



Stainless Steel and Corrosion

Claus Qvist Jessen

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FOREWORD

For most people, stainless steel is a metal with a number of great qualities. It is bright and attractive. It is easy to clean. It emits an aura of quality. And it is as 'stainless' as its name suggests. Or is it? Unfortunately, not always; for, even though stainless steel remains attractive and corrosion-free in a vast majority of cases, from time to time things go wrong and the material will begin to rust. But why?

When sifting through the literature in search of answers, one often ends up in the dense and cryptic world of engineering, full of dull equations and lifeless formulas, while only a limited amount of information is written for lay audience. This book is an attempt to remedy this trend, for, unlike almost all other works on stainless steel, corrosion and metallurgy, it is not written for fully trained engineers. Instead, it is aimed at professional tradesmen who wish to expand their stainless steel horizons.

The target audience notwithstanding, no book is ever written in a vacuum, and I would therefore like to thank Damstahl's CEO, Mikael Sthaalros, who suffers from the same contagious disease as myself: Technical knowledge is fascinating, and fascinating knowledge must be shared - and preferably in a somewhat entertaining manner to prevent readers from nodding off in mid paragraph. After all, knowledge is not worth much if it is not diffused in the right places.

On the professional side of things, I am particularly indebted to Erik-Ole Jensen, Arla Foods and professor Per Møller from MEK, DTU. In addition, Torben Henriksen, Migatronic A/S, Jesper Nielsen, Preben Z Jensen A/S, and Jon Kold, Stålcetrum, have provided valuable input for the book. Furthermore, I would like to thank my former colleagues at FORCE Technology and Cleanodan A/S / Steel-Tech ApS, both in Brøndby, Denmark, for their constructive and professional sparring. It is impossible to be an expert in every field, and I will never be too old to learn something new.

I would also like to take this opportunity to thank my wonderful colleagues at Damstahl, as well as Damstahl's many great clients and course participants who, over the last four years, have bombarded me with so many constructive questions that from the answers an entire book has emerged. There is certainly no harm in building a bridge between knowledge-thirsty clients and Damstahl's corrosion-resistant brain cells.

Last, but not least, I am grateful to my wife, Annette, for her endless patience with my writing excesses over the last year. Not only has stainless steel writing and research invaded our home and many of our nightly exchanges - Annette has also had to live with having her kitchen table taken over by solid masses of stainless steel under decorative corrosive attack. There's nothing quite like a lovely bit of pitting corrosion or stress corrosion cracking served between salad, roast beef and bread.

Skanderborg, Denmark, March 2011

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MIKAEL STHAALROS

HERE YOU GO

Some readers may sit with this book in their hands and wonder:
"Why doesn't Damstahl just concentrate on selling steel instead of releasing a book?"

The answer is easy:
Because we want to be the world's best at winning clients!

And, in order to do so:
We must contribute significantly to our clients' competitiveness and bottom lines.
As a business partner, we must offer much more than simple buying and selling.
We must make our wealth of talent available to our clients – Damstahl is filled with interesting, knowledgeable and experienced professionals.

I am very happy that Claus agreed to "emptying his head" and sharing his immense knowledge with all of us. That was very generous, indeed.

I am also thankful that Claus has employed his lively and inspiring style and tone, so that I, too, am able to understand the content.

Without further ado, I proudly present this book to its readers – everyone and anyone who is interested in stainless steel.

In wind and weather,

Mikael Sthaalros

Group Managing Director, CEO
Damstahl a/s





PER MØLLER

Take good care of it!

Stainless Steel and Corrosion is a book worth owning for tradesmen, students, architects, engineers and even material researchers. It begins with a closer look at the main types and applications of stainless steel. From there it turns to metallurgy, with an introduction to the Schäffler Diagram and other professional aids. Following a description of the mechanical properties of the various types of steel, the book then reviews the role of individual alloy elements. Nickel is naturally given particular attention, as the price of this alloy element has caused stainless steel prices to soar in recent years. In the aftermath of such dramatic price swings, one asks: "Do we have to use nickel in stainless steel?" This question is addressed and answered in the book in a nuanced manner.

And then we come to corrosion.

Corrosion costs a great deal of money and represents around 5% of a country's gross national product. While it is impossible to fully prevent corrosion damages, studies show that corrosion costs can be significantly reduced - by up to 30% in some cases - by possessing the right knowledge. The author thus has good reason for dedicating almost a third of the book to this problem, as there is literally money to be saved by taking the right steps.

Chapter 8 offers help to anyone in need of help navigating the jungle of Werkstoff Numbers and EN designations. The chapter is followed by an overview of stainless steel forms, with a focus on everything from plate surface conditions and coils to pipes and fittings.

Metal working is naturally the next area of focus. The book illustrates that, even after purchasing the optimal material, new problems can quickly arise. This is particularly true if the material is welded - although even simple operations such as cutting, sawing and clipping present their own sets of challenges.

After processing comes surface treatment, which can be performed mechanically, chemically or electronically. Here the book covers everything from sandblasting and pickling, to passivation and electro polishing.

Chapter 13 bears the symbolic title, "In the event of an accident", and contains tips and good advice regarding the prevention and repair of corrosion damages. At the end of the book you will find a glossary of terms and a list of useful references for a full overview of the topic at hand.

On a general note, the book is written in an entertaining style and employs a conversational tone. The author has attempted to grab the reader's attention throughout the book, and does not let go until the message has been delivered. It is tough to put this book down, as it is packed with useful information which everyone should have access to.

Finally, a warning to new owners of this book: Take good care of it! This is not a book that should be loaned out, as you are not likely to see it ever again!

Per Møller

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INTRODUCTION

Stainless steel represents a large group of *passive* alloys, which, together, contain a common main element, iron (Fe), and all of which contain at least 10.5% (Cr) and a maximum of 1.2% carbon (C). The role of Cr is to passivate. Even though Cr is generally a less noble metal than iron, this passivation converts the steel from being a 'normal', active alloy that fits within the electrochemical series, to a passive alloy with a vastly improved corrosion resistance.

And this passivity is exactly what makes stainless steel such an excellent material! The combination of high corrosion resistance, reasonable prices, an attractive appearance and a high degree of workability has made stainless steel by far the most commonly used alloy within the full range of 'critical' applications. Stainless steel is indeed a global 'hit', and it is most certainly not a coincidence that it is extremely popular in dairies, slaughterhouses, the pharmaceutical and chemical industries, households, refineries, construction and design. In short, stainless steel is used anywhere one might desire an attractive, polished look combined with a material that is highly resistant to corrosion and easy to clean. Stainless steel may be the closest one comes to a corrosion-resistant, universal alloy that can be used for everything from mail boxes to skyscrapers.

Stainless steel is ideal for critical applications.



Figure 0.1: *Atomium is a Brussels landmark which displays the iron atom's cubic, space-centred structure (BCC). The sculpture is 105 metres high and was originally made in aluminium for the 1958 World Expo. In 2005 the coating was changed to acid-resistant 4404 (1.2 mm plates) supplied by Aperam. Photo: Thomas Pauly, Euro-Inox [11].*

*Global
production of
stainless steel*

Stainless steel's fantastic potential is reflected both in terms of production and applications. World production (measured as smelted steel) in 2001 was recorded at 19.2 million tonnes, and by 2006 this figure had jumped to 28.4 million tonnes. The global recession of 2008-2009 resulted in a slowdown in both consumption and production, and the figures for 2007, 2008 and 2009 were 27.6, 25.9 and 24.6 million tonnes, respectively [6]. Production rose once again, however, in 2010. As a matter of fact, the first quarter of 2010 resulted in over 23 million tonnes, so there is no doubt that stainless steel is has a very bright future.

While world production has risen steadily over the last ten years, the list of producing *countries* has changed significantly. In 2001, Western Europe produced 8.21 million tonnes, while the Americas and Asia produced 2.29 and 8.40 million tonnes, respectively. By contrast, the same figures from 2009 were 6.44, 1.96 and 7.13 million tonnes, while China alone jumped to 8.81 million tonnes, bringing Asia to a total of 15.94 million tonnes. The stainless steel world is facing East, and there is no sign of this development changing anytime soon.

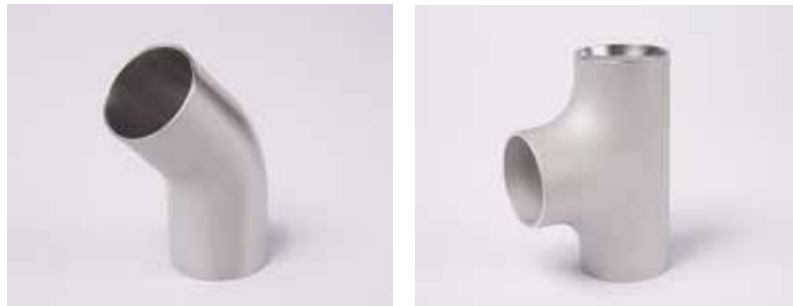


Figure 0.2: *Production of fittings has also risen dramatically in China in recent years, and both the 45° dairy fitting (left) and the T-piece (right) are manufactured in China. Photo: Kenneth Stig Mortensen, Damstahl a/s.*

*Stainless steel is
only 'stainless'
if..*

Unfortunately, even stainless steel is not 100% safe from corrosion. Despite its name, the steel can still rust under certain conditions, which is to say that the material is *conditionally rust-free*, as it must be treated carefully to obtain the most from it. Stainless steel is a lot like a quality car, as even a brand new Rolls Royce with its numerous qualities is not immune from damage. It is of enormous benefit to the car's service life if it is treated properly, and the same is true of metals and alloys - they must be treated properly.

*Stainless steel
is an either/or
material*

This is particularly true of stainless steel. The right steel must be selected for the right task; the right jointing method must be employed; and the right mechanical and chemical finishes must be applied. And even when all of this is done, the user must ensure that the steel is not exposed to conditions that it cannot endure; otherwise, the steel will easily become much less stainless than intended.

For those used to working with low-alloy carbon steel, the switch to stainless steel can be something of a culture shock. The use of carbon steel and galvanised steel most often involves a 'calculated risk', as the user's equipment will slowly deteriorate by corrosion. This means that, if the corrosion speed can be determined, the equipment's service life can be calculated. Stainless steel, on the other hand, is much more of an 'either/or' material: either it works well and the equipment's lifetime is practically endless, or it suffers from corrosion and the service lifetime is extremely short.

This either/or quality also means that the consequences of improper treatment are much greater with stainless steel than with carbon steel or galvanised steel. A mistake with a galvanised piece of equipment may result in a service life reduction from 20 to 15 years, while improper treatment of a stainless steel construction can reduce the service life from eternity to just a few months. Stainless steel is a more 'obstinate' material than galvanised or carbon steel, and the requirements for the various links in the production chain are thus greater.

In order to obtain the most from stainless steel, it is therefore incredibly important to become familiar with the material in question. For example:

- Why is 'acid-resistant' steel better than ordinary stainless steel?
- Is there a steel type more resistant to corrosion than acid-resistant steel?
- Why shouldn't we allow bluish heat tinting near weldings?
- Why does lack of bonding constitute a serious reduction in corrosion resistance?
- Why is fouling a problem?
- What makes ordinary sea salt so terribly corrosive?
- Why do cracks emerge directly beside the welds rather than through them?
- Why is low carbon steel advantageous?
- Why do iron contaminations create cosmetic defects?
- Why is coarse grinding work worse than a fine one?
- What does pickling entail, and why should the pickling be performed after the welding process?



Figure 0.3: *With its 828 metres distributed over 162 storeys, Burj Khalifa, located in Dubai, is the world's tallest building and one of its most impressive constructions. Due to the risk of sea salt, large sections of the building are made of type 4404, acid-resistant stainless steel.*

Constructive laziness: Doing things right the first time

Stainless steel is a science that houses a number of questions. The more one knows about the material, however, the easier it is to avoid serious mistakes and to keep clients satisfied. 'Constructive laziness' means doing things right the first time, and the information contained in the subsequent chapters should help to push you in the right direction.

