



# “CORROSION MANAGEMENT IN OIL AND GAS PLANT”

A

DISSERTATION REPORT

FOR THE FULFILLMENT FOR THE AWARD OF THE DEGREE OF

**MASTER IN BUSINESS ADMINISTRATION**

IN

**OIL AND GAS MANAGEMENT**

(2018-2020)

**Submitted by:**

**Abhishek Kumar Shrotriya**

MBA (Oil & Gas Management)

SAP ID: 500065309

**Under Guidance:**

**Ahmed El-Zeabak**

Process Shift Controller

Dolphin Energy Limited



**CENTER OF CONTINUING EDUCATION**

**UNIVERSITY OF PETROLEUM & ENERGY STUDIES, DEHRADUN**

CENTER OF CONTINUING EDUCATION

UNIVERSITY OF PETROLEUM & ENERGY STUDIES, DEHRADUN



## ACKNOWLEDGEMENT

Research is a high concept, it brings to test our patience, vigor and dedication. Every result arrived at a beginning for higher achievements. Our project in the same interest is just a drop in ocean. No work can be turned as a single person show. It need the help of professionals and proper guidance of experts in the field to achieve something.

We feel highly indebted and give much credit to our Sr. Production Manager (Operations Production department) for helping us to guide in all prospects until completion.

We express our sincere thanks to Mr. Ahmed El-Zeabak (Process Shift Controller, Production department) for guiding us and all the team members of Production and Operations Engineering department, who encouraged and helped a lot in developing the ideas to kill the corrosion issue and helped us with various journals and relevant data from time to time.

**Abhishek Kumar Shrotriya**

MBA (Oil & Gas Management)

SAP ID: 500065309

## DECLARATION

This is to certify that Mr. **Abhishek Kumar Shrotriya** a student of MBA in Oil & Gas Management, SAP ID: 500065309 of UPES has successfully completed this dissertation report on “**Corrosion Management in Oil and Gas Plant**” under my supervision.

Further, I certify that the work is based on the investigation made, data collected and analyzed by him and it has not been submitted in any other University of Institution for award of any degree. In my opinion it is fully adequate, in scope and utility, as a dissertation towards partial fulfillment for the award of degree MBA.

*Ahmed  
25/oct-2019*

Regards:

**Ahmed EL Zeabak**  
Process Shift Controller  
Production Department

F +974 55031657  
M +974 66046155  
Ahmed.ElZeabak@dolphinenergy.com

Dolphin Energy Ltd  
PO Box 22275  
RasLaffan, State of Qatar

Date: 25th October 2019

Place: RasLaffan – Qatar

## Table of Content

Title “Corrosion Management in Oil and Gas Plant”	1
Chapter 1: Introduction	2
1.1: Overview	7
1.2: Background of study	8
1.3: Problem Statement	8
1.4: Objective	9
1.5: Research Hypotheses	9
Chapter 2: Literature Review	11
2.1: Effect of de-aeration and chloride ion concentration on corrosion	11
2.1.1: Sample preparation	12
2.1.2: Solution preparation for the effect of chloride concentration	13
2.1.3: Result and Discussion	13
2.2: Influence of temperature on corrosion in natural gas system	15
2.3: The effect of flow rate on corrosion in natural gas system	16
2.4: Gas hydrates	16
Chapter 3: Corrosion control, research and methodology in natural gas system	18
3.1: Engineering design and control	18
3.1.1: Selection materials of construction	19
3.1.2: Coating	20
3.1.3: Cathodic Protection	21
3.1.4: Change of chemistry of environment	23

3.2: Corrosion monitoring in natural gas system	26
3.2.1: Physical methods of control of properties of metal	27
3.2.2: Monitoring of the environment and technology parameters	28
3.2.3: Examination of the border metal environment	29
3.2.4: Online real-time corrosion monitoring	30
3.3: Efficiency monitoring from corrosion protection	30
Chapter 4: Findings, Analysis and Decision	32
4.1: Boiler emergency shutdown due to Floor Tubes / Primary S/H Tube leaks	32
4.1.1: Findings	32
4.1.2: Casual factor	34
4.1.3: Actions	35
4.1.4: Metallurgical failure investigation report	36
4.2: Off-Gas compressor corrosion deposition	37
4.2.1: ESR: Engineering study for observed deposits	37
4.2.2: Reported acid etching / pit initiation	40
4.3: Pitting corrosion inside the Claus Reactor re-heater	42
4.3.1: Findings	43
4.3.2: Casual factor	43
4.3.3: Actions	44
Chapter 5: Conclusions and Scope for Future Work	45
Bibliography	47
References	48

# “CORROSION MANAGEMENT IN OIL AND GAS PLANT”

## 1:Introduction:

Carbon steel pipelines are the main material choice for both offshore and onshore oilfield production to transport crude oil and gas from well to different separating units. In-service integrity of the pipelines is very important to ensure a safe working environment and continuous production. Unfortunately, internal corrosion of carbon steel pipelines is reported frequently in oil and gas production. According to Nyberg, internal corrosion in wells and pipelines is influenced by many factors such as temperature,  $CO_2$  and  $H_2S$  content, water chemistry, flow velocity, oil or water wetting, composition of the steel, and the surface condition of the steel. The interdependent parameters that influence  $CO_2$  corrosion are shown in Figure 1.1.

Hear, we will discuss about the real scenario of Corrosion Management in Oil and Gas Plant. After starting the plant, in onshore facility, we are receiving the gas along with water, we call it sour water because it contains  $H_2S$ . Then we start getting issues after few years of start-up, we came to know water coming along with gas is containing much calcium and some other salts, which are attacking the metallurgy of the pipes impacting bad effect. We found corrosion at many places, which is mainly hydrocarbon condensate with water. We found corrosion at compressor side, suction drum, suction pipe and overhead stripper column. Stripper we are using to strip-out light hydrocarbon liquid. Overhead line we came to know, it is totally attacked with corrosion.

After findings, analyzing, troubleshooting and research work, it was decided and replaced with upgraded metallurgy. So many other places because of that salts, which is coming along with water is the main cause of corrosion. Engineering start studies on this in order to eliminate from the source in upstream unit, try to segregate water from gas in upstream & treated in to sour water treated unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy.

The aim of this work is to describe, analyze and rectification of corrosion problem in Gas plant. Corrosion phenomena and factors influencing them are discussed as well corrosion control

