A Comparison of the Corrosion Resistance of Cast and Wrought Superduplex Stainless Steel

By:

R. Francis and S. A. Hebdon

Weir Materials and Foundries,
Manchester,
UK.

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1. INTRODUCTION

Stainless steels are widely used in industry for handling corrosive liquids. The components for this service may be cast or wrought according to convenience, ease of manufacture, cost and design. It has often been stated that cast alloys are not as corrosion resistant as their wrought equivalent. There are a number of reasons for thinking this, when considering stainless steels and nickel alloys.

With austenitic alloys high in chromium and molybdenum, such as the 6Mo super austenitic stainless steels and the nickel-base alloys, such as 625 and C-276, there is a strong tendency for elemental segregation across the dendritic structure. This means that chromium and molybdenum are not uniformly distributed across the alloy. The wrought alloys are then hot worked followed by solution annealing and quenching. This refines the grain size and results in a more or less homogenous elemental distribution. With a cast alloy it is only solution annealed and the coarser grain size means that longer annealing times are required to achieve homogeneity. The problem is that during annealing there is usually grain growth. The authors have seen grains 6mm diameter, and larger, in cast 6Mo super austenitic alloys. This obviously reduces the alloy strength and so annealing times tend to be kept short. This means that the casting may not be fully homogenous and, hence, will have reduced corrosion resistance at areas lower in chromium and molybdenum than elsewhere.

Castings also contain more inclusions than wrought products and these are well known to act as preferential sites for the initiation of localised corrosion. The introduction of AOD ladles into foundries is resulting in cleaner melts with reduced levels of inclusions and impurities. There have been other improvements in the foundry arising from the use of a range of techniques and processes. The use of modern ceramics for cores, mould parts and runner systems can result in reduced inclusion levels and better surface finishes. The use of computer based software for the design of runner systems can reduce erosion and turbulance resulting in lower levels of inclusions entering the mould cavity. Finally the use of modern ladle refractories and nozzle systems can further improve cleanliness, whilst gas shrouding during melting and pouring is claimed to give further benefits.

Sometimes, however, the cast version of an alloy can offer advantages over its wrought counterpart. A good example is 316L, which is fully austenitic as a wrought product. However, as a casting (CF8M) the alloy contains 5 to 15% ferrite. This duplex microstructure greatly increases the resistance to chloride stress corrosion cracking, although not as much as with the modern duplex stainless steels, with ~ 50% ferrite. However, in some solutions, eg. ammonium carbamate, the delta ferrite phase can be preferentially attacked.

This paper compares and contrasts the corrosion resistance of a modern superduplex stainless steel in the cast and wrought forms.

2. HISTORY

During the 1970's there was a huge increase in activity in the North Sea by the oil and gas industry. This fuelled a demand for high strength, corrosion resistant alloys for injection pumps. At the time the pumps were mostly made of 316 with alloy 625 weld overlay in critical areas, or in a 25% Cr duplex alloy of the Ferralium type, with a PREN of 35 to 36. The PREN, or pitting resistance equivalent number, is an empirical measure of the corrosion resistance and is usually given by:-

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

During the late 1970's development of an improved duplex stainless steel was underway and resulted in Zeron 100, the first of the superduplex stainless steels. This is a 25% Cr alloy with increased levels of molybdenum and nitrogen to give a minimum PREN of 40.0, thus guaranteeing a minimum level of corrosion resistance, subject to correct heat treatment and chemical balance to achieve the required phase equilibrium.

During the 1980's the alloy was very successful in offshore injection pumps, seawater lift pumps and firewater pumps. A demand grew for a wrought counterpart of the alloy for use in seawater piping systems and the wrought alloy first entered service in 1990. Thus, Zeron 100 is unusual in that it started life as a cast alloy and the wrought alloy was developed subsequently. Since that time Zeron 100 has found a wide range of applications, not only in seawater, but also in a great variety of other corrosive liquids including sour brines, FGD slurries, acids, alkalis and other corrosive chemical media. Below are the results of corrosion tests of both cast and wrought forms of Zeron 100 in a variety of common media.

