ZERON 100 FOR DOWNSTREAM PROCESSING IN ACID LEACH MINING

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ABSTRACT

There is increasing use of acid leach extraction methods at elevated temperatures and pressures by the mining industry. In many locations there are limited supplies of fresh water, and waters with higher chloride contents must be used, making conditions more corrosive. The fluids downstream of the main autoclave are hot, acidic, oxidizing and contain chlorides and present a challenge to the mining community to ensure reliable operation. Zeron 100 is a high strength superduplex stainless steel that offers high corrosion resistance at a cost effective price. The paper presents a combination of laboratory data and service experience, particularly in the aggressive fluids found in downstream processing.

INTRODUCTION

Hydrometallurgy is a cost-effective way of extracting many metals from their ores, including copper, nickel, uranium, gold and zinc. This involves crushing the ore and mixing with water to form a slurry, which is reacted with sulphuric acid in an autoclave, often at high temperatures (>150°C) and pressures (5 to 50 bar). After the autoclave, some of the heat is usually recovered and then the temperature is reduced to about 100°C. The liquid must then be separated from the solids, and the metals present in solution must be separated so that those of value can be recovered. This involves a number of processes over a range of temperatures, many of which are at low pH and frequently contain chlorides. With the drive to reduce costs and maintenance intervals, there is a great interest in more cost-effective materials of construction. Superduplex stainless steel offers the combination of high strength, excellent corrosion resistance and ready availability.

DOWNSTREAM PROCESSING

After the autoclave circuit, the slurry may go to a surge tank, which is essentially a holding tank to maintain the flow should there be an interruption in the autoclave circuit operation. The slurry then goes to the thickeners where the solids and liquids are separated by counter current decantation (CCD). These are large ponds, tens of meters in diameter with long rotating rake arms. Because of the aggressive nature of the slurry, either high integrity coatings or corrosion resistant alloys are required.

After the thickeners, the liquid may go to a precipitation tank. In this the pH is increased slightly to precipitate out metals that are not required for recovery, e.g. iron. The solution is now known as pregnant liquor and may be processed in a number of ways. One of the most common is solvent extraction, where the liquor is mixed vigorously with an organic liquid so that the metal of value transfers to the organic phase. The remaining aqueous phase is termed the raffinate and is piped away for recycling. The metal is then removed from the organic liquid back into aqueous phase by a pH adjustment and is then sent to the tank house for electrowinning. The electrowinning process is carried out in warm, acid solutions that are still corrosive.

As an alternative to the solvent extraction route, which can be complex when there are many metals to separate out, there are some proprietary processes that have been developed for specific process routes. One of the best known is the Sherritt process that is used in the extraction of nickel (and cobalt) from nickel laterite ores. The solutions from such processes then generally go to the tank house for electrowinning, as above.

ALLOYS

Duplex stainless steels are roughly 50/50 austenite/ferrite and combine the ductility of austenite with the strength of ferrite. They contain varying amounts of chromium, molybdenum and nitrogen to give resistance to acids and chlorides. The nitrogen also gives additional strength to the austenite and improves weldability. For each austenitic stainless steel, there is an equivalent duplex alloy. Because duplex alloys contain less molybdenum and nickel than their austenitic equivalents, they are lower cost.

ZERON® 100 was the first of the superduplex stainless steels and was developed by RA Materials during the 1980's, first as a casting alloy and then as a wrought product. Zeron 100 contains additional alloying for increased strength and corrosion resistance. Table 1 shows the nominal composition of Zeron 100 compared with some other common stainless steels.

The elements chromium, molybdenum, tungsten and nitrogen all give resistance to localized attack in chloride-containing solutions. These are often combined to give a pitting resistance equivalent number or PREN, where:

$$\text{PREN} = \%\,\text{Cr} + 3.3(\%\,\text{Mo} + \%\text{W}/2) + 16 \times \%\,\text{N}.$$

Table 1 – The nominal composition of
some common stainless steels

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**	**> 41**
ZERON 100 (Cast)	**bal**	**25**	**8**	**3.5**	**0.25**	**0.7**	**0.7**	**> 41**
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(%Mo + %W/2) + 16 x %N

It can be seen that Zeron 100 has a higher PREN than most of the other alloys in Table 1, similar to the 6% Mo alloys, 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 wrought 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^{o}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.

