REPORT

# THE USE OF ZERON 100 SUPERDUPLEX STAINLESS STEEL IN PHOSPHATIC AND UREA-BASED FERTILISER PLANTS.

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**SUMMARY**

ZERON® 100 is a superduplex stainless steel with high strength and excellent resistance to both corrosion and stress corrosion cracking in a wide range of environments encountered in fertiliser manufacturing. Data is presented to show the resistance of Zeron 100 to localised corrosion in the presence of chlorides, to chloride stress corrosion cracking and to erosion corrosion.

Zeron 100 offers superior resistance compared with commonly used austenitic alloys such as the 300 series. The high strength of Zeron 100 offers the advantage of reduced wall thickness compared with austenitic alloys, resulting in lower costs. The paper shows how the maximum advantage can be obtained by utilising design codes, which take the greatest advantage of the high yield stress of the alloy. This minimises wall thicknesses, reduces fabrication time and hence lowers costs.

A range of applications for Zeron 100 in the production of both phosphatic and urea fertilisers is presented.

## 1.0 INTRODUCTION

Stainless steels have been used by the chemical industry for many years in applications requiring corrosion resistance better than that of carbon steel. Where alloys such as 304L and 316L have proved inadequate there has been a tendency to choose nickel-base alloys such as C-276 (UNS N10276) and alloy 625 (UNS N06625). These alloys have superior corrosion resistance to the 300 series austenitic stainless steels, but at a greatly increased cost.

In the late 1970's and 1980's the current generation of duplex stainless steels was developed. These alloys have a 50/50 austenite-ferrite structure with higher levels of chromium and molybdenum than the 300 series austenitic alloys. Their combination of high strength and corrosion resistance has led to the widespread use of duplex stainless steels by the oil and gas industry, particularly for corrosive, offshore environments. The use of duplex stainless steels by the fertiliser industry has been more limited, but there are now numerous applications where their combination of properties has led to the selection of duplex stainless steel in fertiliser plants.

## 2.0 ZERON 100

Zeron 100 was the original superduplex stainless steel, characterised by its high content of molybdenum and nitrogen, compared with earlier duplex stainless steels, and having a pitting resistance equivalent number (PREN) guaranteed to be greater than 40. (PREN = % Cr + 3.3 x % Mo + 16 x % N). The composition of Zeron 100 is shown in Table 1 and some commonly used austenitic alloys are shown for comparison. The high PREN value of Zeron 100 compared with other alloys indicates its high resistance to localised corrosion in the presence of chlorides.

The mechanical properties of Zeron 100 are shown in Table 2, and the properties of some commonly used austenitic alloys are shown for shown for comparison. The superior 0.2% proof stress of Zeron 100 is clearly shown. Utilising this strength to decrease wall thickness of pipe and vessels can offset the slightly higher cost of Zeron 100 compared with, say, 316L.

## 3.0 CORROSION RESISTANCE

### 3.1 Pitting Corrosion

The relative pitting resistance of stainless steels and nickel alloys is often compared using the ASTM G48 test in ferric chloride. The high chloride content, low pH and highly oxidising nature of this solution is not dissimilar to a number of solutions in use by the chemical industry. The temperature at which pitting is first observed is known as the critical pitting temperature (CPT). Figure 1 shows the CPT for a number of common stainless steels.

It can be seen that the CPT of Zeron 100 is superior to that of 316L, 22%Cr duplex and 904L and while not so great as that of C-276, the value of 70°C for Zeron 100 is adequate for many applications.

3.2 Stress Corrosion Cracking

One recurring problem in chemical plants of all types is chloride stress corrosion cracking (SCC) of 304L and 316L stainless steels. The duplex stainless steels are much more resistant to chloride SCC than the 300 series austenitic alloys, as is shown in Figure 2. Zeron 100 has shown no indications of cracking in 5% sodium chloride solution up to 250℃. Thus Zeron 100 offers a chloride stress cor rosion cracking resistance similar to alloy C-276 at a much lower cost.

