ROLLED ALLOYS

REPORT

TITLE **Zeron 100 Superduplex Stainless Steel In the Mining Industry**

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ZERON 100 SUPERDUPLEX STAINLESS STEEL IN THE MINING INDUSTRY

FIGURES

SUMMARY

This report describes the physical and mechanical properties of Zeron 100 along with its corrosion resistance in a variety of acids and low pH, chloride solutions. The experiences with Zeron 100 in the nickel laterite pressure acid leach process, as well as other applications in gold, copper and uranium mining are described.

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 applications, particularly for pumps and piping, and 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 process industry and mining. Mining and mineral extraction often involve the use of acids, frequently in the presence of chlorides and at high temperatures, which represent an aggressive environment. The present paper highlights the properties of Zeron 100 and describes some applications and experiences with the alloy in mining applications 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:

$$PREN = \% Cr + 3.3 \times \% Mo + 16 \times \% N.$$

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

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 20 and 904L, which were 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 costs and time. The cost advantage of superduplex stainless steel, compared with austenitic, acid-grade 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. Larger vessels have been manufactured to ASME VIII division I, such as a mixed sulphides vessel at a nickel laterite mine, mine that was ~ 3m diameter and 20m long.

Zeron 100 is readily welded by all the commonly used arc welding processes. It is usually welded with Zeron 100X consumables, which contain 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 all these product forms in RA Materials, Manchester warehouse.

3. CORROSION

3.1 Acid Leach

During many mining operations leaching is often carried out with sulphuric acid. Zeron 100 has excellent resistance to sulphuric acid, better than many of the alloys in Table 1, including other superduplex stainless steels such as UNS S32750, as shown by the iso-corrosion curves (0.1mm/y) in Figure 1. This is because the latter alloy does not contain any copper or tungsten.

Sulphuric acid used in extraction processes often contains impurities and a common one is the chloride ion. Figure 2 shows the iso-corrosion curves (0.1mm/y) for Zeron 100 and some other common stainless steels in sulphuric acid containing 2,000 mg/l chlorides. It can be seen that Zeron 100 has superior corrosion resistance not only to the common stainless steels, but also compared with other high alloy stainless steels such as S31254 (a 6% Mo super austenitic) and S32750 (a 25% Cr superduplex).

There are other ions which could be present and which can influence corrosion resistance. Other halides, such as fluorides and bromides, will decrease corrosion resistance in a similar manner to chlorides. Oxidising species, such as ferric and cupric ions, have a beneficial effect and increase corrosion resistance. Figure 3 shows the effect of 50 mg/l ferric ions and 100 mg/l cupric ions on the iso-corrosion curve of Zeron 100 in sulphuric acid. However, halide ions are often also present with these oxidisers and so the exact concentration of each will determine the corrosion resistance. However, Zeron 100 consistently performs well in such solutions.

In some extraction processes hydrochloric acid is preferred and Zeron 100 has good resistance to dilute acid at high temperature as shown in Figure 4, especially when compared with other grades of stainless steel.

Many processes involving sulphide ores utilise oxygen sparging at elevated temperatures in acid environments. An autoclave test was carried out under the following conditions to simulate a typical environment:

$NaCl$	14 g/l
$MgSO_4$	15 g/l
$NiSO_4$	52 g/l

pH	2
Temperature	100°C
Pressure	10 bar (O_2)

Samples of Zeron 100 were tested to assess resistance to general corrosion, crevice corrosion and stress corrosion cracking, with exposure for 3 weeks. The corrosion rate was ~ 0.03 mm/y and there were no signs of crevice corrosion or stress corrosion cracking.

Note that in oxidisation pressure leach applications, the conditions become more aggressive as the chloride and oxidiser (such as ferric and cupric ions) concentrations increase. When both oxidisers and chlorides are at high concentrations, it is possible to get localised pitting, particularly in shielded areas. It is important to consider each project individually under its own specific conditions.

3.2 High Pressure Acid Leaching

High pressure acid leaching of metals from ores has been used in a number of locations around the world and it is being used for extracting nickel from the laterite ores in Western Australia. Plants in other parts of the world are currently under construction. In this method crushed ore is heated to temperatures of about 250°C and the nickel is extracted with sulphuric acid at about 50 bar pressure.

