Stress Corrosion Cracking of Stainless Steels used in Manufacturing Brine Circulating Pumps used in Desalination Plants.

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STRESS CORROSION CRACKING OF STAINLESS STEELS USED IN MANUFACTURING BRINE CIRCULATING PUMPS USED IN DESALINATION PLANTS

By
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A Thesis submitted to the United Arab Emirates University
In Partial Fulfillment of the Requirements for the Degree of Masters of Science in Material Science and Engineering

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Abstract

In earlier works, characterization and stress corrosion cracking of casings of brine recirculation pumps used in desalination plants was investigated. These casings, which were manufactured from two types of Ni resist ductile irons, were reported to show different service lives. Material selection of casings is believed to be one of possible factors to extend the service lives of these pumps. Two types of stainless steels; UNS S31603 and UNS S32750 were recommended as substitutes to Ni resist ductile irons. In this work, mechanical, metallurgical, electrochemical and stress corrosion cracking (SCC) tests were conducted on as received samples, made from these two types of stainless steels. As stress corrosion cracking rig was constructed, calibrated and connected to an internet webcam for monitoring purposes. Results have shown considerable higher yield and tensile strengths and corrosion resistance for the UNS S32750 over the UNS S31603. Electrochemical tests confirmed this behavior and have shown reproduced pitting attack illustrated by measured pitting potentials and visual observations for the UNS S31603 samples. UNS S32750 samples have shown no signs of pitting. Furthermore, Stress corrosion cracking tests in the hot brine environment have shown less resistance to stress corrosion for UNS S31603 samples as demonstrated by sample cracking failures after few days of stress corrosion testing. No stress corrosion cracking was observed for UNS S32750 samples under the same testing conditions.
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Chapter One

INTRODUCTION

&

LITERATURE REVIEW
1.1 Introduction

The service life of a brine circulation pump, used in desalination plants, is one important feature in determining the selection of the pump. Failure of pump casings serving in these plants was reported to be one of the critical factors defining the service life of a pump [1, 2]. A pump casing contains brine water which represents a corrosive environment. Pump casings are frequently manufactured from Ni resist ductile irons. In earlier works [1, 2], it was reported that casings made of two types of Ni resist ductile iron [3,4] and operating under similar working conditions, have shown service failure at two different service lives due to stress corrosion cracking. (figures 1 and 2)

Fig. 1: (a) Brine recirculation pump casing (BRP), made from G material (Ni resist BS3468S2W) failed due to stress corrosion cracking. (b) Close view of the crack.[5]
This work aims to study the mechanical and metallurgical, electrochemical properties of two types of stainless steels, austenitic stainless steel UNS S31603 and super duplex stainless steel UNS S32750. These two types of stainless steels were suggested by pump manufacture for evaluation to substitute Ni resist iron in manufacturing pump casings [6,7]. Resistance to stress corrosion cracking was also investigated by using NACE type A testing apparatus with constant tensile load applied to the samples [8,9]. In this research samples were tested in brine water solution at 55°C to evaluate the two types of stainless steels and their suitability for manufacturing the brine recirculation pumps casings used in desalination plants.

This reports starts with introduction and literature review in the first chapter of this study. Chapter two includes a comprehensive procedure and apparatus for the material and experimental work. Results were reported and discussed in chapter three. Chapter four presents the conclusion and recommendation for future work.
1.2 Literature review

1.2.1 Brine recirculation pumps (BRP) in desalination plants

Brine recirculation pumps are one of the essential parts of desalination plant machinery. Brine recirculation pumps are durable and heavy duty, hydraulically loaded and handle corrosive and highly chloride concentrated environments. Brine recirculation pumps are used to extract the concentrated brine water from the earlier heat rejection section stage (HRS) to pump it through the heat gain section stage (HGS) condensers and the brine heater tubes. They are required to maintain the drop in the pressure that occurs in the condenser tubes, brine heater water box and valves. Hence, the vaporization in the recycle pipes or brine heater tubes is avoided by ensuring their pressures are greater than that of the saturation pressure.[10] Failure of these pumps lead to shut down of the desalination plants with consequent delay in water and electricity production. (Figure 3)

Fig. 3: One BRP removed from the plant during maintenance and awaiting disassembly for inspection. Left side of picture shows failed casing of G material whereas right side shows upper part of the pump [5].
1.2.2 Material used in manufacturing brine recirculation pumps

Materials used in marine services should be compatible with each other in order to resist the highly corrosive environment of the sea water. In multi stage flash desalination plants (MSF) Brine recirculation pumps are usually vertically constructed. The shaft and impeller are the rotating parts of the pumps and they are usually made of stainless steel. The other parts, suction barrel and pressure casings are made from carbon steel lined with rubber or other metallic alloys to enhance the part corrosion resistance in brine solution. The casings are usually made from Ni resist ductile irons (NDI), austenitic or duplex stainless steels. In some cases a combination of these alloys or other types of ferrous alloys are used [11].

1.2.3 Ni resist ductile cast iron

These are iron - carbon alloys having more than 2% carbon. This percentage is more than the carbon solid solubility in austenite. Corrosion resistant at elevated temperature and abrasion resistant properties of these alloys can be improved by adding more than 3% of elements like Ni, Cr, Cu, Si, Mo, V, etc. Nickel and chromium of 13-36% and 1.8 to 6% respectively are added to provide Ni resist alloyed cast iron [12]. These elements help producing corrosion resistant alloys with austenitic matrix and flakes or spheroid of graphite. Nickel as austenite stabilizer is responsible for stabilizing austenite phase, An alloy of this type is called “Austenitic Cast Iron”. Chromium and nickel combinations are effective elements to provide the cast iron with a protective passive layer. This layer shall provide good corrosion resistance and excellent resistance to liquids flow erosions [12].
Rafael and Javier [13] have studied the impact of chemical composition of different alloys on the microstructure and mechanical properties of nodular graphite cast iron. They reported that the copper in combination with carbon enhances the ferrite. The increase of nodule counts can be produced by higher carbon, silicon, and magnesium contents. Chromium action in ductile iron depends on the content of carbon and silicon. Nevertheless chromium is pearlite promoter. Other elements such as nickel, copper, molybdenum affect the hardness, strength and corrosion resistance, therefore it must be well controlled and treated carefully when added to cast iron alloy [13].

