Developments in the use of stainless steels for pumps and valves

R. Francis PhD, MSc, BSc, C Eng, F I Corr, MIM and
Weir Materials & Foundries

L M Phillips BSc, C Eng, MIM
Weir Pumps Ltd

SYNOPSIS

Developments in the use of stainless steels mainly by the marine and oil and gas sectors over the last 20 years are reviewed. The forces that drove the development of the high alloy austenitic and duplex stainless steels are described. The combination of properties that resulted in superduplex stainless steel becoming a preferred alloy for pumps and valves is discussed. Problems with the materials and their incorporation into existing systems are discussed and some new material developments are reviewed with an assessment of their suitability for pumps and valves in the offshore market.

1. INTRODUCTION

The offshore oil and gas industry makes a great deal of use of pumps and valves, both in the seawater cooling circuit and for handling hot process fluids. The principal pumps used are seawater lift, firewater, seawater injection and main oil line (MOL). The purpose of seawater lift and firewater pumps is self explanatory. Injection pumps are used to force deaerated seawater into the oil-producing strata to increase production. MOL pumps are used to pump the oil ashore after it has been separated from any water and gas.

In the early 1970's the principal alloys used for seawater lift and firewater were gunmetal (BS 1400; LG4) and nickel aluminium bronze (BS 1400; AB2). MOL pumps were manufactured from cast iron or steel and injection pumps mainly cast 316 stainless steel, often with nickel alloy 625 weld overlay. This was to prevent corrosion at crevices as the deaerators offshore are often not well maintained and there can be a substantial dissolved oxygen content to support corrosion.

With the increasing fluid pressures in new fields, there was a requirement for higher pressure injection pumps. However, space and weight are at a premium on offshore platforms. It has been calculated that a tonne saved in topside weight requires £100,000 less steel below the waterline. This led to the introduction of the early 25% Cr duplex stainless steels such as Ferralium and Zeron 25, because of their higher strength and corrosion resistance compared with 316 stainless steel. These worked well, but by the end of the 1970's it was clear that a stronger and more corrosion resistant alloy was desirable. This was partly due to further increases in pressure requirements and also a tendency to re-inject corrosive, produced waters, containing CO_2 and H_2S.

Gradwell et al[1] developed Zeron 100, the first of the superduplex stainless steels. This alloy not only has high strength, but also good corrosion resistance, including in chlorinated seawater. The alloy was further developed by the authors' company and was first used for injection pumps in 1983 and for seawater lift pumps in 1986. It quickly gained acceptance offshore and the success created a demand for a wrought equivalent alloy for pipes, fittings and flanges. Wrought Zeron100 was developed in the late 1980's and first entered service for seawater piping in 1990 and process piping in 1991. At the same time the Swedes developed a wrought 6% Mo (6Mo) super austenitic stainless steel for piping (Avesta 254SMO). This has been widely used for both seawater and process piping, particularly in the Norwegian Sector. With the selection of the wrought 6Mo alloy for piping, a cast version was quickly developed for pumps and valves. The paper describes the properties of both these alloys, their advantages and disadvantages and how they have been utilised by the oil and gas industry.

2. THE "SUPER" STAINLESS STEELS

Table 1 shows the nominal composition of cast Zeron 100 superduplex and the cast 6Mo super austenitic stainless steels to the relevant ASTM standards with cast 316 for comparison. Both contain high quantities of chromium, molybdenum and nitrogen, which confer corrosion resistance. In addition the nitrogen improves hot workability and weldability. Both alloys contain a small copper addition. Although this was originally added to improve manufacturing, the addition also increases the resistance to corrosion in non-oxidising mineral acids, such as sulphuric acid[2]. Zeron 100 also contains a small tungsten addition. This was done to reduce the risk of the formation of third phases during manufacturing, but tungsten also improves corrosion resistance in some acids, such as hydrochloric[3].