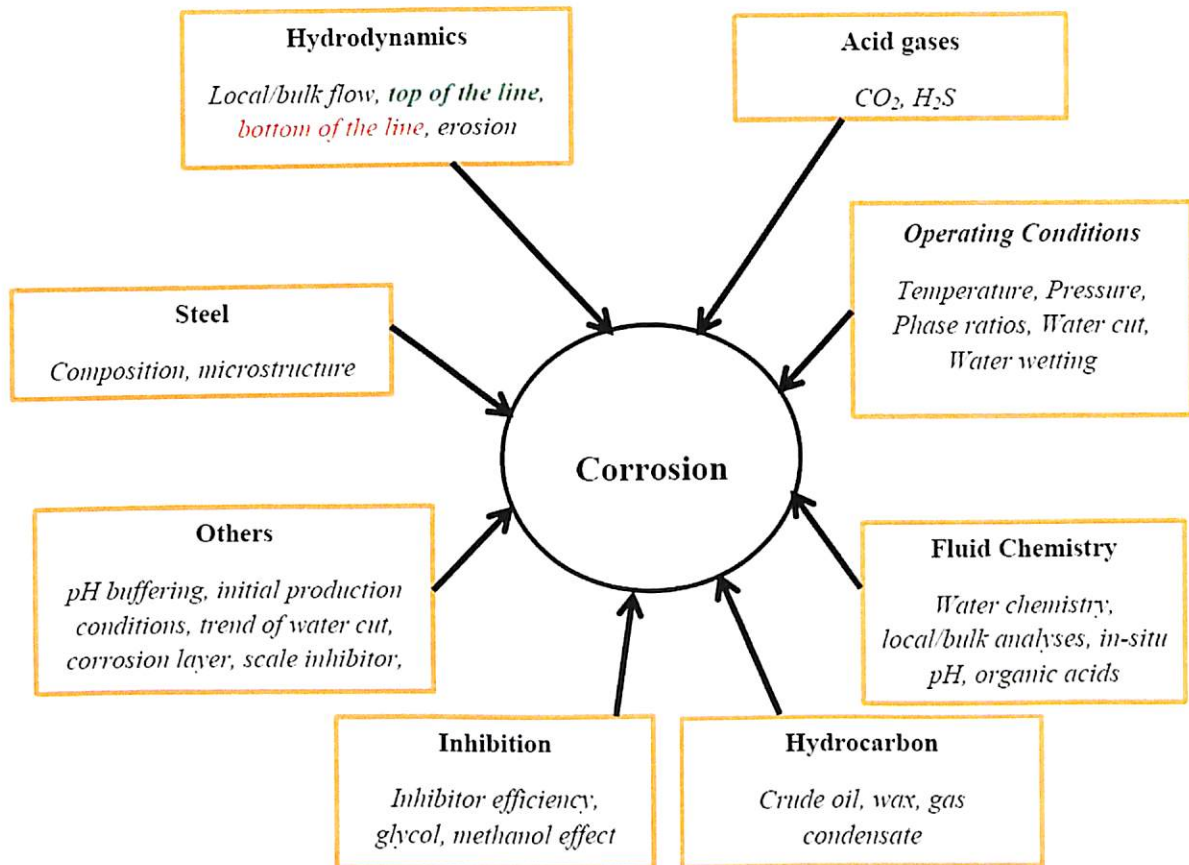


Figure 1.1: **Independent Parameter that influence corrosion**

and monitoring methods are illustrated. Corrosion management play vital role in solving the corrosion problems. Metallic equipment and constructions in the Oil & Gas plant contact natural gas, liquid hydrocarbon along with water and soil. All the processes with participation of aggressive substances occur in metallic equipment at reactive temperature and pressure. Oil & Gas plant units represent a high hazard industry with media which are flammable, explosive,



toxic to the human health or harmful to the environment. The combination of numerous factors makes plant equipment very vulnerable to a variety of corrosion phenomena that can lead to serious accidents.

On the one hand Oil & Gas industry has accumulated large experience, on the other hand development and production of new deep wells in harsh conditions, introduction of new technology, materials, strict requirements of gas and fuels, and the reduction of environmental pollution state new problems to the safe functioning of equipment and construction. In order to understand and to solve corrosion problems, corrosion and material specialists should learn diverse physicochemical processes which are the basis of treatment of oil & gas, production of fuel and other chemicals. There are many ways to avoid or control corrosion hazards: selection of corrosion-resistant or suitable materials, correct design, use of anti-corrosive chemicals, coating, cathodic protection, control of technological parameters, and the most important is inspecting and controlling at all stages of application of these actions.

Compound/ Ions	Name	Present in Bottom	Present at Top
CO <sub>2</sub> , aqueous	dissolved CO <sub>2</sub>	√	√
H <sub>2</sub> CO <sub>3</sub>	carbonic acid	√	√
CO <sub>3</sub> <sup>-2</sup>	carbonate ion	√	√
HCO <sub>3</sub> <sup>-</sup>	bicarbonate ion	√	√
H <sup>+</sup>	hydrogen ion	√	√
OH <sup>-</sup>	hydroxide ion	√	√

$\text{Fe}^{2+}$	iron ion	√	√
$\text{Cl}^-$	chloride ion	√	
$\text{Na}^+$	Sodium ion	√	
$\text{K}^+$	Potassium ion	√	
$\text{Ca}^{2+}$	Calcium ion	√	
$\text{Mg}^{2+}$	Magnesium ion	√	
$\text{Ba}^{2+}$	Barium ion	√	
$\text{Sr}^{2+}$	Strontium ion	√	
$\text{CH}_3\text{COOH}$	Acetic acid	√	√
$\text{CH}_3\text{COO}^-$	Acetate ion	√	√
$\text{H}_2\text{S}$ , aqueous	Dissolved hydrogen sulphide	√	√
$\text{HS}^-$	Bisulphide ion	√	√
$\text{S}^{2-}$	Sulphide ion	√	√
$\text{HSO}_4^-$	Bisulphate ion	√	
$\text{SO}_4^{2-}$	Sulphate ion	√	

**Table 1.1: Species Present in the Pipelines**

Corrosion management of all facilities used in oil and gas is expected to form part of the overall management system which includes the development, implementation, review, and maintenance of corrosion policy.  $CO_2$  and  $H_2S$  gases are both common natural gas contaminants present in oil reservoirs which can be highly corrosive in combination with water. Metal dissolution is drastically reduced whenever there is formation of corrosion products on the metal surface which prevent the metal surface from direct contact with corrosive gases or solution. At high temperature, a more dense and protective corrosion product film of iron carbonate ( $FeCO_3$ ) is precipitated on the surface of the metal, and this will reduce the corrosion rate but when  $H_2S$  is present in addition to  $CO_2$ , iron sulphide ( $FeS$ ) may be formed instead of  $FeCO_3$  at low temperature because  $FeS$  is thermodynamically more stable than  $FeCO_3$ . In wet gas and stratified flow, water vapour (saturated with gases such as  $CO_2$  and  $H_2S$ ) in the gas phase condenses on the pipe wall when the environment outside the pipeline is cooler than the saturated vapour flowing inside the pipe resulting in top-of-the-line corrosion (*TLC*). Basically, a high drop in temperature at the pipe wall results in the formation and precipitation of liquid water at a very high rate which will wet the inner wall of the pipe resulting in corrosion at the wall surface in combination with other corrosive gases. In simple terms, *TLC* occurs in oil and gas pipelines due to the condensation of water (containing dissolved corrosive gases) on the pipe wall typically in the vapour phase close to the 12 o' clock position. *TLC* is a significant problem in wet gas pipelines because of the difficulty in identifying it by conventional monitoring methods. Table 1.1 shows the typical species that are present in pipelines both at the bottom and top of the line. It is evident from the table that the chemical compositions of condensed water are different from the formation water at the bottom of the line (*BOL*). This is an indication that only volatile species and their derivatives are present at *TOL*.

## 1.1: Overview:

After plant start-up in onshore facility, we are receiving the gas, hydrocarbon liquid along with water, we call it sour water because it contains H<sub>2</sub>S. Then we start getting issues after few years of start-up, we came to know water coming along with gas is containing much calcium and some other salts, which are attacking the metallurgy of the pipes impacting bad effect. We found corrosion at many places, which is mainly hydrocarbon condensate with water. We found corrosion at compressor side, suction drum, suction pipe and overhead stripper column. Stripper we are using to strip-out light hydrocarbon liquid. Stripper overhead line we came to know, it is totally attacked with corrosion. Our offshore platform designed to be unmanned, to be controlled & manipulating, checked from onshore control room. There is not any kind of separation on the platform itself. The water along with the hydrocarbon condensate and gas coming out from the wells to the common header and then to the reception facility of onshore. Offshore platform just pumping out the gas along with condensate and water to the onshore reception facility. We are separating and treating these kind of things in onshore, whatever mud, sludge, sour water, anything coming is to be treated in the onshore. We have got some kind of pin hole in the pipe, when we came to know, we have taken some measures, we have done UT scanning and we found thickness loss much as compare to its original state. Then we start taking some measures at many places to identify the healthiness of the plant. We have done UT scanning at many places. We have done the sampling from the gas line, water side and condensate side & it is proven that salts are there in the lab result. These equipment are not designed initially to handle these types of salts.

Opening the equipment it self like knock-out drum of the compressor have proven that from photo, UT scanning, the pitting is there, metals are badly corroded. And it was very clear that is along with salts in the streams.

Engineering start studies on this in order to eliminate from the source in upstream unit, try to segregate water from gas in upstream & treated in to sour water treated unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy. Then it was replaced with upgraded metallurgy. So many other places because of that salts, which is coming along with water is the main cause of corrosion. Engineering start studies on this in order to eliminate from the source in upstream unit, try to segregate water from gas in upstream & treated in to sour water treated unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy.

### **1.2: Background of Study:**

Initial design of our offshore platform designed to be unmanned, to be controlled & manipulating, checked from onshore control room. There is not any kind of separation on the platform itself. The gas along with the hydrocarbon liquid condensate and water coming out from the wells to the common header and then to the reception facility of onshore. Offshore platform just pumping out the gas along with condensate and water to the onshore reception facility. We are separating and treating these kind of things in onshore, whatever mud, sludge, sour water, anything coming is to be treated in the onshore. This water, we called it sour water containing H<sub>2</sub>S and salts. After passing the years, started facing some issues of corrosion during any maintenance work. Following is the way to influence of corrosion in to the system.

