An Investigation on the Corrosion Resistance and Stress Corrosion Cracking Of Ductile NI-Resist Cast Irons in Desalination Plants.

Yahya Abdulla Alzafin

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AN INVESTIGATION ON THE CORROSION RESISTANCE AND STRESS CORROSION CRACKING OF DUCTILE NI-RESIST CAST IRONS USED IN DESALINATION PLANTS.

A thesis Submitted to the Deanship of Graduate Studies Of the United Arab Emirates University

By

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In Partial Fulfillment of the Requirements of The Degree of M.Sc. In Materials Science and Engineering

December/2007
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ABSTRACT

Two cases of stress corrosion cracking failures of brine pumps casings have been reported. These pumps are installed in two desalination plants located on the coast of Arabian Gulf in UAE. The materials of construction of failed parts are Ni-Resist Ductile Irons (NDI) and the environment is brine, which is concentrated seawater. Two brands of pumps had different lives to total failure; one lived 18 years while the other lasted only 5 years. The failed parts of former pumps were made out of NDI material as per American standard ASTM A439 D2 (designated D material) whereas those of latter pumps were made out of NDI material as per the British standard BS 3468 S2W (designated G material).

In this work, the material factor, as one of the possible factors that could have contributed to this different behavior has been evaluated. Metallurgical, mechanical, electrochemical tests and stress corrosion cracking tests were carried out to compare between the two alloys. Results have shown variations in the microstructure, tensile strength and hardness values of both alloys. However, electrochemical tests have shown similar corrosion rates between 0.20 and 0.25 mmpy in brine at room temperature, whereas, cyclic sweeps have shown comparable Tafel plots. To facilitate performing of SCC testing using the direct tensile test method a special testing apparatus has been developed. It comprised proof ring, stressing jig (frame), corrosion test cell and electric heater. The SCC tests have been carried with durations till full fracture or a maximum of 8 to 10 days in case of no fracture. The results have clearly shown different behaviors with respect to SCC resistance. The time to failure of D material was much longer than that of G material. This difference in behavior was attributed to the higher yield strength of D material and its more favorable microstructural features compared to G material. This has confirmed the material factor as a main contributor to the different performance in resistance to SCC of the two Niresist ductile irons.
Acknowledgements

All the praise and gratitude belong to Allah, the one and only God worthy of worship, for without his well, help and favors this study would not have been accomplished.

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The support provided by Mr. Saeed M. Al-Tayer, Managing Director and CEO of Dubai Electricity and Water Authority (DEWA), is highly appreciated. Such support was very vital to the success of this study especially in providing the necessary testing materials, machine shop services and sufficient supplies of brine solution. The support and encouragement received from my Manager Mr. Nassir Lootah, Executive Vice President (Generation), are also very much appreciated. Thanks are due also to my colleagues Mostafa Mokhtar, George Ben, Dyanan, Konder and Shamsuddin for the help they extended during preparation and execution of the experimental work.

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Finally all the love, appreciation and gratitude are due to my wife who encouraged me and stood by me all the time during the course of this study. Her patience and unwavering support were very vital to the success of this study.
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<th>Description</th>
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BRP</td>
<td>Brine Recirculation Pump</td>
</tr>
<tr>
<td>BS</td>
<td>British Standards</td>
</tr>
<tr>
<td>DSS</td>
<td>Duplex Stainless Steels</td>
</tr>
<tr>
<td>MSF</td>
<td>Multi-Stage Flashing Chambers</td>
</tr>
<tr>
<td>NDI</td>
<td>Ni-resist Ductile Irons</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steels</td>
</tr>
<tr>
<td>TDS</td>
<td>Total Dissolved Solids</td>
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<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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</table>
Chapter 1

INTRODUCTION
1. Introduction

1.1 Motivation

Ni-Resist Ductile Irons (NDI) have been widely used in sea water desalination plants. These iron based alloys possess high strength with a moderate ductility [1, 2]. Compared to ordinary cast irons and some steels NDI’s have much better resistance to general corrosion. They also have better resistance to localized corrosion than some types of stainless steels [2, 3, 4]. NDI’s also possess good erosive wear resistance, good machineability and castability and controlled expansion [1,2]. Their microstructure is characterized by uniformly distributed nodular graphite in an austenitic matrix which also contains carbide areas [5, 6].

Stress corrosion cracking (SCC) of pressure parts of brine pumps in a desalination plant located on Arabian Gulf has been investigated in this study. Two brands of pumps had different lives to total failure. The failed parts of former pumps were made out of NDI material as per ASTM A439 D2 (denoted D material in this study), whereas the latter pumps were made out of NDI material as per BS 3468 S2W (denoted G material in this study). Photographs of failed casings are shown in figures 1.1 and 1.2. These two grades of ductile Ni-resists are equivalent according to the applicable standards [5, 6]. Deliberate addition of Niobium in minor percentage gives the S2W better weldability. However performance of these BRPs was not the same. The D material has lasted for around 18 years prior to failure by SCC while the G material has lasted for only around 5 years prior to SCC failure.

The BRP failures cause reliability problems in desalination plants, the main water source in the Arabian Gulf countries, and can lead to catastrophic failures resulting forced and extended outages in case proper and timely corrective actions are not taken. Therefore it was felt necessary to study and evaluate this difference in SCC performance of the above brands of pumps. This difference in resistance to SCC may have been caused by mainly two factors, working individually or in combination. The first is presence of high tensile stress, applied or residual. The second factor is properties and features related to material of construction. The latter is studied in this work.
Figure 1.1: (a) One casing out of many BRP casings of G material (Niresist BS3468 S2 W) found with a crack by stress corrosion and (b) close view of the crack.

Figure 1.2: Pump casing of D material (Niresist ASTM A439 D2) with cracks indicated with arrows. Marks of clamping arrangement, used to strengthen the casing and prevent opening of the cracks during service, are also visible.
1.2 Aims and Objectives

Several types of examinations and testing were performed. The specimens used in this work were all from casings that failed during service. The objectives of this work are:

1. To perform metallurgical examinations, image analysis and mechanical testing. Optical and SEM microscopy as well as standard mechanical testing methods are used.

2. To conduct electrochemical testing using a potentiostat and PC software.

3. To devise a novel testing apparatus to allow easy and repeatable stress corrosion testing using the direct tension test constant load method.

4. To carry out tensile stress corrosion testing using the devised apparatus to compare the performance of two brands of NDI with regards to resistance to SCC.

1.3 Outline of the Thesis

This thesis is comprised of five chapters. The first chapter is an introduction describing the subject, motivation to this work in addition to the aims and objectives. A literature review is provided in chapter two starting on definition and aspects of SCC and description the desalination process. The chapter then provides details on various materials used making internal components and parts of brine pumps in desalination plants and their performance against corrosion in general with an emphasis on stress corrosion cracking of stainless steels and ductile Ni-resist irons. Experimental work including materials examination and various lab tests is detailed in chapter three. The chapter provides details of apparatus used and devices fabricated to facilitate the stress corrosion testing. It also includes sections on testing conditions and procedures. Results and discussion on experimental work is provided in chapter four. The chapter is comprised of five sections. Section one is on materials and chemical composition. Section two is on image analysis, microstructure and hardness tests. Section three is on mechanical testing results. Section four includes electrochemical testing results. Section five is
on examination of specimens with service induced cracking. Section six is on effectiveness of 
SCC testing apparatus. Section seven includes the SCC testing results listing times to failure, 
crack morphology and discussion on the these results. Conclusions are included in chapter five 
with recommendation for further work.
Chapter 2

LITERATURE REVIEW
2. Literature Review

2.1 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is defined as the "cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium." [7] Due to its localized nature, the SCC initiates as fine cracks whereas the remaining material surface in contact with the corrosive environment is virtually free of such type of corrosion attack. The SCC usually takes place at stress values within design stress range. The seriousness of this type of attack is that it can be undetected till failure take place leading to operational problems, process breakdown or even major safety hazards in some cases.

2.2 Potable Water Production by Seawater Desalination

Potable water in the gulf region is mainly produced by desalinating seawater by one or more of 3 methods/technologies namely; multi-stage flashing chambers (MSF) desalination plants, reverse osmosis (RO) plants and multi-effect desalination (MED) plants. MSF desalination is reported to account for producing about 80% of the desalinated water [8].

The following details describe a modern MSF desalination unit as found in the Plant Operation & Maintenance Manuals. It is as usually made of 3 sections namely heat input section, heat recovery and heat rejection sections. A deaerator (D/A), in which fresh sea water is added, is connected to the last stage of the heat rejection section. Figure 2.1 shows a simplified illustration of an MSF desalination plant. The heat input section is a shell and tube type heat exchanger (brine heater) in which steam, imported from steam generating boilers, is fed to heat up the circulating brine. The steam is condensed across the heater tubes and the condensate is collected and sent back to the boiler plant. In modern high capacity MSF desalination plants the heat recovery and rejection sections are made of a series of closed box like chambers of around 19 stages (17 recovery stages and 2 rejection stages).
Figure 2.1: MSF Desalination Process showing brine, seawater, distillate & steam circuits. Evaporation in lower part of chambers (orange lines) and Condensation on tubes (light blue) shown.