It is usually accepted that chloride SCC starts from the bottom of small pits. It is not clear whether it is the more aggressive solution in the bottom of the pit, or the pit acting as a stress raiser that causes this preferred site of initiation. Slow strain rate tests have been conducted on cross-weld tensiles of Zeron 100 at a strain rate of $1 \times 10^{-6}$/sec. The environment was synthetic sea water plus 4.5M NaCl at pH1, which was chosen to represent the conditions inside a pit[1]. The tests were conducted at 45℃. Figure 3 shows the load/extension curve compared with one for a test in distilled water at the same temperature. There was no significant change in the extension to fracture. The elongation ratio (elongation in test solution/elongation in distilled water) was 0.98. This shows the high resistance of Zeron 100 to chloride SCC.

3.3 Erosion Corrosion

The slurries produced during the manufacture of phosphoric acid are not only corrosive, but also erosive. Zeron 100 has excellent resistance to erosion corrosion in the presence of slurries because of its superior strength and hardness compared to austenitic alloys. Figure 4 shows data from pin erosion tests in acidic slurries containing 10.6% wt% calcium sulphate, 0.26 wt% calcium carbonate, 5,000 mg/l chloride and 0.1% fly-ash[2]. This slurry is abrasive mostly because of the fly-ash, but the results in Figure 4 show that Zeron 100 is superior not only to 316L but also to lower alloyed 25%Cr steels (PREN = 37). Zeron 100 has been used as a cast alloy (UNS J93380) in pumps and valves since 1986 and has also been used for the main slurry pumps in the flue gas desulphurisation (FGD) units at the Drax Power Station, UK. These pumps have been in service for over 10 years with excellent results.

## 4.0 DESIGN

The high strength of Zeron 100 combined with its resistance to localised corrosion and chloride SCC makes it very attractive for vessels and pipes operating at high temperatures and / or pressures. To take maximum advantage of the properties it is advisable to use a code which uses design stresses based on 0.2% proof stress values rather than tensile strength, eg. PD5500 for pressure vessels.

By utilising suitable design codes such as PD5500 it is possible to make substantial wall thickness reductions for duplex stainless steels compared to 316L and hence offset the somewhat higher cost of the duplex material. The use of a thinner wall means that there will also be a reduction in fabrication time, leading to further savings.

Table 3 shows the maximum design stress at several temperatures for 316L and ZERON 100 using ASME VIII division 1 and PD5500. The figures clearly show the much higher design stresses permitted by PD5500. This code is widely used by the UK chemical industry, and in many countries application to the national pressure vessel authority will permit the use of internationally recognised standards such as PD5500. Table 3 also shows the much higher design stresses for Zeron 100 compared with 316L with both codes.

## 5.0 PHOSPHATIC FERTILISER PRODUCTION

Phosphatic fertilisers are produced from phosphoric acid, which is mainly manufactured by a wet process, which consists of attacking natural phosphate rocks with sulphuric acid. There are three major steps in the process i.e.:

1. Acidulation of natural phosphate
2. Filtration of the slurry
3. Concentration of the acid

These processes generate a range of corrosion problems, many of which are overcome by the use of corrosion resistant alloys. The following sections outline the resistance of superduplex stainless steel to some of the process media, and highlight the advantages over alternative alloys.

### 5.1 Sulphuric Acid

Concentrated sulphuric acid is used with recycled acid from the filter to react with phosphate rock at about 80°C. This enters the reactor as a slurry and produces a suspension of calcium sulphate crystals in phosphoric acid (~40%). Zeron 100 superduplex stainless steel has excellent resistance to sulphuric acid, as shown in Figure 5. Not only does it have superior resistance to alloys such as 316L and 22%Cr duplex, but also to sulphuric acid grade alloys such as 904L. The performance of Zeron 100 is equivalent to, or superior to, a number of other special sulphuric acid grade austenitic alloys. Because of its lower nickel content, Zeron 100 is less costly, particularly if its superior strength can also be utilised to reduce wall thickness.

