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THE USE OF SUPER DUPLEX STAINLESS STEEL FOR HIGH PRESSURE ACID LEACH CIRCUITS – A SUPPLIER'S PERSPECTIVE.

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ABSTRACT

This paper describes briefly the properties of super duplex stainless steel that first made it attractive for the proposed HPAL extraction from nickel laterite ores. The results of laboratory testing based on initial expectations of process conditions are presented. Following problems during ramp up, the laboratory testing was expanded to cover more severe conditions. The implications of this data combined with service experience are discussed. The areas in HPAL plant where super duplex can be successful are described.

1. INTRODUCTION

Weir Materials and Foundries has been involved in materials selection for high pressure acid leach (HPAL) mining of nickel laterite ores since the concept was being discussed in the mid 1990's. As the projects were developed from concepts to drawings, to plant on the ground, WM&F has carried out a continual programme of corrosion testing and evaluation of materials. The ideas about conditions in the plant and candidate materials of construction have changed over the years and this paper presents the data in a historical perspective. The main emphasis is on super duplex stainless steel, but some other materials are also reviewed.

2. WHAT IS ZERON 100?

Zeron 100 was the first of the super duplex stainless steels and it was invented by WM&F in the 1980's. The alloy started life as a casting material for injection pumps for the oil and gas industry and the alloy was so successful that there was a demand for a wrought equivalent. Following its big success in the oil and gas industry WM&F embarked on research to identify other areas where Zeron 100 could find application. In the last ten years the alloy has been successful in marine, flue gas desulphurisation, desalination, chemical and process, as well as mining applications.

The composition of the alloy is shown in Table 1, compared with some other common stainless steels. Zeron 100 is a duplex stainless steel, having a 50/50 austenite-ferrite ratio, and a balanced microstructure. Although the alloy is covered by UNS S32760/J93380 and it is listed in many ASTM specifications, the composition and thermo-mechanical processing of Zeron 100 are more tightly controlled to give the optimum blend of strength, corrosion resistance and weldability.

The mechanical properties of Zeron 100 are shown in Table 2, where they are compared with some other common stainless steels. It can be seen that Zeron 100 has 3 times the proof stress of 316L and is 22% stronger than 22Cr duplex stainless steel. This offers opportunities for savings not only in wall thickness, but also fabrication time and costs. This becomes more important at higher process temperatures and/or pressures.

Zeron 100 is readily welded by all the common arc welding processes and the alloy has been successfully fabricated in thicknesses from 1mm to 63mm. There is a risk of precipitation of sigma phase when welding small diameter, thin wall pipe. This can be minimised by adherence to the WM&F welding guidelines (1) in terms of joint design, minimising heat input and controlling interpass temperature. Like all high alloy materials. Zeron 100 requires strict adherence to approved & qualified weld procedures using qualified welders to ensure successful fabrications.

3. EARLY DAYS

In the mid 1990's WM&F made contact with Resolute Resources, who were planning to use HPAL for the nickel laterite ores in the Bulong Nickel project. A schematic diagram of a HPAL circuit is shown in Figure 1. This shows the four main areas of potential application, the heaters/ p.d. pumps, the autoclave, the flash tanks and the steam return lines.

Corrosion tests were conducted by Resolute in the USA on a wide range of alloys in the conditions believed to be likely in the autoclaves. Zeron 100 was included in these tests, but the results showed that stainless steels and nickel alloys were unsuitable and only titanium and titanium-palladium alloys resisted attack. In the clad form, this has now become the standard material for the high pressure acid leach autoclaves.

WM&F then entered discussions on the conditions likely to prevail elsewhere in the plant. It quickly became apparent that currently available corrosion data would not be able to predict performance in these environments. Hence, a programme of autoclave tests was undertaken to simulate these environments and investigate the corrosion of candidate materials. The results of these tests were presented at the Ni/Co '97 Conference in Sudbury, Canada, and they are summarised below.

3.1 HEATERS

Direct contact heaters were proposed with hypersaline water being used for the slurry make up. The design was such that the lowest pH expected in the heaters was 3. Hence, tests were conducted in the following solution:-

Na Cl	-	150g/l
$Mg\ S0_4$	-	15g/l
$Fe_2\ (S0_4)_3$	-	0.15g/l
pH	-	3
Temperature	-	203°C
Pressure	-	17.7 bar

Initial thoughts were that alloy 20 would be suitable for applications such as the p.d. pumps. However, these tests showed that alloy 20 could pit in the heater slurry. Zeron 100 showed no indications of pitting or crevice corrosion or stress corrosion cracking in the parent or weld metal and the general corrosion rate was <0.01mm/ly. These results suggested that Zeron 100 would be an excellent material choice for the application.

