THE SELECTION DESIGN, FABRICATION AND PERFORMANCE OF ZERON[®]100 IN SWRO APPLICATIONS.

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<u>Abstract</u>

Super Duplex Stainless Steels (SDSS) are finding increasing use in high pressure feed pipework systems on SWRO plants and in other desalting applications using membrane technology.

This paper details the corrosion resistance of ZERON 100 SDSS in seawater service, comparing and contrasting this with other grades of steel commonly used in SWRO applications.

Key aspects of product design that allow for the construction of lower cost, more mechanically efficient pipework systems and vessels are detailed. Again these are compared and contrasted with other steels used in SWRO plants.

Fabrication practices and procedures are discussed and welding, forming, machining and galvanic compatibility with other steels are considered.

Specific case studies are presented where ZERON 100 SDSS has been successfully used in small scale and large scale new build SWRO applications.

Also presented are cases where the alloy has been successfully used to replace SWRO pipework constructed in other grades of stainless steel that have suffered corrosion failure in service.

Finally the successful use of the steel in novel membrane systems on offshore platforms is also presented.

I. INTRODUCTION

This paper considers the nature of the alloy chemistry of ZERON 100, its microstructure and the resultant properties that make it attractive to the design engineer for Sea Water Reverse Osmosis (SWRO) applications. Aspects of design and fabrication to optimise its commercial attraction and performance in service are also detailed.

II. CORROSION RESISTANCE

The diversity of stainless steel grades, the variation in costs and contradictory reports of their resistance to corrosion in seawater make it difficult for design engineers to establish a settled and undisputed material philosophy. All stainless steels rely for corrosion resistance upon the formation of a Chromium rich, oxide film on their surface, known as a passive film. Other elements, in particular molybdenum, nitrogen and tungsten are known to make the passive film, more difficult to breakdown in the presence of the chloride ion. Figure 1 shows that the passive film in most stainless steels is stable over a wide range of potentials. It also shows what elements extend this range of passivity or enhance corrosion resistance [1]. It can be seen that passivity is lost under highly oxidising (transpassive) conditions and when active, general corrosion occurs. Increased temperature also has a negative effect on passivity.



A convenient, yet empirical, point of entry to differentiate between the corrosion resistance of stainless steels in chloride environments has been provided by Truman [2]. Using linear regression analysis of chemical composition and pitting and crevice corrosion test data, Truman identified a strong correlation between a parameter known as the Pitting Resistance Equivalent (PRE_N) and, both the critical pitting and critical crevicing temperature (CPT/CCT) for a wide range of stainless steels in chloride solution (Figure 2).



FIGURE 2 Critical pitting temperature versus PRE_N for some stainless steels

The validity of this relationship has been confirmed by many subsequent authors. Kovach and Redmond [3] published an excellent review of the history of this work, rationalizing differences and discrepancies in test technique, alloy chemistry and seawater conditions and drawing compelling conclusions as to the relationship between PRE_N and CCT in seawater. By comparing the results of long term crevice corrosion tests in warm seawater with laboratory results from ASTM G48 Method D corrosion tests, these authors found that only those alloys with a CCT of 35°C or higher in the Method D test resisted crevice corrosion in warm seawater (Figure 3).



Further, they were able to relate this behavior to the PRE_N number of a range of stainless steels and determine the PRE_N level necessary to avoid crevice corrosion (Figure 4).



Figure 4 Relationship Between PRE_N and Critical Crevice Temperature (ASTM G48D)

This means that for seawater service only SDSS with a PRE_N of 40 minimum and super austenitic stainless steels (SASS) grades with a PRE_N of 45 minimum should be considered if crevice corrosion is to be avoided. However, this considers only seawater with typical chloride contents of 18-20,000 ppm. On brine rejection circuits this figure may double and we understand developments in membrane technology may further concentrate the reject brine with chloride. Figure 5 shows that under mildly oxidising conditions the CPT of Zeron 100 welds remains at about 50°C as the chloride content increases from 20,000 mg/l to 100,000 mg/l. The crevice corrosion resistance was displaced to even higher temperatures as the chloride content was reduced correspondingly.



FIGURE 5 CCT/ CPT versus chloride concentration at a potential of +400mV SCE

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The performance of high alloy stainless steels and nickel alloys in seawater service is dependent upon their proper chemical formulation, processing, heat-treatment and finishing.