The lower side of the chambers act as a channel in which the circulating brine flows taking it from the preceding chamber (or brine heater for stage 1) to the following chamber through weir gates. In the last stage of rejection section the brine is collected in a sump and most of it is directed to the tubes (upper part) of last stage in heat recovery section through two large heavy duty vertical brine recirculation pumps (BRP). In the upper part of the heat recovery section chambers the brine flows in laterally arranged tube bundles connected from stage to stage by inter-stage piping. The brine flow direction in the tubes from stage to stage is opposite to that in the channel (the lower part). After the brine flowing in the tubes of stage one reaches brine heater tubes it is directed to the first stage channel area (lower part). This way the brine flowing in the tubes progressively picks up the heat of the condensing vapor that flashed in the lower part of each stage. For heat rejection section sea water flows in the tube bundles from last stage (stage 19) to first stage of this section (stage 18). It then divides into two streams. The first is rejected out to dump whereas the other stream goes to the D/A to make-up for the produced distillate and the rejected brine so that fixed flow rate of circulating brine is approximately maintained. The deaerated sea water at the bottom of the D/A flows to stage 19 and mixes with the brine in the
sump where it gets circulated by the brine pumps. During start up the plant is under cold circulation where no evaporation takes place hence no distillate is produced. On admission of heating steam to the brine heater the brine gets heated up slowly till the temperature reaches around 105 deg C. As the pressure in the first stage chamber is kept at around a value of 1 atm a rapid evaporation process takes place in which the circulating brine flashes as water vapor (with high purity) in lower portion of the chambers rising upward and getting in direct contact with the surfaces of the tubes. The brine inside the tubes is cooler that the water vapor. As such the brine absorbs the heat of the vapor which leads to its condensation. The condensate is collected in water trays which are connected in all stages and finally collected in a pipe and pumped away as distillate for further treatment. The evaporation process results in a reduction in temperature of the brine in the chambers due to loss of heat energy by evaporation. To allow the continuation of brine evaporation process with decreasing temperatures from stage to stage; and hence abiding by laws of Thermodynamics, a dedicated vacuum system controls the pressure in a decreasing fashion going from stage 1 to last stage (stage 19). As the evaporation process also increases the salinity of circulating brine during its travel through the stages, it is essential to control the brine salinity keeping it within a specified range. This is achieved by continuously and simultaneously adding fresh sea water in the D/A and rejecting out a controlled quantity of the brine before its return to the heat recovery section of the desalination plant.

As can be seen from the above discussion the circulating medium; i.e. brine, in the MSF desalination process is a very corrosive environment which is very rich in chlorides. Typical salinities of Gulf sea water and brine measured in the desalination plants of failed Brine pump parts are indicated in the Table 2-1.

<table>
<thead>
<tr>
<th>Environment</th>
<th>SEA WATER</th>
<th>BRINE</th>
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<tr>
<td>Total Dissolved Solids [mg / Ltr]</td>
<td>45200 – 45360</td>
<td>61924</td>
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Table 2-1: Actual measurements of sea water and brine Environment salinities.
The average salinity of earth oceans, TDS, ranges from 32000 to 37000 mg/Ltr [9, 10]. As seen from the above table the Gulf, being almost a closed sea, is already very saline which makes the brine itself a much more saline environment.

2.3 BRINE RECIRCULATION PUMPS

It is clear that the two brine recirculation pumps (BRP’s) are essential pieces of machinery that are responsible for circulation of brine in an MSF plant. They are heavy duty pumps that are subject to continuous hydraulic and mechanical loading. They also handle a very corrosive environment with high chloride content. Failure of these critical pumps would result in shut down of the desalination plant. Further upstream in the desalination process, the sea water pumps, SWP’s, are also as critical and are usually of same vertical construction. Figure 2.2 below shows a photograph of one of the BRP’s removed during maintenance.

Figure 2.2: 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.

The BRPs may suffer catastrophic failures due to mechanical loading. They may also fail due to general corrosion as well as localized forms of corrosion. In any case, such failures will result in a shut down of the MSF desalination plant which may have its costly consequences. Unless such failure mechanisms are prevented or at least developing damages are caught and repaired before they lead to a total failure the plants will suffer from unacceptable failures with plant reliability and availability problems.
According to work conducted by Miyasaka [4] the temperature of the brine, in the range of 40°C to 45°C as it enters the brine pumps, and it high salinity can accelerate the SCC process. This temperature is relatively high compared to that of sea water and hence BRP’s tend to suffer more failures due to localized corrosion than sea water pumps.

2.4 Materials for Saline Water Environments:

Following is a technical literature review on performance of above materials of construction against corrosion in saline water environments.

2.4.1 General materials of construction used in brine and Sea water pumps:

In a reference book [3] critical duty of large pumps in power, desalination and industrial plants is highlighted. The book also gives guidelines on use of the various materials in marine service to ensure their compatibility with each other. It discusses in details use of a number of groups of materials for saline water environment. It extensively reviews various types of corrosion attack expected in marine service. In large MSF plants, BRP’s and SWP’s are usually of vertical construction with rotating parts (shaft and impeller) usually made out of Stainless Steels or Duplex Stainless Steels. The stationary parts are suction barrel containing all submerged parts and pressure casings that contain the rotating parts. The suction barrel is usually made of Carbon Steel with special corrosion protective lining of rubber or metallic alloy of high corrosion resistance against brine. The pressure parts (casings) are usually made out of Ni-resist ductile irons (NDI), austenitic stainless steels (ASS), duplex stainless steels (DSS) or a combination of 2 or more of these classes of ferrous alloys.

The above materials are usually used in combinations (mixing of 2 or more materials) considering factors such as cost and required material performance. It has been reported [3, 14] for example that NDI materials provide cathodic protection to ASS parts against pitting corrosion that can take place in stagnant water conditions during standby service or even during flowing conditions at crevices (tight places/pockets with relatively stagnant water condition; e.g. flanged joints). Such a protection however is not needed when pumps are in continuous service provided that a crevice tolerable design is used.
Table 2-2 shows materials combinations indicated [3] to be compatible and of proven experience. The materials not only relate to pressure casings but also other components of BRPs such as rotating parts and low pressure parts such as pump suction barrels. Considerations were given to effects of galvanic corrosion and other properties required in handling saline waters.

<table>
<thead>
<tr>
<th>Part</th>
<th>Reference</th>
<th>Alternative</th>
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<tr>
<td>Transition piece</td>
<td>CF3M, 316L</td>
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<td>ANI-D2W, D2-FSR, 316L</td>
<td>EC steel</td>
</tr>
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<td>ANI-D2W, D2-FSR</td>
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<td>Inlet Bell</td>
<td>ANI-D2W, D2-FSR</td>
<td>ANI-D2W, D2</td>
</tr>
<tr>
<td>Impeller</td>
<td>CF3M, CF8M, CD4MCu</td>
<td>Austenitic &amp; Duplex SS</td>
</tr>
<tr>
<td>Shaft</td>
<td>N04400, 316</td>
<td>N50, DSS2205</td>
</tr>
</tbody>
</table>

Notes: CF3M & CF8M: cast equivalent of 316 & 316L; DSS2205 is a duplex SS. ANI (Ni-Resist= austenitic cast iron types D2 and D2W (weldable)). FSR: furnace stress relieved. EC= epoxy coated.

2.4.2 Austenitic stainless steels (SS):

Moller reported [13] excellent performance of austenitic SS in sea water service flowing at high velocity. He reported occasional failures by severe localized attack by pitting at crevices or under deposits in quiet sea water. Moller concluded that to combat pitting cathodic protection is needed either by using other components lower in the galvanic series or by using sacrificial anodes. He stated that chloride SCC at ambient was not a problem based on field data. He also indicated that fabricated austenitic SS parts can suffer from intergranular corrosion cracking if sensitized (exposed to a specific temperature range for sufficient time during fabrication).
Todd reviewed the various factors [14] that are important for austenitic SS materials selection for marine service. He discusses the issue of localized corrosion in the form of pitting and crevices corrosion discouraging designers against the selection of Austenitic SS. He, however, emphasized good resistance of Austenitic SS to high velocity seawater especially for pumps' shafts and impellers. He pointed out the importance of cathodic protection needed to prevent pitting (in stagnant water conditions) and that such protection can be provided by using less noble materials such as Ni-resist casings.

Flint discussed [15] corrosion resistance of austenitic SS in various naturally occurring waters including seawater, s c e c s S S S known since their inception. He identified the steps needed to minimized localized corrosion of Austenitic SS in seawater environment such as avoiding crevices or minimizing their effects by making them "as open and as shallow as possible", to cathodically protect them and maintenance of high velocity of seawater to prevent permanent deposition of solid.

Malik et al reported [16] varying degrees of corrosion attack on materials used in gulf seawater environment. They studied performance of the materials generally used in this environment with regards to general pitting and crevice corrosion using weight loss and electrochemical techniques. They concluded the following. General corrosion rate is very low in temperature 25°~50°C. In crevice and deposit fee systems, all standard materials are not subject to risk of localized attack. Otherwise only highly alloyed SS appear to have satisfactory performance.