In Western Australia there is a shortage of fresh surface water in sufficient quantities for this process, although there are numerous boreholes producing high chloride brines (15 to 150 g/l chloride). To use conventional plant materials it would be necessary to reduce the salinity of the water substantially by desalination. This would be extremely expensive, both in terms of the cost of the plant and its operating costs. The alternative is to use the borehole water as it is and build the plant of suitable corrosion resistant materials.

Figure 5 shows a simplified schematic diagram of the ore processing chain. Two heating and cooling stages are shown, but in practice there could be four or more stages prior to and after the main autoclave. During heating, a mixture of crushed ore and water is steam heated in stages until it is injected into the main autoclave. Sulphuric acid is added either to the autoclave or immediately prior to it. After reaction in the autoclave the residual slurry is progressively cooled through a series of flash tanks. Steam extracted from each tank is used to provide heat during the heating stages (Figure 5). Following this the slurry is at about 100°C and it must be further cooled, separated and neutralised prior to extraction of the nickel.

3.2.1 Heater Fluids

In the directly heated vessels, as shown in Figure 5, the steam from the flash tank strips most of the oxygen from the incoming slurry, but the carry over of acid can mean that the pH could drop to 3. Under severe upset conditions even lower pH's have been postulated. A series of autoclave tests was conducted in a simulated laterite slurry of the following composition at different pH's at 200°C, a typical autoclave injection temperature:-

$MgSO_4$	-	15g/l
$Fe_2(SO_4)_3$	-	150 mg/l
NaCl	-	150, 17 or 1.7 g/l
pH	-	1,2 or 3

The results in Table 4 show that at normal pH (3) the corrosion rate was low and even at pH2 the corrosion rate was still acceptable. However, at pH1 the corrosion rate was very high and caustic injection or something similar would be required to prevent excessive attack if this occurred in service. Samples were also included to test for crevice corrosion and stress corrosion cracking (SCC). Neither was observed. The direct injection of steam into the heater vessels increases the slurry volume by up to 10% and it has been proposed that indirect heating of the slurry, in a series of heat exchangers, would be more economical. This will depend on the price of steam for the particular project. With indirect heating the slurry inside the tubes is no longer deaerated, and the risk of corrosion is greater.

Independent laboratory tests to simulate the indirect heater environment (high temperature, aerated slurry) showed that all stainless steels cracked at 200°C. Only Ti-Ni (grade 12) and Ti-Pd (grade 16) resisted attack. Heating the slurry from ambient to 200°C requires a large number of heat exchangers in series and superduplex stainless steel is suitable for the first few stages where the temperatures are lower.

3.2.2 Flash Tank Fluids

This environment, which is the spent liquor from the autoclave, is progressively cooled from 250°C to ~ 100°C. Acid concentrations are about 40 g/l with chlorides plus sulphates of nickel and cobalt. Autoclave tests at 177°C showed excessive corrosion of alloy 20, 6% Mo austenitic and Zeron 100. In addition the alloy 20 and 6% Mo austenitic were pitting, and the C-rings showed severe cracking. Tests at different chloride levels gave similar results and the corrosion seems to be controlled more by the acid content. These stainless steels are clearly unsuited for this environment.

The exception to this was at 100°C with 40 g/l acid. Zeron 100 corroded at a low rate (0.015mm/y max) with no localised corrosion or SCC with up to 5g/l chloride. With 20g/l chloride the corrosion rate increased (0.265mm/y) and pitting occurred.

3.2.3 Thickeners

After leaving the final flash tank at about 100°C the slurry may be passed through a heat exchanger prior to separation of the solids and liquids in a series of thickeners. These have long arms with rakes which are normally made of coated carbon steel. Bare metal is used for components such as hangers and pivots, which must be made of corrosion resistant alloys. Alloy 904L is sometimes used but in more aggressive environments the greater corrosion resistance of Zeron 100 is required.

The first thickener contains the most corrosive environment and tests were carried out under the following conditions:

$CoSO_4$	-	1.0 g/l
$FeCl_3$	-	1.5 g/l
$NiSO_4$	-	9.2 g/l

$MnCl_2$	-	2.3 g/l
$MgSO_4$	-	75 g/l
NaCl	-	150 g/l
H_2SO_4	-	15.5 g/l
Temperature	-	60^{o}C

Samples of Zeron 100 were tested for general corrosion, crevice corrosion, pitting or stress corrosion cracking, in a 30 day exposure. The weight loss showed a corrosion rate <0.001 mm/y with no crevice corrosion or stress corrosion cracking, showing the excellent resistance of Zeron 100 to this environment.