Natural rocks contain a wide range of other elements and these can also influence the corrosion behaviour. The presence of chlorides and fluorides, in particular, increases the susceptibility of alloys to corrosion. The high PREN value of Zeron 100 indicates its resistance to localised attack in the presence of halides. This makes it superior to lower grade alloys such as 904L and 316L and similar to many nickel-base alloys. Figure 6 shows the iso-corrosion curves (0.1mm/y) for several stainless steels in sulphuric acid containing 2,000mg/l chloride. Zeron 100 is clearly superior not only to alloys such as 904L, but also to other 25%Cr duplex alloys such as UNS S32750.

The presence of oxidising ions such as $Cu^{2+}$, $Fe^{3+}$, or small quantities of nitric acid all extend the operating range of stainless steels in sulphuric acid. Zeron 100 has been approved for use in a sulphuric acid concentrator that takes the concentration from 70% to 95% by boiling off the water. The acid contains ~0.15wt% nitric acid and tests showed that Zeron 100 corroded at 0.029 mm/y in 70% sulphuric acid at 125°C.

### 5.2 Phosphoric Acid

Many stainless steels have good resistance to pure phosphoric acid, but the impurities in commercial phosphoric acid make it much more corrosive. In addition to the phosphoric acid there is some residual sulphuric acid and, if there were any fluorides in the rocks, hydrofluoric acid. Some of this will react with silica to form fluorosicilic acid. There are usually also substantial quantities of aluminium and iron in the acid. Aluminium tends to reduce the aggressivity of the fluorine-containing compounds, while iron tends to make the solutions more oxidising. In addition the rocks may contain chlorides which increase the corrosiveness of the acid.

RA Materials developed the following synthetic commercial phosphoric acid composition based on typical analyses from plants around the world.

| | | |
|---|---|---|
| Phosphoric acid | - | 350ml/l(30% $P_2O_5$) |
| Sulphuric acid | - | 3.0 wt% |
| Fluorosicilic acid | - | 2.0 wt% |
| Iron (as sulphate) | - | 0.35 wt% |
| Aluminium (as sulphate) | - | 0.40 wt% |

Tests were conducted at 80℃ with a range of fluoride (0 to 0.8%) and chloride concentrations (300 to 3,000 mg/l).

Figures 7 & 8 show the corrosion rates of Zeron 100, 6%Mo austenitic and 22% Cr duplex as a function of fluoride and chloride contents. Both graphs show that Zeron 100 has the lowest corrosion rate, especially at high fluoride and/or chloride contents.

Rocks used in phosphoric acid production frequently contain abrasive particles as well as chlorides and fluorides. This can lead to erosion or erosion-corrosion problems. The high resistance of Zeron 100 to erosion-corrosion, as described previously, makes it eminently suitable for components in the first stage reactor during phosphoric acid production, including pumps, agitators and stirrers.

5.3 Nitrophosphate Plants

Nitrophosphate fertilisers have a number of advantages, both economic and environmental, over conventional phosphates. The main ones are that the process is independent of sulphuric acid, and hence the price of sulphur, and also that there are no solid by-products to dispose of.

The process consists of reacting natural phosphate rocks with nitric acid, which produces nitrophosphoric acid and calcium nitrate. The solution is cooled to crystallise the calcium nitrate, which can then be separated, while the liquor is then concentrated as required. The calcium nitrate can be reacted with $CO_2$ and ammonia to produce calcium ammonium nitrate, which is also used as a fertiliser.

Zeron 100 superduplex is very resistant to hot nitric acid, eg. the corrosion rate is 0.1mm/year in 44 wt% nitric acid at its boiling point (110℃). The acid is strongly oxidising and so the presence of other oxidising ions from the rocks has no significant effect. The presence of chlorides and fluorides does degrade alloy performance however. The corrosion rate depends on the concentration of halides in the rocks being processed.

5.4 Applications for Zeron 100 Super-duplex Stainless Steel

The excellent resistance of Zeron 100 superduplex stainless steel to both sulphuric and phosphoric acids makes it an ideal candidate alloy for the sulphuric acid digesters, sulphuric acid pipework and phosphoric acid vessels. The excellent resistance of Zeron 100 to erosion corrosion in acidic slurries also makes it suitable for agitators, stirrers and slurry pumps, pipework and valves.

