

Preparation of functionalized nanoparticles and Their Use in Corrosion Treatment

BY

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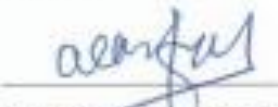
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Dedication

I dedicate this thesis to, my Mother, wife and all family and friends.

I dedicate this thesis to everyone who lends a helping hand, and to those who believe me and led me towards success.

special thanks to my Advisor Prof: Tawfik Abdo Saleh and team member Dr. Abdulrahman Al-Arfaj and Dr. Moataz Qurishi and colleagues for their support and encouragement in my life.

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LIST OF ABBREVIATIONS]

XRF: X-ray Fluorescence

XRD: X-ray Diffraction

SS: Stainless Steel

FTIR: Fourier Transform Infrared Spectroscopy

C.S: Carbon Sulphur Analyzer

LOW: Loss of Wight

SEM: Scanning Electron Microscopy

HM: Hardness Measurements

HAZ: Heat Affected Zone

HCl: Hydrochloric Acid

MSA: Methane sulfonic acid

AA: Acetic Acid

SS: Stainless Steel

ABSTRACT

Full Name : [Abdulaziz Abduulah Alharbi]

Thesis Title : [Preparation of functionalized nanoparticles and Their Use in Corrosion Treatment]

Major Field : [Chemistry]

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Corrosion is one of the greatest adversaries that metals and alloys are still facing in the modern era. Recently, various preventive measurements have been employed to mitigate or inhibit corrosion progression. However, there are certain limitations, such as poor adhesion, incompatibility with the surface, and carcinogenicity of corrosion inhibitors which have to be overwhelmed for effective corrosion prevention. In this regard, this research work or topic was chosen to create a variety of functionalized nanomaterials, such as branches that contain carboxyl, amines, and hydroxyls connected to nanoparticles. It was focused on the various approaches employed for the synthesis, modification, and functionalization of nanostructured such as modified graphene oxide. The potential inhibition applications and their enhancement upon modification of nanostructures have also been discussed in detail. Different Techniques and procedures like Fourier Transform Infrared Spectroscopy(FTIR), Scanning Electron Microscopy(SEM), and Loss of Weight (LOW) are examples of this analysis. The performance of the nanoparticles will be examined for potential use as inhibitors of effective solid corrosion in oil and petrochemical settings.

The research also aims to assess the behavior of stainless steel at different temperatures and also using different chemical solvents with low and high acidity. such as hydrochloric acid (HCl), acetic acid (AA), and methane sulphonic acid (MSA). The advantages of surface functionalization and their applications are also highlighted. This work will be further discussed in metal adjustments using X-Ray diffraction (XRD) and X-Ray Fluorescence.

ملخص الرسالة

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يعد التآكل أحد أكبر الخصوم التي لا تزال المعادن والسبائك تواجهها في العصر الحديث. في الآونة الأخيرة تم استخدام قياسات وقائية مختلفة لتخفيف أو منع تقدم التآكل. ومع ذلك هناك بعض القيود مثل ضعف الالتصاق ، وعدم التوافق مع السطح ، و ضعف مثبتات التآكل التي يجب التغلب عليها لمنع التآكل بشكل فعال .

في هذا الصدد تم اختيار هذا العمل البحثي أو الموضوع لإنشاء مجموعة متنوعة من المواد النانوية الوظيفية ، مثل الفروع التي تحتوي على الكربوكسيل والأمينات والهيدروكسيل المتصلة على الجرافين وقد ركز على الأساليب المختلفة المستخدمة في تخليق وتعديل وتوظيف الجرافين المعدل. كما تمت مناقشة التطبيقات المحتملة وتعزيزها عند تعديل الهياكل النانوية بالتفصيل .

تم ذلك عن طريق استخدام التقنيات المختلفة مثل : اشعة المطياف تحت الحمراء ومجهر المسح الإلكتروني وفقدان الوزن
كما يهدف البحث إلى تقييم سلوك الفولاذ المقاوم للصدأ في درجات حرارة مختلفة وكذلك استخدام مذيبات كيميائية مختلفة ذات حموضة منخفضة وعالية. مثل حمض الهيدروكلوريك وحمض الخليك وحمض الميثان سلفونيك.

يتم هنا تسليط الضوء على المجموعات المختلفة من الجسيمات النانوية ومزايا التشغيل الوظيفي السطحي وتطبيقاتها , ستم مناقشة هذا العمل بمزيد من التفصيل في تعديلات المعادن باستخدام حيود الأشعة الإنكسارية والحيود السينية

CHAPTER1

INTRODUCTION

Corrosion is defined as the degradation of metals caused by electrochemical, chemical, and metallurgical interactions with their surroundings. Steel corrosion is of a significant environmental and economic impact due to its widespread use in many industries. Carbon steel is the most widely used material in the construction of oil and gas wells and petrochemical plants due to its inexpensive cost compared to other materials with similar physical and chemical properties, despite its poor corrosion resistance. In the gas and oil industry, corrosion is estimated to cost the industry £1.3 billion per year in the world due to corrosive chemicals found in crude oil.

The most essential stimulation procedure for increasing oil production is acidizing a petroleum oil well. Acidizing is a method of increasing oil output by injecting acid at a high temperature in the well bore for dissolving rubbles originating in an aged well and building channels in the rocks to let gas and oil reaching the well. Acids are also used to clean the muck out of newly drilled wells before they are put to use for production. Various acids are employed in acidizing treatments, depending on the well's composition and the treatment goal. Examples are hydrofluoric acid (HF), hydrochloric acid (HCl), Sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$), acetic acid (CH_3COOH), chloroacetic acid (ClCH_2COOH), and formic acid (HCOOH).

The most commonly used acid is HCl (with a concentration range between 5 to 28%). The oil well, which is normally composed of carbon steel, is exposed to the hostile corrosive atmosphere using this acidizing procedure. Hydrocarbons with a specified proportion of dissolved carbon dioxide (CO_2) are referred to as "sweet" in the gas and oil industry. "Sour" hydrocarbons have a certain quantity of dissolved hydrogen sulphide (H_2S) in them. CO_2 and H_2S in oil and gas

reservoirs are the results of many physicochemical processes that occur in the formation. Microbial activity can also produce H_2S , a process known as "reservoir sourness." Though gas and oil transported through pipelines undergo numerous treatments to eliminate impurities, they still include pollutants that might compromise the steel pipes' physical integrity because of corrosion. Once a steel pipeline conveys a mixture of water and hydrocarbons with dissolved CO_2 or H_2S , the gases dissolve in the phase, lowering pH and increasing corrosiveness. Metals can be damaged by H_2S corrosion in a variety of ways, including uniform corrosion, pitting, and stepwise cracking. If not treated properly, hydrogen sulfide can result in life-threatening conditions. Workers exposed to H_2S might suffer catastrophic short- and long-term consequences, such as fast unconsciousness, coma, and even death. Corrosion inhibitors, corrosion-resistant materials, coatings, cathodic protection, and using of a corrosion inhibitor are the common ways of controlling corrosion, with inhibitors being the practical, cheap, and effective way of protecting oil wells from corrosion.

During the acidizing process, inhibitors are added to the acid solution to lessen the acid's aggressive attack on oil wells. Acetylene alcohols, alkenyl phenones, aromatic aldehydes, nitrogen-containing heterocyclic, and condensation products of carbonyls and amines are all excellent acidifying inhibitors that are commonly found in commercial formulations. However, these inhibitors are only effective at high concentrations, are poisonous, and are not ecologically friendly. This has necessitated the development of novel, nontoxic, and ecologically friendly corrosion inhibitors. Corrosion inhibitors derived from naturally occurring biological substances have been studied. The majority of them are organic compounds with heteroatoms like nitrogen, sulfur, phosphorus, and/or oxygen atoms. Carboxylates (such as amino or fatty acids) are effective corrosion inhibitors, particularly those having a long hydrophobic alkyl chain and a hydrophobic methyl end-group, such as sodium octanoate and sodium decanoate. They produce self-assembled monolayers (SAMs), which have higher corrosion prevention efficacy due to hydrophobic activities. They act as a barrier between the bulk electrolyte and the metal surface, preventing the transfer of hydrated corrosive species. Self-assembly monolayers (SAMs) can be utilized as efficient inhibitors for several applications. Sodium Octanoate is a good corrosion inhibitor for carbon steel corrosion. reported the use of sodium caprylate as a corrosion inhibitor

against internal corrosion of carbon steel in a 3.5% NaCl solution. In this thesis work, nanomaterials will be synthesized and evaluated as corrosion inhibitors.

1.1 Thesis Objectives

The main objective of the thesis project is to synthesize a series of functionalized nanomaterials such as carboxylates, amines, hydroxyls, etc. attached to nanoparticles. The proposed materials will be characterized using different techniques including FTIR, Raman, SEM, TEM, etc. The proposed materials will be investigated for the possible use as corrosion inhibitors for steel corrosion in acidic media (15% Hydrochloric Acid 15% Acetic acid and Methane Sulfonic Acid 15%). The main objective will be achieved by addressing the following specific objectives:

- (i) To synthesize and characterized new samples of stainless steel (SS) and inhibitors to different pH solution
- (ii) To characterize the SS Using different techniques such as XRD, XRF, CS, and SEM Analyzers.

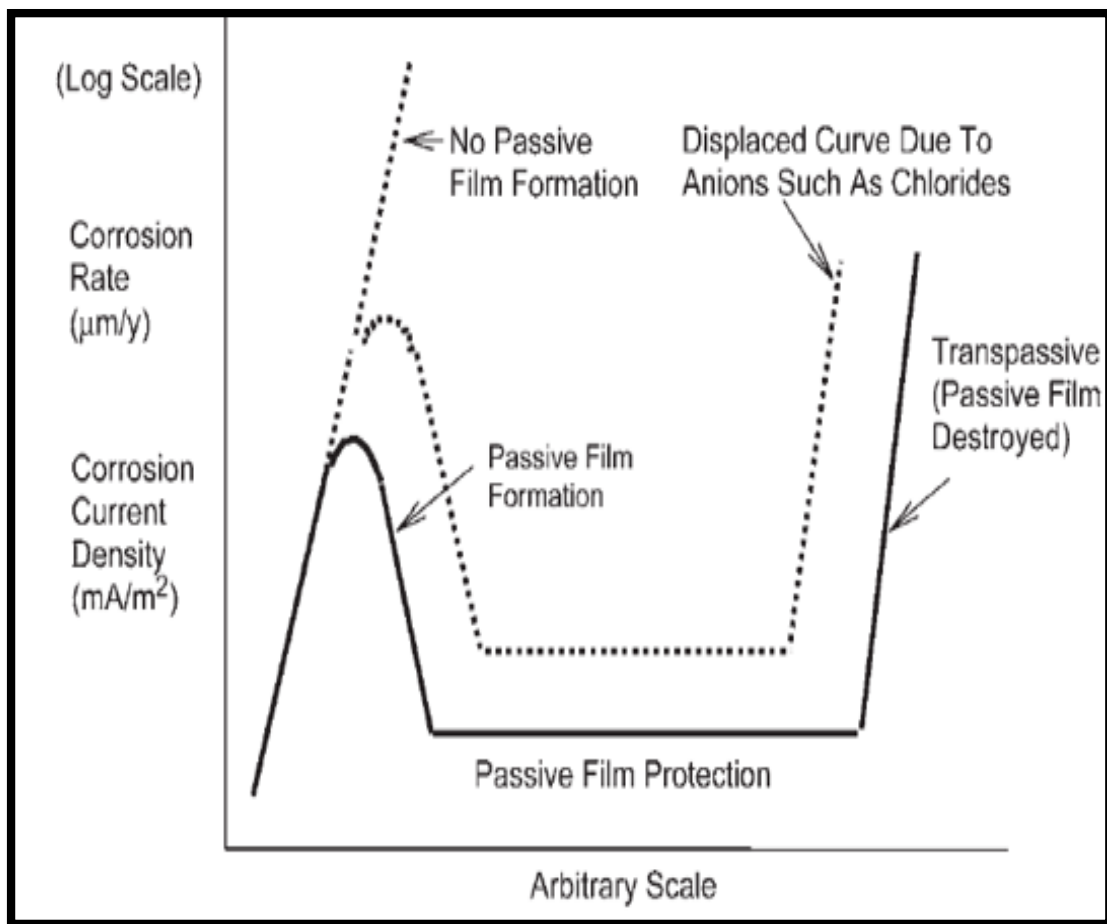
1.2 Types of Stainless Steel (SS)

Corrosion properties of the SSs can be increased by the addition of suitable alloying elements which have a direct influence on the passive film properties. Commonly used alloying elements are Nickel (Ni), Silicon (Si), Molybdenum (Mo) Carbon (C), Nitrogen (N), Titanium (Ti), Aluminum (Al), & Copper (Cu). These alloying elements impart different properties by affecting the microstructure of the materials. Based on microstructure and processing techniques SSs are divided into four major categories. In this case, we will explain one of them.

1. Ferritic SSs
2. Austenitic SSs
3. Martensitic SSs
4. Duplex SS

1.3 Passive Film on Stainless Steel (SS):

The passivation process improves the corrosion resistance of stainless steel parts and returns them to their original corrosion standards. Parts made of stainless steel must be immersed in a citric acid or nitric acid chemical solution for a predetermined amount of time and at a predetermined temperature in order to passivate them. However, it does not remove the heat tint or oxide scale that may have been left behind by welding or heat treatment. This cleans the surface of foreign material like free iron. In the end, the passivation procedure does not alter a part's look or make it noticeably brighter; it only increases corrosion resistance and leaves a clean surface. Comparatively, electro polishing improves the appearance of items manufactured of a larger variety of stainless steel and other metal alloys by removing burrs, heat tint, and oxide scale, Figure 1. While passivating stainless steel can increase its resistance to corrosion, not all grades are suitable for this process, and some parts might need additional cleaning procedures first.]



[CHAPTER2

LITERATURE REVIEW]

2.1 Types of Corrosion

There are several types of corrosion; general, crevice, pitting, stress-corrosion cracking, galvanic, intergranular, dealloying, and erosion. Three of them; crevice, pitting, and stress-corrosion cracking form a group called localized corrosion. In 4 all the localized corrosion types the metal is attacked in certain positions, whereas some of the other types form a uniform corrosion that spreads over the entire metal surface.

2.1.1: Pitting Corrosion

Pitting is a corrosion that occurs where there is for example a local breakdown of the passive film on the metal surface. This breakdown could happen because of ions in the electrolyte. For stainless steel, those anions are often chloride ions. The breakdown also has a dependence on the inhomogeneity's in the atomic structure of the metal. Pitting usually does not occur on surfaces without a strong protecting layer, in these cases, uniform corrosion is more common. For pitting to begin, a critical pitting potential must be reached since that is the potential when the electrochemical process breaks through the protective layer. [1] Pitting can also be initiated if the protective layer is scratched or if there is inhomogeneity's in the composition of the atoms. Pitting is a corrosion type that is very dangerous for materials. Although it does not spread over the entire surface, pitting can cause deep damage to the material that one cannot easily see. A stainless steel surface attacked by pitting corrosion can be seen in Figure 2.



Figure 2: the surface of stainless steel showing clear signs of pitting corrosion.

The initiation of pitting includes three theories; penetration, adsorption, and film breaking. The penetration mechanism is when the ions are penetrating the passive film, causing dislocations between the metal and the oxide film. The adsorption mechanism of the passive layer starts with chloride ions that adsorb onto the layer and forms complexes with the oxide film, thus leading to the dissolution of the film. The dissolving of the passive film further makes the passive film thinner in local areas until the metal is reached and the pitting can begin. The film-breaking mechanism evolves from the principle that chloride ions enter through already existing cracks in the film. Figure 3 shows the three different pitting initiations explained by E. McCafferty.

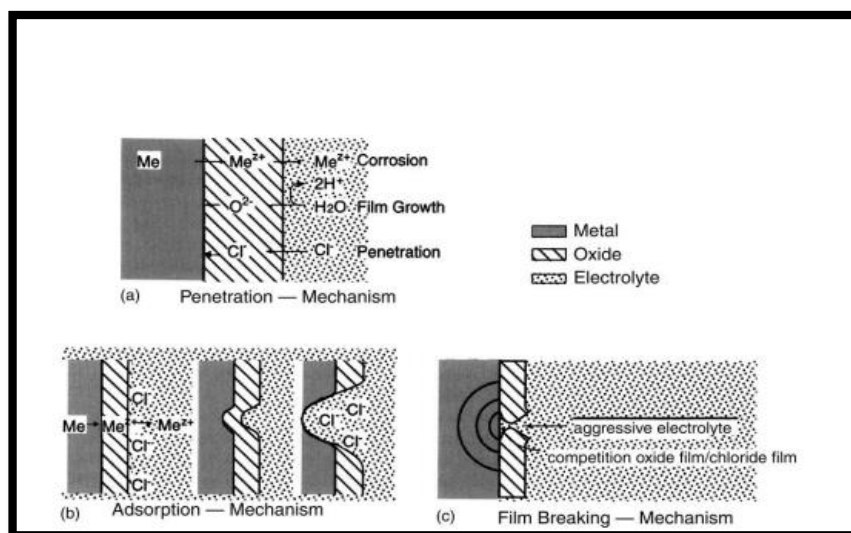


Figure 3: Visualization of the three types of pitting initiation (11)

2.1.2: Crevice Corrosion

Crevice corrosion refers to the attack of metal surfaces by a stagnant solution in crevices, for example around the edges of nuts and rivet heads. When dust, sand, and other corrosive substances are deposited on surfaces, they create an environment where water will accumulate and corrode the part. It can happen between two metals or between a metal and a nonmetal. This causes damage to the metallic part, which is initiated by the concentration gradient in chemicals



Figure 4: the surface of stainless steel showing clear signs of crevice corrosion.

2.1.3: Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is the growth of crack formation in a corrosive environment. It can lead to unexpected and sudden failure of normally ductile metal alloys subjected to tensile stress, especially at elevated temperatures. SCC is highly chemically specific in that certain alloys are likely to undergo SCC only when exposed to a small number of chemical environments. The chemical environment that causes SCC for a given alloy is often one which is only mildly corrosive to the metal. Hence, metal parts with severe SCC can appear bright and shiny, while being filled with microscopic cracks. This factor makes it common for SCC to go undetected prior to failure. SCC often progresses rapidly and is more common among alloys than pure metals.



Figure 5: the surface of stainless steel showing clear signs of stress corrosion cracking.

2.2: Preventing corrosion:

There are several ways to prevent the corrosion of metals. This section will explain some of them. However, it is important to think of the possibility to carry out these prevention techniques depending on the situation where the metal should be used.

- **Coating:**

It is possible to create a corrosion-resisting surface on the metal using different types of coating. Coating with polymers is commonly used and is a very effective way to protect the metal, although some problems are still related to the method. If the coating would crack and corrosion should start in the crack, there might be an environment with very little oxygen in the crack. This will be preferable for corrosion to continue. The coating inside a process can also cause other problems, such as migration into the product and there could be a problem with these coatings at high temperatures such as melting or breaking down.

- **Changes in the media in contact with the metal:**

In some situations, it might be possible to change the media that causes corrosion. The changes can be either an addition of corrosion inhibition substances or a removal of the amount of corroding substances. These changes can be very difficult in many processes since one might not want to change the product in any way [1]. For example, in food processes, one does not want to add the corrosion inhibition chromate to the media for obvious reasons.

- **Changes in the metal composition:**

As for the addition of molybdenum into the stainless steel to improve the corrosive protecting features against pitting, one can add several other substances to get similar effects. This is a very difficult method that requires a lot of research since one change in the alloy composition can alter a lot of the material properties. Some properties that might change are the conducting properties, mechanical properties, the alloys strength, or diffusivity. This method is therefore more expensive.

- **Designing to prevent corrosion:**

When one speaks of corrosion in both buildings and processes there is a major difference of the corrosion resistance depending on the design of the parts in the process. With smart designing of the process, one can avoid a lot of the corrosion. The interesting part of this type of corrosion protection is that it does not necessarily have to be an increased cost if this is taken into consideration before designing the process.

- **Passivation:**

Passivation is another method that can make the metal more resistant against corrosion. Since passivation is a major topic in this master thesis, it will be explained more thoroughly in chapter one.

- **Inhibitor:**

A corrosion inhibitor may be used to slow down the rate of corrosion of a metal exposed to that environment. A material that inhibits a chemical or corrosion process is called a slowing agent.

To lessen the severity of corrosion, corrosion inhibitors are frequently applied occasionally or continually to acids, cooling fluids, steam, and many other situations. Typically, they are applied to clean surfaces, let to permeate, and then left to dry. While many inhibitors are harmful, despite their great efficacy, care must be taken to safeguard both personal safety and the ecology.



Figure 6: Scale formation for inhibitors

2.3 Role of Alloying Elements and Their Characteristics

SSs contain various distinctive alloying components, each of which specifically affects the properties of the steel. The properties of a particular steel grade will accordingly be determined by the amount of alloying elements in that specific grade. A brief review of the alloying components and their effects on the properties and structure of the steel is given below with an explanation that why different elements are added to certain grades.

2.3.1: Chromium (Cr):

This is the most essential alloying element as it provides basic corrosion resistance to SSs. Generally better corrosion resistance is due to the higher content of Cr. At high temperature Cr also upgrades the steel's resistance to oxidation and promotes a Ferritic structure.

2.3.2 Nickel (Ni):

Ni promotes an Austenitic structure. It generally increases toughness and ductility. Ni also provides good effect in an acid environment and lowers the corrosion rate. Ni is used to form intermetallic compounds in precipitation-hardening steels to increase the strength of the steel.

2.3.3 Molybdenum (Mo):

Mo significantly increases the mechanical strength of steels and enhances the resistance to both localized and general corrosion. It also promotes a Ferritic structure and formation of secondary phases in Duplex, Ferritic and Austenitic SSs. At higher temperature, Mo increases the hardness in Martensitic SSs due to its effect on carbide precipitation.

2.3.4 Manganese (Mn):

Mn is used to improve hot ductility in stainless steels. Ferrite / Austenite balance that varies with temperature is affected by the Mn, at high temperatures, Mn is a Ferrite stabilizer and at low temperatures, it will stabilize Austenite. It is used to obtain high Nitrogen (N) contents in Austenitic steel and increases the solubility of N

2.3.5 Copper (Cu):

This element generally promotes Austenitic structure and enhances the corrosion resistance of steels in some acid environments. Cu is used to increase the strength of steel by forming intermetallic compounds in precipitation-hardening steels.

2.3.6 Nitrogen (N):

N promotes an austenitic structure because it is a very strong Austenite former. When N is used in combination with Mo then it enhances the resistance to localized corrosion. It is also used to increase the mechanical strength of steel. N will lead to a significant reduction in corrosion and toughness resistance in Ferritic stainless steels. In Martensitic Austenitic and Martensitic SSs, the addition of N will reduce the toughness of the steel and gradually increases the hardness and strength.

2.3.7 Carbon (C):

C is a strong Austenite former and promotes an Austenitic structure. It also helps in achieving better mechanical strength. Higher C content affects resistance to intergranular corrosion. Higher C content also reduces both corrosion resistance and toughness in Ferritic SSs whereas, in the Martensitic and Martensitic-Austenitic steels, it increases the strength and hardness. In Martensitic steels, strength and hardness is generally increased by reducing the toughness.

2.3.8 Titanium (Ti):

This element is a strong carbide and ferrite former and helps to promote a Ferritic structure and lower the effective carbon content. Ti is added in Austenitic steels to improve the resistance to intergranular corrosion, but at high temperature, it also enhances the mechanical properties of the steel. In Martensitic steels, Ti is used to increase the tempering resistance and reduces the Martensite hardness. By lowering the amount of interstitials in a solid solution, Ti is added to Ferritic stainless steels to improve toughness and corrosion resistance.

2.4 Methods of Determining Corrosion Rates:

Corrosion rates for metals undergoing uniform corrosion can be determined by any of the following methods:

2.4.1 Weight Loss

In this method, previously weighed metal samples are removed from the solution at various timed intervals, and the loss in weight due to metallic corrosion is determined (per unit area of the sample). For this method to be accurate, any solid corrosion products must be removed from the metal surface. If the corrosion products are loose and non-adherent, they can be removed by mechanical means. Tight and adherent corrosion products can be removed by chemical or electrochemical methods, which are usually specific to the metal or the alloy being tested.

2.4.2 Weight Gain Method

This method is generally not useful in aqueous corrosion studies but is more suited to dry oxidation where oxide films or products are more adherent than is in the case of aqueous corrosion. Laboratory weight gain measurements in dry environments have the useful feature that the gain in weight can be measured continuously and without the removal of the specimen from the environment.

2.4.3 Thickness Measurements

Measurement of the thickness of a metal as a function of time is a method to monitor the corrosion behavior of a system. This method is used to survey the practical corrosion behavior of a system in service, rather than as a laboratory technique. Has been used to track the progress of corrosion in railroad hopper cars, storage tanks, and pipelines. Thickness measurements are based on the response of a specimen to an ultrasonic or a magnetic signal

2.4.4 Electrochemical Technique

Each of the methods described previously has an application in either the laboratory or the field. But none of these methods can provide insights into the underlying mechanism of corrosion. Electrochemical techniques have this capability and in addition, offer the possibility of mitigating corrosion by controlling the electrode potential. There are various methods of determining the corrosion rate by electrochemical techniques, but here will consider only the direct current (DC) polarization method and its offshoots. Alternating current (AC) techniques, which are very powerful in determining corrosion rates and in monitoring the progress of corrosion.

CHAPTER 3

EXPERIMENTAL

3. EXPERIMENTAL SET-UP AND PROCEDURES

3.1 X-ray Fluorescence analyzer:

The chemical composition of the sample was determined utilizing Bruker S8-Tiger Wavelength Dispersive X-ray Fluorescence spectrometer (WDXRF). The technique is based on the principle that each element fluoresces characteristically when exposed to X-rays. X-ray fluorescence spectrometry is a non-destructive analytical technique used to identify and determine the concentrations of elements present in solid, powdered, oil, and liquid samples. XRF spectrometers operate by irradiating a sample with a beam of high-energy X-rays and exciting characteristic X-rays from those elements present in the sample (known as X-ray Fluorescence). In a wavelength diffraction X-ray fluorescence (WDXRF) spectrometer, this separation is achieved by diffraction, using an analyzer crystal that acts as a diffraction grating. The specific lattice of the crystal selects the correct wavelengths according to Bragg's law.

The present analysis was carried out using QUANTEXPRESS programmer, which is built on semi-quantitative method provided by the manufacturer. The powder-spent acetylene catalyst samples were placed in a suitable sample cup and measured by the spectrometer. The result of the elements present is reported as oxides. The analysis results in standard less analysis are normalized to 100%, not absolute quantification. The typical accuracies

- Depend on the sample type and are generally not predictable
- Within 5 - 20% of true value for Majors (> 10 wt%)
- Within 10 - 30% of true value for Minors (0.1 - 10 wt%)
- Usually within 20 - 300% of true value for Traces (< 0.1 wt%) Separation of the



Figure7: X-ray Fluorescence Bruker S8 Tiger

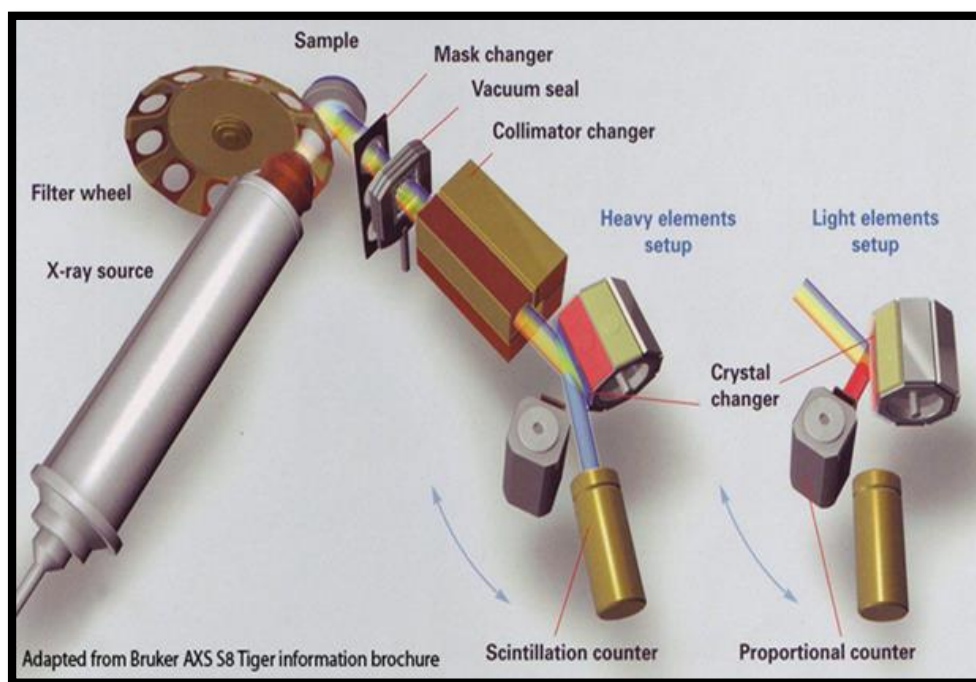


Figure 8: X-ray Fluorescence Bruker S8 Tiger

3.2 Carbon Sulphur Analyzers:

C-S analysis: measures the carbon and sulfur concentration in samples through combustion in an induction furnace and the subsequent analysis of the gaseous combustion products carbon dioxide and sulfur dioxide. The sample is melted in a pure oxygen atmosphere in the induction furnace of the elemental analyzer, causing sulfur to oxidise to sulfur dioxide (SO_2) and the carbon present is oxidised to a mixture of carbon monoxide (CO) and carbon dioxide (CO_2). The carbon dioxide and sulfur dioxide (SO_2) are then detected by infrared cells. The Wt% carbon and sulphur are calculated automatically by the software and are represented as direct read out.

Instrument- ELTRA 2000 CS analyzer

Crucible: Alumina



Figure9: Carbon Sulphur ELTRA CS 2000

3.3 Scanning Electron Microscope (SEM):

A concentrated electron beam is used to scan a sample's surface in a scanning electron microscope (SEM), which creates pictures of the sample. The sample's surface topography and chemical composition are revealed by the signals that are created as a result of the electrons' interactions with the sample's atoms. A picture is created by combining the position of the electron beam with the strength of the signal being detected as it is being scanned in a raster scan pattern. A secondary electron detector is used in the most popular SEM mode to find secondary electrons released by excited atoms (Everhart–Thornley detector). The topography of the specimen is one factor that affects the quantity of secondary electrons that may be detected and, consequently, the signal strength.



Figure10: Scanning Electron Microscope Analyzer QUANTA FEG 250

3.4 X-ray Diffraction (XRD):

X-Ray diffraction analysis (XRD) is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material. It is based on the constructive interference of monochromatic X-rays and a crystalline sample. X-rays are shorter wavelength electromagnetic radiation that are generated when electrically charged particles with sufficient energy are decelerated. In XRD, the generated X-rays are collimated and directed to a nanomaterial sample, where the interaction of the incident rays with the sample produces a diffracted ray, which is then detected, processed, and counted. The intensity of the diffracted rays scattered at different angles of material are plotted to display a diffraction pattern.



Figure 11: X-ray Diffraction Analyzer Rigaku Ultima.

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

Model: Niclot IS 10

SMART iTR

In ATR sampling, the infrared (IR) light travels through a crystal, is totally internally reflected at least once at the crystal-sample interface; and the reflected light travels to the FTIR detector. During the internal reflection, a part of the IR light travels into the sample, where it can be absorbed. This is called the evanescent wave. The penetration depth of the evanescent wave into the sample is defined by the refractive index difference between the sample and the ATR crystal. To account for different sample types and different path length requirements, several materials with different refractive indices are used as ATR sensors



Figure 12: Fourier Transform Infrared Spectroscopy Analyzer Niclot IS 10

CHAPTER4

RESULTS AND DISCUSSION

4.1 Visual Examination

4.1.1: Visual Examination SS 304 H:

The received Pipe sample was photographed in as-received condition as well after cut by the digital camera as shown in Figures 10-12, and several observations were found as follows: - The outer surface of the pipe (OS) shows signs of general corrosion, whereas the inner surface (IS) show the same sign only in the bottom side of the pipe. - The welding area which connects the small tube to the pipe, is repaired - Crack is partially noticeable in the bottom side of the welded area - Bulging at the (IS), opposite side of welding



Figure 13: Photo by digital camera showing the main pipe as received condition.