Almost all books about stainless steel and/or corrosion are written for engineers or engineering students, while more practice-oriented tradesmen often have trouble finding material of a less theoretical nature. In order to remedy this, the author has sought to avoid the use of endless formulas, and has instead spiced up the text with a wealth of more or less decorative examples of corrosion damage. The power of example should not be underestimated, as one can certainly learn from mistakes made in the past.

Before we continue our discussion of stainless steel, we should first say a few words about terms and numbers. Interests of avoiding terminological confusion we have decided to stick with "stainless steel".

For most smiths and engineers, stainless steel is more or less synonymous with 'type 304' or 'acid-resistant type 316' steel. Both names derive from the dated, but unusually long-lived AISI system, which, at best, may be considered to be a bit out of step with reality. It is a bit like referring to a moped as a 'motorised bicycle', as AISI has not classified a new steel type since the 1960s. The fact that many people continue to use AISI terminology is, at best, a bit old-fashioned and, at worst, misleading.

Instead of the AISI numbers, the editorial staff has thus opted for the European EN numbers which, in turn, are based on the old German Werkstoff Numbers (W.-Nr.). A stainless steel type classified by the EN system may, for example, be called 'EN 1.4301'; however, for the sake of simplicity, in most cases we have dropped the 'EN 1.' and instead refer to the steel type as simply '4301'. Readers in need of a 'translation' between the modern EN system and the classic AISI numbers can refer to Table 8.3 page 151.

Stainless Steel and Corrosion

CHAPTER 6

CORROSION OF STAINLESS STEEL

Stainless steel is almost the perfect material for critical applications, but as with all other near-perfect materials stainless steel has its limitations. The steel cannot be subjected to just anything without consequence, and in the majority of cases the limitations of the steel are defined by its resistance to corrosion. Stainless steel is unfortunately not always as stainless as its impressive name suggests.

Repassivation of chromium oxides

Stainless steels usually excellent resistance to corrosion is down to an ultrathin layer of oxides of especially chromium and iron, and although this film is only a few *nanometres* thick, it is still so dense and strong that the steel is effectively 'isolated' from the surrounding environment - similarly to an ultrathin paint. If, despite all precautions, a hole occurs in the protective oxide layer, it quickly restores itself, and the steel is again protected. This mechanism is called *repassivation*.

Unfortunately, even the best-laid plans can go awry. Under unfortunate circumstances, the oxide layer can break down without subsequently being restored, and this may result in serious corrosion attacks. Once the corrosion has commenced, penetration may occur rapidly, and the use of stainless steel therefore often becomes a kind of either/or situation where the difference in between the two extremes is very slight. If corrosion initiation can be prevented, stainless steel will last almost forever. If not, serious corrosion will occur very quickly, and the life of any equipment can become alarmingly short. Stainless steel is only *conditionally stainless*. Depending on the type of steel and environment, stainless steel can be attacked by a whole range of more or less damaging types of corrosion.

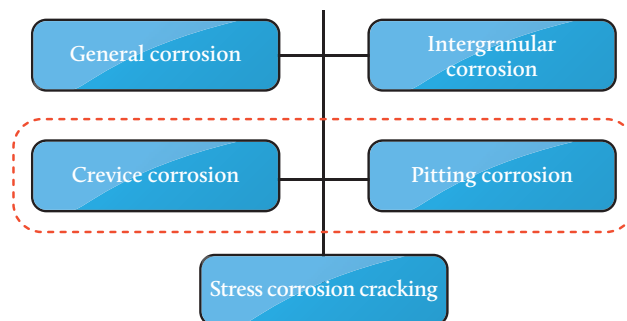


Figure 6.1: *Stainless steel is only "conditionally stainless", and, depending on steel quality and environment, there is a risk of a whole host of corrosion nightmares. Pitting corrosion and crevice corrosion are both quite common and are often collectively referred to as 'local corrosion'.*

General corrosion produces a uniform loss of material

6.1 General corrosion

General corrosion is also called *acid corrosion* as it is a type of corrosion that in stainless steel is often found in *very acidic*, but also in *very alkaline media*. As opposed to the four other types of stainless steel corrosion, general corrosion is characterised by both anode and cathode reactions taking place all over the surface. This means that the *whole surface is activated* and thereby corrodes more or less uniformly.



Figure 6.2: *Stainless steel bolt (4301) after prolonged exposure to strong pickling acid (nitric acid-hydrofluoric acid). Note that the corrosion is very uniform and that the quantity of corroded metal is quite large.*

General corrosion is the only one of the five types of corrosion where the steel does not behave like a fishing line. This is because general corrosion involves a fairly uniform breakdown of the protective oxide layer. Consequently, the loss of material is equally uniform, and while the weight loss, expressed in grams per square metre, may be quite large, the *corrosion rate* (measured in mm per year) is usually quite low. Similarly, the time to penetration is often correspondingly long.

In non-passivating metals and alloys, general corrosion is the most common type of corrosion, but for passivable alloys it is relatively rare. This is because a total activation of the surface can only take place in extreme media. General corrosion is therefore a very uncommon type of corrosion in stainless steel, and it is very rare that general corrosion is the type of corrosion that determines the life of the stainless steel equipment.

General corrosion in strong acids or bases

As stated above, general corrosion takes place in *very acidic* or (more rarely) in *very alkaline media*. Typical media are sulphuric acid, phosphoric acid, etc. while with alkaline media you may encounter general corrosion in very strong and hot sodium hydroxide, potassium hydroxide, etc.

General corrosion in molten salts

In addition to aqueous media, general corrosion is a risk if the stainless steel is exposed to molten salts. Just as in strong acids, liquid, chloride and fluoride salts (e.g. fluxes for soldering, temperatures typically > 400°C) may entail total breakdown of the protective oxide layer of the stainless steel which will result in rapid general corrosion. General corrosion in alkaline media or molten salts is, however, rare. Below the emphasis will therefore be on the strong, aqueous acids. A typical example of general corrosion of stainless steel in molten salts can be found in Figure 6.6.

Even in strong acids, stainless steel can achieve a certain level of passivity, and in practice there is a big difference between an acid that simply thins the passive layer, but does not entirely dissolve it, and an acid that eats away the whole of the passive layer and immediately attacks the underlying steel. Relatively weak and pure acids (e.g. citric acid, acetic acid or formic acid) only thin the naturally occurring oxide layer slightly. The oxide layer is restored with the same speed, and corrosion loss is minimal - at least when the acids are pure. If the acids contain aggressive ions (especially chloride), the situation may become far worse, especially at high temperatures.

6.1.1 Isocorrosion Diagrams

The corrosivity of a certain acid towards various types of stainless steel can be read on a so-called *isocorrosion diagram*. An isocorrosion diagram is a set of curves showing the acid concentration on the x axis and the temperature on the y axis. Each curve shows the conditions that are required to peel off precisely 0.1 mm of steel per year. Above the curve, conditions are more corrosive than 0.1 mm/year, while under the curve conditions are *milder*. An example of an isocorrosion diagram for different types of stainless steel in sulphuric acid can be found in Figure 6.3.

Isocorrosion diagrams indicate combinations of metals and environments with the same corrosion rate

The corrosion rate for a given combination of stainless steel, acid and temperature can be determined by *simple weight loss experiments*. All you need is a sheet with a known area and known weight, and after a certain length of time in the acid the sheet is weighed again - the amount of metal that has corroded away can then be calculated. This technique can only be used for corrosion experiments where the loss of material is entirely or almost entirely homogenous - such as general corrosion. For all other types of corrosion, the weight loss technique will, at best, be an imprecise way of measuring corrosion.

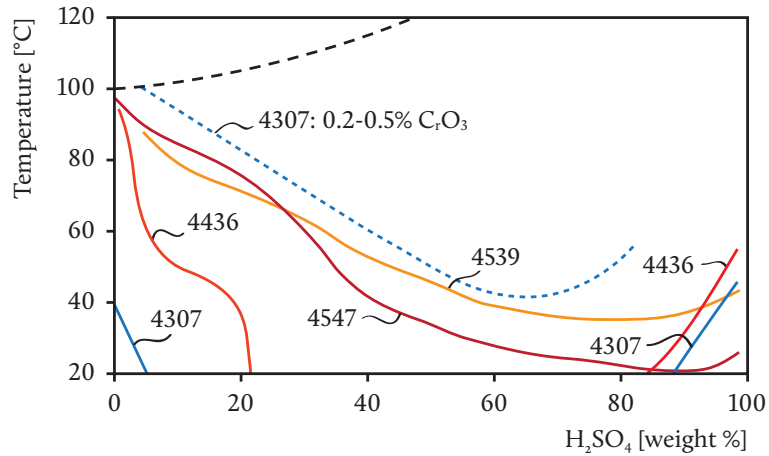


Figure 6.3: *Isocorrosion diagram for different types of stainless steel in aerated sulphuric acid. The curves for each type of steel show the conditions required to remove 0.1 mm of steel per year. Above the curves the corrosion loss is worse than 0.1 mm/year; below it is better. The black dotted line indicates the acid's boiling point, while the blue dotted line shows steel 4307 in sulphuric acid with 0.2-0.5% Cr₂O₃ added as an inhibitor. Both higher and lower content of Cr₂O₃ increase the corrosion rate. Working drawing produced on the basis of [5].*

Corrosion curves make the calculation of corrosion rates possible

A good, but far from cast-iron rule of thumb says that the corrosion rate *doubles* for every 10°C temperature increase. Likewise, a temperature reduction of 10°C will generally result in a *50% reduction* in corrosion rate. It should be noted here that no matter how low the temperature drops, the corrosion rate will never fall to 0 mm/year. Unlike all other forms of corrosion, general corrosion never completely disappears. There will always be a microscopic corrosion loss, even at near-freezing temperatures.

The fact that *expected corrosion loss* can be calculated also means that a pipe system's service life can be estimated. If, for example, corrosion loss is 0.1 mm/year, an *additional 2 mm* of pipe thickness will mean a service life of 20 years. Isocorrosion diagrams for various types of stainless steel exposed to countless acid and chemical compounds can be found in Sandvik's Corrosion Handbook [5].

6.1.2 Environmental Factors in Acids

The risk of general corrosion of stainless steels exposed to acids normally depends on:

- The acid type and concentration (acidity, pH)
- The acid's oxidation capacity
- Temperature
- Type and concentration of impurities

Most often: The higher the acid concentration, the worse the corrosion

The acid's concentration is not as unequivocal as might be expected. For most types of acid, *higher concentrations* generally mean greater weight loss of the steel. However, at extremely high acid concentrations - e.g. > 90% of sulphuric acid (H_2SO_4) - the lack of water actually results in the acid failing to function properly as an acid, which is to say that water is thus the limiting factor. This is only the case, however, with sulphuric acid; for almost all other acids, the following general rule applies: The higher the concentration, the worse the corrosion.

For all non-passivating alloys, it generally follows that the more active the cathode reaction (see Chapter 5), the worse the corrosion, though this is not necessarily the case with *passive* alloys. The formation of passivating chromium oxides requires a certain oxidising effect, and, up to a certain limit, stainless steel thus performs *better* in oxidising acids than in non-oxidising acids.

Oxidising and non-oxidising acids

This effect is illustrated in Figure 5.8 on page 64, where the strong, non-oxidising acids (sulphuric acid, phosphoric acid, etc.) will typically make the steel fall into the yellow "active area" with resulting high corrosion rates. An oxidising acid, on the other hand, such as a pure nitric acid or peracetic acid will make the steel jump up into the green "passive area" where the corrosion rate is far lower despite the higher potential (and thereby theoretically greater driving force). The corrosion rate is not only governed by *energy*, but just as much by *kinetics*.