3. EXPERIMENTAL

3.1 Materials

Samples of cast Zeron 100 were cut from keel blocks from production heats. The variation in composition from heat to heat is small and Table 1 shows the composition range and a typical heat. The wrought test pieces were machined from bar of various diameters. Again the heat to heat variation is small and a typical analysis is shown in Table 1.

The major difference between the cast and wrought product is the maximum nickel content, which is higher for castings. This is because it is essential to obtain a 50/50 austenite/ferrite structure and in a single production operation (sand casting) the higher nickel content is helpful.

3.2 Test Methods

3.2.1 Ferric Chloride

The critical pitting temperature (CPT) was evaluated according to ASTM G-48 method C for triplicate samples.

The resistance to crevice corrosion was evaluated using cylinders 13mm diameter by 35mm long, The crevice was created with neoprene 'O' rings having 10mm id and 2.5mm thickness. Duplicate specimens were exposed at several temperatures to determine the critical crevice temperature (CCT), as in ASTM G48D.

3.2.2 Seawater

Crevice corrosion tests were conducted in synthetic seawater at + 600mV SCE, which is the potential of stainless steel in chlorinated seawater. After the current stabilised, the temperature was increased at 5°C/hour until crevice corrosion initiated, and the temperature at which this occurred was recorded as the critical crevice temperature (CCT).

Two crevice formers were used around the 10 mm od "bullet" samples. One was a 7mm id x 2mm thick 'O' ring. The second was a rectangular cross section, silicone rubber ring, also of 7mm id and 6mm cross section. The silicone rubber ring creates a deeper crevice, which is known to be more severe than that created by a simple 'O' ring.

3.2.3 Acids

Tests were conducted in laboratory grade sulphuric and hydrochloric acids to determine the iso-corrosion curves (0.1mm/y) over a range of temperatures and acid connections. In addition further tests were conducted in sulphuric acid containing 2,000 mg/L chloride.

Exposure tests were also conducted in an acetic acid plant at 186°C. The product was 42% acetic acid with 10% formic acid and 8% propionic acid.

3.2.4 Caustic Soda

Iso-corrosion curves 0.1mm/y) were determined in caustic soda from 10 to 70 wt % concentration. Tests below the boiling point were conducted in electrically heated Zeron 100 vessels, while tests above the boiling point were conducted in alloy C-276 autoclaves.

3.2.5 FGD Slurry

Critical crevice temperatures (CCT) were measured in a synthetic flue gas desulphurisation (FGD) slurry, using the method described by Francis et al (1). The CCT was measured at pH's from 3 to 5 and at a chloride concentration of 40,000 mg/l.

3.2.6 Oil and Gas

A series of tests were conducted with Zeron 100 C-rings to qualify the cast and wrought alloys for inclusion in NACE MR01-75. The C-rings were stressed to 100% of the actual 0.2% proof stress and exposed in an autoclave at 80°C in brines containing various concentrations of chloride and pressurised with 20 bar CO_2 plus 0.2 bar H_2S. After 30 days exposure the samples were examined for signs of localised corrosion/cracking.

4. RESULTS

4.1 Ferric Chloride

In the G48 test pitting first appeared at a temperature of 70 $\pm$ 5°C for both cast and wrought forms of Zeron 100.

The crevice corrosion results are a little more confusing, as shown in Table 2. The area of crevice attack was very small on all the samples and a loss of 1mm^3 of metal corresponds to ~8mg metal loss. The accuracy of the balance used was $\pm$ 1mg, so that the metal loss at 35° and 40°C was very small.

The results for the cast product are fairly easy to interpret, showing the critical temperature to be about 35°C. However, the results for the wrought product are less clear cut, with attack on one sample only at 35°, 40° and 45°C. The fact that at 35°C the wrought sample that showed crevice attack had no measurable weight loss shows that the attack was very shallow. This is similar to the results for cast Zeron 100 at 35°C. Hence, the CCT for wrought Zeron 100 is no more than 5°C higher than for the cast product. The variability in the CCT is thought to be due to the problem of creating a reproducible crevice with an 'O' ring (2).