Prakash et al studied [17] the SCC behavior of mild steel, austenitic stainless steels, 316L and 317L, ferritic SS 430 and nickel based alloy Monel 400, all used in desalination plants, under synergistic action of corrosents such as chlorides, oxidants and hydrogen sulfide (H2S). Using standard proof rings and U-bend samples in NACE and SHELL solutions containing H2S combined with electrochemical polarization measurements threshold stresses for SCC had been determined. Mild steel, alloy 430 and Monel 400 suffered SCC in H2S environment, whereas 316L and 317L were found immune to SCC under test conditions. All above materials were ranked based on the resistance to SCC under above environments.
2.4.3 Duplex stainless steels (DSS):

DSS are a group of stainless steels with austenite areas in a matrix of ferrite both rich in chromium all preferred with a 50% to 50% balance of each phase [3]. These materials are used as pumps materials. Addition of nitrogen has made these materials very useful in pumps adding advantages of improving ductility, repairability and reduced partitioning of chromium between present phases. This has improved pitting resistance of duplex steels.

Tsai et al investigated [18] the behavior of DSS 2205 regarding its resistance to SCC in 26% wt NaCl solution at 90°C. They evaluated its susceptibility to SCC, using slow strain testing method, at both open circuit potential as well as various anodic potentials. They identified potential of -160mV to be critical to resistance to SCC above which material is susceptible. Otherwise they found it immune to this form of localized corrosion attack.

Sophie Jacques et al discuss [19] the importance of using SS and DSS in desalination plants to combat corrosion with emphasis on pitting and crevice corrosion. They conducted tests on some grades of the above stainless steels with regards to pitting and crevice corrosion resistance at conditions similar to those prevailing in desalination plants. The reported results indicated the DSS UNS S32304 to possess same or better pitting corrosion resistance than austenitic SS grade 316L. They also reported that grade DSS UNS S32205 offered a better corrosion resistance than grade 316L especially from crevice corrosion.

2.4.4 Ni-Resist Ductile Iron (NDI) Alloys:

In order to have better understanding of this class of materials it is important to know and discuss the various properties of cast irons and ni-resist cast irons as special classes of metallic engineering materials.

2.4.4.1 Manufacture of cast irons:

Cast iron is manufactured from its oxide ores [1]. Iron is reduced in a blast furnace where coal or coke, limestone and iron oxide ore are charged at the top of the furnace and hot blast air is introduced at the bottom along with some hydrocarbon fuel. The liquid iron ‘pig iron’ (4-5% C, 0.5-1% Si) is collected at the bottom of the furnace and allowed to solidify in various forms.
Subsequent processing with many alloying options in electric or other furnaces is needed to produce the irons or steels of desired properties for the intended applications. Contrary to steel products cast irons have considerably lower ductility or are basically brittle. Therefore cast irons are usually obtained as cast products whereas steels are usually produced in various forms such as plates, beams, bars, cast, etc.

2.4.4.2 Microstructure, main alloying elements and classification of cast irons:

Cast irons are ferrous alloys that have carbon rich phases [1]. The common, i.e. non-alloyed or low-alloyed, cast irons have iron, carbon and silicon as main elements. The matrix in common irons can have the different microstructures such as pearlite or ferrite. The matrix may have different alloying elements in solution. Other phases, i.e. graphite and carbides, also exist.

Moderately and highly alloyed cast irons contain, among other elements, high percentages of alloying elements [1]. These special high-alloy cast irons are manufactured to serve various engineering applications. Such applications may require heat resistance, corrosion resistance, wear resistance or a combination of these desirable properties. Figure 2.3 is a classification of such special cast irons.

![Classification of highly alloyed cast irons](image)

Figure 2.3: Classification of highly alloyed cast irons [1].
2.4.4.3 Role of graphite and its effect on properties of cast irons:

Graphite is believed [1] to give the cast irons three main advantages over steels. The first is by lowering the pouring temperature due to the higher carbon content. The second is by increasing the melt fluidity as the graphite act as a lubricant. The third way is by resulting in moderate shrinkage of the metal during solidification as the graphite increases in volume and compensates for some of the metal shrinkage. These advantages allows for casting the iron in intricate shapes reducing manufacturing costs; e.g. casting is simplest and most direct way of processing metals. As an example, casting in a pattern instead of cold working or welding, gives more consistent product without dimensional change with more uniformity in structure avoiding homogeneity problems or flaws introduced by welding. Graphite can have different shapes depending on liquid treatment, prior to pouring, and chemical composition. Figure 2.4 illustrates the various forms of graphite in cast irons.

The shape, size and distribution of the graphite in cast irons can significantly affect their properties [1]. For example big variation in mechanical strength is a result of difference in graphite morphology as depicted in figure 2.5. All the stress strain curves in the figure indicate lack of linearity or clear yield points. For ductile, also known as nodular, irons the percent nodularity also affect mechanical properties [1]. Ductile irons are usually specified to have greater than 90% nodularity [1]. Low percentages of nodularity can adversely affect mechanical properties, such as 0.2 offset yield and tensile strength, as shown in figure 2.6.

2.4.4.4 Carbide effects on properties:

Carbides in cast irons also affect their mechanical strength properties [1]. Presence of carbides is indicated to affect both 0.2 offset yield and tensile strengths of cast irons. Figures 2.7 and 2.8 below show that as the carbide content increases the 0.2 % offset yield strength increases and the tensile strength decreases respectively.
Figure 2.4: Typical graphite shapes: I, spheroidal graphite; II, imperfect spheroidal graphite; III, temper graphite. IV, compacted graphite; V, crab graphite; VI, exploded graphite; VII, flake graphite [1]
Figure 2.5: Influence of graphite morphology on the stress-strain curve of several cast irons. [1]
Figure 2.6: Influence of nodularity on some mechanical properties of ductile iron. [1]
Figure 2.7: Relationship of carbide content with 0.2% offset yield strength [1].

Figure 2.8: Relationship of carbide content with tensile strength [1].
2.4.4.5 Microstructure and chemical composition of NDI

NDI's are highly alloyed class of cast irons [1, 2]. Their main alloying element is Nickel and its content varies between 18-22% as per relevant standards giving it its austenitic microstructure and its desirable corrosion resistance properties. Other alloying elements such as chromium are present even though in lower percentages than nickel. It has been reported that addition of chromium, as in Ni-resist castings, forms hard carbides and hence higher chromium is believed to increase the propensity for microporosity in the iron castings [2]. NDI come in a variety of compositions depending on the application. For sea water applications which includes brine service two common grades of NDI are indicated in table 2-3.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C Max.</th>
<th>Si</th>
<th>Mn Max.</th>
<th>P Max.</th>
<th>Ni</th>
<th>Cr Max.</th>
<th>Mg</th>
<th>Nb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A439 D2</td>
<td>3.0</td>
<td>1.5-3</td>
<td>0.7-1.25</td>
<td>0.08</td>
<td>18-22</td>
<td>1.75-2.75</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BS3468 S2W</td>
<td>3.0</td>
<td>1.5-2.2</td>
<td>0.5-1.5</td>
<td>0.05</td>
<td>18-22</td>
<td>1.5-2.2</td>
<td>0.06</td>
<td>0.12-0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The microstructure of NDI grades is comprised of austenite matrix containing nickel, among other elements, in solid solution with two other phases namely graphite nodules and carbide areas [2]. Such microstructure is shown in figure 2.9.

![NDI S2W microstructure showing graphite nodules and carbides in Austenite.][1]

---

[1]: ndi_s2w_microstructure.png
2.4.4.6 Mechanical properties of NDI

Data on the 0.2% yield and tensile strength were comprehensively published by the NDI [2]. Table 2-4 shows typical values of NDI grades D2 and S2W.

Table 2-4: mechanical properties of two grades of ductile Ni-resist.

<table>
<thead>
<tr>
<th>Ni-Resist Alloy</th>
<th>Tensile Strength, MPa</th>
<th>0.2% Proof Stress, MPa</th>
<th>Elastic Modulus, GPa</th>
<th>% Elongation, minimum</th>
<th>Brinell Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A439 D2</td>
<td>370-480</td>
<td>210-250</td>
<td>112-130</td>
<td>8</td>
<td>140-200</td>
</tr>
<tr>
<td>BS3468 S2W</td>
<td>370-490</td>
<td>210-260</td>
<td>112-133</td>
<td>7</td>
<td>140-200</td>
</tr>
</tbody>
</table>

2.4.4.7 Corrosion performance and electrochemical properties of NDI in sea water

NDI alloys are reported to have better resistance uniform corrosion than ordinary cast irons and carbon steels [2] as shown in the figure 2.10. They also posses much better erosion/corrosion resistance than these alloys [2]. NDI are located mid range in the galvanic series of alloys tested in sea water environment [2]. Their potentials against SHE range from around -0.53 V to -0.42 V. They become anodic when for example they are coupled with SS316 material as the latter has a free potential of around -0.05 V. Figure 2.11 shows the galvanic series of common alloys in sea water.