The proper combination of alloy chemistry and thermo-mechanical processing is of prime importance. However, Shone [4] also found that:-

- 2.1 Poor pickling was leading to crevice corrosion of alloy 625 that had previously been believed to be immune to crevice corrosion in seawater. Grubb [5] confirmed the significance of pickling with respect to 6% Molybdenum alloys similarly.
- 2.2 Variation in performance between plate and tube products in 6% Molybdenum alloys was attributable to differences in processing.
- 2.3 Small differences in alloy chemistry of duplex and austenitic grades was giving rise to differences in crevice corrosion resistance.

In view of this, designers and specifiers should seek a consistency in supply source of the raw material (bar, billet, plate and seamless pipes). They should ensure all converters of raw material to finished and semi finished products are approved and qualified to manufacture by the supplier of the steel. This should ensure that all thermo-mechanical processing of the material is compatible with the base chemistry of the raw material provided. Without this level of consistency in material, variation in performance can arise [6]. Most reputable steel companies dealing with branded alloys appreciate this and work hard to retain brand integrity across all product forms.

So, purchase specifications should require tests confirming a suitable level of performance. These usually involve ASTM G48 Method A corrosion tests, Charpy impact tests and microstructure tests. This approach has been standardized in the form of ASTM A923. However, the scope of this standard is limited to the detection of intermetallics and does not address fitness for purpose.

III. DESIGN

| | | NON | MINAL C | | 0.2% PROOF | | | | | |
|------------------------|-----|-----|---------|-----|---------------|-----|------|------------------|-----------------|--------------|
| ALLOY | Fe | Cr | Ni | Мо | Cu | W | Ν | PRE _N | STRESS (MPa) | UTS (MPa) |
| 316L | bal | 17 | 10 | 2 | - | - | - | 24 | 170 | 485 |
| 904L | bal | 20 | 25 | 4.5 | 1 | - | - | 35 | 215 | 490 |
| 6Mo Aust. | bal | 20 | 18 | 6 | 0.7 | - | 0.2 | 43 | 300 | 650 |
| Zeron 100 (Wrought) | bal | 25 | 7 | 3.5 | 0.7 | 0.7 | 0.25 | >40 | 550 | 750 |
| Zeron 100 (Cast) | bal | 25 | 8 | 3.5 | 0.7 | 0.7 | 0.25 | >40 | 450 | 700 |

Table 1 shows the composition and mechanical strength of a range of stainless steels used in SWRO plants.

Figure 6 plots the relative localised corrosion resistance as quantified by the PRE_N number against the strength level of these steels. From this it can be seen that the family of duplex steels mirrors the family of austenitic stainless steels in terms of corrosion resistance but with the benefit of 2 x strength and the added benefit of higher resistance to chloride stress corrosion cracking.



FIGURE 6 PRE_N versus 0.2% proof stress for some stainless steels

Table 2 shows the allowable stresses for pipework and vessels of SASS and SDSS alloys according to British and American vessel and pipe codes.

| Table 2. |
|----------|
|----------|

| | DESIGN STRESS FOR TEMPERATURES UPTO 40°C (100°F) | | | | | |
|---------------------------|--|-------------------|-------------------|--|--|--|
| MATERIAL | PD5500 (formerly BS5500) | ASME VIII div 1. | ASME B31.3 | | | |
| 6% Mo (UNS S31254) | 207 MPa (*Note 1) | 185 MPa | 207 MPa (*Note 1) | | | |
| ZERON 100 (UNS S32760) | 319 MPa (*Note 2) | 214 MPa (*Note 2) | 250 MPa | | | |

* Note 1 - Material not listed in code; design stress calculated in accordance with code rules.

* Note 2 - Enquiry case 5500/111 of PD 5500 and code case 2245-1 of ASME VIII.