This effect is clearly seen with stainless steel in sulphuric acid (see Figure 6.3) where even small amounts of the highly oxidising chromic acid, CrO_3 , has a strong inhibiting effect on the corrosion of 4307 steel. This is seen by the curve's high location in relation to the pure sulphuric acid. If the concentration of CrO_3 is increased beyond the indicated 0.2-0.5%, the curve will fall again as a sign of "overdosing". Other oxidants such as *hydrogen peroxide* (H_2O_2) has the same beneficial effect and can therefore be used as a corrosion inhibitor in sulphuric acid. Peroxide-inhibited sulphuric acid is often used as a substitute for nitric acid in applications where remains of nitrates (NO_3^-) for various reasons are unwelcome, e.g. in the cleaning of milk tanks.

Anodic protection due to copper

The temperature is always dangerous

The composition of the steel itself can also affect the oxidation capabilities of the medium. 1-2% of copper in the steel acts as an efficient catalyst for the cathodic hydrogen reaction and thereby pushes the corrosion potential from the low, active region to the higher, passive one. The corrosion potential is increased, but due to the passive effect the corrosion current (and thereby the corrosion velocity) becomes significantly lower. This effect means that copper alloyed steel is significantly better in reducing acids than similar steel types without copper. The effect is called *anodic protection* and is known from e.g. the austenitic 904L (EN 1.4539) and Sanicro 28 (UNS N08028) as well as the superduplex Ferralium 255 (UNS S32250), which are all very resistant in reducing acids such as phosphoric acid and sulphuric acid.

The temperature is a generally very underestimated, but extremely important factor. The temperature works uniformly negatively, and generally the higher the temperature, the higher the corrosion rate – irrespective of the type of acid, type of steel or air pressure over the Azores. In fact, all types of corrosion are affected by temperature, and all else being equal the higher the temperature, the worse things get.

The last factor, the impurities, may be surprising, but as we know stainless steel belongs to the group of passivating alloys and as such the resistance to corrosion is completely dependent on the condition of the passive layer. Any substance affecting the passive layer will therefore affect the resistance to corrosion, and particularly ions like chloride (Cl⁻), fluoride (F⁻) and other halogenides are apt to break down the steel's protective oxide layer and thereby increase the corrosion rate significantly.

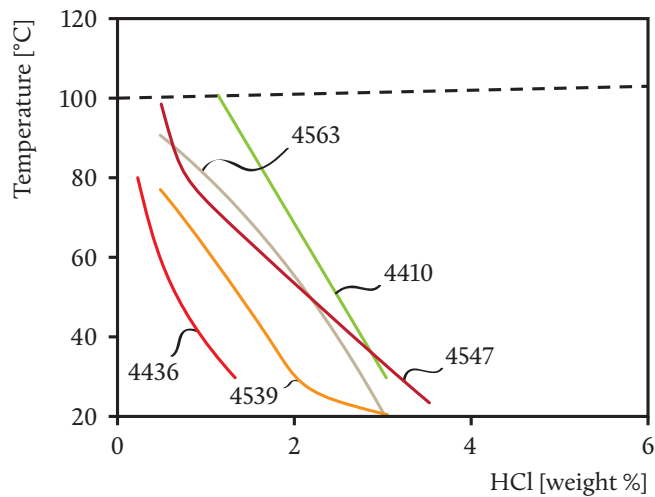


Figure 6.4: Isocorrosion curves (0.1 mm/year) for a number of different stainless steels in hydrochloric acid (HCl). Working drawing produced on the basis of [5].

Of these, *chloride* is clearly the greatest culprit which can clearly be seen in Figure 6.4, which shows the corrosion conditions for different types of stainless steel in *hydrochloric acid* (, HCl). If you compare this with Figure 6.3, it will be noted that hydrochloric acid of 2% at 40°C is far more corrosive to *all types of stainless steel* than a 20% sulphuric acid at the same temperature. This is due to the sad ability of chloride to peel off the steel's oxide layer and then attack the steel itself. By adding chloride to an otherwise relatively harmless acid, you get *diluted hydrochloric acid* which will be far more corrosive to the steel than the pure, chloride-free acid.

Impurities in acids are dangerous

In an acid like phosphoric acid, impurities are usually brought in via the raw materials (raw phosphate), and all else being equal these *impure, 'technical' qualities* are *more corrosive* than similar pure acids. Chloride may, however, also come from water which is why care should be taken about the water used to dilute the acid. EU tap water may contain up to 250 mg/l chloride and water from private wells much more than that – especially in low-lying, coastal areas such as Lolland and Falster in Denmark. Even apparently small amounts of chloride from water can turn otherwise relatively harmless acids into extremely corrosive ones, and acid diluted with tap water will therefore be more corrosive than a similar acid diluted with demineralised water. From a corrosion point of view, all acids should be diluted with demineralised water.

6.1.3 The effect of the alloying elements on general corrosion

When you look at the *sequence* of the various curves in Figure 6.3 and Figure 6.4, it should be noted that 4301 is consistently the lowest indicating the *poorest* resistance. Then comes 4436 (\approx AISI 316 with 2.5-3.0% Mo, see Chapter 8), and even higher is the duplex 4462 and the austenitic 4539 and 4547. The various types of stainless steels are thus not equally resistant to general corrosion which quite naturally is due to the differences in the alloy compositions of the steel.

The elements with the greatest *positive* effect on resistance to general corrosion are:

- Chromium (Cr)
- Molybdenum (Mo)
- Nickel (Ni)
- Copper (Cu) in non-oxidising acids

General corrosion involves uniform activation of the entire surface, and the effect of chromium is therefore generally somewhat *smaller* than when it comes to maintaining the perfect passive layer. This is especially true of non-oxidising acids, while Cr is particularly useful to resistance in the strongly oxidising nitric acid. This has the slightly curious effect that 'standard stainless' steel in the 4301/07 category actually becomes slightly more resistant than 'acid-resistant' steel in pure, strong nitric acid. Here Mo does not help much, whereas the fact that 4307 contains 1% more Cr than 4404 has a positive effect.

When we talk about pitting corrosion (see Section 6.3), Cr and Mo are regarded as having more or less the same effect (with a factor 3.3 difference), but this is not the case for general corrosion as previously explained. In the non-oxidising (reducing) acids, Mo is, however, significantly better than Cr at passivating, and this means that the more Mo in the steel, the better its resistance to corrosion.

Nickel (Ni) is also good against general corrosion across the board. Ni is quite simply a more noble metal than both Cr and Fe, and for this reason it corrodes slower, so the more Ni in the steel, the better. The effect of both Ni and Mo is clearly seen in Figure 6.3, where the acid-resistant 4436 copes significantly better than standard 4301 in sulphuric acid.

*Austenites best
in strong acids*

The significance of nickel against general corrosion is doubled by the fact that the structure of the steel also has a certain influence. Usually the nickel-containing, fully austenitic phase is *more* resistant to strong acids than the ferritic and martensitic phases that contain little nickel. In practice this is often seen by e.g. welded pipes where both the longitudinal and circumferential welds contains a few percentages of ferrite to prevent heat cracks during the welding process. The drawback is that the ferrite phase is weaker in strong acids which can be seen in the darker welds of the specimens in Figure 4.4 on page 46 and Figure 6.5.

The positive effect of copper is due to stainless steel being better suited to oxidising rather than non-oxidising (reducing) acids. Copper (Cu) has an accelerating effect on the cathodic development of hydrogen (Eq. 5.5) which has the useful effect that the steel almost in itself makes the acid more oxidising. As discussed above, this moves the corrosion effect from pure, non-oxidising sulphuric acid in the direction of a more oxidising, but less corrosive acid such as nitric acid, and the steel itself goes from the critical active condition to passive (see Figure 5.8 on page 64). This handy effect can be used commercially, and a couple of highly alloyed, non-corrosive austenites like 904L (4539, UNS N08904) and Sanicro 28 (4563, UNS N08028) and the superduplex Ferralium 255 (4501, UNS S32760) have all had small amounts of copper added to increase resistance to sulphuric acid, phosphoric acid, etc.

*Impurities in the
steel are critical*

*Nitric Acid
Grade and free-
machining steel*

Finally, it should be mentioned that *impurities* and *alien phases* in the steel have a very *negative* effect. Any alien phase is a possible point of attack which is the direct reason that in Germany they use a special variant of 4307, a "Nitric Acid Grade", which is especially designed for nitric acid. This type contains a particularly low level of impurities and other non-metallic phases which benefits the resistance to corrosion.

Another classic is the 0.15-0.35% sulphur (S) added to stainless free-machining steel (EN 1.4305) to make the steel short-chipped, but which is extremely detrimental to all types of corrosion – including general corrosion. This can clearly be seen if you attempt to pickle free-machining steel. While standard stainless steel corrodes relatively uniformly, free-machining steel has a significantly increased corrosion in the chip-breaking manganese sulphides. One example is Figure 4.4 on page 46.



Figure 6.5: *General corrosion in stainless steel shackle (4301) after a long period in a nitric acid/hydrofluoric acid-based pickling bath. Note that the whole item is corroded, but that the end surfaces of the steel bar and welds have been slightly more aggressively attacked than the rest.*

6.1.4 General Corrosion in Alkaline Media

In most cases, general corrosion is something that takes place in strong acids while it may come as a surprise for many that it may also take place in alkaline media. In the strong alkaline media, in particular, many metal salts (incl. oxides) are dissolved as complex ions, and this dissolution of course affects the passive layer negatively. This effect is often seen with metals such as aluminium and zinc which both corrode aggressively in a strong base, but even stainless steel can corrode at an extremely high pH.

Along with the acidic conditions, extreme bases cause a homogenous thinning of the oxide layer and subsequent corrosion of the stainless steel itself. Luckily, this weak, general corrosion is rarely something that affects the life of the steel to any significant degree. Even at 30% sodium hydroxide, NaOH, at 100°C the corrosion loss for both 4301 and 4401 will be approx. 0.1 mm/year, while the loss under gentler conditions and particularly at lower temperatures will be much less. Ferritic stainless steel is generally more sensitive to general corrosion in alkaline media than austenitic.

Strong bases are rarely a problem in austenitic steel



Figure 6.6: Molten salts at high temperatures may have the same effect on stainless steel as strong aqueous acids. This 6 mm thick base plate from an oven made of 4571 ('316Ti') has in just two years suffered from penetration due to contact with a strong fluoride-based flux for the soldering of aluminium. The flux had a fluoride content of up to 50%, and the temperature has been approx. 550°C.

General corrosion in alkaline media is rarely a problem, but there are examples of problems caused by the weak but unavoidable liberation of metal in the solution. In strong alkalines, metals will often deposit as hydroxides which in most 'technical' contexts is unimportant, but if the base subsequently is to be used for e.g. pharmaceutical products, this is unacceptable.

Caustic
brittleness and
stress corrosion
cracking

The biggest risk of corrosion in strong alkaline media is not in fact general corrosion, but *caustic brittleness*, a type of stress corrosion cracking which produces intergranular cracks and which may result in penetration in a very short period of time. This is, however, a risk which for austenitic steel is only a serious factor at temperatures above 140°C.

6.1.5 Transpassivity and Stray Currents

By far the most serious cases of general corrosion occur in the potential that electrochemists call 'the active area' (see Figure 5.8 on page 64). This typically occurs at quite low potentials while general corrosion is rarely a problem in the passive area.

It may, however, be that the potential is forced up so high that the steel enters the *transpassive* area. This hardly ever happens purely chemically, but may occur if the steel is exposed to inexpedient, *electrical* influences such as close contact with cables and wires. If this occurs, the steel may be exposed to an extremely high potential causing the steel's passive layer to dissolve anodically, and corrosion will again occur.

A good example of such transpassive corrosion is sometimes seen on buried pipes located too close to buried electrical cables. The power from the cables generates an electrical field which can 'polarise' the stainless steel and thereby push it into the transpassive area. The result is serious corrosion in those places where the electrical resistance through the ground between cable and stainless steel pipe is the smallest - typically in those places where the physical distance in between pipe and cable is the shortest.



Figure 6.7: Severe penetration in a buried stainless steel pipe (4404) as a result of short distance to a buried, live cable. This has pushed the steel from its ideal passive condition to 'transpassive', and corrosion commences. Note the lack of small corrosion pits.