The 6Mo alloy is fully austenitic while Zeron 100 is produced with a 50/50 austenite/ferrite phase balance. This combines the strength of the ferrite phase with the ductility of the austenite phase.

Table 2 shows the minimum room temperature mechanical properties for both superduplex and super austenitic stainless steels to ASTM A890 and A351 respectively. It can be seen that both alloys are stronger than 316 but the superduplex alloy is ~80% stronger than the super austenitic. This has little significance for low pressure systems, such as firewater and seawater cooling. However, injection pumps now frequently operate at discharge pressures in excess of 300 bar. This means that, for this application, the superduplex stainless steel offers savings in wall thickness, weight and cost.

Both alloys offer good impact toughness. This is not surprising for an austenitic alloy, but the superduplex alloy has been utilised successfully for pumps used in the manufacture of butyl rubber, which cycle between +80°C and –120°C [4].

In sour service (e.g. injection of produced water) NACE MR0175 [5] is used to define the safe operating limits for materials, and both alloys have good resistance to sulphide stress corrosion cracking (SSCC). There used to be hardness restrictions on both these alloys, but these have been removed in the 2003 edition for solution annealed and quenched castings and wrought products. This is in recognition of the fact that only heavily cold worked material, with a higher hardness, has a reduced resistance to SSCC. Castings for pumps and valves are always supplied in the solution annealed and quenched condition.

The corrosion resistance of the two alloys is difficult to compare simply because it is a function of several variables depending on the fluid. In aerated, chlorinated seawater the maximum safe temperature for the 6Mo austenitic alloy is about 30° to 35°C [6], while that of the superduplex is about 40°C [7]. In sour service, the 6Mo alloy can tolerate more H_2S than the superduplex at temperatures of 70°C to 100°C but at temperatures greater than 120°C the superduplex alloy resists SSCC to higher levels of H_2S [5]. For most oilfields the resistance of both alloys to SSCC is more than adequate.

3. APPLICATIONS

The 6Mo alloy was available as a wrought product a little before superduplex, and it was selected for several Norwegian platforms for seawater and firewater systems. This meant that 6Mo castings were also required for the pumps (Figure 1) and valves and, in some cases, large flanges.

The move from copper alloys to high alloy stainless steels was a little later in the UK sector of the North Sea and both superduplex and 6Mo were used for piping. However, the more ready availability of superduplex castings has meant that it was generally used for pumps and valves. The present day situation is that superduplex stainless steel is more widely used in both sectors for pumps and valves because of its high reliability and ready availability.

When high alloy stainless steels began to be used offshore for seawater and firewater systems, it was logical to also consider them for the process system when the fluids were particularly corrosive. Some Norwegian platforms made good use of 6Mo for process piping including valves. However, as temperatures and pressures in new fields increased, the superior strength of superduplex meant that savings in weight, size and cost were possible compared with 6Mo austenitic. Currently super austenitic is rarely used for process systems, while superduplex is an automatic choice for corrosive conditions (Figure 2).

As fields have aged the produced water content with the oil and gas has increased. This has meant that more water is retained with the oil after the separators, as well as CO_2 and H_2S. This has meant that the environment in the MOL pumps has become more corrosive. The trend has been to switch to 13% Cr alloys for the impellers and sometimes also for the cases. In some of the oldest fields 25% Cr alloys (PREN ~36) have been used for impellers under the most corrosive of conditions. To date there has been no requirement to use the more highly alloyed superduplex and super austenitic alloys.

In other industries the super austenitic and superduplex alloys have also been gradually adopted. In some industries they are now first choice materials. A good example is reverse osmosis (RO) desalination. This process uses a large quantity of pumps, valves and piping. In this system seawater is forced through special membranes at high pressure (typically 70bar) to remove salt. It is important that there is no corrosion, because the corrosion products would affect membrane efficiency and would also contaminate the drinking water. Superduplex and super austenitic stainless steels are now first choice materials for RO plants. A good example is the RO plant at Tampa Bay, Florida, USA, which produces 106,000 m^3 per day of drinking water. The plant is half superduplex and half super austenitic and is expected to be the first of many large RO plants in the southern states of the USA, where the demand for drinking water is rising (Figure 3).

