

THE SELECTION OF PUMP MATERIALS FOR HANDLING WASTE WATERS

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ABSTRACT

The term “waste water” can cover a multitude of compositions, and means different things to different people. In the water industry, this can mean treated sewage water or treated effluent from chemical plants. In the oil and gas industry this is often a mixture of sour water, possibly with aerated water and various chemicals from the refinery. Chemical Industry waste can be particularly varied, and can be acidic, neutral or alkaline and may contain small amounts of aggressive species that would severely corrode carbon steel or low alloy CRA's. Of particular importance is the redox potential, which strongly affects performance of many alloys. Impurities such as copper and iron can make the solution oxidizing, while species such as sulphide or nitrite make it reducing. In some processes the waste water will be treated with chemicals, such as potassium permanganate, which is a strong oxidizer. This will significantly affect alloy selection in many cases, and may mean that the first choice material will not last long because of corrosion due to the high redox potential. This paper points out how to evaluate the waste water and select suitably resistant materials for pumps. As many valves also have cast parts, the same principals apply to valve alloy selection. It also stresses the need for suitable procurement specifications, testing and rigorous QA/QC, over and above the requirements of standards like ASTM, if good quality material is to be obtained. Some case studies show how suitable CRA's were selected for these projects and why lower cost materials would not have worked. The paper stresses the need for an experienced corrosion engineer or metallurgist to ensure that all the possible corrosion mechanisms are addressed prior to purchasing.

INTRODUCTION

Waste waters can cover a wide range of compositions and also may vary from reducing to strongly oxidizing. Sometimes corrosion will be controlled by impurities in the water rather than by chloride concentration or pH. This means that material selection for any pipeline to carry this water can be difficult. However, for a pipeline of any length, economics will dictate the use of carbon steel, possibly with a suitable protective coating.

In most pipelines handling waste water one or more pumps are required to keep the water moving at an adequate rate. While it would be desirable to use carbon steel pumps to minimise costs, this is only possible with near neutral waters or chemicals that are not aggressive. In more aggressive fluids coatings are not an option, partly because of the complex shape inside centrifugal pumps, and partly because of the high flow velocities and turbulence inherently present in a pump of this type. This means that corrosion resistant alloys (CRA) are often required and it is important to know the detailed composition of the water to select a CRA that will be adequate, without excessive cost.

All of the factors that must be taken into account when selecting cost-effective materials for pumps were discussed in detail by Phillips and Francis¹. They used examples from the oil and gas industry to illustrate the important points, but the same principles can be used to select materials for waste waters. The most important factor is to get as detailed a view as possible of the likely composition of the waste water and also the likely variations during the

life of the system. This is often very difficult in practice, and then it is wise to estimate a worst case, because if a pump fails unexpectedly there is all the lost working time as well as the cost of replacement.

The present paper briefly reviews the important corrosion characteristics of some common alloy groups with respect to their performance in a variety of waste waters. This is followed by a few case histories examining why particular alloys were chosen for specific projects.

CORROSION

The nominal compositions of all the corrosion resistant alloys discussed in the text are shown in Table 1.

Cast Carbon Steel

The problem with cast carbon steel is that the corrosion rate rises rapidly with flow velocity, as shown in Figure 1 for seawater². It can be seen that at velocities greater than a couple of meters per second, the metal loss rate is unacceptable. Although this is for seawater, the rate of metal loss at higher flow velocities does not reduce that much with chloride content, and at 100 mg/L chloride the rate is only roughly halved. This is compounded because, depending on the pump design, flow velocities in the impeller are often in the range 5 to 10 m/s and the abrupt changes in direction mean that there can be a lot of turbulence.

Where dissolved oxygen contents are low and the pH is near neutral, the corrosion rate is lower, and Figure 2 shows the corrosion rate at 1 m/s for a range of oxygen contents. This means that at oxygen contents of 20 to 50 ppb the corrosion rate can be acceptable, but remember that this is at 1 m/s, and the rate will be significantly higher at 5 to 10 m/s.

The corrosion rate of carbon steel also increases significantly at low pH (<3) and may be high at higher pH if there are aggressive species present.

Copper Alloys

Copper alloys have excellent resistance to corrosion in near neutral pH solutions over a wide range of chloride contents, and alloys such as the gunmetals and nickel aluminium bronze have given good service³. However, they can suffer pitting in the presence of sulphides, or other sulphur compounds, which is accelerated at higher velocities³ (see Figure 3). Sulphides are often produced by sulphate reducing bacteria (SRB) and these can become active under deposits, fouling, or they may already be present in the source water. Where sulphides are a possibility, copper alloys are not a good choice, and they are also not recommended in solutions operating at high or low pH (<5 or >9).