4.1.2: Visual Examination SS 304 L:



Figure 14: Photo by digital camera showing flange sample as received condition



Figure 15 : Photo by digital camera showing the Inner Surface (IS) of the flange condition, as received

4.2 Characterization of SS

4.2.1: Chemical Analysis:

For the purpose of investigating the chemical composition, two samples were cut and prepared. The Elemental Composition analysis was performed by utilizing Bruker- S8 Tiger XRF Spectrometer. And Carbon-Sulphur was determined utilizing Eltra Carbon /Sulphur ELTRA 2000 Analyzer.

The chemical composition of both samples material falls within the specified range of SS304H and SS304L as shown below in Table 1&2:

Table 1: Elemental Analysis by XRF for the main pipe for SS304 H

Chemical Composition		
Elements	Conc %	STD For SS304H
Fe	67.69	
Cr	19.19	18.0 - 20.0
Ni	9.78	11-8
Mn	1.62	2 Max
Mo	0.53	
Cu	0.496	
Si	0.43	1 Max
Al	0.091	
C	0.083	0.04 - 0.10
V	0.063	
Ti	0.02	
P	0.005	0.045 Max
S	0.002	0.03 Max

Table 2: Elemental Analysis by XRF for the flange's material SS304L

Chemical Composition		
Elements	Conc %	STD For SS304L
Fe	67.742	
Cr	19.95	18.0 - 20.0
Ni	9.95	
Mn	1.16	2 max
Si	0.57	1 max
Cu	0.23	
Al	0.18	
Mo	0.08	
C	0.03	0.03 max
V	0.064	
P	0.018	0.045 max
Ti	0.009	
S	0.017	0.030 max

4.2.2 Microstructure Examination for SS304 H:

To study the microstructural properties of the tube, seven samples were cut; five samples from the main pipe (two samples from the cracked area (at the bottom side of the pipe), two samples from the un cracked area for comparison, and one cross-sectioned sample from the bottom side of the pipe). The other two samples were cut from the small tube (one sample to analyze the welding area, and the other sample is cross sectioned from the top of the tube to analyze observed pitting). The samples were prepared as per ASTM E3, ground, polished, etched using oxalic acid as per ASTM E407-0 to reveal the microstructure. After that, the samples were examined using Leica Inverted Light Microscope (Leica CTR6500) as etched condition. The images that were taken as etched on all samples show typical austenitic microstructure with annealing twins. In addition to that, the five samples from the main pipe show an oxide layer at IS. For the cracked samples, wide cracks were observed in both IS & OS, and were mainly filled with oxide as confirmed by SEM-EDS analysis. The cracks in the IS are traveling through the grain boundaries (Intergranular Cracks), while most of the cracks in the OS are (Transgranular) in a dagger shape which is typical of thermal fatigue cracks. The analysis of the welded sample from the small tube shows the welded area, HAZ (Heat Affected Zone), and base metal. Results are shown in Figures (16-26).

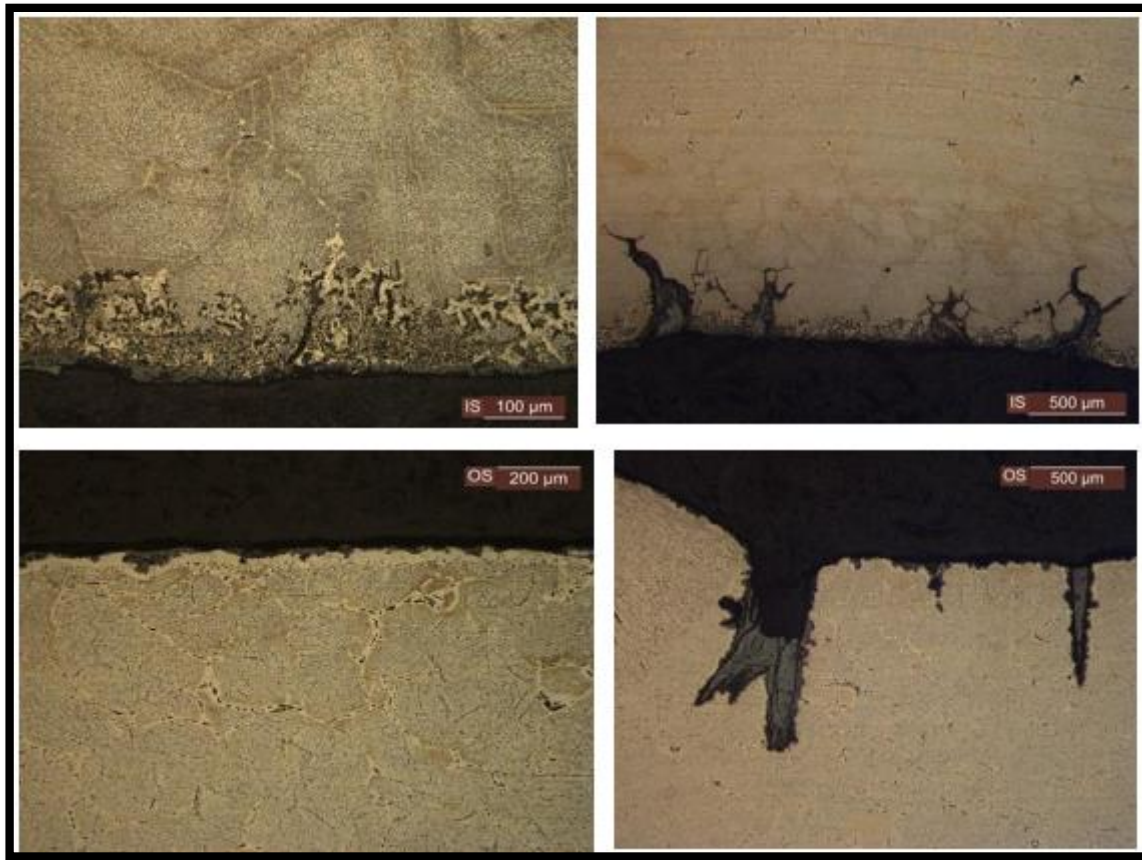


Figure 16: Photos by light microscope of the 1st cracked sample next to the welding that connects the pipe and the tube as etched condition. Note: cracks in top right picture (Intergranular) are going through the grain boundaries, while the circled crack in bottom right picture is (transgranular).

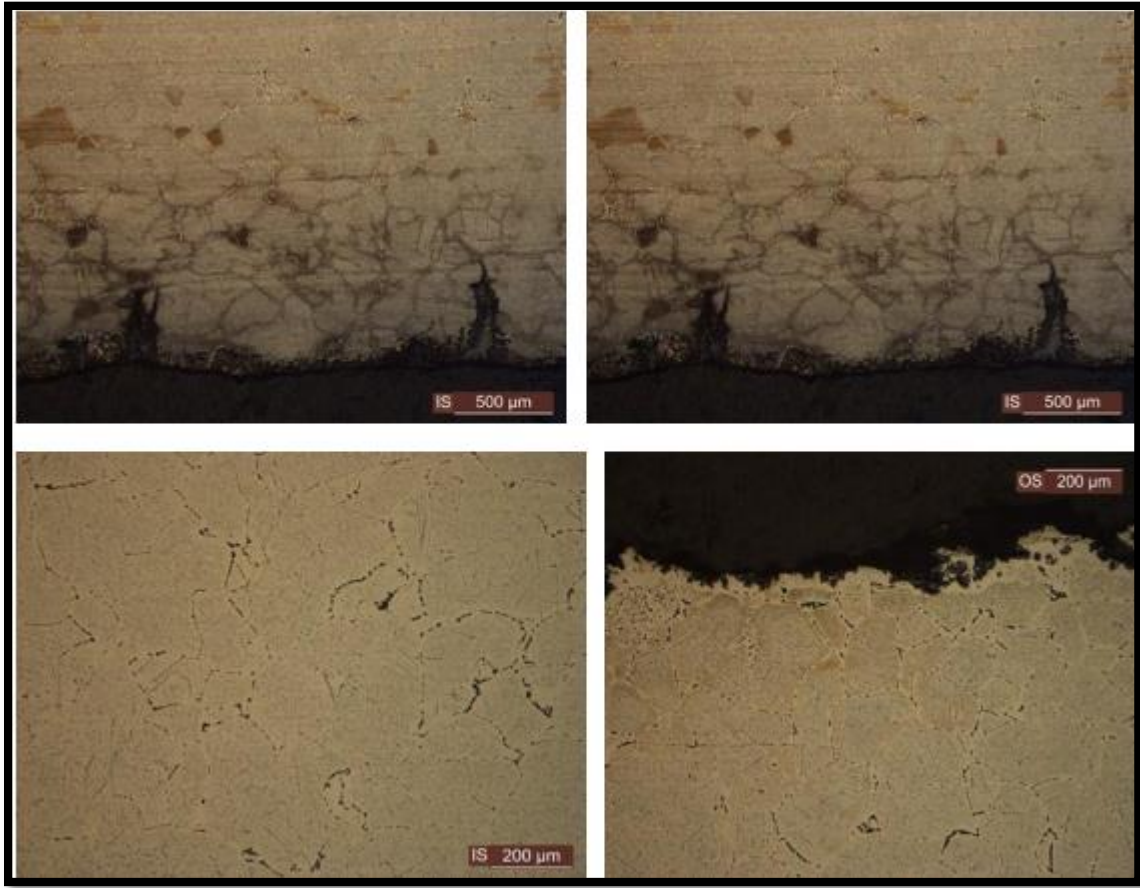


Figure 17: Photos by light microscope of the 2nd cracked sample as etched condition. Note: cracks in top pictures (Intergranular) are going through the grain boundaries

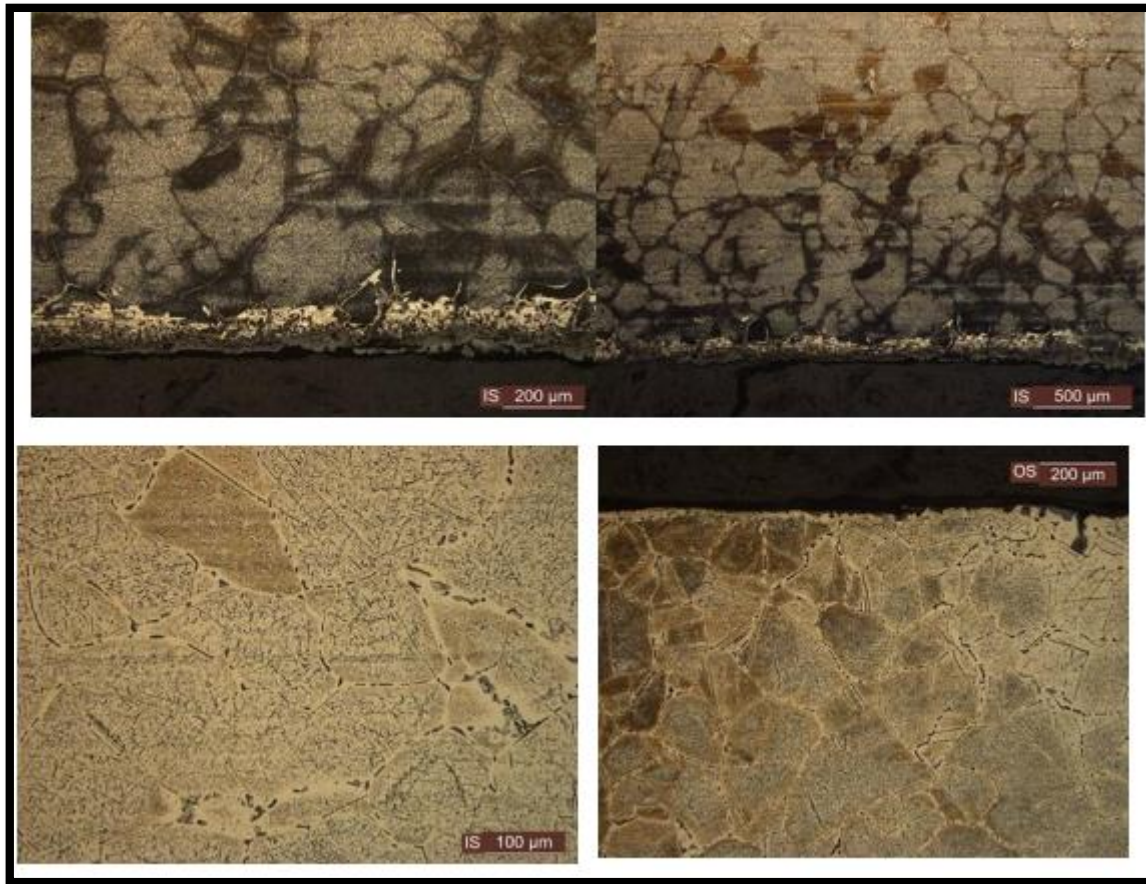


Figure 18: Photos by light microscope of the 1st uncracked sample next to the welding that connects the pipe and the tube as etched condition

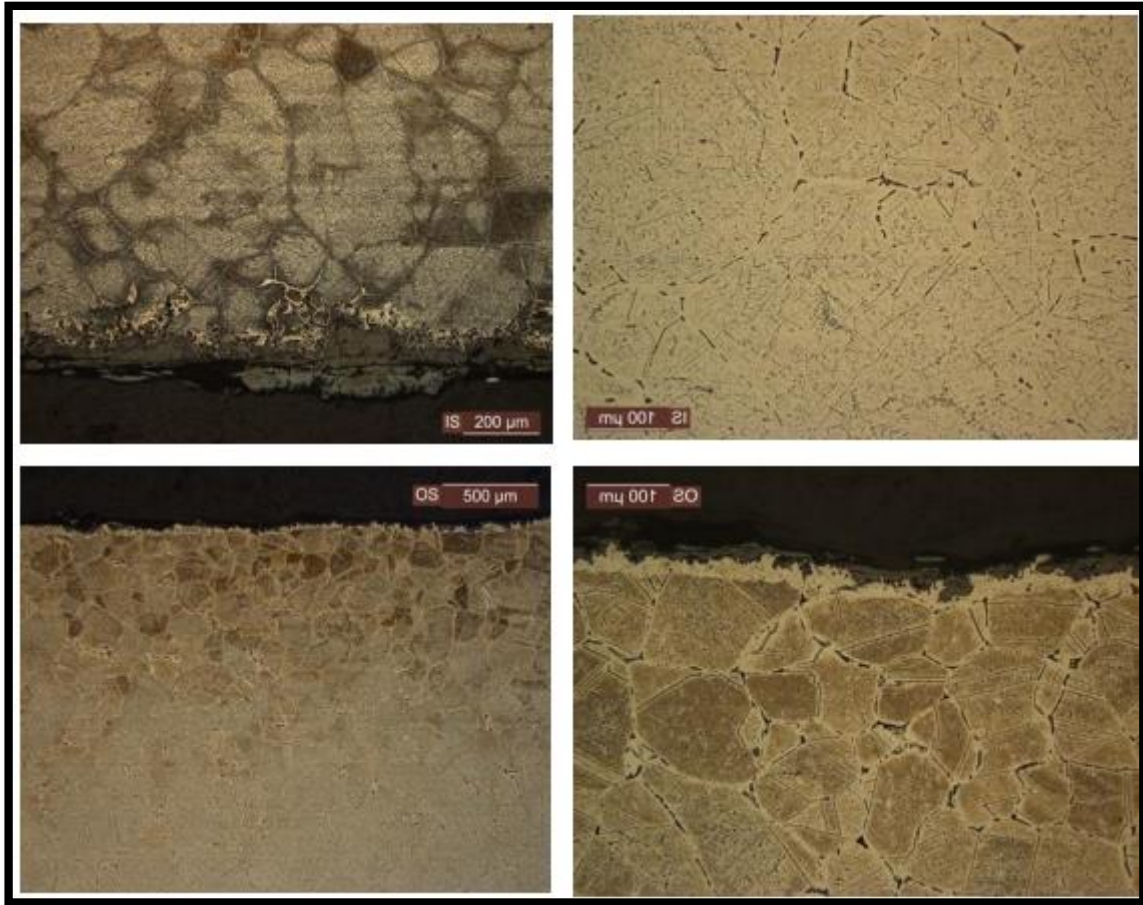


Figure 19: Photos by light microscope of the 2nd cracked sample as etched condition

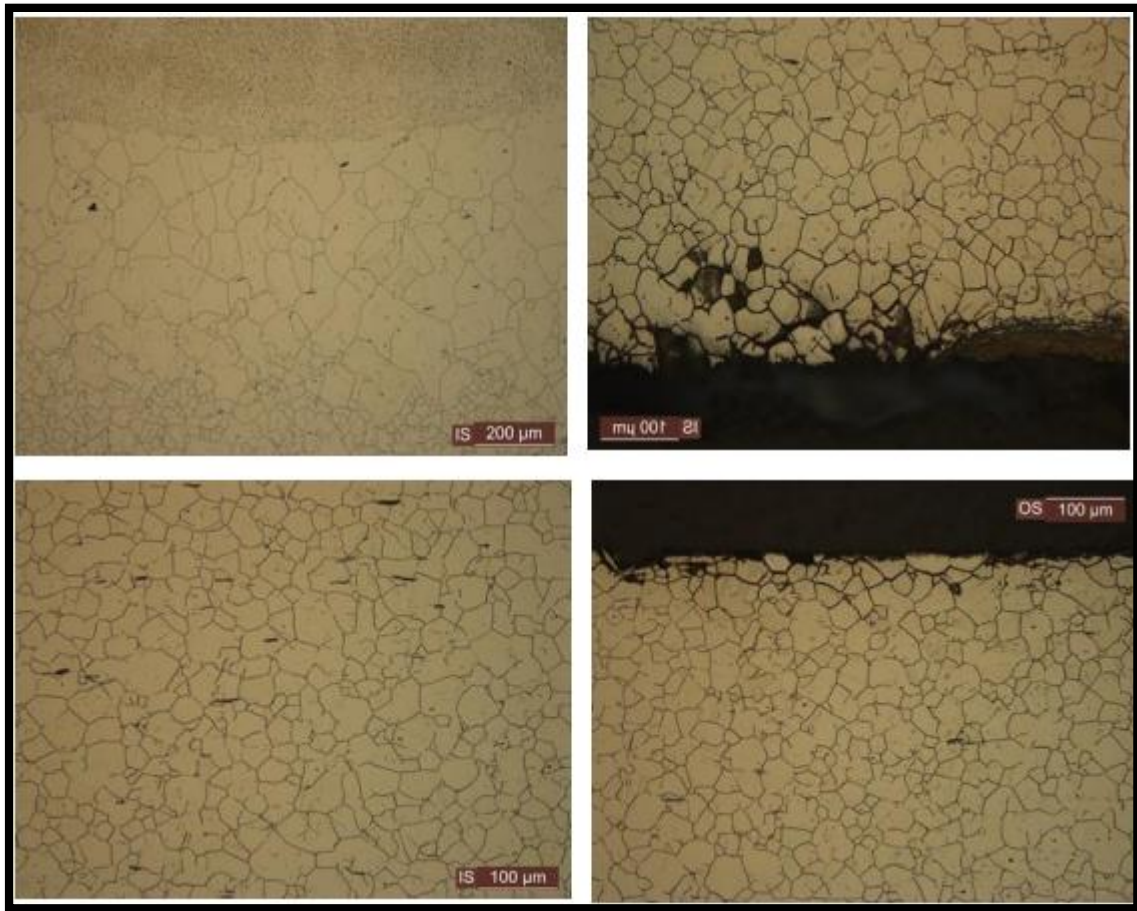


Figure 20: Photos by light microscope of the welded sample from the small tube as etched condition

Note: top left picture shows welding area (top), HAZ (middle), base metal (bottom).

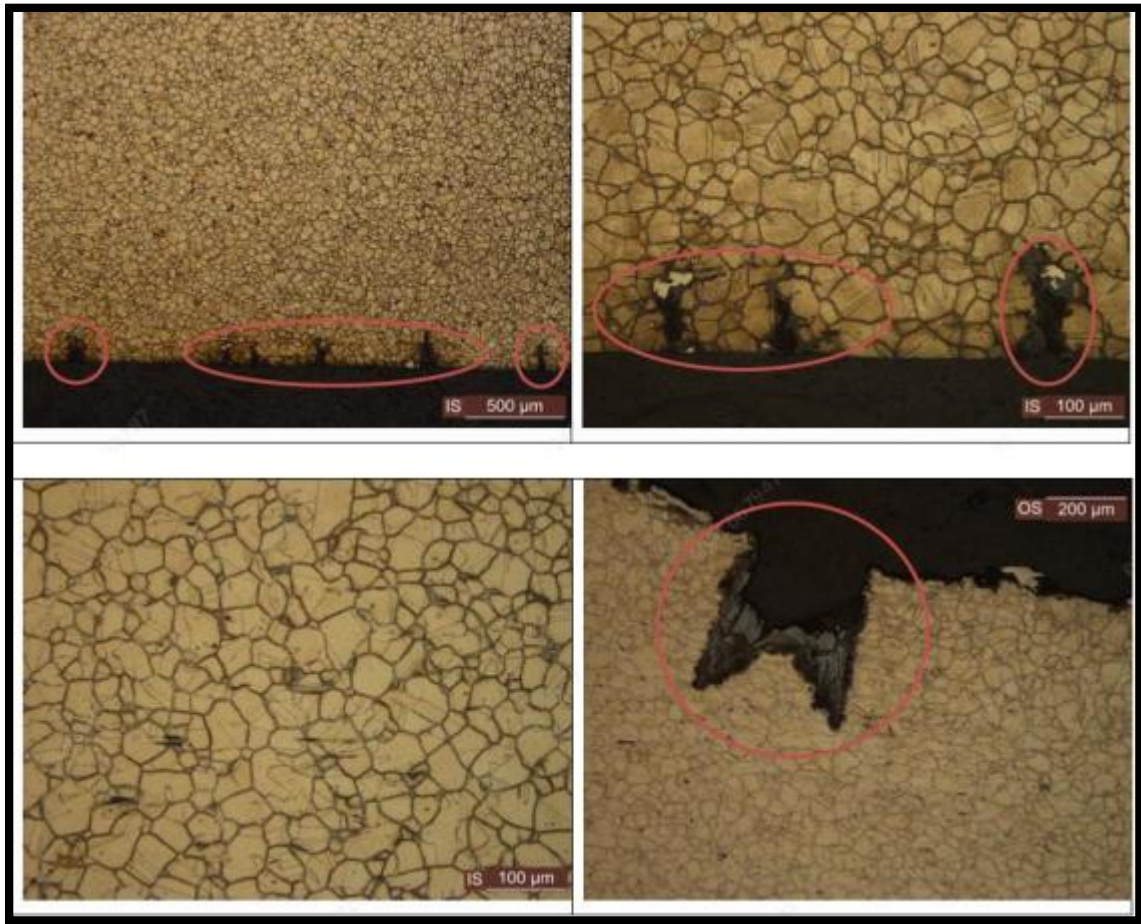


Figure 21: Photos by light microscope of the cross sectioned sample from the small tube as etched condition.

Note: pitting are clearly observed as circled in red.

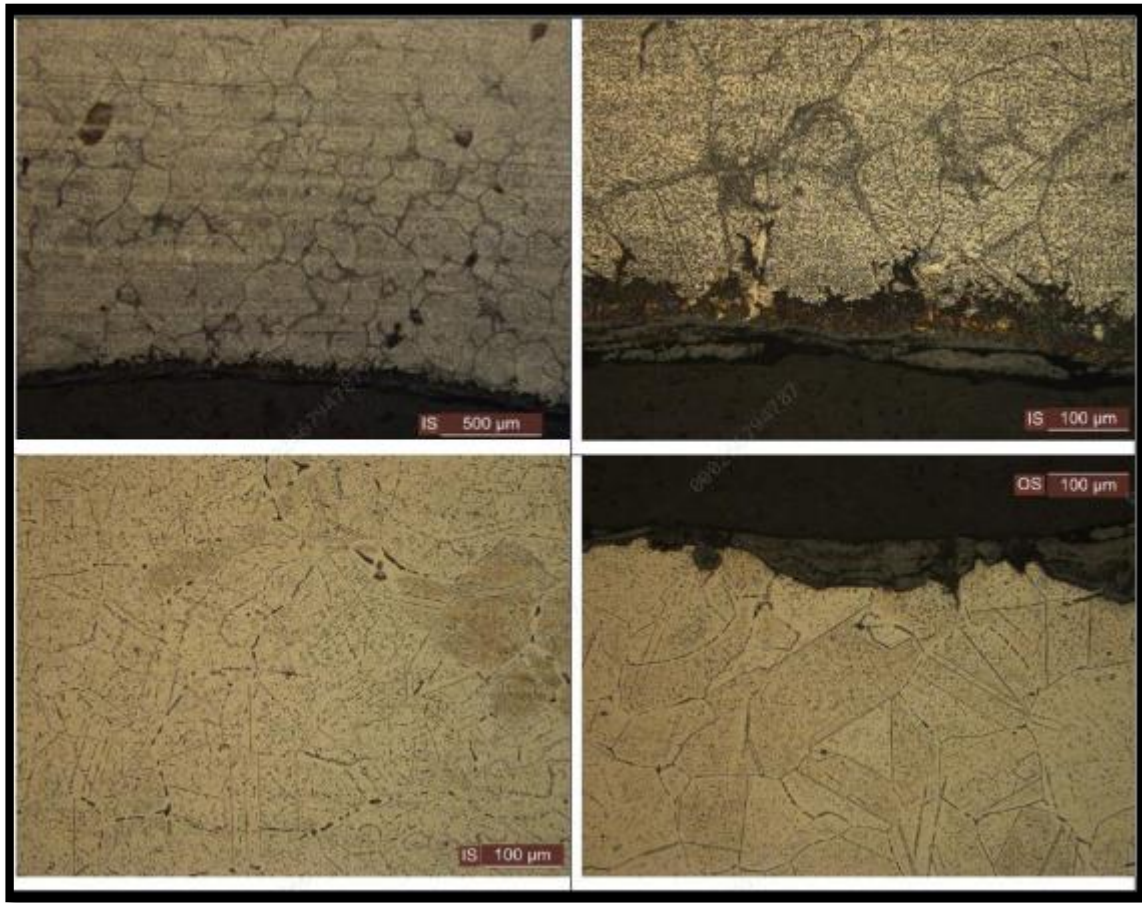


Figure 22: Photos by light microscope of the cross sectioned sample from the main pipe as etched condition.

During the examination of the microstructure, dual structure was observed (where ditches are located at grain boundaries; in addition to that, steps between grains but not completely surrounded) which could be a sign of sensitization. Moreover, the SS 304H grade is susceptible to sensitization since it contains the regular amount of carbon [2]. Therefore, sensitization test was done on four of the seven prepared samples which are one of the cracked sample, one of the uncracked sample, crossed sectioned sample from the main pipe, and the welded sample from the tube. The sensitization was done by 10% oxalic acid as per ASTM A262-10. As a result of that, the three samples from the main pipe looked sensitized by observing the ditch structure (where one or more grains are completely surrounded by ditches). On the other hand, the welded sample from the tube seems to be more sensitized at one side than the other which is the bottom side of the tube (closer to the main pipe). Results are shown in Figures (22-26)



Figure 23: Photos by light microscope of the 1st cracked sample after sensitization test.

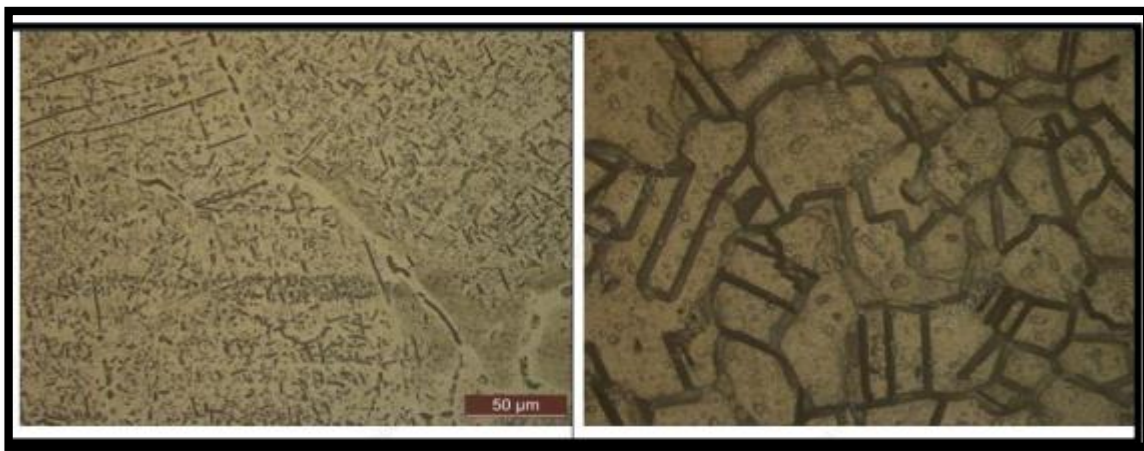


Figure 24: Photos by light microscope of the 1st un cracked sample after sensitization test.

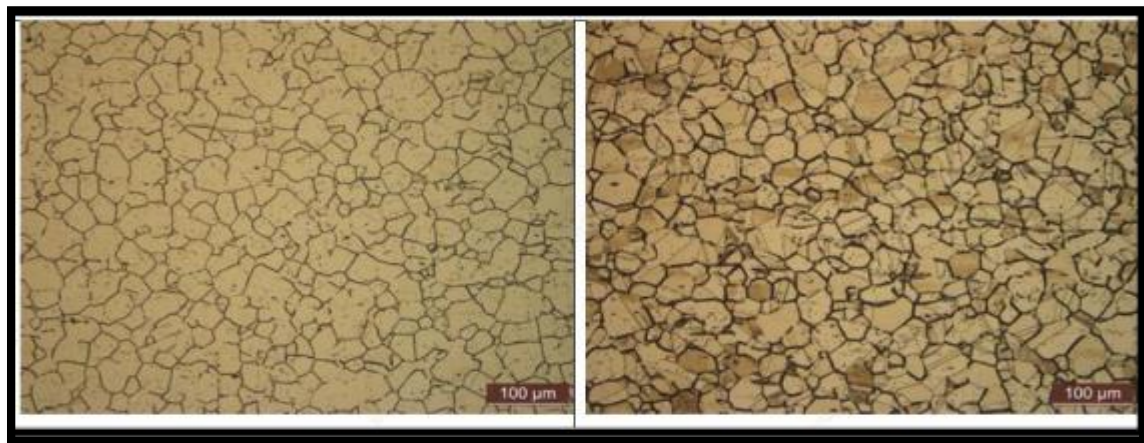


Figure 25: Photos by light microscope of the welded sample after sensitization test.

Note: the right picture is the bottom side of the tube which is close to the pipe, while the left picture is the top of the tube.