In the Middle East drinking water is also made by the multi-stage flash process (MSF), which essentially involves boiling the seawater and condensing the steam. The main seawater circulation pumps have traditionally consisted of stainless steel impellers with austenitic cast iron cases. However, there has been a series of failures of these pump cases by stress corrosion cracking (SCC) (Figure 4). Research has shown that austenitic cast iron is particularly susceptible to SCC in the warmer waters of the Middle East. The first choice for replacements has been superduplex stainless steel because of its corrosion resistance, reliability and availability. Some companies are now specifying that all new pumps must be superduplex stainless steel.

High alloy stainless steels have also been adopted for corrosive service in other industries. Flue gas desulphurisation (FGD) by the wet limestone process produces a slurry that is both abrasive and corrosive. The high strength and hardness of superduplex stainless steel means that it has good erosion resistance, superior to both conventional stainless steels and the 6Mo austenitic alloy [8]. Superduplex stainless steel was chosen for the slurry recirculation pumps, valves and agitators at the Drax power station in the UK (Figure 5). Despite the aggressive conditions these pumps regularly go 30,000 to 40,000 hours between major refurbishment.

The mining industry also produces slurries that are both erosive and corrosive and Zeron 100 has been used for the wetted components on positive displacement slurry injection pumps. These pumps inject slurry at ~180°C and pH 2 to 4 into the main autoclaves at two nickel laterite plants in Australia (Figure 6).

Because Zeron 100 has a high resistance to corrosion in a wide range of fluids it is now being used increasingly by the chemical industry for pumping corrosive liquors. A good example of this is sulphuric acid. Figure 7 shows the iso-corrosion curves (0.1mm/y) for some common stainless steels in sulphuric acid[3]. It can clearly be seen that Zeron 100 offers superior corrosion resistance to stainless steels such as 316L and 6Mo austenitic and, for most acid concentrations, it is superior to alloy 20 (CN7M as a casting). This good performance has led to the alloy being considered for sulphuric acid production plants where acid concentrations vary from 96% to 100% and temperatures vary from 80° to 200°C. The alloy is currently on trial at several sulphuric acid plants in North America.

4. PROBLEMS

There are a number of problems with both super austenitic and superduplex alloys. Some of these are production problems, while others have occurred in service.

The 6Mo austenitic alloys are difficult to cast in thick sections. The alloy is very susceptible to hot cracking and it is often necessary to build in a finite scrap rate. Another problem is grain growth during heat treatment. The 6Mo austenitic alloys are typically solution annealed at 1225°C minimum (e.g. NORSOK), but this can result in grains 6mm or more in diameter. This can mean it is difficult to meet the minimum strength requirements. The alternative is a much longer anneal at a lower temperature (e.g. ASTM A351 allows 1150°C min). This must be sufficiently long to ensure the re-dissolution of any second phases, e.g. sigma. Also the quench after annealing must be sufficiently fast to prevent the formation of secondary phases during cooling.

There have been crevice corrosion problems with 6Mo austenitic components in seawater and firewater lines. These appear to stem from poor manufacturing processes, resulting in alloy segregation or even third phases, which reduced localised corrosion reisistance[9].

None of these problems occur with superduplex, which is annealed at a lower temperature than 6Mo austenitic. The two-phase microstructure also means that grain growth does not occur. It is still essential to anneal for a sufficient time to re-dissolve all precipitates and then to quench fast enough to prevent their formation on cooling. Overall superduplex stainless steel is regarded as an easier alloy to cast in thick sections than the 6Mo austenitics. This is probably because the superduplex alloy was developed initially as a casting alloy, while the 6Mo alloy was developed from an existing wrought alloy.