Code cases for Zeron 100 have been processed by the relevant authorities for PD5500 (Europe) 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 1, such as a mixed sulphides vessel at a nickel laterite mine that was ~ 3m diameter and 20m long.

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

ALLOY	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (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
22%Cr Duplex	289	177	207
Alloy 20	NL	158	161
6%Mo Aust.	NL	185	207

NL – not listed

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 Rolled Alloys warehouses in Europe and North America.

CORROSION

Acids

Zeron 100 has excellent resistance to sulphuric acid, better than many of the alloys in Table 1, including 2507 (UNS S32750), which is a superduplex similar to Zeron 100, but which contains no copper or tungsten. This is shown in the iso-corrosion curves (0.1mm/y) in Figure 1. These curves demonstrate the benefits of the tungsten and copper additions to Zeron 100 on acid corrosion.

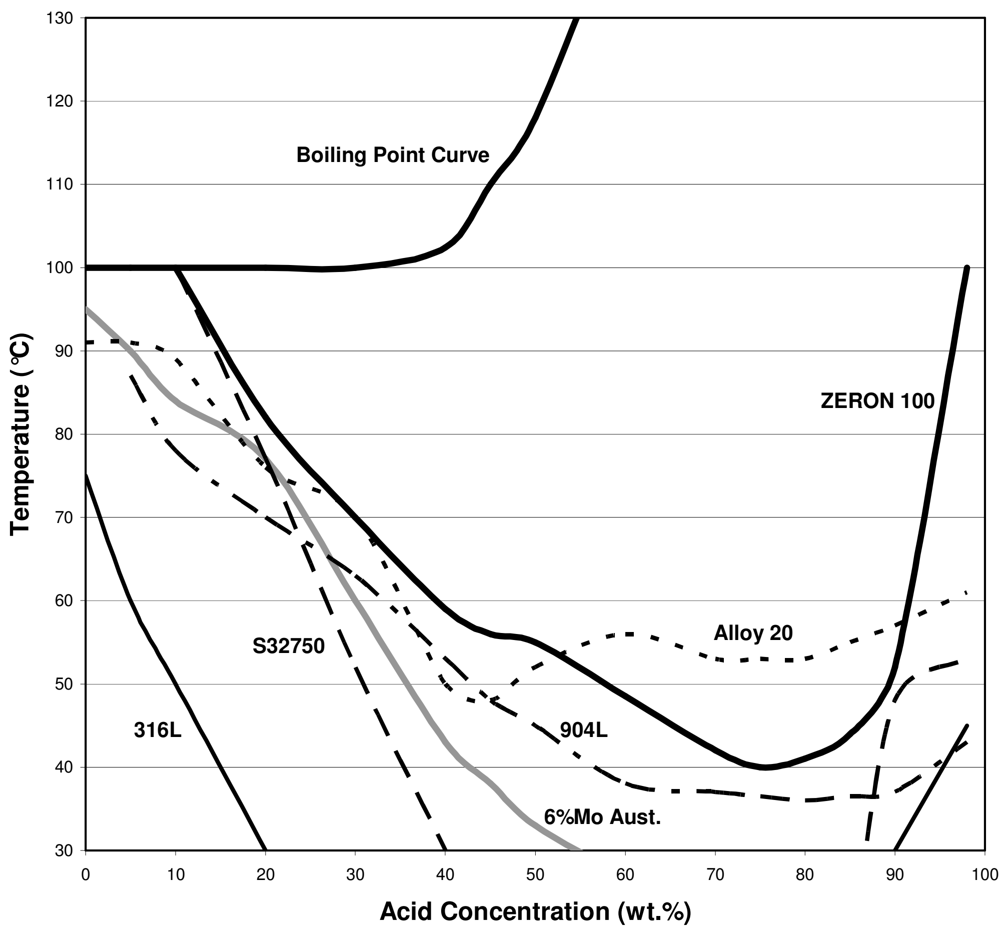

Figure 1 – Iso-corrosion curves (0.1mm/y) in sulphuric acid for some common stainless steels

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).