3.3 Raffinates and other Acid Solutions

Spent fluids or raffinates from acid extraction systems typically contain 1 to 15g/l sulphuric acid, chlorides, and metals such as copper, iron, zinc, cobalt, nickel and manganese. Because of its high resistance to dilute sulphuric acid containing chlorides and oxidisers, Zeron 100 is highly suitable for handling raffinates and other spent acid liquors. Table 5 shows the composition of some of the raffinates currently being handled by Zeron 100 in the field. Problems can arise with high concentrations of oxidisers and chlorides, when pitting is possible. RA Materials has carried out extensive testing to show the limits of use of Zeron 100 in such fluids.

The only problem arises when the conditions become reducing. In an Australian plant, nickel powder was added to sulphuric acid (3 to 10g/l) at 90℃ to form nickel sulphate. The agitator was a Zeron 100 shaft with Zeron 100 blades attached by welding. Severe corrosion occurred at the fusion line of the welds. The conditions were strongly reducing and the corrosion occurred at the fusion line because it was the weakest area from a corrosion point of view.

3.4 Erosion

In addition to its excellent corrosion resistance, Zeron 100 also has good resistance to erosion and corrosion in abrasive slurries. This is discussed in detail elsewhere[1] and Figure 6 shows the relative performance of a number of stainless steels tested at 40 m/sec in a brine containing 25 g/l chloride and 640 mg/l sharp sand at 55^{o}C and a pH of 3.5. These results show the high resistance of Zeron 100 to erosion in this environment.

4. SERVICE EXPERIENCE

4.1 Centrifugal Pumps

Zeron 100 has been used in the mining industry for some years, principally in the cast form for pumps, as shown in Table 6. The potash mines have found the alloy to be very reliable and in Canada the Zeron 100 pumps are described as "bullet proof". They handle a mixture of KCl and NaCl (~ 300 g/l) with some sand at about 80^{o}C. The fluids in the USA potash mines also contain H_2S, which increases the aggressivity, but the Zeron 100 pumps are performing well.

In the nickel and gold mines the main use of pumps has been for handling acid mine waters with high solids burdens. The resist2ance of the alloy to both corrosion and erosion means that the pumps generally have long lives.

In the copper mining industry the extraction of the copper is often by sulphuric acid and electroplating. Zeron 100 has been used for pumps handling the spent acid, which is oxidising because of the presence of Cu^{2+} ions, it may contain chlorides and it is typically at about 60°C. The spent acid can also be abrasive because of the presence of residual solids. Zeron 100 gives excellent performance at 60°C up to ~ 35 wt% acid. Figure 7 shows a Zeron 100 pump in a copper mine in the USA.

4.2 Copper Extraction

Because of its excellent resistance to hot sulphuric acid, particularly in the presence of chlorides and copper, Zeron 100 has found applications in copper extraction plants. The Escondida mine in Chile has used NPS 48 and NPS 20 Zeron 100 piping to handle spent acid liquors. These pipes replaced rubber lined carbon steel, where the rubber detached from the steel after only a short time in service. Zeron 100 has been used by the same project for seawater lift pumps, taking seawater up to the mine site because of the shortage of fresh water.

The Spence project in Chile uses a bio-leach reactor to extract copper from the ore. Sulphur oxidising bacteria produce sulphuric acid as a by-product, dissolving copper from the ore. Zeron 100 has been used for the pipes carrying the dissolved copper, which also includes spent sulphuric acid and chlorides.

When copper is plated from solution, it is usual to use 316L stainless steel starter plates. These have polished faces so that the copper can be easily separated from the stainless steel at intervals. When the acid solution contains high levels of chlorides, the 316L can pit and these pits act as keys preventing the copper from detaching easily. With its high resistance to chlorides in acid solutions Zeron 100 is a candidate to replace 316L for starter plates. The Cyprus Bagdad Copper Company has used Zeron 100 starter plates at its plants in Arizona, USA and at El Abra in Chile.