This effect is sometimes called 'stray currents', and the way to prevent these is to ensure sufficient electrical resistance between cables and steel pipes either by avoiding the pipes and cables being too close or by ensuring that the water content in the ground is kept sufficiently low - and that addition of electrically conductive salts is avoided. Alternatively, an 'insert' can be introduced, e.g. carbon steel, which can function as an 'electric screen' between the cable and the stainless steel pipe.

6.2 Pitting corrosion

The mechanism of pitting corrosion is the complete opposite of general corrosion. While general corrosion causes an even and homogenous breakdown of the protective oxide layer and subsequent homogenous corrosion, pitting causes *local breakdown* of the oxide layer. This local breakdown makes the steel produce an 'internal galvanic coupling' (see Chapter 5) where the small, corroding stain functions as an *anode* while the rest remains an inert cathode.

'Fishing line corrosion'

Pitting corrosion is the perfect example of an either/or type of corrosion. Where general corrosion produces large material loss expressed in g/m^2 , pitting corrosion, on the other hand, results in a *very small* loss of material. However, as the attack is local rather than general, penetration may occur very quickly. Pitting corrosion is the ultimate 'fishing line corrosion' (see Figure 5.12 on page 71), where either things go perfectly well forever or where penetration takes place in a very short period of time.

Whether general corrosion or pitting corrosion takes place is usually a question of the acidity of the solution. At very low or very high pH a general

Passivity = risk of local corrosion attacks

activation of the surface of the steel will take place, and the result is general corrosion as in the yellow active area in Figure 5.10 on page 69. In the large, wide area between the extremes, typically from pH 2 to pH 12, the steel will, to a greater or lesser extent, passivate (see Figure 5.10 on page 69, the green passive area), and then we have the risk of local corrosion attacks – such as e.g. pitting corrosion. A drawn model of the difference between the total activation during general corrosion and the very local activation during pitting corrosion can be found in Figure 6.8.

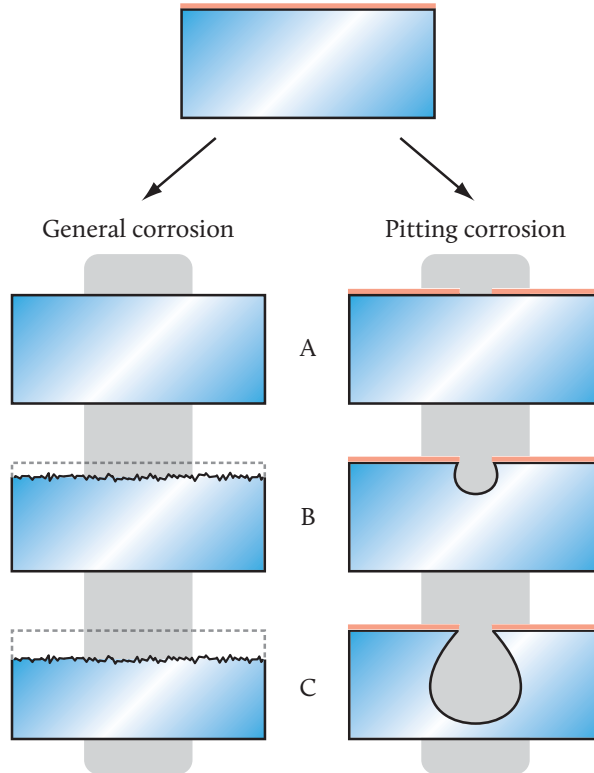


Figure 6.8: *Illustration of the differences between the mechanisms for general corrosion and pitting corrosion respectively. While general corrosion will produce by far the greatest loss of material, pitting corrosion will produce the fastest penetration.*

Crevice corrosion is similar in its mechanism to pitting corrosion, but differs in that it takes place in geometrically difficult accessible areas where all fluid replacement takes place by *diffusion* rather than *convection*. Pitting corrosion and crevice corrosion are often called by their generic name of 'local corrosion', but due to the differences in their mechanisms, crevice corrosion has been given its own subsection. All the following observations about environmental factors and alloying elements do, however, generally apply to both pitting corrosion and crevice corrosion.

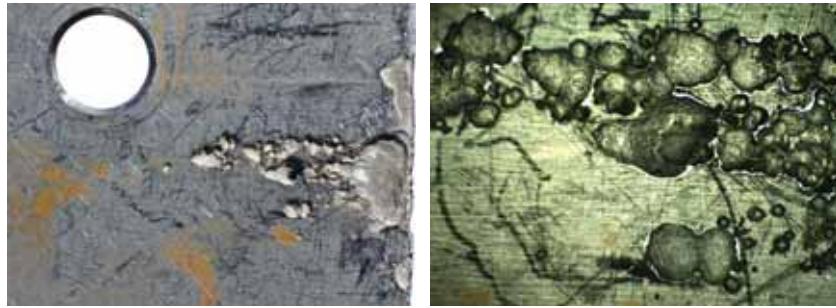


Figure 6.9: *Pitting corrosion in 0.5 mm thick, stainless steel 4301 sheet after only a few days immersed in a mixture of salt (NaCl) and hydrogenperoxide (H_2O_2). While 99% of the surface is completely unaffected, four day's of corrosion was sufficient to produce penetration. The picture on the right is a microscope photo of the same item; the penetration is right in the center.*

6.2.1 Environmental factors in pitting corrosion

General corrosion is, as described above, a type of corrosion which is *always* taking place. Depending on the type of acid, pH, temperature, impurities, type of steel and other factors, the corrosion will take place at a faster or slower pace, but it will never be zero. Compared to general corrosion, pitting corrosion is much more an either/or type of corrosion. Either things go incredibly well or else they go very, very badly. There is nothing in between.

The environmental factors influencing the risk of *pitting corrosion* for a given type of stainless steel are usually the following:

- Chloride concentration
- Temperature
- Corrosion potential (type and concentration of oxidants, the cathode reaction)
- pH (acidity)

In general the risk of pitting corrosion *rises* with *increasing chloride concentration*, *increasing temperature*, *increasing corrosion potential* (cathode reaction) and *decreasing pH* (more acidic solution).

6.2.2 Critical Pitting Temperature (CPT)

The interaction between, in particular, chloride concentration and temperature can be measured using the 'critical pitting temperature' (CPT). For a certain type of steel in a certain medium (and at a determined corrosion potential), the CPT is the temperature above which pitting corrosion will take place. In practice, CPT is measured by exposing a steel electrode to the medium concerned. The temperature is slowly increased step by step, and the temperature at which pitting corrosion occurs is defined as CPT.

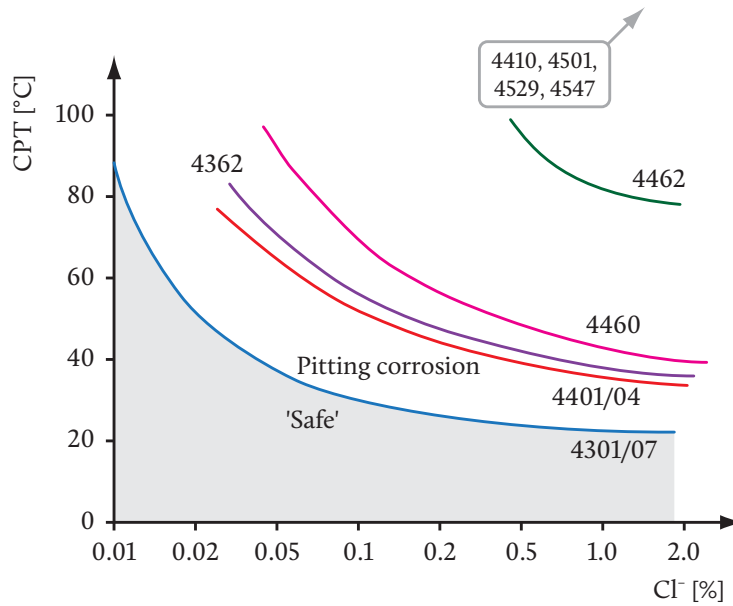


Figure 6.10: Laboratory measurements of the critical pitting temperature (CPT) for different kinds of stainless steel at varying chlorine contents. The experiments were carried out under conditions equivalent to "well aerated tap water". For every type of steel, the environment has been constant while the temperature has been increased until pitting corrosion occurs [1, 5].

CPT = critical pitting temperature

Such a series of CPT measurements for different qualities of steel in different media can be seen in Figure 6.10. It should be noted that all tested types of steel produce the same *shape* of the curve: the higher the content of chloride in the water, the lower CPT will be measured – and vice versa. Similarly, the lower the chloride concentration, the higher is CPT. In practice, this shows that the higher the chloride, the lower is the temperature to which the stainless steel equipment may be exposed to – regardless the steel type. This illustrates very well that both increased chloride and a rising temperature have a uniformly negative effect on the corrosion resistance of the steel, but if one factor is improved, greater deviation is allowed in the other.

CPT v. chloride content

Curves such as those in Figure 6.10 have all been carried out under conditions equivalent to "well aerated, pH-neutral water". By experience, *well aerated water* is the equivalent of a corrosion potential of $300 \text{ mV}_{\text{SCE}}$, where SCE stands for 'Saturated Calomel Electrode', a reference electrode 246 mV above the defined zero of $0.000 \text{ mV}_{\text{SHE}}$ (see Chapter 5). $300 \text{ mV}_{\text{SCE}}$, thus corresponds to $546 \text{ mV}_{\text{SHE}}$.

This kind of CPT graph can be used as a *material selection guide*. The curve for each steel type marks a kind of limit and *under* each curve there is a reasonable certainty against pitting corrosion, while *above* the curve there is great risk of corrosion. If "normally aerated, pH-

*Pressure testing
of pipe systems*

neutral water" (with e.g. 250 mg/l chloride, the maximum in EU tap water) is used, it is seen from Figure 6.10 that steel type 4301 only lasts to approx. 50°C without suffering from pitting corrosion. If the chloride content is increased to 500 mg/l, the temperature is reduced to 38°C and at 2000 mg/l (= 0.2%) only 25°C is possible.

The higher the chloride concentration, the poorer the corrosion resistance, which needs to be taken into consideration for e.g. pressure testing of pipe systems. It is possible that the steel will be fine in standard tap water with max. 250 mg/l during the pressure testing itself, but remaining drops of water may cause problems. The water evaporates, but the salts do not, and the chloride content can easily become much higher than the original 250 mg/l in the drops of water. This is the same evaporation effect that over thousands of years has created the Dead Sea, and several times corrosion has occurred due to evaporation of the pressure testing water. Corrosion at the bottom of pipes after pressure testing indicates such damage.

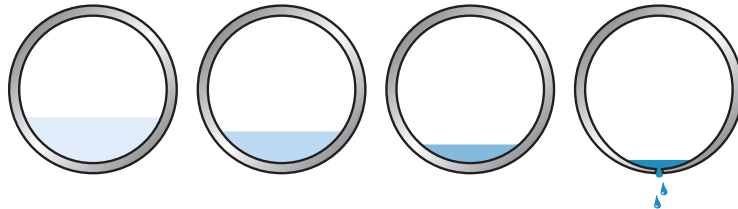


Figure 6.11: *Remaining drops of water from e.g. pressure testing of pipe systems may cause unpleasant surprises. As the water evaporates, the salt content increases, and the conditions gradually become more corrosive. The risk of bacterial growth does not improve the situation.*

If you look at the CPT curves in Figure 6.10, it can be seen that very high chloride concentrations almost make the curves run completely horizontally. This is a sign that there is no great difference between the corrosion conditions at 1% Cl⁻ and 2% Cl⁻. At the lower end, a doubling of the concentration has much greater effect which is not really as strange as it seems. With more than 1% chloride, the corrosive agents are so dominant that a bit more makes no difference.

*Extreme salt
concentrations
give low oxygen
solubility*

In practice, one may even encounter a 'softening effect' at very high salt concentrations as the solubility of oxygen is lower in strong solutions than in weak ones. This often means that a *high* salt content is accompanied by a *lower corrosion potential* which may even *improve* the resistance to corrosion (see below in Section 6.2.3). Concentrated salt solutions are thus not necessarily worse than diluted ones as the increase in chloride is compensated for by a reduction in the corrosion potential - the driving force of the corrosion.