Electrochemical properties of NDI in 3% NaCl solution at 25dC were studied by Smart et al [20] using rotating disc voltammetry. They have found that corrosion potential values and their dependence on rotating speed indicated oxygen reduction as the cathodic process and that it is of kinetic control type rather than mass transport control. They have also found that two Tafel regions existed in the anodic process one with a slope ca 70 mV decade⁻¹, occurring at low current densities, and the other, at higher current densities, with a slope of ca 49 mV decade⁻¹. They have stated that Tafel slope extrapolation method was not suitable in determining corrosion current due to large errors in Tafel slope determination.
Figure 2.10: Corrosion performance of Ni-resist compared to ordinary cast iron and carbon steels in aerated sea water environment [2].
Figure 2.11: Galvanic series of alloys in flowing seawater [2.4-4.0 meter/sec] at ambient temperatures [10-27°C]. [2]
2.4.4.8 SCC of Ni-resist and cracking in other selected ductile irons:

Miyasaka et al studied [4] SCC behavior of Ni-resist cast irons type ASTM A436, type 2 and A439, type D2 in NaCl solution using constant load method and smooth round specimens. They examined influence of applied stress, temperature, NaCl and oxygen concentrations, potential and alloying elements on SCC behavior. They found among other findings, Ni-resists are susceptible to SCC and type D2 (ductile) being more resistant to SCC than type 2. They found that SCC mechanism was of active path corrosion cracking, and that life to SCC failure is inversely proportional to applied stress, potential and temperature.

Kauczor reported [21] that SCC is transgranular and runs in straight lines through the material with sharp branches that are usually at right angles. He stated that the cleavage surfaces could almost be mistaken for grain boundary fracture. He also stated that the types of crack behavior could be distinguished in the fracture surface from being that of grain boundary fracture by comparing the scanning electron micrographs (SEM) with sufficiently magnified optical micrograph that would show grain boundaries and cracks through the grains.

Dawson and Todd [22] examined SCC susceptibility of Ni-resist D2 with verifying amounts of carbides at 45°C. The results indicated that within chemical composition range required by ASTM standard various carbide contents can occur and that the form of SCC is influenced by amount of the carbides. The results also showed that high carbide contents promote more severe cracking if these carbides tend to form network. The authors recommended good silicon inoculation practice and high silicon and less chromium contents. They also recommend heat stress relieving the Ni-resist castings to minimize total stress.

Roger Covert et al reported [2] that Ni-resist are highly resistant to SCC even though some failures had likely occurred by this form of corrosion. They stated that proper stress relief heat treatment after casting, welding and machining operations would greatly alleviate or even eliminate such failures. They questioned what others reported with regards to ranking some Ni-resist grades over other in their resistance to SCC. They preferred to treat them equally as they believed that other reasons such poor quality of castings, corrosion fatigue and other failure mechanisms should be considered.

Raman et al [23] studied failure of a cast iron component exposed to caustic solution during Bayer process used in processing alumina. They examined cracks in the component using
metallography, SEM, TEM and Auger electron spectroscopy. Cracks were attributed to intergranular SCC and embrittlement of grain boundary at crack tip front. Argument was made on possibility of hydrogen assisted crack propagation.

J. Kim and J. Ji [24] carried out fatigue tests on ductile cast irons that were subject to super rapid induction quenching treatment. The effect of the developed hard layer on fatigue crack initiation and propagation was emphasized in the study. They found that the applied quenching treatment resulted restriction on crack initiation due to development of martensitic shells around the graphite nodules as well as the compressive residual stress in the hard layer. Crack propagation was found to be retarded by these developed features.

Over the last two to three decades there have been many cases in which NDI materials failed by stress corrosion cracking (SCC) especially in the Arabian Gulf region [4, 11, 12, 21]. Due to economic and reliability considerations in desalination process, these failures make re-evaluation of and further studies on performance of these materials and investigation on use of other candidate materials for pressure casings of paramount importance.

Preliminary investigation by the author has revealed that the failures of the pump casings made out of NDI grades by two different manufacturers were not related to carbide phases forming a network or quality of castings. It is however cracking through austenite matrix without preference to any microstructural features. Therefore there is a need to study and compare the different behavior of the two grades of NDI’s with respect of their resistance to the SCC in brine service. Even though the difference in behavior could be due to a single or a combination of factors, only material related factors will be investigated in this study. This will be achieved by conducting SCC testing on these two materials while neutralizing other contribution factors, such as residual or applied stresses, temperature, galvanic effects, etc. The study will be carried out using specially designed SCC test cell and apparatus. The study will also include mechanical, microstructural and electrochemical testing to compare the properties of these two grades and investigate their relationship to SCC resistance of the two D and G materials.
Chapter 3

EXPERIMENTAL WORK
3. Experimental Work

3.1 Materials

The test materials used in this study were designated, sourced and identified as follows:

- Designation: The material that had a longer service life prior to failure by SCC is designated as D material (used in desalination plant named D) whereas the one that had shorter service life prior to its failure by SCC is designated G material (used in desalination plant named G). The D material was manufactured as per ASTM A439 D2 [5] and G material as per British standard BS3468 S2W [6] which according to standard is more weldable than D material due to addition of Niobium in small amounts.

- Test materials of both D and G materials were cut out from pump casings that failed by SCC. Locations at which test materials were cut is selected to be as near to crack area as possible to ensure to the extent possible that microstructure of test material is same as that of cracked areas. Figure 3.1 show pump casings with cut out portions. The chemical compositions as reported by pump manufacturers were used in the comparison. X-ray fluorescence (XRF) instrument was used to compare between percentages of main elements of the two types of materials.

3.2 Specimens Fabrication and Preparation for Testing

Specimens of different shapes and sizes were fabricated to suit the various examination and testing techniques used in this study. The specimens used in both electrochemical and SCC testing had their surface finished to 600 grit size. Specimens used for image analysis were finished as discussed in section 3.3. Prior to electrochemical tests specimens were washed with fresh water followed by acetone wash and air drying. Other specimens were stress relieved by heat treatment according to ASTM A439 [5]. During heat treatment D and G materials were stress relieved in same oven in same batch. Typical heat treatment chart is shown in figure 3. To facilitate microscopic examination chemical cleaning by Hexa methylene tetra amine solution was used according to ASTM G1 [25] to remove as much as possible of corrosion products from samples that failed during service and those subjected to SCC laboratory tests. Same cleaning
method was used to clean specimens subjected to stress relief heat treatments from high temperature scale prior to grinding and polishing these specimens for corrosion testing.

Figure 3.1: BRP casings of D material (a) and G material (b) with test material cut out.
Figure 3.2: Typical stress relief heat treatment according to ASTM A439 [5].
3.3 Image Analysis and Hardness Tests:

Round specimens of 0.5” thickness and 1” diameter were fabricated for microscopic examination of the microstructure as well as hardness testing. Specimens are shown in figure 3.3. Necessary surface grinding was carried out using a rotary grinder with grinding paper, up to 2400 grit size. Ground specimens were polished using a rotary polishing machine with diamond paste up to 0.25 μm. Samples were then etched using 2% Nital solution (2% Nitric acid in 98% Ethanol). Classification of graphite nodules, in both types of cast irons, in terms of average nodule diameter, number of nodules per square millimeter and average aspect ratio of nodules was determined using SEM images and KS 300 Kontron Elektronik image analysis software. Hardness tests were conducted using standard Vickers hardness tester. Brinell hardness tests were also arranged through a specialist laboratory.

![Figure 3.3: The two specimens used for microstructural examination.](image)

3.4 Mechanical Tensile Tests:

Tensile test specimens 2 of each of the two D and G materials (total 4) having a gauge diameter of 12.5 mm were machined from failed pump casings. Tension tests were conducted as per ASTM E8 standard [26] using 100 MN MTS tensile testing machine. The specimens used in SCC testing were of size 6.25 mm, to suit proof ring stressing capability. Therefore, in order to examine the effect of specimen size on tensile properties, two round tensile specimens size 6.25 mm were prepared and then tested using MTS machine. Due to small gauge length the available extensometer could not be used and strain gauges were used instead. The stress strain curves were obtained.
3.5 Electrochemical Testing:

Hollow cylindrical test specimens having 12.4 mm outside diameter and 7.94 mm height both D and G materials were used. Following machining, specimens were stress relieved following the ASTM guidelines [5], chemically cleaned as per ASTM [25] and mechanically polished to 600 grit size. Specimens were then degreased with acetone and cleaned with fresh water prior to electrochemical testing.

The brine used for testing was arranged from the desalination plants in which the failures of G material by SCC took place. Storage tanks were used to store brine at roof level to allow for a once through gravity assisted flow and hence avoid use of pumps. Figure 3.4 shows the desalination plant and a brine tank being filled with brine.

ACM potentiostat and software system were used for testing. The test apparatus and shape of test specimens used in electrochemical tests are shown in Figure 3.5.

Figure 3.4 Filling the brine tank with brine used in corrosion testing: (a) the desal plant and (b) the tank being filled with brine.
Using the available software prepared specimens were subjected to long term linear polarization resistance measurement (for corrosion rate determination) and long term rest potential measurement. These measurements were carried out over a period of about two days at room temperature (25 ± 2°C). The duration was chosen to allow for surface stabilization to ensure repeatability of results. The above tests were directly followed by potentiodynamic sweep tests to compare between the corrosion behaviors of both material types. Standards ASTM G3, G59 and G61 [27, 28 and 29] pertaining to these tests were used.