Another advantage of the superduplex stainless steels is corrosion resistance. In many fluids Zeron 100 is as, or more, corrosion resistant than the 6Mo alloys. No fluid has yet been tested where Zeron 100 has inferior resistance to the 6Mo alloys. The advantages of superduplex over cast 6Mo have been realised by the oil and gas industry and the majority of high alloy stainless steel castings are in superduplex stainless steel.

The superduplex alloys have been cast in thick sections, up to about 300mm, but there is a size limit for large castings. The size is limited by section thickness, casting weight and the effectiveness of the quench facility. Until recently this limited the size of pump that could be produced in superduplex stainless steel. In 2002 the author's company supplied 5 large recirculation pumps to a nitrogen plant in Mexico, using cast impellers and cases fabricated from wrought product (Figure 8). These pumps supply the seawater cooling for the heat exchangers and replaced earlier copper alloy pumps that failed due to the high sand loading (up to 50,000 mg/l). This method of construction is now being considered for other large circulation pumps.

5. NEW DEVELOPMENTS

Because of the corrosion problems in the North Sea with some 6Mo austenitic components, some manufactures have developed even more highly alloyed austenitic stainless steels. These are all proprietary alloys, but they follow the same trends. They contain increased levels of chromium or molybdenum and double the nitrogen content. The latter is achieved by increasing the manganese content of the alloy. The wrought alloys all show an increased resistance to crevice corrosion in warm seawater. Because these alloys are being considered for piping etc., castings are needed for pumps and valves.

The author's company recently supplied valve bodies in a cast version of UNS S34565, a super austenitic alloy containing Fe/24Cr/18Ni/5Mo/6Mn/0.5N. Like all of the new super austenitic alloys it is still susceptible to hot cracking and grain growth. A sample of the casting was evaluated in the laboratory for crevice corrosion resistance in synthetic seawater at +600mV SCE. This is the potential typically adopted by high alloy stainless steels in chlorinated seawater. The critical crevice temperature (CCT) is shown in Table 3, along with that of Zeron 100 for comparison. It is usual, when making engineering decisions, to use the minimum CCT value. Using this criterion the CCT of the cast S34565 was only ~6°C greater than that of Zeron 100. This seems a small increase for an alloy that is more expensive and difficult to cast than superduplex.

The answer to the question "What is happening with superduplex stainless steels?" is "Everything and nothing". The composition of Zeron 100 was carefully selected to optimise ease of casting with high strength and corrosion resistance. If the alloy was modified to substantially increase, say, the corrosion resistance, it would require substantial modifications to the composition to ensure the alloy remained balanced. By this we mean that the 50/50 phase balance is retained and the segregation of elements between the phases is such that the properties of one phase are not inferior in any respect. Such a change would severely tighten the production constraints to achieve this. The discussion in the previous sections has demonstrated that cast superduplex stainless steel is a very versatile alloy with good strength and high corrosion resistance in a range of fluids. Instead of creating a new alloy, the alloy can be varied from heat to heat to accentuate particular properties for a specific project. Hedbon[10] has described these in detail, but a few examples will suffice. A small increase in the ferrite content will produce a higher strength where this is required. If good impact toughness at low temperature is required, then the austenite fraction can be increased. This was the method used to achieve the impact toughness requirement at –120° C for the Exxon butyl rubber pumps[4].

Finally the corrosion resistance can be modified to suit special fluids. London Underground (LUL) was suffering corrosion and cracking problems with cast iron tunnel linings on a quarter mile stretch of the Northern Line. This was caused by sodium chloride in the ground water combined with sulphuric acid, produced by microbial action. Superduplex stainless steel was selected as having the correct combination of strength and corrosion resistance for the projected 400 year life (Figure 9). The resistance to corrosion by dilute sulphuric acid containing chlorides was increased by increasing the nominal copper content from 0.7% to 1.0 wt%. This produced a significant increase in the resistance to pitting in this environment.