Zeng et al [14] have investigated the enhancement of corrosion resistance of Ni resist ductile iron by laser surface alloying. They reported that high copper content of more than 2% is not compatible with the production of spheroid graphite and decreases the mechanical properties of Ni resist cast iron. in addition, there is a limited solubility of copper percentage in ferrite or austenite which should be less than 1% in equilibrium conditions. Excesses copper will be isolated in the austenite matrix in shape of globules that will initiate galvanic corrosion. Laser surface alloying is a technique used to enrich the surface with adequate copper. This technique allows rapid melting and solidification of the deposited layer and substrate to form an alloyed region at shallow depth from the surface. The two authors reported that the corrosion current \( (I_{corr}) \) of the laser treated samples is about one order of magnitude less than untreated samples. The formation Cu\(_2\)O oxide film on the alloyed surface was reported to be the reason of the good corrosion resistance in chloride solution [14].
Neville et al [15] have studied the grey cast iron in liquid erosion and liquid – solid erosion conditions of grey cast iron in which weight loss in combination with electrochemical measurements were used to evaluate the corrosion resistance. In their study, they demonstrated important interactive effect between mechanical, electrochemical, and process quantification.

1.2.4 Austenitic stainless steel

The most extensively used grades of austenitic stainless steel are those with chemical composition comparable to AISI 300 series alloys. They are originally based on 18Cr-8Ni alloys, having almost completely austenitic structure [12]. Stainless steels having 16-25% Cr, 8-20% Ni and 0.03-0.10 % C are the simplest ones. Austenitic alloys can be used in cryogenic applications as they have high ductility with low stacking fault energy and less ductile to brittle transition temperatures. Austenitic stainless steels have an FCC structure. Some austenitic stainless steel alloys are unstable when cold worked, therefore phase transformation to martensitic phase can occur. As chromium is a good former of carbides, low temperature annealing can lead to precipitation of carbides in the matrix and in grain boundaries. This shall reduce the percentage of chromium to less than 12%, which is needed to have good resistance to corrosion. General and localized corrosion resistance in halide environment can be improved by adding Molybdenum [16].
Fig. 4: Effect of elements shown on resistance of austenitic stainless steels to stress corrosion cracking in chloride solution. [16]

Berthome et al. [17] have investigated the metastable pitting of austenitic stainless steel in oxidizing electrolytes containing chloride. They reported that increasing the exposure time shall decrease the number of pitting events and reported that potential recovery is being referred to discharging of the interfacial capacitance after the repassivation.

In Austenitic stainless steel, the fracture mode of stress corrosion cracking is transgranular, intergranular or mixture of both [16]. Austenitic stainless steel exhibits stress corrosion cracking in general environments such as hot aqueous chloride solutions, hot caustic solutions, and high temperature high pressure oxygenated water. The effect of
an alloy changes can vary from its composition range to the tested environment. The effect of minor additions is complex. Figure 4 shows the effect of many elements and its susceptibility to stress corrosion cracking in chloride containing solution [16].

1.2.5 Duplex (Ferritic – Austenitic) stainless steel

Duplex stainless steel normally has 30% to 70% ferrite and the rest are austenite. Alloys with low ferrite content normally have 17% to 21% Cr and 5% to 12% Ni. While the alloys with high ferrite content normally have 18.5% to 26% Cr and 4.5% to 7% Ni. Ferrite to austenite proportion and chemical compositions are affected by heat treatment or welding processes [16].

Duplex stainless steels have higher strength than austenitic stainless steels, good corrosion resistance as well as good pitting resistance with high threshold stress for stress corrosion cracking. Super duplex stainless steel was defined [18] as the steels for which the pitting resistance equivalent number (PREN=wt% Cr + 3.3 wt% Mo + 20 wt % N) is greater than 40. Compared with ordinary duplex stainless steels, super duplex stainless steels show higher strength and better corrosion resistance, especially the local pitting resistance and stress corrosion cracking in high chloride environments which brings wide applications in marine and petrochemical industries [18, 19, 20, 21, 22] The structure of duplex or super duplex stainless steel consists of the two phases; ferrite and austenite. The two phases structure is stronger than the single phase since the two phase alloy will enjoy the high yield strength of ferrite and the high ultimate strength of austenite. An increase of 1% delta ferrite increases the tensile strength by 2.2 MN/m2 and 0.2% proof stress by 2.5 MN/m2. The ultimate tensile strength of super duplex stainless steel at room
temperature rise to maximum at about 70% -80% ferrite. Further increase in the ferrite content above this range would cause a drop in the ultimate tensile strength of the two phase alloy to approach the tensile strength of ferrite [12].

Tan et al [18] have studied the effect of annealing temperature on the pitting corrosion resistance of super duplex stainless steel. They have reported that beside chemical composition, the annealing treatment is another important factor influencing the corrosion resistance of duplex stainless steels. At a given chemical composition, varying the annealing temperature can change the proportion of ferrite and austenite phases and adjust the redistribution of alloying elements in the two phases. This can result in the variation of the corrosion resistance of each phase.

Tsai and Chen [23] have studied the electrochemical behavior of each phase of super duplex stainless steels. They found that at active to passive transition region of the polarization curve two distinct peaks corresponded to the respective anodic peaks of the single austenite and ferrite phases in 2 M H₂SO₄ + 0.5 M HCl mixed solution. Austenite and ferrite phases were reported to exhibit a polarity reversion in mixed H₂SO₄ + HCl solution and HNO₃ solution. Austenite has found to be the cathode when exposed to (2M H₂SO₄+ 0.5 M HCl) mixed solution while it was found to be anode in HNO₃.

Antony Comer and L. Loonney [24] have investigated the corrosion resistance of the weld of one type of super duplex stainless in synthetic sea water. Under high imposed electrochemical potentials, it was reported that the corrosion resistance of the weld metal was similar to the base metal when positively polarized in synthetic sea water of ambient
temperature. They have reported an increase in the crack propagation rates for the base and weld metal by over a factor of 2 compared to rates in laboratory air. They have also reported that high temperature solution reduces the pitting potential and delays repassivation.

Donik et al [25] have reported that there are three different techniques used to produce thin oxide layers on polished duplex stainless steel. They utilized oxygen inside vacuum chamber, ambient conditions for 24 hours and plasma oxidizing. The common characteristics of all produced oxide layers is the double oxide stratification with higher concentration of iron oxides regions closer to the surface and higher concentration of chromium oxide at more in-depth.