### **1.3: Problem Statement:**

In the problem statement, we will discuss about, how's the issues of water discovered and how the problem was mentioned?

We have got some kind of pin hole in the pipe, when we came to know, we have taken some measures, we have done UT scanning and we found thickness loss much as compare to its

original state. Then we start taking some measures at many places to identify the healthiness of the plant. We have done UT scanning at many places. We have done the sampling from the gas line, water side and condensate side & it is proven that salts are there in the lab result. These equipment are not designed initially to handle these types of salts.

Opening the equipment it self like knock-out drum of the compressor have proven that from photo, UT scanning, the pitting is there, metals are badly corroded. And it was very clear that is along with salts in the streams.

#### **1.4: Objective:**

Objective is to describe, analyze and rectification of corrosion problem in Gas plant, elimination of the salts content from the gas and hydrocarbon condensate completely from the source itself in upstream unit, try to segregate water from gas in upstream & treated in to sour water treatment unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy.

#### **1.5: Research hypothesis:**

After few years of starting of the plant, we start getting issues in the plant, we came to know water coming along with gas is containing much calcium and some other salts, which are attacking the metallurgy of the pipes impacting bad effect.

We have started taken several measure like UT scanning on many places, sampling from the gas, water and condensate side and we came to know because of salt content in the water.

We found corrosion at many places, which is mainly hydrocarbon condensate with water facilities. We found corrosion at compressor side, suction drum, suction pipe and overhead

stripper column. Stripper we are using to strip-out light hydrocarbon liquid. Overhead line we came to know, it is totally attacked with corrosion.

Engineering start studies on this in order to eliminate from the source in upstream unit, try to segregate water from gas in upstream & treated in to sour water treatment unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy.

Following methods being used to identify the issues, root cause of the problem and to eliminate the issues:

**UT Scanning:** UT scanning being conducted at many places to identify the thickness of the pipes and equipment.

**Sampling:** Sampling taken from the many places, for the gas, sour water and hydrocarbon condensate side.

**Inspection of Equipment:** Opening of the equipment itself like Compressor, suction knock-out drum of compressor, stripper column, column overhead lines etc.

**Elimination:** Elimination by replacing the lines with upgraded metallurgy, which can handle these types of salts.

## **2:Literature Review:**

Initially your offshore platform designed to be unmanned, to be controlled & manipulating, checked from onshore control room. There is not any kind of separation on the platform itself. The gas along with the hydrocarbon liquid condensate and water coming out from the wells to the common header and then to the reception facility of onshore. Offshore platform just pumping out the gas along with condensate and water to the onshore reception facility. We are separating and treating these kind of things in onshore, whatever mud, sludge, sour water, anything coming is to be treated in the onshore. This water, we called it sour water containing  $H_2S$  and salts. After passing the years, started facing some issues of corrosion during any maintenance work. Following is the way to influence of corrosion in to the system.

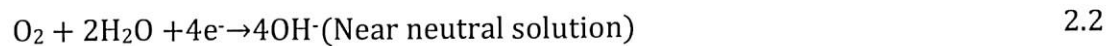
### **2.1: Effect of de-aeration and Chloride ion concentration on Carbon Steel Corrosion:**

This preliminary study was introduced to understand the carbon steel corrosion in different chloride ion and oxygen concentrations. Many oil & gas reservoirs contain large amounts of brine which are trapped in sediment pores. It has been reported that the chloride concentration of produced brine during oil and gas production could be as high as 50,000mg/L. The presence of chloride ions in the formation water poses significant corrosion problems during drilling during oil and gas production. Other reports also confirmed that chloride ions are the main cause of carbon steel pipeline corrosion. Cheng et al also explained that chloride ions increased the electrolyte conductivity which invariably increases the dissolution rate. Most of the formation water in sweet ( $CO_2$ ) wells also contain different varieties of salts and carbonate ions at different concentration which could pose corrosion threats with the exception of carbonate ions which can form an adherent protective scale on metal surface. The solubility of oxygen at room temperature ( $\sim 20^\circ C$ ) in water is about 8ppm. The focus of this section is to understand the



effect of chloride ion concentrations on carbon steel corrosion. Likewise, investigation of the mechanism of carbon steel corrosion at different de-aeration time was introduced. It is also important to know that de-aeration (using  $N_2$  gas) is necessary (in the laboratory) before saturating the environment with  $CO_2$  gas. However,  $CO_2$  gas was not introduced in both cases so that the presence of  $CO_2$  gas would not influence the corrosion process.

This was carried out via immersion tests, which subsequently are denoted as ‘bottom of the line’ corrosion test. Riser pipelines are almost exclusively constructed of carbon steel for both onshore and offshore applications. Corrosion (metal loss) of the pipelines is due to oxidation of iron (Equation 2.1) on the metal surface to give ferrous ions which goes into solution while the electrons are consumed by a cathodic reaction, depending upon solution  $pH$  (Equations 2.2 and 2.3)



The rate of the reduction reaction is limited by the reactant concentrations present in the environment. Carbon steel always experiences unacceptable corrosion rates in the presence of dissolved oxygen and chloride ions.

### 2.1.1: Sample Preparation:

Sample preparation for both experiments is the same and is summarized in Table 2.1. The material used as working electrode for both experiments is carbon steel rod from a parent material *BS970* supplied by Merseyside Metal Services Ltd. UK, and its chemical composition is shown in Table 2.1. The cylindrical rod is cut into test sample with working area of  $0.283\text{cm}^2$ ,

and it is spot-weld using copper wire at the opposite side that would be exposed to the electrolyte. Opposite end of the copper wire used for the spot-weld will serve as a point of connect for the electrochemical measurements insulated by 8mm PVC tube. The sample is put in a 30mm acrylic mould and filled it up with araldite resin and araldite hardener in ratio 11/1, and left for 24hrs for complete curing. Thereafter, the surface of the working electrode were mechanically polished using silicon carbide papers of grades: 320, 400, 600, 800, 1200, 2400, and 4000 in order to remove oxide/scale from the surface and achieve a mirror surface with no scratches, then rinsed with ethanol and air dried. Saturated calomel electrode and platinum electrode were used as reference and counter electrode respectively.

C (%)	Si (%)	Mn (%)	P (%)	S (%)	Fe (%)
0.170	0.200	0.780	0.020	0.023	Bal

Table 2.1: **Chemical composition of carbon steel rod used in working electrode:**

### 2.1.2: Solution Preparation for the Effect of Chloride Concentration:

The experiment is also carried out in a 1L glass cell. Different concentrations of sodium chloride (*NaCl*) salt; 0.0585% (0.01M), 0.3% (0.05M), 3.5% (0.6M), 5.8% (1M), and 10% (1.7M) *NaCl* was added to make up the 1L solution of the electrolyte used for each experiment. Likewise, the solution was thoroughly mixed using a magnetic stirrer to dissolve the high concentration of salt in each solution, and maintained at room temperature all through the experiment. The experiment is an open system to allow the electrolyte to be saturated with dissolved oxygen to simulate seawater corrosion. Electrochemical measurements were used to determine the corrosion rates.

### 2.1.3: Result and Discussion:

The free corrosion potential ( $E_{corr}$ ) of each sample was conducted for a period of 2hrs.

The  $E_{corr}$  showed a downward shift of the equilibrium potential (more negative values) as the de-aeration time increased. The results of the potentiodynamic polarization also indicated a similar downward shift of the corrosion (equilibrium) potential,  $E_{corr}$  as the de-aeration time increased. The anodic metal dissolution reaction (Equation 2.1) showed a significant shift of Tafel slope to the right after 30mins de-aeration but then remains almost the same thereafter. The anodic reaction is a charge transfer control. It can be established that there is high rate of metal dissolution below 30mins de-aeration time because the concentration of oxygen at this temperature is assumed to be close to 8ppm (the maximum oxygen solubility in water at this temperature), and above 30mins de-aeration time, the concentration of oxygen is much less. The cathodic Tafel slope also shown a significant shift to the left (indicated reduced corrosion rate) with low corrosion current density,  $i_{corr}$ , but gradually reduced thereafter. The simple interpretation of the curve is that the concentration of oxygen in the electrolyte has been reduced to below 100ppb after 1hr de-aeration. The  $i_{corr}$  also shifted to the left after 30mins de-aeration which is an indication of reduction in corrosion rate. The cathodic Tafel slope can also be used to interpret the mechanism of corrosion that take place during the de-aeration process. The mechanism of corrosion changes from mass transfer control oxygen reduction reaction (Equation 2.2) to water reduction reaction (Equation 3.4) as the cathodic reaction



The metal will corrode in the active state followed by hydrolysis to form  $\text{Fe}(\text{OH})_2$  as shown in equation 2.5 and 2.6.