Zeron 100 was originally developed as an alloy to resist seawater, and so it is eminently suitable for use in sea water cooled heat exchangers, both for tubing and for tube plates. Zeron 100 has been used in seawater heat exchangers for many years, cooling a variety of aggressive chemicals.

Superduplex stainless steel can be considered for the same kind of applications in nitrophosphate plants as sulphuric/phosphoric acid plants i.e. digesters, reactors, pipework, pumps, valves and agitators. The aggressiveness of the fluids in any plant will be strongly influenced by the quantities of other ions present in the natural rocks being processed. Halides will decrease alloy performance, while oxidising species will improve it. Hence, it is desirable to conduct corrosion tests prior to alloy selection for major components.

Norsk Hydro has used Zeron 100 for recirculation pipework on the primary reaction vessel, where nitric and phosphate rocks are reacted. They had previously used 316L, but problems had occurred due to corrosion and erosion. Zeron 100 was chosen because of its high corrosion resistance. This makes it more tolerant of impurities such as fluorides and chlorides and enables the plant to use lower grade rock, which contains high levels of halides. Zeron 100 has extended the life of the pipework by over 500%. In addition to the pipework, the first stage sedimentation tank has also been constructed from Zeron 100 plate, again because of its resistance to corrosion and erosion.

Because of its good resistance to general corrosion and erosion corrosion Zeron 100 was used for several components in a phosphate reactor recirculation pump in an East European plant. The environment consists of about 33% phosphoric acid plus fluorides, chlorides and undigested rock at about 100°C. In this instance Zeron 100 was chosen as a more cost effective alternative to the nickel alloy C-276 (UNS N10276).

One problem that does arise is the fact that many plants are licensed by the large chemical companies, who specify the materials of construction. These specifications are not always reviewed at regular intervals, and do not take account of the newer, more cost effective alloys such as superduplex stainless steel. It requires pressure from both users and alloy producers to ensure that designs encompass current technology, to produce the most cost effective plants.

## 6.0 UREA FERTILISERS

Urea is increasingly popular as a fertiliser because of its high nitrogen content compared with ammonium nitrate. Urea is produced by reaction of ammonia and carbon dioxide to form ammonium carbamate, followed by decomposition of the carbamate into urea and water. Unconverted carbamate is removed and recycled into the reactor.

Ammonium carbamate is corrosive towards stainless steels and grades with higher levels of chromium and molybdenum perform better than 304L and 316L. For this reason Zeron 100 superduplex would be ideal for the carbamate re-cycling pumps and pipework, and also for the carbamate coolers.

Notten (3) has described the use of the Streicher test (ASTM A262 Method B) for qualifying stainless steels for carbamate service. The pass level for 25%Cr duplex stainless steel is a weight loss not exceeding 0.9 $g/m^2/h$ and selective phase or intergranular attack not exceeding a depth of 100µm. The results for Zeron 100 in Table 4 show that it not only exceeds the requirements for 25%Cr duplex stainless steel but also that for Safurex, a proprietary grade of duplex stainless steel developed for carbamate service.

The reactor vessel could be constructed of superduplex stainless steel, but this may run into materials specification problems from the licensing companies as described above

Zeron 100 has excellent resistance to wet gases containing $CO_2$ and/or $H_2S$ at high temperatures. This has lead to its widespread use by the oil and gas industry for handling sour process fluids[4, 5]. Zeron 100 is currently working in such environments up to at least 200℃, with no corrosion problems. In urea plants the $CO_2$ may well contain sulphur gases and hence Zeron 100 will be ideal for $CO_2/H_2S$ strippers. Zeron 100 is also resistant to ammonia and so could be used for ammonia pipework and vessels operating below 300℃.