If strong oxidants are present (e.g. peroxide or hypochlorite), the reduced solubility of oxygen unfortunately does not play a role, and the corrosion conditions uniformly become worse at higher concentrations of chloride. Trying to improve the corrosion conditions by increasing the salt concentration is therefore not recommended.

6.2.3 Corrosion Potential and pH

The significance of the *cathode reaction* (see Chapter 5) is reflected in the *corrosion potential* which may be translated into the 'oxidation power' felt by the steel. The higher the corrosion potential, the more actively the cathode reaction works as electron consumer and the easier it is for the steel to yield electrons - i.e. to corrode.

CPT v. corrosion potential

Figure 6.12 shows a series of CPT experiments with the same, acid-resistant type of steel (4401/04) in the same media, but exposed to three different corrosion potentials. The 300 mV_{SCE} curve thus corresponds to the 4401 curve from Figure 6.10, while the curves for 200 and 400 mV_{SCE} simulate less oxidising and more oxidising conditions, respectively.

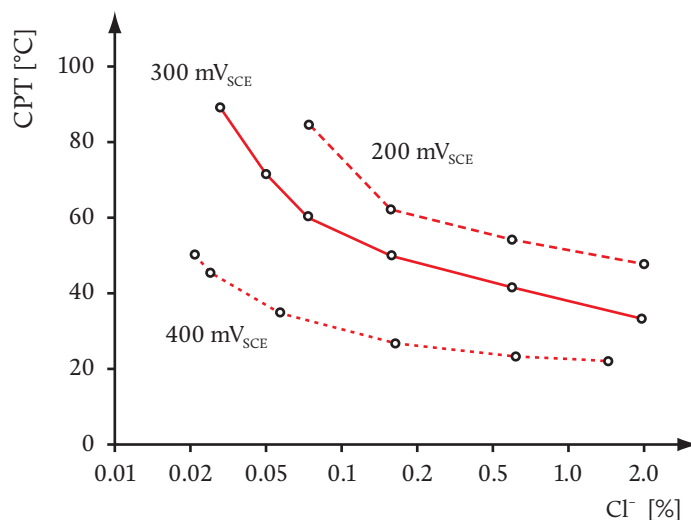


Figure 6.12: *The critical pitting temperature (CPT) for acid-resistant 4401/04 steel carried out in the same media but at three different corrosion potentials. The 300 mV_{SCE} corresponds to the maximum achievable for standard aerated tap water, while the +200 and +400 mV_{SCE} indicate less oxidising and more oxidising conditions, respectively [1, 5].*

Note that the curve at 400 mV_{SCE} is significantly lower than the curve at 300 mV_{SCE}, which indicates that less is required to fall into the wrong side of the curve. Inversely, the curve at 200 mV_{SCE} lies significantly higher as a good indication that the steel becomes *more* resistant to pitting corrosion. Although 100 mV does not sound like much, it is quite a lot in terms of electrochemistry (cf. Table 5.1 on page 55), and the negative effect of an increased corrosion potential is in practice very important. The more active the cathode reaction, the higher the corrosion potential and the lower the steel's resistance to corrosion.

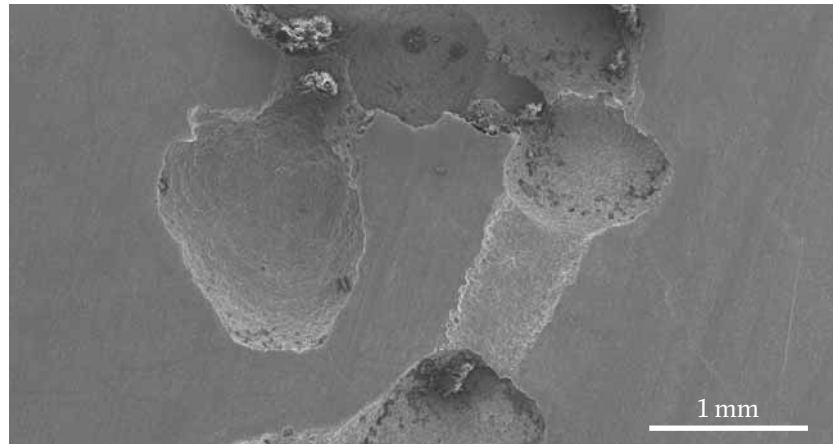


Figure 6.13: *Pitting corrosion photographed with a scanning electron microscope (SEM). The specimen originates from the same trial series as the one in Figure 6.9, i.e. 4301 exposed to a critical mixture of salt and hydrogen peroxide. Note the local nature of the pitting. Photo: Metallographer Laila Leth, MEK/DTU.*

Hydrogen peroxide is a powerful oxidant and an excellent electron eater which can be seen from its position in the electrochemical series Table 5.1 on page 55. In practice, hydrogen peroxide can force the corrosion potential of the steel above $+500 \text{ mV}_{\text{SCE}}$ ($+746 \text{ mV}_{\text{SHE}}$), which is the direct cause why the corrosion experiment in Figure 6.9 produced penetration in such a short period of time.

*Oxidising
disinfectants*

Many *cleaning agents* contain strong oxidants such as peracetic acid, persulphate, chlorine, hypochlorite or the above hydrogen peroxide, which all help to speed up the corrosion potential considerably. The combination of saline media and the remainder from strong oxidising cleaning agents is pure poison for stainless steel and a frequent cause of serious corrosion damage at dairies, abattoirs and other locations where frequent and efficient cleaning takes place. The solution is to ensure that the cleaning time is *kept short* (typically 15-60 minutes) so that long-term effects are avoided and so that the corrosion does not initiate at all.

*Cathodic
protection of
stainless steel*

The opposite, positive effect is seen when coupling *immersed*, stainless steel constructions with mild steel or galvanised steel. Just as in Figure 5.8 on page 64 and Figure 5.9 on page 65 the most precious metal (stainless steel) will be protected while the least precious metal (mild/galvanised steel) will be exposed to additional corrosion. As the area of e.g. reinforcement bars is very large compared to the area of stainless steel, the additional contribution from the galvanic coupling will be relatively small. Thereby, the stainless steel will be cathodically protected without consequence to the mild steel reinforcement bars. Because of its wide and efficient passive zone (see Figure 5.10 on page 69) stainless steel is actually well suited to cathodic protection

although in many cases this happens by chance, e.g. by screwing the swimming pool's stainless steel ladder into the reinforcement bars of the concrete.

The last key factor is the acidity of the water, *pH*. In the large neutral range, pH usually has a relatively *small* effect on the steel itself, but may nonetheless affect the corrosion conditions considerably. pH is an expression of the concentration (or more correctly *the activity*) of hydrogen ions (H^+) in the water, and the higher the concentration of H^+ , the lower the pH. Any reaction involving H^+ will therefore depend on the pH, and here it should be noted that several of the relevant *cathode reactions* in Table 5.1 on page 55 involve precisely H^+ . The acid reaction itself, the oxygen reaction, the hydrogen peroxide and hypochlorite (as cathode reactions) use H^+ , and all reactions are therefore accelerated by an increased concentration of H^+ – i.e. a falling pH.

6.2.4 Impurities, Salts and Other Unknown Factors

In addition to the environmental factors discussed above, a wide range of other factors may affect the corrosion resistance of the steel and thereby the position of the CPT curves. First, it is worth noting that *all* CPT curves created in the laboratory are at best rose-coloured depictions of a much more complex reality. The experiments are all carried out with *perfectly processed laboratory samples* without cracks, grinding marks, welds, heat tinting, inclusions or other weaknesses, and the results of the curves are therefore to be regarded as a *best case scenario*. The only thing that is certain is that reality will never be better than the laboratory data, and in practice reality is often much worse (see Chapter 10). Therefore the CPT curves should only be regarded as a guide – not as absolute truths. The CPT curves are nonetheless excellent for showing how, in particular, chloride and temperature affect the steel's resistance to pitting corrosion, but like the corrosion potential (see Figure 6.12) different factors may move the curves up and down and thereby influence the steel's resistance to corrosion.

As illustrated in Figure 6.12 oxidants generally have a *negative* effect on the steel's resistance to pitting corrosion, but also substances that are not electronically active may affect the position of the CPT curves and thereby the resistance of the different types of steel. A good rule of thumb here is that substances that are *not* either oxidising (such as oxygen or peroxide) or destructive to the passive layer (chloride) often affect the resistance to corrosion *positively*. '*Impurities*' such as sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) are not electrochemically active under normal conditions, and they do not degrade the steel's protective oxide layer, but just like chloride they may adsorb to the surface of the steel and this effect alone can be beneficial. The more of the surface taken up by the corrosion-neutral ions, the less room there is for chloride, and, by experience, sulphate in the same *molar* concentration as chloride can provide 10°C extra in terms of CPT. Under normal conditions sulphate

All measurements are for 'ideal test samples'

Impurities in the water

thereby acts as a corrosion inhibitor, but the effect is not completely certain. There are examples of pitting corrosion in completely chloride-free media where microbiological activity can use sulphate to create an unfortunate local environment.

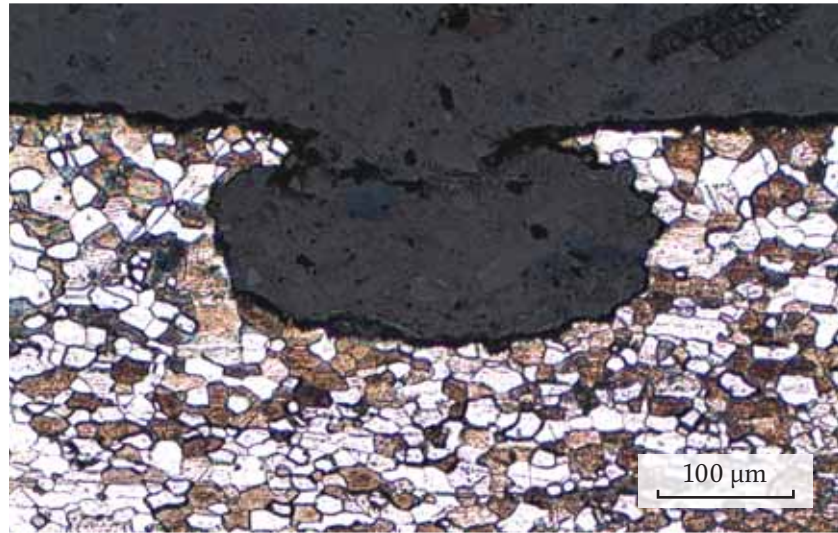


Figure 6.14: *Micro-section of pitting corrosion through a 1 mm thick sheet of ferritic stainless steel, type 4512. Note how the corrosion is very aggressive in one place while the rest remains unaffected. The corroding part has been active while the rest of the steel has remained passive.*

Organic substances inhibit corrosion

An even better inhibitor effect may be achieved with *organic substances*. Many organic substances such as fats, proteins, glycol and similar substances adsorb effectively to the stainless steel surface, and, all else being equal, the conditions will be *less corrosive* than pure water without organic substances. In practice many examples are known of relatively low alloyed stainless steel (e.g. 4301) surviving hot, seawater-like conditions without pitting corrosion occurring - simply due to a very high content of organic substances. It is thus not unusual that a quality of stainless steel can be used which in terms of corrosion is poorer (and as a rule cheaper!) than the one 'recommended' by the CPT diagrams.

It should, however, be emphasised that the effect of both organic and inorganic substances in the water may vary considerably, and with complex media it is recommended that an actual corrosion testing is carried out to ascertain the optimum steel type. This can be done by carrying out accelerated short-term experiments (e.g. cyclical polarisation, CYP, or the above determination of the critical pitting temperature, CPT) or, less common, long-term exposure. The latter is required if crevice corrosion is to be tested or if microorganisms are involved. A description of the various corrosion tests can be found in [1].