Stainless Steels

Stainless steels contain more than 11% Cr and often have additions of other elements such as nickel, molybdenum, copper, and nitrogen. The main classes of stainless steels used for pumps, i.e. as castings, are martensitic, austenitic and duplex. The selection of the grade depends strongly on the water composition, the redox potential, the pH and the dissolved oxygen content.

Martensitic stainless steels are not very resistant to pitting and crevice corrosion in aerated waters containing chloride, but they have excellent resistance to corrosion in the presence of sulphides, such as H₂S, as is found in many waste streams in the oil and gas industry. Under conditions where no oxygen can be present, then the corrosion risk is sulphide stress corrosion cracking (SSCC), and the limits of use are given by ISO 15156⁴.

Austenitic stainless steels are widely used for pumps and the common grades are CF8 and CF8M, the cast versions of 304 and 316. There are cast versions of the 6% Mo austenitic alloys, but these are rarely used for waste waters because they are more expensive than superduplex stainless steel. In aerated chloride-containing solutions, the risk is crevice corrosion and Figure 4 shows the limits of use of the lower alloyed austenitic and duplex stainless steels⁵.

The common duplex stainless steels are grade 4A (the cast version of 2205) and grades 5A and 6A, the cast versions of 2507 and Z100 superduplex. Figure 4 shows the limits of use for 2205, and while they are greater than for 316, it is still not suitable for high chloride aerated waters. The cast superduplex alloys have been used in a wide range of aerated chloride-containing waters including seawater and higher chloride brines⁵. Figure 5 shows the critical crevice temperature (CCT) for both 2205 and Z100 superduplex as a function of chloride concentration and the open circuit potential⁶. A potential of +600 mV SCE is very oxidizing, while one of +200 mV SCE is mildly oxidizing. It is clear that the CCT is not affected very much by chloride concentration over the range 3,000 to 100,000 mg/L chloride.

In deaerated waters the limits of use increase and 2205 can be used with 50 ppb of oxygen up to ~60°C with 100,000 mg/L chloride⁷. For superduplex the CCT for cast Z100 was 80°C with 410 ppb oxygen and 100,000 mg/L chloride⁷. In fully deaerated waters with H₂S, the limits of use to avoid SSCC for austenitic and duplex stainless steels are given by ISO 15156⁴.

In chemical waste waters, stainless steels have good resistance to a wide range of alkaline and acidic chemicals^{5, 8}. The choice of alloy depends on the specific chemical, its concentration and the temperature. Sulphuric acid can often appear in chemical waste and in this liquid, grade 6A superduplex out performs grade 5A because of its deliberate copper addition (Figure 6). Where acid concentrations and temperatures are low, lower alloy stainless steels can be used (Figure 6). Where there are impurities with the acid, such as chloride, the alloy ranking can change significantly. Such data as is available is reviewed in references 5, 8 and 9.

Another form of corrosion that can affect stainless steels in waste waters is microbially influenced corrosion (MIC), which can occur when a stainless steel is handling a biologically active water. It is not the bacteria that attack the metal, but their metabolic by-products, and there is a wide range of aerobic and anaerobic bacteria that can affect the corrosion of stainless steels⁵. In natural, aerated waters a biofilm forms in a period of two or three days to two or three weeks. This film depolarises the cathodic reaction, the reduction of dissolved oxygen, with a resultant increase in potential to anywhere in the range 250 to 400 mV SCE. This can result in pitting or crevice corrosion of lower alloyed stainless steels. As the biofilm thickens, the oxygen next to the metal can be depleted and anaerobic bacteria, such as SRB become active. It is well known, for example reference 5, that 300 series stainless steels are particularly susceptible to MIC and Francis references some failures⁵. The higher alloy stainless steels, such as the 6% Mo austenitic and superduplex grades do not appear to be susceptible to MIC under most service conditions⁵.

Nickel Alloys

The nickel base alloys, such as the nickel-copper and nickel-chrome-moly alloys are considerably more expensive than stainless steels and waste waters are not usually aggressive enough to justify the expense. However, the wrought alloys, such as K-500 and 625 are sometimes used for small components in areas at high risk of corrosion damage.