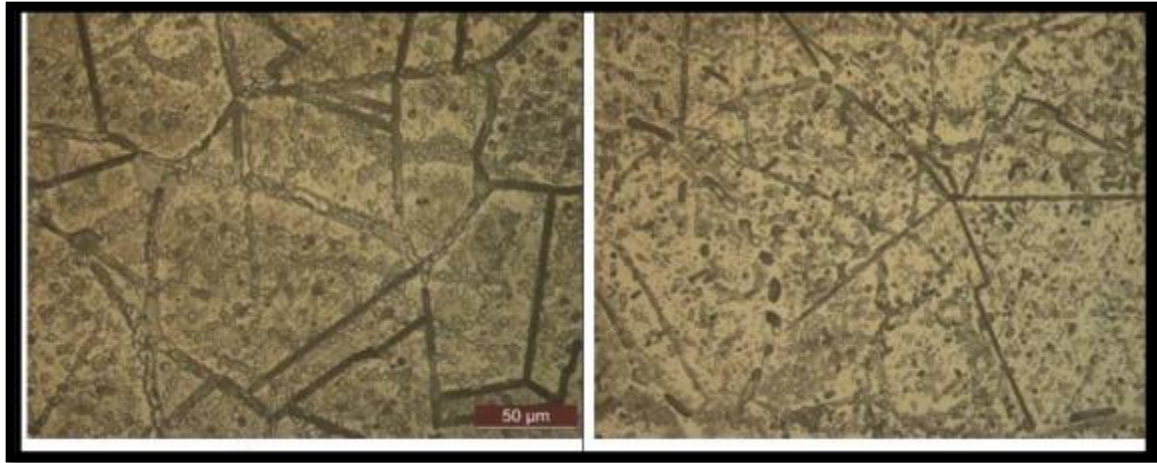


Figure 26: Photos by light microscope of cross sectioned sample after sensitization test.

4.2.3 Microstructure Examination for SS304 L:

Three Samples were cut to study the microstructure of the flange's neck at different locations. One of those samples was to investigate the inner surface (IS) and the type of cracks on it, while the other two were cross-section cut samples for the purpose of examining the inner surface (IS) from the welding area at the top to the base metal in the bottom going through Heat Affected Zone (HAZ). The samples were prepared as per ASTM E3, ground, polished then examined using a light microscope in polished condition. Then etched by preparing oxalic reagent to reveal the microstructure for stainless steel materials referring to ASTM E407. Classification: General Business Use The images of all samples were taken in polished condition, but only two of them as etched condition (the third sample was used for the hardness test). Huge cracks traveling within the grain boundaries (intergranular cracks) were observed in all samples, especially, in the middle of the IS sample, and on the inner surface of the cross-section samples. The photographs show a typical austenitic structure with a lot of twins which is a sign that the metal is annealed. Moreover, titanium nitride particles (orange) and chromium carbide particles (blackish) were observed all over the microstructure of all samples which were confirmed by SEM as well. Results are shown in Figures 27 to 29.

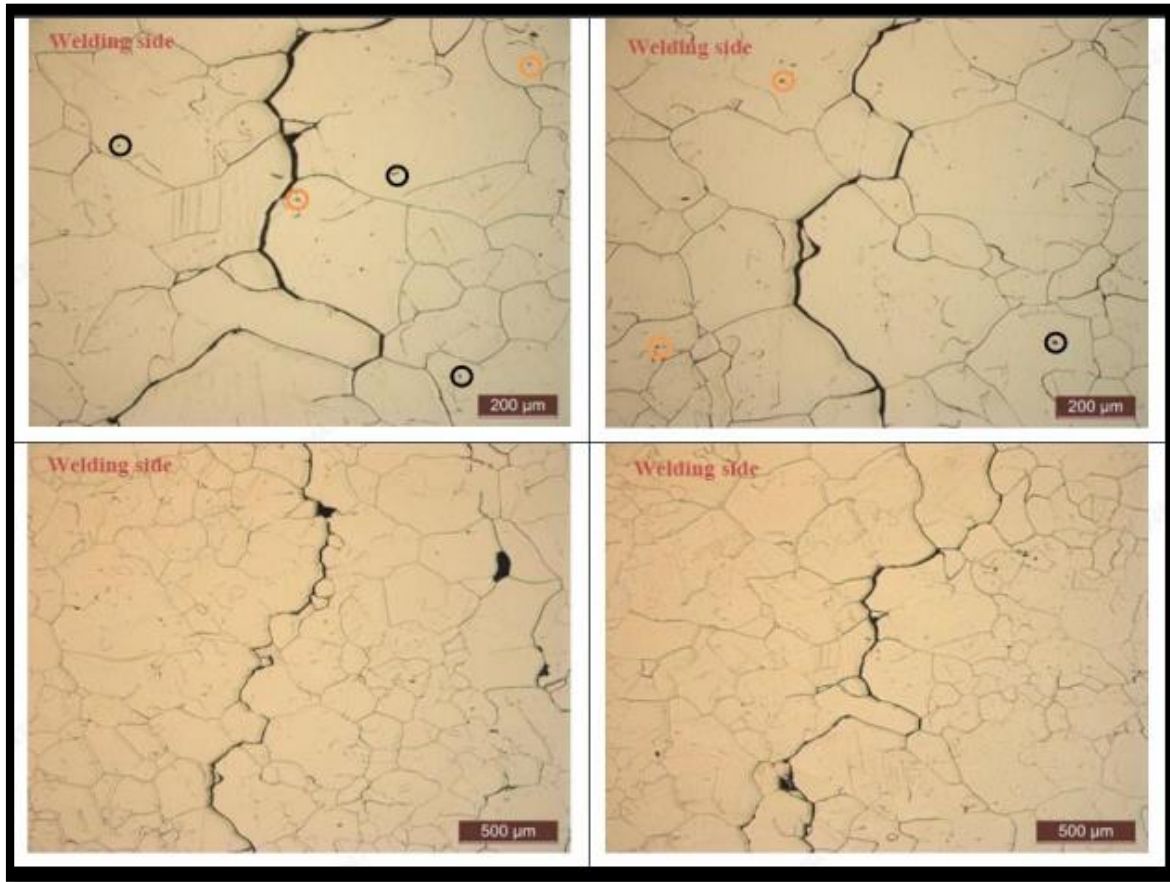


Figure 27: Photo by light microscope of Inner surface sample as etched, showing the microstructure with Intergranular crack

Note: titanium nitride particles clarified in orange circles, while chromium carbides particles clarified in black circles.

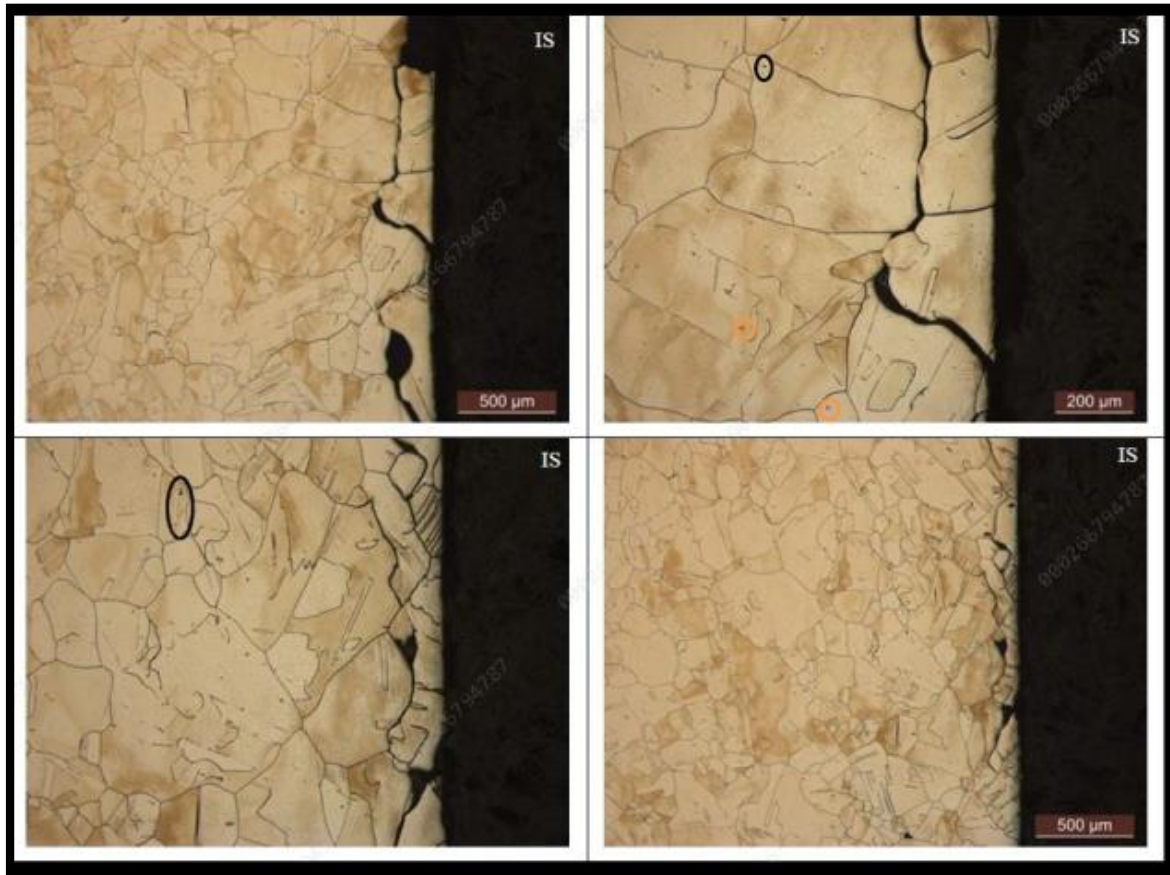


Figure 28: Photo by light microscope of a cross section sample as etched, showing the microstructure with Intergranular crack prevailing from IS to OS.

Note: titanium nitride particles clarified in orange circles, while chromium carbides particles clarified in black circles.

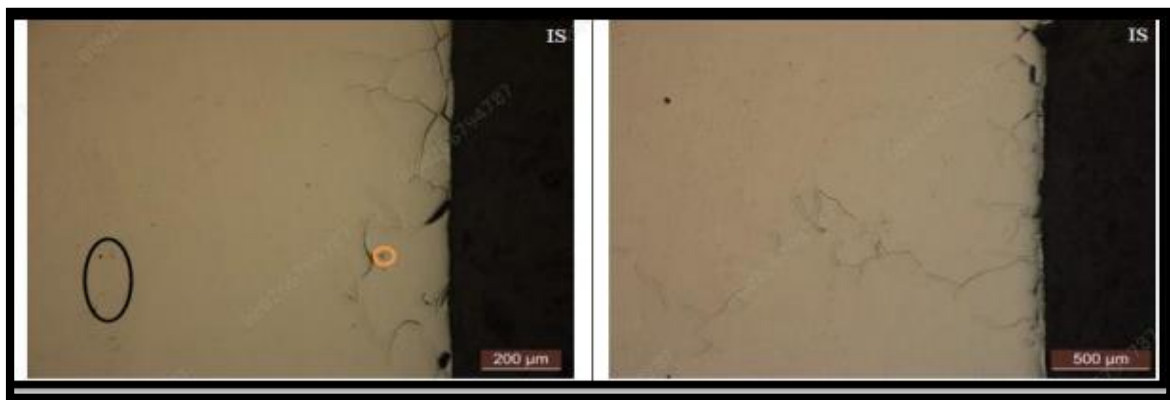


Figure 29: Photo by light microscope of a cross section sample as polished, showing the microstructure with Intergranular crack prevailing from IS.

Note: titanium nitride particles clarified in orange circles, while chromium carbides particles clarified in black circles.

4.3 SEM Analysis:

4.3.1 SEM Examination for SS304H:

Performing a full investigation requires planning and deep analysing. Therefore, two samples were examined as received condition (a sample from the main pipe, and another one from the tube), and after preparation four samples were examined as well (three from the main pipe and one from the tube) by scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS) to study the surfaces morphology and analyse the materials inside of cracks to identify the present elements. The SEM-EDS analysis of the sample from the main pipe as received condition shows the main elements in general but the Cr was little in some spots with higher O in the same spots. This indicates that those spots are oxidized. Results are shown in Figures 30 and 31, and in Table 3-4. For the sample from the small tube, the target was to analyse the deposit on it. The reddish area shows high S and Si compared to the base metal. However, the whitish area in the deposit, has even very much more S and Si than the reddish area. The S reached 6, 7, and 12 %, while Si 4, 5, 6%; in addition to that, four different areas have more than 2% of N and one spot with 11% of Ca. At the dark area which is directly below the whitish, the S and Si dropped dramatically in some spots while staying high in other, and the main elements such as Cr and Fe keeps fluctuating with the enormous presence of O in in some area which indicates that this dark blackish area is oxidized. Results are shown in Figures 32-34 and, and Tables 5-7

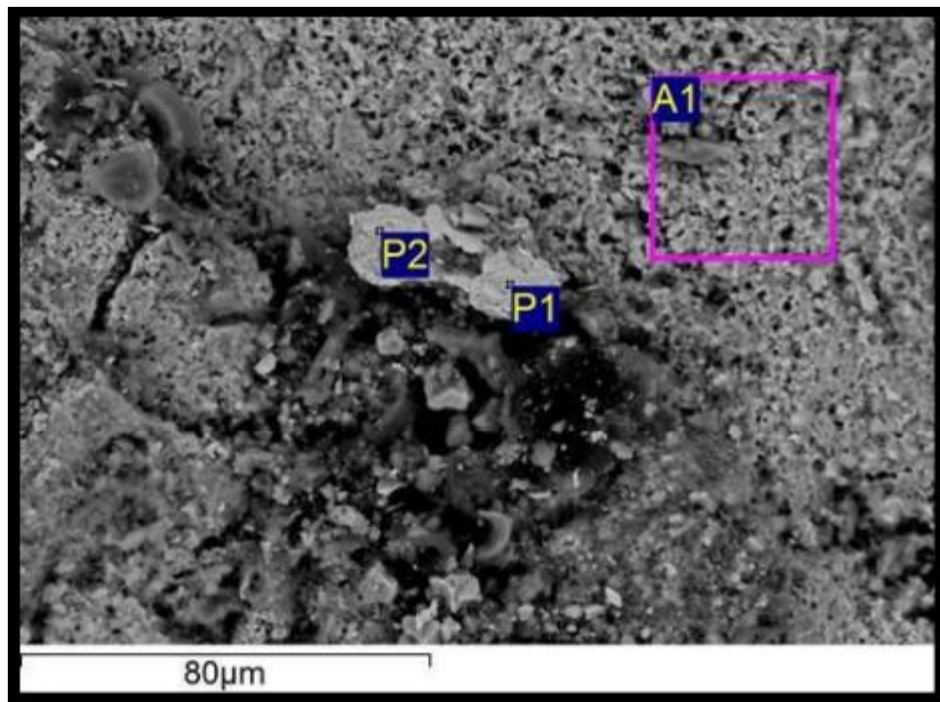


Figure 30: Photo by SEM for the sample from the main pipe as received condition

Table 3: SEM-EDS Analysis of the sample from the main pipe as received condition.

Spectrum	C	O	Na	Mg	Si	S	Cl	Ca	Cr	Mn	Fe	Ni	Total
P1	13.24	4.60			0.57	0.12			15.87	1.16	56.31	8.13	100.00
P2	8.84	4.03		0.34	0.71	0.10		0.23	16.94	1.29	59.10	8.41	100.00
A1	6.63	32.12	0.94		0.76	0.37	0.51	1.22	28.18	0.60	23.12	5.55	100.00

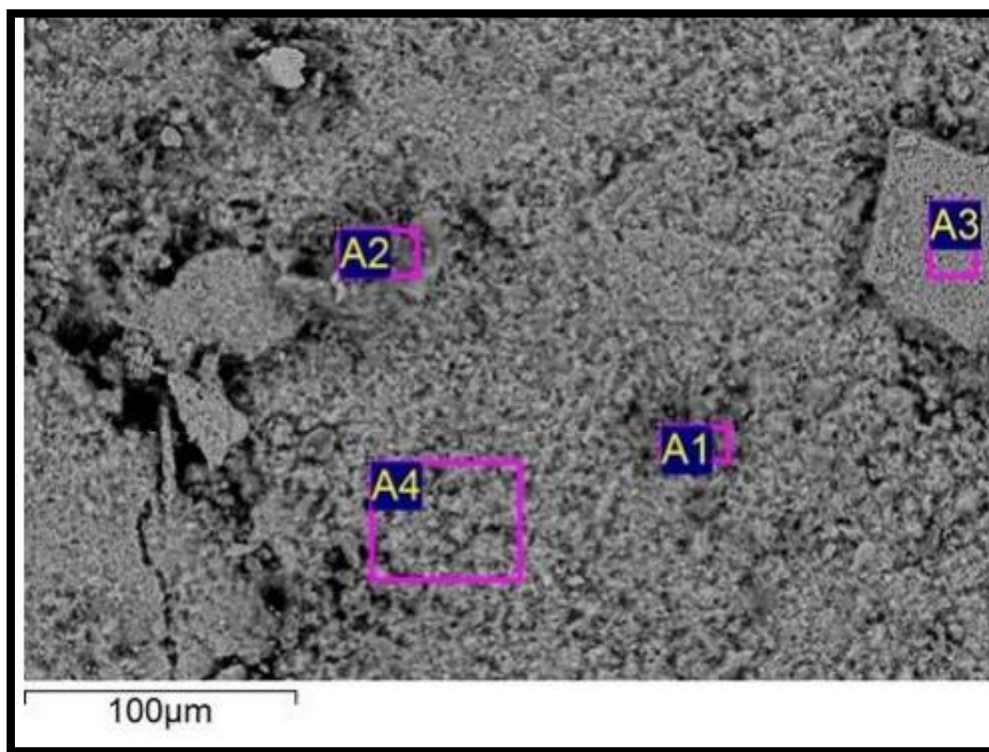


Figure 31: Photo by SEM for the sample from the main pipe as received condition

Table 4: SEM-EDS Analysis of the sample from the main pipe as received condition.

Sp	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Mn	Fe	Ni	Total
A1	8.17	29.72	1.32	0.88	2.51	10.12	1.96	0.66	0.51	3.58	12.44	0.63	22.43	5.06	100.00
A2	12.87	41.62	1.58	2.50	1.31	3.04	1.26	0.79	0.26	5.91	9.96	0.46	14.34	4.11	100.00
A3	9.88	32.96	0.88	0.43	0.46	0.96	0.37	0.30		0.62	2.24	0.76	48.60	1.53	100.00
A4	6.01	30.92	1.45	0.52	0.60	1.89	0.95	0.90	0.16	0.85	19.27	0.54	26.71	9.24	100.00

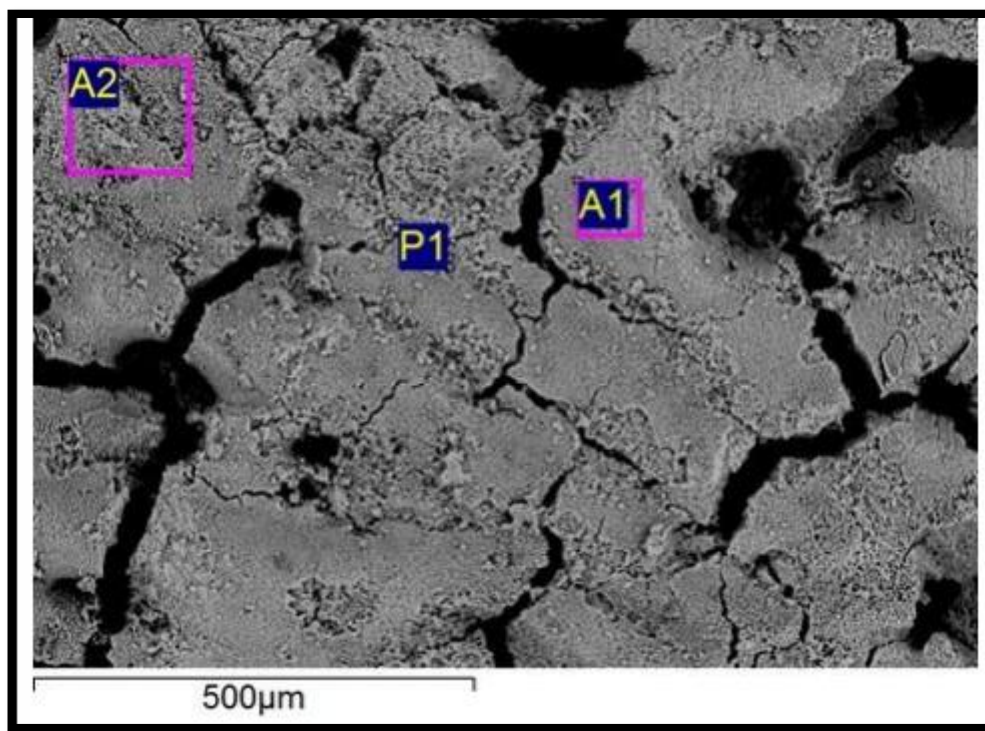


Figure 32: Photo by SEM for the sample from the small tube (reddish area) as received condition.

Table 5: SEM-EDS Analysis of the sample from the small tube (reddish area) as received condition

Spectrum	C	O	Si	S	Ca	Cr	Fe	Ni	Total
A1	7.56	43.14	0.29	1.40		10.22	32.70	4.70	100.00
P1	9.67	51.39	0.39	1.66	0.25	7.98	24.87	3.78	100.00
A2	7.54	46.78	0.36	3.51		8.91	29.29	3.61	100.00

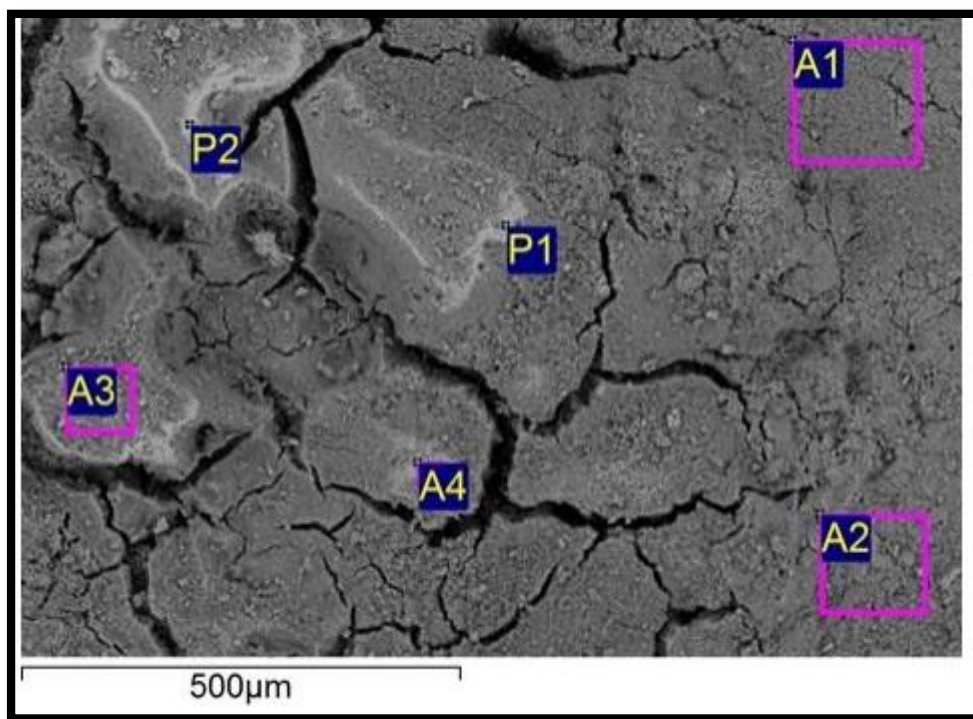


Figure 33: Photo by SEM for the sample from the small tube (whitish area) as received condition.

Table 6: SEM-EDS Analysis of the sample from the small tube (whitish area) as received condition.

Spectrum	C	N	O	Mg	Al	Si	S	K	Ca	Ti	Cr	Fe	Ni	Total
A1	10.57	2.66	56.70		0.12	1.70	7.75		0.17		5.81	14.23	0.29	100.00
A2	10.13	2.38	52.43			4.76	6.79				7.79	15.34	0.38	100.00
P1	17.54	3.34	61.61			1.31	6.39		0.63		2.82	6.00	0.37	100.00
P2	9.33		56.53	0.42	11.00	5.70	1.76	0.12	11.41	0.84	0.95	1.62	0.33	100.00
A3	18.06	2.81	57.58	0.13	0.18	3.04	7.75		0.38		4.69	4.17	1.21	100.00
A4	11.71		55.67			3.36	12.51				8.21	5.70	2.85	100.00

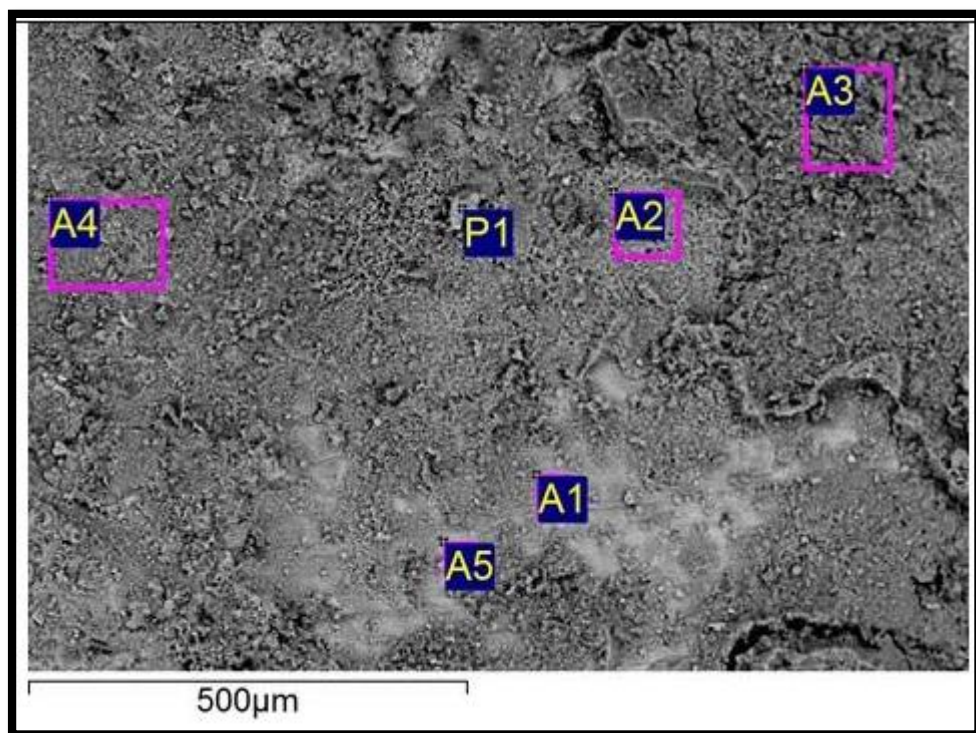


Figure 34: Photo by SEM for the sample from the small tube (blackish area) as received condition.

Table 7: SEM-EDS Analysis of the sample from the small tube (blackish area) as received condition

Sp	C	N	O	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Ni	Cu	Total
A1	7.99		34.04			4.54		1.23			13.76	0.66	34.05	3.26	0.47	100.00
A2	7.23	1.61	51.32			1.05	0.13	5.20		0.24	6.33		26.62	0.26		100.00
A3	12.46	2.37	51.76		0.16	6.02		7.03		0.61	5.03		14.33	0.24		100.00
A4	9.11	2.25	53.80		0.12	2.67		6.78		0.36	8.51		15.90	0.51		100.00
A5	8.76		30.71			5.41		0.99			15.96	0.65	33.17	3.92	0.43	100.00
P1	9.27		58.29	1.44	2.54	5.76		2.50	0.27	1.43	1.05	0.15	17.30			100.00

The investigation of the samples as prepared was mostly for the purpose of looking into present particles on the surface and the deposits inside of the cracks. Two samples out of the three from the main pipe were from the cracked area, the particles were confirmed to be manganese sulphide and aluminium oxide. The cracks in IS & OS in both samples contain mostly O with little different elements such as Cu, Mn, Ni, and Si. Results are shown in Figures 35-37 and Tables 8-10. The third sample from the pipe was a cross-section from the bottom of the pipe. The middle surface shows the main elements of the SS 304H with very little Mo, However, the IS has a very high presence of S up to 38% and 13 % of Ni. Results are shown in Figure 38 and Tables 11. The fourth sample which is from the small tube shows high O and fluctuating present of Si, S, and Ni on the pitting. Results are shown in Figure 39 and Table 12.

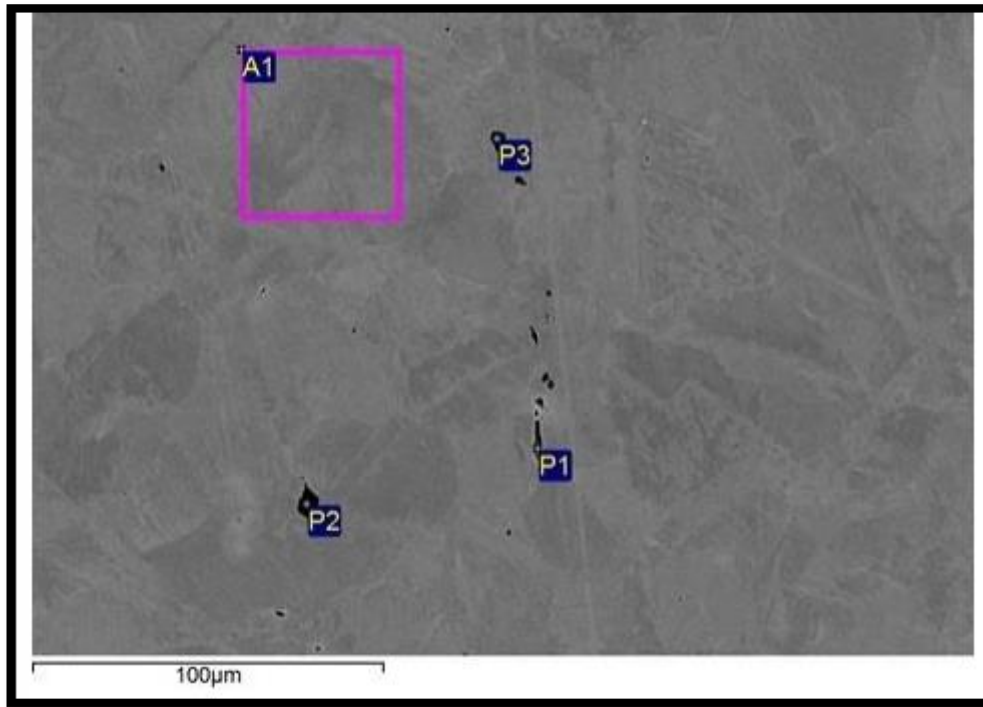


Figure 35: Photo by SEM for the crack sample from the main pipe as prepared condition.

Table 8: SEM-EDS Analysis of the crack sample from the main pipe as prepared condition.

Spectrum	C	O	Al	Si	S	Ti	V	Cr	Mn	Fe	Ni	Total
P1	9.03				20.33			7.90	34.37	25.71	2.66	100.00
P2	3.13	43.15	37.91			0.47		6.78		7.72	0.85	100.00
P3	3.50	37.86	14.64			2.66	0.42	15.07	24.11	1.75		100.00
A1	6.55			0.49				17.86	1.30	66.34	7.47	100.00

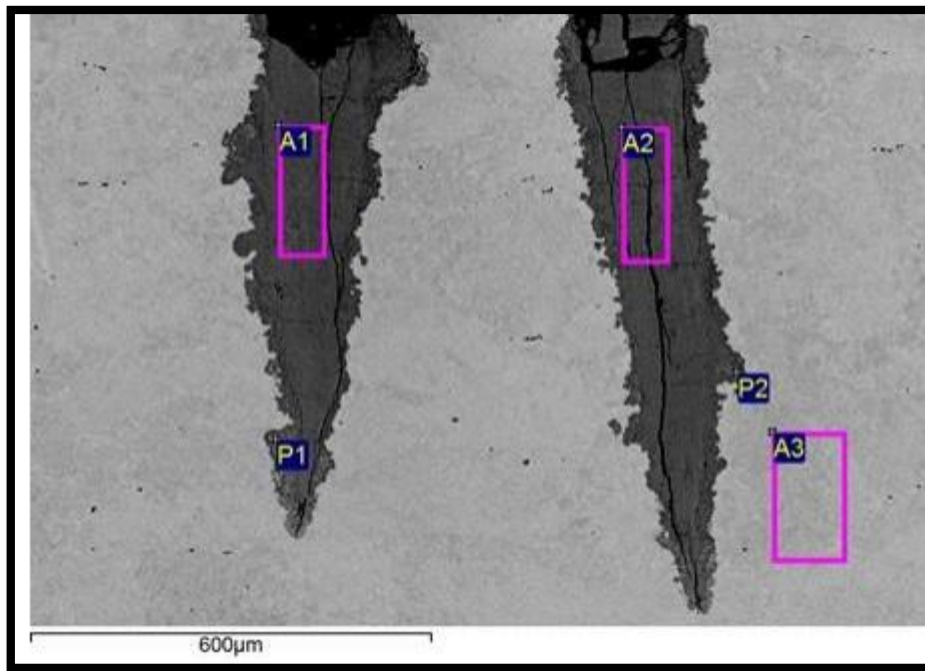


Figure 36: Photo by SEM for the crack sample (OS) from the main pipe as prepared condition.