6.2.5 The Effect of Alloying elements Against Pitting Corrosion

If you look at Figure 6.10, it is clear that not all types of steel are equally effective in resisting pitting corrosion. Some types of steel are clearly better than others, and, by experience, the most important alloying elements include:

- Chromium (Cr)
- Molybdenum (Mo)
- Nitrogen (N)
- Impurities, sulphur (S), phosphorus (P), etc.

Cr, Mo, and N all work against pitting corrosion

Chromium is our main alloying element and contributes strongly to the formation and maintenance of the steel's passivating oxide layer. In general it is therefore true that *the higher the content of Cr, the better the resistance to pitting corrosion*. Steel with 18% Cr can be regarded as a fishing line with a breaking strength of 18 kg, and it will always be stronger than a line with a breaking strength of 17 kg (17% Cr), which will always be better than 16, 15, 14 and 13 kg respectively. The more Cr, the better, and this effect is unequivocal.

Molybdenum also contributes strongly to the passivation of the steel, and its effect is even more positive than Cr. The higher the Mo, the better, but the two elements are not completely 'parallel'. There are certain differences in the way Cr and Mo work, as Mo better than Cr maintains the passive layer in *acidic environments*. On the other hand, Mo is sometimes less effective than Cr in strongly oxidising environments.

Nitrogen (N) also affects the passivity of the steel positively, and, just as for Cr and Mo, the following rule applies: The more, the better. In addition, N is the only passivating element which is also an *austenite stabiliser* which is why extra nickel (Ni) is not required to maintain the austenite structure. The disadvantage is that N, like other gasses, is only marginally soluble in a 1500°C steel melt which sets low limits for how much can be added to the steel (see Chapter 4, 'Alloying elements').

The last factor is the amount of impurities in the steel. As is the case with other metals and alloys, stainless steel is not 100% homogenous, but consists of grains – the "bricks" of the steel (see Chapter 3). These bricks are separated by a kind of mortar, and it is often here that we find impurities. Unfortunately, it is also here that you find the 'weakest link in the chain', and with a material that, as in Figure 5.12 on page 71, behaves like a fishing line, it is vital to keep the resistance to corrosion in the weakest link as high as possible.

Of non-metallic impurities, (S) in particular is problematic. As described in Chapter 4, S, in conjunction with manganese (Mn) forms manganese sulphides, which makes the steel short-chipped but also lowers the corrosion resistance drastically. Manganese sulphides work as a point of attack for almost all types of corrosion, and as Mn is a necessary element to improve the hot rolling properties of the steel, it means that the higher the content of S in the steel, the poorer the resistance to corrosion.

6.2.6 Pitting Resistance Equivalent, PREN

As Cr, Mo and N all affect the corrosion resistance of the steel *positively*, the question may well be asked: How good are the different elements? Is 1% Mo the same as 1% Cr - and what about N?

Comparing Cr, Mo and N is a bit like having your pocket full of money in different currencies. That DKK 100 is more than DKK 75, which is more than DKK 50, is simple enough, but how much is DKK 100 compared to DKK 40 + USD 5 + GBP 8? For this sort of thing you need the exchange rates between the various currencies after which you will be able to convert to a common monetary unit (e.g. DKK).

*Stainless
currency
exchange rates*

Similarly, "stainless steel currency exchange rates" can be used. If Cr is used as the common monetary unit, dozens of laboratory experiments have shown that 1% Mo protects just as much as 3.3% Cr, and 1% N is just as good as 16% Cr. Thereby, we can develop a kind of 'currency gauge' named 'Pitting Resistance Equivalent' (PRE or PREN). The designation "PRE" is often used if only Cr and Mo are used in the calculation while "PREN" is used if nitrogen, N, is included.

$$\text{Eq. 6.1:} \quad \text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N}$$

Two types of stainless steel with the same PREN will have approximately the same resistance against the *initiation* of pitting corrosion. The higher the PREN, the better, and it is worth noting that theoretically it does not matter whether 1% Mo or 3.3% Cr is added. It is the *increase* in PREN that is decisive.

With Eq. 6.1 as the starting point it is possible to analyse the alloy composition of the steel and on the basis of the content of Cr, Mo and N evaluate how great is the resistance towards pitting corrosion. By looking at the alloy composition in the various types of steel, a chart can be drawn up – a kind of scorecard showing the different steel type's resistance towards pitting corrosion. Such a list of various commercial steel qualities along with their content of Cr, Mo and N is attached in Table 6.1. Note that all data are based on the steels' *minimum values* for the various, useful alloying elements. Steel of the type 4307 may contain from 17.5% to 19.5% Cr, but it would be too optimistic to rely on the 19.5%. The only thing that is guaranteed is at least 17.5% Cr.

EN	AISI / UNS / Popular Name	Cr	Mo	N	PREN
• 2.4819	Hastelloy C-276	14.5	15.0	-	64.0
• 2.4856	Inconel 625	20.0	8.0	-	46.4
• 1.4547	254 SMO	19.5	6.0	0.18	42.2
• 1.4529	904LhMo	19.0	6.0	0.15	41.2
• 1.4410	Super duplex; UNS S32750	24.0	3.0	0.20	37.1
• 1.4507	Super duplex	24.0	3.0	0.20	37.1
• 1.4501	Super duplex; UNS S32760	24.0	3.0	0.20	37.1
• 1.4462	Duplex 2205 / UNS S32205	22.0	3.0	0.14	34.1
• 1.4539	904L	19.0	4.0	-	32.2
• 1.4462	Duplex 2205 / UNS S31803	21.0	2.5	0.10	30.9
• 1.4460	AISI 329	25.0	1.3	0.05	30.1
• 1.4536	-	19.0	2.5	0.10	28.9
• 1.4438	AISI 317L	17.5	3.0	-	27.4
• 1.4435	AISI 316L, 2.5-3.0 Mo	17.0	2.5	-	25.3
• 1.4432	AISI 316L, 2.5-3.0 Mo	16.5	2.5	-	24.8
• 1.4436	AISI 316, 2.5-3.0 Mo	16.5	2.5	-	24.8
• 1.4408	Cast alloy: 316	18.0	2.0	-	24.6
• 1.4162	Lean duplex	21.0	0.1	0.20	24.5
• 1.4362	Duplex 2304	22.0	0.1	0.05	23.1
• 1.4404	AISI 316L	16.5	2.0	-	23.1
• 1.4401	AISI 316	16.5	2.0	-	23.1
• 1.4571	(AISI 316Ti)	16.5	2.0	-	23.1
• 1.4521	AISI 444	17.0	1.8	-	22.9
• 1.4526	-	16.0	0.8	-	18.6
• 1.4318	AISI 304LN	16.5	0.10	-	18.1
• 1.4306	AISI 304L (high Ni)	18.0	-	-	18.0
• 1.4418	-	15.0	0.8	0.02	18.0
• 1.4307	AISI 304L	17.5	-	-	17.5
• 1.4301	AISI 304	17.5	-	-	17.5
• 1.4509	AISI 441	17.5	-	-	17.5
• 1.4305	AISI 303	17.0	-	-	17.0
• 1.4541	AISI 321	17.0	-	-	17.0
• 1.4371	AISI 202	17.0	-	-	17.0
• 1.4104	AISI 440A	15.5	0.2	-	16.2
• 1.4109	(AISI 430F)	16.0	-	-	16.0
• 1.4510	AISI 430Ti / 439	16.0	-	-	16.0
• 1.4016	AISI 430	16.0	-	-	16.0
• 1.4310	AISI 301 / 302	16.0	-	-	16.0

EN	AISI / UNS / Popular Name	Cr	Mo	N	PREN
• 1.4034	AISI 440B	14.0	0.5	-	15.7
• 1.4057	AISI 431	15.0	-	-	15.0
• 1.4542	AISI 630	15.0	-	-	15.0
• 2.4816	Inconel 600	14.0	-	-	14.0
• 1.4021	AISI 420	12.0	-	-	12.0
• 1.4003	AISI 410S	11.5	-	-	11.5
• 1.4006	AISI 410	11.5	-	-	11.5
• 1.4512	AISI 409	10.5	-	-	10.5

Table 6.1: *List of the content of Cr, Mo and N in a range of standard stainless steel and the calculated PREN according to Eq. 6.1. For all types of steel the values for Cr, Mo and N are minimum values according to the standards (see Chapter 8). The colour of the dots indicates steel type: Austenitic (red), ferritic (blue), duplex (green), pH alloys (yellow), martensitic (purple) and nickel alloys, austenitic (black).*

Again it helps to regard stainless steel as a fishing line. If so, PREN can be regarded as the fishing line's breaking strength, and the higher the breaking strength, the smaller the risk that the line will break at a given load. In principle, choosing stainless steel is therefore 'just' a question of finding a steel with a sufficiently high 'breaking strength' towards corrosion.

Unfortunately, a higher level of useful alloying elements also entails a significantly higher price and usually also increased processing costs. The solution to the problem is therefore not to build everything using 254 SMO or super duplex, but to find a suitable balance in between corrosion resistance and price. You have to find out what is required and then you 'just' have to choose steel on the right side of the limit – of course with a healthy safety margin.

PREN;
4301 v. 4401

Take e.g. the classic 4301 (AISI 304). This type of steel contains min. 17.5% Cr and neither Mo or N which is why $PREN_{4301}$ will be 17.5. The acid-resistant steel, 4401, contains only 16.5% Cr, but at the same time at least 2.0% Mo, which pushes $PREN_{4401}$ up to 23.1. Just by observing the alloy composition of the two types of steel, it is possible to *predict* that 4401 has a better resistance to pitting corrosion than 4301. If you look at the duplex '2205' (4462), $PREN_{4462}$ ends up at 30.9 as proof of even better resistance against pitting corrosion.

That PREN is not just pure invention can be seen from Figure 6.10 which shows the corrosion resistance for different types of stainless steel in different media. Note that the higher the steel's PREN, the higher the curve for the steel concerned *regardless of the chloride content of the water*. Steel such as the acid-resistant 4401 is therefore better in *all media* than the non-acid-resistant 4301 steel. This does not mean that 4401 is immune to pitting corrosion, but that it takes more to initiate pitting corrosion in 4401 than for its younger brother 4301. If 4301 can keep up, so can 4401, and if 4401 suffers from pitting corrosion, so will 4301.

In the middle there is a middle group of environments where 4401 remains undamaged while 4301 does not – the area between the curves in Figure 6.10. In practice this area is extremely important, and there are numerous examples of the difference between the acid-resistant (4401 category) and the standard stainless steel (4301-) being the difference between success and failure. In Northern Europe, stainless steel installed outdoors will be subject to a harsh salt fog during winter-time. Such conditions are very corrosive towards stainless steel, and while acid-resistant steel (the 4401 class) may be ok, standard stainless of the 4301 class hardly ever is (see Section 7.2 on page 134).

Different types of acid-resistant steel

As far as acid-resistant steel is concerned, it should also be noted that the AISI 316(L) group is covered by several different EN standards. It should especially be noted that while 4401 and 4404 both have a minimum of 2.0% Mo, the lower limit for 4432, 4435 and 4436 is 2.5%. The increased Mo content has a positive effect on PREN, and thereby the resistance to pitting corrosion (see Table 6.1). So if there is a working drawing specifying 4432, 4435 or 4436, 4401 or 4404 cannot be used nor can the titanium stabilised 4571. But there are very rarely any problems in replacing 4404 with 4432 or 4436 – apart from the price, of course! The difference between the different standards is described in Chapter 8.

So what about the impurities of the steel? As mentioned above, it is particularly sulphur which is able to generate the resistance to corrosion, and if fair is fair S should be included in the PREN equation in Eq. 6.1 – with a great, negative factor indicating that S has a very negative effect. The size of this factor has been much discussed, but $\div 123(!)$ has been suggested for both S and P which gives the following, modified PREN:

$$\text{Eq. 6.2: } \text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N} - 123 \cdot (\% \text{S} + \% \text{P})$$

This means that only 0.1% S needs to be compensated by 12.3% extra Cr or 3.7% extra Mo just to maintain the resistance towards pitting corrosion. For most commercial sheets and tubes, the upper S limit is 0.015% while up to 0.030% is accepted in steel bars and flat steel. This corresponds to a negative effect of 1.85% and 3.70% Cr, respectively. Table 6.1 does not include S which is the direct reason for 4305 being aligned to 4301 although the maximum permissible 0.35% S theoretically is capable of lowering the PREN to under $\div 26!$ Free-machining steel is significantly less resistant to all types of corrosion than the corresponding, sulphur-free qualities.