1.2.6 Stress corrosion cracking

Stress corrosion cracking refers to a cracking process that requires the simultaneous action of corrosive and sustained tensile stress. This excludes corrosion reduced sections, which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion, which can disintegrate an alloy without either applied or residual, stresses [26].

Theories or discussion talking about the stress corrosion cracking and its mechanisms supported by the fundamentals of anodic dissolution or hydrogen related phenomena. Studies with attempts over the last 30 years are utilized to clarify the controlling mechanism. It was shown that there are various factors affecting the stress corrosion cracking process. Factors such as chemical composition of alloys, metallurgical
condition, and chemistry of service environment, electrochemical state, and condition of mechanical stress have a complicated role in the process of stress corrosion cracking [27].

1.2.7 Stress corrosion cracking mechanisms

In order to have a better understanding of the process, single mechanism is considered. Stress corrosion cracking is the phenomenon of one of the interactions between passivation and activation processes. An oxide film produced by alloy system makes a protective layer on the metal surface and makes it more resistant to the corrosive environments. A stress corrosion cracking process often starts as a process of crack nucleation when the protective layer is broken down or localized electrochemical reaction occurs to reach the propagation condition. Figure 5 illustrates the sequence of a stress corrosion cracking process where a corrosion pit formation is initiated at the surface followed by the initiation and growth of a stress corrosion crack [27].

Fig. 5: Sequence of events (left to right) in a stress corrosion cracking test on an initially smooth specimen. For low alloy steels in sea water, the rate of growth of SCC is faster than it is for pitting by a factor of about 106, and fast fracture propagates at about 1010 times faster that SCC [27].
1.2.8 Factors influencing stress corrosion cracking (SCC)

A stress corrosion cracking process responds to one of four basic variables; Alloying and metallurgical factors, mechanical stress factors, electrochemical factors, and environmental factors [27].

1.2.8.1 Alloying and metallurgical factors

Stress corrosion cracking behavior can be affected by alloying additions as it can disturb the creation of a protective layer on the surface of the alloying system. Alloying addition can eventually affect the metallurgical condition and hence the electrochemical state of the system. Precipitation processes, and segregation can produce a microstructural conditions and second phases, which is inhomogeneous and more or less resistant to crack propagation. Stress corrosion cracking can be affected by yield strength and grain size. In case of having intergranular cracking, grain size has a considerable influence on that crack path [27]. The chemical composition, orientation of grains, distribution of precipitations, dislocation, progress of phases transformation, degree of metastability are all factors affecting the susceptibility to stress corrosion cracking when it interact with the environmental conditions [28].

Zeman et al [29] have reported that cold working of austenitic stainless has slightly positive influence to general or localized corrosion processes in super critical water reactor conditions used in nuclear power plants.
1.2.8.2 Mechanical stress factors

The mechanical stress condition is one of the major considerations for the stress corrosion cracking to start. The crack tip advances as the local stresses increase due to loading of engineering structures. This can lead, in certain environments or services to a sudden failure if a crack initiates and its propagation growth process is allowed to continue. [27]. It was reported generally that stress corrosion cracking produces three stages, initiation, growth and failure or fast fracture process [27].

![Generalized SCC kinetics](image)

Fig. 6: Generalized SCC kinetics. Fast fracture at one of the points marked $K_{IC}$ may preclude development of region III or of region II and III. There may be a true threshold $K_{ISC}$ or the kinetics may simply decrease continuously to over smaller but finite values as $K$ is decreased, denoted by broken line prolongation of region I.[27].

Often exhibiting a lengthy period of stage II growth period where crack growth rate is independent of observed stress intensity or associated local stress as shown in figure 6. This plateau region was observed in numerous materials -environment systems. The mechanisms that were proposed for stress corrosion cracking require that certain events occur in sequence to sustain crack propagation [31]. These requirements explain the plateau region in which the rate of crack propagation is independent of the applied
mechanical stress. That is a sequence of chemical reactions and processes is required and the rate limiting steps of these sequence of events determines the limiting rate of plateau of crack propagation until mechanical overload fracture starts contributing the fracture process in stage III in figure 6.

Figure 7 illustrates a crack tip in which crack propagation results from reactions in metal a head of the propagating crack. The figure shows that the crack growth rate – determining steps include: mass transport along the crack to the crack tip, reactions in solution near the crack, surface adsorption at or near the crack tip, surface diffusion, surface reaction, absorption into the bulk material, bulk diffusion to the plastic zone ahead of the advancing crack, chemical reaction in the bulk, the rate in the atomic bond rupture. Changes in the environment, which significantly retard the rate of any of the above mentioned required steps in the sequence, could make that step the crack propagation rate – determining step.

Fig. 7 : Schematic of crack tip processes that may be the rate –determining step in environmentally assisted crack propagation [31]
It was reported [31] in aqueous solutions the rate of absorption and surface reaction are usually very fast compared with the rate of mass transport along the crack to the crack tip. As a result, bulk transport into this region or reaction in this region frequently is believed to be responsible for determining the steady state crack propagation rate or plateau velocity. Several different environmental parameters were reported [31] to influence the rate of crack growth in aqueous solutions. These parameters include but are not limited to: temperature, pressure, solid specious, solid concentration and activity, pH, electrochemical potential, solution viscosity, and stirring or mixing. It is well known and generally accepted that the environment at occluded sites, such as a crack tip can differ significantly from the bulk solution. If an alteration to the bulk environment allows the formation of critical stress corrosion cracking environment at crack nuclei, then crack propagation will result. If this bulk environment cannot maintain this local crack tip environment then crack propagation will stop. As a result, slight changes to the environment may have a dramatic influence on crack propagation. In addition to these environmental parameters stress corrosion crack propagation rates are influenced by; the magnitude of the applied stress on the stress intensity factors, and crack geometry which includes length, width, and aspect ratio.

Kamaya and Haruna [30] have investigated the initiation behavior of stress corrosion cracking and the influence of the applied stress. They have reported that the crack initiation time and fracture time decrease when the applied stress increases. Further more crack initiation time and the stress around the tips to contribute to the acceleration of a new crack initiation around the tips. Thus, the fracture was caused by coalescence of
multiple cracks rather than by growth of some primary cracks increase in stress intensity at crack tip, which consequently accelerates the crack initiation rate.