Table 9: SEM-EDS Analysis of the crack sample (OS) from the main pipe as prepared condition.

Spectrum	C	O	Si	Cr	Mn	Fe	Ni	Cu	Total
A1	5.00	34.50	0.21	3.35	0.89	53.78	2.28		100.00
A2	9.64	35.11		2.03	0.82	50.72	1.68		100.00
A3	6.90		0.40	17.73	1.70	64.62	8.10	0.54	100.00
P1	5.08	21.97	0.63	27.42	3.31	24.27	16.22	1.11	100.00
P2	4.85	28.28	0.52	22.98	3.17	16.33	22.47	1.41	100.00

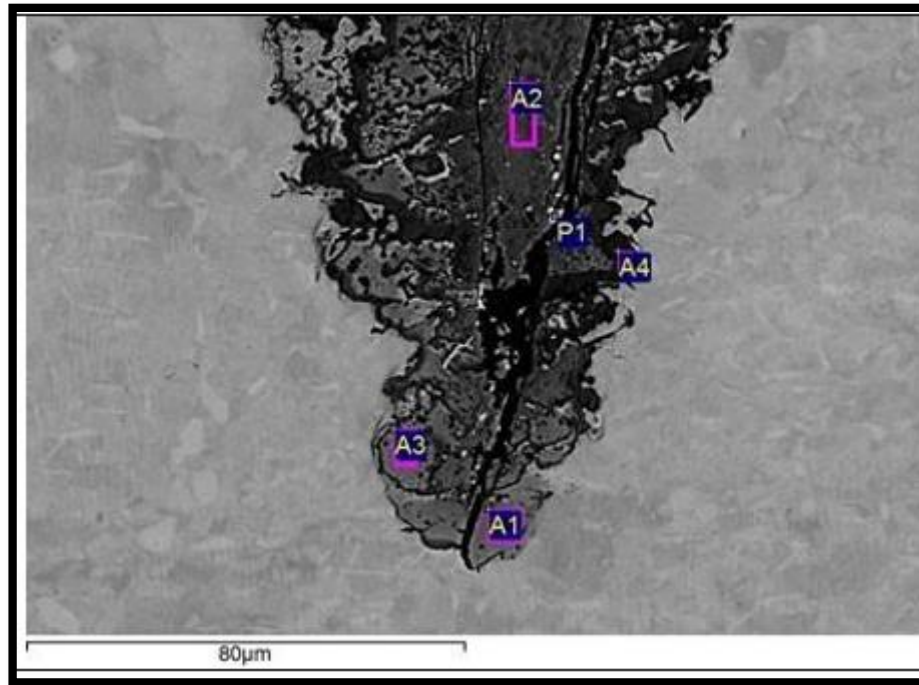


Figure 37: Photo by SEM for the crack sample (OS) from the main pipe as prepared condition.

Table 10: SEM-EDS Analysis of the crack sample (OS) from the main pipe as prepared condition.

Spectrum	C	O	Si	S	V	Cr	Mn	Fe	Ni	Cu	Total
A1	4.28	21.42	0.52	0.14		21.29	1.70	39.64	10.99		100.00
A2	4.14	27.36				1.37	1.39	65.11	0.64		100.00
P1	11.55	3.03				1.74		28.40	52.16	3.12	100.00
A3	4.97	23.40	0.50	0.14		21.52	1.95	32.47	14.26	0.78	100.00
A4	3.38	34.52	0.53	0.09	0.27	40.41	2.74	17.36	0.70		100.00

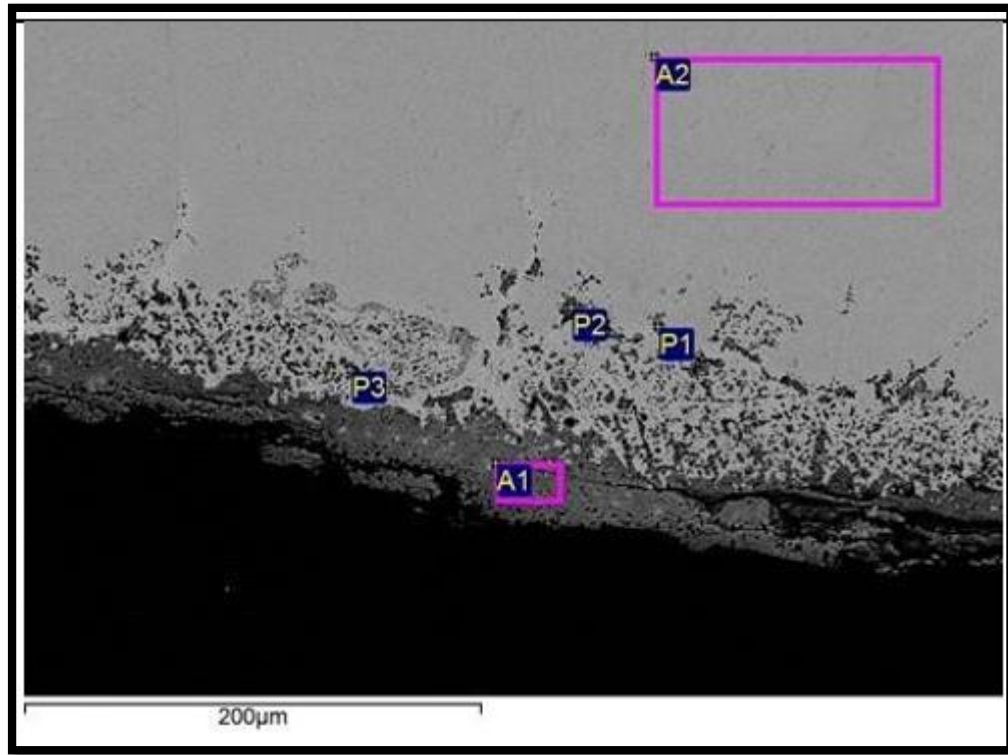


Figure 38: Photo by SEM for the cross sectioned sample from the main pipe as prepared condition.

Table 11: SEM-EDS Analysis of the cross sectioned sample from the main pipe as prepared condition.

Spectrum	C	O	Si	S	V	Cr	Mn	Fe	Ni	Cu	Mo	Total
A1	4.25	32.02	0.72	0.31		35.21		24.96	2.53			100.00
P1	12.03			38.95	0.35	35.55	0.72	11.26	0.51	0.64		100.00
P2	13.10	20.35	2.28	1.80	0.85	47.79	2.49	7.82	3.51			100.00
P3	12.37	12.59	3.51	0.54	0.37	33.28	1.83	22.15	13.35			100.00
A2	7.91		0.37			18.13	1.70	63.55	7.72		0.62	100.00

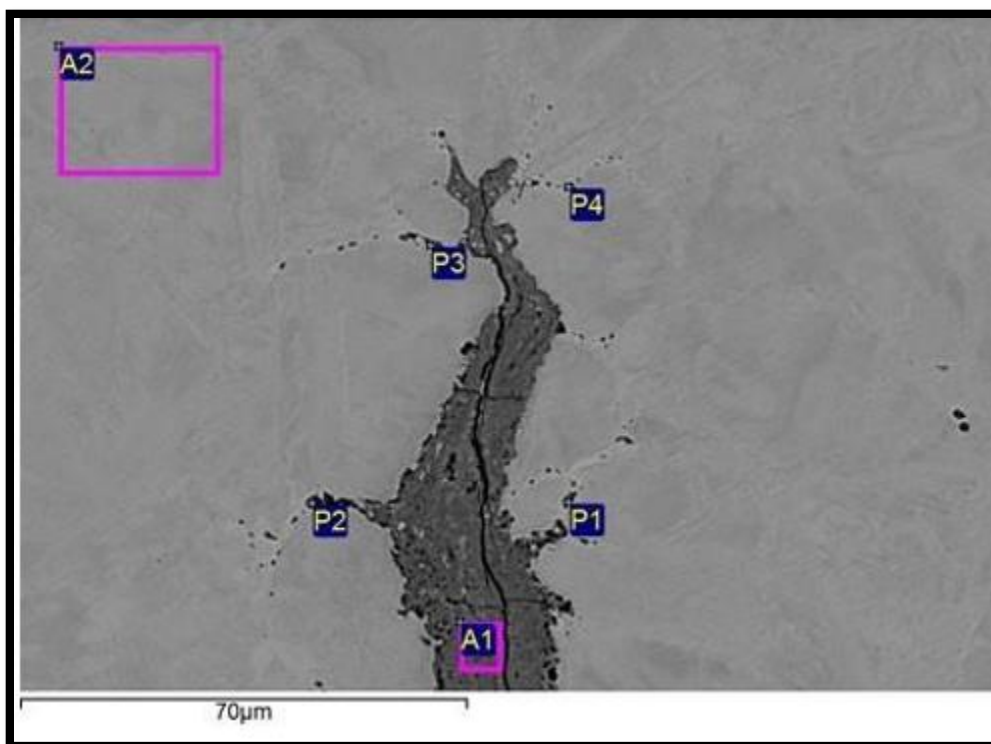


Figure 39: Photo by SEM for the pitting sample from the small tube as prepared condition

Table 12: SEM-EDS Analysis of the pitting sample from the small tube as prepared condition

Spectrum	C	O	Si	S	V	Cr	Mn	Fe	Ni	Total
A1	3.76	31.10	0.61	1.24		16.34	1.63	42.93	2.39	100.00
P1	8.27		0.34	8.22		14.37	0.89	58.07	9.83	100.00
P2	7.10	22.92	6.26	7.27	0.42	30.51	1.92	19.84	3.75	100.00
P3	4.26	21.32	1.44	1.17	0.27	25.47	3.18	37.33	5.54	100.00
P4	6.44		0.45	6.23		15.51	0.62	58.07	12.68	100.00
A2	5.54		0.56			18.27	1.32	67.38	6.93	100.00

4.3.2 SEM Examination for SS304L:

Performing a full investigation requires planning and deep analyzing. Therefore, all three samples were examined after preparation as polished by Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to study the flange's surface morphology and analysis the materials inside of cracks to identify the present elements.

The SEM-EDS analysis on the IS sample demonstrates the expected elements regarding the results of the chemical composition test that was done on the material. Moreover, the high percentage of Ti, and N in the second spot (S2) confirms that those orange particles on the microstructure were Titanium Nitride, results are shown in Figures 40 & 41 and Tables 13 & 14. In Figures 42 to 43 and Tables 15 to 16 show the outcomes of analysed cracks surfaces on the inner and outer surfaces of the cross-section sample (1). The analysis shows the unexpected presence of Mg, and Al elements; in addition to that, Cl was inside some cracks and their branches which is a sign of Chloride Stress Corrosion Cracking (ClSCC).

Last but not least, the inner surface of the cross section sample (2) results demonstrate nothing out of expectations but a little of Mg, and Al next to a crack, results are shown in Figures 44 & 45 and Tables 17 & 18.

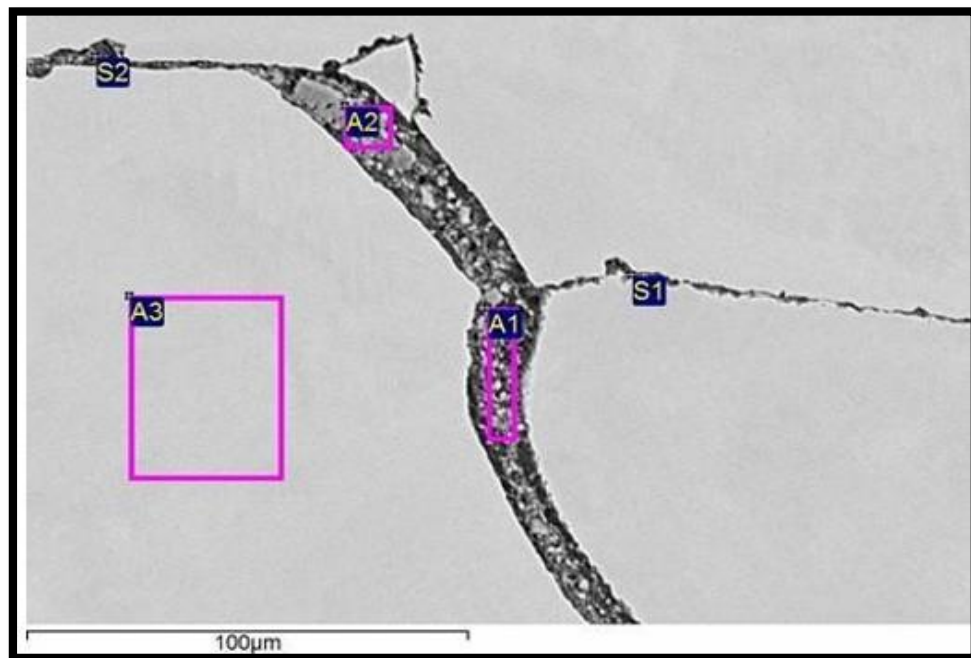


Figure 40: Photo by SEM showing the crack's surface of IS sample as polished condition.

Table 13: SEM-EDS Analysis of crack's surface of IS sample as polished condition.

Spectrum	C	N	O	Si	P	S	Ti	V	Cr	Mn	Fe	Ni	Cu	Total
A1	18.03		31.10	0.30	0.13	0.12			5.06	0.52	42.97	1.76		100.00
A2	14.72		33.30	0.19					2.19	0.42	48.30	0.88		100.00
S1	15.70		13.79	0.32		0.19			16.36	1.23	46.58	5.44	0.40	100.00
S2	3.67	35.87	3.59				50.89	0.94	3.79		1.24			100.00
A3	6.41			0.67					17.87	1.53	64.65	8.36	0.51	100.00

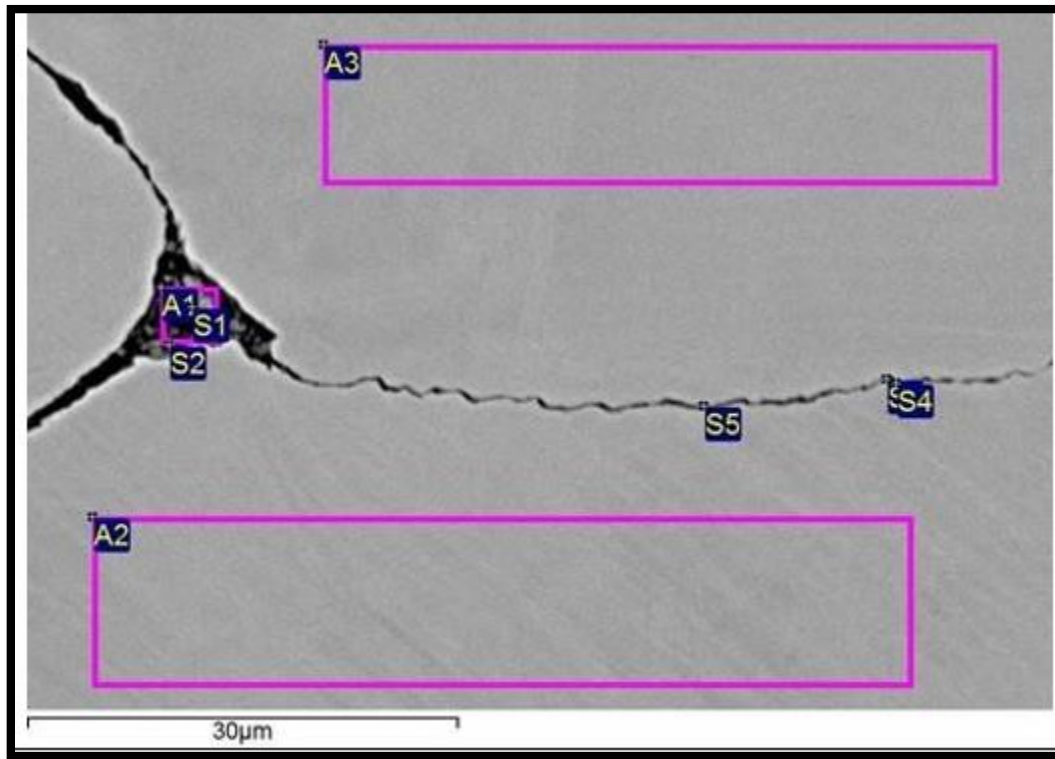


Figure 41: Photo by SEM showing the crack's surface of IS sample as polished condition.

Table 14: SEM-EDS Analysis of crack's surface of IS sample as polished condition.

Spectrum	C	O	Al	Si	P	S	Cr	Mn	Fe	Ni	Cu	Total
A1	9.03	33.99	0.20	0.44	0.10	0.12	5.58	0.41	46.58	3.55		100.00
S1	6.28	35.81		0.22		0.08	2.52		53.23	1.85		100.00
S2	9.24	34.34		0.38	0.17	0.11	8.39	0.71	43.15	3.51		100.00
S3	5.02	7.00		0.40			18.20	1.23	61.97	6.18		100.00
S4	7.55			0.49			19.37	1.22	64.43	6.53	0.41	100.00
S5	6.02	8.61		0.45		0.07	18.09	1.13	59.51	6.11		100.00
A2	6.17			0.59			17.95	1.30	66.64	6.88	0.47	100.00
A3	6.08			0.58			17.78	1.35	67.23	6.98		100.00

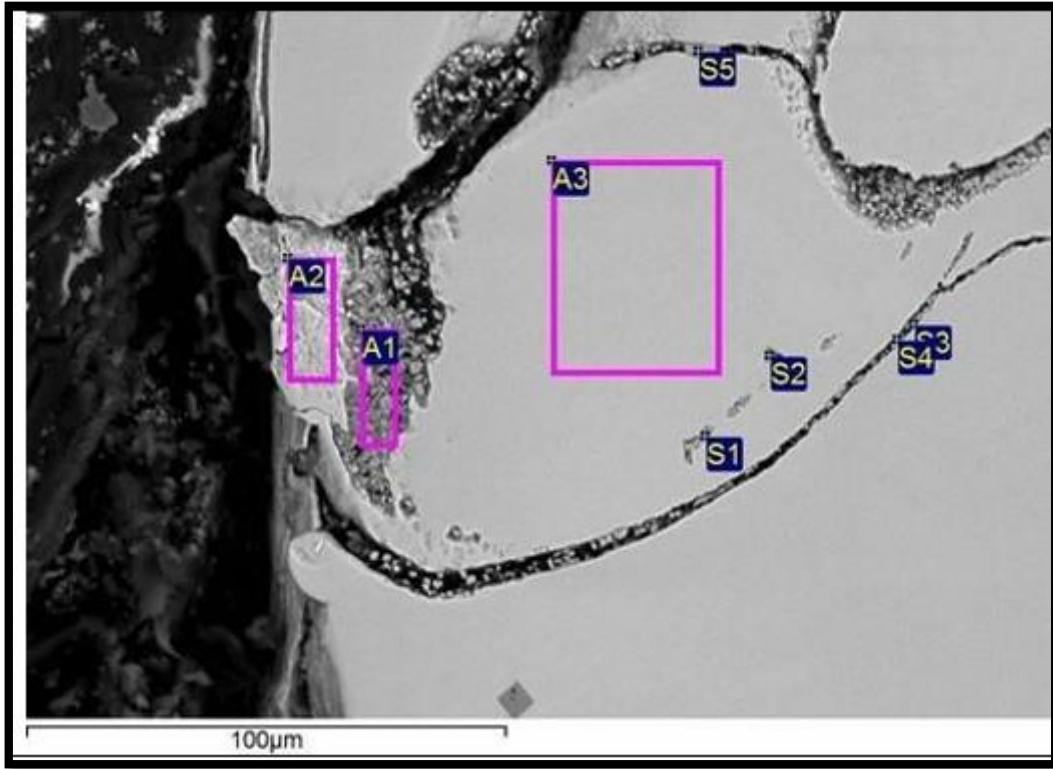


Figure 42: Photo by SEM showing the crack's surface on the Inner surface of cross section sample (1) as polished condition.

Table 15: SEM-EDS Analysis of the crack's surface on the Inner surface of cross section sample (1) as polished condition.

Spectrum	C	N	O	Mg	Al	Si	P	S	Cl	Ca	Ti	V	Cr	Mn	Fe	Ni	Zn	Total
A1	18.70		34.43			0.17	0.11			0.10			3.79	0.34	40.29	1.68	0.39	100.00
A2	12.65		7.71			0.71							15.93	1.22	55.67	6.10		100.00
A3	8.12					0.66							17.68	1.40	65.13	7.01		100.00
S1	7.05		34.27			0.50	0.11	0.08					11.21	0.67	41.88	4.23		100.00
S2	2.14	20.37	30.07	2.39	5.06			0.07			29.15	0.54	4.16		5.65	0.40		100.00
S3	10.68		34.39			0.43	0.16	0.07	0.05				9.24	0.52	40.73	3.73		100.00
S4	24.69		37.47			0.35	0.12						7.08	0.27	27.38	2.63		100.00
S5	8.13		37.55			0.45	0.28						4.75	0.37	44.94	3.51		100.00

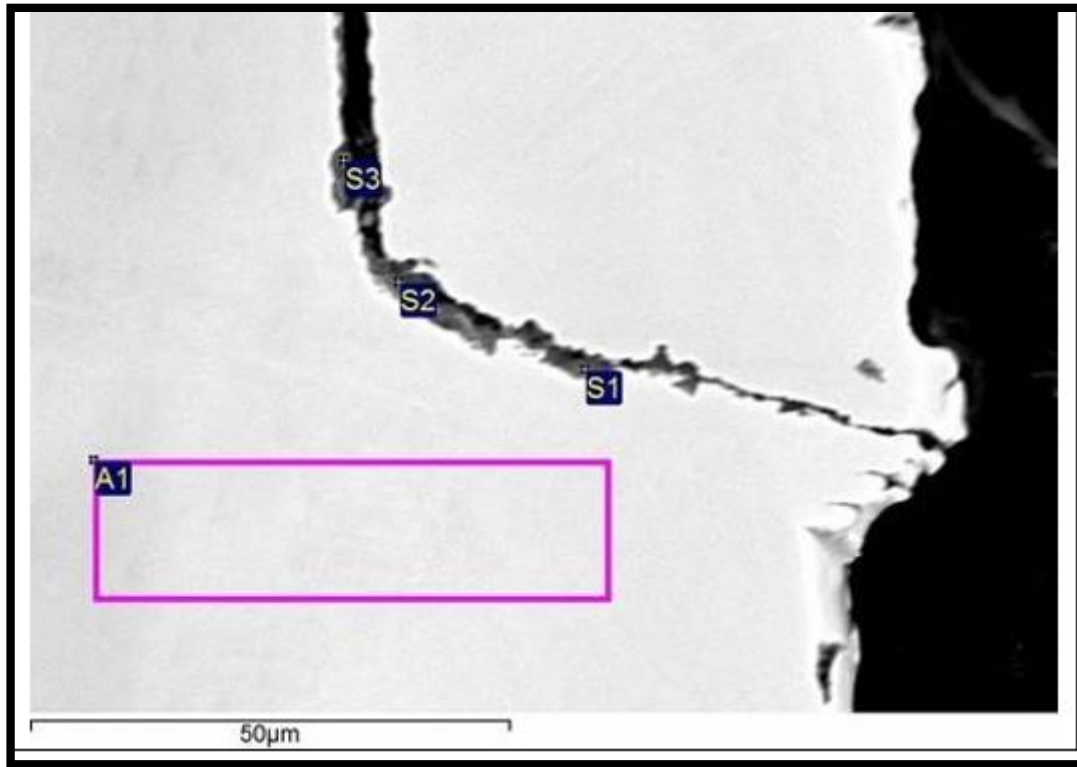


Figure 43: Photo by SEM showing the crack's surface in the outer surface of cross section sample (1) as polished condition

Table 16: SEM-EDS Analysis of the crack's surface in the outer surface of cross section sample (1) as polished condition

Spectrum	C	O	Na	Si	S	Cl	Cr	Mn	Fe	Ni	Total
S1	11.60	39.91	0.55	1.13	1.43	1.47	18.61	0.60	22.68	2.02	100.00
S2	19.02	41.96	0.39	0.93	2.37	2.71	21.30		10.26	1.07	100.00
S3	50.14	32.25		0.33	0.44	1.06	3.58		11.48	0.72	100.00
A1	10.77			0.86			17.47	1.29	62.50	7.12	100.00

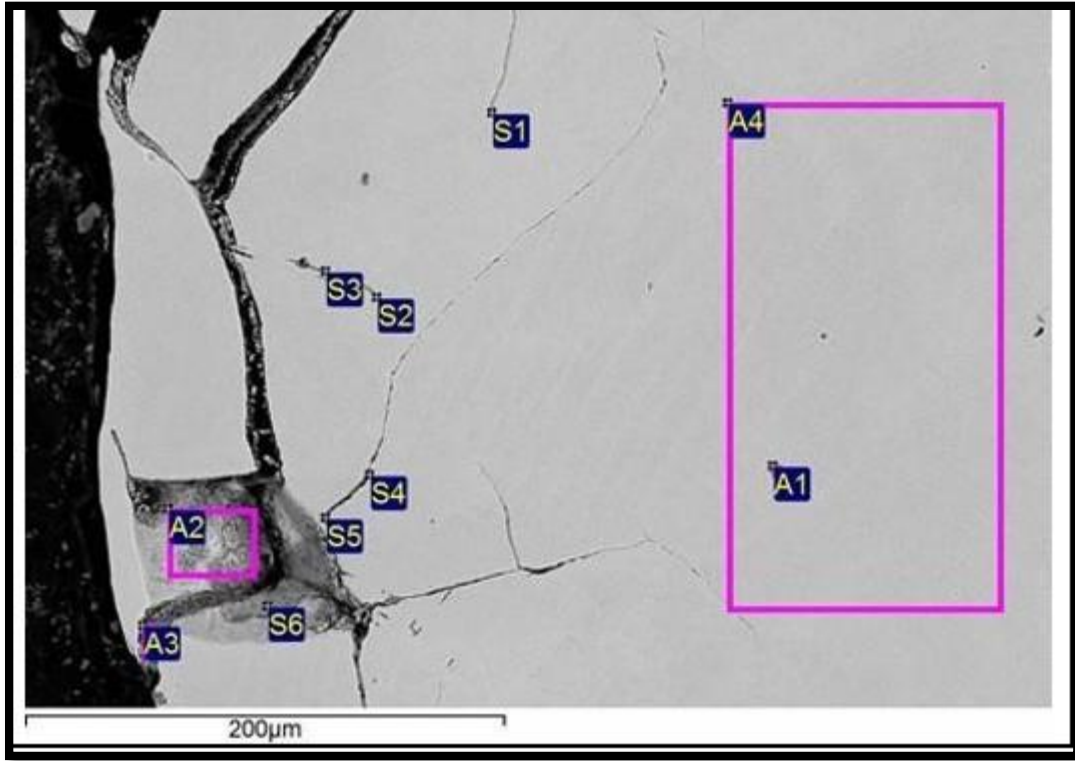


Figure 44: Photo by SEM showing the crack's surface on the Inner surface of cross section sample (2) as polished condition.

Table 17: SEM-EDS Analysis of the crack's surface on the Inner surface of cross section sample (2) as polished condition.

Spectrum	C	N	O	Mg	Al	Si	P	Ca	Ti	V	Cr	Mn	Fe	Ni	Total
A1	1.80	22.98	15.00	1.23	2.57				39.86	0.89	6.28	0.26	8.34	0.79	100.00
S1	6.19		25.08			0.57					12.38	0.72	49.62	5.44	100.00
S2	4.86		26.63			0.50					10.60	0.61	51.61	5.19	100.00
S3	7.44		25.15			0.40	0.14				11.53	0.60	50.07	4.66	100.00
S4	14.97		16.78			0.38					11.85	0.78	50.30	4.94	100.00
S5	12.32		26.40			0.48					9.52	0.57	46.18	4.54	100.00
S6	24.81		39.42			0.24					3.72	0.31	29.92	1.58	100.00
A2	13.51		18.16			0.46					12.82	1.00	49.72	4.34	100.00
A3	28.06		32.10			0.24		0.69			2.29		34.89	1.73	100.00
A4	5.86					0.60					18.13	1.35	66.57	7.49	100.00

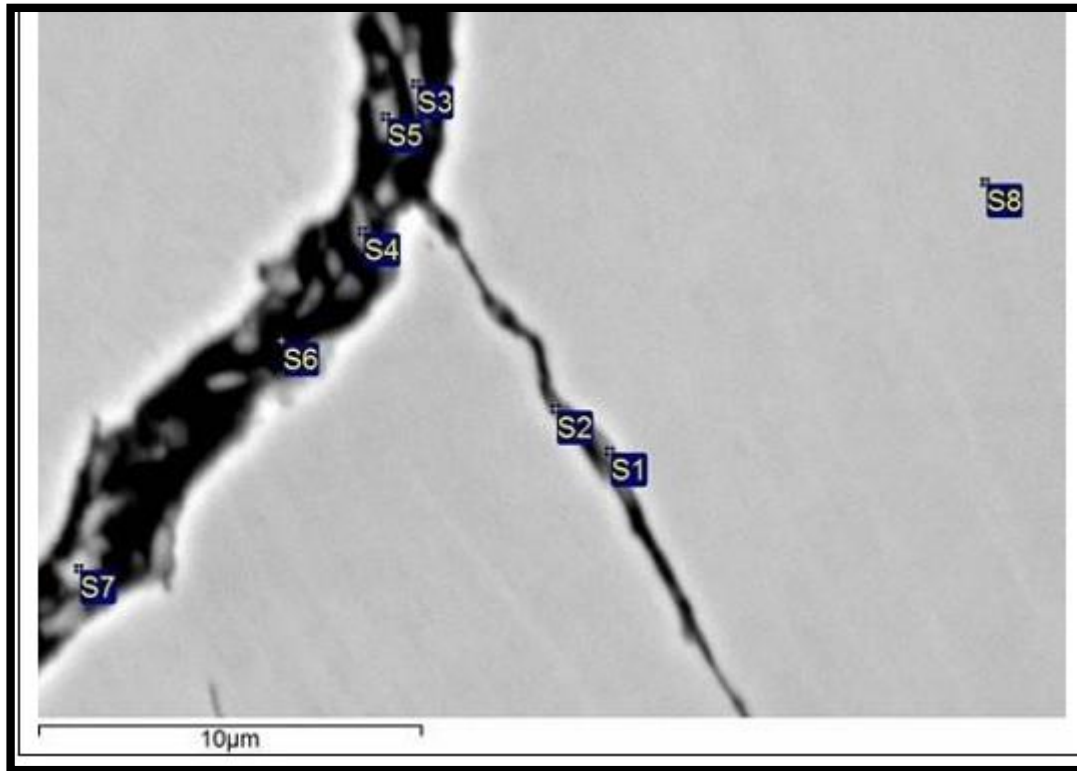


Figure 45: Photo by SEM showing the crack's surface on the Inner surface of cross section sample (2) as polished condition.

Table 18: SEM-EDS Analysis of the crack's surface on the Inner surface of cross section sample (2) as polished condition.