PUMP COMPONENTS

The three main components in a pump are the case, the impeller(s) and the shaft. The first two are usually castings, while the shaft is wrought. Of these three, the shaft is the most important, because if even a small amount of localised corrosion (pitting or crevice corrosion) occurs on the shaft, it will act as a stress raiser. This will be followed soon after by a very expensive fatigue failure of the shaft. Hence, it is common practice to make the shaft from an alloy with superior corrosion resistance to the case and impeller. Where these are in a very corrosion resistant alloy, such as superduplex stainless steel, then the shaft may be in the wrought version of the same alloy. The shaft will have seals, the impeller and other items fastened on it that can create crevices, so it is important that the shaft resist crevice corrosion.

The author has seen two major pump failures where the shaft was in Ni-Cu alloy K-500 and crevice corrosion occurred, followed by a fatigue failure during operation. The repairs in both cases were very expensive.

Because the case and impeller are castings, it is important to select an alloy that has reasonable castability, to avoid excessive costs. Phillips and Francis reviewed the main features required to minimise costs while obtaining satisfactory properties in pump components¹. Francis and Hebdon pointed out that the duplex stainless steels are easier to cast than the 6% austenitic alloys¹⁰. They also compared castings in grade 5A and grade 6A superduplex stainless steels, and showed that grade 6A is easier to cast in thicker sections. The lower alloy stainless steels are relatively easy to cast.

The production of good quality castings in the higher alloy stainless steels requires care and Francis and Hebdon discuss in detail what the technical requirements are and the need to audit foundries to ensure compliance with the technical specification¹⁰. Although they were reviewing seawater pumps, the same considerations apply to pumps handling waste waters.

CASE HISTORIES

Case History 1

It is well documented that when a stainless steel is immersed in an aerated natural water, the potential increases over a period of a few days to weeks, finishing in the range +250 to +400mV SCE. This has been found for both seawater and fresh waters. The ennoblement is due to the formation of a biofilm that cathodically depolarises the reduction of dissolved oxygen. This makes the initiation of localised corrosion more likely.

These electropositive potentials can mean that an alloy is taken past its pitting or crevice potential. The potential of such materials then decreases and this is often used as an indicator that crevice corrosion has initiated (Figure 7). With SRB, the H₂S produces local reducing conditions and negative potentials. Iversen¹¹ demonstrated this by exposing stainless steels in some Swedish waste water plants. In the early stages a biofilm formed that produced electropositive potentials, similar to those seen in seawater. However, over time the potential slowly decreased to very negative values. This was ascribed to the formation of a thicker biofilm such that SRB became active beneath it. With this electronegative potential, no localised corrosion initiated. However, some waste water plants add oxidizing chemicals, such as potassium permanganate, as part of the waste treatment process. This can change the local redox potential such that corrosion can occur because sulphide can lower the threshold potential for localised corrosion.

Iversen describes the results of exposure tests of 304L, 316L and 2205 at six Swedish waste water plants^{12, 13}. The results showed that 304L suffered MIC at 4 plants, all where the

chlorides exceeded 200mg/L, which is above the threshold for crevice corrosion of 304L at room temperature (Figure 4). 316L corroded at one plant, where the chloride exceeded 500mg/L and there were lots of deposits on the metal. This is below the chloride threshold for crevice corrosion of 316L at room temperature in sterile solutions (Figure 4). Alloy 2205 suffered no corrosion in any of the plants. Iversen concluded that chloride alone could not predict the likelihood of MIC¹². These results show that in waste waters where MIC is possible, it is necessary to consider a higher alloy than would be required under sterile conditions.

Case History 2

The author was asked to consider materials for a main oil line pump, which was pumping oil from an offshore platform to a treatment plant. This would normally require a carbon steel because oil per se is not corrosive. However, this was an ageing field and there was a significant water content with a high chloride content. In addition there was some H₂S and CO₂ present, and the possibility of some oxygen ingress. The oxygen ingress was sufficiently low that it would be mopped up by the H₂S, and so the fluid could be treated as a sour water with oil.

The pump company was considering a 22% Cr duplex pump, which would have been satisfactory, but the author pointed out that under the conditions in the design specification, a cast 13% Cr martensitic alloy would also be satisfactory, using ISO 15156. This resulted in significant cost savings for the large multi-stage pump. This demonstrates the requirement for knowledge as to how components in the fluid will interact to optimise materials selection.