1.2.8.3 Electrochemical factors

Electrochemical factors can have a clear effect on stress corrosion crack behavior of alloy steels. It was reported [27] that for low alloy steel such as 4340 heat treated to various yields strength levels, applied potential was demonstrated to have little effect on threshold stress corrosion cracking intensity ($K_{\text{th}}$). However significant effect was reported on the crack growth rate at stress intensity levels above the threshold value ($K_{\text{th}}$) as shown in figure 6. It was also reported that for maraging steels, impressed electrochemical potentials have a significant effect on ($K_{\text{th}}$). These effect can further be worsened by crack tip chemistries, which can be substantially different from that bulky chemistry [31]. This can produce changes in number of variables affecting SCC behavior including mass transport to the crack tip, protective film attack, absorption and diffusion and reaction with material.

1.2.8.4 Environmental factors

Stress corrosion cracks are expected in many mediums. Additionally stress corrosion cracking occurs in other specific liquid metals, non aqueous inorganic liquid and fused salts. Oxides have pronounced influence on tendencies to cracking. The presence of dissolved oxygen is critical to the cracking of austenitic stainless steel in chloride solutions as cracks will not occur if oxygen is removed from the medium. For various alloying systems, there is always a new found environment, which contributes the cause of stress corrosion cracking. Therefore, it is necessary to evaluate any given alloy to
stress corrosion cracking resistance at a given environment. Increasing the service
temperature also increases the stress corrosion cracking [28].

Prakash and Malik [33] have studied the SCC behavior of different alloys used in
desalination plants under different environments. The study has included the stress
corrosion cracking behavior of these alloys resulting from the synergistic action of
corrodents such as chloride, oxidants and H₂S. The studied alloys include mild steel ,
316L , 317L , 430, and Monel 400. The test results have shown that intergranular and
intragranular SCC fracture of mild steel and alloy 430 in H₂S environment occur only in
the limited potential environment where as the alloys 316L and 317L were found to be
immune to SCC under the same test conditions. The alloy Monel 400 was reported
however susceptible to SCC in the presence of H₂S, which may present in some where in
desalination plants due to pollution of sea water.

1.2.9 Stress corrosion crack morphology

Stress corrosion cracks give the appearance of a brittle mechanical fracture when, in
fact, they are the result of local corrosion processes. Both intergranular and transgranular
stress corrosion cracking are observed. Intergranular cracking proceeds along grain
boundaries, while transgranular cracking advances without apparent preference.
Intergranular and transgranular cracking often occur in the same alloy, depending on the
environment or the metal structure. Such transitions in crack modes are known in high
nickel alloys, iron chromium alloys, and brasses [28].
Cracking proceeds generally perpendicular to the applied stress. Cracks vary also in degree of branching. In some cases the cracks are virtually without branches and in other cases they exhibit multibranched "river delta" patterns. Depending on the metal structure and composition and upon the environment composition, crack morphology can vary from a single crack to extreme branching [28].
Chapter Two

EXPERIMENTAL WORK
2. Experimental work

2.1 Material preparation and tensile tests

Two strips of hot rolled plates of UNS S31603 and UNS S32750 having a thickness of 12.7 mm were cut into samples having dimensions of 250 X 50 X 12.7 mm. Chemical analysis, by weight percentage of elements in each type of steel is shown in table 1[34,35]. Tensile test samples for each type of stainless steel were prepared as per the ASTM standard [36]. Machining of all samples was carried out using a machining coolant to avoid overheating the samples.

Table 1: Chemical composition of the two as received types of stainless steel*

<table>
<thead>
<tr>
<th>Material</th>
<th>C%</th>
<th>Mn%</th>
<th>P%</th>
<th>S%</th>
<th>Si%</th>
<th>Cu%</th>
<th>Ni%</th>
<th>Cr%</th>
<th>Mo%</th>
<th>N%</th>
<th>Co%</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS S31603</td>
<td>0.025</td>
<td>1.360</td>
<td>0.029</td>
<td>0.003</td>
<td>0.268</td>
<td>0.468</td>
<td>10.056</td>
<td>16.804</td>
<td>2.176</td>
<td>0.051</td>
<td>0.213</td>
</tr>
<tr>
<td>UNS S32750</td>
<td>0.017</td>
<td>0.893</td>
<td>0.031</td>
<td>0.0004</td>
<td>0.370</td>
<td>0.126</td>
<td>6.651</td>
<td>24.681</td>
<td>3.755</td>
<td>0.280</td>
<td>-</td>
</tr>
</tbody>
</table>

*The balance of the two compositions is iron

2.2 Metallographic and hardness tests

Samples from the as received material of both austenitic UNS S31603 and super duplex UNS S32750 were cut into thin sections using a thin sectioning cutter. A cutting coolant was used during cutting to avoid overheating. Thin sections were then mounted in phenol moulds to be ready for grinding and polishing. Grinding emery papers having grids of 240, 400, 600, 1000, and 2400 were used. Polishing was performed in two stages using 6μm, and 1μm diamond pastes.

Austenitic stainless steel samples were electrolytically etched using 10% oxalic acid at 3 volts, whereas, super duplex samples were etched using an electrolyte of 20% NaOH and 100 ml of distilled water at 3 volts for 20 s. Samples were then examined using an...
optical microscope and a digital image camera was used to capture microstructures of both steels [37]. For hardness tests, a load of 200 gm was applied on different locations of the microstructure for each tested sample by using Vickers micro hardness testing device. For each type of steel, an average of five different readings were calculated [32].