4.3 Nickel Laterite Ores

Zeron 100 has been extensively used in the laterite ore processes in Australia, particularly on the Murrin Murrin Project and to a lesser extent in the Bulong Nickel and Cawse projects, Table 6 shows some of these applications, as well as those from some other mining projects.

RA Materials have supplied pipes, fittings and flanges to project suppliers for a variety of areas within the laterite mining projects. In addition Zeron 100 has been supplied to the manufacturers of original engineered equipment such as agitators and mixers.

The positive displacement slurry pumps are very large, as shown in Figure 8, and use a mixture of cast and wrought Zeron 100 for the wetted parts. They operate at ~ 180°C at pH values down to ~3. The process vessels in the Murrin Murrin project are very large and Figure 9 shows the mixed sulphides vessel. During start up and shut down of re-oxidation vessels the conditions can go strongly reducing and the greater acid resistance of Zeron 100 can be an advantage over 22%Cr duplex, which has experienced severe corrosion under these conditions on some projects.

In the steam return lines from the flash tanks to the heater vessels the acid carry-over is estimated to be 1-3 g/l. Depending on the chloride concentration in the slurry, this could be a mixture of sulphuric and hydrochloric acids (high chloride) or mostly sulphuric acid (low chlorides). Superduplex stainless steel has been used for the steam return lines in some laterite ore projects. On the Murrin Murrin project they were replaced by titanium due to excessive slurry carry-over from the flash tanks. With improved flash tank design, acid slurry carry-over should not occur and Zeron 100 should work well.

Laboratory corrosion tests have shown that the corrosion rate of Zeron 100 is low (<0.1mm/y) in both the vapour and the condensed liquid in steam return lines at temperatures of 225°C and acid concentrations up to 1g/l (~pH2) with various concentrations of chloride[2.]

4.4 Other Applications

In addition to the laterite ore projects, Zeron 100 has been used in a variety of other applications. Table 7 shows a range of mining projects where Zeron 100 has been used in both wrought and cast forms. The slurry at Olympic Dam, which extracts both uranium and copper, is very corrosive and Zeron 100 was used for the wetted parts of both the thickeners and agitators to replace 904L.

The Lihir gold project was using Ti-Nb oxygen sparge pipes in the main autoclave (40g/L H_2SO_4 at 205°C) but these were eroding in the abrasive slurry and required regular replacement. Zeron 100 offered a lower cost alternative, and the first set of pipes was in good condition after one year of service. Figure 10 shows a set of sparge pipes awaiting despatch. The project is also having problems with erosion of the agitators, also in Ti-Nb, and is looking to replace these with Zeron 100.

A titanium dioxide refinery in the Middle East is using Zeron 100 pipework for the spent acid lines. This plant uses the chloride route and so the spent acid contains hydrochloric acid. Zeron 100 was chosen because of its high resistance to this acid. A titanium dioxide plant in the UK uses sulphuric acid in the production of rutile and Zeron 100 was chosen for the centrifuges separating ferrous sulphate crystals from the spent acid (~ 20% acid at 40°C). These were to replace 316L centrifuges that were corroding rapidly and required frequent replacement.

5. CONCLUSIONS

Zeron 100 has excellent resistance to corrosion in sulphuric acid, even when it contains chlorides as are found in many mineral extraction processes. This resistance has led to the extensive use of the alloy not only in nickel laterite ore projects, but also in other processes for the extraction of gold, copper and uranium.

Reference

1) R. Francis, WM&F Technical Note TN781 R1 July 1994.

2) H. Dykstra, Bacon Donaldson, Private Communication.

TABLE 1 The composition of some stainless steels commonly used in acid leach mining.

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	-	-	34
Alloy 20	bal	20	35	2.5	-	3.5	-	28
904L	bal	20	25	4.5	-	1.5	-	35
6% Mo Aust.	bal	20	18	6	0.2	0.7	-	43

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

TABLE 2 Minimum mechanical properties of some stainless steels commonly used in acid leach mining.