Case History 3

A collection line was being installed to collect waste waters from a number of chemical plants, and the fluids were likely to contain a wide variety of chemicals. These included organic and inorganic acids, alkalis, aerated waters of high chloride content, and other chemicals. The concentrations were relatively low and the temperature was ambient, so it was thought that 22%Cr duplex would be satisfactory. However, part of the line passed through a tunnel with restricted access, and the tunnel owners did not want a leak at any time in the future if the fluids became more aggressive. Hence, the piping was upgraded to superduplex stainless steel. Because of the strong possibility that the waste fluid mixture would become more aggressive over time, the pumps were also made in grade 6A superduplex.

Case History 4

A collection line was being installed at a Middle Eastern plant to take what were described as waste sour fluids for treatment and disposal. These were basically high chloride waters with varying contents of CO₂ and H₂S, but in addition some of the waters could be aerated. Because the oxygen content was unknown, but likely to be variable, an alloy was required with a good tolerance of sour deaerated waters and also of aerated high chloride waters. The 1km line was installed with NPS 24 superduplex stainless steel pipe, valves and pumps, and it has performed well for over 15 years.

CONCLUSIONS

The selection of materials for waste water pumps is a complex operation and requires experience of materials, corrosion and the interaction of chemicals in the specific fluid. In addition it is important to know whether MIC is possible, because this can significantly reduce the limits of operation of some materials.

Without a suitably qualified corrosion engineer, the consequences in additional cost and lost production can be enormous. In addition, the corrosion engineer needs to be involved at all stages from design to delivery.

If you hire a corrosion engineer at the beginning of a project it will cost you a little money. If you do not hire them, don't feel bad about it, as you will be giving them much more work later on. Corrosion resistance is added at the specification stage, and once the equipment is built, it is difficult to add it later on.

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TYPE	UNS No.	COMMON NAME	NOMINAL COMPOSITION (wt.%)												
			Fe	Cr	Ni	Mo	N	W	Cu	Al	Sn	Zn	Pb	Other	
Cu-Base	C83600	Gunmetal	-	-	-	-	-	-	-	Bal	-	5	5	5	-
	C92410	Gunmetal	-	-	-	-	-	-	-	Bal	-	7	2	3	-
	C95800	NAB	4	-	4.5	-	-	-	-	Bal	9	-	-	-	-
Aust. SS	J92620	304	Bal	18	9	-	-	-	-	-	-	-	-	-	-
	J92800	316	Bal	17	10	2	-	-	-	-	-	-	-	-	-
	J94651	6%Mo	Bal	20	24	6	0.2	-	0.3	-	-	-	-	-	-
	J93254	6%Mo	Bal	20	18	6	0.2	-	0.7	-	-	-	-	-	-
Duplex SS	J92205	Grade 4A	Bal	22	5	3	0.16	-	-	-	-	-	-	-	-
	J93404	Grade 5A	Bal	25	7	4	0.25	-	-	-	-	-	-	-	-
	J93380	Grade 6A	Bal	25	8	3.5	0.25	0.7	0.7	-	-	-	-	-	-
Ni-Base	N05500	K-500	1.5	-	65	-	-	-	-	Bal	3	-	-	-	0.4 Ti
	N06625	625	3	21	Bal	9	-	-	-	-	-	-	-	-	3.5 Nb

Bal = Balance

TABLE 1 Nominal compositions of the alloys discussed in the text.

