REPORT

ZERON 100 SUPERDUPLEX STAINLESS STEEL IN THE CHEMICAL AND PROCESS INDUSTRIES

Prepared by: Roger Francis
Corrosion Services Manager

Approved by: Glenn Byrne
Managing Director

CIRCULATION

Division	Engineering
Job No.	
Reference No.	
Report No:	TN1387
Iss No.	3
Date:	Nov 2008

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SUMMARY

This report describes the physical and mechanical properties of Zeron 100, as well as its corrosion performance in a range of common fluids found in chemical plants. Some examples are given to demonstrate the diversity of uses of Zeron 100 by the chemical and process industries.

1.0 INTRODUCTION

Zeron 100 superduplex stainless steel was developed during the 1980's in both cast and wrought forms to produce an alloy with high strength, easy formability, good weldability and excellent corrosion resistance. Initially the main market for Zeron 100 was seen as sea water, particularly for pumps and piping. The alloy was very successful in this application with the offshore oil and gas industry during the late 1980's and early 1990's. The alloy was then used for process pipes, fittings, flanges, manifolds etc. particularly with sour wells. Other applications then began to emerge, where the combination of properties offered by Zeron 100 was commercially attractive. These included flue gas desulphurisation (FGD), the chemical and process industry and mining. The chemical and process industry often involves the use of aggressive liquids, including acids and alkalis, frequently with the presence of halides and at high temperatures. The present paper highlights the properties of Zeron 100 and describes some applications and experiences with the alloy in the chemical process industry from around the globe.

2. ALLOY PROPERTIES

Zeron 100 is a superduplex stainless steel comprising both austenite and ferrite with a nominal 50/50 phase balance. The composition of the alloy is shown in Table 1, with some other common stainless steels for comparison. The elements chromium, molybdenum and nitrogen all give resistance to localised attack in chloride-containing solutions. These are often combined to give a pitting resistance equivalent number or PREN, where:

$$\text{PREN} = \%\ \text{Cr} + 3.3\%\ \text{Mo} + 16\%\ \text{N}.$$

It can be seen that Zeron 100 has a higher PREN than most of the other alloys in Table 1, and it is the only alloy to have a guaranteed minimum PREN.

The PREN of 6%Mo austenitic is slightly higher than that of Zeron 100, but it has been shown (1) that the PREN of high alloy austenitic alloys needs to be 2 to 3 PREN points higher, to have equivalent resistance to crevice corrosion to a duplex stainless steel. The PREN of alloy C-276 is much higher than that of Zeron 100, but in many commercial solutions Zeron 100 has similar or better performance compared with nickel-base alloys.

The elements copper and tungsten are well known to confer extra resistance to sulphuric acid and it can be seen that both of these elements are present in Zeron 100. Copper is also present in alloy 904L, which was originally developed for sulphuric acid service.

The mechanical properties of Zeron 100 compared with some common alloys are shown in Table 2. It can clearly be seen that Zeron 100 is much stronger than the other alloys, even the 22% Cr duplex alloy. The strength differential increases above 150°C because the loss of strength with increasing temperature is much less for Zeron 100 than other CRA's such as 6%Mo austenitic stainless steel. If this strength is used during design then the opportunity for substantial cost savings exists, not only because of the reduced wall thickness, but also because of the consequent savings in fabrication cost and time. The cost advantage of superduplex stainless steel, compared with austenitic, and nickel-base alloys, is further enhanced because of its low content of nickel and other strategic elements.

Code cases for Zeron 100 have been processed by the relevant authorities for PD5500 and ASME VIII division 1 for vessels and ASME B31.3 for pipes. The approved design stresses at room temperature are shown in Table 3 and it can be seen that Zeron 100 offers the highest design stresses. With vessels, PD5500 is preferred for design because of the greater potential wall thickness savings. The largest vessel designed to PD5500 in Zeron 100 is 3.5m diameter, 4.5m tall and 20mm thick and it has been in service with a UK pigments manufacturer since 1996 with no problems.