## 7.0 AVAILABILITY

Zeron 100 has the advantage that it is available in all wrought product forms (plate, bar, pipe etc.) as well as in cast form and so it is possible to construct complete items in super duplex. This has the advantage of removing galvanic corrosion problems, and fabrication problems between different grades of alloys. Zeron 100 is readily welded with its own welding consumable (Zeron 100X) by all the common techniques GTAW, MMAW, SAW etc[6]. Like all high alloy stainless steels, Zeron 100 needs care in welding and requires qualified welders working to approved procedures. Zeron 100 has been welded in thicknesses from 1mm to 65mm without problems.

## 8.0 CONCLUSIONS

Zeron 100's combination of high strength and excellent corrosion resistance to a whole range of fluids make it an eminently suitable and cost effective material for a wide range of applications in the phosphatic and urea fertiliser industries.

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**TABLE 1: Nominal composition of some commonly used stainless steels.**

| ALLOY | UNS NO. | COMPOSITION (wt%) | | | | | | | PREN* |
|---|---|---|---|---|---|---|---|---|---|
| | | Fe | Cr | Ni | Mo | N | Cu | W | |
| 316L | S31603 | Bal | 17 | 11 | 2.1 | - | - | - | 24 |
| 904L | N08904 | Bal | 20 | 25 | 4.5 | - | 1.5 | - | 35 |
| 6%Mo Aust | S31254 | bal | 20 | 18 | 6 | 0.2 | 0 .7 | - | 43 |
| C-276 | N10276 | 5 | 15 | bal | 15 | - | - | 3.5 | 64 |
| 22%Cr Duplex | S31803 | Bal | 22 | 5 | 3 | 0.16 | - | - | 35 |
| **ZERON 100** | **S32760** | **Bal** | **25** | **7** | **3.5** | **0.25** | **0.7** | **0.7** | **>40** |

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

**TABLE 2: Specified minimum mechanical properties of some common stainless steels.**

| ALLOY | UNS NO. | 0.2% Proof Stress (MPa) | UTS (MPa) | Elongn. (%) |
|---|---|---|---|---|
| 316L | S31603 | 210 | 500 | 45 |
| 904L | N08904 | 230 | 530 | 40 |
| 6%Mo Aust | S31254 | 300 | 650 | 35 |
| C-276 | N10276 | 365 | 785 | 59 |
| 22%Cr Duplex | S31803 | 450 | 680 | 25 |
| **Zeron 100** | **S32760** | **550** | **750** | **25** |

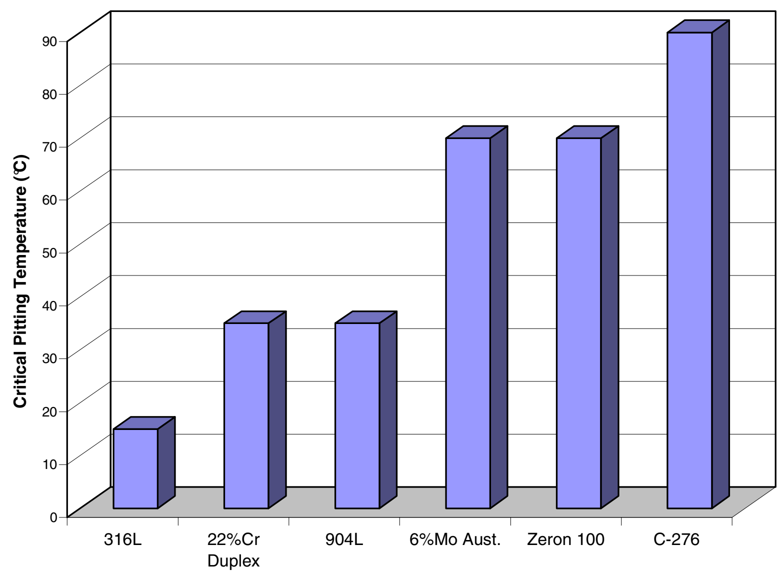
**TABLE 3: Design stresses permitted by different vessel codes at various temperatures for 316L and Zeron 100**

| CODE | ALLOY | DESIGN STRESS (MPa) | | |
|---|---|---|---|---|
| | | 25°C | 100°C | 200°C |
| ASME VIII DIV. 1 | 316L | 115 | 115 | 109 |
| | Z100 | 214 | 212 | 200 |
| PD5500 | 316L | 150 | 134 | 110 |
| | Z100 | 319 | 300 | 269 |