3.6 Examination of Specimens Having Service Induced Cracks:

To permit SEM examination of the fracture surface initiated by SCC during service one specimen each from both D and G materials of a size approximately 2" by 1" by 1" and having cracks with crack front were cut out from failed casings. Holes with threads were prepared and special fixtures were fabricated to open the crack surfaces up using the MTS without damaging the crack surface. Figure 3.6 illustrates the G specimen ready for crack opening. Two other specimens with SCC cracks were also prepared for optical microscopy to examine nature of crack propagation in the matrix and other phase present. They are shown in Figure 3.7.
Figure 3.6: The specimen prior to crack opening with the SCC appearing at top. The top threaded hole (out of two used to hold specimen) is shown at top surface.

Figure 3.7: The two specimens (G to the left and D to the right) with SCC cracks removed from failed pumps casings. These were specifically used for optical microscopic examination of SCC cracks.
3.7 Tensile Constant Load SCC Testing Apparatus Development

Due to its simplicity the constant load method using direct tension tests a proof ring was selected to evaluate and compare the materials resistance to SCC and as per ASTM standard G49 [30]. Due to limited resources, commercially available proof rings could not be arranged. This required developing a proof ring of suitable capacity to handle Ni-resist materials. After the fabrication of the proof ring it was loaded and calibrated using MTS. A calibration table was prepared. It indicates the load values achievable against the deflection values of the ring. The proof ring with specimen holding bolts and tightening nut are shown in the figure 3.8.

To allow proper and accurate stressing of the specimens a special jig was devised. A rectangular opening at the holding bracket through which the top stressing bolt is inserted ensures that by turning the nut the bolt does not turn. Hence the specimen receives only tensile loading without torsion stress. This is important as only tensile loading should be present during SCC testing. Figure 3.9 and 3.10 show stressing jig before and after proof ring-specimen assembly whereas figure 3.11 shows the stressing of the proof ring and specimen. The jig also made it possible to accurately measure the reduction (deflection) of the diameter of proof ring using a digital vernier caliper. For this purpose, the internal diameter of the proof ring would be measured in vertical direction. The required load to be applied on the specimen and the corresponding compression was identified using the proof ring calibration table. Figure 3.12 shows how measurement is made.

The test cell was then designed and fabricated using plastic materials. The main body is a transparent plastic pipe 2 inches in diameter. The two open ends were provided with Teflon caps which contained holes for solution inlet and outlets. The specimen would be inserted at the center of the cell in vertical arrangement. The cell was also designed to permit electrochemical testing. The cell has holes for accommodating the working (specimen), counter and reference electrodes in addition to holes for thermometer and venting tubes. Figure 3.13 shows top and side views of the cell with some of the items fitted in holes. The cell would be supported in inclined arrangement. During the trial testing the proof ring-cell assembly was seated on the stressing jig as shown in Figure 3.14. However in order to overcome leakage of electric currents
observed during initial testing a non-conducting round Teflon bar with opening to carry the proof ring-cell assembly was devised as shown in figure 3.15. It has grooves at the sides so as to be fitted on the side walls of the drainage pan with the cell in inclined position as is shown in figure 3.16. The inclination of the cell allows hydrogen gas, evolved during the electrochemical process at the cathode, to be vented at inlet side for the cell through a narrow vent tube. The ventilation prevents downward displacement of the brine in the cell by gas evolution hence ensuring all time immersion of the specimen.

Special attention was given to preparation of specimens for SCC in the brine solution. After machining them they were stress relieved and chemically cleaned. After that they had to undergo surface preparation by fine grinding to grade 600. They were then prepared for coating the two reduction portions of specimen by resin so as to ensure two purposes. The first was to seal the test cell as the specimen would penetrate the cell at top and bottom. The second was to ensure a crevice free surface at gauge length. This is shown in Figure 3.17.

Figure 3.8: The proof ring with top bolt, stressing nut and bottom bolt.
Figure 3.9: The proof ring stressing Jig with the proof ring on left side.

Figure 3.10: The proof ring-cell-specimen assembly fixed in the stressing jig.
Figure 3.11: Stressing of the proof ring-specimen assembly using the stressing jig.

Figure 3.12: A photo that shows how the proof ring compression is measured.
Figure 3.13: A top view (a) and a side view (b) of the test cell with all connections fitted except the tensile specimen.
Figure 3.14: A side view (a) and a front view (b) of the test apparatus using the stressing jig as a seat
Figure 3.15: The round Teflon seat used for the proof ring-cell assembly.

Figure 3.16: A front view of the test apparatus using the Teflon bar as a seat.
Figure 3.17: Photos (a) to (c) that show how a specimen is prepared for resin coating application at the section reduction portions. Teflon half rings are clamped at center and threaded ends are wrapped with Teflon tape. Photo (d) shows how the specimen looks like after application of the resin. The solution side of the resin is angled in a way to minimize crevice effect.
3.8 SCC Testing Conditions:

In order to accelerate the SCC testing the specimens were subjected to following test conditions. These were adopted after consulting the literature as well as relevant standards.

1. Apart from the brine solution corrosion aggressiveness it was aerated by allowing atmospheric air to enter the overhead brine tank. Continuous supplies of the brine ensure that the brine in the test cell stays fresh and rich in chlorides hence maintaining its corrosiveness.

2. The brine solution temperature was raised to around 55°C using a specially fabricated heater. This temperature was chosen based on work by Miyasaka [4] which suggested that higher temperature would not accelerate SCC significantly. A specially made electric heater was used for this purpose. To overcome the electric element damage by brine corrosion attack observed during initial trial tests a containment cylinder housing the element was used. The cylinder was made out of SS316 material and contains automotive radiator coolant fluid which transfers the electrically generated heat to the cylinder and subsequently to the flowing brine. Figure 3.18 below shows the heater.

![Figure 3.18: The electric brine heater wrapped with thermal insulation material.](image)
3. The specimens were all anodically polarized by 100 mV with respect to their free corrosion potential. This polarization is believed to be moderate and representative of actual situation during service as niresist is usually coupled with SS316 [3].

4. The specimens were stressed to values ranging from just over 70% to 102% of the yield stress of both materials. This was chosen in order to accelerate the SCC and based on the fact that stress values were within proof ring capacity and that higher stress values could not be accurately determined based on measured stress strain data.

3.9 Tensile Constant Load SCC Testing Procedure:

Actual tensile SCC testing was performed on a total of 8 specimens; i.e. 4 specimens of G material and 4 of D material. Following procedure was used:

1. The specimens were first stress relieved using HT curves as per ASTM standard [5].
2. The applied stresses were chosen as follows. Two G specimens and two D specimens were stressed at around 220 MPa. This is 100% of G specimens yield stress and 86% of D material yield stress. For unbiased comparison, two G specimens were also stressed and tested at 86% (190MPa) of G material yield stress. Two other D specimens were tested at 190 MPa and 206 MPa.
3. The design of the cell necessitated that the stressing of the specimens is carried out, using the proof ring, after inserting the specimen in the test cell. Using a set of spanners the proof ring is tightened to the desired stress levels using the calibration table and a digital vernier caliper as discussed in a previous section.
4. Once the specimen is stressed the whole assembly is placed on the seating arrangement and various connections are made. The end caps are then fitted to the cell. This is followed by fitting all inserts namely; vent tube at inlet side, thermometer to the right of vent, the reference electrode next to specimen and the counter electrode.
5. Further, the heater would be set at 55° C using the heater element thermostat. It is essential that the heater is allowed sufficient time to warm up to around the set temperature. This can be known with the power supply indication lamp.

6. The PC connected camera is then hooked around the test cell using rubber bands and aimed at the specimens. The camera software is set so as to take photos at intervals of 15 minutes.

7. The ACM software is then set with the required data such as specimen surface area, polarization, scans rate, etc. Now the apparatus is ready for testing.

8. After admitting the brine solution and reaching at the test temperature (55+ 3° C) the camera is activated, the potentiostat is run and the time to full fracture will be monitored and recorded visually with the camera.

The above procedure was repeated for all the specimens. The criterion of comparing the resistance to stress corrosion cracking is the time to full fracture.
Chapter 4

RESULTS AND DISCUSSION
4. Results and Discussion

4.1 Materials and Chemical Composition:

The chemical composition of both D and G materials are shown in Table 4-1 as reported by pump manufacturers. ASTM A439 [5] and BS3468 [6] ranges of composition are also shown in the table. A Niton portable XRF analyzer model XLT898W was used to compare the alloy contents. Due to limitation of this method in detecting Carbon and Silicon in cast iron it was used just as a support to confirm composition reported by OEMs especially regarding contents of major elements such as nickel and chromium. The chemical compositions so measured are indicated.