3.2 FLASH TANKS

In the flash tanks the slurry from the autoclave is cooled in three or four stages from 250°C to ~100°C, with steam being extracted to heat the incoming slurry. A test was conducted in the following, simulated slurry:-

Na Cl	-	150g/l	$Fe\ Cl_3$	-	1.5g/l
$Mg\ SO_4$	-	75g/l	$Mn\ Cl_2$	-	2.3g/l
$Ni\ SO_4$	-	9.2g/l	$H_2\ SO_4$	-	38g/l
$Co\ SO_4$	-	1.0g/l	pH	<	1

Temperature	=	177°C
Pressure	=	57 bar

The results showed that the corrosion rates of 6Mo austenitic stainless steel and Zeron 100 were very high, with pitting of the 6Mo austenitic alloy. In addition stress corrosion cracking was observed. It was concluded that stainless steels were not suitable for the flash tanks under these conditions.

3.3 STEAM RETURN LINES.

It was estimated that with the steam there would be 1 to 3g/l of acid carry over into the heaters. Zeron 100 has good resistance to sulphuric acid, as shown by Figure 2. As the acid would be vapour during normal operation, no serious corrosion was expected. Condensation during start up and shut down would give a little corrosion, but this was not expected to be serious as it would only be transient. It was concluded that Zeron 100 would be suitable for the steam return lines.

4. THE INTEREST QUICKENS

In the late 1990's, interest in HPAL of nickel laterite ores increased and three projects were launched in Australia. Super duplex stainless steel was specified for a variety of applications in all three projects.

It was quickly apparent that the chloride content of the make up waters at Cawse and Murrin Murrin would be lower than at Bulong Nickel. With lower chloride contents it was possible that Zeron 100 might be suitable for the flash tanks, and so further autoclave tests were undertaken. These used a similar slurry to that in section 3.2, above, but with chlorides of 1,000 mg/l at temperatures of 177° and 135°C.

The results, in Figure 3, show that the corrosion rate remained high even when the chloride content was greatly reduced. Reducing the temperature from 177°C to 135°C had only a small effect on the corrosion rate. No stress corrosion cracking was observed at either temperature. Hence, the corrosion in flash tank fluids appears to be largely controlled by acid concentration. Note that the flash tank slurry is highly oxidising because of the high Fe^{3+} content, which increases susceptibility to attack.

When the slurry leaves the flash tanks there is sometimes a requirement for a surge or holding tank. As the temperature here is ~100°C, further tests were conducted in the same simulated flash tank slurry. The results, in Figure 4, show that at 20,000mg/l chloride, corrosion rates were moderate but both Zeron 100 and 6Mo austenitic showed pitting attack. At 2,000mg/l chloride the corrosion rates were very low, even for welded material, and there was no pitting. No stress corrosion cracking was seen in either test.

Hence, at the lower temperature of the surge tanks, chloride content is important, but stainless steels are only suitable at lower chloride concentrations.

5. THE PROJECTS GO LIVE

All three Australian projects were built and ramp up began in 1999. Problems occurred in a number of areas, not just due to corrosion (3). Corrosion of super duplex was observed in the steam transfer lines, the heater vessels and the slurry injection pumps. This was not confined to Zeron 100, but was also seen with other super duplex grades, such as S32750

This mostly took the form of pitting, but stress corrosion cracking from the base of the pits was also seen in the steam transfer lines and the heater vessels. Details of the attack can be seen in Figures 5 and 6.
A test programme was initiated to try and reproduce the attack in the laboratory. Discussions with project personnel indicated that the pH in the heater vessels may have decreased to 2 or even 1 because of excessive slurry recycling with the steam. Previous tests (section 3.2.) showed that Zeron 100 corrodes at a high rate in flash tank slurry, so the attack in the steam return lines, presumably where slurry settled on the pipe walls, was not surprising.

Tests in simulated heater slurry were conducted over a range of chloride concentrations at pH's of 1 to 3. The results are summarised in Table 3. Corrosion rates were still low at pH2, hardly any greater than at pH3, but at pH1 there was a high rate of metal loss. However, there was no pitting and no stress corrosion cracking, and the attack did not appear as in Figure 5.