Zeron 100 is readily welded by all the commonly used arc welding processes. It is usually welded with Zeron 100X consumables, which contain 2 to 2.5% extra nickel to ensure the correct phase balance of the weld metal in the as-welded condition. Like all high alloy stainless steels, Zeron 100 requires welders experienced in stainless steel fabrication working to approved and qualified procedures.

Supply is not a problem because Zeron 100 is readily available in all the common product forms, including castings, pipes, fittings, flanges, plates, bar, billet, fasteners etc. A large stock is currently held in RA® Materials, Manchester warehouse in all these product forms.

3. CORROSION

3.1 Seawater/Brines

Zeron 100 was invented initially as a seawater grade alloy for pumps, valves and piping. It has been in service as castings since 1986 and as a wrought alloy since 1990. Seawater applications cover Europe, the Middle East and the Far East. Because seawater is a common coolant in many chemical and process plants, Zeron 100 is an attractive alloy for heat exchangers cooling aggressive chemicals.

Zeron 100 also resists localised corrosion in neutral chloride solutions over a wide range of concentrations and temperatures. The alloy has found uses in brine discharge lines in desalination plants as well as in crystallisers and evaporators.

3.2 Stress Corrosion Cracking

In hot fluids containing chlorides, stress corrosion cracking (SCC) can cause failures of some stainless steels. Figure 1 shows the threshold temperature for chloride SCC of some common alloys in 3% sodium chloride. The results show that Zeron 100 has superior resistance to chloride SCC compared with both 316L and 22% Cr duplex and similar to that of alloy C-276. Although 6%Mo austenitic can be used to higher temperatures than 22%Cr duplex, it is not as resistant to chloride SCC as Zeron 100.

The safe operating temperature increases as the chloride content decreases. However, the safe temperature decreases if more aggressive cations are present, such as magnesium.

3.3 Mineral Acids

Zeron 100 has excellent resistance to mineral acids. Figure 2 shows the 0.1mm/y iso-corrosion curve for Zeron 100 compared with some other alloys in sulphuric acid. It is clear that Zeron 100 has superior resistance to sulphuric acid compared with many other common grades of stainless steel. Its resistance is similar to that of alloy C-276 over most of the concentration range, except from 50% to 90wt% acid. At acid contentrations >90 wt% Zeron 100 has excellent resistance to corrosion and the alloy finds uses in the heat recovery sections of sulphuric acid plants where the 98% acid is around 200°C (2).

In the presence of oxidisers, such as ferric ions, cupric ions, nitric acid etc. the performance of Zeron 100 increases substantially. A good example of this is the reconcentration of sulphuric acid containing 0.15% nitric acid, used in the manufacture of explosives. Acid at 70wt% concentration is heated at 125°C as part of the concentration process. The corrosion rates with and without nitric acid are shown below.

70% acid (no nitric); corr. rate >> 1mm/y
70% acid (+ 0.15% HNO_3); corr. rate = 0.029mm/y

The performance of Zeron 100 in sulphuric acid is discussed at length in another publication (2).

In some processes the sulphuric acid contains chlorides. Figure 3 shows the iso-corrosion curves in sulphuric acid containing 2,000mg/l chloride. The data shows the excellent performance of Zeron 100 compared with some other stainless steels. In the presence of oxidisers (e.g. Fe^{3+}) the performance can improve, but if the concentration of oxidiser is too high the potential can exceed the pitting potential and localised attack will occur. No data was available for alloy C-276 in this environment.

In hydrochloric acid Zeron 100 also shows good resistance, better than most stainless steels and similar to data for alloy C-276 up to ~7wt % acid (Figure 4). This has led to some applications, as described in section 4.

Zeron 100 has good resistance to phosphoric acid, particularly in the presence of halides, as occurs in the production of fertilisers. This is described in detail elsewhere (3).