The results of the electrochemical impedance spectroscopy (*EIS*) gave more understanding of the mechanism of corrosion of mild steel during the de-aeration process. The results showed one time constant which related to the corrosion process at the metal/electrolyte interface. The solution resistance significantly decreased after 30mins de-aeration and almost the same thereafter. This might probably due to low ionic conductivity of oxygen in solution. The comprehensive impedance data obtained are presented in Table 2.1. It is evident from the table that polarization resistance,  $R_p$  value increases with de-aeration time which is an indication of reduction in corrosion rate. The result also indicated that the removal of oxygen changed the mechanism of the electrochemical process to water reduction reaction. Both graphs also showed increase in polarization resistance as the de-aeration time increase; indicating a corresponding decrease in corrosion rate. *EIS* reproducibility results for 12hrs de- aeration data. Phase shift the impedance is primarily resistance above 100Hz and primarily capacitance below 100Hz with maximum values of  $60^\circ$  and  $46^\circ$  recorded at intermediate and low frequencies respectively. It is also evident from the phase shift plot that the solution resistance,  $R_s$  decrease with de-aeration time while  $R_p$  and  $n$  values increased with de-aeration time. The ' $n$ ' values in all cases are close to unity which shows that the impedance of *CPE* is capacitor but decrease with de-aeration time. The plot of the variation of corrosion rate with de-aeration time was a drastic reduction in corrosion rate after 30mins de-aeration, and gradually reduced thereafter.

## **2.2: Influence of temperature on corrosion in natural gas systems:**

Temperature and pressure affect the number of phases (liquid, gas, solid) which in turn can cause extraordinary corrosion. Temperature rise accelerates the rates of electrochemical corrosion reactions and the transfer of participants: aggressive substances to the surface of metals and corrosion products from the surface to the environment. Increase of temperature causes a decrease of pH of water. As a result, corrosion rate should go up with the increase in temperature. On the other side, solubility of aggressive gases ( $H_2S$ ,  $O_2$ , and  $CO_2$ ) decreases with

increase of temperature. Therefore, temperature has complicated effect on corrosion rates. Up to a certain temperature, corrosion rate increases with increase of temperature. After a certain temperature, corrosion rate decreases due to the reduction of corrosive gas solubility in aqueous solutions. Usually maximum is at 60-80°C depending on the chemical composition of the liquid phase. In addition to this, temperature increases the rate of sedimentation and the formation of a protective  $\text{FeCO}_3$  film.

### **2.3: The effect of flow rate on corrosion in natural gas systems:**

Flow regime and flow rate affect the corrosion significantly. The increase in flow rate defines the coming of aggressive substances to metal surface, removing corrosion products and protective layers (such as corrosion inhibitors and  $\text{FeCO}_3$ ). As a result, corrosion rate increases. For example, increase of flow rate from 1 to 10 m/s causes increase of corrosion rate from 1 to 3 mm/y in aqueous solution containing  $\text{CO}_2$  (1bar and 20°C) in the absence of protective layer  $\text{FeCO}_3$ . The flow effect occurs especially in interferences such as valves, expansion lines, restrictions, elbows, and bends. Flow regime defines the type of wetting of the metal surface, resulting in the occurrence of corrosion at the top of the pipe. High flow rate can cause erosion corrosion. At low flow rates, aggressive materials have sufficient time to be in contact with the metal surface, different deposits can accumulate and cause localized corrosion.

### **2.4: Gas hydrates:**

Ensuring of gas flow in the field of gas technology is very important. Natural gas flow should reach from the field to the production line without blockages. There are three areas of concern:

- a) Wax deposits, asphaltenes, and other heavy organic materials.
- b) Inorganic deposits.
- c) The formation of solid gas hydrates (similar to ice)

Organic deposits can be removed by means of "pigs". Inorganic deposits can cause problems of equipment in gas wells but not in large lines. Cleaning with acids is the solution for removing of inorganic sediments. Gas hydrates can clog and shut lines for a few minutes without warning. Sometimes they accumulate over months and years and can be set by the pressure drop. Gas hydrates are formed when water molecules form a cage structure and a molecule of methane or other gas are trapped inside. This happens at certain temperature and pressure. Molecules of other gases ( $H_2S$ ,  $O_2$ ,  $N_2$ ) containing in the natural gas can be included together with molecules of methane. Gas hydrates can be formed anywhere in the pipeline, but usually after orifices and valves due to significant cooling as a result of the expansion of the gas according to Joule-Thomson

Phenomenon.

Three methods are used for preventing the formation of hydrates:

- a) Maintaining temperature and pressure outside of the formation of hydrates. Usually it is not practical.
- b) Drying of natural gas from water.
- c) Injection of inhibitors that prevent the formation of hydrates. Methanol and ethylene glycol at ~ 50% are commonly used for this purpose.

### **3: Corrosion control, Research and Methodology in natural gas systems:**

Selection of corrosion control measures are based on the influence of chemical composition of natural gas (corrosive impurities) and process conditions (temperature, pressure, and flow rate regime) on corrosion. Three major factors affect corrosion: metal type, environmental features and conditions, and the border metal environment. Thus, we take care of three factors above to prevent corrosion in natural gas systems. We classify all the methods into three groups: the metal treatment (selection of material), the treatment of the environment (neutralization, removing of water,  $CO_2$ ,

H<sub>2</sub>S, O<sub>2</sub> and salts) and boundary metal-environment (injection of inhibitors, use of coatings, and cathodic protection). We can add technological methods, which means maintaining the process conditions (temperature, pressure, flow rate). We will start from engineering design.

### **3.1: Engineering design and control:**

Engineering design includes:

- a) The use of standards, specifications, procedures, reports, and any new information.
- b) The use of knowledge of principals, processes and possible corrosion phenomena in natural gas system. It is necessary to take in to account the geometry of the account to make less crevices, to control flow rate, to control air infiltration, to avoid “dead legs” (gathering areas and stagnation of water)
- c) Selection of suitable materials of construction, methods of protection, control and corrosion monitoring for designed period of service. Choosing suitable coating, corrosion inhibitor, biocides, ant-scaling agent, cathodic protection and removing corrosive impurities (H<sub>2</sub>S, H<sub>2</sub>O, and O<sub>2</sub>) belongs to this group.
- d) Selection corrosion monitoring methods: monitoring from construction materials behavior, corrosive environment and efficiency of methods of protection against corrosion.

#### **3.1.1: Selection materials of construction:**

Materials selection marks the use of metals and alloys, polymer and composite materials (composites) suitable for different environments in the technology of natural gas. There is no ideal material that is resistant to all media under all conditions. It is acceptable to call stainless steels and alloys based on nickel as corrosion resistant materials. Really general corrosion rates of these alloys in natural gas systems are much lower than values for carbon steel. But stainless steels and nickel alloys are susceptible to pitting and crevice corrosion, intergranular corrosion, and stress

corrosion cracking. Therefore, it is better to use the term materials compatible with corrosive media. A proper method for selecting alloys is based on information and experience which are included in the standards, procedures, reports, and articles. The disadvantage of this approach is that changes in the environment (even at the same gas field) can alter the corrosion resistance of alloys. In the selection of alloys, it is necessary not only to relate to general corrosion but also to local corrosion, for example, by chlorides, oxygen, bacteria, hydrogen, etc.

Metals and alloys. Carbon steel occupies more than 90% of all the materials in natural gas systems. Drill pipes are used according to the standard API 5D, casings and tubes – API 5CT, and line pipes – API 5L. Design of carbon steel use should be made with calculation of corrosion allowance and suitable heat treatment. Use of carbon steel in natural gas systems must be accompanied by injection of corrosion inhibitors to prevent internal corrosion, the use of coatings, and cathodic protection to prevent external corrosion of underground and submerged structures and equipment. It is possible to use materials resistant to corrosion better than carbon steel: metals and alloys with addition of chromium, nickel and molybdenum (stainless steels), alloys based on nickel, cobalt, copper, titanium, and aluminum, polymers, and composite materials. The most common alloy among stainless steel in natural gas systems is 13Cr that is used in wells and in sea

water. Generally selection of alloys for use in hot gas wells and other applications occurs in the next direction: carbon steels → stainless steel martensitic 13Cr → stainless steels austenitic → duplex stainless steels → austenitic nickel alloys. It is possible to select specific alloy suitable at particular temperature, pressure and  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NaCl}$  concentrations when the general corrosion rate will be less than 0.05 mm/year. Titanium alloys can be used in natural gas wells at high pressures and temperatures in the presence of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . Iron-nickel (9%) alloys are used as material for cryogenic tanks for storage of liquefied natural gas (LNG) at  $-162^\circ\text{C}$ .