Spectrum	C	O	Si	P	S	Cr	Mn	Fe	Ni	Cu	Total
S1	5.94	10.32	0.43			16.76	1.19	58.60	6.26	0.48	100.00
S2	6.78	10.13	0.47			16.48	1.10	58.27	6.21	0.57	100.00
S3	19.20	31.92	1.00	0.11		8.24	0.43	35.92	3.18		100.00
S4	21.58	21.60	1.01			11.62	0.64	39.85	3.70		100.00
S5	15.42	30.42	1.25	0.16		7.97	0.41	40.58	3.80		100.00
S6	33.63	12.47	0.53		0.10	11.80	0.64	37.45	3.38		100.00
S7	25.72	33.25	0.60	0.12		5.41	0.28	31.59	3.03		100.00
S8	6.06		0.60			17.90	1.40	66.91	7.13		100.00

4.4 Hardness Measurements:

4.4.1 Hardness Measurement of SS304H:

The hardness of both tubes was measured using Struers digital micro hardness tester at room temperature 22.3°C and load 1000gf. The hardness was performed on three of the prepared samples which are the cracked sample from the bottom side of the big tube, the uncracked sample from the top side of the big tube for comparison, and the welded sample from the bottom of the small tube.

For the cracked and the uncracked samples, two lines of hardness measurement (from IS to OS) were done on each of them. In the 1st measurement line on both samples, which is located on the big tube side, the cracked sample has a higher value especially at the (IS) and both of the 7th & 8th indentations. While the mid area for both samples seems to be in the same range. For the hardness measurements line that is going through the weld in both samples, the cracked samples have a much higher value exactly at the (IS). In addition to that, both samples show a drop of hardness at the (HAZ), which is at the 8th indentation for the cracked sample and the 7th for the uncracked sample. Results are shown in Tables 19&20 and Figures 46-49. For the third sample, three measurement lines were conducted (all going from IS to OS), one going from the base metal through the welding area while the other two are on each side of the sample. The hardness measurement that is going from base metal through welding,

shows high values at the first two indentations at the (IS). After that, all other readings have little drop but in the same range except the indentation at the (HAZ) which has a noticeably less value than others. For the other two measurement lines at the edges of the sample, the hardness values at IS and OS are a little higher at the bottom side of the tube which is closer to the mining pipe, while the middle area of

both sides are in the same range. Results are shown in Table 21 and Figures 50&51.

Table 19: Hardness value measurements of cracked sample from main pipe.

Indentation No (IS to OS)	Main Pipe Bottom Side (HV)	Through Welding (HV)
1	325.70	354.40
2	206.30	226.10
3	218.30	207.50
4	208.40	207.70
5	207.10	210.40
6	220.30	218.50
7	240.40	195.80
8	225.10	178.10
9	208.10	202.30
10		204.90
11		202.10
12		182.20
13		173.50
14		191.80
15		201.30
16		194.60
17		199.10
18		191.10
19		199.90
20		201.30
21		199.30

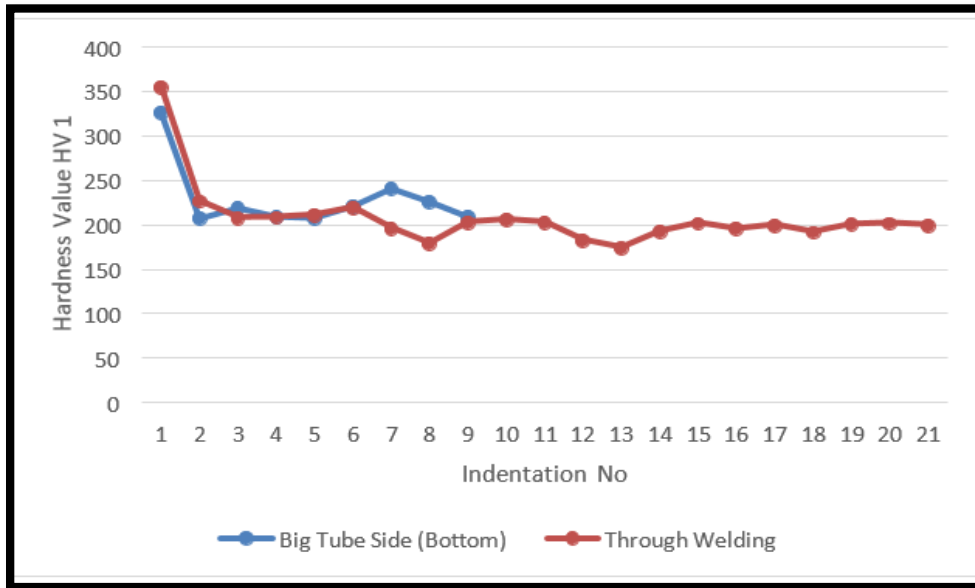


Figure 46: Hardness value profile of cracked sample from the main pipe.

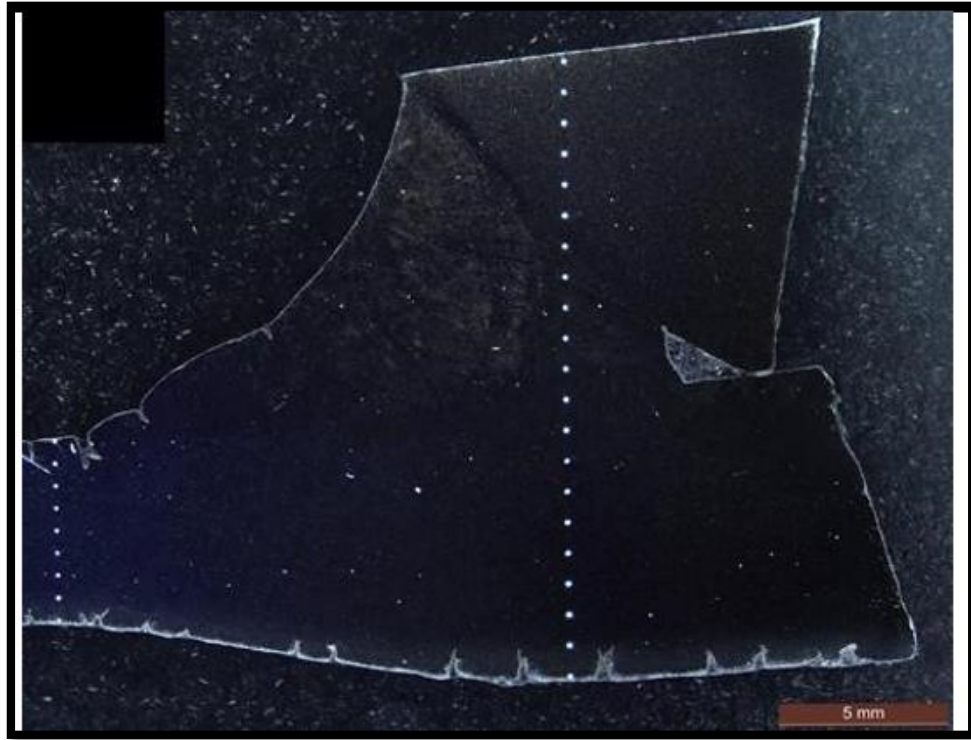


Figure 47: Photo by stereo microscope showing the cracked sample with indents after hardness test.

Table 20: Hardness value measurements of un cracked sample from main pipe.

Indentation No (IS to OS)	Main Pipe Top Side (HV)	Through Welding (HV)
1	237.70	295.00
2	195.20	214.60
3	192.00	211.00
4	187.50	207.20
5	202.10	207.50
6	190.00	208.40
7	187.50	183.50
8	180.90	206.00
9	208.10	202.20
10		205.10
11		196.60
12		186.80
13		192.80
14		190.10
15		193.10
16		191.10
17		202.40
18		204.60
19		200.90
20		209.90
21		197.80

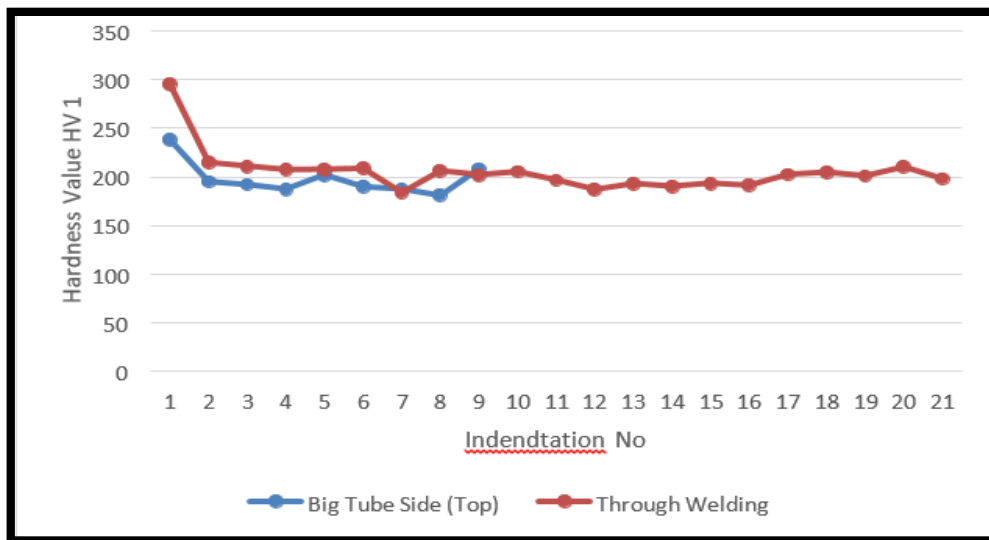


Figure 48: Hardness value profile of cracked sample from the main pipe.



Figure 49: Photo by stereo microscope showing the un cracked sample with indents after hardness test.

Table 21: Hardness value measurements of welding sample from small tube.

Indentation No (IS to OS)	Bottom Side (HV)	Top Side (HV)	Through Welding (HV)
1	255.00	228.60	236.9
2	206.10	212.20	239.5
3	185.70	192.60	212.2
4	173.70	183.80	197.3
5	162.20	170.80	172.4
6	173.30	176.20	158.6
7	166.30	184.20	169.7
8	173.00	180.10	173.2
9	218.40	199.30	165.3
10			172.2
11			162.2
12			170
13			173
14			172.6
15			172.8
16			176.9

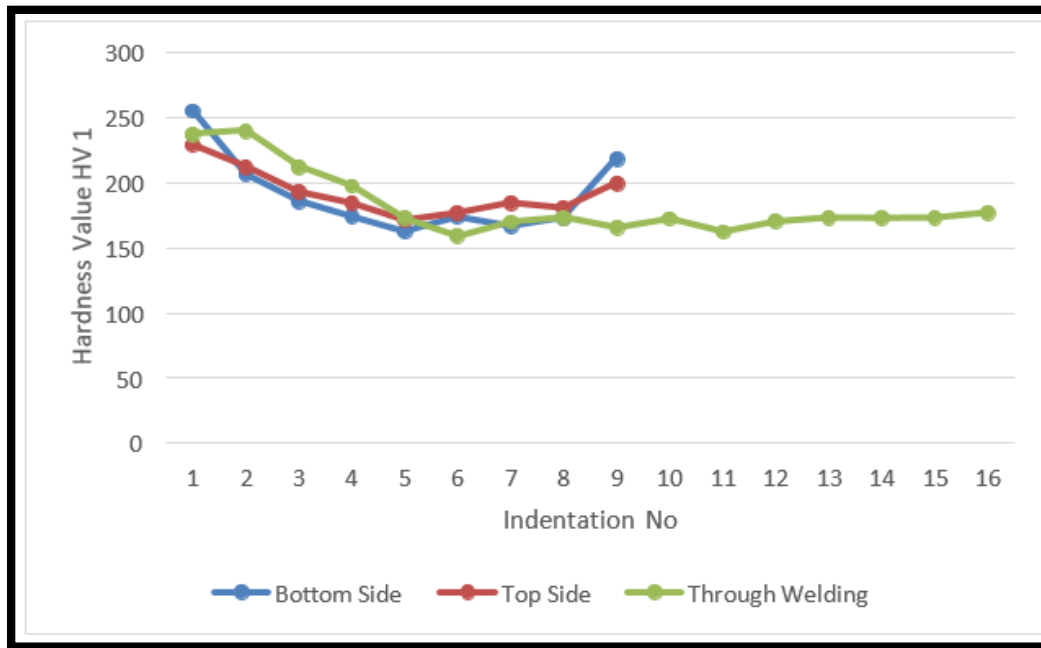


Figure 50: Hardness value profile of welding sample from small tube.

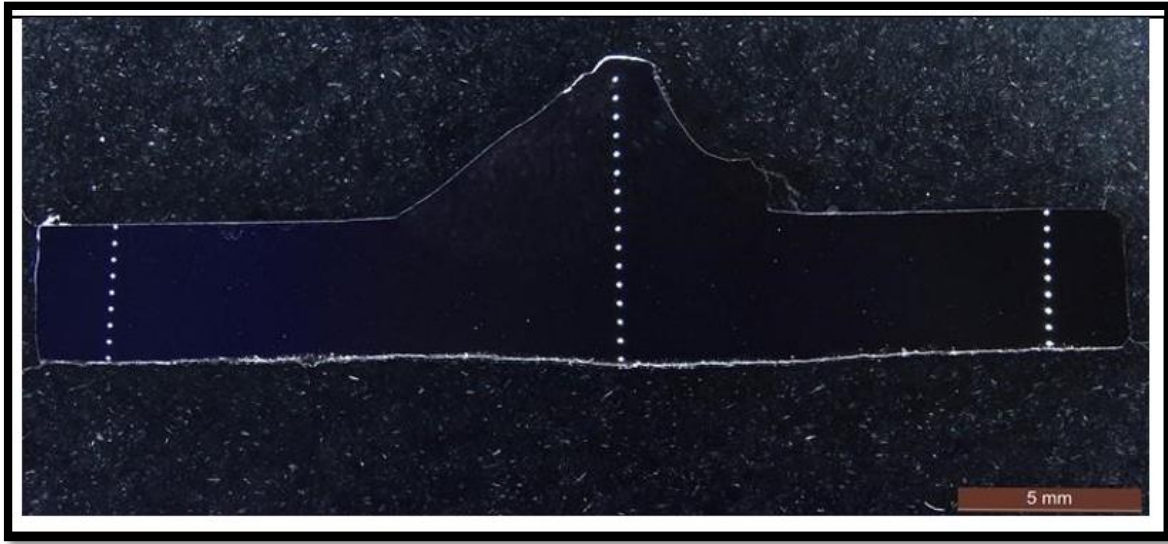


Figure 51: Photo by stereo microscope showing the welding sample with indents after hardness test.

4.4.2 Hardness Measurement of SS304L:

The hardness of the flange sample was measured using Struers digital micro hardness tester at room temperature 22.5°C and load of 500gf. The hardness was performed on one of the cross section samples to measure all of weld metal (WM), heat affected zone (HAZ), and base metal (BM) areas so we can see the full picture of the sample hardness. The hardness measurements were taken twice, once from the top to the bottom of the sample so we cover all mentioned areas, while the other time was only on the HAZ area going from the outer surface to the inner surface of the sample.

On the first reading, the hardness measurements of the welded area were very close until it slightly dropped before entering the HAZ area, and it kept going around the same hardness except for a very little drop in the 8th indentation. On the second reading, the hardness of the HAZ area was almost identical except for a single drop and jump in indentations 3 & 5 respectively. The detailed results are shown in Tables 22&23 and Figures 52&53

Table 22: Hardness value measurements of flange sample top to bottom.

Indentation No	HV
1 (Weld)	246.10
2 (Weld)	248.90
3 (Weld)	247.20
4 (Weld)	251.60
5 (Weld)	234.70
6 (HAZ)	233.30
7 (HAZ)	230.40
8 (HAZ)	217.80
9 (HAZ)	238.70
10 (HAZ)	226.60
11 (HAZ)	241.50
12 (BM)	236.90

Table 23: Hardness value measurements of flange sample on HAZ area OS to IS.

Indentation No	HV
1 (OS)	219.60
2	186.80
3	219.10
4	219.20
5 (IS)	230.60

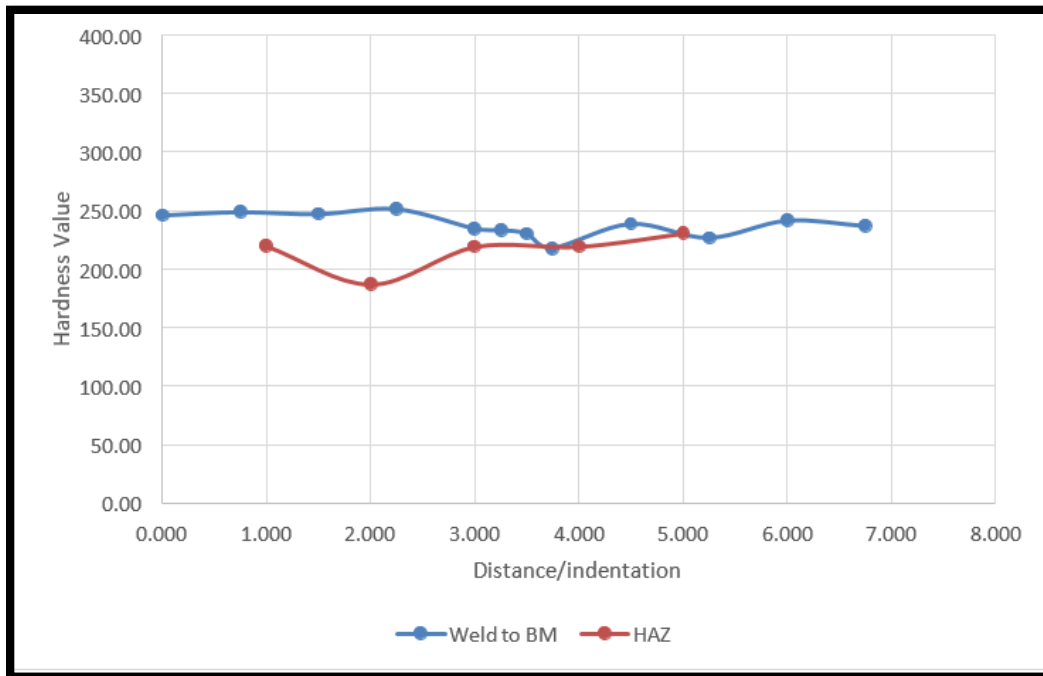


Figure 52: Hardness value profile of flange samples.

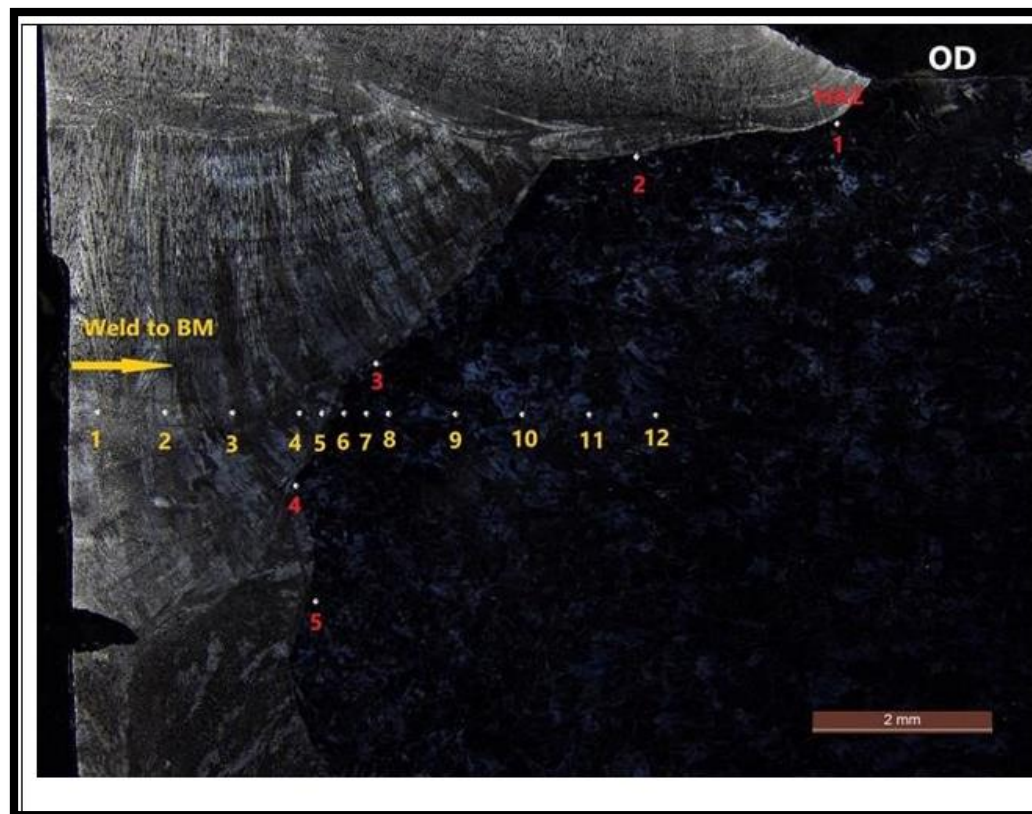


Figure 53: Photo by Stereoscope showing locations of indentations of both measurements

4.5 Loss of Wight

The reaction basin used in this method was a graduated cylindrical plastic. vessel 5 cm inner diameter and has a total volume of 150 mL. 50 mL of the test solution was employed in each experiment. The test pieces were cut nearly 3cm * 3cm and the thickness 1 cm. we prepared the samples and drop it in the cylindrical plastic, and we dipped them into the different solutions and different concentrations. After specified periods of time, the samples were taken out of the test solution, rinsed in doubly distilled water, dried as before, and weighed again and the mean value of weight loss has been reported in below Table.

$$\text{Corrosion rate (mm/year)} = \frac{W \times 8.76 \times 10^4}{A \times T \times D}$$

Corrosion Rate Equation

W: mass loss

A: area in cm²

T: Time of exposure in hours

D: Density in g/ cm³

$$\%IE_{Wt\ Loss} = \frac{CR_o - CR_i}{CR_o} \times 100$$

Inhibitor Efficiency

CR₀: Wight loss for Blank

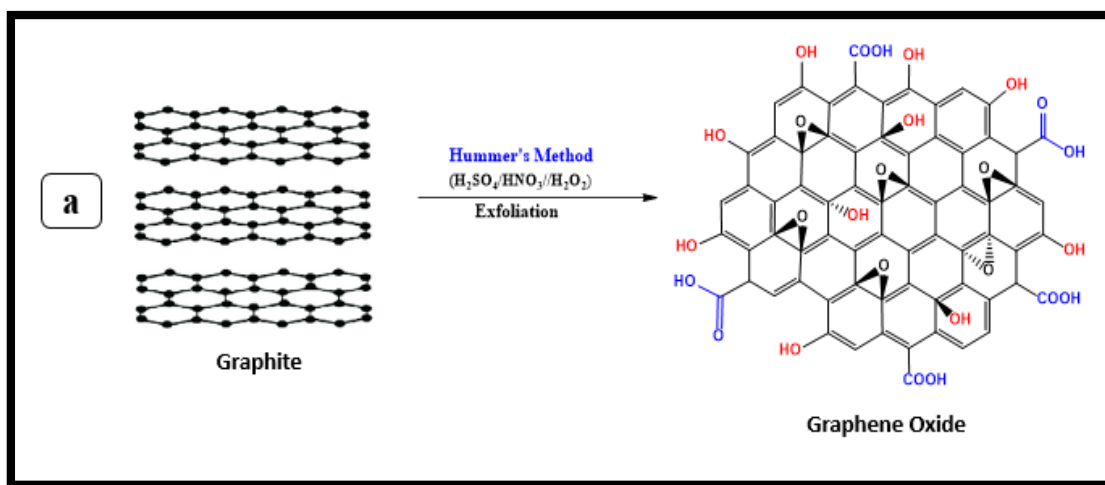
CR_i: Wight loss for sample with inhibitor

4.5.1: Synthesis of inhibitor:

The work includes the preparation of functionalized nanoparticles. Several modified nanoparticles including modified silica and modified graphenes. Among them, initial testing indicated that the modified graphene displayed good inhibition performance. Thus, the synthesis and testing in corrosion treatment of this material is reported as in the following sections.

An aqueous solution of chitosan (0.2 g) was obtained by dissolving it in 40 mL of 0.33 M acetic acid for 24 h, and 12 mmol of polyaniline monomer was dissolved in 20 mL of 0.8 M $\text{NH}_2\text{SO}_3\text{H}$. This polyaniline solution was added to the chitosan solution and stirred for 30 min to form a homogeneous solution. An ammonium persulfate (10 mmol) solution was prepared by dissolving it in 0.33 M CH_3COOH , which was then added dropwise to a homogeneous solution for 1 h at $0 - 5^\circ\text{C}$. The molar ratio of oxidant to monomer was 1: 2, with the polymerization reaction, carried out at $0 - 5^\circ\text{C}$ for 6 h. The precipitated composite was collected by filtering and washing with water and ethanol, respectively, and then dried at 50°C for 12 h in a vacuum oven.

Conductive polyaniline chains were electrostatically grafted on the GO sheets through a common in-situ oxidative polymerization utilizing ammonium peroxide sulphate as redox initiator. For this aim, first, 15 mL HCl solution (1 M) containing aniline (3.2 mM) and ammonium peroxide sulphate (0.8 mM) was prepared and added to 15 mL deionized water solution containing stable dispersion of graphene oxide (25 g/L). The reaction mixture was stirred for 24 h at room temperature ($25 \pm 3^\circ\text{C}$), reaching a dark green mixture that visually confirmed the polyaniline (PANI) deposition on the GO sheets. In the end, the product was filtered and washed three times with deionized water. The final product was coded as GO-PANI, hereafter.



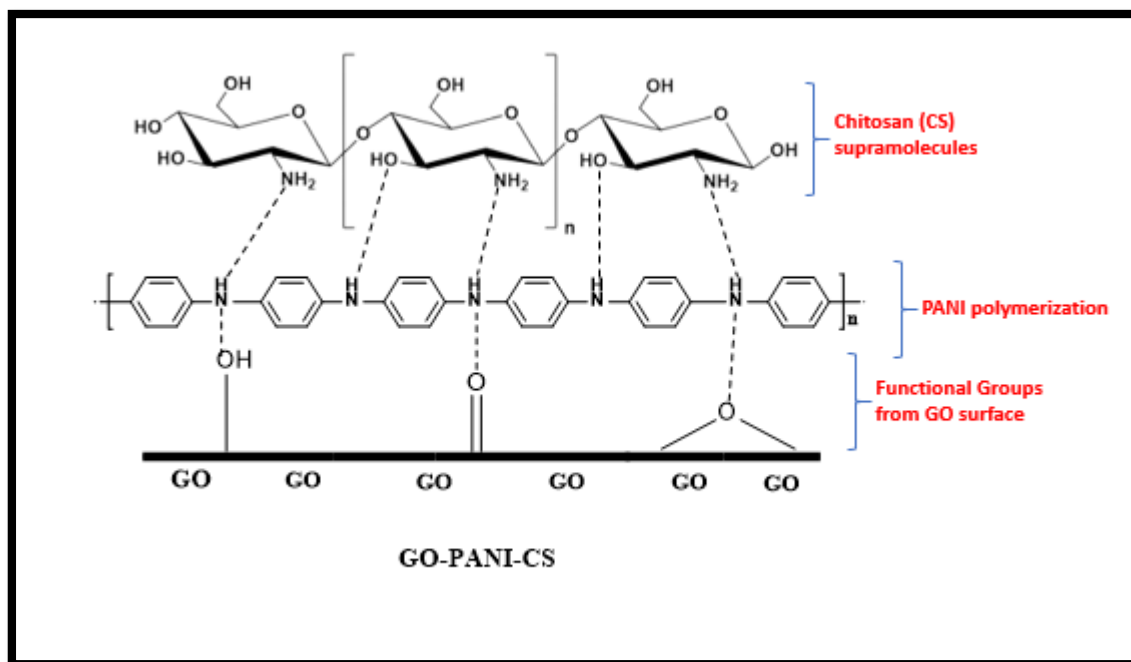
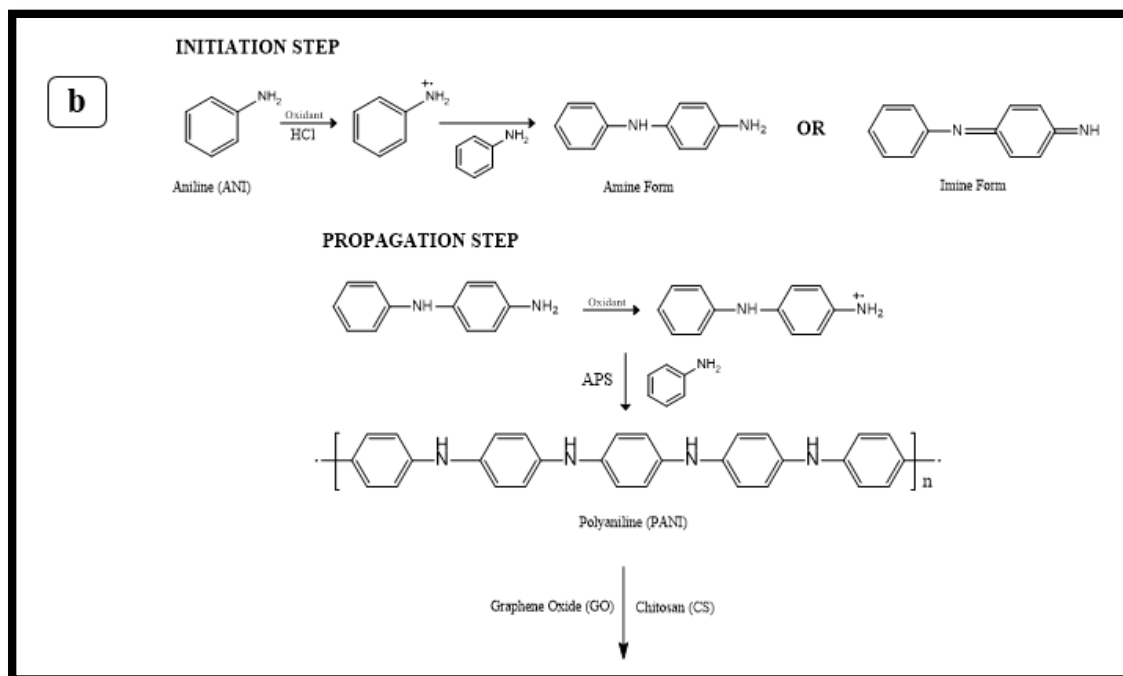


Figure 54: Synthesis of the prepared inhibitor:

4.5.2: Sample preparation and Testing Metallurgical:

Regarding the SS304 H we cut 12 samples from the pipe as shown in Figure 51, while for the SS304 L we cut 12 samples from flange as shown in Figure 56. For the total samples we have 24 samples, 12 samples for each grade. The dimension of the samples 3cm * 3cm and the thickness 1cm. we grind and polish the samples with UNIPOL-820, and we are used for polishing Silicon Carbide paper 240 Cw. We prepared the HCl with different concentrations 15 & 7 M. the first step placed the samples in plastic containers and added hydrochloric acid and we drop different concentrations of inhibitors 1,5,25,75,100,200,300,400 and 500 ppm. To identify the best concentration. After that, we change the parameters to see what is the best condition for the inhibitor to protect the SS from corrosion. We found the best concentration for inhibitor 200 ppm. We repeat the analysis using 200 ppm from the inhibitor for different temperatures and solutions.

- Acetic Acid (CH_3COOH) 15 M
- Methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) 15 M
- (CH_3COOH 15 M & HCl 15 M) 50% for each solution
- ($\text{CH}_3\text{SO}_3\text{H}$ 15 M & HCl 15 M) 50% for each solution

The detailed results are shown below.