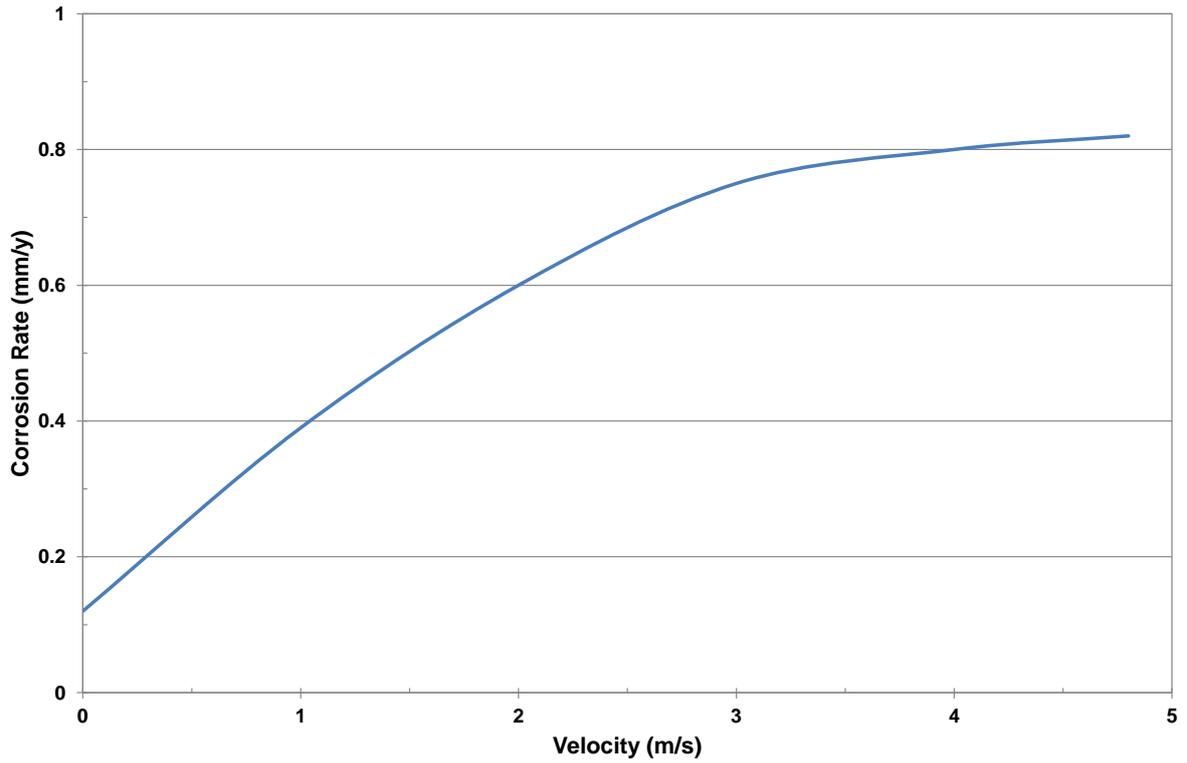


FIGURE 1 The effect of velocity on the corrosion rate of carbon steel in seawater².

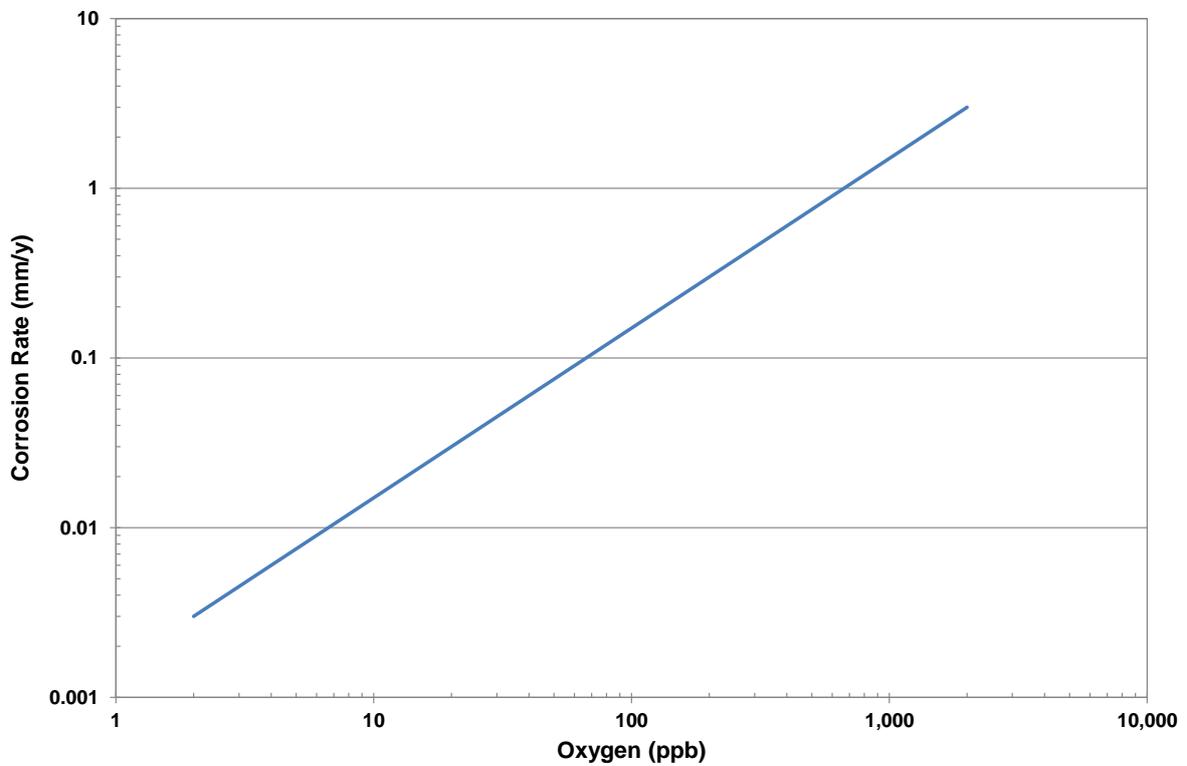


FIGURE 2 The corrosion rate of carbon steel in sodium chloride as a function of oxygen content at 1 m/s.