3.4 Organic Acids

Most pure organic acids are not very corrosive and can be handled by alloys such as 316L up to quite high concentrations and temperatures. The exception is formic acid, which is quite aggressive. Formic acid is produced during the manufacture of acetic acid and the mixture can be very aggressive. Superduplex stainless steel has very good resistance to such mixtures (4), as shown in Figure 5. The results show that superduplex performs better than many common stainless steels and was equivalent to alloy C-276.

Zeron 100 was exposed in a commercial acetic acid plant under oxidising conditions for two years, with the following results:

Acetone 2%	Water 19%
Formic Acid 10%	Acetic Acid 42%
Propionic Acid 8%	

Temperature - 188°C Pressure - 680 psi

Alloy C-276	-	0.100mm/y
Alloy 20	-	0.075mm/y
Zeron 100	-	0.045mm/y

Zeron 100 outperformed the then currently used nickel alloys.

In some processes halides, such as chlorides or bromides, are present and these make the process more corrosive. Laboratory tests in 80wt% acetic acid with 1.5g/l bromide ion and 0.5g/l manganese ion at 90°C, showed the excellent corrosion resistance of Zeron 100 compared with other stainless alloys (Figure 6).

Test were conducted at high temperature to simulate conditions found in the production of terephthalic acid and dimethyl terephthalate. The results, in Table 4, show the significantly lower corrosion rate of Zeron 100 compared with alloy 317L.

3.5 Caustic Soda

Figure 7 shows the iso-corrosion curves (0.1mm/y) for Zeron 100 in caustic soda compared with 316L. The results show the superior corrosion resistance of Zeron 100, particularly at dilute concentrations (0-30wt%). The presence of chloride up to several wt% has no effect on the corrosion of Zeron 100 in caustic soda (5). Under highly oxidising conditions, Zeron 100, like many other stainless steels, can suffer caustic cracking. However, the threshold conditions for caustic SCC are over a narrow concentration range and at much higher temperatures than are required to cause cracking of 316L. Zeron 100 also offers a more cost effective option compared with nickel alloys over a wide range of temperatures and concentrations.

3.6 Erosion

In addition to its excellent corrosion resistance, Zeron 100 also has good resistance to erosion and corrosion in abrasive slurries, and this is discussed in detail elsewhere (6). Figure 8 shows the relative performance of a number of stainless steels tested at 40m/sec in a brine containing 25g/l chloride and 640mg/l sharp sand at 55°C and a pH of 3.5. These results show the high resistance of Zeron 100 to erosion in this environment.

4. SERVICE EXPERIENCE

Below are some examples of the use of Zeron 100, showing the diverse range of applications in the chemical and process industries.

Zeron 100 has been used in synthetic rubber production. Winnik el al (7) described the use of Zeron 100 for the pump and pipework in a polymerisation reactor cycle (Methyl chloride plus $AlCl_3$ catalyst). This application involves cycling between – 120°C and + 82°C. Hence the superduplex has to have proven fracture toughness at the lowest operation temperature. The material consistently passed the charpy test specification of 40J minimum and 0.38mm lateral expansion at –120°C. The successful use of Zeron 100 for this application has led to several repeat orders. Zeron 100 was chosen because of its combination of high strength and corrosion resistance. The alternative was a nickel alloy, which would have been much more expensive. All of the reactors in the USA and UK have now had Zeron 100 pumps fitted.

The resistance of Zeron 100 to corrosion in strong brines and other concentrated solutions was described above. Zeron 100 was used for the pump discharge piping in a sodium sulphate crystallizer installed in South Africa. The unit operates at 105°C with a 30 wt% solution of sodium sulphate plus solids. The concern in the discharge pipework was both corrosion and erosion. The 1200mm diameter ducting was fabricated from Zeron 100 plate and it has been in successful service since 2001.

Weir Materials delivered in 1995 the largest super duplex vessel at that time (approximately 3.5m diameter and 5.6m long) (Figure 9). The vessel operates at 135°C and is used for solvent recovery by a major pigment producer. The environment varies from acid to alkaline and contains chlorides. A previous vessel had been cast-iron, but with the upgrading of the process and the increase in the temperature, the corrosion allowance would have resulted in excessively thick castings. Zeron 100 proved to be a cost effective alternative with proven resistance to both corrosion and stress corrosion cracking in the working fluid.