These few examples show the versatility of superduplex stainless steel castings. It is expected to be a workhorse alloy for machinery in corrosive environments well into the 21st Century.

6. CONCLUSIONS

1. During the 1980's and 1990's cast superduplex and super austenitic stainless steel castings became used increasingly for pumps and valves in the oil and gas business.

2. The high strength and corrosion resistance of the superduplex grade meant that it became specified increasingly for applications involving high pressure and/or temperature.

3. The success of the superduplex and super austenitic alloys in the oil and gas industry has led to their use in other industries where high corrosion resistance is required.

4. More highly alloyed austenitic grades are now available and cast versions are being developed.

5. The versatility of superduplex stainless steel combined with its high strength and corrosion resistance mean it will remain a workhorse alloy for fluid machinery for many years to come.

REFERENCES

1. K J Gradwell and C V Roscoe, Paper 34
Duplex Stainless Steel '86 Conference, The Hague, Holland. Oct 1986 126.

2. J Sedriks, "Corrosion of Stainless Steels", 2nd edition, published by John Wiley.

3. R Francis, Paper 387, Corrosion '94, Baltimore, MD, USA. March 1994, NACE International.

4. S Winnik and B Fitzgerald, Paper 131,
"A User Perspective of Duplex Stainless Steel in Petrochemical Service".
Duplex Stainless Steel '94, Glasgow, UK, Nov 1994, TWI.

5. MR0175-2003, "Materials for Sulphide Stress Cracking and Stress Corrosion Cracking Resistance in Sour Oilfield Environments", NACE International.

6. B Wallen, Duplex Stainless Steel '97, Maastricht, Holland, Oct 1997. Published by KCI, page 59.

7. R Francis & G Byrne, Paper 255 Corrosion 2003, San Diego, CA, USA,
March 2003, NACE International.

8. X Hu and A Neville, Paper 189, Corrosion 2002, Denver, Co, USA,
March 2002, NACE International.

9. O Strandmyr and O Hagerup, Paper 707, Corrosion '98, San Diego, CA, USA.
March 1998, NACE International.

10. S Hebdon, "The Manufacture of High Quality Duplex and Superduplex Castings".
SFSA National T&O Conference, Nov 1999. SFSA.

TABLE 1. Composition of superduplex and super austenitic stainless steels to ASTM A890 and A351 respectively.

ALLOY		COMPOSITION (WT%)							PREN*
		Fe	Cr	Ni	Mo	N	Cu	W	
316 (CF8M)	min	-	18.0	9.0	2.0	-	-	-	24
	max	Bal	21.0	12.0	3.0	-	-	-	
Superduplex (Grade 6)	min	-	24.0	6.5	3.0	0.20	0.5	0.5	>40
	max	Bal	26.0	8.5	4.0	0.30	1.0	1.0	
Super Austenitic (CK3MCuN)	min	-	19.5	17.5	6.0	0.18	0.5	-	43
	max	Bal	20.5	19.5	7.0	0.24	1.0	-	

Bal = balance

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

TABLE 2. Minimum mechanical properties at room temperature for superduplex (ASTM A890) and super austenitic (ASTM A351) stainless steels.

ALLOY	0.2% Proof Stress (MPa)	UTS (MPa)	Elongation (%)
316 (CF8M)	205	485	30
Superduplex (Grade 6)	450	690	25
Super Austenitic (CK3M Cu N)	260	550	35

TABLE 3. Critical crevice temperature at +600mV SCE in synthetic seawater for some cast stainless steels.