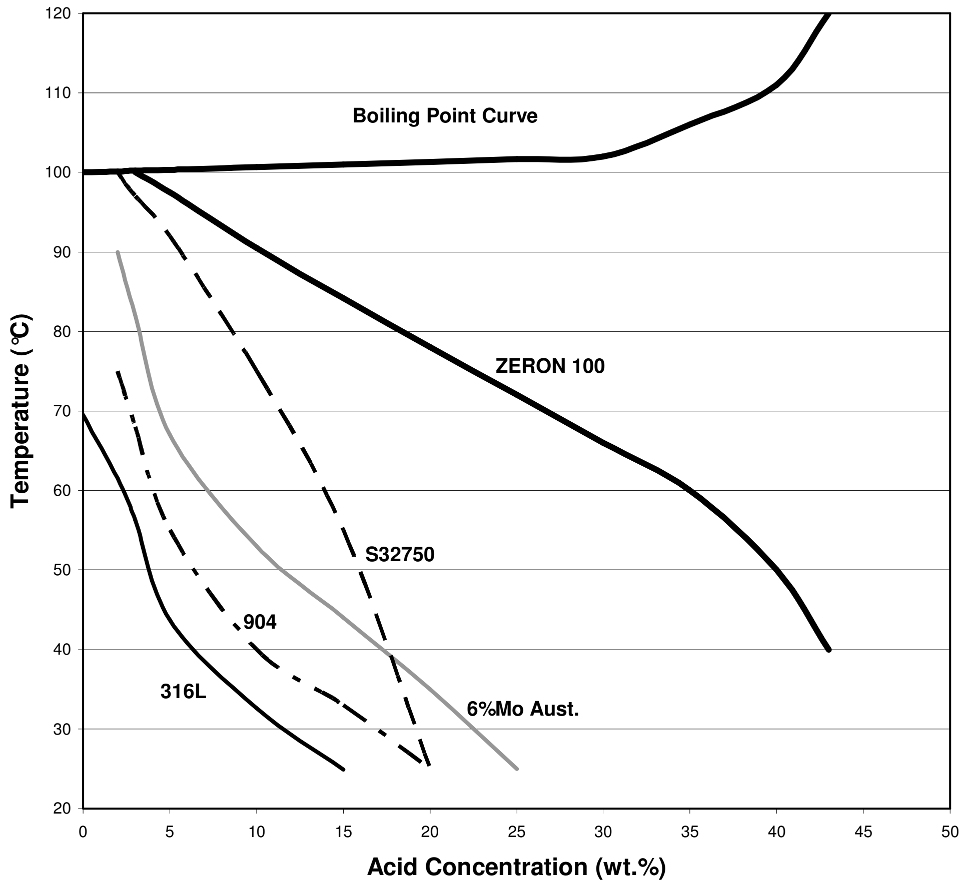

Figure 2 – Iso-corrosion curves (0.1mm/y) in sulphuric acid plus 2,000mg/L chlorides for some common stainless steels

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. Oxidizing 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 oxidizers and so the exact concentration of each will determine the corrosion resistance. When there is sufficient chloride, then the pitting potential may be exceeded as the cupric/ferric ion concentration increases. This causes increased corrosion, but it is now as small deep pits. Figure 4 shows the effect of cupric and chloride ions on the iso-corrosion curves of Zeron 100 in 5wt% sulphuric acid. The decrease in performance at high chloride and copper ion contents is due to pitting.