Table 4-1: Reported chemical compositions of the D and G-types Ni Resist austenitic cast iron in relation to the permissible range of composition as per the ASTM.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Mg</th>
<th>Nb</th>
<th>Cu</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A439</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2 Range</td>
<td>3.0*</td>
<td>1.5-3</td>
<td>1.25</td>
<td>0.08*</td>
<td>18-22</td>
<td>1.75-2.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>D material:</td>
<td>2.69</td>
<td>2.58</td>
<td>0.83</td>
<td>0.013</td>
<td>18.9</td>
<td>2.12</td>
<td>*</td>
<td>0</td>
<td>0</td>
<td>72.87</td>
</tr>
<tr>
<td>XRF D Mat'l</td>
<td>-</td>
<td>-</td>
<td>.93</td>
<td>-</td>
<td>21.45</td>
<td>2.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>74.92</td>
</tr>
<tr>
<td>BS3468-S2W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>3.0</td>
<td>1.5-2.2</td>
<td>0.5-1.5</td>
<td>0.05</td>
<td>18-22</td>
<td>1.5-2.2</td>
<td>0.06</td>
<td>0.12-0.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>G material:</td>
<td>2.77</td>
<td>1.94</td>
<td>1.03</td>
<td>0.015</td>
<td>20.1</td>
<td>1.66</td>
<td>0.043</td>
<td>0.15</td>
<td>0.08</td>
<td>72.21</td>
</tr>
<tr>
<td>XRF G Mat'l</td>
<td>-</td>
<td>-</td>
<td>1.08</td>
<td>-</td>
<td>21.07</td>
<td>1.79</td>
<td>-</td>
<td>.13</td>
<td>-</td>
<td>75.31</td>
</tr>
</tbody>
</table>

* amount not indicated though controlled amount of about 0.045% is needed to produce nodular graphite in ductile irons.
The reported data fall within ranges specified in ASTM A439 for D material and in BS2346 for G material. The data measured by XRF method show that contents of nickel, chrome and manganese are close to those reported by manufacturers of failed pumps. Slight variation in composition exists as carbon and silicon could not be detected due to inherent limitation of XRF method.

4.2 Image Analysis, Microstructure and Hardness:

Figure 4.1 shows SEM micrographs, illustrating the difference between the microstructures of the D material (a) and the G material (b). Table 4-2 shows the image analysis results for both types of cast iron. These results show that the number of graphite nodules per square millimeter for the D material cast iron is almost half the number of that for the G material. However, the average nodule diameter of the D material is greater than that for G material. Table 4-2 shows also that the graphite nodules of the D material are more circular in cross section than the nodules of the G material cast iron. This is illustrated by the higher average aspect ratio of the D material nodules as compared to the average aspect ratio of the G material nodules. The SEM micrographs of Figure 4.1 show also higher amounts of carbides with more uniformly distribution within the microstructure of the D material compared to G material. Higher chromium content can cause this [2]. This can explain the relatively higher hardness of this type of cast iron, as can be seen from the Vickers hardness indentations shown in Figures 4.2 as well as Brinnel hardness measurements discussed below. Average Vickers hardness values, HV5 of 220 and 200 have been measured for the D and G materials respectively. Brin nel Hardness testing using a 30 kgf load was also arranged separately. Averages of 5 measurements on each of the two materials were done and values are as follows. G material had an average value of 133 HB whereas D material had an average value of 139
BH. The ASTM and BS standards [5, 6] require minimum values of 139 BH and 140 BH respectively. Figure 4.3 shows SEM micrographs, illustrating chromium carbide area and a distorted graphite nodule within the matrix of G-type. The EDX chemical analysis within the field area of these micrographs shows that Cr basically exists in carbides rather than being in the matrix. Same can be said about D material as both materials belong to equivalent grades of same material.

Figure 4.1: SEM micrographs showing the difference between the microstructures of the D material (a) and the G material (b) of the Ni-resist cast irons.
Table 4-2: Image analysis of the D and G-Types of the Ni-resist austenitic cast irons.

<table>
<thead>
<tr>
<th>Material</th>
<th>DMat'l</th>
<th>G Mat'l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field area (mm²)</td>
<td>4.505</td>
<td>4.505</td>
</tr>
<tr>
<td>Number of nodules</td>
<td>113</td>
<td>227</td>
</tr>
<tr>
<td>Number of nodules / mm²</td>
<td>25.08</td>
<td>50.39</td>
</tr>
<tr>
<td>Average nodule diameter (µm)</td>
<td>43.67</td>
<td>31.54</td>
</tr>
<tr>
<td>Average aspect ratio</td>
<td>0.717</td>
<td>0.645</td>
</tr>
<tr>
<td>Percentage area of graphite to the total field area</td>
<td>3.8 %</td>
<td>2.09 %</td>
</tr>
</tbody>
</table>

Figure 4.2: Vickers hardness indentations for (a) the D and (b) the G materials
(a) SEM micrograph showing carbides with the corresponding EDX analysis in the field area for the G material cast iron.

(b) SEM micrograph for a distorted graphite nodule with the corresponding EDX analysis in the field area for G material. This micrograph confirms that Cr exists in carbides only.

Figure 4.3: SEM micrographs of (a) chromium carbide area and (b) a distorted graphite nodule within the matrix of the G material.
4.3 **Mechanical Tensile Testing:**

The tensile tests results are shown in Figures 4.4 (a) and (b). They show stress strain curves with ultimate strengths of 347MPa for D material and 355MPa for G material were measured. They also show that G material has a higher ductility (9.2%) than D material (3.0%). The D ductility is below the minimum required by the standard. The figures however do not show clear yield points. This is typical of cast irons as discussed by Fontana [7]. Also, it was not possible to accurately identify modulus of Elasticity of both materials as there was no clear linear elasticity region.

To try to identify yield points the 0.2% offset method as per ASTM E8 [26] was used to approximate the yield points. In order to do that the stress strain curves of figures 4a and 4b were superimposed up to small strain values (strain scale expanded) as shown in Figure 4.5. Accordingly, it was found that the D material has higher 0.2 % offset yield strength of 260 MPa compared to G material for which the value is 220MPa. The modulus of D is found to be 131 GPa. The G material’s modulus is found to be 110 GPa. Both yield and modulus values show that the D material is on the upper side of the range whereas the G material is on the lower side of range reported in the standard [5, 6]

The variation in mechanical properties is attributed to the higher carbide content in D material in its microstructure compared to G material. This effect was reported by R. Covert et al [2]. However, even though curve of D material is the upper within the comparable strain ranges (up to 3%) the curve of G material having higher ductility makes its ultimate tensile strength slightly higher than that of D material.

Figure 4.6 shows stress strain curves obtained using sub-size specimens of both materials. The curves are shown with strain values between 1% to 2%. Strain gauges detached from the test specimens beyond these values. The curves are very similar to those obtained using standard 1/2" specimens indicating that size effects are negligible.
Figure 4.4: Stress strain curves for D material (a) and G material (b) shown till fracture. Curves D2 and G2 are offset by 1% and 2% respectively for clarity.
Figure 4.5: Stress-strain plots for the D (upper curves) and G (lower curves) specimens. 2 plots of each material are shown. The curves are shown to low strain values to show 0.2% offset yield points.
Figure 4.6: Stress strain curves of sub-size specimens of both D and G materials. 0.2% Yield stresses are indicated by arrows. Curves are limited to strains at which strain gauges detached from test specimens.
4.4 Electrochemical Testing:

Results of corrosion rates, rest potential and cyclic sweeps measurements are shown in figures 4.7, 4.8 and 4.9 respectively.

![Corrosion rate graph](image)

**Figure 4.7:** Corrosion rates of 4 specimens (2 from each type of cast iron)

![Potential graph](image)

**Figure 4.8:** Potentials of 4 specimens (2 from each D & G materials). Potentials are measured versus Ag/AgCl reference electrode.
The corrosion rates stabilized between 0.2 to 0.25 mmpy and the rest potentials ranged between -450 mV to -500 mV all with respect to Ag/AgCl reference electrode. Similar results have been reported by Covert[2].

Figure 4.9 shows the Tafel plots obtained from the cyclic sweeps. Both materials showed similar behavior in shape of curves without any distinctive pattern for either D or G materials. The rest potentials varied from -500mV to -650mV which is negligible knowing that the such variation is not uncommon in these materials as seen in Figure 2.11 in chapter 2. Similar behavior was reported by Smart [20] in synthetic sea water environment (3% NaCl) solution at 25 °C. Severe corrosion process took place at potentials greater than -400mV (Ag/AgCl RE) anodic to rest potential with blackish thin corrosion layer accompanied with rigorous bubbling at the surface of the counter electrode. The curves also indicate that Niresists are non passivating materials unlike stainless steels.
4.5 Examination of Specimens with Service Induced Cracks:

The two specimens sampled for examination of the crack surfaces were opened up as planned using the special holders prepared for the purpose. Figure 4.10 (a) shows sample of G material during this process. Figure 4.10 b/c shows fracture photographs surfaces of both materials taken after opening the cracks. They show corroded as well as mechanically fractured areas. Figure 4.11 shows micrographs of the microstructures of the two D and G materials with SCC induced during service. They indicate that all cracks pass through the matrix without preference to phases present. Figures 4.12 and 4.13 show SEM micrographs of fracture surfaces of both the cracked samples of D and G materials. They indicate distinctive regions of mechanical fracture and SCC fracture surfaces. The SCC surfaces are similar to those reported by Kauczor [21] as shown in Figure 4.14.