Although the CCT's of wrought and cast Zeron 100 were very similar in ferric chloride solution, the weight losses were much greater for cast material when corrosion did initiate. This shows that, while the conditions for initiation of crevice corrosion are similar for both product forms, the propagation rate is faster in cast material. This is probably due to the coarser grain size of cast material and the fact that, even after solution annealing, the material will not be perfectly homogenous. Corrosion always follows the path of least resistance i.e. areas lower in corrosion resisting elements. In finer grained, wrought material there will be a lesser degree of inhomogeneity, and hence better corrosion resistance.

4.2 Seawater

The results of the CCT tests are shown in Table 3. With the neoprene 'O' ring the wrought form was clearly more resistant to crevice corrosion than the cast product. However, with the silicone rubber ring the difference in the CCT between the two forms was small. The neoprene 'O' ring type crevice represents the sort of crevice created by, for example, a flanged joint, while the silicone rubber ring creates the kind of tight crevice such as occurs at threaded joints. All of these CCT values are high numbers for a superduplex stainless steel, compared with normal operating temperatures (up to 40°C).

4.3 Acids

Figures 1 and 2 show the iso-corrosion curves (0.1mm/y) for Zeron 100 in sulphuric and hydrochloric acids. There was no difference in the performance of the cast and wrought products. Figure 1 also shows the curve for Zeron 130. This is a casting made with a higher copper content to improve sulphuric acid performance.

Figure 3 shows the iso-corrosion curves for Zeron 100 in sulphuric acid containing 2,000 mg/l chloride ions. Again there was no difference between the cast and wrought product forms.

In the acetic acid plant the results from coupon tests after 2 years exposure were:

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

The cast and wrought products gave the same results and less corrosion than the nickel alloys currently in use.

4.4 Caustic Soda

Figure 4 shows the iso-corrosion curve (0.1mm/y) for Zeron 100 in caustic soda. There was no difference between the wrought and cast product forms. Some tests included chloride additions up to 19,000 mg/L, which had no effect on the corrosion rate (3).

4.5 FGD Slurry

Figure 5 shows the CCT results for wrought and cast Zeron 100 in the pH range 3 to 5. The results clearly show a substantially lower resistance of the cast alloy to crevice corrosion at pH3 compared with the wrought form, while at pH 5 there was little difference and, by extrapolation, there would be no difference at pH 5.5.

4.6 Oil and Gas

The initial tests to qualify Zeron 100 for sour service in NACE MR0175 were carried out with 0.2 bar H_2S and 120,000 mg/L chloride. Both cast and wrought forms showed no signs of pitting or cracking after 30 days at 80°C. This is the temperature of greatest susceptibility to sulphide stress corrosion cracking for duplex stainless steels (4).

5. DISCUSSION

The relative performance of the cast and wrought forms of Zeron 100 shows a great deal of variability in the tests reported above.

The resistance to chlorides is well known to depend on the chromium, molybdenum and nitrogen contents of stainless steels. These are often linked together in the pitting resistance equivalent number or PREN, where:-

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

The higher the PREN the greater the resistance to localised attack, such as pitting and crevice corrosion. Zeron 100 is made to a PREN> 40 in all forms. However, not only is the composition important, but also homogeneity and inclusions. There is usually more segregation of elements in a casting compared with a wrought alloy and a greater number of inclusions. However, the solution treatment of all product forms of Zeron 100 (1120 ± 20°C) ensures this is kept to a minimum. Localised attack due to chlorides usually takes place at inclusions and the more numerous and the larger the inclusions, the greater the risk of attack. Castings traditionally contain more and larger inclusions than wrought material and, hence, would be expected to be more susceptible to attack by chlorides.

However, the differences between the cast and wrought product forms varied considerably from medium to medium. The FGD data clearly show that differences are a function of pH. Although there were large differences between the cast and wrought forms at pH3 in FGD slurry, the differences were small in ferric chloride solution, which has a pH of 1.2 to 1.5. This may be because the ferric chloride solution behaves more like a dilute acid with chlorides (Figure 3), than an acidic chloride solution.