Polymeric materials and composites occupy a certain place in their application in natural gas systems. Chemical resistance of these materials is much higher in contact with various



gases and solvents. The disadvantages of polymers are low resistance to high temperatures and low mechanical properties compared with metals. Polymeric materials are used in natural gas systems as seals, gaskets, rings, sumps, tanks and pipes in contact with water, sea water, cooling water, fire-fighting water, solutions of acids and alkalis, atmosphere, and soil. Polymeric materials are

characterized by mechanical, thermal, electrical properties, and chemical resistance. Temperature drastically affects the properties of polymers and composites. When heating the polymer material can chemically breakdown. When cooling it can be hard and brittle. Selection of the type of polymer and composite depends on the purpose for use in natural gas systems. Therefore, it is necessary to analyze all properties of polymers and composites before application. Polymeric materials and composites are used in coatings.

### 3.1.2: Coatings:

Use of any coating is based on the fact that metal must be isolated from the aggressive environment. All coatings can be differentiated into three groups according to the nature of basic material: organic, inorganic, and metallic. Organic coatings may be paints, polymeric materials, greases, and other paraffinic mixtures. Inorganic coatings may be enamels, ceramics (among them cement), and glasses. Metallic coatings are any metal or alloy. All three groups of these coatings are used for the protection of pipes, tanks, pumps, columns, numerous structures and equipment in contact with natural gas, atmosphere, water, soil, and different technological solutions. Natural gas systems are situated in different geographical areas. Therefore, it is important to create coating specifications that protect structures and equipment under various conditions: resistant to gas, fuels, water and aqueous solutions, atmosphere, soil, high temperature, and under thermal insulation.

### 3.1.3: Cathodic protection:

The philosophy of cathodic protection use is that organic coatings` application on metallic structures is the main (leading) method of corrosion control, and cathodic protection is a complement to protect the defects that are always exist or appear in organic coatings during application and service. Electrochemical mechanism of corrosion of metals in solutions of electrolytes allows the use of electric current and electric potential to protect metal surface from corrosion. Therefore, cathodic protection works only in solutions of electrolytes and does not work in media of high electrical resistivity which cannot conduct electrical current: in natural gas, air, oil, and fuels. Two ways exist for cathodic polarization in practice: connection the main metal to be protected (for example, iron) to less noble metal (aluminum, zinc, magnesium, or their alloys), or connection to the negative pole of outer power supply (rectifier or battery). The first method is based on sacrificial anodes use, because they are sacrificed being dissolved as anode, and turn the metallic construction to cathode which does not corrode. Sometimes this method of cathodic protection is called a passive one (there is no relationship to passivity), because we connect equipment to be protected to a sacrificial anode, and “forget” about corrosion for some period. The second method of cathodic protection is based on the connection to the negative pole of the rectifier and use of impressed electric current. This method is called sometimes an active method of cathodic protection. Cathodic protection is one of wide spread methods of corrosion control of underground and submerged metallic structures and equipment. Cathodic protection works only on external surfaces that contact with the electrolyte and it does not mean the media flowing or stored inside: gas, oil, fuel, or water. Many standards exist to implement cathodic protection, testing methods and monitoring efficacy. High temperatures, destroyed coatings, shielding, microbial attack, areas of pipes and tanks that are not in contact with the electrolyte and dry soil are the conditions when cathodic protection is not effective or is working only a part of time. Cathodic protection does not work for thermal insulating structures. It is important to

remember that cathodic protection is working when the following components exist: an anode, a cathode, an electrolyte, and a complete electrical circuit. The absence of one of these components prevents the activity of the cathodic protection. Sometimes people forget about it and try to use cathodic protection for hot pipes when hot water evaporates and there is no electrolyte for the passage of an electric current. American engineer Robert Kuhn was the first who used cathodic protection on pipelines for transporting natural gas in the U.S. in 1928 and more widely in the 1930s. There are several methods to test the efficacy of cathodic protection. The most common method is to check the electrical potential of the protected pipe. Its corrosion rate decreases to two orders of magnitude when electric potential lower than  $-0.85$  V with respect to a saturated copper/copper sulfate reference electrode. Keep in mind that the corrosion rate of cathodically protected structure is never zero but very low value and acceptable for safe use without corrosion risk. In the early years (1920-1950) of use of cathodic protection, it was generally accepted that corrosion structures could be fully protected in soil and water. Then cathodic protection was begun to use in combination with coatings. Cathodic protection is not an alternative to the protection by coatings of pipes and tanks but an addition. Coatings allow to reduce electric current on several orders of magnitude and to extend the service life of structures. It should be noted that cathodic protection can be used for the protection not only carbon steel but also cast iron, ductile iron, stainless steel, brass, and aluminum. Cathodic protection can cause the following problems:

- a) Impressed current systems may cause stray current corrosion if metallic constructions are in the region of cathodic protection activity and are not connected to impressed current.
- b) Coating de-bonding.
- c) Hydrogen embrittlement (in the case of overprotection, less than  $-1$  V with respect to a saturated copper/copper sulfate reference electrode and as a result of water decomposition and hydrogen evolving).

d) Corrosion of aluminum (because hydroxyl ions forming during cathodic protection are harmful to aluminum).

### 3.1.4: Change of chemistry of the environment:

There are several options to change the chemical composition of the environment and protect metals. These methods are injection of corrosion inhibitors, biocides, pH control, removal of water, CO<sub>2</sub>, H<sub>2</sub>S, and O<sub>2</sub> from natural gas. Corrosion inhibitors occupy an important role in preventing and reducing corrosion in natural gas systems. The first inhibitors were amines that were used as the only means of corrosion control in natural gas pipelines in the 1940-1980s. Only in the 1980s with the discovery of deep wells at high temperatures and high pressures inhibitors were not effective, and special alloys were begun to use under these conditions. There is no common classification of inhibitors. We will describe a few of them.

a) Classification according to the influence on corrosion reactions. For example, anodic inhibitors slow down anodic reactions on the surface of the metal. Cathodic inhibitors retard cathodic reactions. There are mixed inhibitors that suppress both anodic and cathodic reactions simultaneously.

b) Classification by the type of metal to be protected. For example, corrosion inhibitors that protect carbon steel, copper, aluminum and their alloys.

c) Classification by the environment: water and aqueous solutions of electrolytes; acids; alkaline solutions; the gaseous phases; oil and fuels; coatings; concrete.

d) Organic and inorganic inhibitors.

Mechanism of action of inhibitors is based on their adsorption on the metal surface and preventing the coming of aggressive substances to the metal surface. Therefore, usually increase of concentration of inhibitors reduces the metal area exposed to aggressive components. We will describe corrosion inhibitors using in natural gas systems. Most corrosion inhibitors using in gas

systems are “filming amine” that produce a protective film on the metal surface. When crude oil enters into an aqueous phase its ingredients are able to protect the inner surface of the pipes from corrosion. Organic compounds containing nitrogen (amines, amides and their salts), heavy carboxylic acids and their salts, imidazoline, phenols, thiourea, phosphonates, benzoates, saturated hydrocarbons, aromatics and resins containing in oils act as corrosion inhibitors. Most corrosion inhibitors injecting into natural gas pipelines are nitrogen organic substances. Inhibitors are not always able to prevent corrosion at the top of the pipelines. Volatile corrosion inhibitors and inhibitors that are introduced into the foam matrix are recommended in these cases. Inhibitors produce a thin layer of molecules on the surface of the metal. An intensive flow of gas, liquid or liquid-gas mixture is able to remove this layer. Inhibitor efficiency decreases in the presence of suspended solids and sand because they attract molecules of the inhibitors. Inhibitors are attracted to scale and corrosion products that reduce their effectiveness. It is recommended to carry out chemical cleaning before the start of corrosion inhibitor injection. It is necessary to carry out periodic cleaning using “pigs”. Inhibitors used in natural gas systems are organic materials that decompose at temperatures above 200°C.