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	170	485	40	22
22% Cr Duplex	450	650	25	28
Alloy 20	240	550	30	22
904L	220	490	35	22
6% Mo Aust.	300	650	35	22

* - maximum

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
22Cr Duplex	289	177	207
Alloy 20	NL	158	161
6Mo Aust.	NL	185	207

NL – not listed

TABLE 4 The corrosion of Zeron 100 in a simulated laterite heater fluid versus chloride and pH at 200°C

SAMPLE	pH	CHLORIDE (mg/l)	CORR^n RATE (mm/y)
A	3	90,000	<0.01
B	3	90,000	<0.01
C	2	1,000	0.06
D	2	1,000	0.02
E	2	10,000	0.014
F	2	10,000	0.014
G	2	90,000	0.005
H	2	90,000	0.014
J	1	1,000	4.0
K	1	1,000	7.2

TABLE 5 The composition of raffinates in some service environments utilising Zeron 100.

Sulphuric Acid (g/l)	Chloride (g/l)	Copper (g/l)	Iron (g/l)	Temperature (°C)
21	-	2	-	55
10	40	1	0.8	50
156	90	0.1	0.5	60
15	0.2	1	1	95

TABLE 6 Some experiences with Zeron 100 pumps in the North American mining industry.

MINERAL	PROJECT	NO. OF PUMPS
Potash	Potash Corporation (Canada) Saskatchewan IMC (Canada) Kalium (Canada + USA) Cominco-Agrium (Canada)	4 7 6 1
Gold	Bousquet (Canada) [mine water]	1
Nickel	INCO, Sudbury Froude mine [drainage water]	12
Copper	Arizona, USA [sulphuric acid + solids]	4 + 1

TABLE 7 Some applications of Zeron 100 in mining and mineral extraction.

ITEM	PROJECT	APPLICATION
Slurry Pumps	Bulong Nickel	Nickel (laterite)
Slurry Pumps	Murrin Murrin	Nickel (laterite)
Thickeners	Olympic Dam	Uranium
Thickeners	Bulong Nickel	Nickel (laterite)
Thickeners	Murrin Murrin	Nickel (laterite)
Mixers	Olympic Dam	Uranium
Mixers	Murrin Murrin	Nickel (laterite)
Vessel (Mixed Sulphide)	Murrin Murrin	Nickel (laterite)
Pipes/Fittings/Flanges	Murrin Murrin	Nickel (laterite)
Sparge Pipes	Lihir	Gold
Piping	-	Rutile
Piping	Escondida	Copper
Piping	Spence	Copper
Centrifuges	Tioxide	Rutile

FIGURE 1 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid

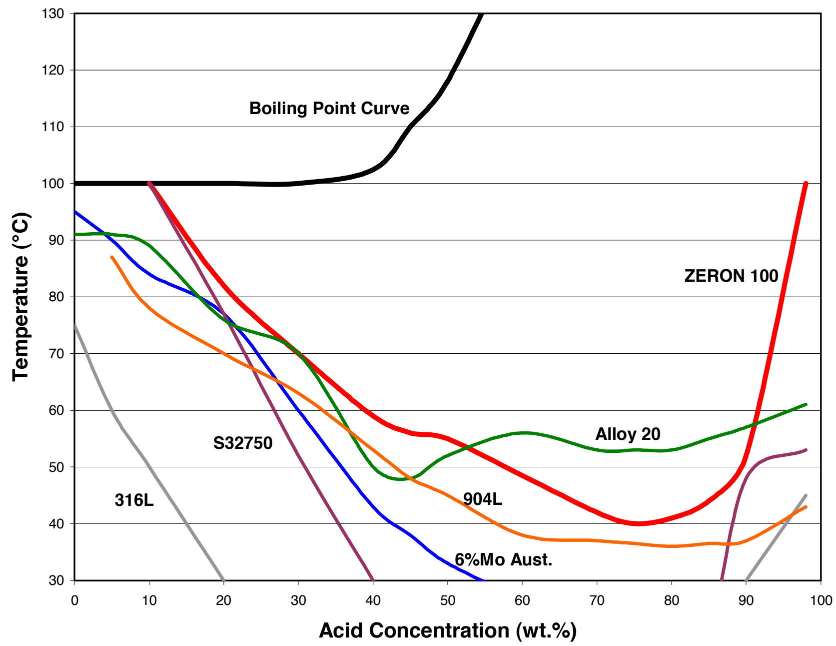


FIGURE 2 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid plus 2,000mg/l chloride