FIGURE 3 An NAB impeller suffering severe erosion corrosion due to sulphides.

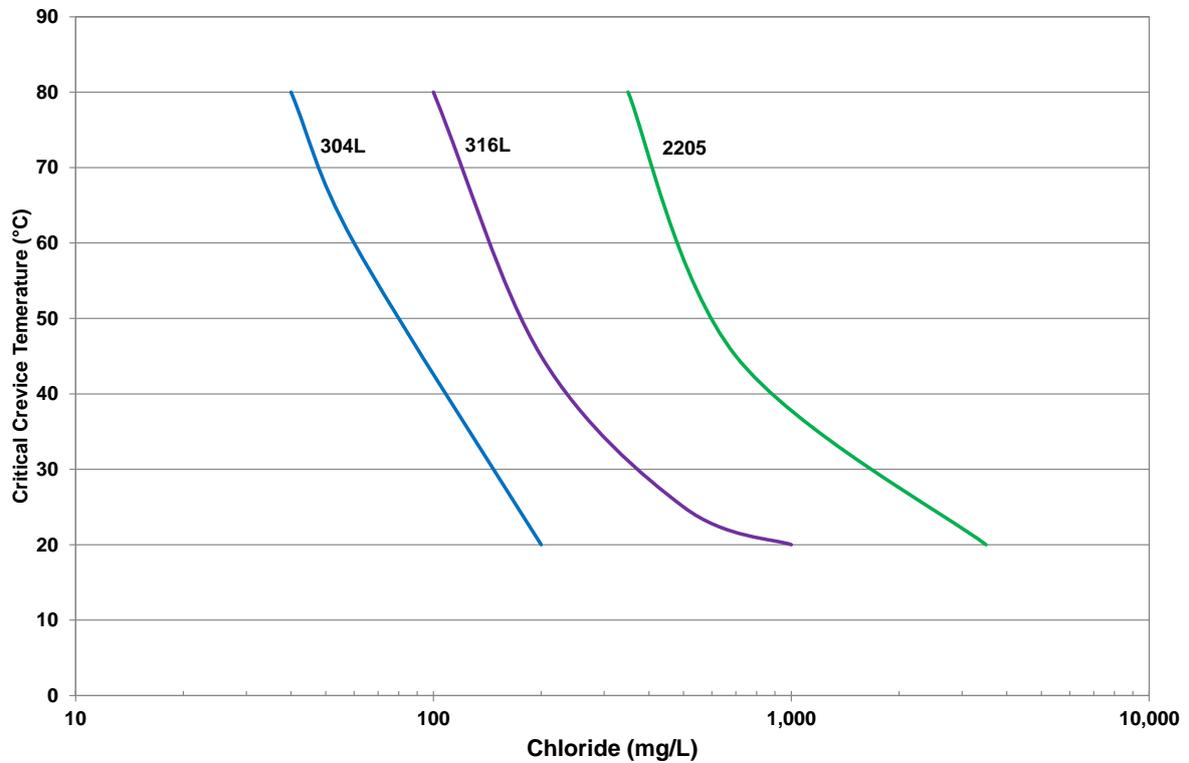


FIGURE 4 Critical crevice temperatures for some stainless steels versus chloride concentration⁵.