In pure, non-oxidising mineral acids there were no differences between the two product forms. It is well known that copper alloying additions improve resistance to these acids (5), and the cast form with a deliberately higher copper content shows a significant improvement in performance over the wrought or cast product with ~ 0.6 wt % copper.

Although hydrochloric acid is high in chlorides, there was no difference between the corrosion resistance of the cast and wrought product forms. This was also true in sulphuric acid with 2,000 mg/l chlorides. General dissolution seems to dominate over localised corrosion at the low pH of these solutions. Both of these liquids are non-oxidising, while ferric chloride solution, sea water and FGD slurry are all oxidising. Differences between cast and wrought Zeron 100 might be expected in sour brines (high chlorides at pH 3.5) but the presence of H_2S means that this fluid is reducing. Under these conditions no differences between the cast and wrought forms were seen.

In caustic soda there are a number of differences compared with acid and neutral solutions. Firstly, the protective film is rich in iron and, especially, nickel (6) because chromium and molybdenum salts are soluble at high pH (7).

Chlorides do not affect the corrosion in caustic soda because they work by creating local acidification by hydrolysis. This is not possible at the very high pH of caustic soda (>14). It might be expected that the cast alloy, with ~ 1% greater nickel content, would perform, better than the wrought alloy, but no significant differences were seen. This may be because the dissolution of the chromium and molybdenum contents masked this effect.

The conclusion is that in many environments there is little or no difference in the corrosion resistance between cast and wrought Zeron 100. Where a difference is seen, it is manifested as a lower crevice corrosion resistance for the cast product. However, this only occurs in oxidising, chloride-containing solutions from approximately pH2 to 8. The greater the redox potential, the higher the pH at which the difference shows e.g. in FGD slurry at +300 mV SCE the difference only shows below pH 5.5, while at +600 mV, in seawater, the difference is still apparent at pH 8 with some crevice geometries.

One issue that has not been addressed is that of surface finish. In the tests reported above, all the samples had a good quality, fine machined finish. However, components supplied to a project can have a variety of finishes. Wrought material is generally smooth with a pickled surface. Castings may also be pickled after solution annealing, but they could also be machined, shot blasted or glass bead blasted. The critical differences between cast and wrought material have been in crevices in chloride-containing solutions. The smoother the metal surface, the tighter the crevice and the greater the likelihood of attack. This suggests that wrought material should be more susceptible to crevice corrosion.

However, there is another factor and that is the effect of small, surface-emergent defects in castings. These can behave like a crevice and are usually detected by NDE, principally dye penetrant testing. The level of defects that are permitted varies from specification to specification, but they are rarely totally removed. These defects may act as initiation sites for corrosion under very severe conditions. An example from service, is under FGD slurry deposits during stagnant periods. Such defects are much fewer in wrought products and may be another reason for the differences between cast and wrought products under severe operating conditions.

Castings have one particular advantage over wrought material and this is that the composition and heat treatment can be modified slightly from heat to heat to enhance specific properties. Hebdon (8) described this in detail for Zeron 100 and a few examples will suffice to make the point. Zeron 110 is a modification guaranteed to increase the minimum 0.2% proof stress over the standard alloy, while Zeron 120 gives exceptional impact toughness at low temperatures (minimum lateral expansion of 0.38 min at –120°C). Finally Zeron 130 has increased resistance to corrosion in sulphuric acid (Figure 1). This alloy was used for two quarter mile sections of the London Underground (Figure 6). The original cast iron sections were suffering severe corrosion and cracking due to an aggressive ground water containing high chlorides and sulphuric acid. The cast Zeron 130 tunnel segments have a planned life of 400 years.

6. CONCLUSIONS

1. Zeron 100 is readily manufactured in both cast and wrought product forms and in many fluids there is no difference in the corrosion resistance.