ALLOY	CCT (°C)		
	min	max	mean
S34565	60.6	68.4	62.8
Zeron 100	54.7	64.0	59.3

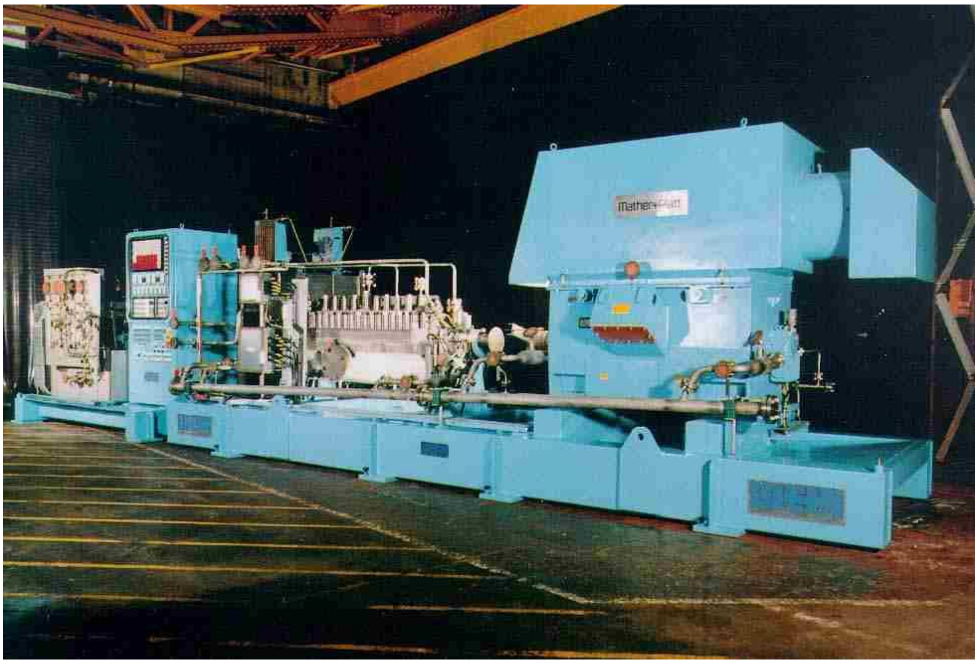

FIGURE 1 Injection pump in cast 6Mo austenitic stainless steel supplied to Middle East

FIGURE 2 Firewater pump in superduplex stainless steel.

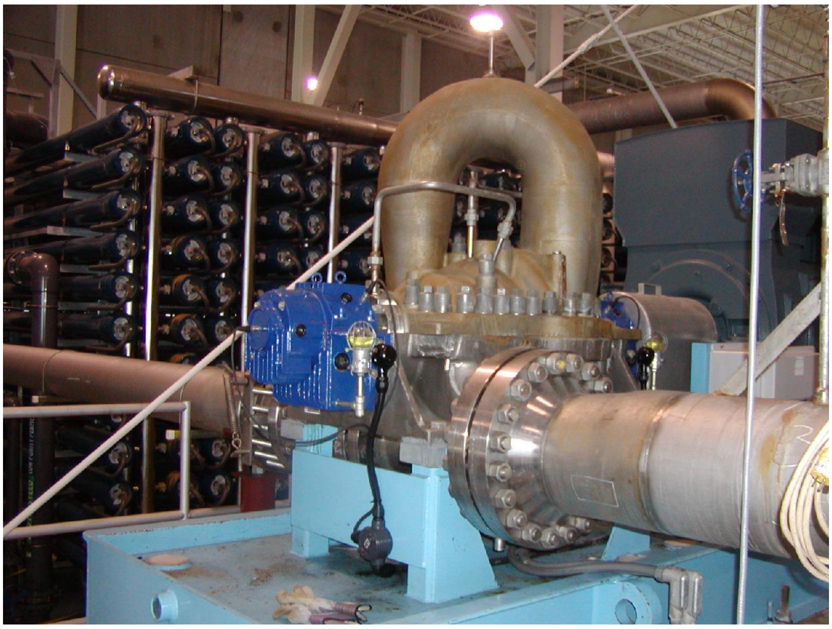

FIGURE 3 Superduplex and super austenitic stainless steels at a Florida reverse osmosis desalination plant.