4.5.3 Hydrochloric Acid HCl

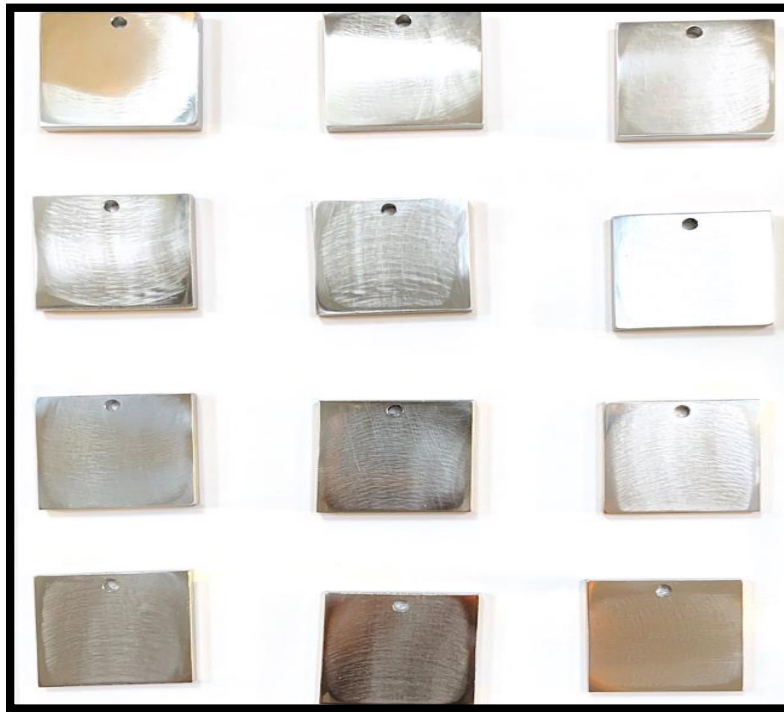


Figure 55: 12 Samples from SS304 H After polishing by Silicon Carbide paper 240 Cw

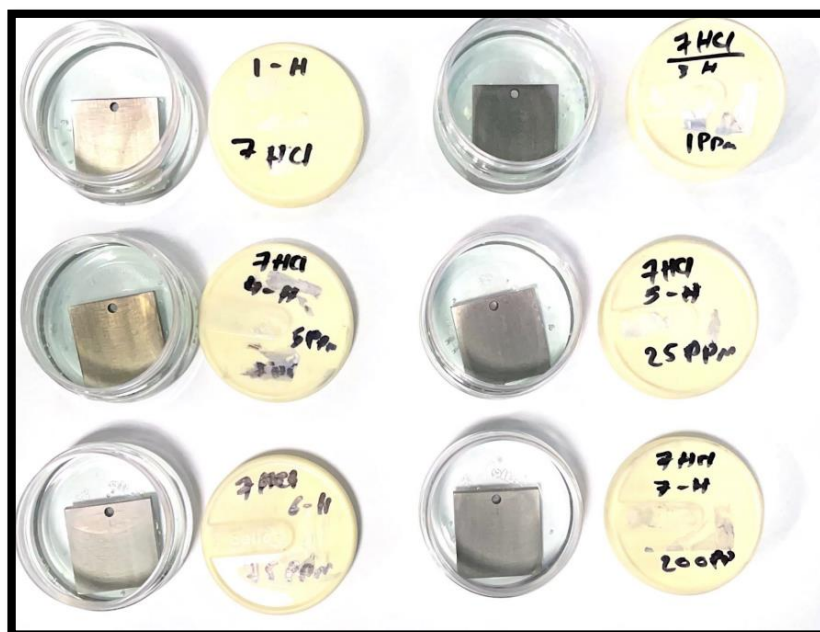


Figure 56: SS304 H 7%HCl



Figure 57: SS304 H 7%HCl – Dry Air

Table24: SS304H (HCl 7%) Inhibitor result

SS304-H							
Sample	Conc of HCl (%)	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	7	Blank	79.1149	78.9291	0.1858	1.131522	
2	7	1	78.9285	78.8927	0.0358	0.218022	80.7
3	7	5	78.9213	78.8855	0.0358	0.218022	80.7
4	7	25	78.963	78.9287	0.0343	0.208887	81.5
5	7	75	79.0477	79.0131	0.0346	0.210714	81.4
6	7	100	79.0514	79.0233	0.0281	0.171129	84.9
7	7	200	78.9241	78.8989	0.0252	0.153468	86.4
8	7	300	78.8994	78.8718	0.0276	0.168084	85.1
9	7	400	78.9432	78.9109	0.0323	0.196707	82.6
10	7	500	78.7496	78.7244	0.0252	0.153468	86.4

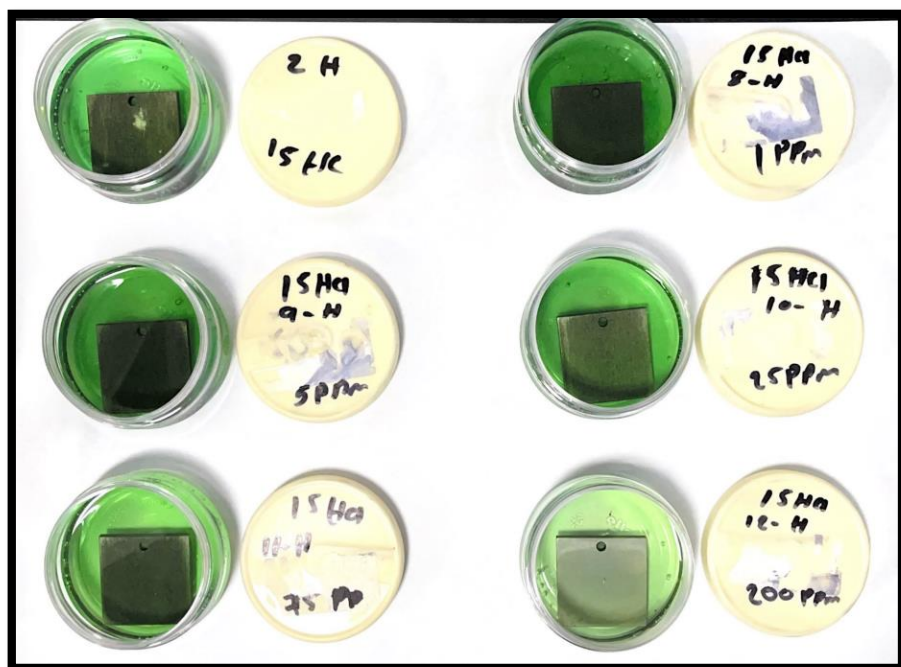


Figure 58: SS304 H 15%HCl



Figure 59: SS304 H 15%HCl – Dry Air

Table25: SS304H (HCl 15%) Inhibitor result

SS304-H							
Sample	Conc of HCl (%)	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	15	Blank	78.8391	78.34	0.4991	3.039519	
2	15	1	78.9133	78.6823	0.231	1.40679	53.7
3	15	5	63.7129	63.4825	0.2304	1.403136	53.8
4	15	25	63.5841	63.3528	0.2313	1.408617	53.7
5	15	75	64.2735	64.0507	0.2228	1.356852	55.4
6	15	100	78.4124	78.3067	0.1057	0.643713	78.8
7	15	200	63.6154	63.5299	0.0855	0.520695	82.9
8	15	300	63.4464	63.3147	0.1317	0.802053	73.6
9	15	400	78.301	78.1726	0.1284	0.781956	74.3
10	15	500	63.3044	63.1917	0.1127	0.686343	77.4



Figure 60: 12 Samples from SS304 L After polishing by Silicon Carbide paper 240 Cw

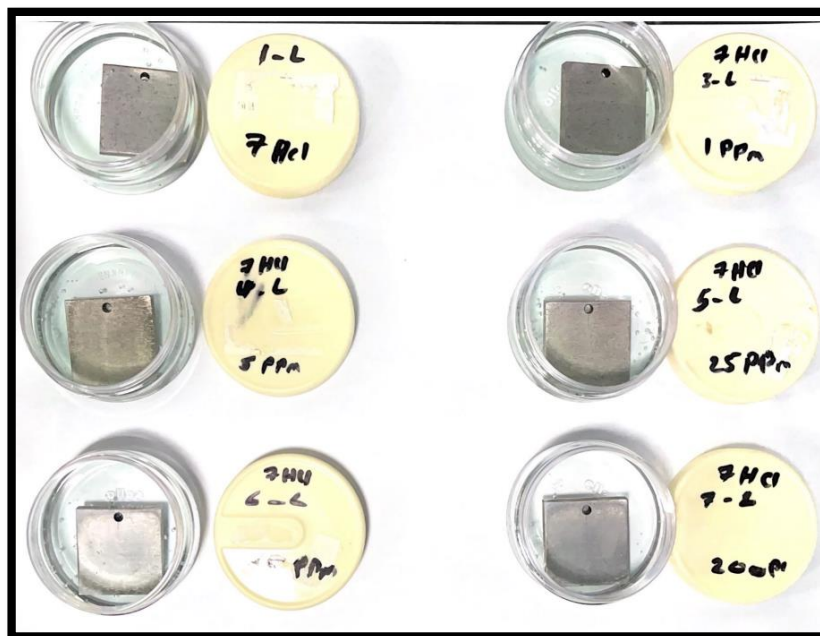


Figure 61: SS304 L 7%HCl



Figure 62: SS304 L 7%HCl – Dry Air

Table26: SS304L (HCl 7%) Inhibitor result

SS304-L							
Sample	Conc of HCl (%)	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	7	Blank	89.7552	89.5593	0.1959	1.193031	
2	7	1	91.8942	91.8576	0.0366	0.222894	81.3
3	7	5	105.6433	105.607	0.0363	0.221067	81.5
4	7	25	104.8785	104.8437	0.0348	0.211932	82.2
5	7	75	102.7613	102.7279	0.0334	0.203406	82.9
6	7	100	91.768	91.7374	0.0306	0.186354	84.4
7	7	200	102.8948	102.8669	0.0279	0.169911	85.8
8	7	300	105.5115	105.4791	0.0324	0.197316	83.5
9	7	400	104.7682	104.7362	0.032	0.19488	83.7
10	7	500	89.5894	89.5577	0.0317	0.193053	83.8

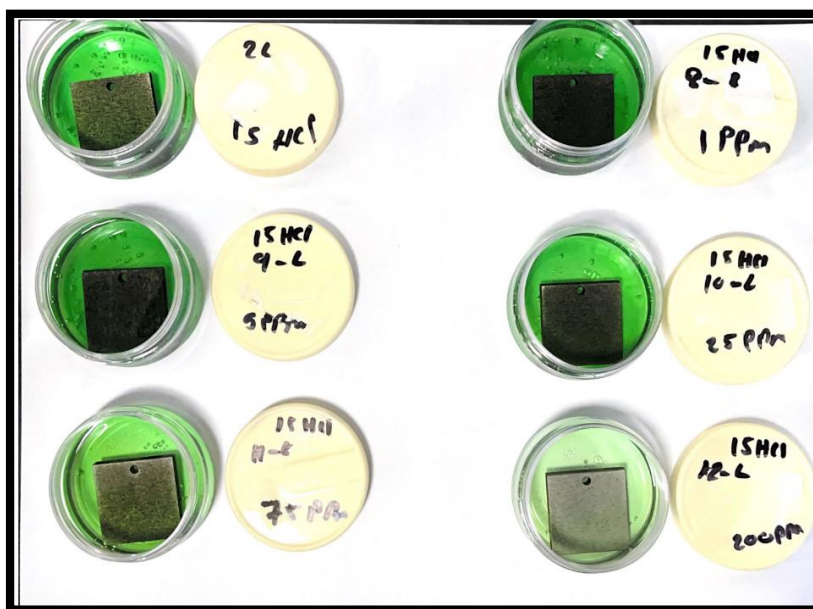


Figure 63: SS304 L 15%HCl



Figure 64: SS304 L 15%HCl – Dry Air

Table27: SS304L (HCl 15%) Inhibitor result

SS304-L							
Sample	Conc of HCl (%)	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	15	Blank	92.5477	92.0019	0.5458	3.323922	
2	15	1	104.651	104.3646	0.2864	1.744176	47.5
3	15	5	104.6997	104.4219	0.2778	1.691802	49.1
4	15	25	105.0349	104.7739	0.261	1.58949	52.2
5	15	75	104.895	104.7185	0.1765	1.074885	67.7
6	15	100	104.5742	104.4527	0.1215	0.739935	77.7
7	15	200	91.6414	91.54	0.1014	0.617526	81.4
8	15	300	92.1993	92.0722	0.1271	0.774039	76.7
9	15	400	104.3025	104.1685	0.134	0.81606	75.4
10	15	500	104.3698	104.2529	0.1169	0.711921	78.6

4.5.4 Acetic Acid (CH_3COOH)

4.5.5 Methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$)

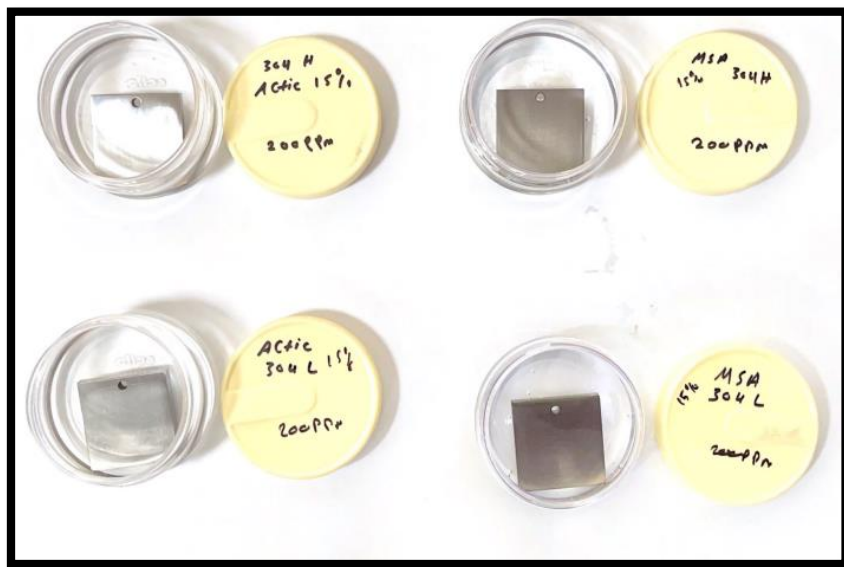


Figure 65: SS304 (H and L) (15% MSA & 15% Acetic acid)

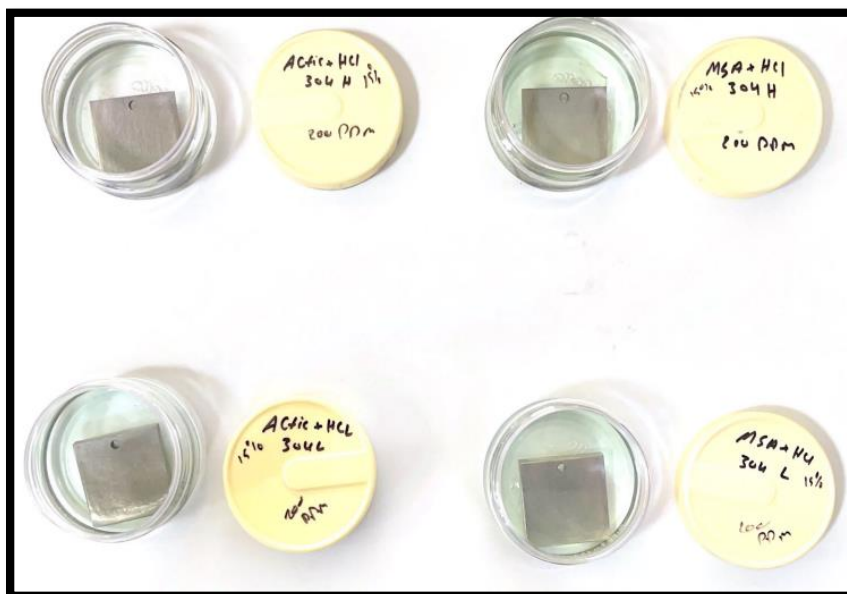


Figure 66: SS304 (H and L) (15% MSA & 15% Acetic acid) Mix solution

Table28: SS304H Acetic Acid, MSA, (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result

SS304-H							
Sample	Solution 15%	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	Acetic Acid	200	78.5897	78.5893	0.0004	0.002436	55.6
2	MSA	200	78.8349	78.82	0.0149	0.090741	29.4
3	Acetic Acid + HCl	200	62.9982	62.9659	0.0323	0.196707	87.1
4	MSA+ HCl	200	63.8711	63.8299	0.0412	0.250908	84.2

Table29: SS304L Acetic Acid, MSA, (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result

SS304-L							
Sample	Solution 15%	Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	Acetic Acid	200	102.6212	102.6202	0.001	0.00609	75.6
2	MSA	200	102.7749	102.7499	0.025	0.15225	20.6
3	Acetic Acid + HCl	200	104.5631	104.519	0.0441	0.268569	83.9
4	MSA+ HCl	200	91.492	91.4349	0.0571	0.347739	80.2

4.5.6 Acetic Acid (CH_3COOH) (Blank)

4.5.7 Methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) (Blank)

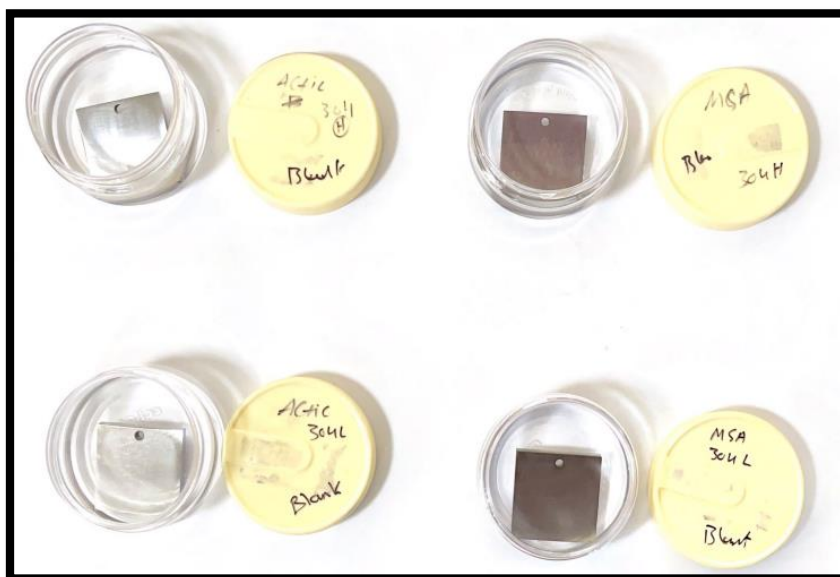


Figure 67: SS304 (H and L) (15% MSA & 15% Acetic acid) Blank

Table30: SS304H Acetic Acid and MSA Blank

SS304-H Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	Acetic Acid (Blank)	78.9509	78.95	0.0009	0.005481
2	MSA (Blank)	78.8401	78.819	0.0211	0.128499

Table31: SS304L Acetic Acid and MSA Blank

SS304-L Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	Acetic Acid (Blank)	91.7051	91.701	0.0041	0.024969
2	MSA (Blank)	105.4362	105.4047	0.0315	0.191835

4.5.8 SS304-H & SS304- L at 60 & 90 °C



Figure 68: SS304 (H and L) (15%HCl), (15% MSA &15% HCl) and (15% Acetic Acid &15% HCl) at 60 & 90 °C

Table32: SS304H HCl , (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result at 60 °C

SS304-H at 60 Temperature							
Sample	Solution 15%	Conc of Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	HCL	200	77.8905	77.033	0.8575	5.222175	71.8
2	HCL + MSA	200	78.6926	78.5577	0.1349	0.821541	82.1
3	HCL + Acetic Acid	200	62.9883	62.8652	0.1231	0.749679	74.5

Table33: SS304L HCl , (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result at 60 °C

SS304-L at 60 Temperature							
Sample	Solution 15%	Conc of Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	HCL	200	91.7456	90.6781	1.0675	6.501075	71.9
2	HCL + MSA	200	104.1921	104.0374	0.1547	0.942123	84.2
3	HCL + Acetic Acid	200	89.453	89.3099	0.1431	0.871479	80.6

Table34: SS304H HCl , (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result at 90 °C

SS304-H at 90 Temperature							
Sample	Solution 15%	Conc of Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	HCL	200	78.1207	74.2845	3.8362	23.362458	32.8
2	HCL + MSA	200	62.9268	61.8827	1.0441	6.358569	56.8
3	HCL + Acetic Acid	200	78.5733	77.8282	0.7451	4.537659	59.3

Table35: SS304L HCl , (HCl + MSA) and (HCl + Acetic Acid) Inhibitor result at 90 °C

SS304-L at 90 Temperature							
Sample	Solution 15%	Conc of Inhibitor (ppm)	Initial weight	Final weight	Initial - Final	Corrosion rate	IE%
1	HCL	200	104.6272	99.6519	4.9753	30.299577	19.6
2	HCL + MSA	200	104.019	102.5822	1.4368	8.750112	59.5
3	HCL + Acetic Acid	200	104.0691	102.9212	1.1479	6.990711	57.5

4.5.9 SS304-H & SS304- L at 60 & 90 °C (Blank)

Table36: SS304H HCl , Acetic Acid and MSA 60 °C Blank

SS304-H at 60 Temperature Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	HCL	76.36	73.3153	3.0447	18.542223
2	HCL + MSA	78.3569	77.6045	0.7524	4.582116
3	HCL + Acetic Acid	62.5985	62.1166	0.4819	2.934771

Table37: SS304L HCl , Acetic Acid and MSA 60 °C Blank

SS304-L at 60 Temperature Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	HCL	89.9385	86.136	3.8025	23.157225
2	HCL + MSA	91.6311	90.6542	0.9769	5.949321
3	HCL + Acetic Acid	89.1991	88.4601	0.739	4.50051

Table38: SS304H HCl , Acetic Acid and MSA 90 °C Blank

SS304-H at 90 Temperature Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	HCL	78.6822	72.9695	5.7127	34.790343
2	HCL + MSA	78.7027	76.2882	2.4145	14.704305
3	HCL + Acetic Acid	63.73	61.8991	1.8309	11.150181

Table39: SS304L HCl , Acetic Acid and MSA 90 °C Blank

SS304-L at 90 Temperature Blank					
Sample	Solution 15%	Initial weight	Final weight	Initial - Final	Corrosion rate
1	HCL	105.2986	99.1135	6.1851	37.667259
2	HCL + MSA	102.6833	99.1383	3.545	21.58905
3	HCL + Acetic Acid	102.5535	99.8515	2.702	16.45518

4.6 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier transform infrared spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

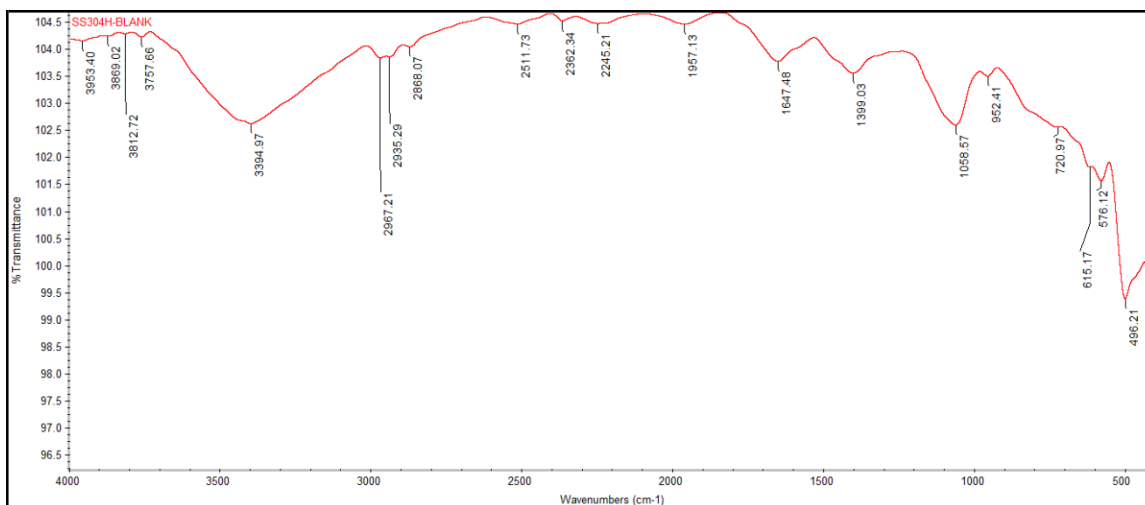


Figure 69: FTIR spectrum of the SS304 H Blank

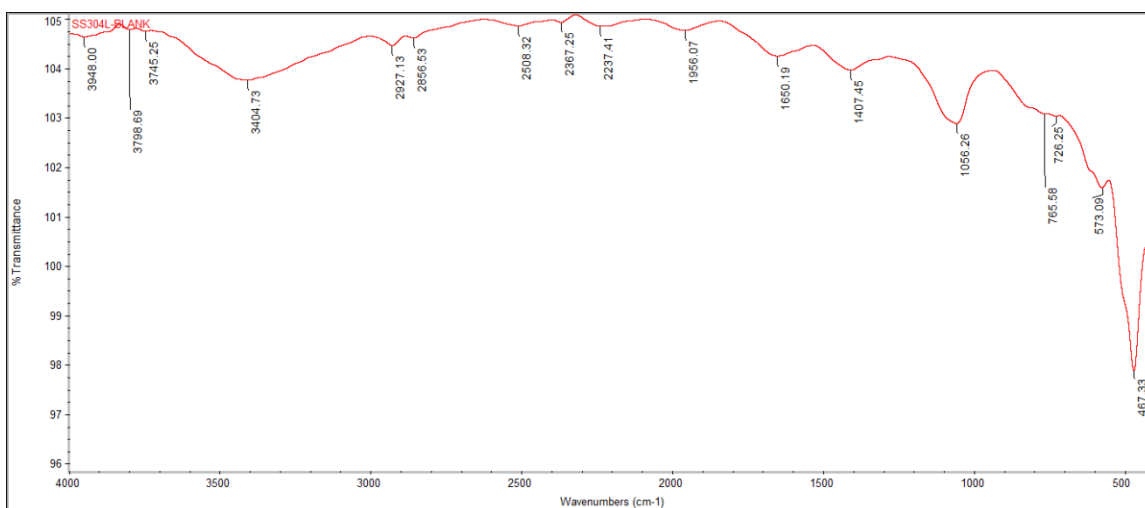


Figure 70: FTIR spectrum of the SS304 L Blank

4.6.1 HCl Solutions

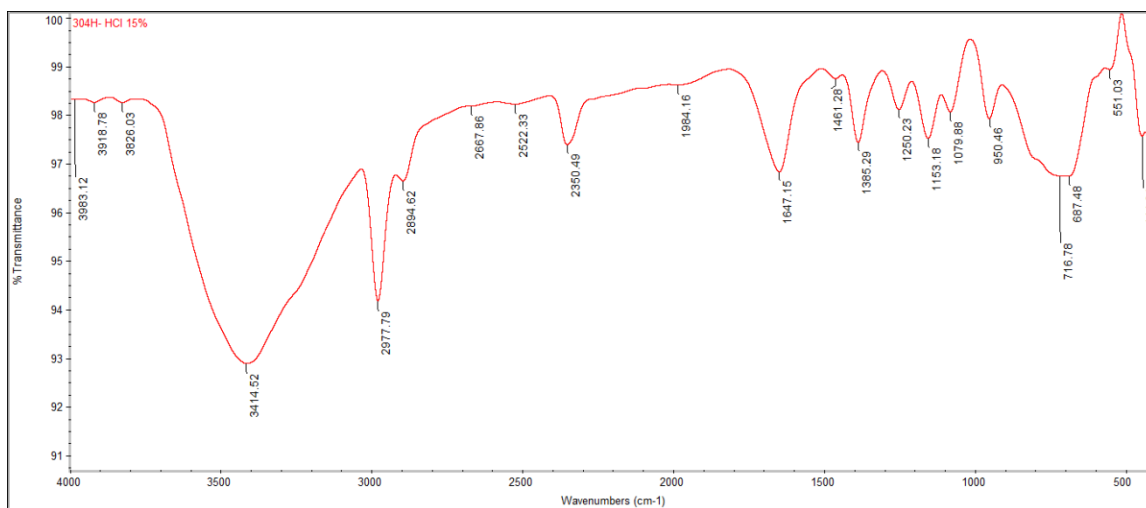


Figure 71: FTIR spectrum of the SS304 H HCl 15 M

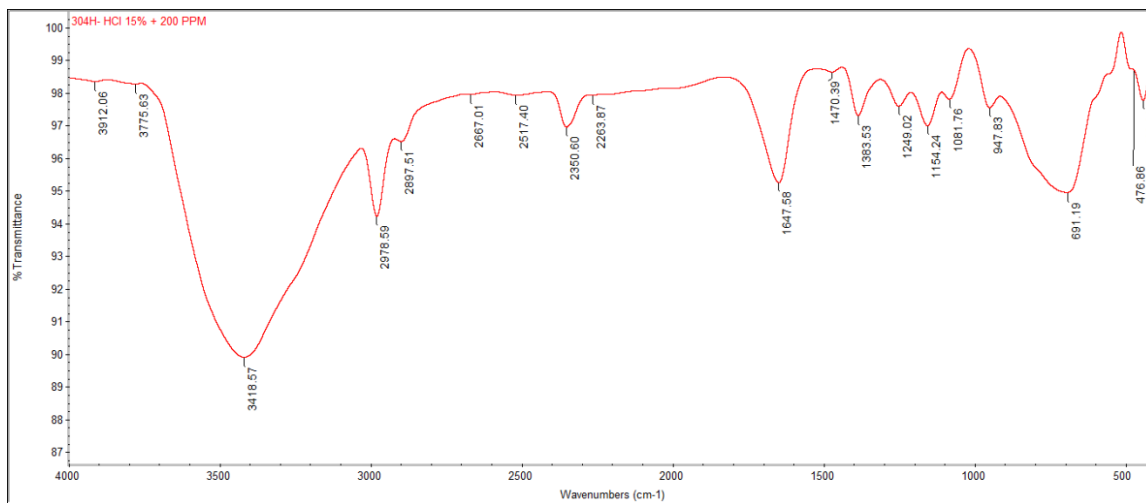


Figure 72: FTIR spectrum of the SS304 H HCl 15 M % 200 ppm inhibitor

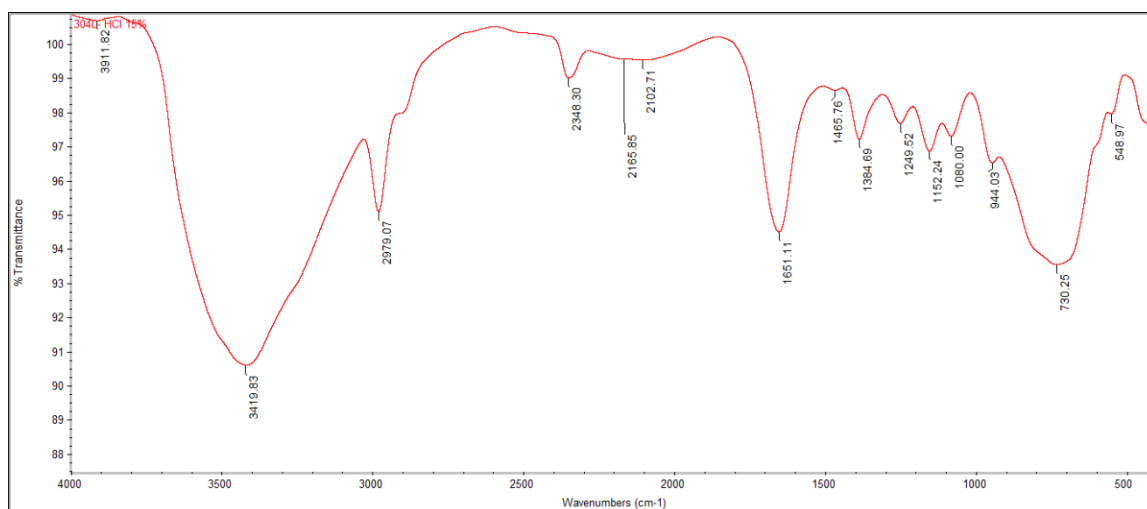


Figure 73: FTIR spectrum of the SS304 L HCl 15 M

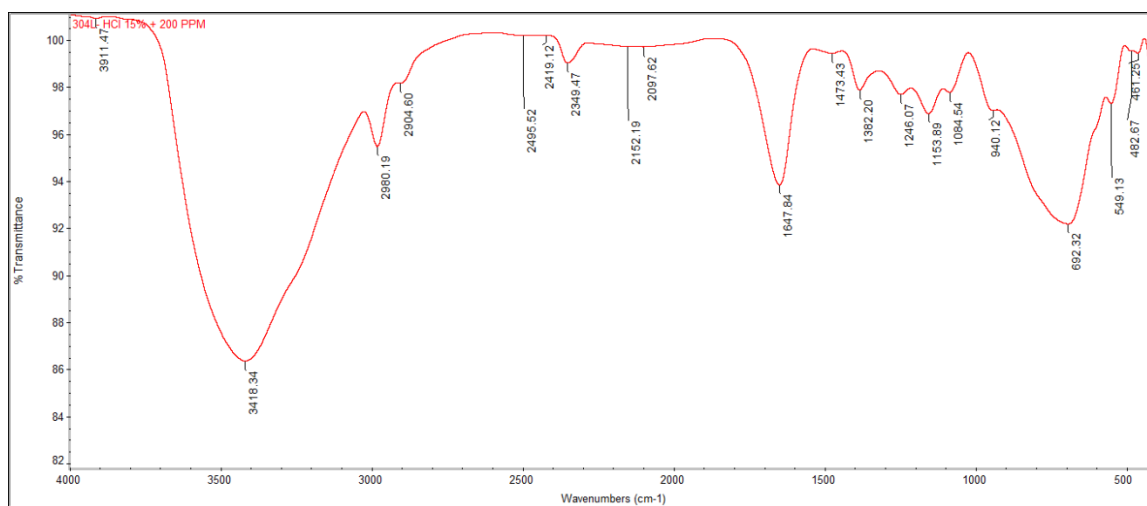


Figure 74: FTIR spectrum of the SS304 H HCl 15 M % 200 ppm inhibitor

At room temperature, there is no change in the peaks. However, the prepared 200 ppm inhibitor caused a reduction in the strength of the peaks, which indicates that the inhibitor formed a protective layer on the surface of the metal that is resistant to corrosion.