The Zeron 100 vessel was fabricated from 20mm plate whereas the cast iron would have been 150mm thick. The weight of the Zeron 100 vessel was 20 tonnes, whereas a cast-iron vessel would have exceeded 100 tonnes. This is an example of vessel design using PD5500 to take maximum advantage of the mechanical properties of Zeron 100. The vessel was inspected after 2 years in service and was found to be in excellent condition. Following this a 316L vessel suffering chloride SCC has been replaced with Zeron 100 at the same plant.

The successful trials of Zeron 100 at a UK acetic acid plant described in a previous section, have led to the installation of a Zeron 100 valve and piping, replacing shorter lived nickel alloy components. Zeron 100 pipes, fittings and flanges have also been used in parts of the acetic acid plant in the Jubail Acetyl Complex, Saudi Arabia, due to come on line in 2009.

In vinyl chloride monomer production, part of the process involves the cooling of gaseous products. Under certain conditions this results in hydrochloric acid condensing on the heat exchanger tubes. Zeron100 was selected for the heat exchanger tubes because of its excellent resistance to both the brackish water cooling medium and hydrochloric acid on the process side (8). Figure 10 shows the unit during construction. Zeron 100 has been selected for the heat exchanger tubes in two subsequent plant expansions.

Another hydrochloric acid application involved the production of rutile by the hydrochloric acid route at a plant in the Middle East. The resistance of Zeron 100 to hydrochloric acid led to its selection for the spent acid lines.

Zeron 100 is also widely used by original equipment manufacturers because of its ready availability. Components such as agitators, filters, mixers etc. are routinely produced. Figure 11 shows the basket from a centrifuge at an FGD plant where gypsum is separated from a corrosive limestone slurry. Similar baskets have been used in the UK in a plant producing rutile by the sulphuric acid route, to separate ferrous sulphate crystals from spent acid. This has resulted in large annual savings in maintenance compared with the previous 316L baskets, which corroded rapidly.

Some other applications include a citric acid plant in Norway, paper machines in Australia, a TPA plant in the USA and a fertiliser plant in Norway.

5. CONCLUSIONS

1. Zeron 100 has excellent resistance to general corrosion, pitting and stress corrosion cracking in a wide range of fluids.

2. The high strength of Zeron 100 offers potential cost savings over austenitic alloys, particularly at higher temperatures and pressures.

3. Zeron 100 can offer benefits not only over lower alloyed stainless steels, but also over nickel-base alloys for some applications.

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TABLE 1. The composition of some stainless steels commonly used by the chemical and process industries.

ALLOY	Nominal Composition (wt%)							PREN*
	Fe	Cr	Ni	Mo	N	Cu	W	
ZERON 100 (Wrought)	bal	25	7	3.5	0.25	0.7	0.7	> 40
ZERON 100 (Cast)	bal	25	8	3.5	0.25	0.7	0.7	> 40
316L	bal	17	10	2	-	-	-	24
22% Cr Duplex	bal	22	5	3	0.16	-	-	35
904L	bal	20	25	4.5	-	1.5	-	35
6%Mo Aust.	bal	20	18	6	0.2	0.7	-	43
C - 276	5	15	bal	16	-	-	3.5	68

bal = balance
PREN = %Cr + 3.3%Mo + 16%N

TABLE 2. Minimum mechanical properties of some stainless steels commonly used by the chemical and process industries.

ALLOY	0.2% PROOF STRESS (MPa)	UTS (MPa)	ELONG[n] (%)	*HARDNESS** (HRC)
ZERON 100 (Wrought)	550	750	25	28
ZERON 100 (Cast)	450	700	25	24
316L	213	500	45	22
22%Cr Duplex	450	650	25	28
904L	230	530	40	22
6%Mo Aust.	300	650	35	22
C – 276	283	690	40	100+

* - maximum
\+ - HRB

TABLE 3. Design stresses for some common stainless steels at room temperature.