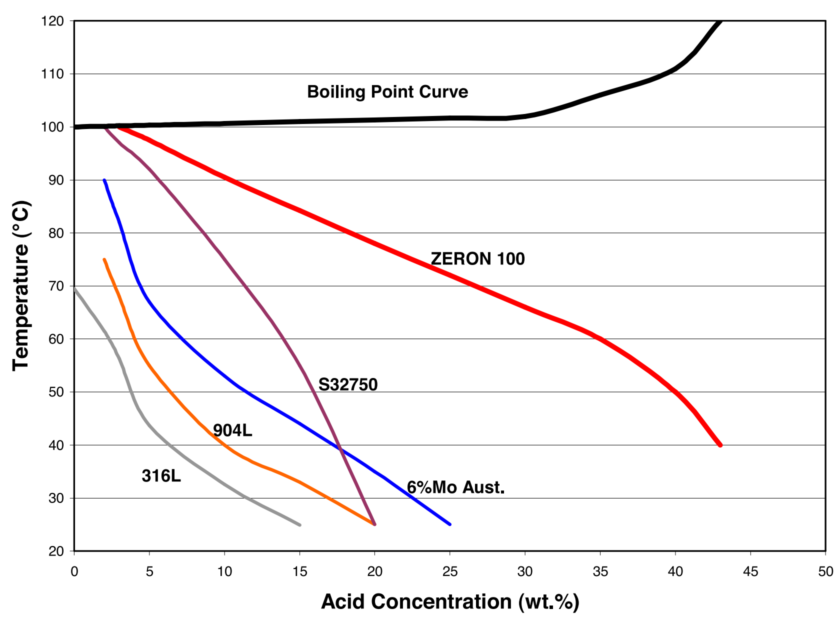


FIGURE 3 Iso-corrosion curves (0.1mm/y) for Zeron 100 in sulphuric acid with oxidizers

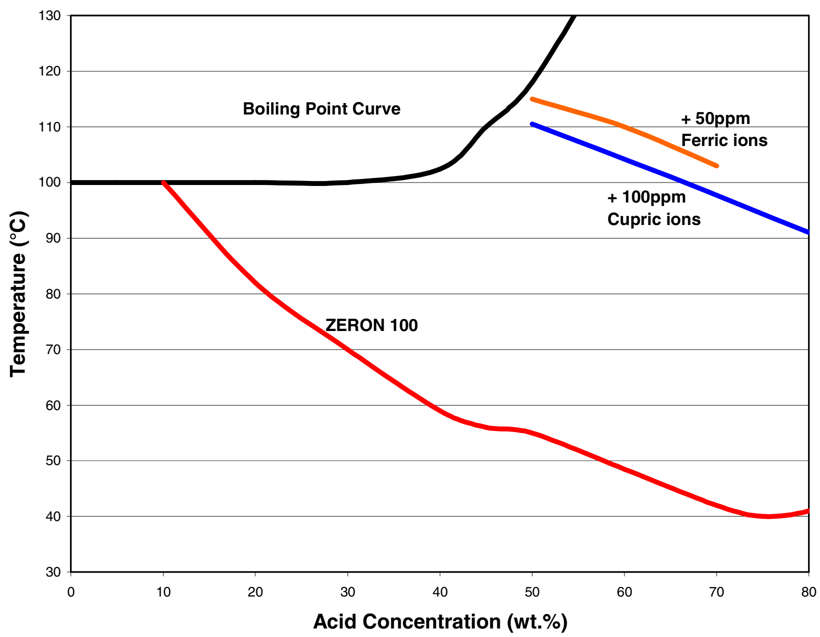
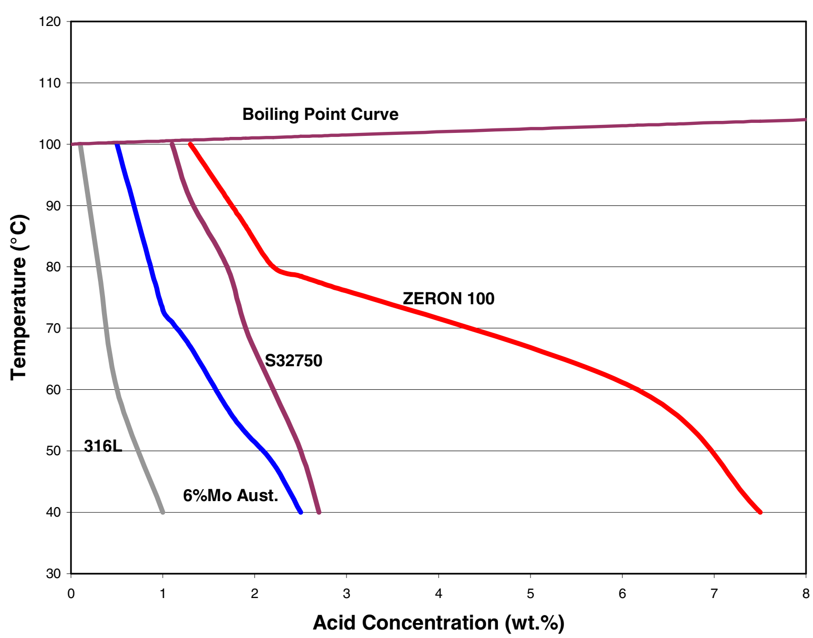