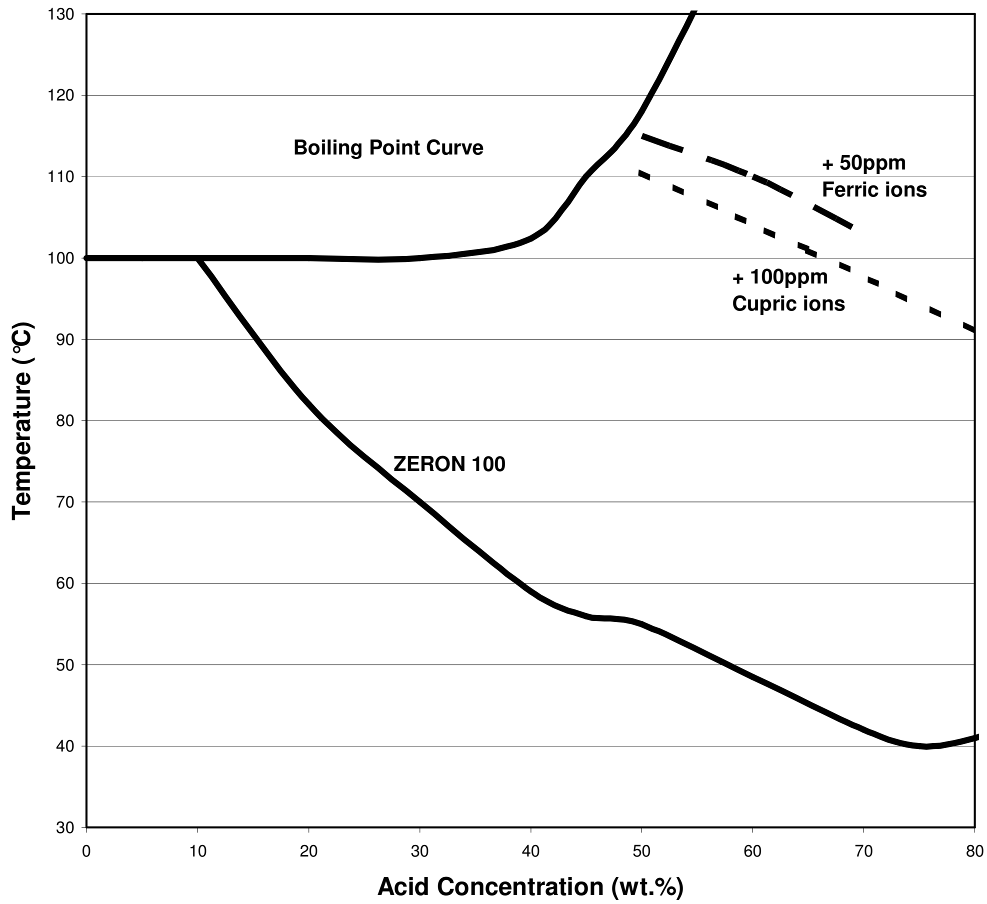

Figure 3 – Iso-corrosion curves (0.1mm/y) for Zeron 100 in sulphuric acid plus oxidizers

The performance of alloys in such liquids is a function of four variables, acid strength, temperature, chlorides and oxidizer (e.g. cupric ions) concentration. RA Materials has collected an extensive database on Zeron 100 over a wide range of these variables to determine its suitability for a wide range of downstream applications.

Erosion Corrosion

The hardness of the solids in mining slurries means that they can be very abrasive, particularly if silica is present. Figure 5 shows the results from an accelerated laboratory test in a slurry containing 25g/L chloride and 640mg/L sharp sand at a velocity of 40m/s and a temperature of 55°C. The results show the high resistance of Zeron 100 to erosion. This has been supported by the extensive use of Zeron 100 pumps in abrasive fluids, such as flue gas desulphurization slurries and acidic mine waters with significant solids contents.

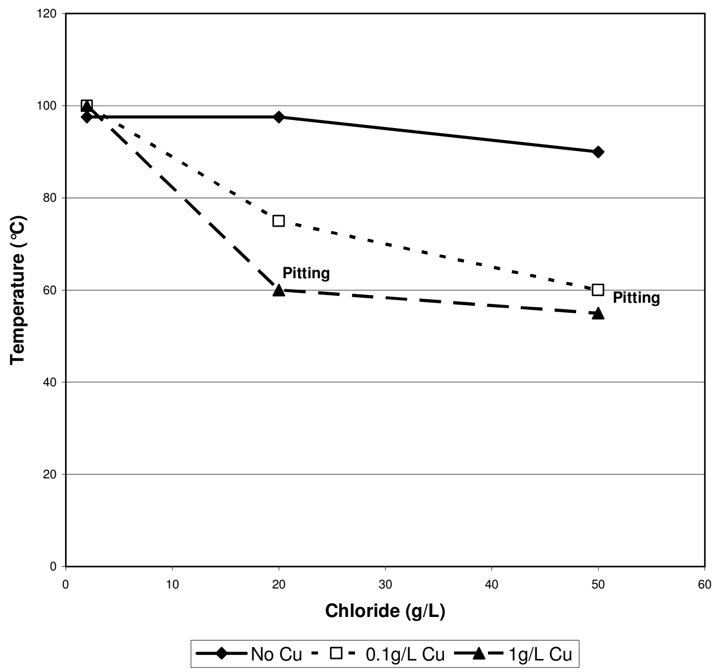

Figure 4 – Iso-corrosion curves (0.1mm/y) showing the effect of chloride on the corrosion of Zeron 100 in 5 wt% sulphuric acid with different cupric ion additions