ALLOY	DESIGN STRESS (MPa)		
	PD 5500 (Vessels)	ASME VIII Div. 1 (Vessels)	ASME B31.3 (Pipes)
ZERON 100 (Wrought)	319	214	250
316L	150	115	115
22%Cr Duplex	289	177	207
6%Mo Aust.	NL	185	207
C-276	NL	188	188

NL – not listed

TABLE 4. The results of corrosion tests in simulated TPA fluids.

ALLOY	CORROSION RATE (mm/y)	
	FLUID 1*	FLUID 2+
317L	0.44	0.67
Welded 317L	0.47	0.68
Zeron 100	0.004	0.011
Welded Zeron 100	0.006	0.016

* - Fluid 1: 75% Acetic Acid with traces of Br, Cu and Mn @ 175°C.

\+ - Fluid 2: 96% Acetic Acid with traces of Br, Cu and Mn @150°C.

FIGURE 1 Threshold temperature for chloride SCC of some alloys in 3% sodium chloride

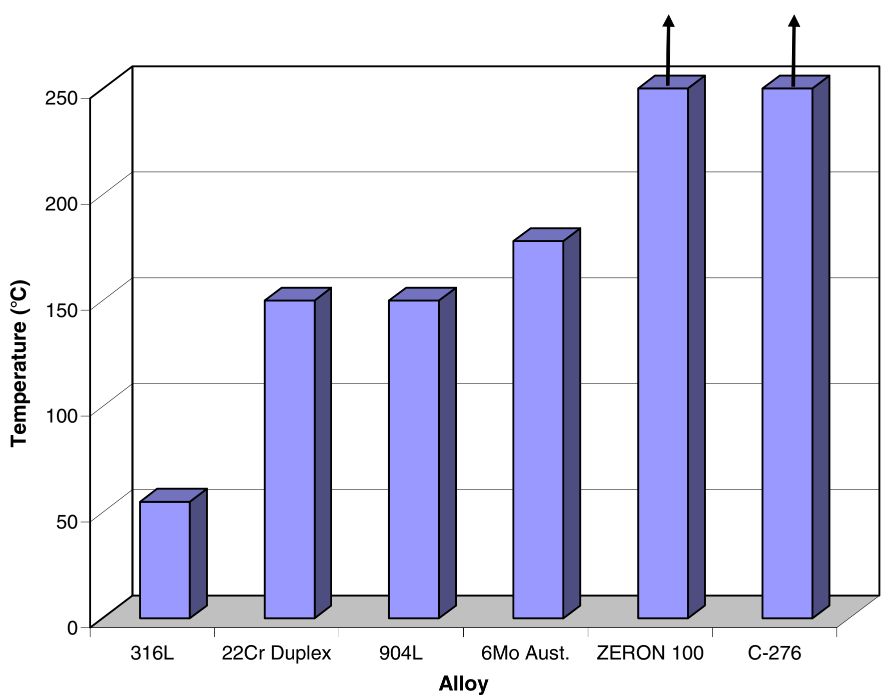

FIGURE 2 Iso-corrosion curves (0.1mm/y) for some stainless steels in aerated sulphuric acid