4.6.2 Acetic Acid 15 M Solution:

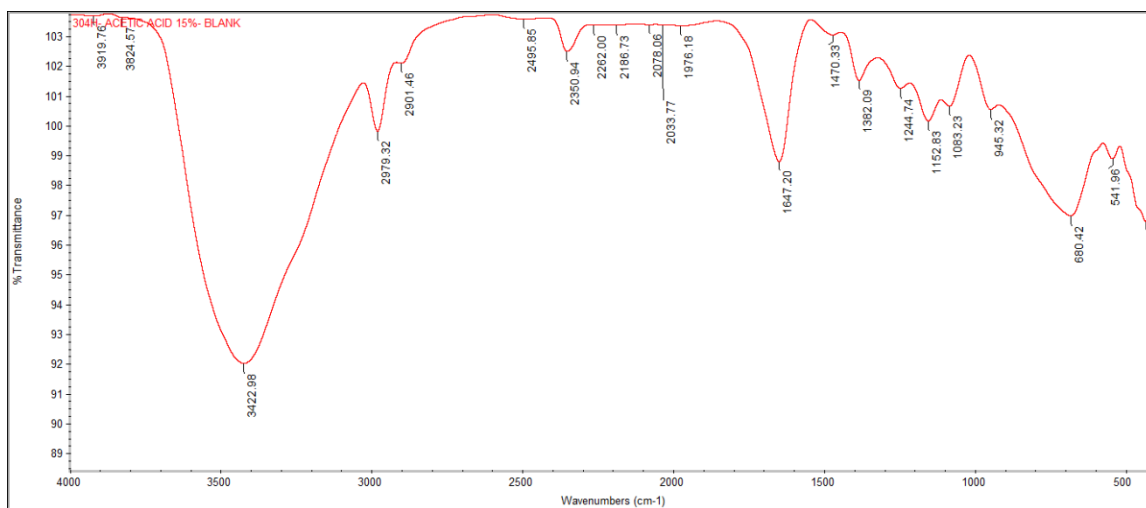


Figure 75: FTIR spectrum of the SS 304 H Acetic Acid Solution 25 °C blank

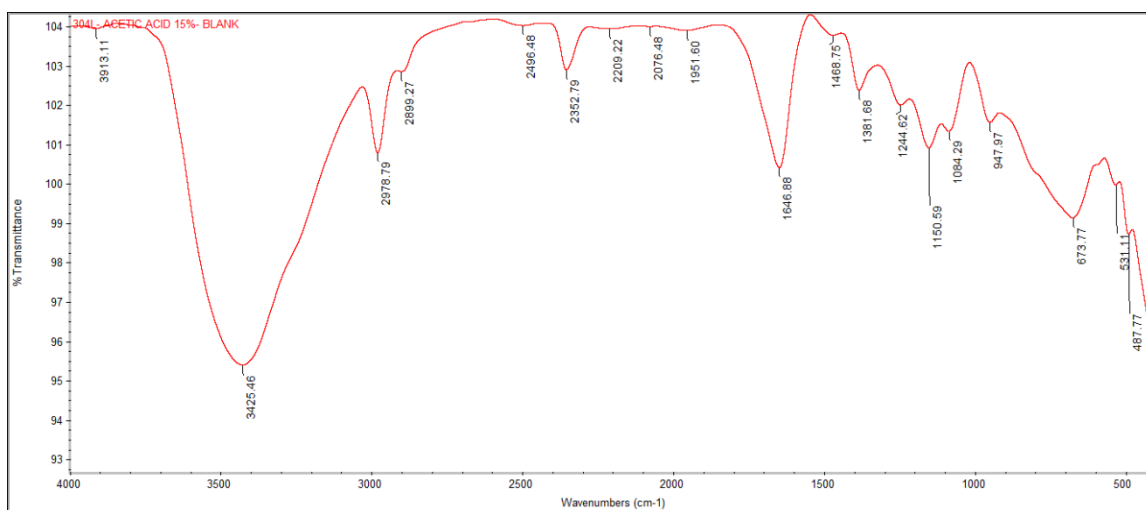


Figure 76: FTIR spectrum of the SS 304 L Acetic Acid Solution 25 °C blank

4.6.3 MSA 15 M Solution:

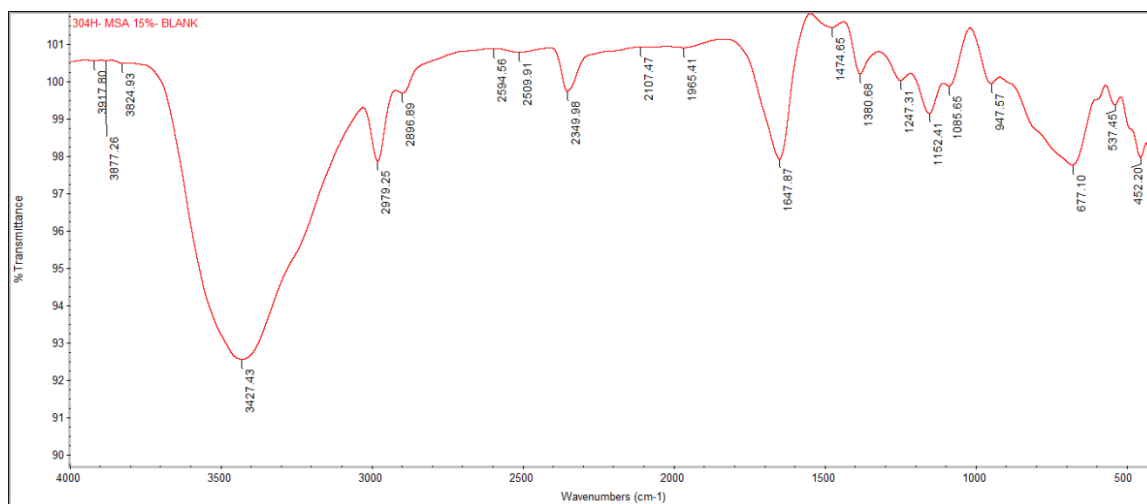


Figure77: FTIR spectrum of the SS 304 H MSA Solution 25 °C blank

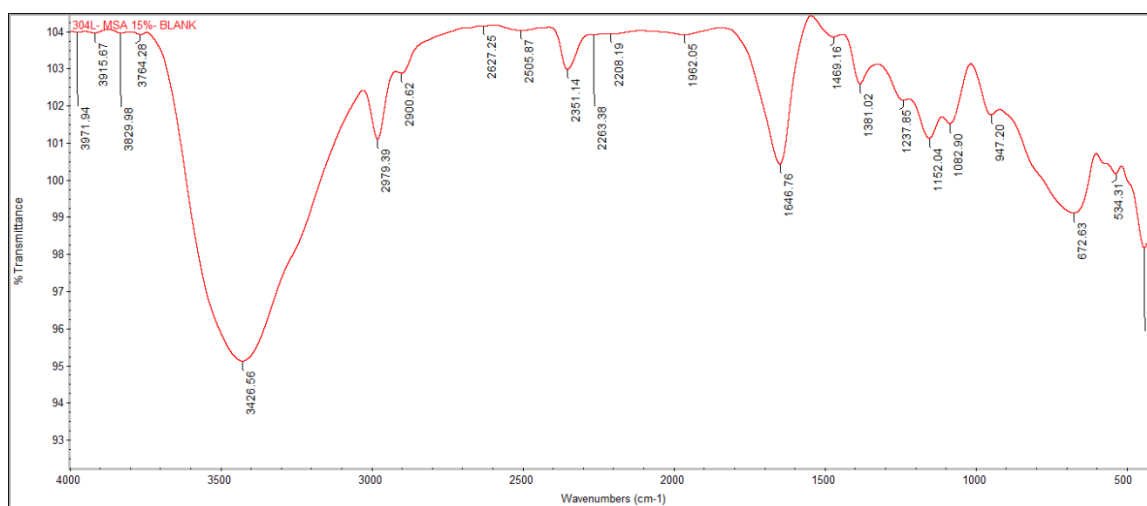


Figure78: FTIR spectrum of the SS 304 L MSA Solution 25 °C blank

4.6.4 SS304 H at 60 & 90 °C

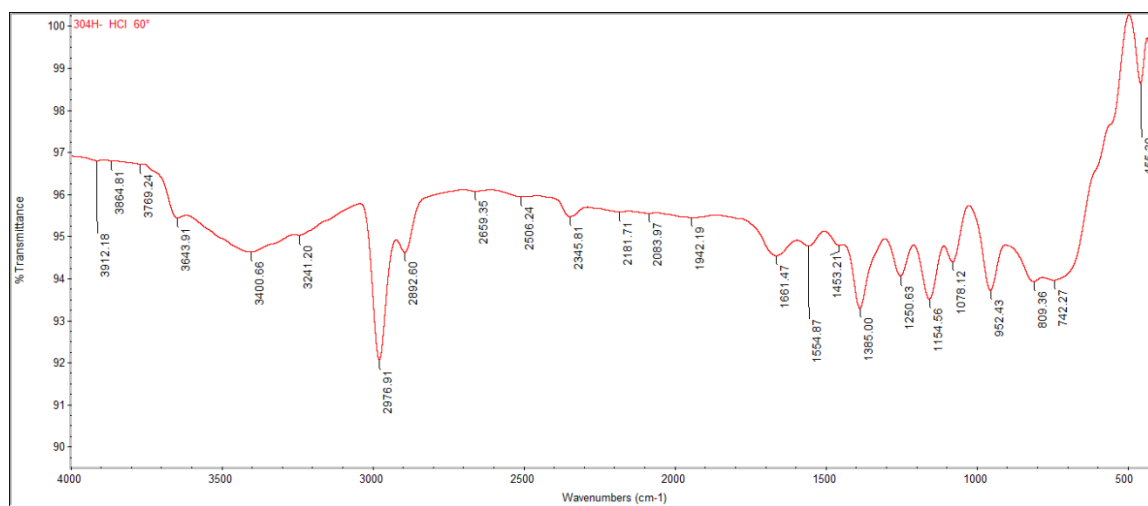


Figure79: FTIR spectrum of the SS304 H / HCl 15M at 60 °C

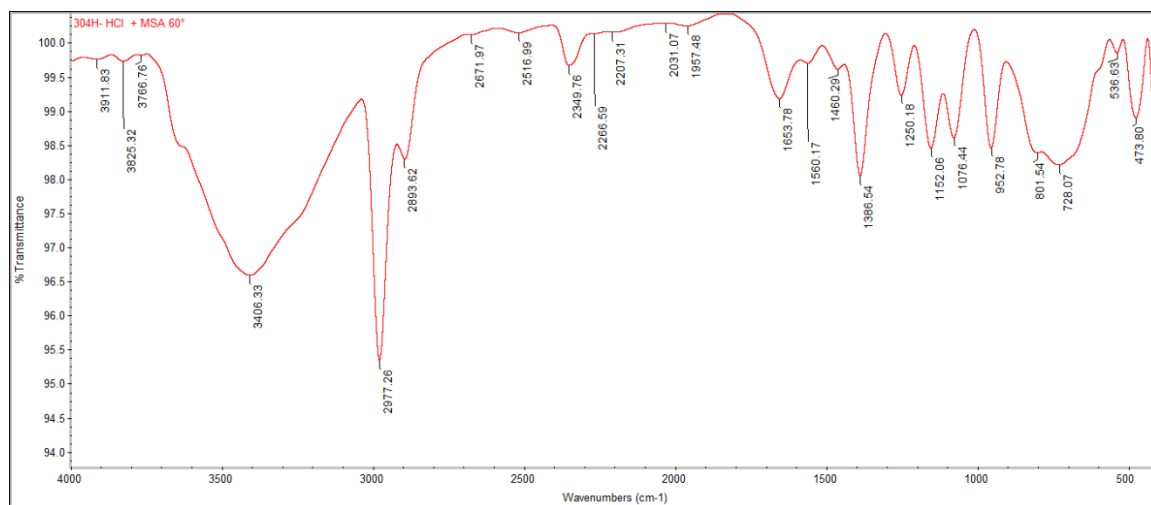


Figure 80: FTIR spectrum of the SS304 H / (HCl + MSA)15M at 60 °C

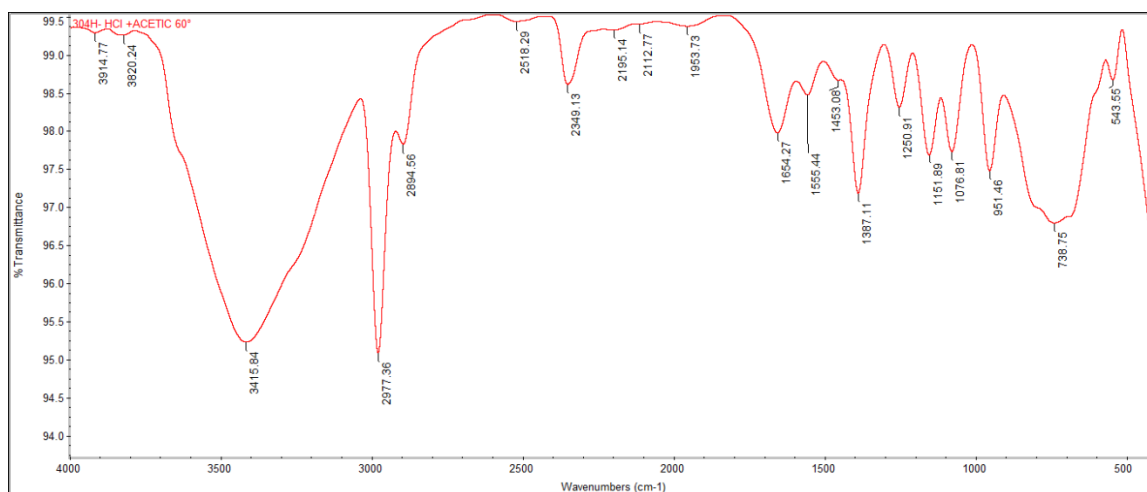


Figure 81: FTIR spectrum of the SS304 H / (HCl + Acetic Acid)15M at 60 °C

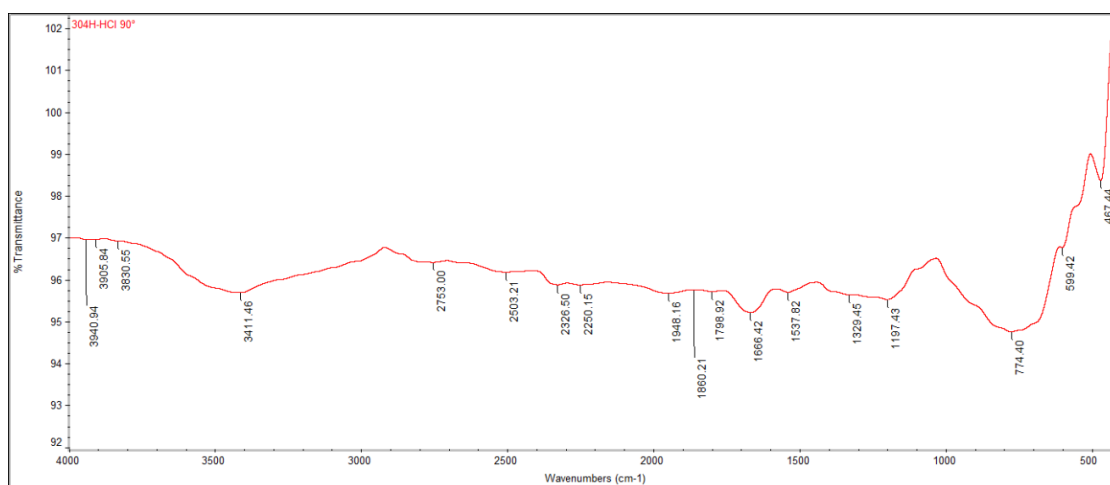


Figure 82: FTIR spectrum of the SS304 H / HCl 15M at 90 °C

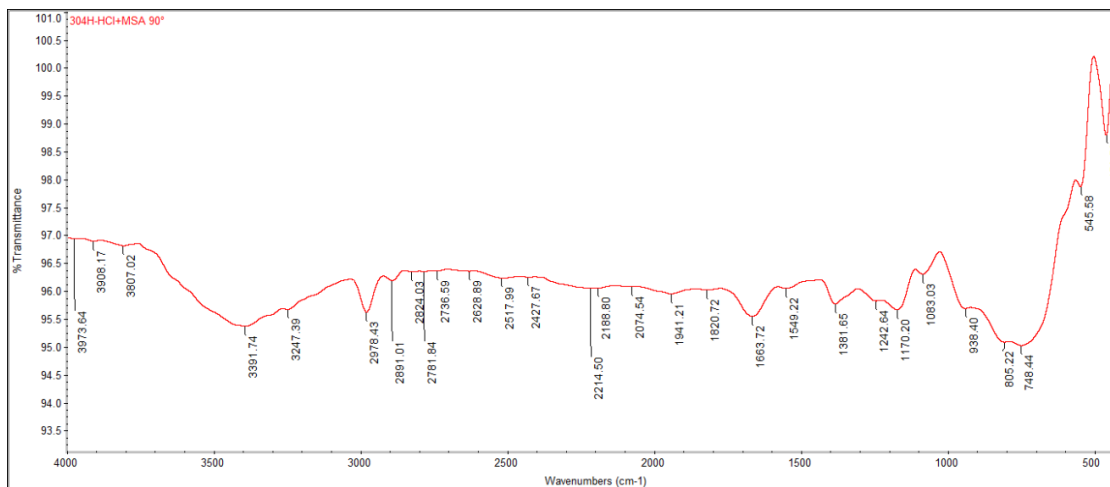


Figure 83: FTIR spectrum of the SS304 H / (HCl + MSA)15M at 90 °C

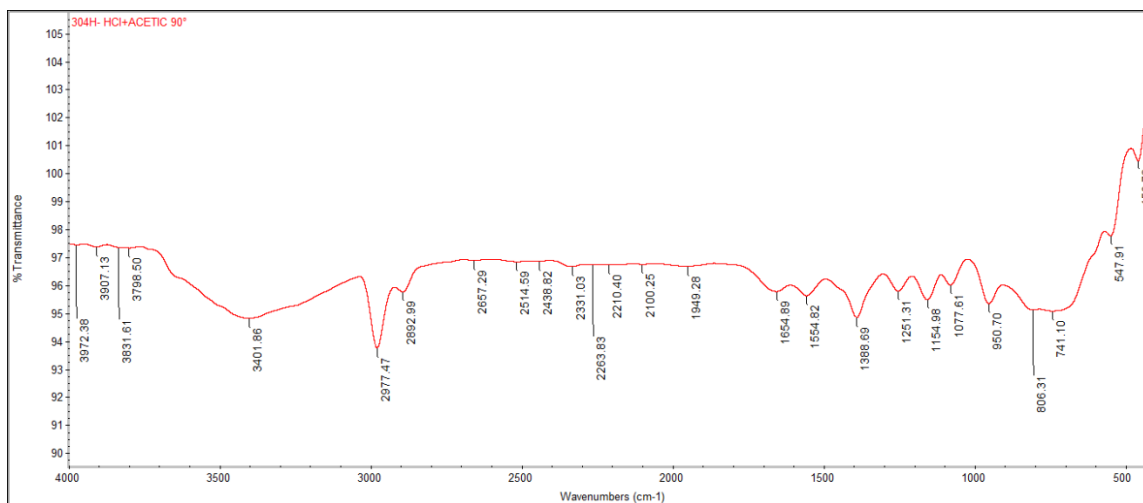


Figure 84: FTIR spectrum of the SS304 H / (HCl + Acetic Acid)15M at 90 °C

As compared with the blank, the peaks shift significantly at high temperatures (60°C and 90 °C), which indicates that the inhibitor is not forming any protective layer, hence ineffective at high temperatures. Also, possibly the nature of the corrosion at higher temperatures is different as compared to room temperature.

4.6.5 SS304 L at 60 & 90 °C

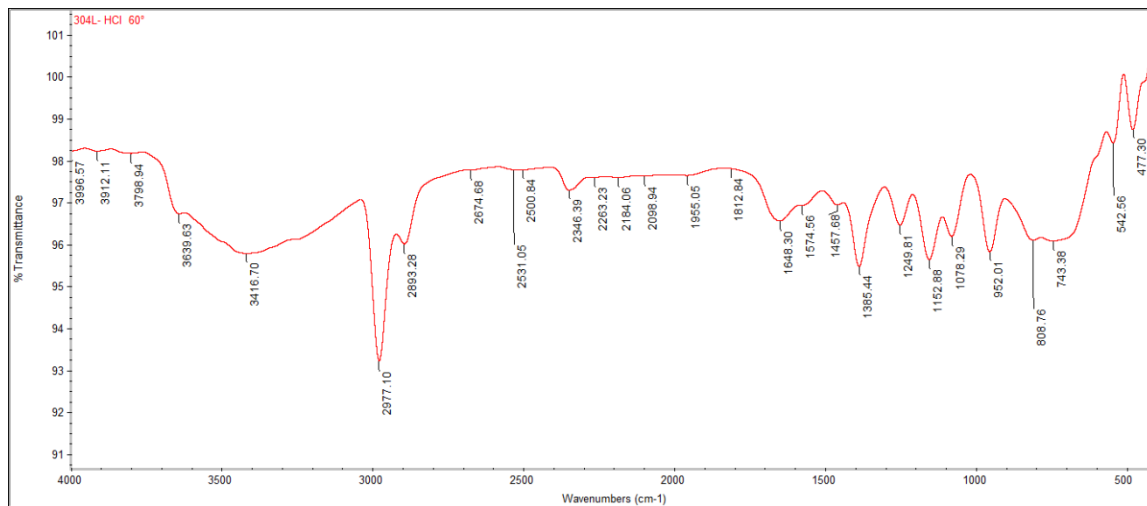


Figure 85: FTIR spectrum of the SS304 L / HCl 15M at 60 °C

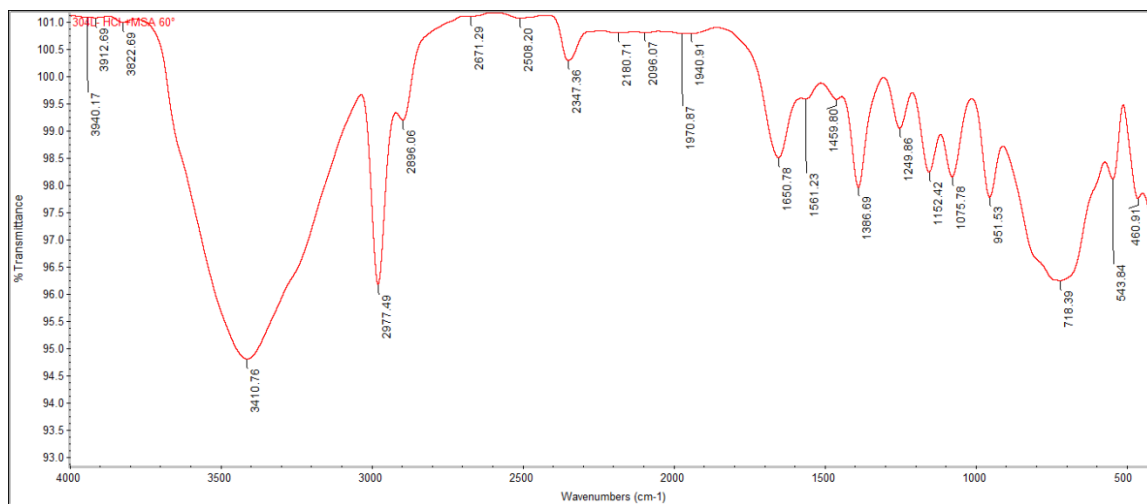


Figure 86: FTIR spectrum of the SS304 L / (HCl + MSA)15M at 60 °C

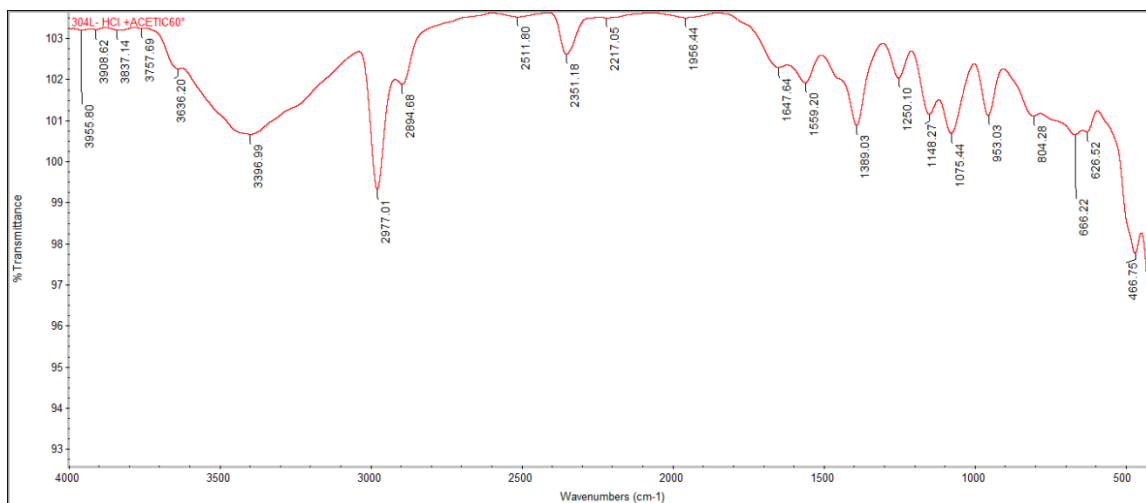


Figure 87: FTIR spectrum of the SS304 L / (HCl + Acetic Acid)15M at 60 °C

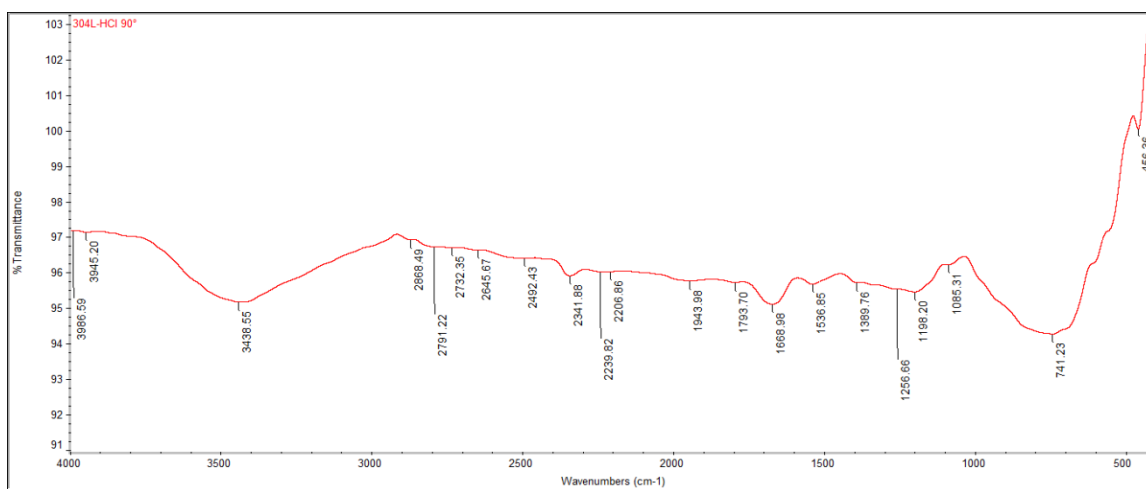


Figure 88: FTIR spectrum of the SS304 L / HCl 15M at 90 °C

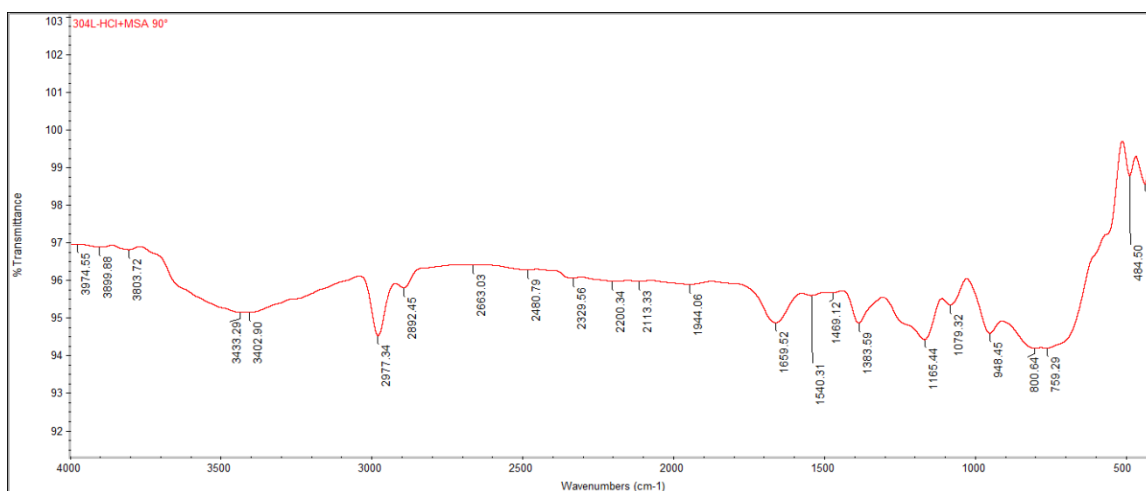


Figure 89: FTIR spectrum of the SS304 L / (HCl + MSA)15M at 90 °C

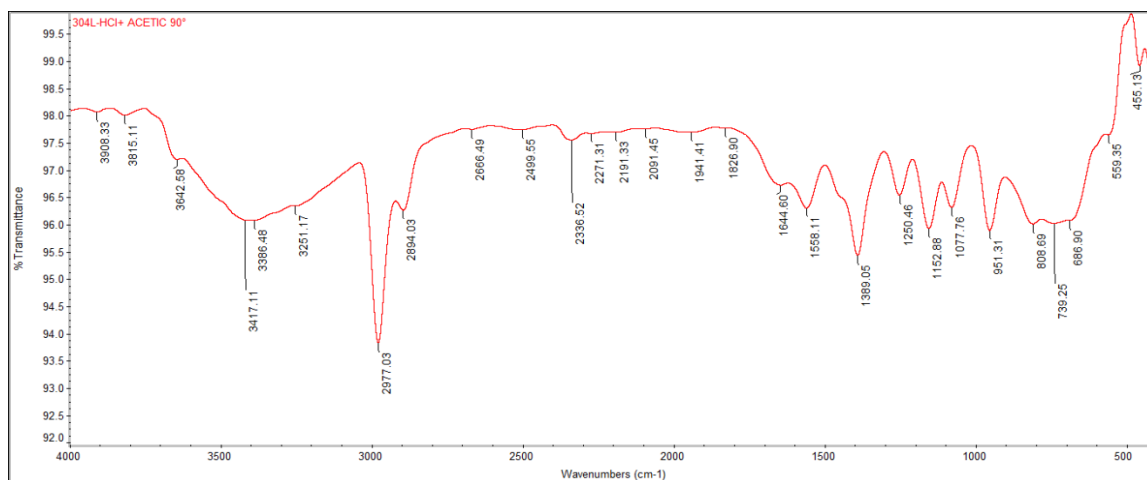


Figure 90: FTIR spectrum of the SS304 L / (HCl + Acetic Acid)15M at 90 °C

As compared with the blank, the peaks shift significantly at high temperatures (60 °C and 90 °C), which indicates that the inhibitor is not forming any protective layer, hence ineffective at high temperatures. Also possibly the nature of the corrosion at higher temperatures is different as compared to room temperature.