2.3 Electrochemical tests

2.3.1 Sample preparation

Two set of polarization test samples from the as received austenitic and super duplex stainless steels were cut and machined to a dimension of 10X70X5mm. Each set, consisting of one super duplex and three austenitic stainless steel samples, was connected to insulated copper wires. The assembly was then molded in an epoxy mixture consisting of a resin and a hardener to ensure complete electrical insulation among samples. Extra care was taken during the molding process to avoid having air gaps between stainless steel samples and epoxy and hence avoid possible crevice corrosion. Molded samples were manually ground with 100, 200, 400, 600, and 1000 emery papers, degreased using 5% caustic soda solution and rinsed in fresh water. Copper wires were passed through water seal PVC tubes and fittings for perfect insulation during immersion in water. Ends of copper wires were identified and labeled as, austenitic stainless steel working electrode, super duplex stainless steel working electrode, and two austenitic stainless steel samples as reference and auxiliary electrodes as shown in figure 8.
Fig. 8: (a) Identification of electrodes in one sample set. (b) Molded samples in epoxy and copper wire passing through water seal PVC tube. (A clear non pitted picture would be better in a above)

2.3.2 Long term potential measurements

An ACM potentiostat Gill 6 connected to a computer was used to perform the electrochemical tests, whereas, Sequencer software was used to control and record the test results. Samples were immersed in Pyrex container filled with a temperature controlled brine solution, as shown in figure 9. The brine solution, which is a concentrated sea water of Arabian Gulf having an average chloride concentration of 34,000 ppm, was arranged from the desalination plant where pump failures have occurred.
Fig. 9: ACM potentiostat and testing apparatus set up.

Open circuit potentials of the as received austenitic and super duplex stainless steel samples were measured using long term potential measurements. Samples were immersed in brine water at 60° C and pH of 8.31 for one hour before running the test to take potential measurements for a duration of one day [39].

2.3.3 Cyclic sweep

Cyclic sweep testing was performed under the above mentioned conditions on stainless steel samples of both types. For austenitic stainless steel, the start potential was set to -250 mV and the reverse potential to +750 mV with reference to its open circuit potential. For super duplex stainless steel, the start potential was set to -250 mV and the reverse potential was set to +1000 mV with reference to its open circuit potential. The sweep rate was 30 mV/Min [39,40].
2.4 Stress corrosion cracking test

2.4.1 Sample preparation

Two strips of hot rolled plates of UNS S31603 and UNS S32750 having a thickness of 12.7 mm were cut into samples having a dimensions of 250 X 50 X 12.7 mm. Samples were then machined to confirm with the requirements of ASTM tensile test and NACE type A stress corrosion cracking test method [8,9]. Figure 10 shows a photograph of a machined stress corrosion cracking test sample. The shoulder diameter of the sample is 10 mm and the gauge diameter and length are 6.24 mm and 40 mm respectively. All samples were machined to have the same dimensions. Machining of samples was carried out using a coolant to avoid overheating of the samples. Samples were manually ground with 100, 200, 400, 600, and 1000 emery papers, degreased using acetone solution, and rinsed in fresh water [8,9,36].

Fig. 10: A stress corrosion cracking test sample.
2.4.2 Stress corrosion cracking testing rig

Figure 11 shows a photograph for the designed and constructed stress corrosion cracking test rig. The rig was designed to simulate real service conditions under which pump casings had failed during service in the desalination plant. Inside the testing chamber, stainless steel samples are subjected to a controlled tensile stress through the proof ring. Samples are subjected also to circulated hot brine of controlled temperature.

The testing chamber is shown in figure 11 together with the attached electrodes, hot plate, wiring to the ACM potentiostat and a computer. The figure shows also the attached dial gauge that used to monitor the deflection of proof ring during stress corrosion cracking testing and the webcam camera. The set up shown in figure 11 consist of the following items;

a. Proof ring

A proof ring (figure 12) made from a duplex stainless steel material was used to control the load on the stress corrosion cracking test samples. The proof ring which has an inside diameter and wall thickness of 195 mm and 7 mm was welded to upper and lower bosses. Both bosses were drilled through the ring. The lower boss was used to fix the ring in place, whereas the upper boss was used in monitoring the stress corrosion cracking test sample. A 100 kN MTS tension compression testing machine was used to calibrate the bossed ring convert its axial deflection into axial tensile force. Figure 13 shows the calibration curve obtained for the used proof ring.
The stress corrosion cracking test rig designed and constructed following the guidelines of the NACE Type A testing method [8,9].
Fig. 12: Proof ring, tightening screws and fixture apparatus.

Fig. 13: Proof ring calibration curve.
c. Testing chamber

A testing chamber made from transparent acrylic tube having an inside diameter of 90 mm was used to contain the stress corrosion cracking testing sample, circulated hot brine solution, electrodes and a thermocouple. A top and bottom Teflon covers with one circular O ring seal in each of them were used together with the acrylic tube to have the testing chamber. The top and bottom Teflon covers were pressed to the acrylic tube through four stud and nut sets. Four holes were drilled to fit the working electrode (stress corrosion cracking sample), auxiliary electrode, reference electrode, and thermocouple. Four corresponding O ring seals were used for these holes to seal the insert places against brine leak. Figure 15 shows photographs for the assembled testing chamber.

Fig. 15: Stress corrosion cracking testing chamber.
d. Hot water container and heating plate

A Teflon coated aluminum container was used to contain the brine solution to be heated and delivered by gravity to the stress corrosion cracking testing chamber. A hot plate with controlled power switch was used to test the brine in the Teflon coated container to the required testing temperature (55°C). The testing temperature of the brine inside the testing chamber was monitored by a thermocouple. This thermocouple was connected to the power switch of the hot plate through a temperature controller. Figure 16 shows a photograph for the storage and disposal brine solution tanks. Both tanks were made from GRP composite material and having a capacity of 30 USG. The storage tank is connected from a higher level to the Teflon coated container. Thus, causing a gravity driven delivery of brine to the container. An over flow floating valve was used to prevent the brine over flow from the container.

Fig. 16: Brine solution storage and disposal tanks Storage tank is at the to level and the disposal are at the lower level.
e. Monitoring camera

An automatic monitoring camera was mounted in front of the dial gauge to take one shot each 30 minutes in order to detect any movements of the dial gauge indicator and hence failure of samples. Photo records were stored in the computer memory with the aid of camera software.

f. Electrodes

Auxiliary and reference electrodes made from as received austenitic stainless material were immersed inside the chamber through the top Teflon cover as shown in figure 11.