2. Where a difference does occur it shows as a reduced resistance to crevice corrosion in oxidising, chloride–containing fluids in the approximate pH range 2 to 8, depending on the redox potential.

3. The performance of the cast alloy can be improved in some fluids by modifying the alloy composition e.g. increasing the copper content for sulphuric acid service.

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TABLE 1 Composition limits for cast and wrought Zeron 100 and typical heats.

FORM		COMPOSITION (wt %)							PREN *
		Fe	Cr	Ni	Mo	Cu	W	N	
Cast	Min	-	24.0	6.0	3.0	0.5	0.5	0.2	>40
	Max	bal	26.0	8.5	4.0	1.0	1.0	0.3	
	OC11748	bal	25.3	8.3	3.57	0.85	0.56	0.21	40.4
Wrought	Min	-	24.0	6.0	3.0	0.5	0.5	0.2	>40
	Max	bal	26.0	8.0	4.0	1.0	1.0	0.3	
	OC11747	bal	25.1	6.98	3.56	0.57	0.58	0.22	40.4

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

TABLE 2 Results of the crevice corrosion tests of Zeron 100 in 10% ferric chloride solution (ASTM G48C).

TEMP (°C)	CAST		WROUGHT	
	Wt. loss (mg)	Pitting	Wt. loss (mg)	Pitting
30	0 0	No No	0 0	No No
35	0 2	No Yes	0 0	Yes No
40	5 5	Yes Yes	1 0	Yes No
45	11 21	Yes Yes	0 2	No Yes

TABLE 3 Results of the crevice corrosion tests of Zeron 100 in synthetic seawater at + 600mV SCE.

Crevice Former	CAST		WROUGHT	
	CCT (°C)	Mean CCT (°C)	CCT (°C)	Mean CCT (°C)
'O' Ring	58.2 67.6	62.9	> 78 > 78	> 78
Silicone Ring	54.2 59.1	56.7	54.7 64.0	59.4