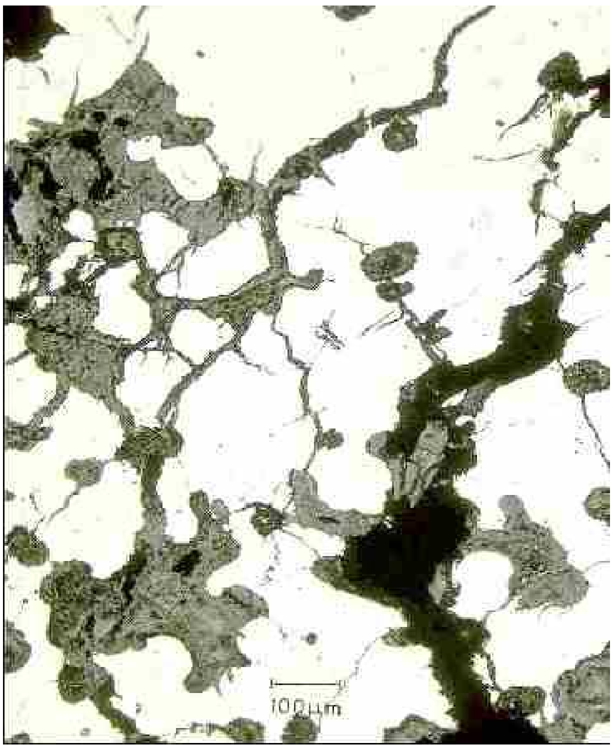

FIGURE 4 Stress corrosion cracking in an austenitic cast iron pump case.

FIGURE 5 Superduplex stainless steel pumps to handle FGD slurry.

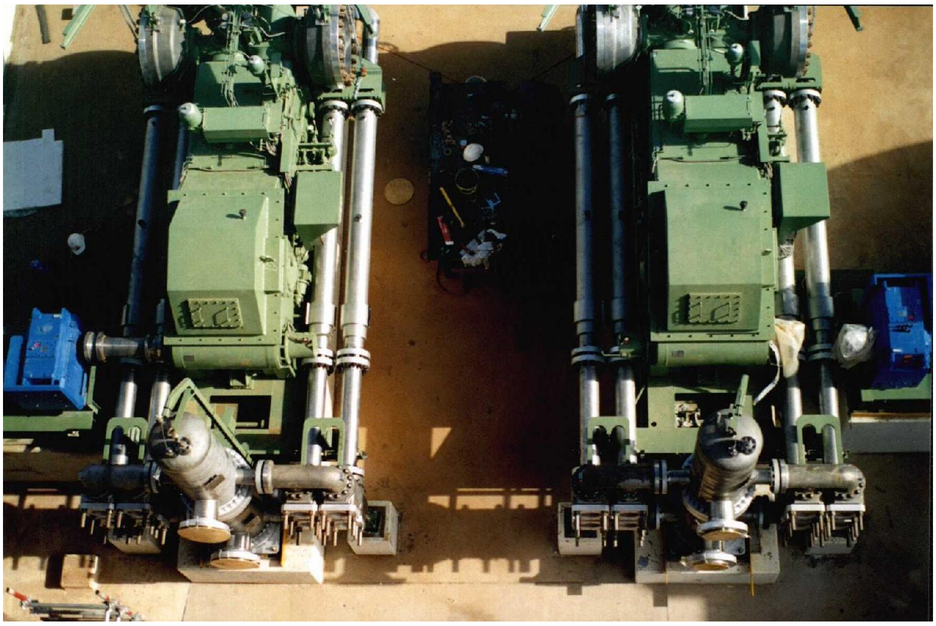

FIGURE 6 Positive displacement pump handling hot, acidic slurry at a nickel laterite plant