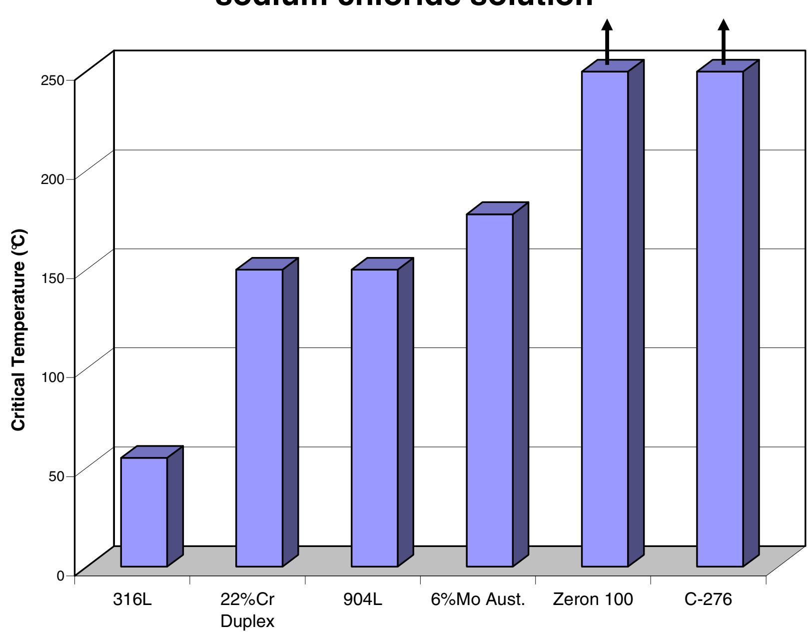
**TABLE 4: Requirements for duplex stainless steels in the Streicher test and the results for Zeron 100 (Ref 3).**

| ALLOY | MAX WT LOSS ($g/m^2.h$) | MAX. DEPTH OF ATTACK (µm) |
|---|---|---|
| Requirement for 25%Cr duplex. | 0.9 | 100 |
| Requirement for Safurex. | 0.7 | 100 |
| Wrought Zeron 100 | 0.20 | 12 |
| Cast Zeron 100 | 0.27 | 32 |
| TIG Welded Zeron 100 | 0.38 | 26 |

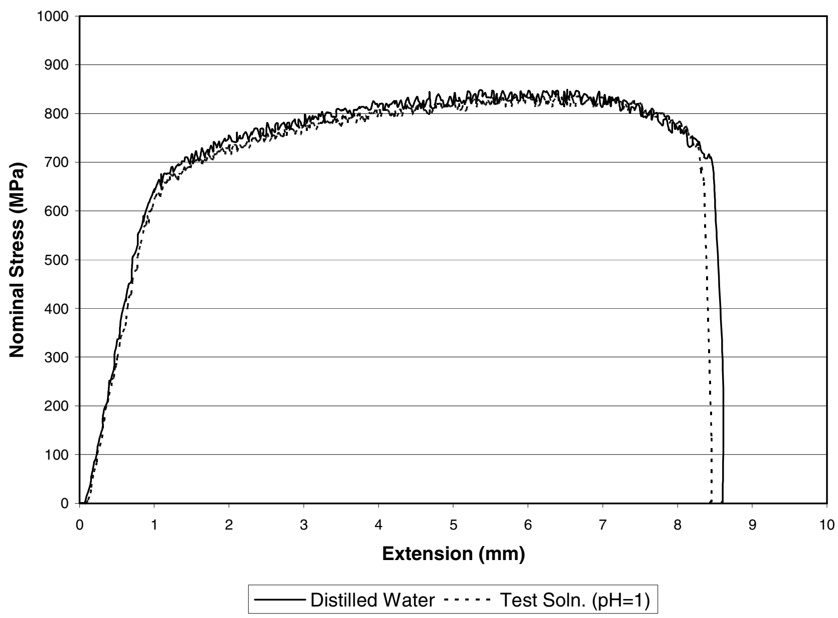
## FIGURE 1 Typical critical pitting temperature in 10% ferric chloride (ASTM G48A)