FIGURE 1 Iso-corrosion curve (0.1mm/y) for Zeron 100 in sulphuric acid

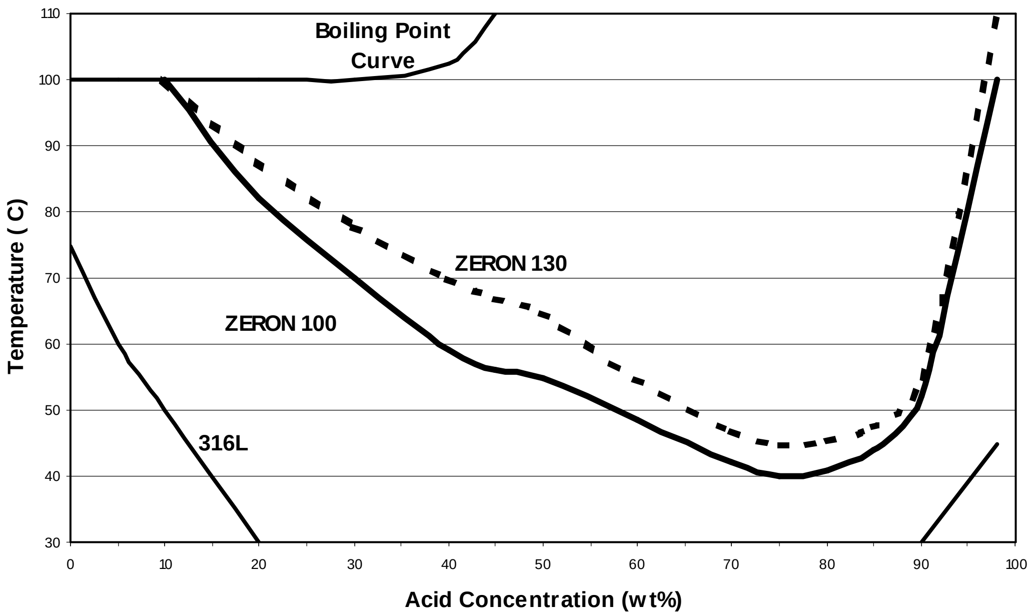


FIGURE 2 Iso-corrosion curve (0.1mm/y) for Zeron 100 in hydrochloric acid

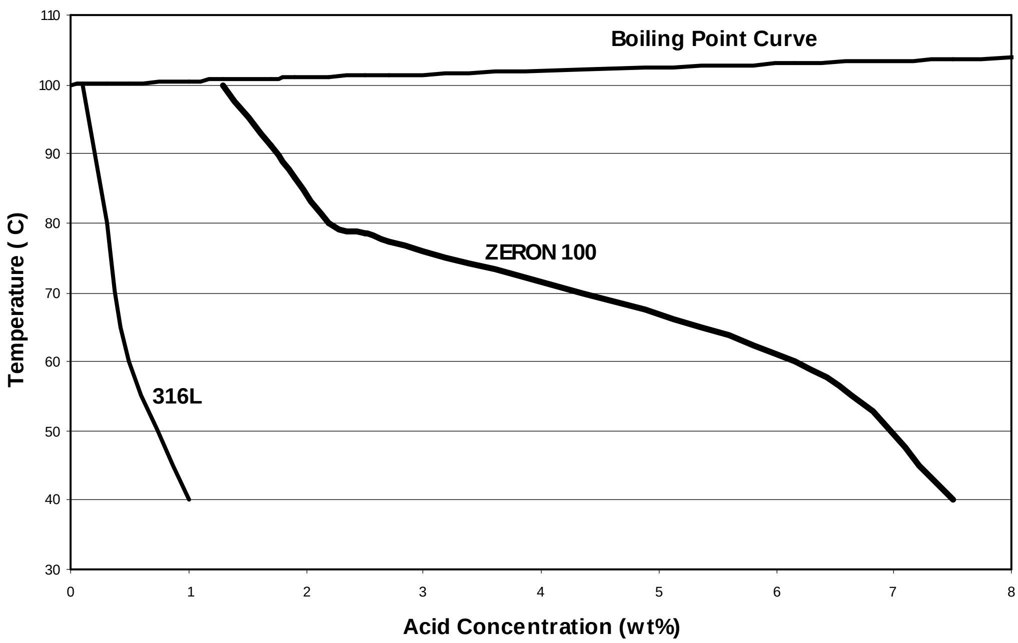


FIGURE 3 Iso-corrosion curve (0.1mm/y) for Zeron 100 in sulphuric acid plus 2,000mg/L chloride