2.4.3 Operation of stress corrosion cracking test rig

A working electrodes (test samples) made from the as received austenitic stainless steel or super duplex stainless steel was fixed inside the test chamber where the applied stress was controlled by means of the tightening nut and screw system. The tightening nut was used to maintain the proofing deflection to a level corresponding to the required tensile load as given by the calibration table of the proof ring. Hot brine solution flowed by gravity from the main storage tank to the Teflon coated container where the brine solution was heated to the required temperature. Brine solution was then supplied to the stress corrosion cracking test chamber through an inlet on the bottom chamber cover. Brine solution was constantly drained off through an outlet on the top chamber cover to the disposal tank. A dial gauge used to show the proof ring deflection. A web monitoring camera was mounted to record a shot every half hour. An ACM potentiostate model Gill 6 and shown in figure 9 was used to apply the required accelerated anodic potential for the test. Sequencer software was used to record the test results.
2.5 Stress corrosion cracking test

An offset anodic potential of +400 mV with respect to the rest potential for each as received austenitic stainless steel and super duplex stainless steel materials was applied with potentiostatic test facility of ACM software [39]. The value of this accelerating anodic potential was determined from cyclic sweep tests based on the pitting potential values observed for austenitic stainless steel. Austenitic and Super duplex stainless steel samples were subjected to a constant load of 8403 N supplied by deflecting the proof ring. This load represents 95% of the yield load of the as received austenitic stainless steel material and 43% of the yield load of the as received super duplex stainless steel. Each stress corrosion cracking test was stopped upon sample fracture or completion of 335 testing hours. (14 days). The fracture of a sample was confirmed by the reading of dial gauge as indicated by a zero deflection reading.

2.6 Stress corrosion cracking fracture sections

Samples, which were not fractured by stress corrosion cracking tests, were mechanically fractured by applying a tensile load. Fracture sections of the mechanically fractured samples were examined using the scanning electron microscopy and compared with the fracture sections of fresh fractured samples. The ultimate tensile loads of both fresh fractured and mechanically fractured tested samples were also compared.
Chapter Three

RESULTS AND DISCUSSION
3. Results and discussion

3.1 Mechanical tensile tests

Table 2 shows all tensile test date and average results of testing of both types of stainless steels. Austenitic Stainless steel enjoys better ductility on the expense of its yield and tensile strengths as compared to super duplex stainless steel. The table illustrates considerable differences in the yield and ultimate strengths of the two types.

The results agree with the corresponding ones reported by material manufacturer [34,35].

Table 2: Average mechanical testing date of the as received two types of stainless steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Dia mm</th>
<th>Area mm²</th>
<th>IGL mm</th>
<th>YL kN</th>
<th>YS N/mm²</th>
<th>UTL N</th>
<th>UTS N/mm²</th>
<th>EL %</th>
<th>RoA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic stainless steel</td>
<td>6.30</td>
<td>31.17</td>
<td>25</td>
<td>8.85</td>
<td>284</td>
<td>18.60</td>
<td>597</td>
<td>52</td>
<td>73</td>
</tr>
<tr>
<td>(UNS S31603)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Super duplex stainless steel</td>
<td>6.27</td>
<td>30.83</td>
<td>25</td>
<td>18.74</td>
<td>608</td>
<td>27.25</td>
<td>852</td>
<td>35</td>
<td>68</td>
</tr>
<tr>
<td>(UNS S32750)</td>
<td></td>
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</tbody>
</table>

3.2 Hardness and metallographic test

Results of hardness testing have also shown a noticeable difference between both types. Austenitic steel was found to have an average hardness of HV 202.6, whereas, super duplex gave an average hardness of HV 265. Difference in the hardness test results of the two materials found to be matching the difference in the ultimate tensile strength.

The ratio between the ultimate tensile strength of the austenitic stainless steel and the super duplex stainless steel is 0.70 which is found to be close to the ration of their vicker’s hardness number: 0.76 [32].
Figure 17 shows micrographs for the austenitic stainless steel microstructure, taken at two magnifications. The micrographs illustrate grains of two phases. The austenite, which is the majority phase and appears in the micrograph as the light phase and ferrite, which is the minority phase and appears as the dark phase. The elongated grains in the micrographs indicate the rolling direction [37, 38, 41].

![Microscopic images for the austenitic stainless steel UNS S31603 a) at 100X and b) at 500X.](image)

Figure 18 illustrates micrographs for the as received super duplex stainless steel. In this case, the micrographs show that ferrite is the majority phase. The change in chemical composition between the two types of stainless steel is the major factor in the change of microstructure of each of them. Less nickel, high chromium, molybdenum and silicon promote the ferrite phase on expense of the austenitic phase [16]. The difference in microstructure can explain the higher strength of super duplex stainless steel. It was reported in literature [12] that an increase of ferrite content in stainless steel is associated
with a corresponding increase in the ultimate tensile strength. Also, it was reported that austenite grains deform at lower stress levels than ferrite grains [16]. On the top of that austenite was reported to be cathodically protected by ferrite [16]. In general, the two phase structure of stainless steel was reported to be stronger than the single phase structure [12].

Fig. 18: Microscopic images for the as received super duplex stainless steel UNS S32750, (a) at 100X and (b) at 500X.

3.3 Electrochemical tests

3.3.1 Long term potential measurements

Figure 19 shows the open circuit potential graphs for the as received austenitic and super duplex stainless steels. All potentials were measured against austenitic stainless steel reference electrode. The average values of the open circuit potentials recorded for the last 4 hours of testing of both types are shown in table 3. These values could indicate that the corrosion tendency for super duplex steel is less than that of austenitic steel when
it is measured under the same environmental conditions of brine solution at 60°C. The immunity of super duplex stainless steel behavior is believed to be due to the higher content of Cr and Mo, which enhance the passivity. Similar results were reported by Kwok et al [43]. They have shown through free corrosion potential measurements that super duplex stainless steel 32760 has a less corrosion tendency that that of austenitic stainless steel UNS S31603.

![Data Graph](image)

**Fig. 19:** Open circuit potential against time for the as received austenitic and super duplex stainless steels. All potentials are measured against austenitic stainless steel reference electrode in brine water at 60°C.