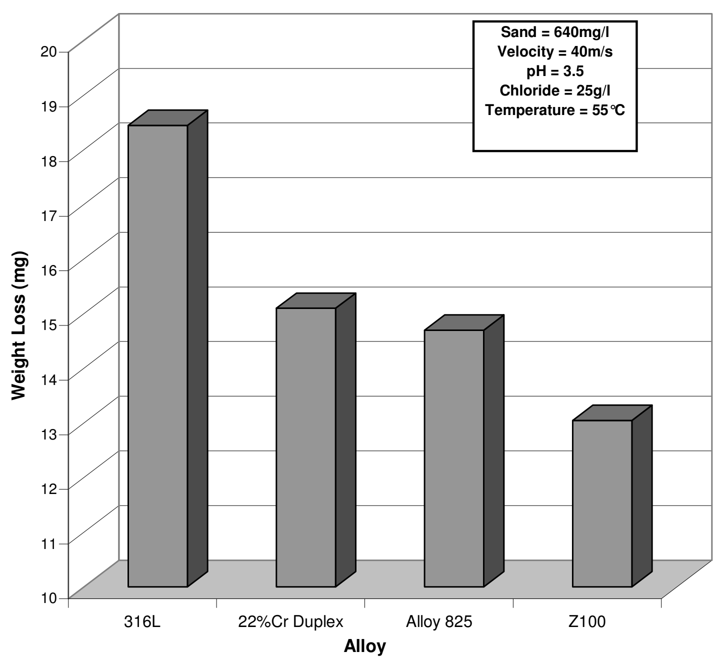

Figure 5 - Erosion of several alloys in a sand laden brine at 55°C

MINING APPLICATIONS

Surge Tanks and Thickeners

The discharge slurry from the autoclave circuit is typically around 100°C with 5 to 50g/L acid and chlorides, often with oxidizers such as cupric and ferric ions. Figure 6 shows the corrosion rate of Zeron 100 in a simulated slurry containing 38g/L acid at 100°C with varying chloride contents. It can be seen that the 6% Mo alloy, Zeron 100 and welded Zeron 100 all performed well up to 5g/L chloride, but pitted with 20g/L chloride. This was because there was a significant content of oxidizing ions (>1g/L).

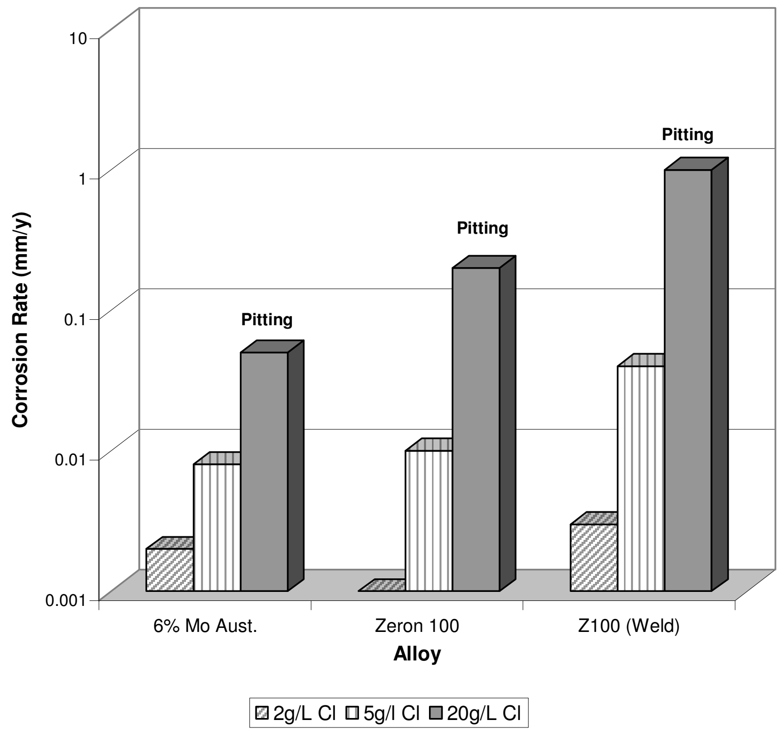

Figure 6 – The corrosion rate of 6%Mo austenitic and Zeron 100 stainless steels in a simulated autoclave circuit discharge slurry

The slurry enters the thickeners at around 100°C, but it cools as it goes from thickener to thickener, decreasing to maybe 50° or 60°C. As the temperature decreases, the chloride tolerance of Zeron 100 increases and it has resisted pitting at 60°C in a liquor similar that described above with 60g/L chloride.