PREN; free-machining steel

6.2.7 Flying Rust

Everyone with a dishwasher knows the problem: The knives get rusty while forks and spoons usually don't get tainted at all. On top of this, it is not the whole knife that gets rusty; usually only the blade looks bad, and when you ask the local shop, you are told that this is 'flying rust' from the dishwasher's white-painted mesh.

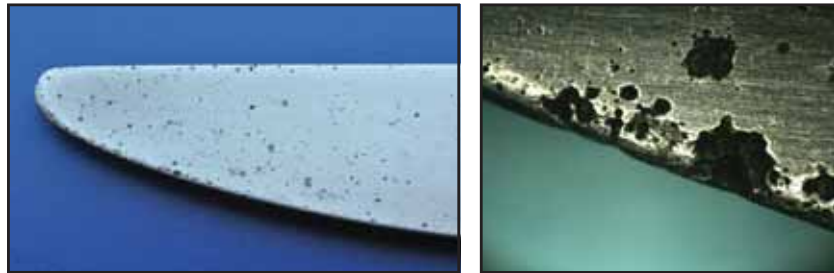


Figure 6.15: *Pitting corrosion on stainless steel knife blades (steel type 4021, 13.5% Cr). The corrosion has arisen during the dishwashing process, the so-called 'flying rust', due to the fact that the PREN of the knife blade is too poor. The picture on the right is a microscope photo of the cutting edge of the same knife blade.*

Martensitic knife blades are often attacked by pitting corrosion = 'flying rust'

Nonsense. Had the rust stains been caused by particles from the mesh, all knives, forks, spoons, plates and glass would be stained, but it is always only the knife blades. The cause is to be found in Table 6.1 which shows that all martensitic steel qualities have a quite poor resistance towards pitting corrosion. Most martensites have a PREN of between 12 and 15, and this makes them significantly *less* resistant to pitting corrosion than 4301 (PREN 17.5). The knife blades are simply less resistant to pitting corrosion, however, as adding more Cr or Mo to the steel is not possible as this will affect the hardening of the blades. Instead, the solution is to ensure a short contact time which is easily done with short washing cycles or (even better) washing by hand.

Should your knives, despite all precautions, suffer from 'flying rust', the best way to remove the rust stains is to use hot citric acid (see Section 12.3.2 on page 263). This removes the rust stains, but of course not the small micro pits created by the corrosion which is why the best solution is always to prevent corrosion attack by using mild washing methods. Lower temperature and/or shorter time are a couple of good steps in the right direction.

6.2.8 Ferritic Stainless Steel and Nickel Alloys

Please note that carbon does not affect the calculation of PREN. 4301 and the low carbon version 4307 both have a PREN of 17.5. Similarly, 4401 and 4404 are equal although the limits for carbon are very different (max. 0.07 against 0.03%; Chapter 8). As regards pitting corrosion on its own, it does not matter whether you choose low carbon or standard steel, however, in practice you should nearly always choose low carbon or titanium stabilised steel due to the risk of *intergranular corrosion* (see Section 6.5) which may later switch into pitting corrosion or crevice corrosion.

Nickel does not affect PREN

It is also worth noting that nickel (Ni) does not affect PREN. This is clearly seen when comparing the ferritic steel 4509 and the austenitic 4301. The former contains 0% Ni while 4301 has 8%, however, it is the 17.5% Cr in both types of steel that does the trick; both alloys have a PREN of 17.5. The performances of the ferritic, nickel-free 4509 versus the austenitic, nickel-containing 4307 towards the initiation of pitting corrosion have been demonstrated in several corrosion testings by the Technical University of Denmark [38], among others. Similarly, it has also been shown that the ferritic 4521 is at least as resistant to the *initiation* of pitting corrosion as the acid-resistant, austenitic 4401 (4404).

Although nickel does not affect the *initiation* of pitting corrosion, it has some significance as the *propagation* (development) of pitting corrosion very much depends on the nickel content. When the damage is done and corrosion has commenced, the steel has been activated, and then the important thing is that nickel is a more noble/precious metal than both chromium and iron. The higher the nickel, the lower the corrosion rate so while chromium, molybdenum and nitrogen determine *whether* corrosion commences or not, it is nickel that determines *how quickly* the steel penetrates once the corrosion gets going. In this context, nickel works as a corrosion safety belt. Nickel does not prevent the accident, but reduces the consequences.

The choice of stainless steel (with the exception of general corrosion) is, however, nearly always based on a desire to completely prevent corrosion in the first place. Whether pitting corrosion produces penetration in three, four or five months is rarely relevant, and this means that it is often possible to 'throw the nickel away'. By only focusing on a high content of chromium and molybdenum, if applicable, the traditional high-nickel austenites can, in many applications, be replaced with the nickel-free ferrites without compromising on the resistance to pitting corrosion. In addition, the ferritic steel provides far better resistance to stress corrosion cracking (see Section 6.4) while on the minus side a poorer elongation (see Chapter 3) and a more complicated welding process to avoid intermetallic phases (see Chapter 10) should be expected.

Ferritic steel grades are stable in price

Another benefit to using ferritic steel is its relatively low and very stable price which does not depend upon the high and volatile price of nickel (see Figure 4.2 on page 43). The price of the ferritic steel is therefore much more stable than for the austenitic which naturally sparked a certain interest around 2006 and 07. As the price of nickel subsequently fell sharply between 2008 and 2009, interest fell correspondingly, but at the time of publication it is slowly on its way up again. This does not, however, change the fact that in the ferritic world there is a much poorer range of steel qualities and supply forms than for the austenites. Especially the stabilised, ferritic steel (e.g. 4509 and 4521) are currently difficult to find in any other form but thin steel sheets (Section 9.1 on page 169).

Release of nickel into food

Apart from the price, the ferrites have the psychological advantage that the risk of release of nickel from nickel-free steel is zero which makes the ferritic steel particularly suitable for food-related applications. 4016 is especially popular for many catering applications both in the UK and Italy, and the weldable 4509 is used widely for both interiors and exteriors of refrigerators, cf. Figure 2.4 on page 18. For further information about food-grade stainless steel please see Section 6.9.1.

Note also that three nickel-based alloys have crept their way into Table 6.1: Inconel 600, Inconel 625 and Hastelloy C-276. Nickel alloys can be treated in parallel with the stainless steel when it comes to pitting corrosion, and increased resistance to corrosion is achieved, of course, by adding as much chromium and molybdenum to the steel as possible. Unfortunately, this needs to be balanced by an equivalent quantity of nickel (see Figure 3.2 on page 26), and at some point so much nickel will have been added that iron (Fe) simply becomes a minority constituent and we get a nickel alloy instead. It is therefore reasonable to regard the high corrosion-resistant nickel alloys as natural extensions of stainless steel.

Mechanical strength of nickel alloys

At the other end of Table 6.1 it is interesting that Inconel 600, despite at least 72% Ni, falls way down the table. In the case of simple pitting corrosion, Inconel 600 simply performs *poorer* than standard 4301 which is because the alloy only contains 14% Cr. The 72% Ni do not help much in the creation of the passive layer, but there is nothing odd about that. Inconel 600 and its relative Inconel 601 (21-25 Cr, 58-63 Ni) were developed for their good mechanical strength at high temperatures and excellent resistance towards corrosive flue gases, but they are no good under oxidising conditions at room temperature. A bit like a Ferrari which is brilliant on a racetrack, but performs poorly on a bumpy gravel road. A 4WD Land Cruiser has the opposite strengths and weaknesses - and the same goes for metals. All alloys have their strengths and limitations, and the trick is always to find the combination of properties that best meet the needs of each individual project.

6.3 Crevice corrosion

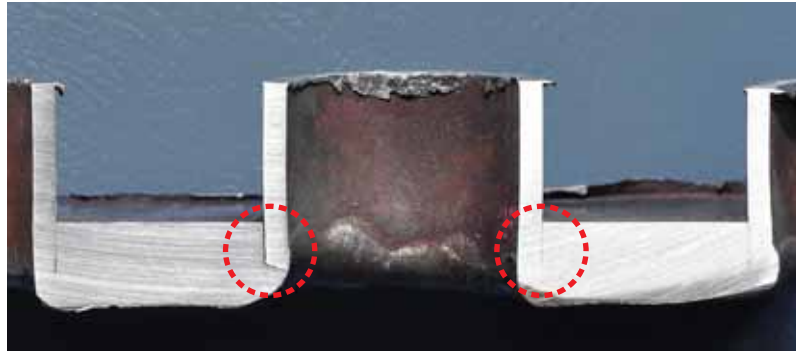


Figure 6.16: *All narrow spaces in a construction can work as crevices. All transport is governed by diffusion, and the environment in the crevice can easily become far more corrosive than is the case outside. In tubular heat exchangers, the risk of crevices between the base and welded pipes is critical and something that needs to be considered in the choice of steel.*

Crevice corrosion is due to poor transport conditions

Crevice corrosion is very similar to pitting corrosion, and they are often jointly referred to as 'local corrosion'. The difference is that while pitting corrosion takes place on the 'free surfaces', crevice corrosion occurs in crevices, flange joints, under bolts, threads, pores and other narrow locations where there is no convection, and where the water is completely stagnant. All transport takes place by diffusion, and in these locations the stainless steel has a tendency to create an environment on its own which is significantly more corrosive than outside the crevice. The weak passive current, which is required to maintain the steel's protective layer of chromium oxides, gives rise to a very, very weak release of positive and acidic metal ions. They need to be balanced in terms of charge which gives a certain diffusion of negative chloride ions into the crevice.

The combination of rising chloride and falling pH makes the medium inside the crevice significantly *more corrosive* than the 'bulk medium' outside. In extreme cases, this mechanism may create diluted hydrochloric acid (HCl) inside the crevice while the medium outside is just standard tap water, and this naturally has a great effect on the corrosion conditions inside the crevice. At some point the bubble will break, and corrosion will initiate - and when this happens, the crevice acts as an anode while the rest of the steel is cathode. This is the same, unfortunate galvanic coupling that can be seen in pitting corrosion, but in crevice corrosion the mechanism is based on geometry.

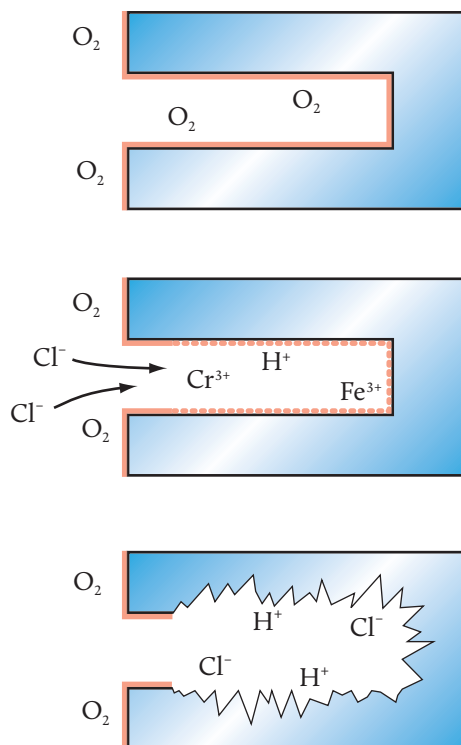


Figure 6.17: *Top: The maintenance of the passive layer entails an ultra-weak diffusion of positive metal ions into the liquid in the crevice. Middle: The positively charged metal ions require charge balancing and therefore attract the negatively charged ions - especially the corrosive chloride. Bottom: Chloride breaks down the steel's protective oxide layer, and the crevice is activated. The crevice hereby becomes anode while the area outside the crevice acts as cathode.*

Crevice corrosion is a greater risk than pitting corrosion

Because of this mechanism where the extremely corrosive chloride is pulled in from a large liquid phase, the crevice corrosion can only take place under fully immersed conditions. On the other hand, the large concentration of chloride in the crevice means that the risk of crevice corrosion is always greater than the risk of pitting corrosion. An old rule of thumb for *austenitic* steel says that the *critical crevice corrosion temperature* (CCT) is 20-25°C lower than the equivalent *critical pitting temperature* (CPT). In other words, this means that there is a risk of crevice corrosion at a temperature which is 20-25°C below the temperature for pitting corrosion which must be particularly considered when designing the equipment. If your chosen steel is close to the corrosion 'pain threshold' (according to e.g. Figure 6.10), it must be ensured by hook or by crook that there are no crevices in the system. If this cannot be ensured, a more corrosion-resistant steel should be chosen in which an extra large safety margin has been included – more than 25°C.