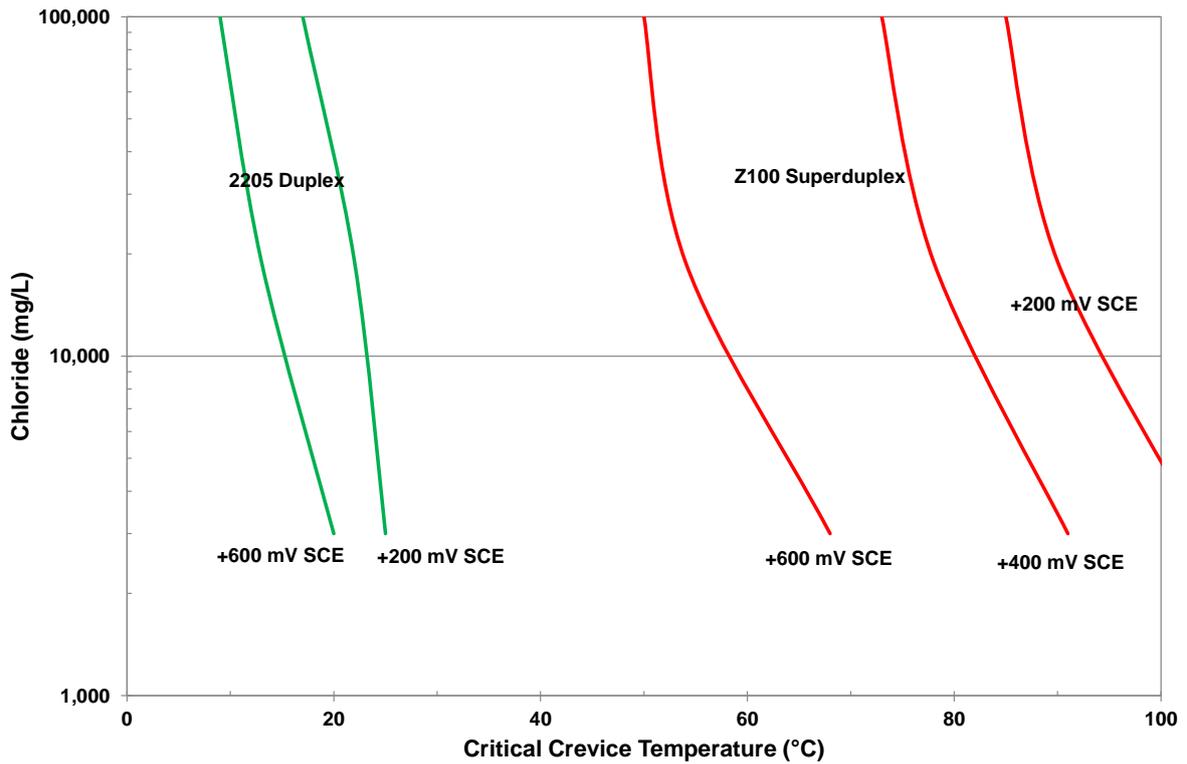


FIGURE 5 Critical crevice temperatures versus chloride at various potentials⁶.