Figure 7 shows a typical thickener arrangement and Zeron 100 has found uses in these applications. The thickener tanks are usually concrete with a rubber liner and the rake arms are metallic. Sometimes they are all corrosion resistant alloy (CRA), but more commonly they are coated carbon steel with CRA's used at complex joints and hinges, where a coating would be impractical. Zeron 100 was used to replace 904L at a uranium/ copper mine in Australia, where the high chloride content caused severe attack of the 904L. The Zeron 100 parts have been in service for over ten years. The thickeners at the Murrin Murrin nickel laterite plant in Australia used Zeron 100 from new and it has performed well over a period exceeding ten years.

Figure 7 A typical thickener arrangement in an acid leach process.
(Photo courtesy of F L Smidth)

Solvent Extraction

In the pump mixers the organic and aqueous solutions are stirred vigorously to make an emulsion, where the metal being recovered transfers to the organic phase. This is still an aggressive environment with acid and chlorides. Zeron 100 is an excellent choice for the pump mixers because of its high resistance to acid chloride solutions, its excellent resistance to erosion corrosion and its availability in both wrought and cast forms.

After the pump mixers the emulsion goes to the settling tanks, where the aqueous and organic phases are separated. These are often long tanks with a 180° turn at the end. Although the tanks are usually made of non-metallics, Zeron 100 is ideal where metallic components are required, such as for the turning vanes.

The aqueous phase is now termed the raffinate and it still contains acid and chlorides and is warm. The raffinate is usually recycled and may be injected into the feed slurry or somewhere a little downstream. This is to recover more of the metal of interest, as the solvent extraction system is not 100% efficient. Raffinates are commonly between 40° and 60°C and are, therefore, corrosive. Zeron 100 was used for the raffinate lines on the Spence copper project in Chile. It was also used to replace 48” rubber-lined carbon steel raffinate lines at the Escondida project in Chile.

The Sherritt Process

The Sherritt process is proprietary and has been used as an alternative to solvent extraction on some nickel laterite projects. As part of the process, the liquor is re-leached with H_2S, typically at a pH around 3. However, pH excursions to lower values are possible, particularly at start up and shutdown and it is important that the re-leach vessel does not suffer sulphide stress corrosion cracking, as H_2S is very toxic. Zeron 100 was selected for the mixed sulphides vessel on the Murrin Murrin project in Australia (Figure 8), where it has performed well. Rolled Alloys has also supplied Zeron 100 to the Ambertovy nickel project for a similar vessel.

Figure 8 The mixed sulphides vessel for the Murrin Murrin project in Australia

Electrowinning

The metal sulphate solution is removed from the organic phase back into aqueous phase for electrowinning. The discharge liquor from the Sherritt process can also go for electrowinning. The solution is warm, with a pH of 1 to 1.5 and there may be some chlorides that have carried over. The starter plates for the cathodes are often polished 316L so that when the desired thickness of metal has been plated, it can easily be detached from the starter plate. However, when chlorides are present, 316L can pit and the plated metal can become keyed to the starter plate at the pit sites. Zeron 100 is much more resistant to pitting in these solutions and has been used as starter plates at two copper mines in Arizona and Chile to combat this problem. The plates have been in service for over eight years without problems.

The electrowinning tanks are non-metallic but metals are needed for various fittings, clamps, electrical points etc above the tanks. This means that acid vapour from the tanks can condense on these fittings and cause corrosion if they are low alloy materials. Zeron 100 offers a high reliability, low maintenance option for all these fittings.

CONCLUSIONS

1. Zeron 100 has excellent resistance to acid-chloride solutions at elevated temperatures, even in the presence of oxidizers.
2. The high strength and hardness gives the alloy good resistance to erosion in corrosive mining slurries.
3. There is a range of applications in acid leach downstream processing where Zeron 100 offers a high reliability, low maintenance option.

REFERENCE

1. R Francis, Stainless Steel World Volume 22, page, 53, January 2010, KCI