Figure 4.10: Opening up of G material using universal tensile test machine (a). D was opened similarly. Photo (a) show D material chemically cleaned and (b) G material as fractured prior to cleaning.
Figure 4.11: Service induced SCC cracks of D material at (a) 30X, (c) 100X, (e) at 200X and those of G material at (b) 30X, (d) at 100X and (f) at 200X. Cracks propagate through matrix without preference to phases.
Figure 4.12: SEM micrographs of D material failed during service. The top photo shows dimpled mechanically (upper-right area) and flat SCC fractured areas (lower-left) magnified at X35 whereas the bottom photos shows (b) an area fractured by SCC alone and (c) an area fractured mechanically alone magnified at X200. Mechanical fractures were produced using universal testing machine.
Figure 4.13: SEM micrographs of G material failed during service. The top photo shows dimpled mechanical (upper-left area) and flat SCC fractured areas (lower-right) magnified at X35 whereas the bottom photos shows (b) an area fractured by SCC alone and (c) an area fractured mechanically alone magnified at X200. Mechanical fractures were produced using universal testing machine.
4.6 Effectiveness of Devised SCC Testing Apparatus:

During initial testing trial on a sacrificial G specimen two problems had been faced. These are listed below.

1. The first was heater not heating after a day or two. Investigation revealed damage of element by corrosion attack of copper coil of the element. This was solved by provision of a small SS316 cylinder to encase the heater element and a coolant fluid.

2. Cell getting drained of brine. This was solved by introducing vent tube and draining bottle at outlet tube.

Testing on the second G specimen (designated G1) was successful with close monitoring (by attending start up and first 8 to 10 hours and then lab visits every 5 to 7 hours). The apparatus devised and used in this study successfully achieved the intended purpose which is conducting SCC using the constant load method using a proof ring. Figures 4.15 and 4.16 show the development of brownish corrosion layer on the specimen at start of test and during the test.
Figure 4.15: A photo taken while SCC test is in progress. The tensile specimen is seen in the cell with brownish layer of corrosion products.
Figure 4.16: A picture (a) at a close distance focused at the exposed portion of the specimen at onset of test. The surface is still shiny and yet to be covered by corrosion products (ferrous oxides). The RE is seen to the left. Photo (b) of specimen after 15 minutes with a developed dark layer of ferrous oxide and photo (c) after 30 minutes with the blackish layer of ferrous oxide getting covered with (tiny globes) reddish ferrous oxide. In photo (d) the specimen is covered with stable thick red-brownish layer after 4 hours.
4.7 SCC Testing Results

Following SCC testing of tensile specimens the times to failure of specimens were determined to nearest 30 minutes. This was based on review of photographs of specimens showing full fracture. Some typical photographs of a specimen before and after failure to full fracture during testing are shown in figures 4.17 and 4.18. Photographs of all specimens removed after the SCC tests are shown in Figure 4.19. Figure 4.20 shows specimens D2 to D4 after cleaning them using silicon carbide paper up to 400 grit size and after conducting dye penetrant crack detection method. No cracks were detected. The life times to full fracture of the various specimens tested are indicated in Table 4-3. SEM micrographs of fracture surfaces of both D and G materials are shown in figures 4.21 to 4.25. In addition to SCC the specimens were simultaneously subjected to uniform corrosion under anodic polarization applied to accelerate the SCC. The effect of uniform corrosion on specimens' sectional area was examined by measuring their diameters after the SCC tests. Details are shown in Table 4-4.

Figure 4.17: Two photograph of specimen during SCC testing: (a) before and (b) after full fracture.

Figure 4.18: Another specimen during SCC testing: (a) before and (b) after fracture.
Figure 4.19: photographs of the 4 fractured G material specimens (a) and those of 4 D material specimens with only D1 fractured.
Figure 4.20: A photograph of specimens D2, D3 and D4 after application of dye penetrant method for crack detection. No cracks detected.

Table 4-3: Performance of G and D materials with regards to SCC resistance (time to failure).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Applied Stress, MPa</th>
<th>Stress, 0.2% offset Yield stress*</th>
<th>Time To Failure, hours</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>225</td>
<td>102.3</td>
<td>37.6</td>
<td>Full Fracture</td>
</tr>
<tr>
<td>G2</td>
<td>216.5</td>
<td>98.4</td>
<td>86.5</td>
<td>Full Fracture</td>
</tr>
<tr>
<td>G3</td>
<td>190.8</td>
<td>86.7</td>
<td>100.5</td>
<td>Full Fracture</td>
</tr>
<tr>
<td>G4</td>
<td>190.3</td>
<td>86.5</td>
<td>72.5</td>
<td>Full Fracture</td>
</tr>
<tr>
<td>D1</td>
<td>224.5</td>
<td>86.4</td>
<td>167.5</td>
<td>Full Fracture</td>
</tr>
<tr>
<td>D2</td>
<td>216.5</td>
<td>83.4</td>
<td>184.8</td>
<td>No failure. Test stopped.</td>
</tr>
<tr>
<td>D3</td>
<td>190.6</td>
<td>73.3</td>
<td>254</td>
<td>No failure. Test stopped.</td>
</tr>
<tr>
<td>D4</td>
<td>205.9</td>
<td>79.2</td>
<td>209</td>
<td>No failure. Test stopped.</td>
</tr>
</tbody>
</table>

* Percentage of yield stress of materials D & G as applicable. Stress (0.2% offset yield) of G = 220 MPa. Stress (0.2 offset yield) of D = 260 MPa (refer mechanical results)
Figure 4.21: SEM micrographs of G material specimen G1 (a) at X70 showing both SCC area at upper right and mechanically fractured area at lower left. Photo (b) is an X200 magnification of selected SCC area of photo (a).
Figure 4.22: SEM micrographs of G material specimen G2 (a) at X70 showing both SCC area at upper right and mechanically fractured area at lower left. Photo (b) is an X200 magnification of elected SCC area of photo (a).
Figure 4.23: SEM micrographs of G material specimen G3 (a) at X70 showing both SCC area at upper right and mechanically fractured area at lower left. Photo (b) is an X200 magnification of elected SCC area of photo (a).
Figure 4.24: SEM micrographs of G material specimen G4 (a) at X70 showing both SCC area at upper right and mechanically fractured area at lower left. Photo (b) is an X200 magnification of elected SCC area of photo (a).
Figure 4.25: SEM micrographs of D material specimen D1 (a) at X50 showing both SCC area at upper part and mechanically fractured area at lower part. Photo (b) is an X250 magnification of elected SCC area of photo (a).
Table 4-4: Effect of specimen section reduction due to uniform corrosion on final state of stress.

<table>
<thead>
<tr>
<th>Spin</th>
<th>Load, N</th>
<th>Initial Dia. mm</th>
<th>Initial Stress</th>
<th>Final Dia. mm</th>
<th>Reduction in Diameter, %</th>
<th>Stress Rise*, MPa</th>
<th>Final Stress*, % Ultimate Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>6836</td>
<td>6.22</td>
<td>225</td>
<td>6.11</td>
<td>1.77</td>
<td>8.2</td>
<td>65.7</td>
</tr>
<tr>
<td>G2</td>
<td>6452</td>
<td>6.16</td>
<td>216.5</td>
<td>5.86</td>
<td>4.87</td>
<td>22.7</td>
<td>67.4</td>
</tr>
<tr>
<td>G3</td>
<td>5723</td>
<td>6.18</td>
<td>190.8</td>
<td>6</td>
<td>2.91</td>
<td>11.6</td>
<td>57.0</td>
</tr>
<tr>
<td>G4</td>
<td>5856</td>
<td>6.26</td>
<td>190.3</td>
<td>6.18</td>
<td>1.28</td>
<td>5.0</td>
<td>55.0</td>
</tr>
<tr>
<td>D1</td>
<td>6757</td>
<td>6.19</td>
<td>224.5</td>
<td>6.09</td>
<td>1.62</td>
<td>7.4</td>
<td>66.9</td>
</tr>
<tr>
<td>D2</td>
<td>6190</td>
<td>6.19</td>
<td>216.5</td>
<td>5.8</td>
<td>6.30</td>
<td>17.8</td>
<td>67.5</td>
</tr>
<tr>
<td>D3</td>
<td>5940</td>
<td>6.3</td>
<td>190.6</td>
<td>6.15</td>
<td>2.38</td>
<td>9.4</td>
<td>57.6</td>
</tr>
<tr>
<td>D4</td>
<td>6379</td>
<td>6.28</td>
<td>205.9</td>
<td>6.09</td>
<td>3.03</td>
<td>13.0</td>
<td>63.1</td>
</tr>
</tbody>
</table>

*Excluding stress rise due to crack effect on section reduction.