Consideration of the slurry composition indicated that slurry recycling with the steam would include ferric ions. In addition, the reduced pH in the heater slurry would also increase dissolution of iron in the incoming heater slurry. Ferric ions are a powerful oxidising agent and an increase in the redox potential increases the risk of localised pitting. It was not possible to conduct electrochemical tests at 200°C in an autoclave, but an indication of the effect of ferric ions was obtained by adding quantities from zero to 100mg/l to a solution of sodium chloride with 10,000mg/l chloride at pH2 and 90°C. The results, in Figure 7, show an increase of ~200mV when the ferric ion content was increased from 10mg/l to 300mg/l. This clearly represents a significant increase in the risk of localised attack. To investigate this further an autoclave test was conducted in a solution containing 10,000mg/l chloride and 500mg/l ferric ion at pH2 and 200°C for 21 days. No sulphate was included, as this can act as a mild inhibitor of localised attack. Also, the autoclave was pressurised with nitrogen, but no attempt was made to purge residual oxygen i.e. simulating start up conditions. This was felt to represent aggressive conditions.

At the end of the test the pH had risen to 2.7 and there was no stress corrosion cracking. However, small pits were observed on the C-rings, as shown in Figure 8. Although not as large as those in Figures 5 and 6, it seems reasonable to suppose that they would have been larger if the test had been longer and the pH a little lower. This test suggests that the role of ferric ions in the corrosion attack is critical.

A further test has been conducted to examine the effect of frequent start up and shut down cycles. Under this regime there would be oxygen in the system for an extended period. A test with 10,000mg/l chloride and 10mg/l ferric ion was carried out at 200°C. The autoclave was pressurised with nitrogen but no attempt was made to flush out the residual oxygen, Every five days the autoclave was cooled to room temperature, flushed with air and then repressurised with nitrogen and heated back up at 200°C.

All the samples showed signs of broad, shallow pitting attack, as shown in Figure 9. This was not dissimilar in appearance to the attack in Figures 5 and 6. Research continues to evaluate the effect of chloride content on this type of attack.

6. DISCUSSION

6.1 HEATERS / PUMPS

From the extensive testing in simulated heater fluids and the service experience on start up it is clear that a low pH and a high ferric ion content can lead to localised pitting of super duplex stainless steel. Once pitting is established, the pit geometry ensures that it acts as a stress concentrator. In addition the hydrolysis of chromium ions within the pit further reduces the pH. This all increases the risk of stress corrosion cracking from the base of pits. The data suggest that Zeron 100 will be corrosion resistant at pH3 and above, and should cope with short excursions to pH2. Excursions to lower pH, with high ferric ion contents should be avoided, as should frequent shut downs and start ups, which introduce a lot of oxygen into the system.

So far no mention has been made of indirect heating. The advantage of this method is that it reduces the water content of the slurry entering the autoclave and increases the efficiency. From a corrosion point of view we now have a fully aerated slurry being heated up to 200°C by acid steam. This means that conditions on the slurry side of the heater are more aggressive. This method of heating is not currently in commercial use but the benefits, pitfalls, and materials problems were discussed in two papers presented at the ALTA 2000 Ni-Co conference (4,5).

6.2 AUTOCLAVES

The early testing in the USA, plus the service experience has clearly demonstrated that titanium and titanium-palladium alloys are the most suitable for this application. The combination of high acid content with the oxidising nature of the slurry makes it very aggressive. Unless a new, more cost effective alloy is developed, there is no reason to consider an alternative choice.

6.3 FLASH TANKS

The tests in these fluids have shown that the corrosion is controlled more by acid content than chloride. Even in the cooler flash tanks the corrosion rates of stainless steels are high. At present acid brick lined steel or titanium clad steel seem the best materials options for this application.

If a surge or holding tank is fitted after the flash tanks then Zeron 100 super duplex stainless steel is suitable with 2g/l chloride, but not with 20g/l chloride. Further corrosion testing is required to determine the upper chloride limit in this environment.

6.4 STEAM RETURN LINES

The service experience has shown that severe pitting and cracking of super duplex stainless steel occurs when large quantities of slurry enter this line. In a good design little slurry should enter and Zeron 100 would be a suitable material choice. If slurry can enter the return lines then it will be necessary to select a more corrosion resistant alloy.

One candidate is titanium, but if the conditions in the return lines go reducing (i.e. no ferric ions) this will result in a high rate of attack. An alternative might be one of the newer nickel-base alloys, such as alloy 33. However, the resistance of this material to very hot acids with chlorides has not been evaluated. In addition it may not be available in all the required product forms. It is strongly recommended that testing be carried out before any expensive, corrosion resistant alloys are selected for this application.