Injection of methanol or ethylene glycol to prevent the formation of gas hydrates also inhibits corrosion due to dilution of aqueous phase. Inhibitors should function in accordance with other chemicals injecting into gas systems for various purposes. We can start or replace inhibitors without stopping and disruption of a process of production, transportation, and manufacturing. This is a big advantage over other methods of corrosion control. In addition, continuous monitoring of the efficiency of inhibitors can be performed and it is possible to change their concentrations in accordance with changes of corrosivity of natural gas.

Cooling water systems. Three chemicals are injected in these systems for control of corrosion, microbiological growth and scale formation: corrosion inhibitors, biocides, and anti-scaling agents. Corrosion inhibitors in such systems are mixtures of anodic inhibitors (e.g. phosphates), cathodic inhibitors (e.g. zinc salts), organic inhibitors (e.g. phosphonates), and

copper corrosion inhibitors (azole). We can use inorganic inhibitors ( $\text{NaNO}_2, \text{Na}_2\text{SiO}_3$ ) in closed cooling water systems for chilling pumps and compressors. Sodium nitrite protects carbon steel in fuel-water mixtures. Now there is a tendency to use “green” or “environmentally friendly” inhibitors. They should be evaluated in terms of health, safety and damage to the environment. It is important to assess the efficiency of potential inhibitors in laboratory and in field in order to select a suitable inhibitor for particular natural gas well. We can calculate efficiency (E %) of inhibitors according to the following formula:

$$E \% = \frac{(CR_o - CR_i)}{CR_o} \cdot 100\%$$

where  $CR_o$  and  $CR_i$  – the corrosion rate of metal without and in the presence of inhibitor respectively. Corrosion rate can be measured using the method of “weight loss (coupons)” or “electrical resistance (ER-probes)”. The dosage should be chosen very carefully and then keep it in the system. Any change in dosage can affect the efficiency drastically. Inhibitors are injected continuously or in portions periodically. The first dose is always big to cover the entire surface of the metal. Then we can lower its concentration to the minimum necessary to maintain inhibitor layer on the metal surface. Corrosion monitoring by means of coupons or electrical resistance (ER-probes) is used to check the efficiency of inhibitors and to change its concentration if needed. It is important to install sensors and coupons inside pipeline in places that could be affected by corrosion and scale and to follow all internal space of the tube. We have to take into account that corrosion is a random process and can vary from place to place and over time. It is necessary to combine coupons and ER-probes that are complementary to each other. We should take into account the natural gas field can age, and chemical composition, temperature and pressure can vary with time. As a result, corrosiveness of natural gas can also change.

### **3.2: Corrosion monitoring in natural gas systems:**

It is important to follow the corrosion in natural gas systems because there is a high danger to humans and the environment in the case of holes and leaks of toxic and explosive gases. The philosophy of preventive anti-corrosion methods also intends to follow their effectiveness. The purpose of corrosion monitoring is to monitor corrosion situation of metallic equipment and structures, aggressiveness of the environment, and efficiency of corrosion control measures. There are several ways to classify corrosion monitoring methods. For example, direct and indirect methods. Direct methods of measurement belong to parameters that vary directly from corrosion. For example, a wall thickness of the pipe or a mass of a metal coupon. Indirect methods of measurement belong to parameters which influence indirectly (temperature, pressure, pH, concentrations of aggressive substances to metals) or are affected (metal dissolved ions because of corrosion and detection of leaking gases or liquids due to holes caused by corrosion). Direct methods are divided into intrusive methods (e.g. weight loss) and nonintrusive (for example, the wall thickness measurement). Indirect methods can be online and off-line. Online measurements are performed without removal of the sensor from the process. Off-line method means removing a metal sample from the process stream for testing. We should distinguish between corrosion monitoring and inspection. Monitoring allows to measure corrosion parameters in real or approximately real time. Inspection has time delay between an incident and an investigation. Inspection collects data about the event that has already happened. We classify corrosion monitoring methods on physical methods, test methods of the environment (chemical analytical) and measure the border metal-environment.

#### **3.2.1: Physical methods of control of properties of metals:**

Historically, physical methods were first: the human eye, sometimes with a magnifying glass. Now there are many optical devices: video cameras, microscopes, stereo video microscopes, and borescope. They can be used for examination of corroded metal surface. Different devices

and techniques based on physical phenomena are used for measuring the wall thickness of pipes and tanks in natural gas systems: Ultrasonic Technique, Acoustic Emission, Eddy Current Technique, Magnetic Flux Leakage, and radiographic methods (X-ray). In addition, there are other physical

methods: Infrared thermography, chemical analysis (non-destructive) of alloys on the site, and penetrant testing. Weight Loss (WL) method is based on inserting of a metal sample (called coupon) of a known mass and area into a flow process, immersion for a certain period (usually between 30 to 300 days, and time depends on the aggressiveness of the environment), removing, cleaning from corrosion products and other deposits, and weighing. A loss of coupon weight per unit area during some period is the rate of corrosion of a metal in a specific environment. Weight loss method is standardized and the most accurate among all the existing methods of corrosion monitoring.

Electrical Resistance (ER) method is based on measuring the electrical resistance of the sensor (corrosometer) made from the same metal of a tube (or other equipment) with time. Corrosion of the sensor (decrease of thickness of a sensor and respectively cross-sectional area  $A$ ) causes increase of electrical resistance  $R$  of a sensor material:

$$R = \frac{(\rho \cdot L)}{A}$$

where  $R$  – the electrical resistance of conducting material (sensor), Ohm;  $\rho$  – the specific electrical resistivity of conducting material, Ohm · m;  $L$  – the length of a sensor, m;  $A$  – the cross-sectional area of a sensor, m<sup>2</sup>. ER-method is an analog of weight loss method with advantage that corrosion rate can be measured continuously. Special 'flush' probes are used in pipelines when cleaning and inspection is performed by means of 'pigs' in natural gas systems when multiple liquid-gas phase is flowing inside. This method is standardized. We can use ER-probes up to 537°C and 700 bar. Both methods (WL and ER) are used for corrosion monitoring in natural gas systems because there is no restrictions on the electrical conductivity of the environment. We can



use these two methods for measuring of corrosion rates of metals in gases, in air, and in conductive and nonconductive solutions. There is a restriction of physical methods: they assume that the corrosion rate is constant throughout the measurement period. In fact, failure because of corrosion occurs rarely with a steady rate. In most cases, failures occur suddenly and often relate to operational events: shutdown of facilities, changes in temperature, pressure, concentrations of substances, velocity and flow regime, operating system, etc.

### 3.2.2: Monitoring of the environment and technological parameters:

Environmental testing includes chemical analytical, physicochemical, physical, and microbiological methods. These methods are used to determine aggressive components in the environment: pH, CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, suspended solids, hardness, corrosion-inducing bacteria, and particles that cause erosion. On the other hand, physicochemical analytical methods (Inductively Coupled Plasma and Rotated Disc Electrode Atomic Optical Emission Spectroscopy) are used for determination of concentration of metals which corrode in liquids with sensitivity ~ 1 ppm and less. Physical and chemical analytical methods should be integrated in natural gas systems. The question is what is the dangerous values of chemical analytical parameters which define the intensity of corrosion (high or low) in the system? Allowable values depend on the specific system (type of a metal and the environment) and corrosion phenomenon type.

Gas detectors have been developed (PID – photoionization detectors) which can detect hydrocarbon gases at concentrations of 1 ppb. These gas detectors are lightweight and portable.

In many cases, it is important to follow not after absolute values, but after a trend that can suddenly change, and thus we can detect the start of corrosion. Testing of concentrations of corrosion inhibitors, neutralizers, oxygen and hydrogen sulfide removers (scavengers), and

biocides in different media and water drainage are important in determination of the efficiency of treatment against corrosion and for the environment.

Monitoring of technological parameters includes measurement of flow rate, temperature, pressure, and dew point temperature.

Advantage of physicochemical analytical methods is their high sensitivity.

The disadvantages are that the chemical composition of the environment points on a qualitative assessment of corrosion; the presence of corrosion products on metal surface can lead to wrong results; sometimes these methods require a long time to obtain results.