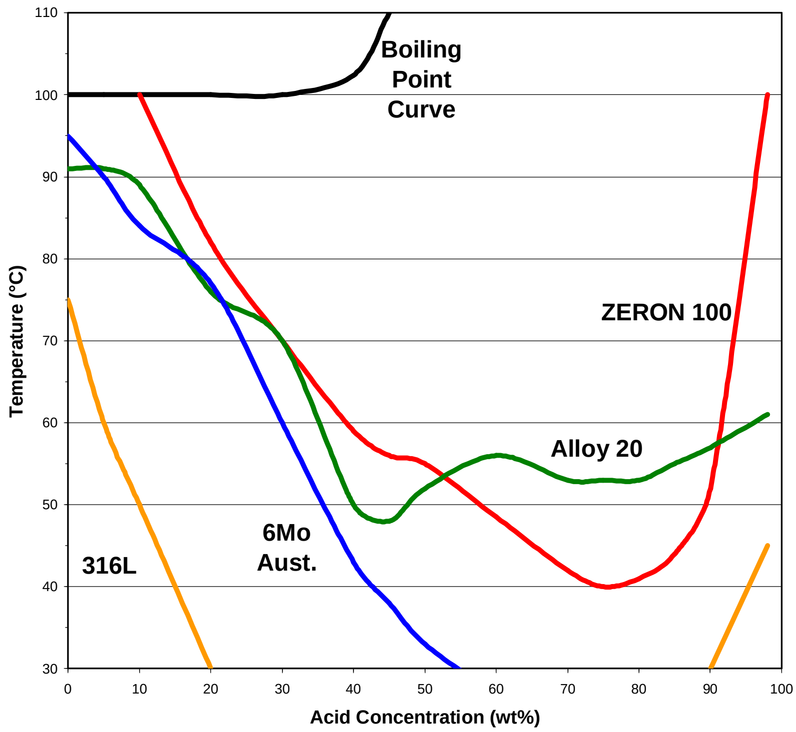

FIGURE 7 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid

FIGURE 8 Seawater circulation pump in superduplex with a fabricated case

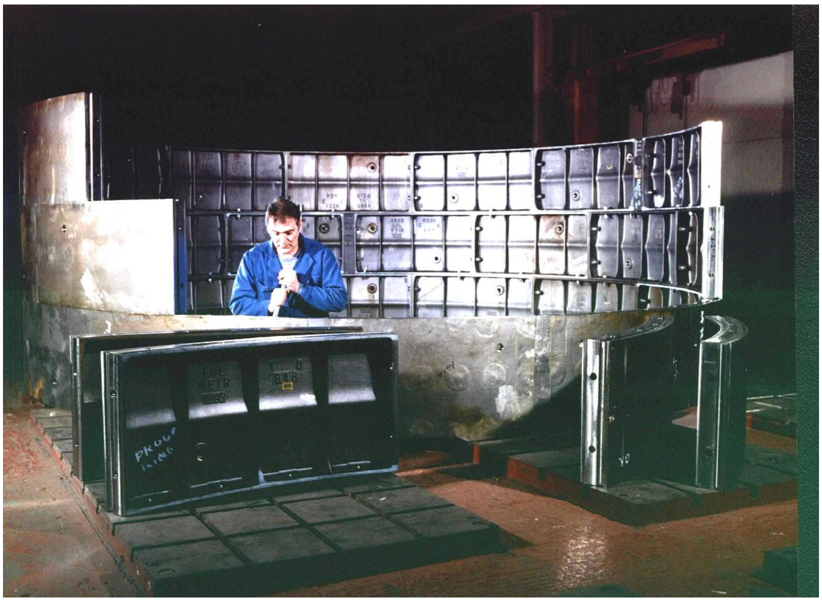

FIGURE 9 Cast tunnel lining in modified superduplex for LUL