6.5 GENERAL

The former discussion of materials performance in HPAL circuits has highlighted one very critical point. That is the importance of having reliable information on the process conditions. Even when corrosion testing is being carried out, the results may not be relevant if important “minor” constituents are omitted, or some part of normal operating procedure is not simulated. To do this effectively requires close collaboration between process engineers and corrosion engineers. The benefits are big reductions in unplanned shut downs and maintenance.

This discussion has concentrated solely on the HPAL circuit because of the problems there during ramp up of the Australian projects. There are many applications for super duplex stainless steel in downstream processing, and where the alloy has been utilised it has been successful.

7. CONCLUSIONS

In HPAL mining of nickel laterite ores it is concluded that:-

1. The corrosion of stainless steels in the heater fluids is strongly influenced by pH, ferric ion content and regular influxes of oxygen.
2. Zeron 100 is satisfactory in this environment at pH3 and above, and can tolerate short excursions to lower pH, if frequent shut down can be avoided.
3. Zeron 100 is unsuitable for the autoclaves or the flash tanks and titanium or titanium-palladium is preferred.
4. Zeron 100 is satisfactory for the steam return lines only if there is minimal slurry recycling.
5. Optimum materials selection requires a detailed knowledge of process conditions and operating practices.

REFERENCES

1. “Guidelines for Welding Zeron 100 super duplex stainless steel”. Weir Materials & Foundries.

2. R Francis, G Byrne and G Warburton
" The uses of super duplex stainless steel in the nickel mining industry" Nickel-Cobalt '97, Sudbury, Ontario, Canada. August 1997. Published by CIM, Vol. IV, page 25.

3. A Griffin, G Becker,
"Bulong Nickel Operations – Post Commissioning "
Alta 2000 Nickel/Cobalt
Perth, Australia. May 2000. Publ[d] by ALTA.

4. K Lamb and J Galyas.
" The Heating of Nickel Laterite Autoclave Feed Slurries."
Ibid.

5. I Hanter and B Moll.
"Indirect Heating, the Effects of Slurry Rheology and Cost Effective HPAL Slurry Heating".
Ibid.

TABLE 1 The composition of some common stainless steels

ALLOY	NOMINAL COMPOSITION (wt.%)							PREN*
	Fe	Cr	Ni	Mo	N_2	Cu	W	
316L	Bal+	17	10	2	-	-	-	24
22Cr Duplex	Bal+	22	5	3	0.14	-	-	35
6Mo Aust.	Bal+	20	18	6	0.2	0.7	-	43
Zeron 100	Bal+	25	7	3.5	0.25	0.7	0.7	>40

*** PREN = %Cr + 3.3%Mo + 16%N_2**
+ Bal = Balance

TABLE 2 The minimum mechanical properties of some common stainless steels at room temperature

ALLOY	0.2% PROOF STRESS (MPa)	UTS (MPa)	ELONGATION (%)
316L	170	485	35
22Cr Duplex	450	620	25
6Mo Aust.	300	650	35
Zeron 100	550	750	25

TABLE 3 Corrosion rate of Zeron 100 in simulated HPAL heater slurry at 200°C. (Fe^{3+} = 30mg/L)

pH	CHLORIDE (mg/L)	CORROSION RATE (mm/y)
3	90,000	<0.01
2	90,000	0.014
2	90,000	0.005
2	10,000	0.014
2	10,000	0.014
2	1,000	0.017
2	1,000	0.059
1	1,000	4.1
1	1,000	7.2