4.7 X-ray Diffraction (XRD)

X-Ray diffraction analysis (XRD) is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material.

The analysis was performed by utilizing RIGAKU Ultima. And the software used to identify was PDXL2.

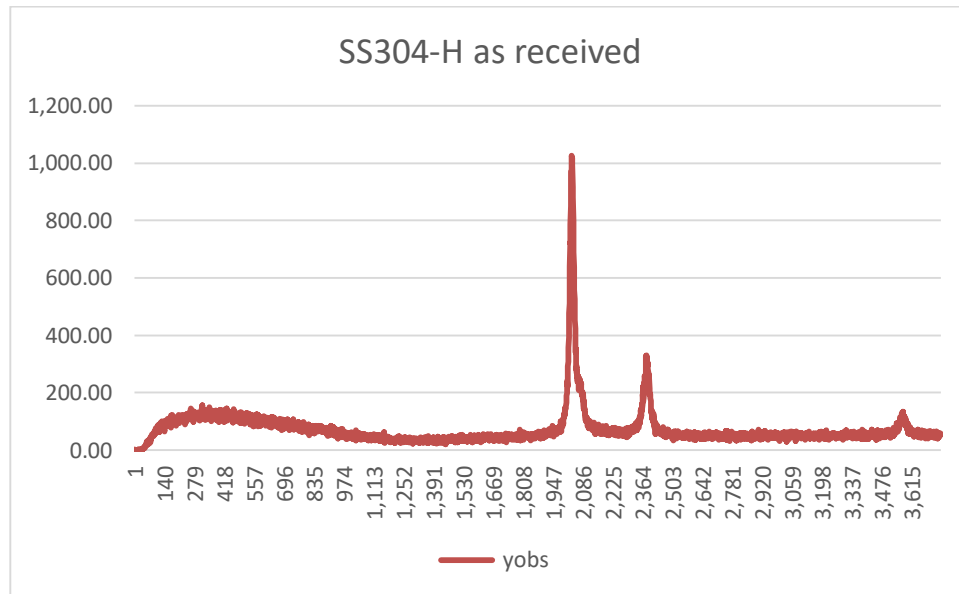


Figure 91: XRD peak for SS304H as received

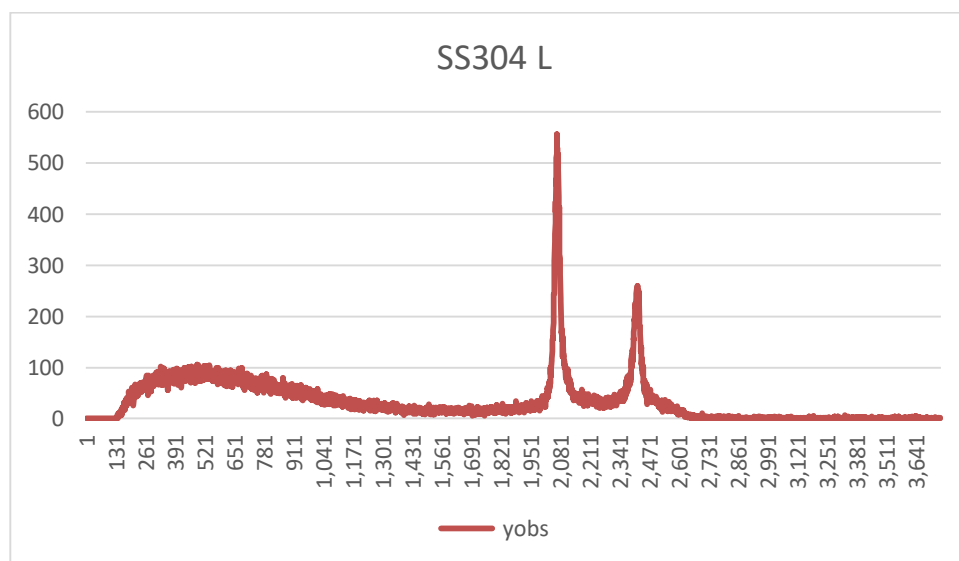


Figure 92: XRD peak for SS304L as received

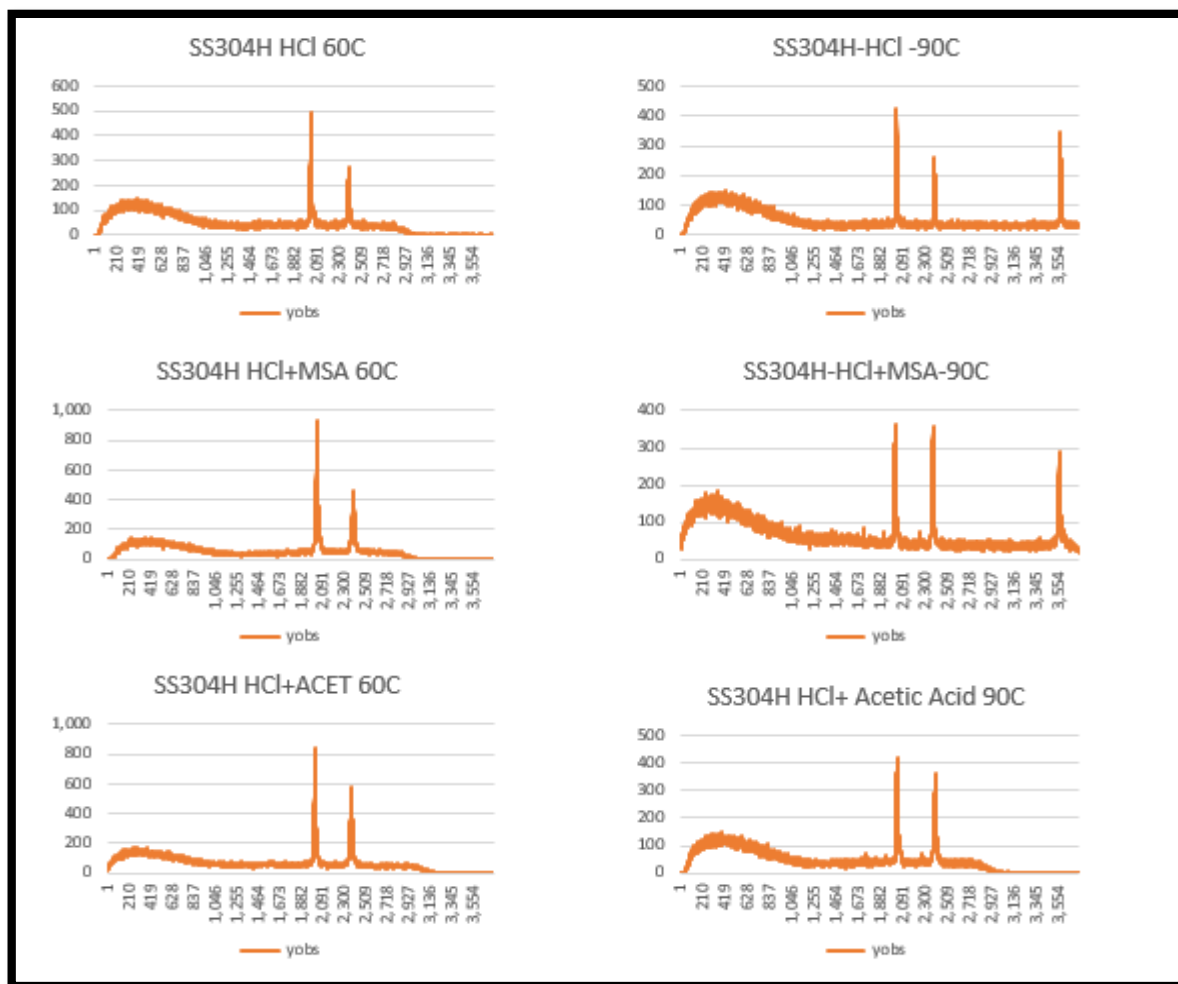


Figure 93: XRD peaks for SS304 H in Different Solutions

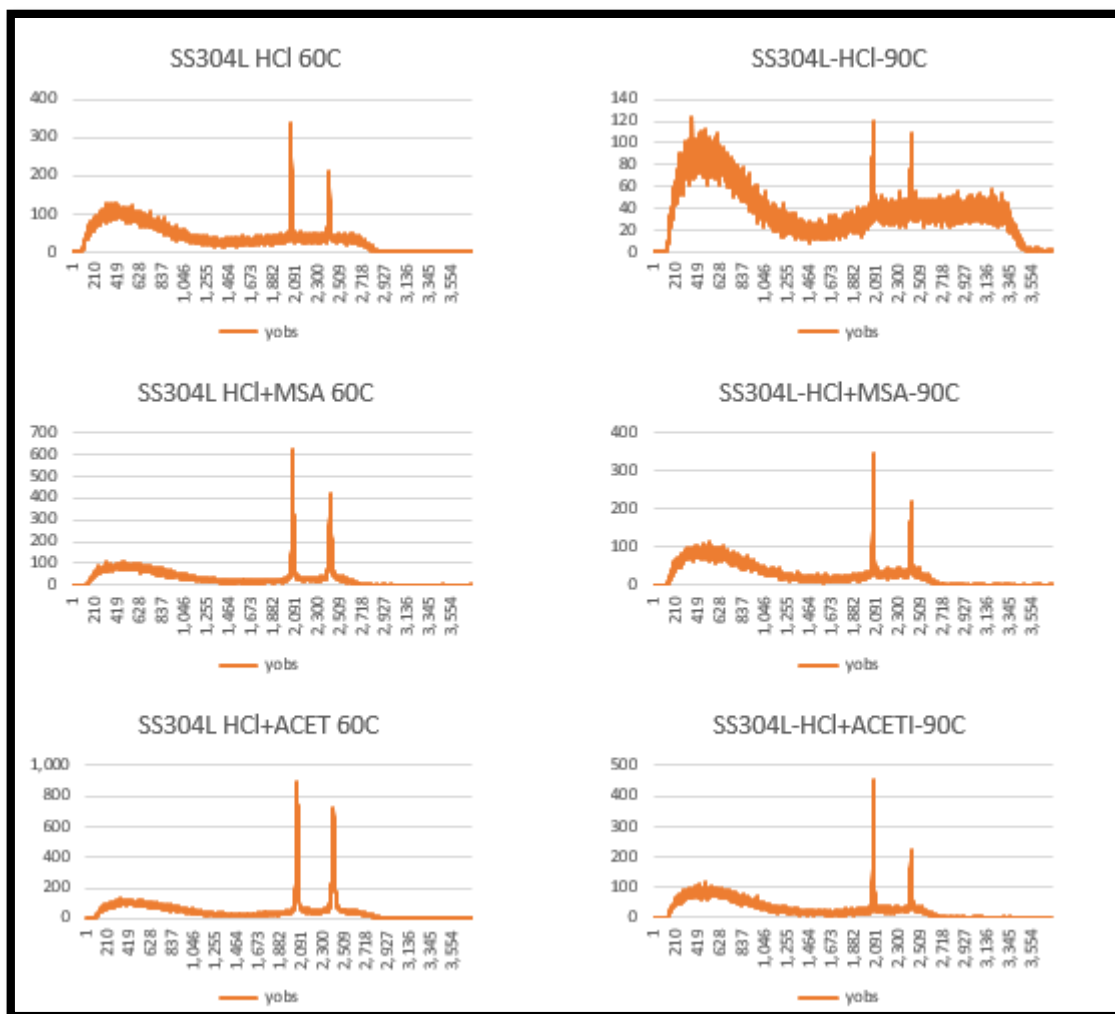


Figure 94: XRD peaks for SS304 L in Different Solutions

As can be seen that the vast majority of the peaks may be found in the same general position; the only thing that distinguishes them from one another is the magnitude at their respective locations.

With the exception of (SS304 HCl 90 °C and MSA + HCl 90 °C), there are three peaks, as seen in the Figures above. The phase identification was performed and identified phases are shown below.

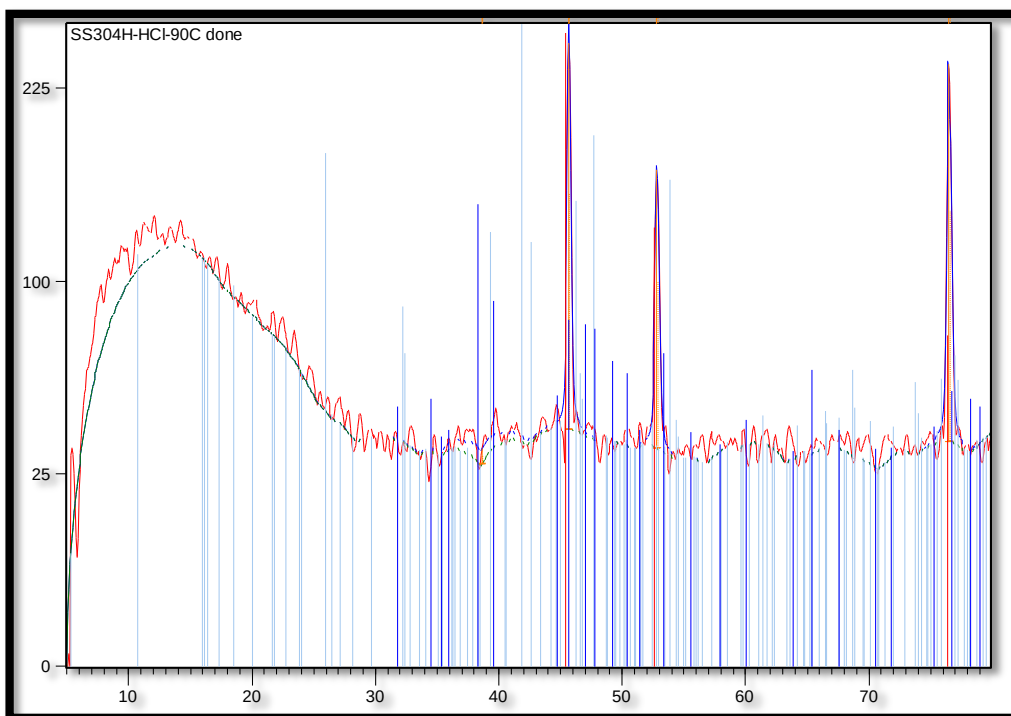


Figure 95: XRD Pattern for SS304H HCl 90 °C

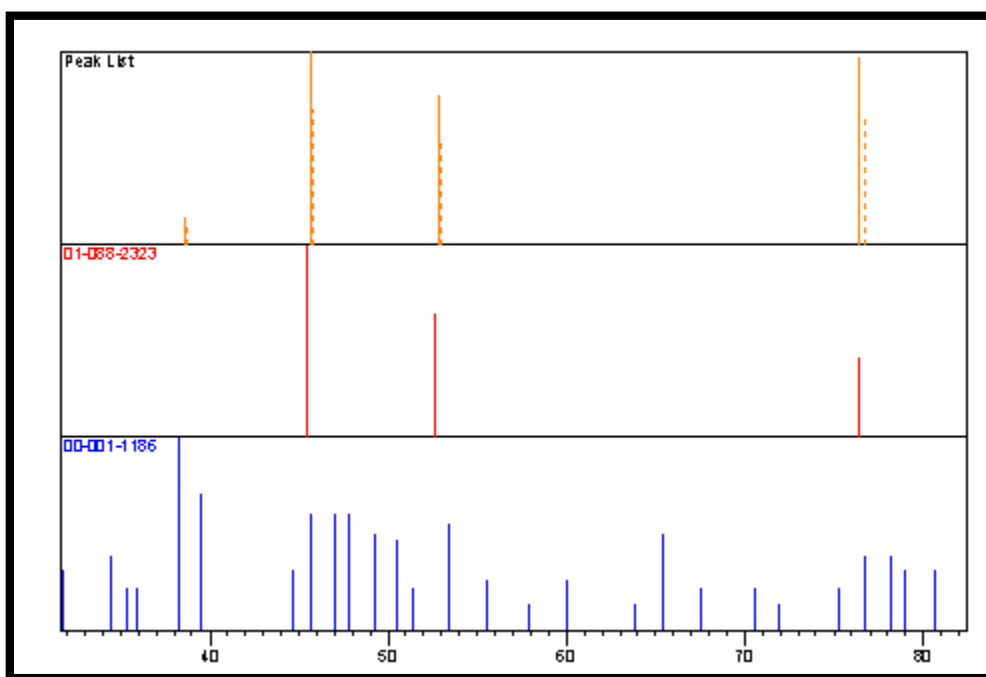


Figure 96: Plot of identification phases by XRD for SS304H HCl 90 °C

Table40: Identified pattern list by XRD for SS304 H 90 °C

Visible	Ref. Code	Compound Name	Chemical Formula
Major Phase	01-088-2323	Chromium	Cr
*	00-001-1186	Chromium Carbide	Cr ₃ C ₂

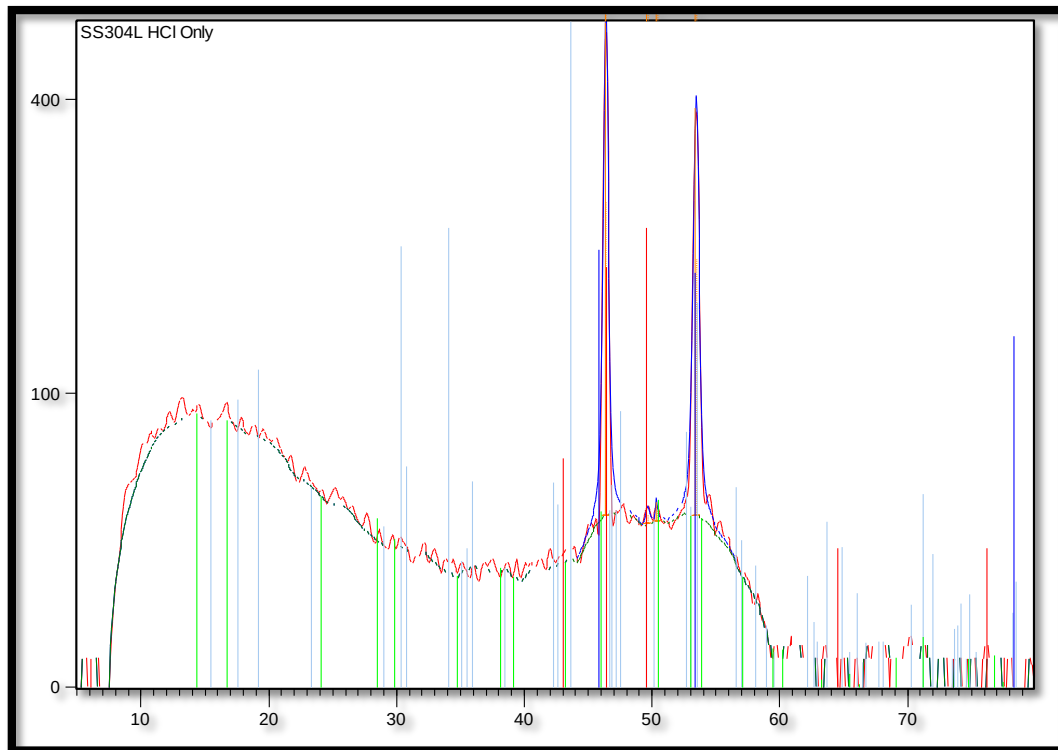


Figure 97: XRD Pattern for SS304L HCl only

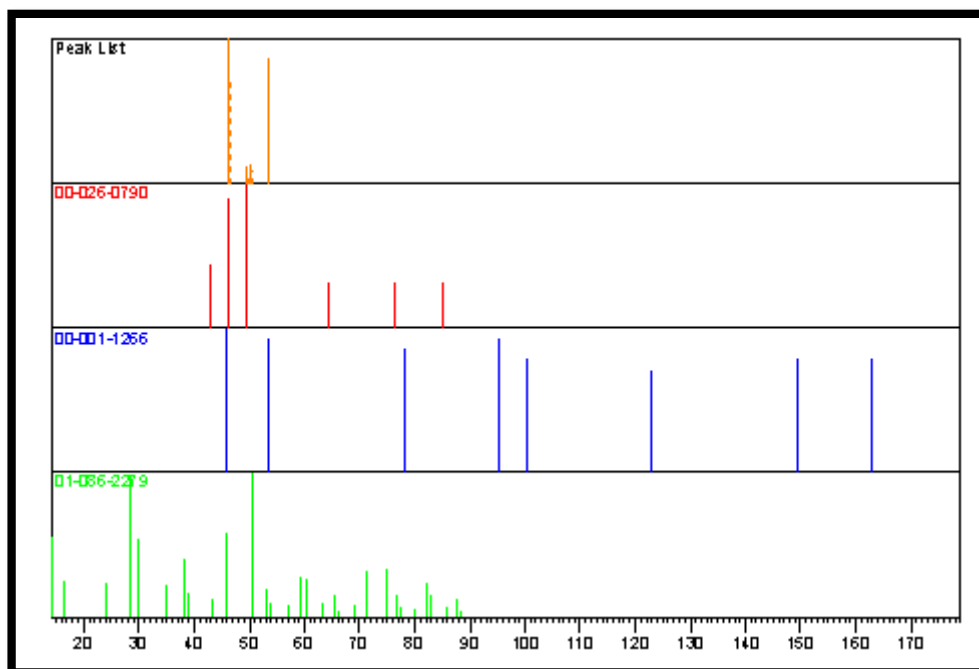


Figure 98: Plot of identification phases by XRD for SS304L Only

Table41: Identified pattern list by XRD for SS304 L only

Visible	Ref. Code	Compound Name	Chemical Formula
Major Phase	00-026-0790	Iron Nickel	(Fe , Ni)
*	00-001-1266	Nickel	Ni
*	01-086-2279	Pentlandite	Fe _{4.2} Ni _{4.8} S ₈

4.8 Microstructure after inhibitors

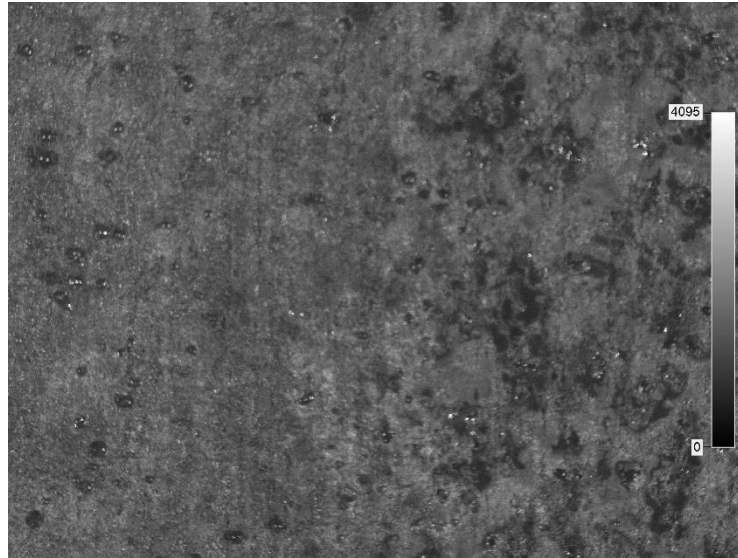


Figure 99: Spectroscopic image of the 15 % HCl SS304H -Blank

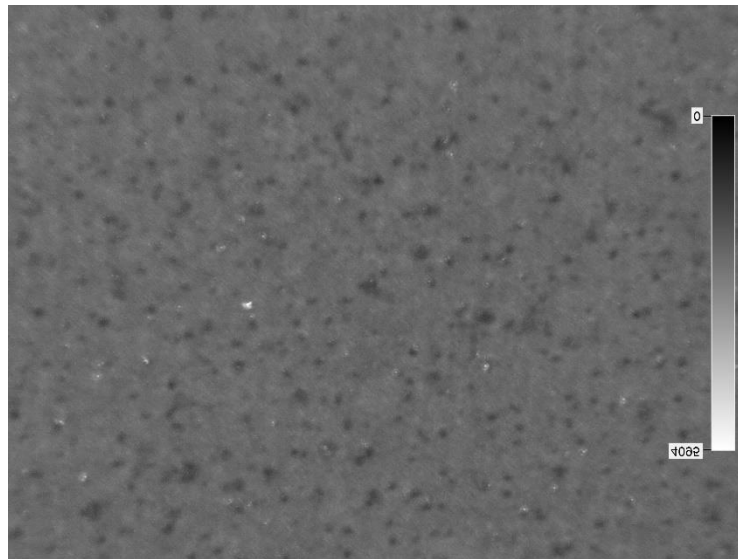


Figure 100: Spectroscopic image of the 15 % HCl SS304H -200ppm

Note: as you can see in Figure 99, there are some spots that lead to have formed as a result of acid or pitting corrosion after dropping the sample 48 h at room temperature. While Figure 100 the inhibitor makes a protective layer on the sample surface leading to inhibiting the corrosion.

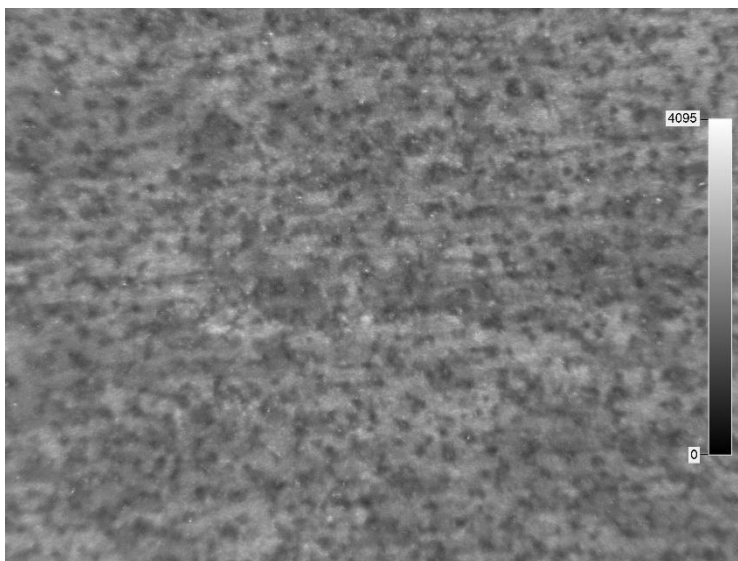


Figure 101: Spectroscopic image of the 15 % HCl SS304L -Blank

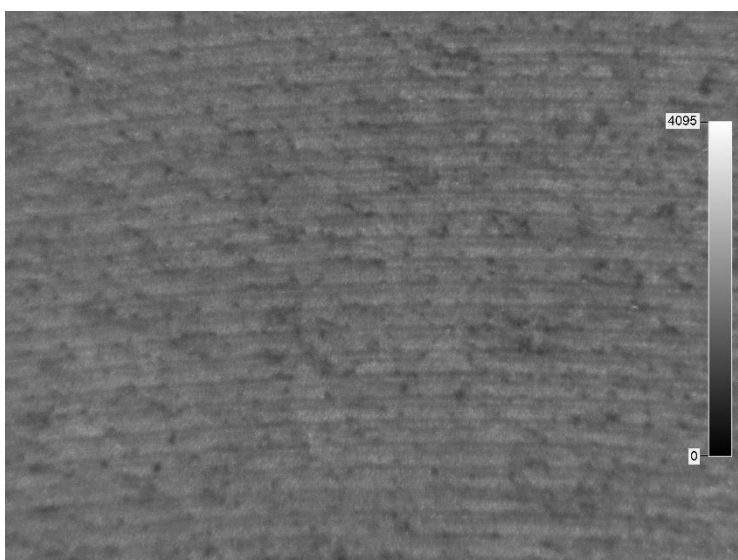


Figure 102: Spectroscopic image of the 15 % HCl SS304L -200ppm

Note: as you can see in Figure 101, there are some spots that lead to pitting corrosion after dropping the sample 48 h at room temperature. While Figure 102 the inhibitor makes a protective layer on the sample surface leading to inhibit the corrosion.

CHAPTER 5

CONCLUSION

SS 304 H

- Visually, outer surface (OS) of the pipe shows signs of general corrosion, and the crack was partially noticeable on the welded area from the bottom side.
- Chemically, the composition falls within the known range of SS 304H.
- The microstructure images austenitic microstructure with intergranular cracks in IS, and mostly trans-granular cracks in OS; moreover, sensitization test confirms that the samples are sensitized.
- SEM confirmed particles as manganese sulphide and aluminium oxide, in addition, cracks are mostly filled with Oxide.
- The hardness value of cracked and uncracked samples are higher at IS, while they noticeably dropped at HAZ. The small tube has a higher hardness in the bottom side (closer to the main pipe).
- The FTIR results show At room temperature, there is no change in the peaks, however, the prepared 200 ppm inhibitor caused a reduction in the strength of the peaks, which indicates that the inhibitor formed a protective layer on the surface of the metal that is resistant to corrosion. As compared with the blank, the peaks shift significantly at high temperatures (60 °C and 90 °C), which indicates that the inhibitor is not forming any protective layer
- In the XRD part the vast majority of the peaks may be found in the same general position; the only thing that distinguishes them from one another is the magnitude at their respective locations, With the exception of (SS304H HCl 90 °C and MSA + HCl 90 °C), there are three peaks, as seen in section 4.7.
- Based on the chemical composition the highest value of Carbon, Chromium and Nickel make the materials more resistant to corrosion
- At room temperature the corrosion rates it's lower compared with high temperature. However, in the general case the corrosion rates it's lower than SS304 L
- The corrosion rate it's increased with HCl > MSA > AA
- The inhibition efficiency s high at this grade compared with SS304 L.

SS 304 L

- Visually, the flange had no signs of corrosion, damages, or thinning. Moreover, there was a welding area in the top of the flange's neck.
- The images were taken after the DPT show transverse and longitudinal cracks at the IS of the flange's neck under the welding area.
- Chemically the composition falls within the known range of 304L stainless steel.
- The microstructure images were taken to study the cracks which were found to be intergranular
- The SEM-EDS analysis shows the presence of Cl in inside of some of the cracks surfaces, which a sign of (Cl SCC).
- The hardness measurements were not vary from each other in both readings, except for 15% drop in 3rd indentation and 6% increase in 5th indentation on the second reading
- The FTIR results show at room temperature, there is no change in the peaks. However, the prepared 200 ppm inhibitor caused a reduction in the strength of the peaks, which indicates that the inhibitor formed a protective layer on the surface of the metal that is resistant to corrosion. As compared with the blank, the peaks shift significantly at high temperatures (60 °C and 90 °C), which indicates that the inhibitor is not forming any protective layer.
- In the XRD part the vast majority of the peaks may be found in the same general position, the only thing that distinguishes them from one another is the magnitude at their respective locations
- Based on the chemical composition the lowest value of Carbon makes the materials lower resistant to corrosion.
- At room temperature the corrosion rates it's lower compared with high temperature. However, in the general case the corrosion rates it's higher than SS304 H.
- The corrosion rate it's increased with $HCl > MSA > AA$
- The Inhibitors efficiency it's lower at this grade compared with SS 304 H

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