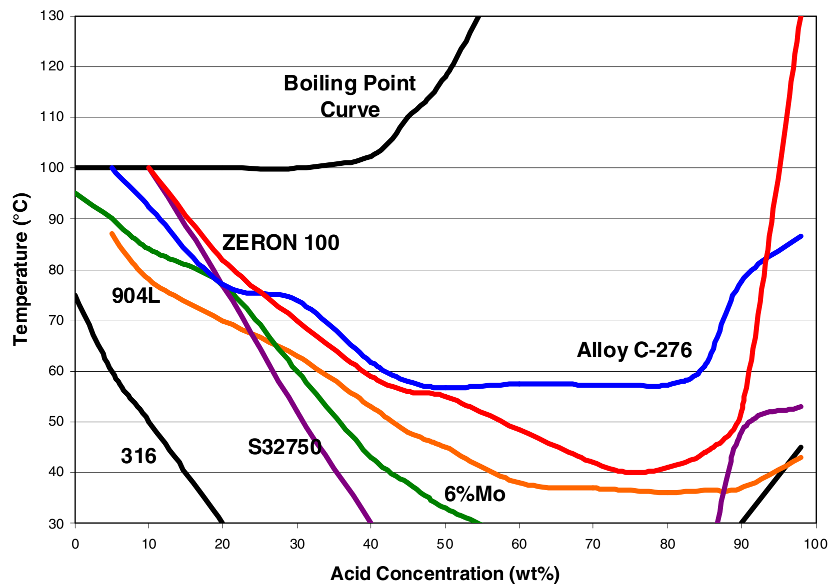

FIGURE 3 Iso-corrosion curves (0.1mm/y) in sulphuric acid plus 2,000mg/l chloride

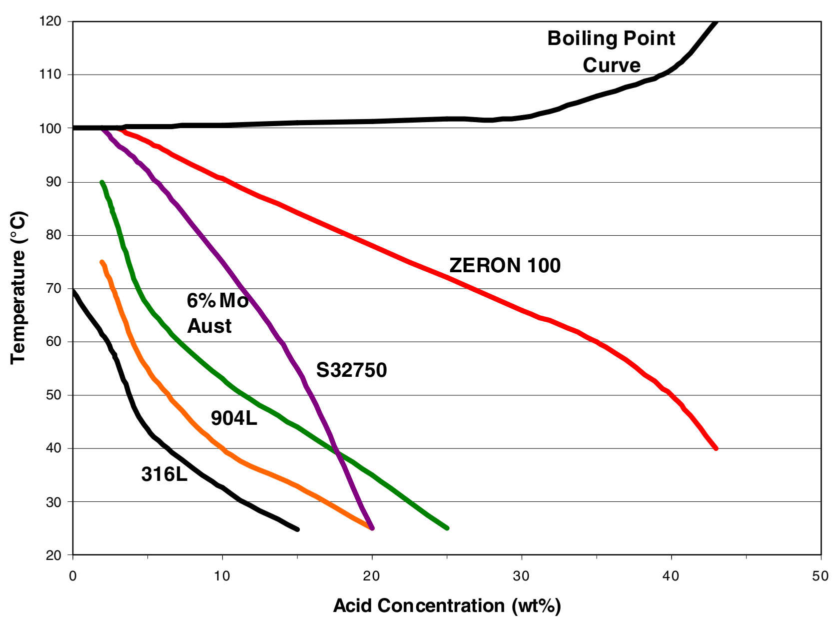

Figure 4 Iso-corrosion curves (0.1mm/y) of some stainless steels in hydrochloric acid

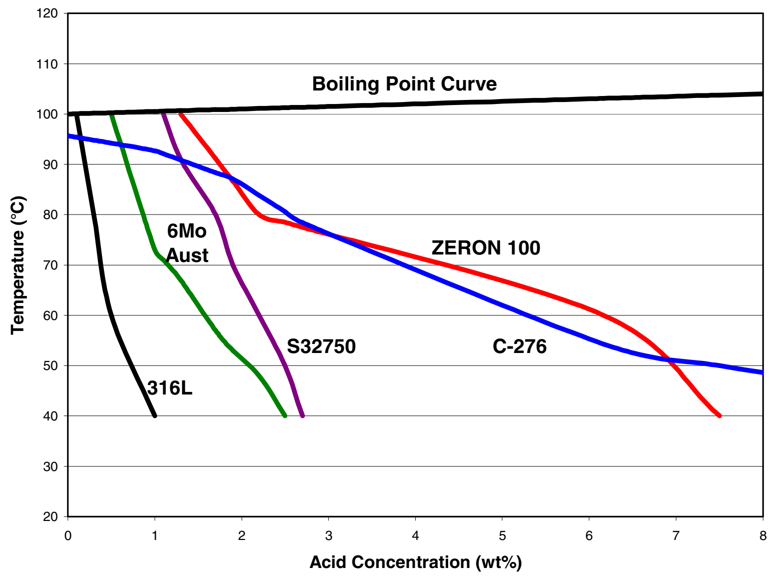

FIGURE 5 Corrosion of some common stainless steels in boiling 50% acetic acid plus formic acid