### **3.2.3: Examination of the border metal-environment:**

These methods are based on physicochemical properties of the border metal-environment and include electrochemical methods, identification of corrosion products and other deposits on metal surface, and surface morphology of corroded metal. Electrochemical methods (examination of electrical potential and current) can be used only in solutions of electrolytes. These methods are used for monitoring of the efficiency of cathodic protection of underground and submerged pipelines, tanks, and other structures.

Physicochemical methods, such as Scanning Electron Microscopy (SEM), Tunneling Scanning Microscopy (STM), Atomic Force Microscopy (AFM) are used for examination of the surface morphology of the metal, Energy Dispersive Spectroscopy (EDS), Energy Dispersive X-ray Fluorescence (ED-XRF), X-ray photoelectron spectroscopy are used for identification of corrosion products, deposits and inhibitors on the metal surface. Microbiological testing of deposits and different media is very important to determine the causes of MIC and ways to prevent it.

### 3.2.4: Online, real-time corrosion monitoring:

On-line measurements are continuous measurements of weight loss and corrosion rate of metals, physicochemical parameters of the system and the environment; data are obtained without disruption of the monitoring processes. Off-line measurements are periodic measurements with a disruption of the monitoring process. Real-time information is obtained immediately, usually for a few minutes. Continuous real-time corrosion monitoring of pipelines is mostly developed

It is necessary to perform its integration with process control system, which means to follow technological parameters with corrosion-state data. Here are some corrosion monitoring systems of pipelines:

- a) The Resistance Corrosion Monitoring (RCM) – continuous measurements of pipe wall thickness using the method of ‘electrical resistance’.
- b) The Field Signature Method (FSM) – Electrical resistance method for determining the wall thickness of pipes: uniform corrosion, corrosion pits, erosion, and cracks.
- c) Advanced ER on-line corrosion probes with fiber optic communication links – Monitoring the effectiveness of anticorrosive chemical injections.
- d) In-Line Inspection (ILI) – Survey for evaluating corrosion of pipes and damages. Combination of physical techniques, chemical analytical and physicochemical methods gives wide information of corrosion situation in natural gas pipelines.

### 3.3: Efficiency monitoring from corrosion protection:

Monitoring and examination of the effectiveness of cathodic protection of pipelines are defined in standards. In practice, two criteria for definition of efficiency and integrity of cathodic protection are used. The first criterion is the electrical potential of a protected buried pipeline in soil should be less than  $-0.85$  V with respect to a saturated copper/copper sulfate reference

electrode. The second criterion is a minimum of 0.1 V of cathodic polarization between the structure surface and a stable reference electrode contacting the electrolyte.

Close Interval Potential Survey (CIPS) and Direct Current Voltage Gradient (DCVG) are widely used for examination of efficiency of cathodic protection of underground pipelines. DCVG method is based on the potential difference measurements at distances of about one meter above underground pipe that is protected by cathodic protection. The more dimensions of defect in coating, the more the difference in potentials. This method allows to detect defects ~1 cm in coatings on pipes buried in the ground at a depth of 1-2 meters.

#### **4: Findings, Analysis and Decision:**

Here we will discuss about the problem statement of our plant. Our first finding, which shows us sign of thickness loss of pipelines. We observe corrosion in many places, which is mainly liquid hydrocarbon condensate with water. During turnaround, while opening of all equipment for maintenance, we found corrosion at compressor side, suction drum, suction pipelines, and overhead stripper column. Stripper overhead line was completely attacked with corrosion.

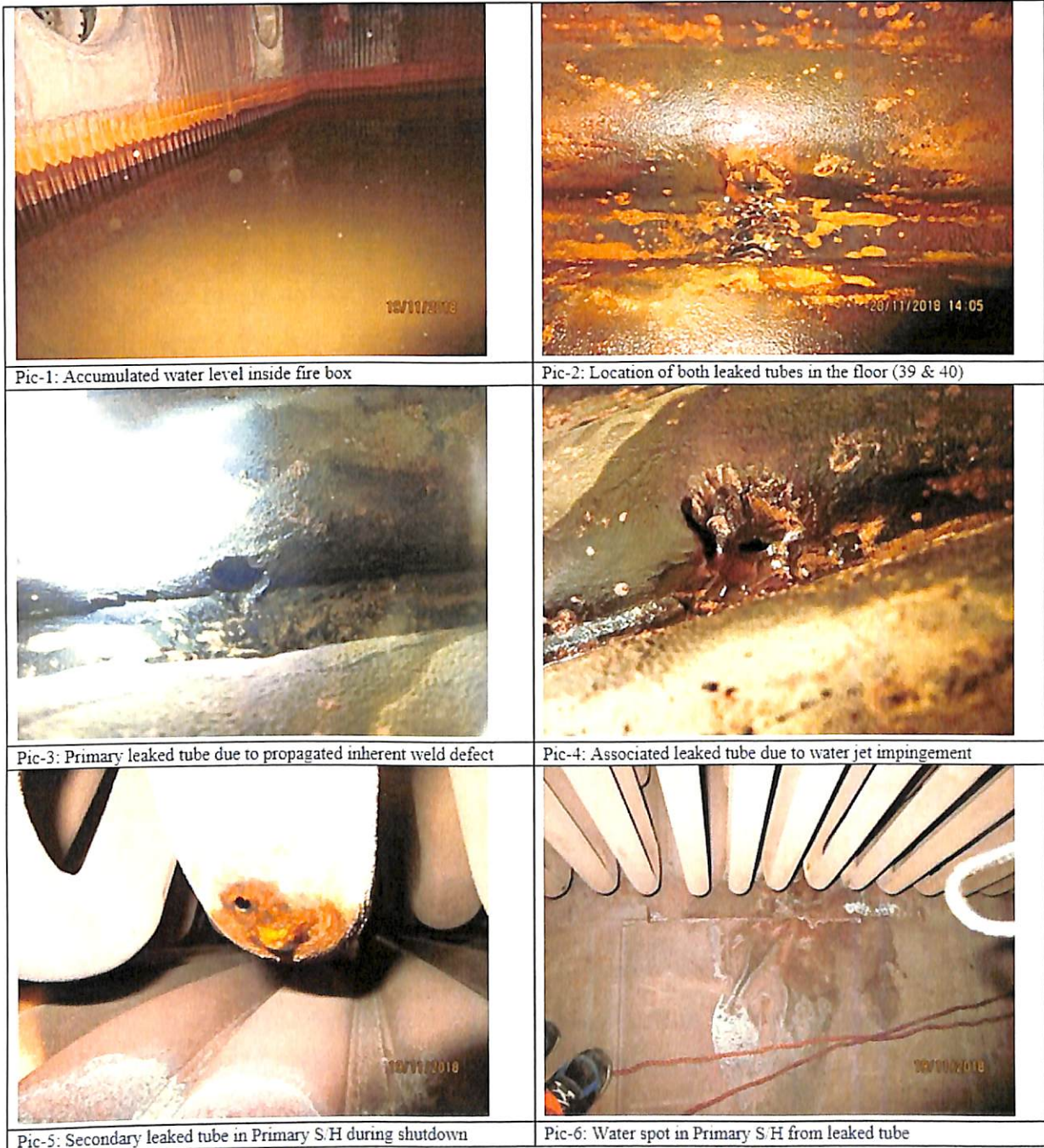
Engineering started studying on problem statement of plant in order to eliminate the issue of corrosion from the upstream itself, try to segregate water from gas in upstream & treat it in a sour water treatment unit rather than to pass it to the stabilization unit & pass through the other unit which is immediately impacting the metallurgy.

#### 4.1:BoilerEmergency shutdown due to Floor Tubes / Primary S/H Tube leaks:

##### 4.1.1:Findings:

- Reported leak in Boiler, post shutdown inspection revealed:
  - Two leaks were identified in floor tubes #39/40
  - One leak was identified in Primary S/H tube #35
  - Accumulated Water level inside Fire Box ~0.5 m

**Figure 4.1.1: Formal Anomaly Snapshot: Boiler Emergency Shutdown due to floor tubes:**



#### 4.1.2: Casual Factor:

##### **Primary Leak:**

- Identified in floor tube #39 adjacent to fin file weld area east side @ 3 o'clock position,
- Root cause: Most probably due to inherent weld defect (construction defect – anticipated arc strike or burn through) which propagated during operation, From the rough surface of the hole and no observed reduction in the cross section, it seems the leak start from very small pinhole and enlarged faster due to high velocity of water eject.