** Average percent rise in stress is found to be 5.7% in both materials.

As can be seen from the table 4-2 all G specimens fractured during the tests. Out of the 4 D specimens only specimen D1 fractured. The SEM micrographs of fractured surfaces clearly indicate two different crack surface morphologies. While much of the fracture surface has dimpled non-flat areas characteristic of purely mechanical fracture, there are flat areas extending from edges of specimen. They also contain sudden vertical steps and transverse cracks do exist in the flat areas in many instances. All of these findings match the original pump casings crack features as was seen in figures 4.12 and 4.13. They also are characteristic of transgranular SCC agreeing with those available in literature as reported by Kauczor [7]. The results also tend to agree with times to failures observed in actual plant service with D material outperforming G material (G failed in 5 years whereas D failed in around 18). Hence it can be said that as other
factors are neutralized the material factor has a significant role in the contrasting performance of NDI's with respect to resistance to SCC. Furthermore, the used test method and apparatus can be considered successful in achieving the intended purpose of obtaining viable results that allow comparative ranking of materials resistance to SCC in brine or similar environments.

The discussion below is an effort to explain the above variation in performance of these two materials.

As was discussed in the mechanical testing results section the 0.2% offset yield stress of D material is higher than G material by 40 MPa. According to Miyasaka [4] the log of time to failure by SCC is inversely proportional to applied stress. Even though the ultimate stresses of both materials are approximately equal the yield stress would practically have a more pronounced effect on SCC resistance. This viewpoint is supported by the fact that SCC takes place at stresses much lower than yield stress as seen in Table 4-2 above and reported by Miyasaka [4]. For a stress value of say 260 MPa the G material would be subject to a strain value of around 1% whereas D material would be strained to a value of 0.33% only. This is shown in Figure 4.26. With higher strain values in G material the bonding between the atoms in the matrix would be stretched 3 times more than D material. This would certainly make G material more prone to SCC compared to D material.

Another possible reason for this contrasting behavior in SCC resistance is characteristics of graphite nodules in each material. As indicated in the microstructure section of this chapter, the nodules of D material are bigger and fewer than G material. The former has an average diameter that is around 40% larger than the latter's average diameter. Also number of D material nodules are half that of G nodules in the same size of field area. As the SCC is a surface phenomenon, i.e. it takes place at surface of material that is in contact with the corrosive environment, the size of graphite nodules and their number may be significant. The nodules are non-load bearing and incoherent phase in the iron as clearly seen in SEM micrographs above which illustrate voids left by nodules and gaps between the matrix and periphery of exposed nodules. Raman [23] has studied the caustic SCC of ductile iron. He found that "where crack encountered graphite nodules, further propagation involved decohesion in the nodule-matrix
interface." As such, surface nodules can be considered as micro-cracks or notches. From a fracture mechanics viewpoint the smaller the diameter of these natural notches the more is the stress concentration at these points. Also the nodule count may also have contributed to the different behavior in resistance to SCC. The higher the number of nodules in the exposed surfaces of the material higher the possibility of a crack to initiate at the surface. Furthermore, the higher the number of nodules in the matrix the higher is the possibility of crack propagation. This is supported by Raman's findings [23]. The above makes the time to failure by SCC of G material shorter compared to D material.

Figure 4.26: A reconstruction of Figure 4.5 showing strain values (indicated with circles) of 0.33% for D and 1% for G materials at a stress value of 260 MPa.
Standard ASTM G49 [30] discusses stress considerations during SCC testing emphasizing on the effects of uniform corrosion accelerated by polarization on final state of stress in tested specimens. It can be seen from the Table 4-4 that the average percent in diameter reduction in D material (3.33%) is relatively higher than that observed in G material (2.71%). The consequent average stress rise in D material (14.6MPa) is also relatively higher than G material (11.88MPa). However, such stresses are still much below the ultimate stresses of both materials with percentages in the range 55% to about 68% of the respective ultimate strengths. This indicates that the results obtained are not biased by area reduction due to uniform corrosion.

Covert [2] indicated that "assigning of degrees of susceptibility (to SCC) is of questionable merit." To the contrary to this statement the results in this study indicate that ranking of Niresists with respect to SCC resistance is viable. This is also in agreement with what Miyasaka [4] had reported.

Further, the results clearly indicate that the relevant standards for Ductile Niresists do not provide the required protection against SCC in marine service even after subjecting the cast materials to suitable stress relief heat treatments again in contrary to what Covert reported [2].

For better field performance the standards need modifications based on further studies with regards to carbide contents, nodule features and mechanical properties so as to arrive at an optimized microstructure leading to best resistance of NDI to SCC in marine service. Such modifications would necessitate more stringent quality control and assurance procedures in manufacturing facilities. On the other hand the surface modification techniques may give favorable results. As an example, Kim [24] had found that a super rapid induction quench treatment gives nodular cast irons a better resistance to fatigue failure. A hard layer at surface would provide compressive stresses and also encapsulate the nodules with martensitic shells retarding crack propagation. Application of such a treatment may be promising in the case of NDI’s. On the other hand, use of alternative materials of better performance should be evaluated. As an example, super DSS has found wider use in marine service in [12] recent years and many brine and sea water pumps got their failed NDI casings replaced with such superior materials.
Chapter 5

CONCLUSIONS AND RECOMMENDATIONS
5. Conclusions and Recommendations

5.1 Conclusions

Two cases of SCC failures of brine pumps in desalination plants were investigated in this study. Such failures cause operational problems and costly shutdowns and repairs. The study included microstructural, mechanical, electrochemical and SCC testing. Based on findings from this study following conclusions are made:

1. The microstructure of both types of cast irons is different in terms of nodularity of graphite nodules, nodule count per square millimeter and content, uniformity and distribution of chromium carbides. This difference in microstructure is reflected in a variation in hardness and tensile strength of both alloys. The D material has relatively higher bulk hardness.

2. Though the ultimate stresses are very close to each other, the mechanical tests showed significant variations in yield stress values, moduli of elasticity and ductility. D material has higher 0.2% yield stress, higher stiffness but lower ductility than G material.

3. Electrochemical corrosion tests in brine solution at room temperature have shown similar corrosion behavior, in term of corrosion rates and potentials. Tafel plots showed similar non-passivating behavior.

4. Stress corrosion cracking tests have indicated that D material lasted longer than G material before cracking.

5. SCC tests have also indicated effectiveness of devised testing apparatus and stressing proof rings used in this study.
6. Further, SEM micrographs indicated that SCC failed specimens had distinctive fracture surface features composed of flat surface which may have cracks and steps as well as mechanically fractured surface with dimpled surface which is similar to fracture surfaces seen in NDI and ordinary cast irons that fail under pure tensile loading.

7. The difference in behavior in resistance to SCC is attributed to mechanical and microstructural properties.

8. Effects of uniform corrosion on tensile SCC specimens and consequent reduction in diameters and increase in final state of stress is found similar in both materials. As such results were not biased by such effects.

5.2 Recommendations

The study has concluded that D material possessed better resistance to SCC in brine than G material. This different behavior was attributed to the higher yield strength of D material and its favorable microstructure. Further studies are needed on the following:

1. Effects of carbides features and nodules feature in NDI on resistance to SCC. This will allow optimization of SCC resistance of these materials.

2. Austenitic and duplex SS materials are gaining more popularity as pump casings materials than NDI in such service. It is therefore recommended to study the resistance of austenitic and duplex stainless steels to SCC in brine service using the test apparatus devised in this study.
3. J. Kim and J. Ji [24] have studied the effect of surface modification by application of the super rapid quench treatment on fatigue resistance of ductile iron. Similar study on effect of such treatment on NDI resistance to SCC may be conducted as it may offer improved resistance.
References


12. Private communication from Bryan Johnson, CSS Technical Support, Sulzer UK Pumps


18. Wen-Ta Tsai, Corrosion Science 42 (2000) 545-559


21. Case Histories in Failure Analysis. Includes articles by various authors. Reorganized by ASM, 1979


الملخص

لقد كانت هناك حالات تدخل غير متوقعة المتعلقة بالمضخات، وحدثت خلال تحليل المياه في الخليج العربي. هذه المضخات مصنوعة من مادة الصلبة المكونة من الزئبق المرتبط، وهو نوع من المضخات المصغرة اختراعها من NDI (Brine).

البيئة التاكلية هي مياه بحر عاليهالترسب. المضخات الأمريكية (NDI-D) والإنجليزية (NDI-G) حسب المواصفات الأمريكية (NDI-D) والإنجليزية (NDI-G) حسب المواصفات البريطانية. المضخات الأولى تظهرت خلال حوالي 18 عاماً في حين الأخرى خلال حوالي 5 أعوام. في هذه الدراسة تم تقييم الفرق بشكل مباشر بين الخصائص الميكانيكية والنكروكيميائية. أظهرت الدراسة فوارق في الخصائص الميكانيكية والنكروكيميائية وتشابه في الخصائص الكهروكيميائية بالإضافة إلى فارق كبير في مقاومة التشقق التاكل الإجهاد. إن هذا الفارق سبب ارتفاع الخصائص الميكانيكية والنكروكيميائية والخصائص الكهروكيميائية بالإضافة إلى الفارق. أثبتت الدراسة بشكل مباشر أن المواد كانت مضخنة في هذا الصرف المحلول في الاداء في مقاومة التشقق التاكل الإجهاد.
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رسالة مقدمة من الطالب

يحيى عبد الله الزفئين

إلى

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