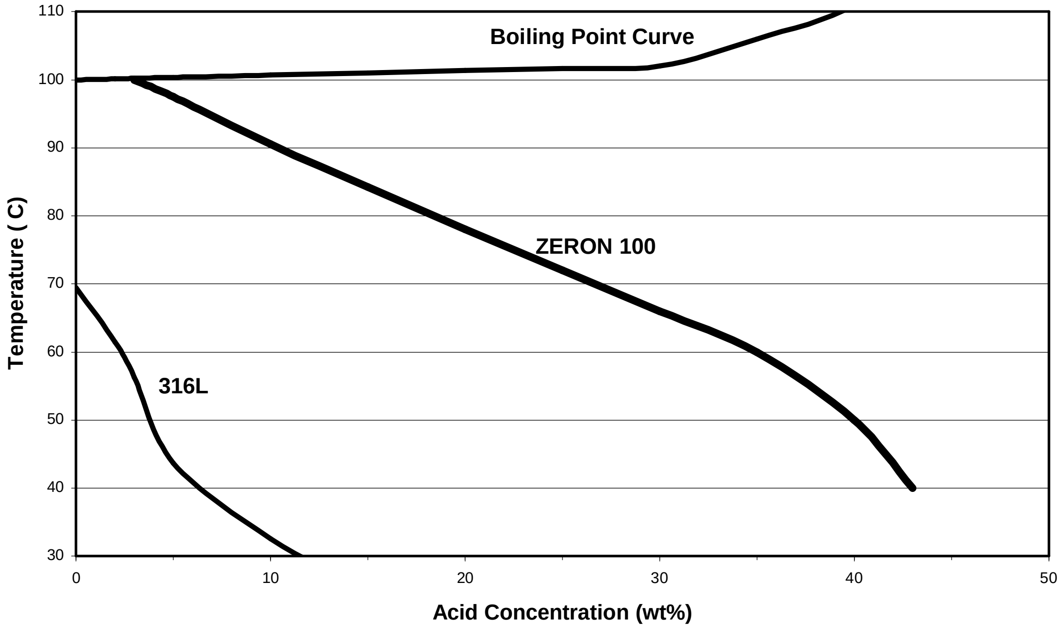


FIGURE 4 Iso-corrosion curve (0.1mm/y) for Zeron 100 in caustic soda

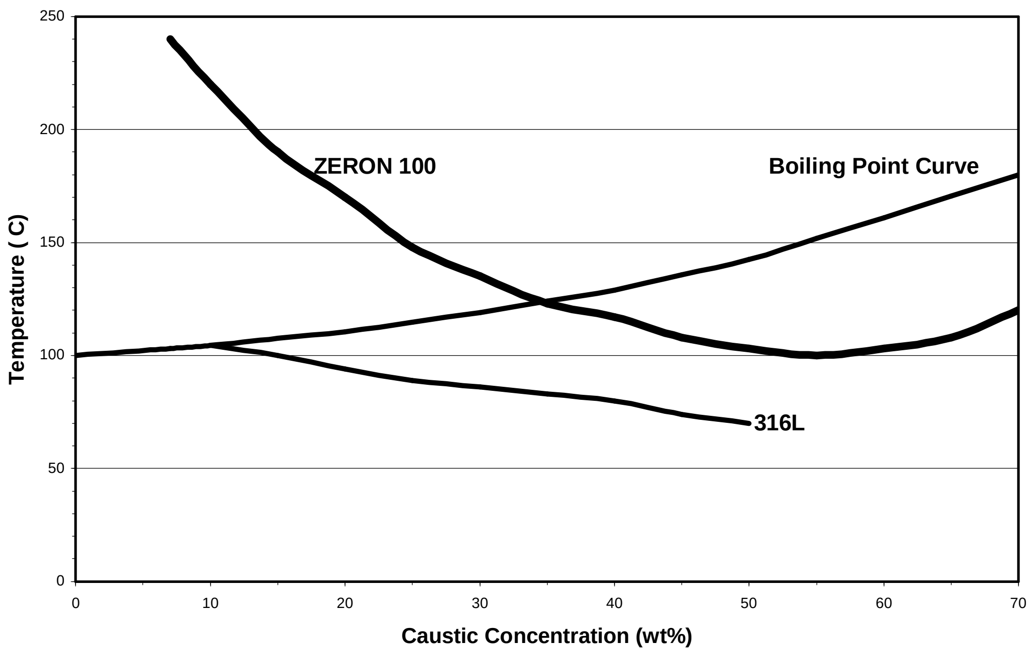
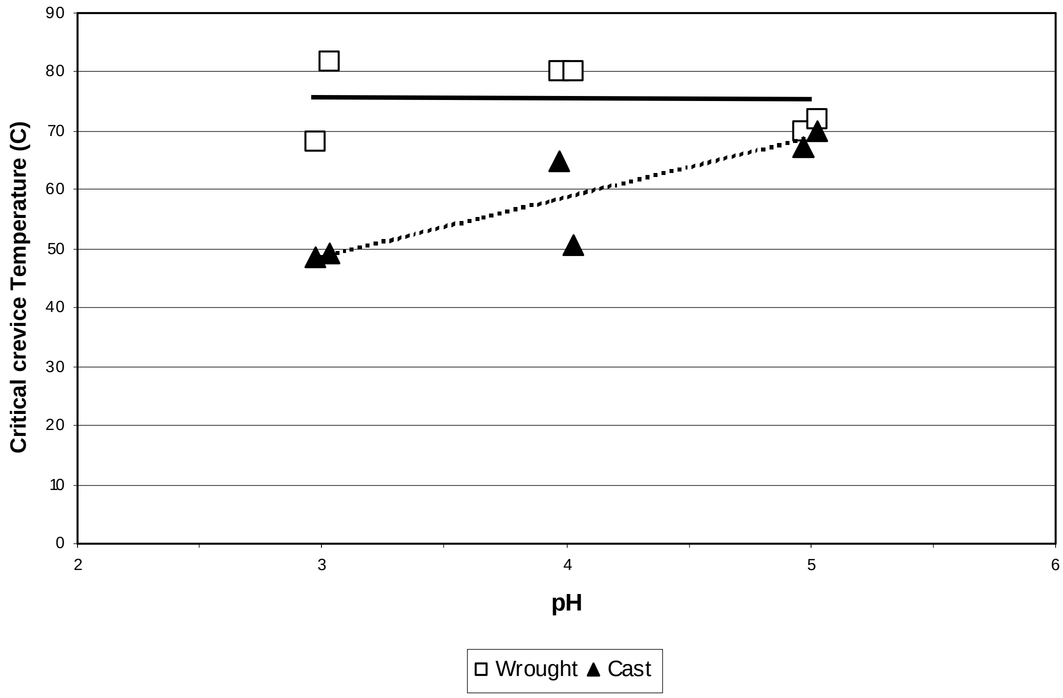