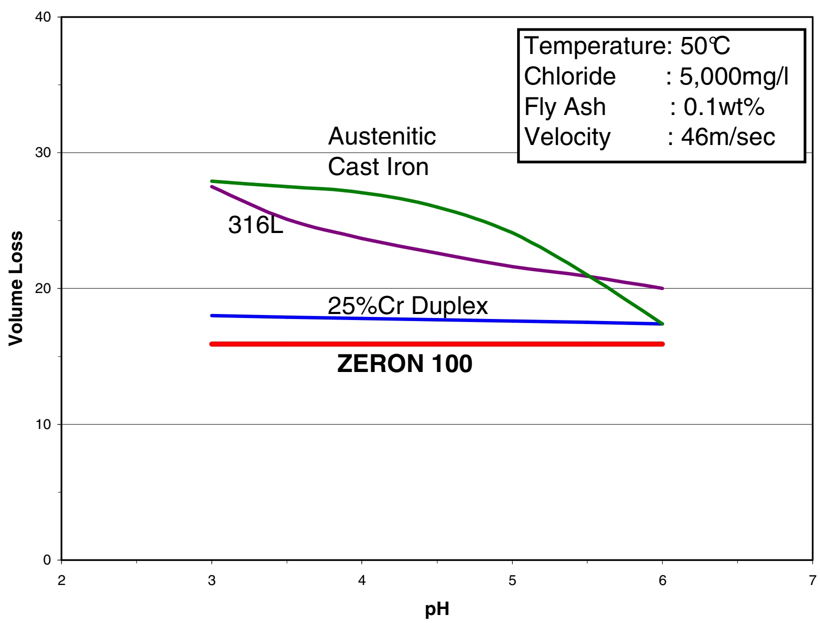

## FIGURE 2 Critical temperature for the onset of chloride stress corrosion cracking in 5% sodium chloride solution



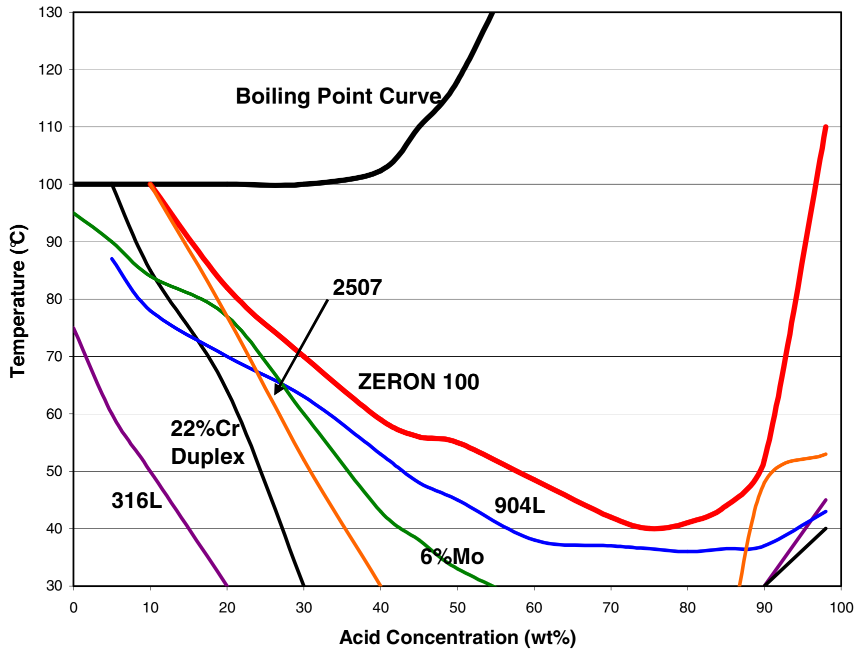
## FIGURE 3 Slow strain rate data for welded Zeron 100 in sea water + 4.5M NaCl at pH1 and 45°C