Taking typical SWRO conditions of 70 bar max pressure and 40°C max design temperature it is possible to calculate for a given pipe diameter the wall thickness required to contain the pressure. The result of this exercise for a range of pipe sizes is shown in Table 3.

| Table | 3. | | | | | | | | |
|--------|---|-----|-------|--------|-------|------------|-------|--------|--------|
| PIPE V | PIPE WALL THICKNESS CALCULATED PER ASME B31.3 | | | | | | | | |
| INTER | INTERNAL PRESSURE 70 Bars (1015 psi), at 100°F (40°C) | | | | | | | | |
| | | | | | | | | | |
| NPS | Nom. | | | | Nom. | | | | Saving |
| | Wall | Sch | (mm) | Nom. | Wall | Sch | (mm) | Nom. | lb/ft |
| | (mm) | | | Weight | (mm) | | | Weight | |
| 1.5 | 0.921 | 10S | 2.77 | 2.09 | 0.763 | 10S | 2.77 | 2.09 | 0 |
| 4 | 2.181 | 10S | 3.05 | 5.61 | 1.807 | 10S | 3.05 | 5.61 | 0 |
| 6 | 3.211 | 10S | 3.40 | 9.29 | 2.660 | 10S | 3.40 | 9.29 | 0 |
| 8 | 4.180 | 20 | 6.35 | 22.36 | 3.463 | 10S | 3.76 | 13.40 | 8.96 |
| 14 | 6.785 | 20 | 7.92 | 45.61 | 5.620 | 10 | 6.35 | 36.71 | 8.90 |
| 16 | 7.754 | 20 | 7.92 | 52.27 | 6.423 | 20 | 7.92 | 52.27 | 0 |
| 18 | 8.724 | 30 | 11.13 | 82.15 | 7.226 | 20 | 7.92 | 58.94 | 23.21 |
| 20 | 9.693 | 30 | 12.70 | 104.13 | 8.029 | 20 | 9.53 | 78.60 | 25.53 |
| 22 | 10.662 | 30 | 12.70 | 114.81 | 8.832 | 20 | 9.53 | 86.61 | 28.20 |
| 24 | 11.631 | 30 | 14.27 | 140.68 | 9.635 | 30 | 14.27 | 140.68 | 0 |

Weight (in bold) and therefore, cost savings become apparent at the 8" and larger sizes. Some argue that for smaller diameter pipes the requirement to use mechanical joints like Victaulic couplings mitigate against the use of schedule 10S pipework systems. However, the use of rolled grooves [7], or the use of schedule 40S pipe "pup pieces", complete with machined Victaulic grooves and taper bored on the ID to suit schedule 10S pipe makes the schedule 10S system a reality.

Today, consideration is being given to SWRO systems with pressures up to 100 bar. Large diameter energy recovery systems with pipework up to 24" NB are being considered. This particular case is detailed in Table 4 which compares 6% Molybdenum against ZERON 100. As the system pressure and pipe diameter increases the case for ZERON 100 SDSS application becomes even stronger.

| Table 4 | 4. | | | | | | | | |
|--|--------|-------------|-------|--------|--------|-----|-------|--------|--------|
| PIPE WALL THICKNESS CALCULATED PER ASME B31.3 | | | | | | | | | |
| INTERNAL PRESSURE 100 Bars (1450 psi), at 100°F (40°C) | | | | | | | | | |
| | | S 31 | 254 | | | | | | |
| NPS | Nom. | | | | Nom. | | | | Saving |
| | Wall | Sch | (mm) | Nom. | Wall | Sch | (mm) | Nom. | lb/ft |
| | (mm) | | | Weight | (mm) | | | Weight | |
| 1.5 | 1.308 | 10S | 2.77 | 2.09 | 1.085 | 10S | 2.77 | 2.09 | 0 |
| 4 | 3.098 | 40S | 6.02 | 10.79 | 2.569 | 10S | 3.05 | 5.61 | 5.18 |
| 6 | 4.561 | 40S | 7.11 | 18.97 | 3.782 | 40S | 7.11 | 18.97 | 0 |
| 8 | 5.938 | 20 | 6.35 | 22.36 | 4.923 | 20 | 6.35 | 22.36 | 0 |
| 14 | 9.638 | 40 | 11.13 | 63.44 | 7.991 | 30 | 9.53 | 54.57 | 8.87 |
| 16 | 11.014 | 40 | 12.70 | 82.77 | 9.133 | 30 | 9.53 | 62.58 | 20.19 |
| 18 | 12.391 | 40 | 14.27 | 104.67 | 10.274 | 30 | 11.13 | 82.15 | 22.52 |
| 20 | 13.768 | 40 | 15.09 | 123.11 | 11.416 | 30 | 12.70 | 104.13 | 18.98 |
| 22 | 15.145 | 60 | 22.23 | 197.41 | 12.558 | 30 | 12.70 | 114.81 | 82.60 |
| 24 | 16.522 | 40 | 17.48 | 171.29 | 13.699 | 30 | 14.27 | 140.68 | 30.61 |