**Table 3:** Average open circuit potentials for austenitic and super duplex stainless steels during the last four hours of testing in brine water at 60°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Austenitic Stainless steel UNS S 31603</th>
<th>Super duplex Stainless steel UNS S 32750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average open circuit potential, mV</td>
<td>7.13</td>
<td>-24.01</td>
</tr>
</tbody>
</table>

45
3.3.2 Cyclic sweep tests

Cyclic sweep test plots are shown in figure 20 for austenitic and super duplex stainless steels. Results of these tests indicated that pitting takes place for austenitic steel at potentials ranging from 275-398 mV measured versus austenitic reference electrode. This was confirmed by visual inspection of working electrode as shown in figure 21. Figure 21 captures a photograph showing pitting of the austenitic sample following to the cyclic sweep. Figure 21 also capture visual inspection for the super duplex working electrode which shows no signs of pitting following to the cyclic sweep testing. The less immune passive film of the austenitic SS lost its protection at a lower anodic potential and lead to sever localized attack in the form of pitting. The pits are believed to be the initiation sites for any possible stress corrosion cracking behavior that the material could undergo with specific combination of environment and stress. On the other hand a much immune behavior is shown for the super duplex stainless steel under the same testing environmental conditions. No breakdown for passivity and no pitting potential were observed, this was also confirmed by the visual examination for the working electrode.
Fig. 20: Cyclic sweep plot potential against current density for the as received (a) austenitic and (b) super duplex stainless steels. All measured potentials are measured versus austenitic stainless steel reference electrode.

The above results are in complete agreement with the corresponding ones reported in the literature. It was reported [24,43] that austenitic stainless steel has lower pitting resistance than super duplex stainless steel. The pitting resistance of stainless steels is primarily determined by their chemical compositions. The three elements, which have a significant beneficial effect, are chromium, molybdenum, and nickel The pitting resistance equivalent number (PREN) gives their relative contribution [18]. The pitting resistance equivalent number of the UNS S 32750 super duplex stainless steel was calculated and found to be 42.7 as compared to 25.0 for the austenitic UNS S 31603 stainless steel.

Fig. 21: Pitting on austenitic sample (a) as compared to no pitting on super duplex sample (b) after one run of cyclic sweep testing.
3.3.3 Stress corrosion cracking tests

Stress corrosion cracking test results and consequent time to failure were recorded for austenitic stainless steel and super duplex stainless steel and are shown in table 4. As electrochemical tests suggested, this table shows that the first sample of austenitic stainless steel failed after 160.29 hours. After this time the proof ring was found to be returned to its original diameter and deflection measurements recorded 0 mm. During the test, many pits were noticed on the surface of this austenitic stainless steel sample. Further visual examinations have carried out after sample failure. This examination showed many small cracks on the surface and some of them were combined together to form a bigger one. Cracks and sample failure are attributed to stress corrosion cracking.

The second sample of austenitic stainless steel failed after a less time than the required to fail the first sample. The second sample failed after 76.38 hours only with clear rupture and separation. This result confirms the failure of the first sample and the stress corrosion cracking as a cause of failure.

Table 4: Time to failure for austenitic and super duplex stainless steels under stress corrosion cracking test condition.

<table>
<thead>
<tr>
<th>Material</th>
<th>Austenitic steel UNS S 31603</th>
<th>Stainless steel UNS S 32750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to failure (Hours)</td>
<td>Sample 1: 160.29</td>
<td>Sample 2: 76.38</td>
</tr>
<tr>
<td></td>
<td>No failure¹</td>
<td>No failure²</td>
</tr>
</tbody>
</table>

¹ Fracture clearly observed
² & ³ Test stopped after 335 hours

Super duplex stress corrosion cracking test results are shown also in Table 4. Again and as electrochemical results suggested, the results show no failure in super duplex stainless steel and test were intentionally stopped after 335 hours of testing.
Proof ring deflection measurements for austenitic stainless steel samples were recorded and are described by the plots shown in figure 22. These plots confirm failure of both austenitic stainless steel samples. Deflection at the end of testing was decreased to 0 indicating total failure of both samples as the proof ring returns to its original diameter before deflection. The plots of figure 22 shows that the stress corrosion cracking failure of austenitic stainless steel takes place in four steps. During the first step cracks are nucleated under the original constant adjusted load. In step 2 major cracking takes place, leading to a drop in the applied load. In step 3 cracking is arrested for certain time due to drop in loading and the need for some time for brine solution bulk diffusion. It was reported [31] that there are several facts that determines the crack propagation rate. In aqueous solution, the rate of absorption and surface reaction are usually very fast compared with the rate of mass transport along the crack to the crack tip. As a result, bulk transport of brine solution into this region or reaction in this region, frequently is believed to be responsible for determining the crack propagation rate [31]. In step 4, cracks propagate again to cause final complete failure.
Fig. 22: Deflection against time for austenitic stainless steel a) sample 1 and b) sample 2
Fig. 23: Deflection against time for super duplex stainless steel a) sample 1 and b) sample 2.
Figure (23 a,b) shows the plots of the proof ring deflection versus time for the super duplex stainless steel samples. The plots show that there is no cracking in both samples as demonstrated by the original constant deflection of the proof ring throughout testing. Visual observations of both super duplex samples after 335 hours of testing revealed that one of the sample has a completely clean surface without any pitting, while the other sample has only one shallow pit on its surface.

3.3.4 Stress corrosion cracking fracture sections

The fracture section of the completely separated austenitic stainless steel sample was examined using the scanning electron microscopy, SEM. The other partially failed sample was brought to complete separation using the MTS machine and the resulted maximum load recorded for sample separation was found to be a 2,911.81 N versus 18,640.0 N, the maximum load for fresh sample. The fracture section of the partially failed sample was also examined using the scanning electron microscopy after sample separation.

One super duplex stainless steel sample was fracture sectioned after 335 hours of stress corrosion cracking test using the MTS machine. The maximum load was found to be the same as that of the corresponding fresh material. This indicates that the super duplex sample was not affected during the 335 hours of stress corrosion cracking testing. Fracture section of this sample was also examined using the scanning electron microscopy.
Figure 24 shows the cross section of one of the as received austenitic stainless steel samples under scanning electron microscope (SEM). The sample fractured after it was tested using mechanical tensile testing. The morphology shows typical ductile fracture of austenitic stainless steel where necking and cup and cone fracture can be identified in figure 24-a. Dimpled fracture section, a characteristic of fracture sections of ductile materials [44] is also shown in figure (24-b).

![SEM fracture section of fresh austenitic stainless steel sample fractured using mechanical tensile testing at a) 35X and b) at 1500X.](image)

Figure 25 shows the fracture section of an austenitic stainless steel sample, failed by stress corrosion cracking testing. The micrograph shown in figure (25-a) clearly illustrates two different morphologies. One morphology is associated to stress corrosion cracking and the other one corresponds to fast mechanical failure. The micrograph shown in figure (25-b) shows step like fractures together with stress corrosion cracking facets which are one analogous to cleavage facets [45].
Fig. 25: SEM fracture morphology of an austenitic stainless steel sample fractured due to stress corrosion cracking at a) 200X, b) 3500X.