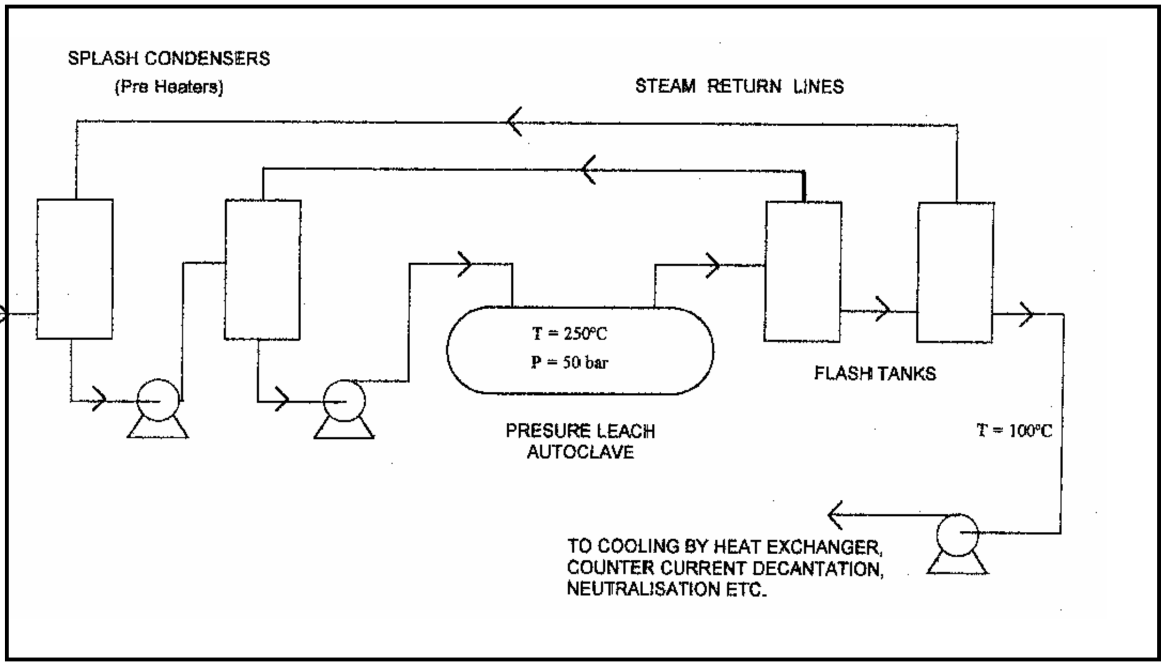


FIGURE 1 Schematic diagram of a HPAL circuit

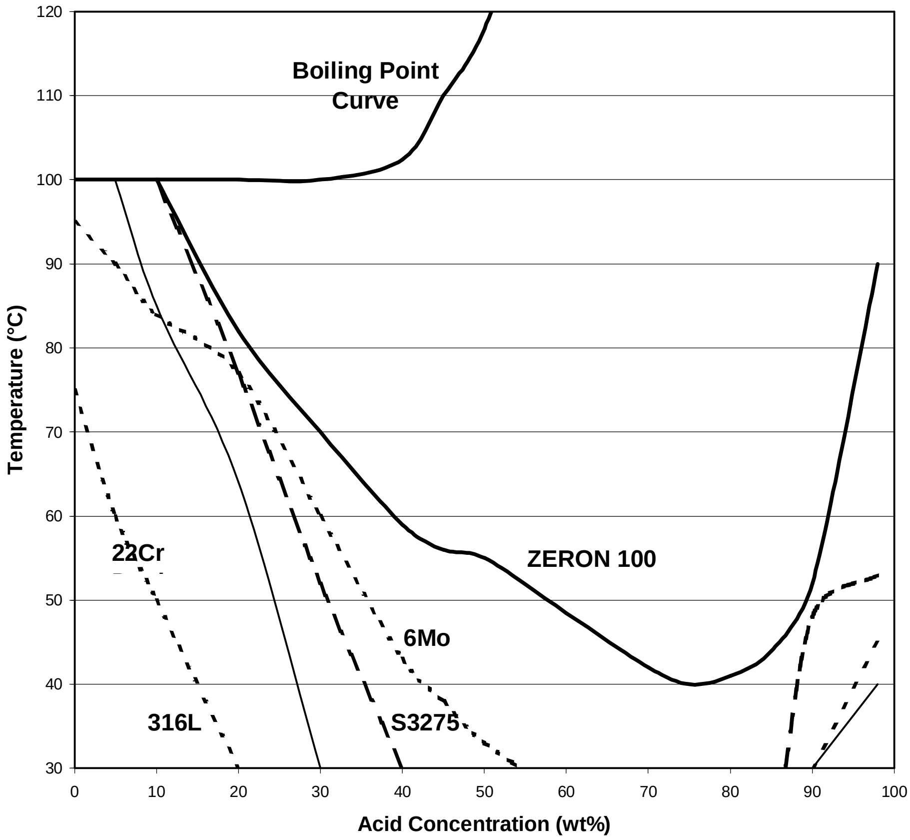


FIGURE 2 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid

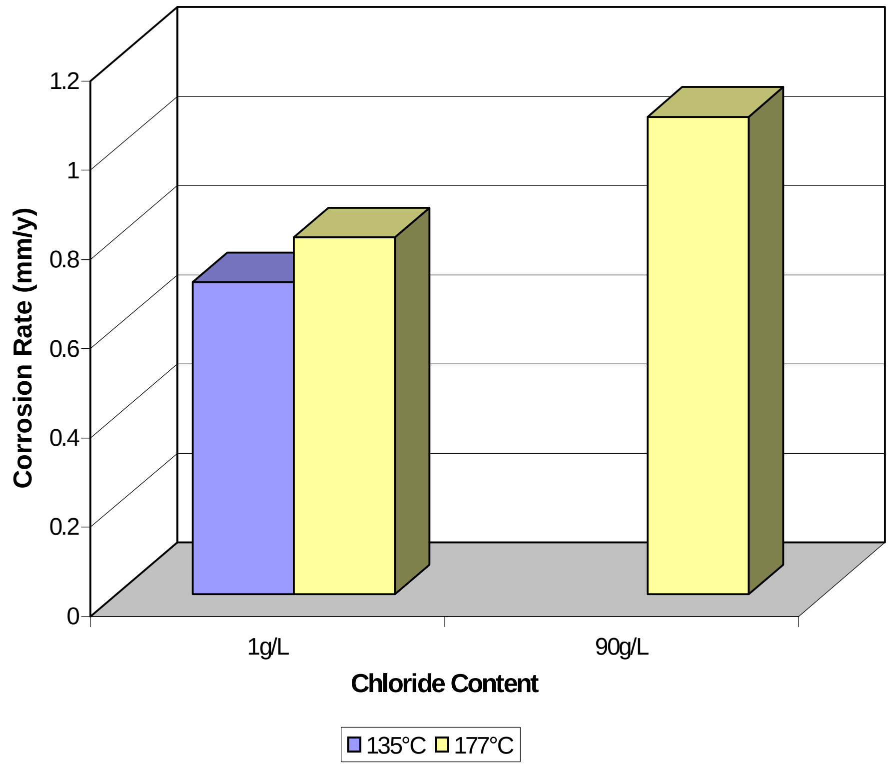


FIGURE 3 Corrosion rate of Zeron 100 in a simulated flash tank slurry

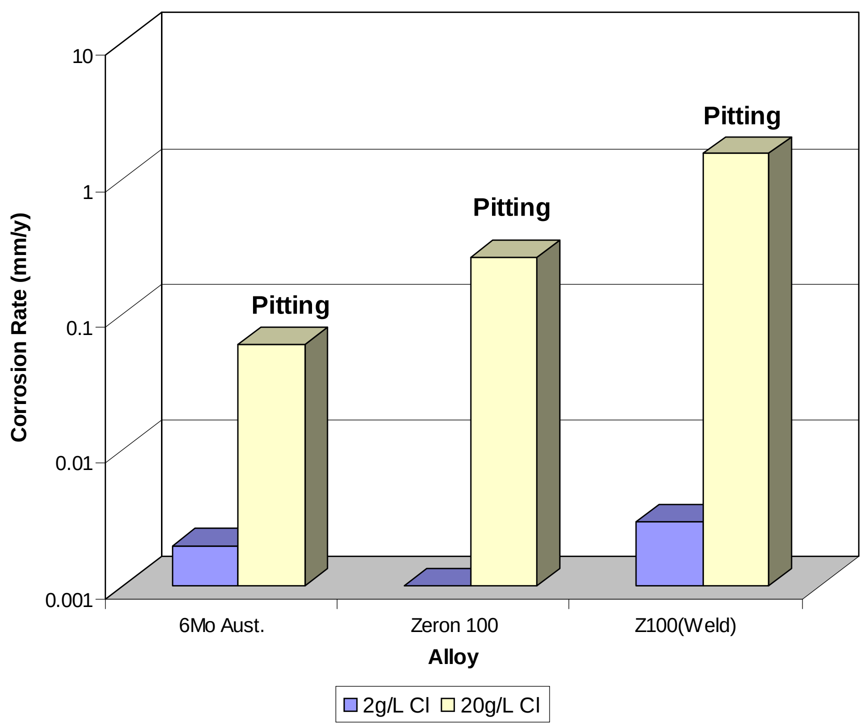