We have come across contractors who design SDSS pipework systems using 6% Molybdenum design stresses, we have come across contractors who have used allowable stresses for vessels (ASME VIII div 1) instead of ASME B31.3 to design pipework systems and there are those who build in their own additional factor of safety into the coded design stresses for both SDSS and SASS systems. Such practices fail to take full advantage from these steels and constitute poor value engineering. We have not encountered these practices in any other industry that we deal in.

IV. FABRICATION

4.1 Welding

Fabrication by welding of all high alloy stainless steels should be carried out by qualified welders working to qualified procedures. Qualification of procedures should follow the requirements of ASME IX but be augmented with a corrosion test to ASTM G48A, Charpy impact testing and a microstructure check. Similarly welder qualifications should be in accordance with ASME IX and should also be augmented with a G48A corrosion test and a microstructure check.

The corrosion resistance of welds, in both ZERON 100 and SASS's can be reduced as a consequence of a broadly similar metallurgical response to the weld thermal cycle, and similar metallurgical phenomena occurring during solidification of the weld metal [8]. Both alloys are susceptible to the formation of sigma phase if the weldment is too hot for too long. Sigma phase is a brittle, chromium-rich precipitate that causes the adjacent matrix to be depleted in Chromium, which lowers its corrosion resistance. Early assessments of the extent to which corrosion resistance can be diminished by sigma phase formation were based upon isothermal heat treating of stainless steels in furnaces to generate sigma and then measuring the corrosion resistance. However, it has been shown [9,10] that simulations of this nature significantly over estimate the detrimental effect on corrosion resistance of sigma phase formation in real welds.

Leonard et al [11] systematically examined the effect of intermetallic phases on the corrosion resistance of SDSS and SASS GTA weldments. The welding conditions examined covered welding arc energy representing typical industrial practice, the high heat input end of the typical range and heat inputs in excess of manufacturers recommended values (abusive practice) respectively.

Table 6 shows the peak and average volume fractions of intermetallic phases found in each of the welds. Both grades show a tendency to increasing volume fractions of intermetallic with increasing heat inputs. The austenitic grades precipitated more sigma phase than the duplex steels. This is attributable to the higher alloy 625 type welding consumables used. Overall the level of sigma phase precipitated as a consequence of these weld thermal cycles was low.

| ARC | V | olume F | | | | | |
|-----------|---------------|----------------|----------------------|------|-------------------------|------|----------------------|
| (kJ/mm) | TYP (0.9 t | ICAL o 1.6) | HIGH (1.1 to 2.0) | | ABUSIVE (1.9 to 3.2) | | PRECIPITATE SIZE |
| ALLOY | PEAK | AVE. | PEAK | AVE. | PEAK | AVE. | |
| 31254 | 1.8 | 1.4 | 2.1 | 1.9 | 2.4 | 1.8 | 4µm dia |
| ZERON 100 | 0.2 | 0.3 | 0.8 | 0.6 | 1.7 | 0.5 | 2µm wide x 10µm long |
| 32750 | 0.8 | 0.2 | 2.6 | 0.3 | 1.3 | 0.4 | 2μm wide x 10μm long |

Table 6.

These welds were then exposed to aerated, chlorinated (0.5 to 1.0 ppm) seawater at 40°C for 62 days and then (following examination) at 53°C for a further 29 days. It should be recognized at this stage that aerated chlorinated seawater is a highly oxidising, aggressive medium, more so than the chemically treated seawater encountered in HP feed pipework in SWRO systems.

The results of the seawater exposure were that none of the weldments exhibited corrosion attack. Moreover, there was no significant difference between any of the welds. Weight loss measurements indicated corrosion rates of less than 0.001 mm/yr. maximum.