FIGURE 4 Iso-corrosion curves (0.1mm/y) for some stainless steels in hydrochloric acid



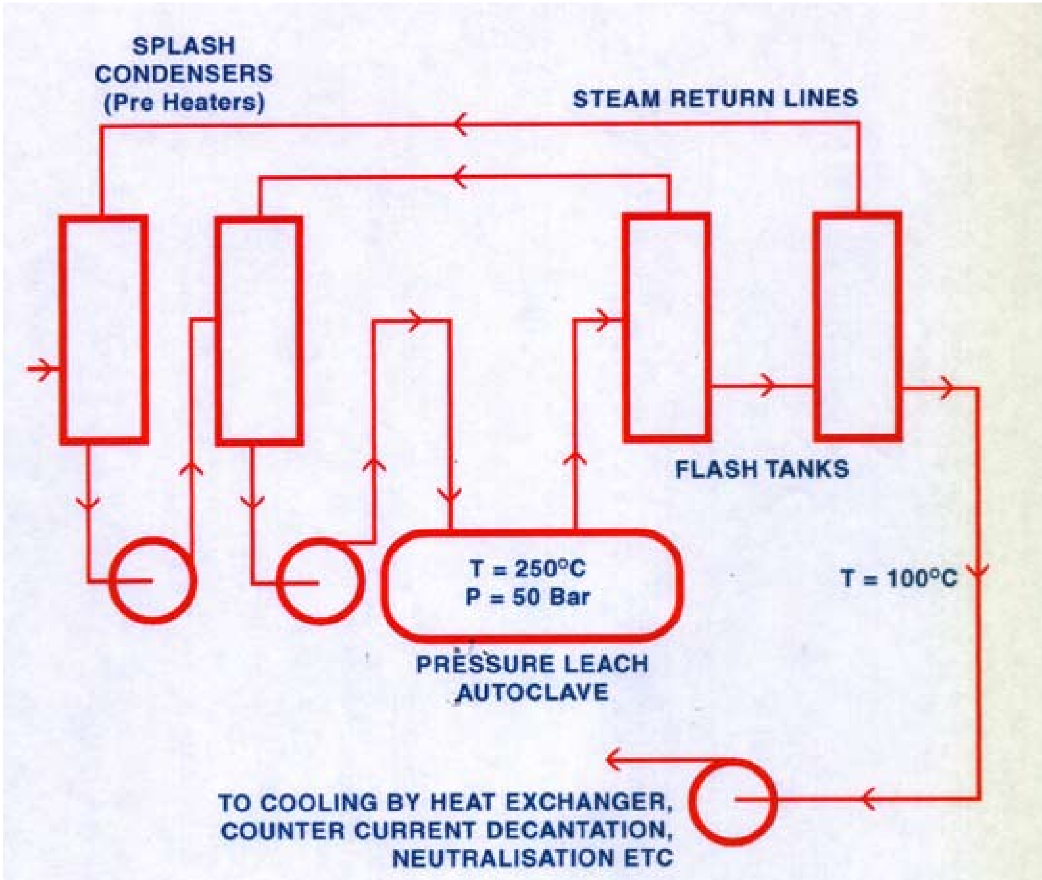


FIGURE 5 Schematic diagram of the high pressure acid leach section of a nickel laterite plant.