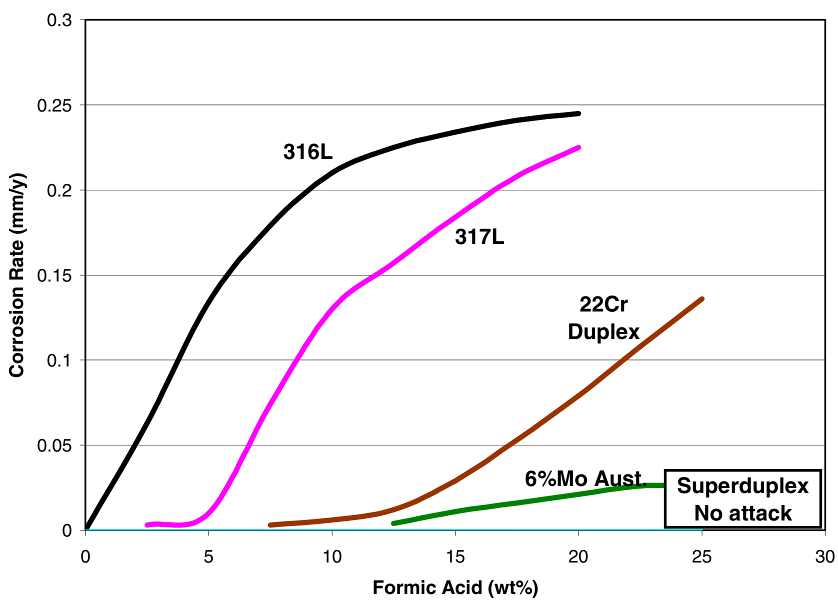

FIGURE 6 Corrosion of some common stainless steels in 80wt % acetic acid plus 1.5g/L bromide and 0.5g/L manganese at 90°C

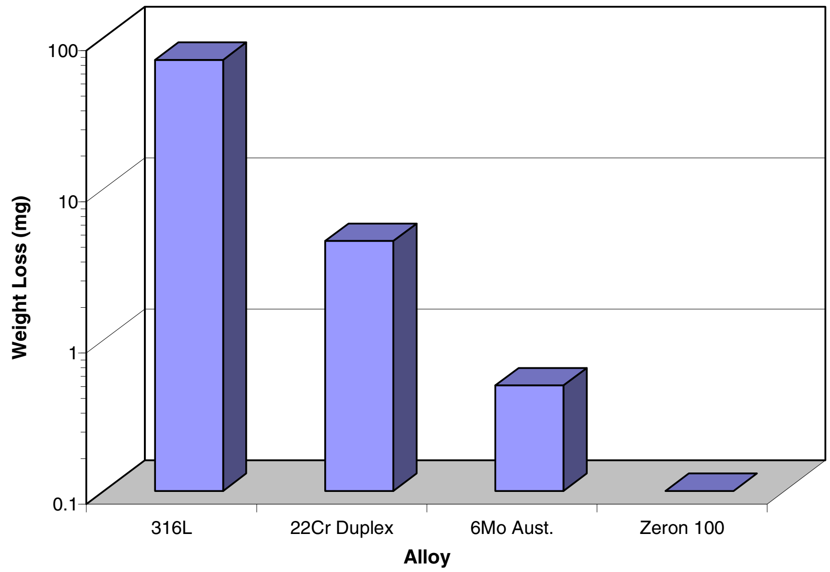

FIGURE 7 Iso-corrosion curves (0.1mm/y) for some stainless steels in caustic soda