The difference between the corrosion resistance of real welds that contain sigma phase and simulated samples containing isothermally transformed sigma is the size and distribution of the precipitates. Isothermally formed sigma particles have time to nucleate and grow under roughly equilibrium conditions. Diffusion processes cause the adjacent matrix to be depleted in Chromium and Molybdenum, locally lowering the PRE_N of the materials immediately adjacent to the precipitate. This zone of depletion increases as the particle size increases. In real welds the thermal cycle is dynamic. Nucleation and growth of precipitates is an incremental process occurring far from equilibrium, across a temperature gradient and is essentially integrated over the relevant temperature ranges of the weld thermal cycle. This has the effect of restricting the growth and diffusion processes in real welds, so minimizing the width of the denuded zone of lower PRE_N material surrounding the precipitate. For pitting corrosion to propagate, the depleted zone must be sufficiently large to contain a stable pit. In real welds this is more difficult to achieve than in isothermal heat treatments. In essence, it is the size of the sigma precipitate that determines its adverse effect on corrosion resistance not its volume fraction. Francis [9] showed that the size of particles formed in isothermal treatment are 7 to 10 times larger than the precipitates formed in welds, for the same overall volume fraction.

Taking a semi quantitative approach encompassing diffusion and percolation theory, Francis and Warburton [12] were able to show that for precipitates of about $2\mu m$ in diameter (typical for real welds) a volume fraction of around 4% would be necessary before corrosion resistance would be affected. This theory was supported by seawater testing of real welds, deliberately manufactured to give a wide range of sigma phase volume fraction, as shown in Figure 7.



FIGURE 7 Depth of attack versus sigma content in chlorinated sea water at 35°C

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These findings have subsequently been supported by others [8,11] working in the laboratory and by the performance of real welds in the field [13,14].

These results and experiences demonstrate that within the range of practical fabrication there is no discernible difference between the pitting corrosion resistance of SASS, other SDSS and ZERON 100 weldments in seawater. Indeed, should the designer feel it necessary to further optimise the corrosion resistance of the welded joint the option remains to pickle the fabricated spools. Francis et al [15] have shown that for ZERON 100, this can increase the CPT of welds in seawater by ~17°C for acid immersion of spools at 55°C and for welds pickled with special acid paste at room temperature. Of course this would require spools to be of a manageable size and have flanged connections for site assembly to avoid closure welds on site that could not be pickled.

These results and practical experience shows that the level of tolerance of welded joints in SASS and SDSS to welding conditions beyond the manufacturers recommended levels is good. This is in agreement with Shone [4] who also considered practical fabrication implications on corrosion. This should give the design engineer confidence in the robust performance and pitting corrosion resistance of weldments in both these steels in SWRO applications.

4.2 Forming

Other fabrication issues relate to the forming of branch connections on manifold pipework feeding the membranes. Such branches can be produced as "set-on" arrangements or as cold formed branches with a stand up height of the branch suitable to allow orbital welding. Previously, some contractors questioned the credibility of cold forming branches in such high strength steels on a consistent basis. However, the limit is provided by the mechanical capacity of the machine to form the branch and not the ductility of the steel. Both G48 Method A and electrochemical testing in seawater has shown that the cold work induced during forming of these branches does not impair the pitting resistance of the steel [16]. Infact, Charles [17] has shown that the cold forming behavior of SDSS, as defined in cupping tests, is very similar to the SASS.

4.3 Machining

Machinability and guidelines for duplex stainless steel are detailed in a recent IMOA publication [18]. Gunn [19] has observed that SDSS and SASS are more difficult to machine than standard grades. In his comparison of these alloys though he found no clear trend. For SDSS processes such as end milling were easier to perform whilst intermittent cutting operations were more difficult to perform when compared with SASS. In any case both alloys are machinable by all the common processes (sawing, turning, facing, milling, drilling etc) as would be expected for engineering steels.

4. 4 Assembly and Galvanic Compatibility

Assembly of pumps, vessels, pipe spools, valves and instruments does not generally cause a problem. However, care does need to be taken in the selection of gaskets suitable for seawater service that do not promote crevice corrosion of flange faces. Kain [20] has considered different types of gasket and their relative influence of crevice corrosion. He found that gaskets best suited to seawater service were natural and synthetic elastomer-type gaskets. (Neoprene, Fluorelastomer, Butyl and Nitrile). Those gaskets more likely to promote crevice corrosion were PTFE and graphite or carbon filled fibre gaskets. Rogne [21] has noted that those gaskets less likely to promote crevice corrosion were all water absorbent to some degree. It is thought that this absorbed water may dilute the environment inside the crevice making it less severe and so less likely for propagation of crevice corrosion. The gaskets that do enhance crevice corrosion can be considered to be of two types. There are those that do not absorb water (like PTFE), and there are the graphite filled ones, where it is believed that the graphite enhances the cathodic reaction to facilitate crevice corrosion. All stainless steels are susceptible to this negative influence on crevice corrosion resistance