FIGURE 5 The CCT of Zeron 100 versus pH in a simulated FGD slurry with 40g/L chloride (Ref 1)



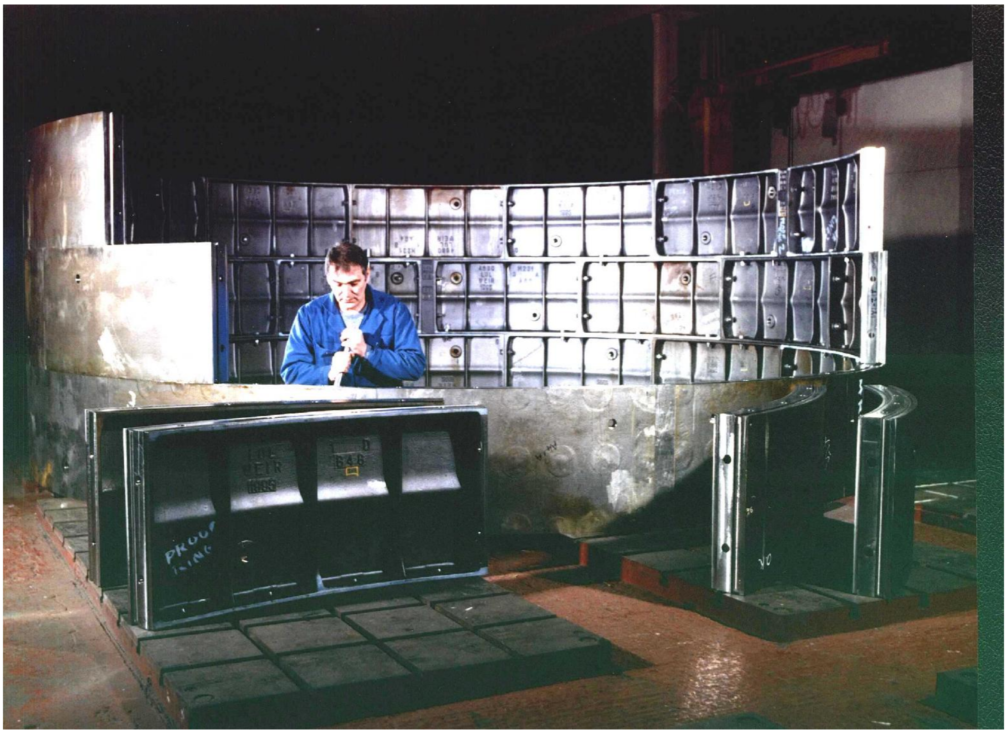


FIGURE 6 Zeron 130 castings for London Underground tunnel lining