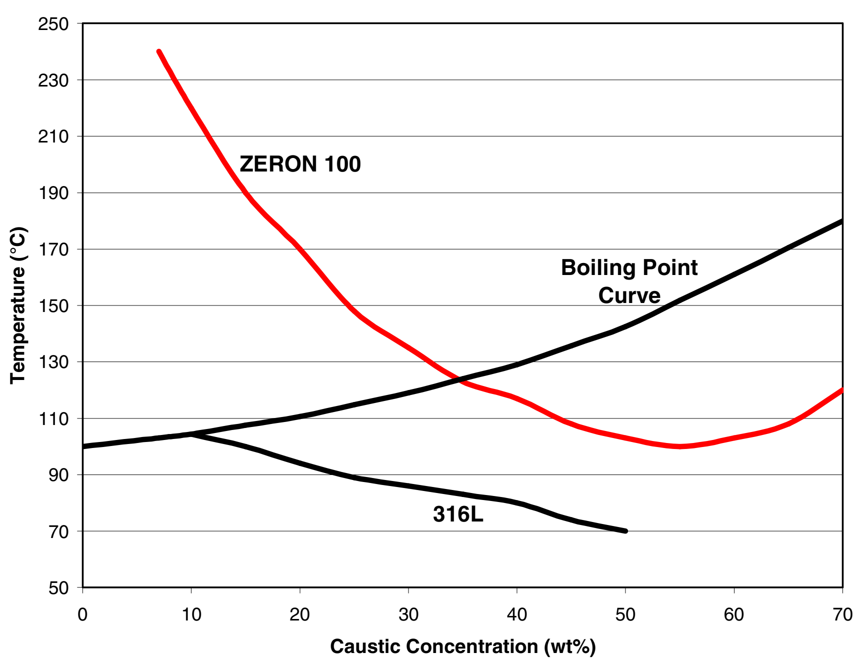

FIGURE 8 Weight loss in erosion test at 40m/sec (pH=3.5; temperature=55°C; chloride=25g/l)

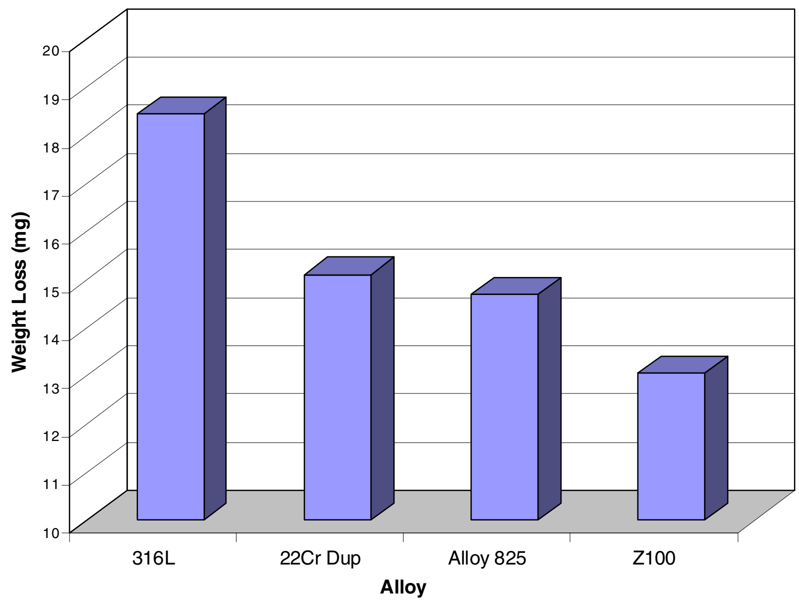

FIGURE 9. Zeron 100 vessel supplied to a UK pigments manufacturer

FIGURE 10. Condenser in Zeron 100 for a VCM plant

FIGURE 11. Centrifuge basket in Zeron 100 for an FGD plant