FIGURE 4 Corrosion rate in a simulated flash tank slurry at 100°C

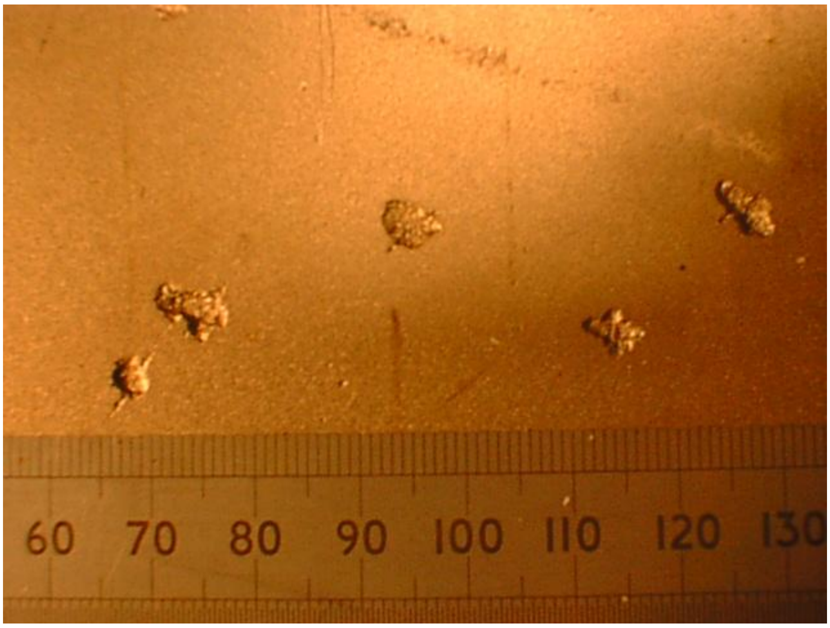
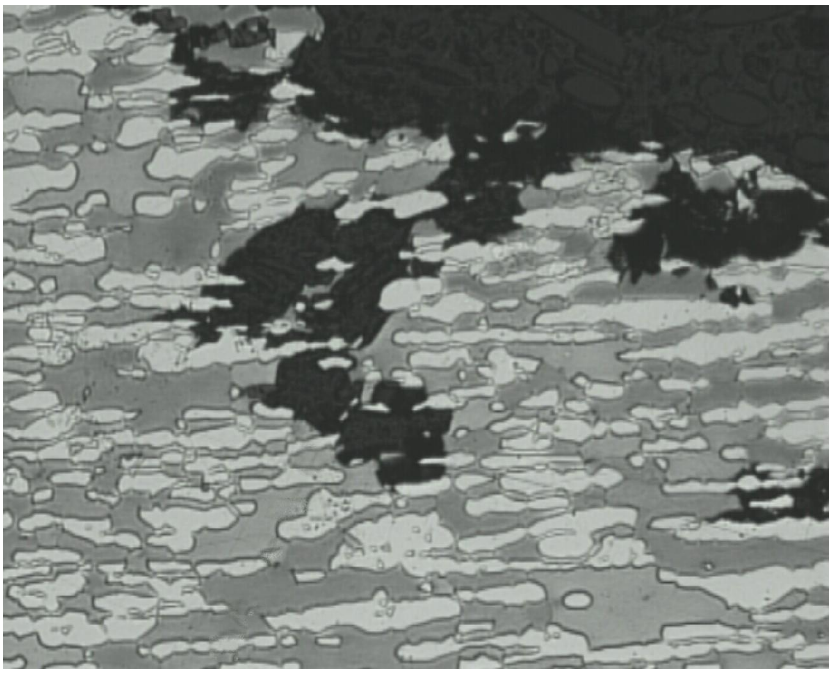