Figure 26 shows the fracture section of fresh as received super duplex stainless steel sample fractured using mechanical tensile testing. Typical ductile fractures characteristics are shown by these micrographs where dimpled fracture and cup, and cone can be identified.
Fig. 26: a) SEM fracture section of a super duplex stainless steel sample fractured using after mechanical tensile testing at a) 50X. b) 2000X.

Figure 27 shows the pits appeared on the surface of one of the super duplex stainless steel samples.

Fig. 27: Few or no super duplex stainless steel pits found on the gauge length after 335 hours of stress corrosion cracking testing at 100X.
Fig. 28: a) SEM fracture section of super duplex stainless steel sample fractured using mechanical tensile testing after 335 hours of stress corrosion cracking testing a) at 35X. b) at 1000X.

Figure 28 shows SEM micrographs for fracture section of one super duplex stainless steel sample fractured using mechanical tensile testing after 335 hours of stress corrosion cracking testing. Comparing the micrographs of figure 26 and 28 reveals that they are identical and no signs for stress corrosion morphology zone appear.
Chapter Four

CONCLUSIONS
4. Conclusions

The following conclusions are drawn on the basis of the current research work and investigations:

- Super duplex stainless steel UNS S32750 has higher yield and tensile strengths. It enjoys also higher hardness on the expense of lower ductility as compared to austenitic stainless steel UNS S 31603.

- Microstructures of both steels consist of ferrite and austenite phases. The percentage amount of ferrite phase in super duplex exceeds its corresponding one in austenitic steel and can explain its superiority in hardness and strength.

- Results of electrochemical tests have shown that the corrosion resistance of the super duplex steel is higher than that of the austenitic steel under the test conditions. This was demonstrated by a less anodic corrosion potential or corrosion tendency.

- Under anodic polarization, cyclic sweeps, and under the test conditions, it was demonstrated that no pitting was observed for the super duplex steel specimens.

- Under anodic polarization, cyclic sweeps, and under the test conditions, it was also demonstrated that severe pitting was observed for austenitic stainless steel specimens. This was illustrated by a distinct pitting potential and visual observation for specimens by the end of the sweep.

- The PREN for super duplex stainless steel is calculated and found to be considerably higher than that of the austenitic stainless steel. This could also help explain the above mentioned pitting behaviors of both steels.
- Austenitic stainless steel shows susceptibility to stress corrosion cracking when loaded to 95% of its ultimate tensile strength, polarized to a potential close to its pitting potential and exposed to brine solution water at 55° C. The pitting tendency of same material would create weak spots on metal surface at which cracks initiation would also occur and hence is considered a significant contributor to start stress corrosion cracking mechanism.

- Super duplex stainless steel is immune to stress corrosion cracking when it is exposed to the above mentioned test conditions.

- The lower pitting resistance and lower strength of austenitic stainless steel are the main reasons for its lower stress corrosion cracking resistance as compared to super duplex stainless steel.

- Pitting is the mode of attack of most passive material and can also be found on super duplex stainless steels possibly at higher corrosion accelerating potentials as well as higher applied stresses. However under the above test conditions it did not lead to further pitting and no cracking to place as a result.

- Fracture sections of failed stress corrosion cracking austenitic stainless steel consists of two regions the first region has step like features and facets analogous to cleavage facets, and the second region corresponds to a dimpled fracture section, characteristic of mechanical failure.
References

[34] “Mill Test Reports”, provided by INDUSTEEL: the material manufacturer, 2007.
[38] ASTM Standard E562-02 (2002).
المخصّص

في بحث سابق تم دراسة خصائص التصدع الناتج عن الإجهاد الميكانيكي و التآكل الكيميائي للأغطية الخارجية لمضخات تدوير مياه البحر المركزة في محطات تحلية المياه. هذه الأغطية كانت قد صنعت من نوعين من حديد الزهر المرن ذو نسبة عالية من النيكل. لوحظ وجود اختلاف في العمر التشغيلي لكل النوعين من المضخات. هناك اعتقاد بأن اختيار المواد الداخلية في تصنيع الأغطية يشكل أحد العوامل المهمة في تحديد العمر التشغيلي لهذا النوع من المضخات. ولذا اقترحت نوعين من الحديد المقاوم للصدأ UNS S31603 و UNS S32750 كمواد بديلة عن حديد الزهر المرن ذو نسبة عالية من النيكل. في هذا البحث تم إجراء الفحوصات الميكانيكية والمعدنية، والأشعة تحت الحمراء في حديد المقاوم للصدأ. تم إنشاء جهات فحص التصدع الناتج عن الإجهاد الميكانيكي و التآكل الكيميائي على عينات حضرت من كل النوعين من الحديد المقاوم للصدأ. ثم ربطه بكاميرا لمراقبة الفحص. النتائج أظهرت أن الحديد المقاوم للصدأ من نوع UNS S32750 و UNS S31603 يمنع بمقاومة UNS S32750 و UNS S31603 ان التصدع الناتج عن الإجهاد الميكانيكي و التآكل الكيميائي. في كل النوعين من حديد المقاوم للصدأ. من خلال الفحص الأليكترونيكي اظهر وجد النقر في هذا النوع من الحديد المقاوم للصدأ. فلم يلاحظ UNS S32750 و وجود النقر على سطح العينات المفحوصة. نتائج فحص التصدع الناتج عن الإجهاد الميكانيكي و التآكل الكيميائي أظهرت أن الحديد المقاوم للصدأ نوع UNS S31603 له مقاومة أقل للفشل UNS S32750. الناتج عن الإجهاد الميكانيكي و التآكل الكيميائي من الحديد المقاوم للصدأ نوع UNS S31603 بعد عدة أيام من تعرضها لظروف الفحص. أما العينات المصنعة من نوع UNS S32750 فلم تفشل عند تعرضها لنفس ظروف الفحص.
جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج علوم وهندسة المواد

التصدع الناتج عن الإجهاد الميكانيكي والتفاعلات الكيميائية للصلب المقاوم للصدأ والمستخدم في تصنيع مضخات تدوير مياه البحر المركزية في محطات تحلية المياه

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حزيران 2009