This rule of thumb applies to the *austenitic* types of steel while the nickel-free ferrites (e.g. 4509, 4521, etc.) re-passivate more poorly and it must therefore be expected that greater distance between crevice corrosion and pitting corrosion applies. For the ferritic steel greater sensitivity to crevice corrosion must therefore be expected than is the case for the equivalent austenites.

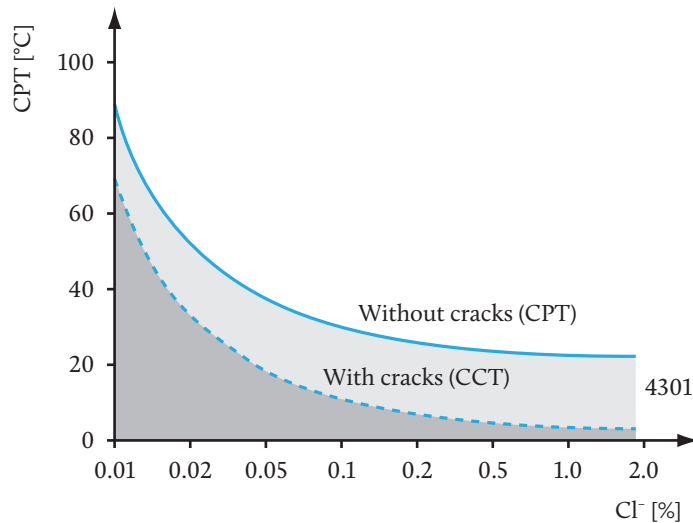


Figure 6.18: The CPT curve for stainless steel 4301 (after Figure 6.10) and an equivalent simulated CCT curve minus 25°C. The bottom curve simulates the resistance to crevice corrosion. Note that crevice corrosion will always occur before pitting corrosion.

Geometry of the crevice

Not all crevices are equally critical. In addition to the materials involved, the geometry of the crevice is of great importance, and the deeper the crevice, the more critical it becomes. Very narrow crevices are more critical than more open ones simply because convection is more difficult so that transport becomes more and more dependent on diffusion. For this reason alone metal/rubber crevices are usually more critical than metal/metal joints. Seals are there to make the joints tighter, but also have the disadvantage that the crevices potentially become more sensitive to corrosion.

Numerous other factors may also affect the behaviour of the crevices, and all in all crevice corrosion is a type of corrosion which is extremely difficult to simulate and thereby to predict. Not only is the crevice *geometry*, as mentioned, of great importance, but it takes a long time to create the corrosive environment. The latter means that it is almost impossible to carry out simple and fast corrosion experiments in a laboratory that are capable of simulating real conditions. Instead the resistance to pitting corrosion is measured (e.g. CPT experiments) and 25°C is then subtracted as is the case in Figure 6.18. This method is by no means 100% accurate, but is useful for a quick choice of materials.



Figure 6.19: *Crevice corrosion in a welding nipple of 4404 exposed to an aqueous solution of copper chloride (CuCl_2). Note that the corrosion is concentrated in the seal track.*

6.3.1 Microbially Induced Corrosion (MIC)

Another, if possible, even more unpredictable aspect of this is the occurrence of microorganisms. Bitter experience tells us that microorganisms can affect the corrosion of stainless steel in very unfortunate ways - partly by forming actual fouling which can act as crevices and partly by creating a biolayer which changes the environment locally.

One of the measurable effects of certain types of bacteria is that they can increase the corrosion potential of the steel to levels far above what is usually seen in pure tap water (typically 150-300 mV_{SCE} in tap water; more than 400 mV in purified waste water – see Figure 6.20). The result is that the CPT curves in Figure 6.10 are pushed radically downwards, and conditions thereby become far worse for the steel.

Crevices are breeding grounds for microorganisms

In addition, the *existing* crevices will be better than the free surfaces at acting as fertile ground for microorganisms which is why microbially active environments will often make the steel far more sensitive to crevice corrosion than to pitting corrosion. As described above, there is usually a temperature difference between crevice corrosion and pitting corrosion of 20-25°C (see Figure 6.18), but in microbiologically active media this temperature difference may become far greater. Examples are known particularly from sewage plants where acid-resistant 4404 has been attacked by severe crevice corrosion in cold water of 12-15°C but with less than 100 mg/l chloride, although the curves say that CPT should be well over 100°C. If so, one should expect crevice corrosion to be a problem at temperatures above 80°C, however, it sometimes occurs at far lower temperatures.

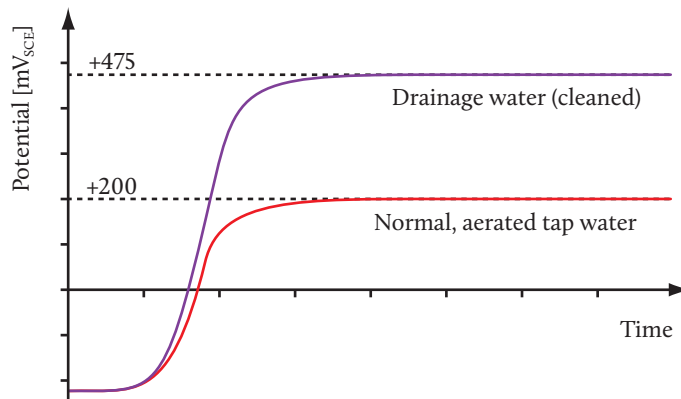


Figure 6.20: Outline measurements of the corrosion potential of passive stainless steel in standard tap water and purified waste water respectively. The measurements have been carried out over a period of more than 14 days, and the corrosion potential for both is initially very low, but increases dramatically after about a week. Note that the end potential (due to bacterial activity) is far higher for stainless steel in purified waste water than in pure tap water.

Waste water can be extremely corrosive to stainless steel

An excellent example of this is waste water, and stainless steel in sewage plants can behave very 'strangely'. The immediate reaction would be that the malodorous, *impure intake* at a sewage plant would be most problematic, but this is not the case. In the inlet, large concentrations of extremely oxygen-hungry microorganisms can be found, and in practice these make the water almost *oxygen-free*. This gives a very *low* corrosion potential which, in turn, gives an extremely good resistance to corrosion for *all* types of stainless steel. It is thus more the rule than the exception that standard stainless steel in the 4301 category remains intact at the intake end.

Acid-resistant steel is not always enough in sewage plants

It is a completely different story at the pure outlet end (settling tanks, sand filters, etc.) where the water is almost as clean as tap water. Here the water behaves far more oxygenising than standard aerated tap water, and precisely because of the bacterial growth corrosion potentials of more than 400 mV_{SCE} can often be measured (unofficial Danish record: +475 mV_{SCE}!) equivalent to the level for stainless steel in diluted hydrogen peroxide. In these media even acid-resistant stainless steel in the 4401/4404 category can be attacked by crevice corrosion which is why the welding specifications for sewage plants frequently contain a clause that states that neither pores nor crevices may be present. The behaviour of stainless steel in waste water is described in detail in [16].



Figure 6.21: *Crevice corrosion in press fitting (left) and tubes (right) of 4404 as a result of bacterial growth in tap water installation. The corrosion arose in water with a temperature of 45-50°C with less than 100 ppm of chloride, and it should be noted that the corrosion (the light grey areas on the right) has commenced in the narrowest places where the sleeve has been clamped around the tube.*

The effect of bacteria and biolayers is not, however, limited to sewage plants. All non-sterile media (i.e. nearly all media!) have the capacity for bacterial influence on the corrosion conditions, and even otherwise clean drinking water can hold unpleasant surprises. As the press fitting system was introduced more than 20 years ago, all pipes and fittings were made of standard 4301 which *should* in theory be enough for cold tap water at least with chloride under 100-150 mg/l (see Figure 6.10 and Figure 6.18). This was not the case, and modern press fittings are all made of the superior, acid-resistant steel (4404). This works in by far most cases, but there are rare examples of bacteria (or combinations of bacteria) that are so aggressive that even acid-resistant steel will suffer from crevice corrosion.

6.3.2 Combating Crevice Corrosion

Due to the slightly odd environmental conditions, the time factor, the effect of microbiology and the impossible task of creating a 'well-defined crevice', crevice corrosion is one of the most difficult forms of corrosion to fight. The alloying elements that best fight crevice corrosion are usually the same as the ones that are useful against pitting corrosion. A ranking of the various types of steel will therefore look very much like Table 6.1.

But there are certain differences between pitting corrosion and crevice corrosion. Molybdenum passivates significantly better in *oxygen-poor* media (and thereby crevices) than chromium, and the steel's molybdenum content should therefore be expected to mean more in crevice corrosion than pitting corrosion. From experience it can be seen that molybdenum is therefore even more important in combating crevice corrosion than pitting corrosion, and it should therefore be expected that the PREN factor between chromium and molybdenum in crevice corrosion would be higher than the 3.3 described in Eq. 6.1 and used in Table 6.1.

*Molybdenum
is good
against crevice
corrosion*

Additionally, the mechanism of crevice corrosion itself means a weak, *general* corrosion and consequently a release of tiny quantities of positive metal ions (see Figure 6.18), and here nickel has some positive effect. Usually it is so, however, that the stainless steel types that have the best resistance against pitting corrosion also have the best resistance against crevice corrosion. Consequently, it is not a bad idea to look upward in the table in order to enhance the performance of the steel.



Figure 6.22: *Saltwater is one of the most corrosive environments for stainless steel. The main risk is crevice corrosion, and if this is to be avoided, 'super alloys' are required. This cooling water system from an oil rig in the Danish part of the North Sea is made of 4547 (254 SMO). Photo: © Maersk Oil.*

*Baby ointment
and crevice
corrosion*

An excellent method is, of course, to avoid crevices in the system completely. This is only rarely possible with e.g. welding pores and lack of bonding, but for 'planned crevices' such as bolt joints and flanges a small trick is possible, which may not be scientifically advanced, but which works in practice. By lubricating the bearing surface with a *thin layer of vaseline* the crevice becomes water-repellent whereby the mechanism in Figure 6.18 just cannot take place. In theory this trick is only temporary, but in practice the effect lasts for a very long time, especially if, instead of vaseline, a mixture of vaseline and alkaline zinc oxide is used – the same as is used in baby ointment! In fact, the baby ointment available from pharmacies is excellent for this purpose although it should, of course, be ensured that the use of vaseline and/or zinc oxide cannot in any way affect the medium.



Stainless steel is one of the greatest technical advancements of the past century. If you were to produce a top ten hit list of our most important alloys, stainless steel would be very close to the no. 1 spot, and nowadays it is very difficult to imagine a dairy or pharmaceutical factory that does not consist of almost 100% stainless steel. Stainless steel is here to stay.

Unfortunately, stainless steel is not always stainless. If conditions are sufficiently aggressive, the steel can be attacked by a wide range of corrosion types, but by knowing your 'enemy' you are much better placed to fight these problems. The right steel must be selected for the right task, the right processing method must be employed, and the right surface treatment must be used.

If steel is used correctly, it will last forever.

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