FIGURE 6 Erosion of several alloys in a sand laden brine at 55°C

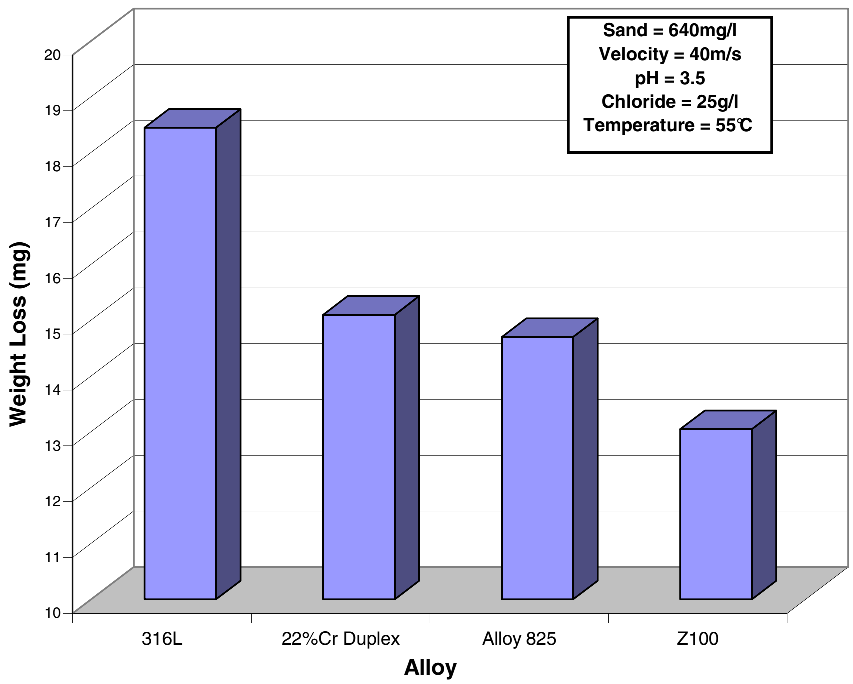


Figure 7 A Zeron 100 pump in a copper mine in the USA

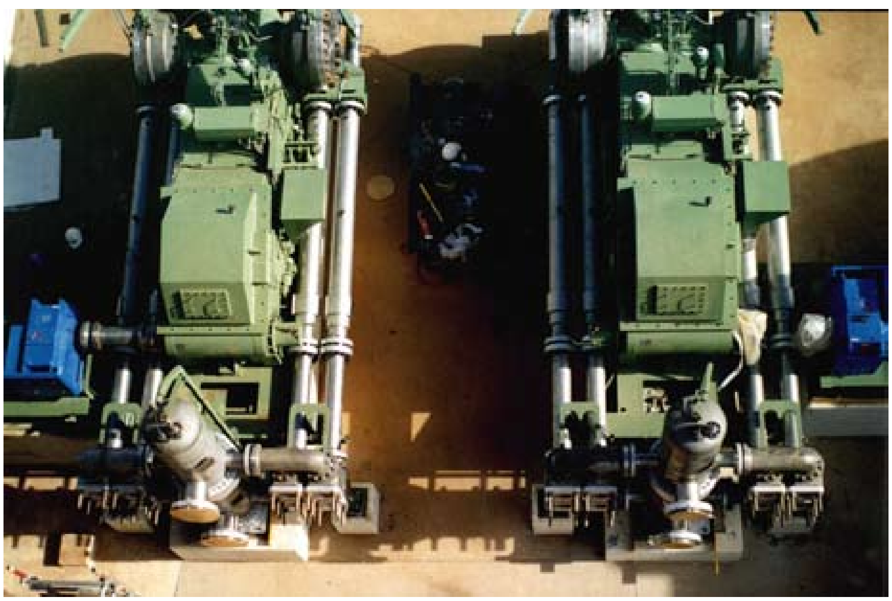


Figure 8 Geho positive displacement pumps in Zeron 100 for a nickel laterite mining project in Australia

Figure 9 Mixed sulphides vessel for a nickel laterite mining project

FIGURE 10 Oxygen sparge pipes for main autoclave at Lihir gold mine, PNG