FIGURE 5 Appearance of pits on super duplex stainless steel from a HPAL heater



50μm

FIGURE 6 Pitting corrosion on super duplex stainless steel from a HPAL heater

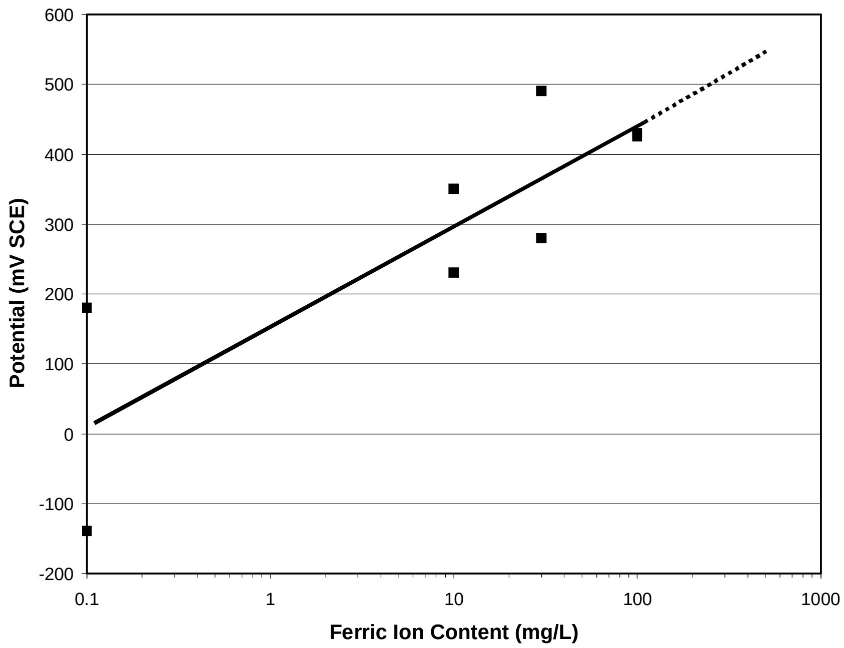
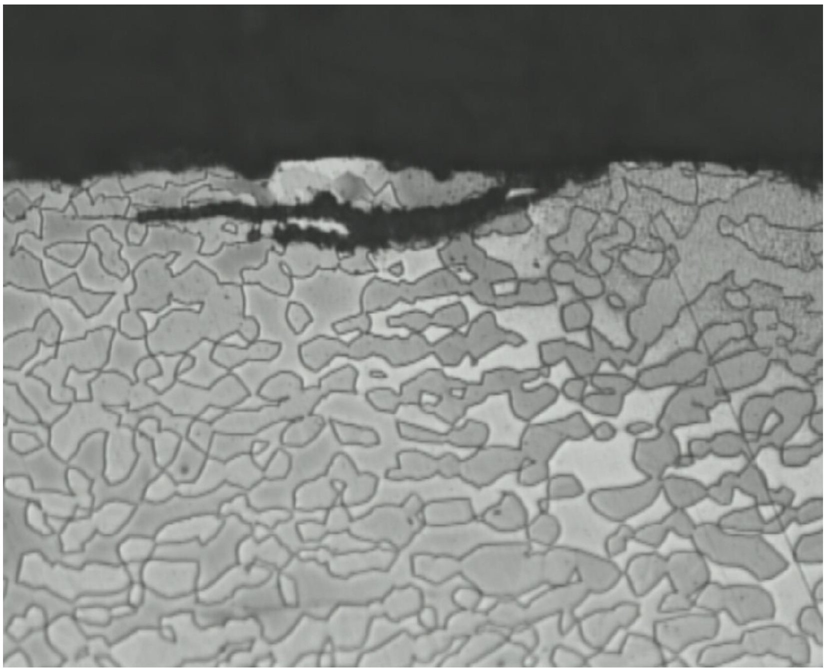
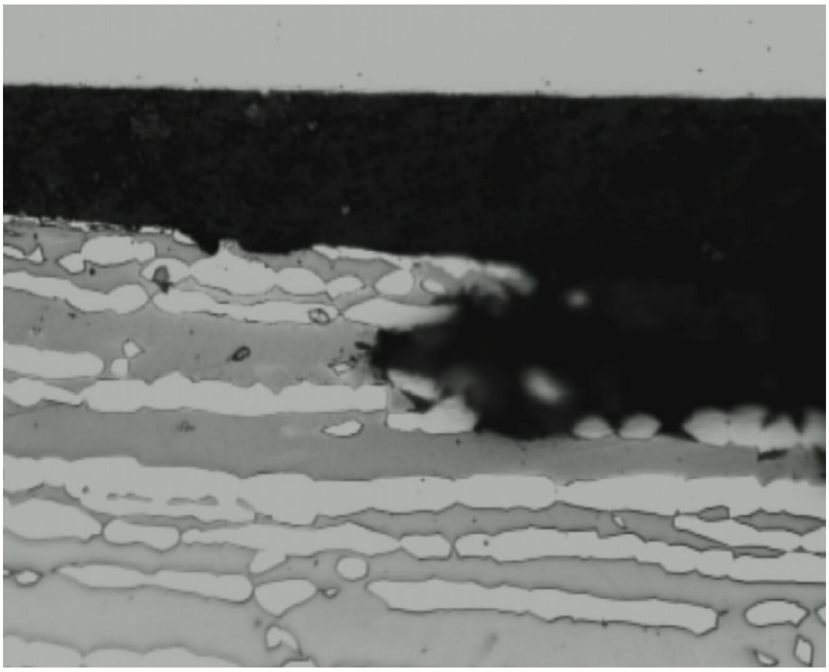


FIGURE 7 Potential of Zeron 100 versus ferric ion content in 10g/L chloride solution at pH2 and 90°C



20µm

FIGURE 8 Pitting corrosion of Zeron 100 tested in 10g/l chloride plus 500mg/L Fe^{3+} at 200°C



20µm

FIGURE 9 Pitting corrosion of Zeron 100 in 10g/L chloride plus 10mg/L Fe^{3+} at 200°C after repeated start-ups