Designers should also be sure that when spiral wound gaskets are selected in seawater applications the actual winding material is galvanically compatible with the parent material. For example alloy 400 or 316L windings would suffer corrosion. The corrosion products formed are often aggressive with respect to the flange material and can cause corrosion [22]. Compatible windings for ZERON 100 flanges in seawater service are Titanium, SASS, alloy 625 or alloy C276.

Often it may be necessary to construct pipework systems containing different grades of steel i.e. SDSS pumps connected to SASS pipes or dissimilar metal valves or instrumentation in a pipework system. In such cases the risk of galvanic corrosion must be addressed. At least three major projects to determine the galvanic compatibility of dissimilar metal joints between notionally marine corrosion resistant alloys have been carried out. Shone et al [4] concluded that provided two materials were intrinsically resistant to crevice corrosion in seawater in their own right, then they could be coupled together without risk of galvanic corrosion. This view has been subsequently confirmed by Kain [23] and Turnbull [24] and by almost 20 years of experience of the use of SDSS pumps and valves in SASS seawater cooling systems used in the Norwegian sector of the North Sea [27].

Table 7 [28] categorizes what material grade couples are galvanically compatible in seawater and those that should be avoided or engineered with care.

| CATEGORY | ТҮРЕ | ALLOY |
|----------|---------------------|--|
| 1 | Noble; passive | Nickel-chrome-molybdenum alloys (Mo>7%), |
| | | 6% Molybdenum austenitic stainless steel, Super Duplex |
| | | Stainless Steel, Titanium and its alloys |
| 2 | Passive; not truly | Alloy 400/K-500, 904L, 22% Cr duplex, Alloy 825 |
| | corrosion resistant | Alloy 20, 316L |
| 3 | Moderate corrosion | Copper alloys |
| | Resistance | Austenitic cast iron |
| 4 | Poor corrosion | Carbon Steel / Cast iron |
| | Resistance | Aluminium alloys |

TABLE 7. Alloy Groupings for Seawater at Ambient Temperature.

V. APPLICATION CASE STUDIES

In the early 1990's the Spanish Ministry of Water were actively seeking materials options for SWRO systems to compete with 904L and 6% Molybdenum grades. Availability of products and costs were the main issues, that they needed to address. The drive was to build plants in the Canary Islands that would provide water for drinking and agriculture and would accommodate the seasonal swell in the population of the islands during the summer months.

The plants generally were of modular construction producing m³/day and 7000 capable of expansion.(These plants now operate at 27,000 m^3/day). Adeje-Arona (Figure 8) was the first plant quickly followed by Playa De Las Americas. Then came Rogue Prieto-Guia, again in Tenerife and then Boca Barranco in the Gran Canaria. These plants have all worked well since their installation and deployment of ZERON 100 in similar applications around the world continues.

Figure 8



There have also been several cases where ZERON 100 has been used to replace 316L and 22% Chromium duplex stainless steels that were suffering corrosion in SWRO applications. In the UAE two 2,500m³/day facilities and more recently in Saudi Arabia a 14,000m³/day facility, originally constructed in 316L material, have been retrofitted with ZERON 100 pipework The 316L pipe spools had suffered pitting at welds and in the mother pipe and crevice corrosion at flange faces. The UAE systems were fabricated in the territory while the system for Saudi Arabia was fabricated in the U.K. and assembled on site.

In the Philippines seawater feed pipework had been constructed in 22% Cr duplex steel in two plants, both of which had suffered pitting at welds and in pipes. These systems were retrofitted with ZERON 100 in 1995 with no problems reported since.

As well as main seawater feed pipework systems, ZERON 100 has been used for pumps, valves vessels, energy recovery systems and permiate ports. The largest SWRO project to date to utilise ZERON 100 has been the 106,000m³/day Tampa Bay Water Project, (Figure 9) where the large diameter seawater feed pipework has been constructed in the grade.

