and geothermal applications.
The high strength can also facilitate weight savings compared with conventional stainless steels such as the 304 or 316 series materials.

2.5 Titanium

Titanium is a very reactive metal that shows remarkable corrosion resistance in oxidizing acid environments by virtue of a passive oxide film. It performs best in oxidizing media such as hot nitric acid. The oxide film formed on titanium is more protective than that on stainless steel, and it often performs well in media that cause pitting and crevice corrosion in the latter (e.g., seawater, wet chlorine, organic chlorides). While titanium is resistant to these media, it is not immune and can be susceptible to pitting and crevice attack at elevated temperatures. It is, for example, not immune to seawater corrosion if the temperature is greater than about 110°C.

3. Corrosion produced by Cl (chlorines) and SO2 (Sulphur dioxide)

The resistance of materials against corrosion is measured in "**PREN**" (**P**itting **R**esistance **E**quivalent **N**umber)

Pitting resistance equivalent number (PREN) is a predictive measurement of a stainless steel's resistance to localized pitting corrosion based on its chemical composition. In general: the higher PREN-value, the more resistant is the stainless steel to localized pitting corrosion by chloride.

PREN is frequently specified when stainless steels will be exposed to seawater or other high chloride solutions. In some instances, stainless steels with PREN-values > 32 may provide useful resistance to pitting corrosion in seawater but is dependent on optimal conditions. However, crevice corrosion is also a significant possibility and a PREN > 40 is typically specified for seawater service.[1][2][3]

These alloys need to be manufactured and heat treated correctly to be sea water corrosion resistant to the expected level. PREN alone is not an indicator of corrosion resistance. The value should be calculated for each heat to ensure compliance with minimum requirements, this is due to chemistry variation within the specified composition limits.

There are several PREN formulas. The most common is PREN = 1 × %Cr + 3.3 × %Mo + 16 × %N

There are a few stainless steels which add tungsten (W), for those the following formula is used PREN = 1 × %Cr + 3.3 (%Mo + 0.5 × %W) + 16 × %N

Exact pitting test procedures are specified in the ASTM G48 standard

As can be seen in the formula, the quantity of C and Ni in the alloy has no influence on the PREN value. The effect of Ni is that it reduces the speed of corrosion once the process has started. This means that higher Ni content gives a longer lifetime to the component exposed to corrosion.

Generally stainless steels are divided into four categories of corrosion resistance, based on their PREN value here some examples:

Category I – Low corrosion

Steel types				PREN value
UNS	**AISI**	**ASTM**	**DIN**	
S41000	410	A182 F6A	1.4006	12,0 / 13,0
S42000	420	A276 420T	1.4021	12,0 / 14,0
S42000	420	A276 420	1.4031	12,0 / 14,0

Category II – Low corrosion, low content of Cl and SO2 – Accessible components

Steel types				PREN value
UNS	**AISI**	**ASTM**	**DIN**	
S37400	347	A182 F347	1.4550	17 / 19
S30400	304	A182 F304	1.4301	20 / 21
S30403	304L	A182 F304L	1.4306	20 / 22
S32100	321	A182 F321	1.4541	17 / 19

Category III – medium corrosion – Medium content of Cl and SO2 – Not accessible components

Steel types				PREN value
UNS	**AISI**	**ASTM**	**DIN**	
S31635	316Ti	A182 F316Ti	1.4571	25 / 30
S31600	316	A182 F316	1.4401	25 / 28
S31603	316L	A812 F316L	1.4404	25 / 28

Category IV – High corrosion by Cl and SO2

Steel types				PREN value
UNS		**ASTM**	**DIN**	
S31803	DUPLEX	A182 F51	1.4462	31 / 36
S32760	SUPERDUPLEX	A182 F55	1.4501	38 / 44

The selection of stainless steel for a specific application must be done according to the mechanical requirements of the component, the process conditions (pressure & temperatura) and the content of corrosive elements.
It shoul always be considered that not only the normal process conditions must be considered, also abnormal conditions, like that the equipment is over a longer period of time out of service, and corrosive components can accumulate.

4. Corrosion produced by CO_2 (carbon dioxide) and H_2CO_3 (carbonic acid)

Dry carbon dioxide (CO2) is not corrosive for all metals at all temepratures. When there is a presence of water (H2O) the combination with the CO2 forms carbonic acid (H2CO3) which is corrosive.
The corrosivness of metals depend of many factors, like temperature, pH value, content of water and chlorine.
This description can only give a general guidness for the selection of a specific material for a component.

The next table applies for liquids

CO2 partial pressure	Relative corrosion	Recommended materials		Notes
≤ 0,5 bar	There is no corrosion	No restrictions		
0,5 up to 2,1 bar	Light corrosion	1.4006 1.4021 1.4313	AISI 410 AISI 420 AISI 415	Cr13 steels
≥ 2.1 bar	Medium to high corrosion	1.4301 1.4541 1.4401 1.4462	AISI 304 AISI 321 AISI 316 A182 F51	Cr17 steels Cr22 steels

The partial pressure can be calculated as follows: in gas with a pressure of 100 bar with a CO2 content of 2%, the CO2 partial pressure is 2 bar.