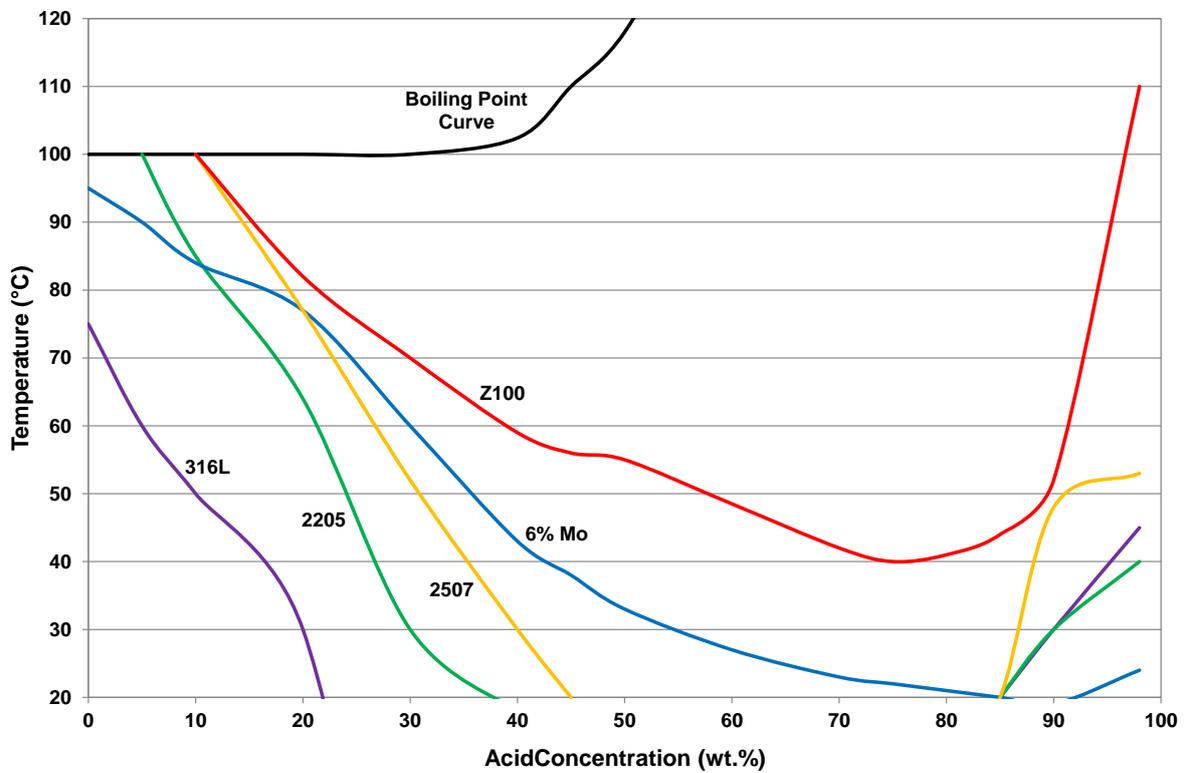


FIGURE 6 Iso-corrosion curves (0.1mm/y) in sulphuric acid for some common stainless steels^{5, 8}.

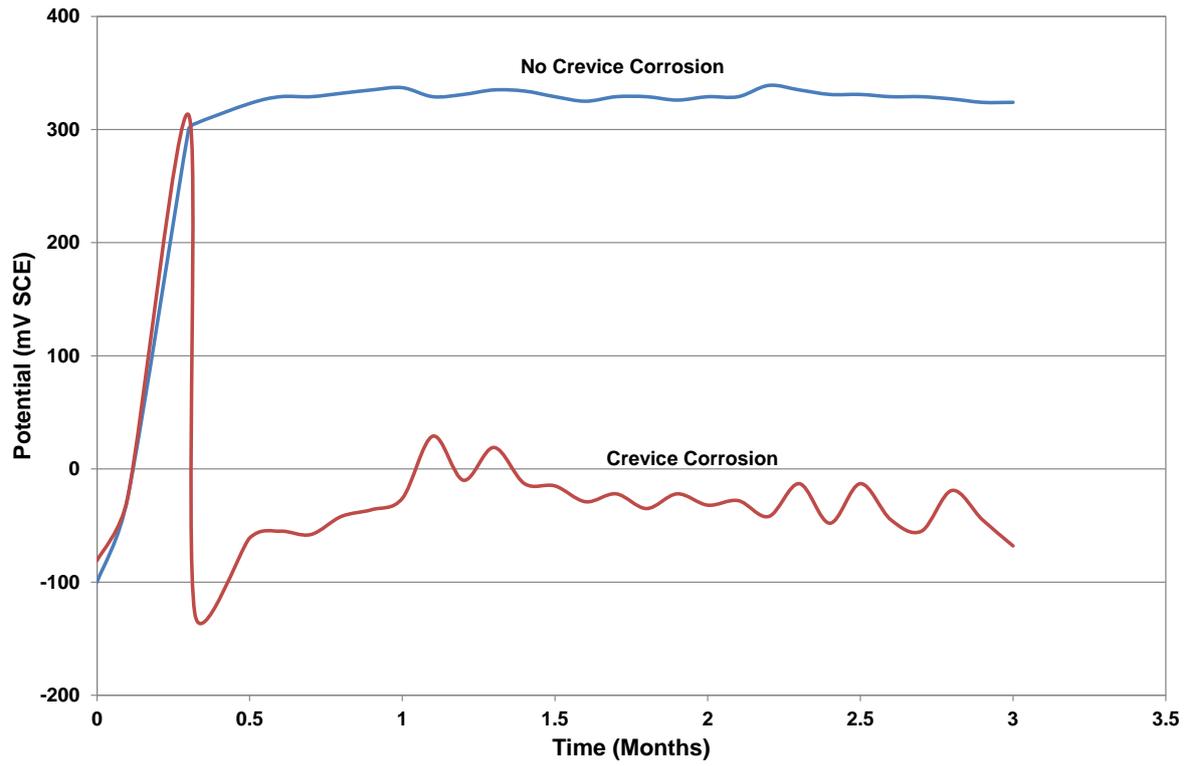


FIGURE 7 Potential versus time curves for stainless steel in water with a biofilm, showing the effect of the initiation of crevice corrosion^{11, 12}.