ZERON 100 has also been deployed in a novel application of membrane technology used by the offshore oil and gas industry. In circumstances where oil wells are becoming depleted and the pressure in the formation is falling, operators revert to secondary recovery processes. One such process involves injection of seawater into the formation to repressurize the well and enhance recovery. However, when the reservoir contains significant amounts of barium or strontium, seawater injection can cause the corresponding sulphate salts to be formed as scales. This reduces the permeability of the well and

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Figure 9.

causes scaling of the tubulars with salts that are difficult to remove [29]. Moreover, McEihiney et al [30] note that injection of seawater into the formation will provide sulphate nutrients that otherwise dormant, sulphate reducing bacteria will metabolise. As a consequence they will form low molecular weight fatty acids (thereby lowering the pH locally) and generate the sour gas H_2S . This causes a corrosion problem, can mean that the products are unsaleable and creates a health hazard.

To mitigate against these phenomena, operators can install Sulphate Removal Plant (SRP). These plants pass seawater through nanofiltration membranes that extract sulphate from the seawater, prior to injection. The process minimizes scaling, helps to optimise oil recovery and avoids the possibility of reservoir souring.

Figure 10.

These packages are supplied as modularized units (Figure 10), to suit lift capabilities on offshore platforms or floating production vessels. Essentially, this involves constructing and installing filtration systems on offshore platforms and vessels, where process piping and marine code requirements have to be rationalized.



ZERON 100 has performed well in this application since the early 1990's and continues to find applications in this sector.

V1. CONCLUSIONS

- 1. The crevice corrosion resistance of ZERON 100 and SASS's in warm natural seawater is good. A minimum PRE_N criterion can be applied to maintain an acceptable level of crevice corrosion resistance provided if these steels are properly processed in manufacture.
- 2. During welding some sigma phase formation can be expected in welds for both SASS's and ZERON 100. However, in the practical welding range this has no effect on corrosion resistance. This constitutes a high tolerance level to variations in fabrication before problems of pitting of welds are encountered in SWRO systems.
- 3. ZERON 100 can be cold formed without loss of pitting corrosion resistance, it is machinable and can be assembled in connection with SASS's and other passive alloys without risk of galvanic corrosion. Assembly with lower category alloys can give rise to corrosion of the less noble material.
- 4. Vessels and pipework can be designed and built in accordance with international codes and standards. The high mechanical strengths of ZERON 100 allows significant cost savings to be realized especially at larger pipe diameters and at higher system pressures.
- 5. ZERON 100 has been deployed in numerous SWRO applications around the world with good success.

V1I. REFERENCES

- 1. Sedriks A. J. "Metallurgical Control of Localized Corrosion of Stainless Steels" Proc. Conf. Stainless Steels '87, York, England, Sept 14-16, 1987, P127-137.
- 2. Truman S. E. "Effects of Composition on the Resistance to Pitting Corrosion of Stainless Steel". Proc. Conf. UK Corrosion '87. Brighton, England, Oct 26-28 1987.
- Kovach C.W. and Redmond J. D. "Correlations Between the Critical Crevice Temperature, PRE Number and Long Term Crevice Corrosion Data for Stainless Steels". Proc. Conf. NACE 93 New Orleans, USA. March 1993, Paper No. 267.
- 4. Shone E.B., Malpas R.E. and Gallagher P. Trans Inst. Mar. Eng., <u>100</u> part 4 (1988) Paper 14, Page193.
- Grubb J. F. and Maurer J. R. "Correlation of the Microstructure of a 6% Molybdenum Stainless Steel with Performance in a Highly Aggressive Test Medium". Proc. Conf. NACE '95, Orlando, Florida, USA. March 1995, Paper No. 300.
- 6. Byrne G, Francis R & Warburton G "Variation in Mechanical Properties and Corrosion Resistance of Different Alloys within the Generic Designation UNS S32760". Proc. Conf. Duplex America 2000, Houston, Texas, USA, 29th Feb 1st March 2000, Paper 113-125.
- Francis R, Byrne G & Jones K "Performance at Reduced Cost; Zeron 100 Super Duplex Stainless Steel Sets the Pace". IDA World Congress on Desalination and Water Reuse, Oct 1997. Madrid, Spain, Vol 111.
- 8. Gooch T. G. "Corrosion Behavior of Welded Stainless Steels" Welding Journal, Vol 75, No. 5, May 1996, pages 135-154.
- 9. Francis R. "Discussion on the Influence of Sigma Phase on General and Pitting Corrosion Resistance of SAF 2205" British Corrosion Journal, Vol 27, No. 4 April 1992, pages 319-320
- 10. Gunn R. N. "Intermetallic Formation in Super Duplex Stainless Steel Heat Affected Zones" Proc. Conf. Duplex Stainless Steels 97, Maastricht, Netherlands. Oct 21-23 1997, pages 335-345
- Leonard A J, Woollin P, and Buxton D. C. "Effects of Intermetallic Phases on the Corrosion Resistance of Super Duplex and Super Austenitic Stainless Steel Weldments". Proc. Conf. Stainless Steel World 2001, The Hague, Netherlands, 13-15 Nov 2001, Paper P0185, pages 375-384
- Francis R. and Warburton G. W. "A Model for Corrosion of the Depleted Zones Around Sigma Precipitates Produced During Welding of Super Duplex Stainless Steel".
 Proc. Conf. Stainless Steel World '99. The Hague, Netherlands Oct. '99. Paper 99006.
- 13. Shrive S. "Seawater Materials The British Experience" Proc NITO Conf Stavanger, Norway, Jan 19th, 1999.