## FIGURE 4 Comparative erosion corrosion data for some slurry pump alloys



## FIGURE 5 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid




## FIGURE 6 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid plus 2,000mg/l chloride

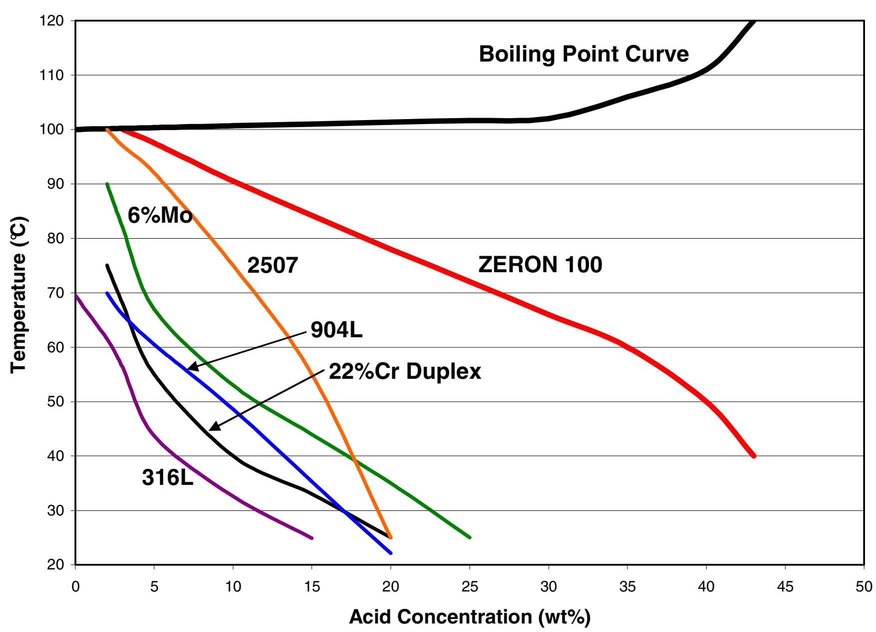


**FIGURE 7 Corrosion of some stainless steels in simulated commercial phosphoric acid with 1,000mg/l chloride at 80℃**

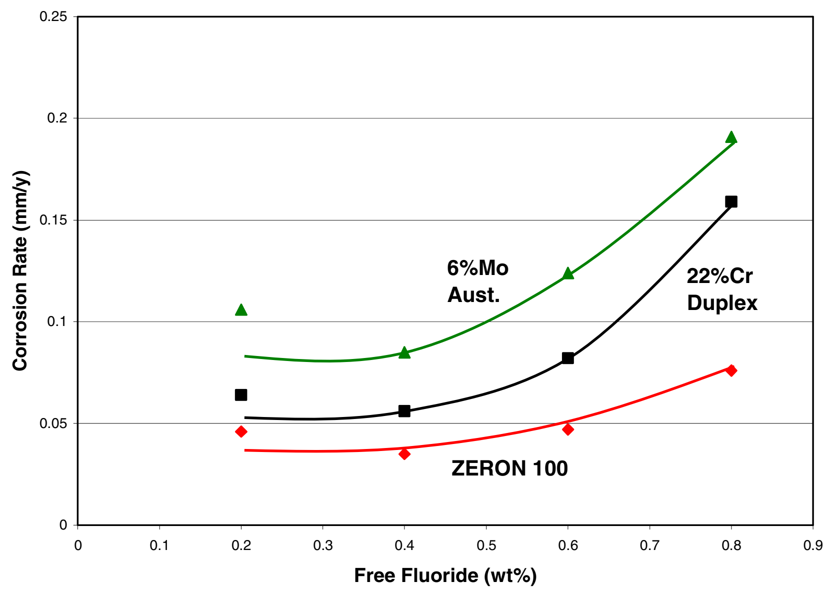



**FIGURE 8 Corrosion of some stainless steels in simulated commercial phosphoric acid with 0.2% free fluoride at 80℃**