- 14. Mohagen S. T. "25Cr Duplex Stainless Steel: Manufacturing and fabrication Experience" Stainless Steels Europe, Dec 1994, page 24.
- Francis R and Warburton G R "The Effects of Post Weld Surface Treatments on the Corrosion Resistance of Super Duplex Welds in Seawater" Proc. Conf. NACE. Corrosion 2000, USA. March 2000, Paper 00630.
- 16. Healiss T. WM&F Technical Note TN 1434, "Examination and Corrosion Testing of a 1¹/₂" Pulled Branch on a 6" Sch 40 Pipe", March 2003.
- 17. Charles J. "Super Duplex stainless steels: structure and properties" Proc. Conf. Duplex Stainless Steels '91, Beaune, France, 28-30 October 1991, Vol 1, page 3 to 48.
- 18. International Molybdenum Association "Practical Guidelines For The Fabrication Of Duplex Stainless Steel". Published 1999.
- 19. Gunn R. N. "Duplex Stainless Steels" Abington Publishing 1997 page 52.
- 20. Kain R. M. "Gasket Materials and Other Factors Influencing the Crevice Corrosion Resistance of Stainless Steel Flanges". Proc. Conf. NACE '98 San Diego, USA. March 1998 Paper 702.
- 21. Rogne T. & Drugli J.M. "Crevice corrosion testing of Stainless Steel", Proc. Conf. Stainless Steel World '99, The Hague, Netherlands, Nov 1999. KCI. Page 529.
- 22. Wallen B & Andersson T. 10th "Galvanic Corrosion of Copper Alloys in contact with a Highly Alloyed Stainless Steel in Sea Water". Scandinavian Corrosion Congress, Stockholm 1986, Stockholm Corrosion Institute, Page 149.
- 23. Aylor D.M, Hays R.A & Marshall L.S., "Galvanic Corrosion Evaluation of High Performance Naval Seawater Valve Materials in Quiescent Natural Seawater". Proc. Conf. NACE Corrosion 2000, Orlando, USA, March 2000, Paper 00640.
- 24. Griffiths A. & Turnbull A. "Galvanic Coupling of Corrosion Resistant Alloys in Seawater at Elevated Temperatures". Stainless Steel World, Jan/Feb 1998, Page 38.
- 25. Strandmyr O. & Hagerup O. "Field Experience with Stainless Steel materials in seawater systems". Proc. Conf. NACE Corrosion 98, San Diego, USA, March 1998, Paper 707.
- 26. Francis R., Galvanic Corrosion A Practical Guide for Engineers, published by NACE 2001.
- 27. Baillie B. Weir Techna, Private Communication
- 28. McElhiney J.E & Davis R.A. "Desulfated Seawater and Its Impact on t-SRB Activity: An Alternative Souring Control Methodology". Proc. Conf. NACE Corrosion 2002, Denver, USA, April 2002, Paper 02028.

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