##### **Associated Leak:**

- Identified in floor tube #39 in opposite of tube #40, leak adjacent to welded fin west side @ 9 o'clock position
- Root cause: Due to water jet impingement from tube #39, Observed external erosion / metal loss around observed leak shows that it is a consequence to the primary leak in the adjacent tube.

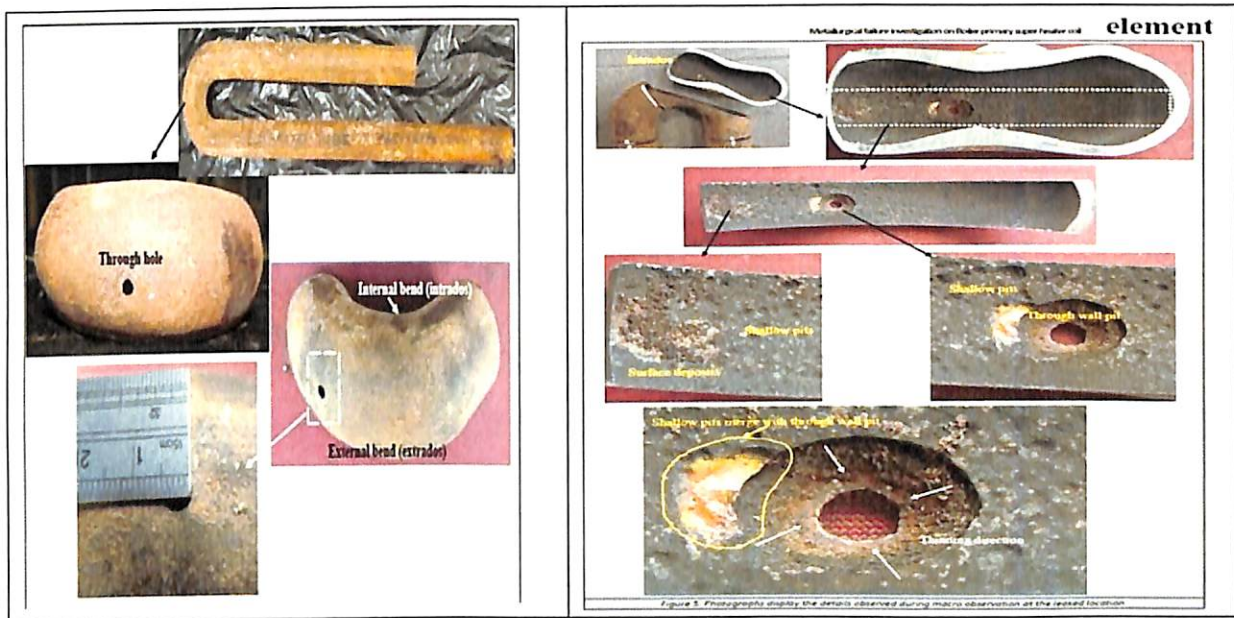
##### **Secondary Leak:**

- Identified in Primary S/H tube # 35 due to aggravated wall thinning, during Boiler shutdown period.
- Root cause: Size of water spot beneath the leaked tube and no detected accumulated water inside the S/H section confirm this leak occurred during Boiler shutdown. Tube was suffering internal pitting corrosion / wall thinning before as identified in May-2018.

4.1.3: Action(s):

- Comprehensive inspection for leaked tubes and adjacent tubes in both locations to identify defected sections for required cut/out and replacement,
- Thoroughly inspection for Primary S/H tubes to identify any additional defected tube to eliminate future on-stream leak until next planned outage for entire Primary S/H coils replacement,
- IWL issued after inspection activity completed.
- Rectified as per IWL.

**Figure 4.1.2: Study Report for Boiler Integrity Threats:**





#### 4.1.4: Metallurgical Failure Investigation report:

Metallurgical failure investigation report on Boiler Primary Super Heater Coil's tube failure (Leak Incident) was received and approved.

#### **Conclusion:**

Based on the results achieved from this metallurgical investigation and from detailed discussion the following observations can be drawn:

1. No significant anomaly/deviation observed w.r.t chemical composition, hardness and microstructure. Super heater coil tube material is satisfactory in terms of metallurgical and mechanical properties.

2. Macro examination showed localized corrosion attack at the inner surface of extrados location. Tube wall thinning noticed from ID to OD.

3. SEM analysis complements the findings made during macro examination. EDS probed the presence of Fe, O, Na, K, S, Cl on the ID corrosion deposits.

4. To conclude, the corrosion failure of Boiler primary super heater coil can be attributed to **“Caustic gouging or Caustic corrosion”**. The localized internal corrosion, which occurred through under deposit corrosion mechanism. The tube bend location acted as a potential site for pitting initiation, further the accumulation of surface deposits at bend location made that zone more vulnerable for pitting corrosion attack. Indication of **oxygen pitting** was also observed that might partially have influenced the internal corrosion.

#### 4.2: Off-Gas Compressor Corrosion Deposition:

**Figure 4.2: Plant Anomaly Snapshot: Off Gas Compressor 1<sup>st</sup> Stage Suction Drum:**



Off Gas Compressor 1<sup>st</sup> stage suction drum is suffering severe pitting / under deposit corrosion.

- Measured pitting depth is 1 mm in Alloy 825 internal cladding (3 mm).
- These drums were newly installed (upgraded from SS316L into Alloy-825)

##### 4.2.1: ESR: Engineering study for observed deposits:

**ESR: Engineering Study for observed carryover Deposit and excessive Sour Water inside Off Gas Compressor 1st Stage Suction Drum & providing suitable internal coating on the bottom as interim mitigation:**

- Interconnecting piping (which was upgraded from SS321 to Alloy-825 as per FMP) may suffer different grade of corrosion especially at dead-log / stagnate location where possibility of deposition will be high.

**Table 4.2: Scale and Sludge Analysis report of Off Gas Compressor 1<sup>st</sup> Stage Suction Drum:**

APPEARANCE/PHYSICAL PROPERTIES( <i>color, pH, consistency, wet/dry, sticky, particle size incidental odor – do not sniff, etc.</i> )		Dry, Black Granules Sample.	
ANALYSIS (As delivered -Wet basis)	wt of sample(g):	7.7134	RESULT (Weight %)
<b>Loss @ 110°C</b> (maybe water, light volatiles)	wt of loss(g):	0.8171	10.59
ANALYSIS (Dry basis)	wt of sample(g):	6.8963	RESULT (Weight %)
<b>Loss @ 500°C</b> (maybe volatiles, organic matter)	wt of loss(g):	2.8941	41.97
<b>Loss @ 800°C</b> (maybe ash)	wt of loss(g):	0.8731	12.66
<b>Residue @ 800°C</b>	wt of residue(g):	3.1291	45.37

ANALYSIS (on Residue)	wt of sample(g):	0.4380	RESULT (Weight %)
<b>Acid Insoluble</b> (maybe silicates, refractory matter)	wt of insoluble(g):	0.2983	68.11
<b>Acid soluble</b>	wt of soluble(g): (by difference)	0.1397	31.89

RESIDUE CATIONS	RESULT (weight % of residue)	RESIDUE ANIONS	RESULT (weight % of residue)
Iron	17.93	Chloride	0.01
Calcium	0.38	Sulphate	11.87
Magnesium	N/D	Carbonate	NIL
Manganese	0.24	Phosphate	N/A
Nickel	35.44	Nitrate	N/A
Sodium	0.33	Nitrite	NIL
Silica as SiO <sub>2</sub>	37.76		
Silicon as Si (calculated from SiO <sub>2</sub> )	17.65		

Please note that During Off-Gas Compressor outage for intersection piping inspection and temporary replacement we inspected 1<sup>st</sup> Stage Off-Gas Compressor Suction Drum as we did in previous trains and observation as below:

**AOI:**

- Moderate deposit brownish color was observed at the bottom dished end, fine deposit was found also on bolts / nuts / support ring, stiffeners channel, etc.,.
- Perforated plate below KRANJI fittings looks clean and free from any deposit for bottom projection only,
- Internal parts / mesh could not be inspected as were not removed for detailed inspection,
- This drum was installed with upgraded material Incone-825 and with KRANJI internals (part of FMP) and this was the first time to be offered for internal inspection since that date.

**DI:**

- Surface etching / corrosion initiation / under deposit corrosion are prominent at the bottom-dished end after flushing and deposit removal.

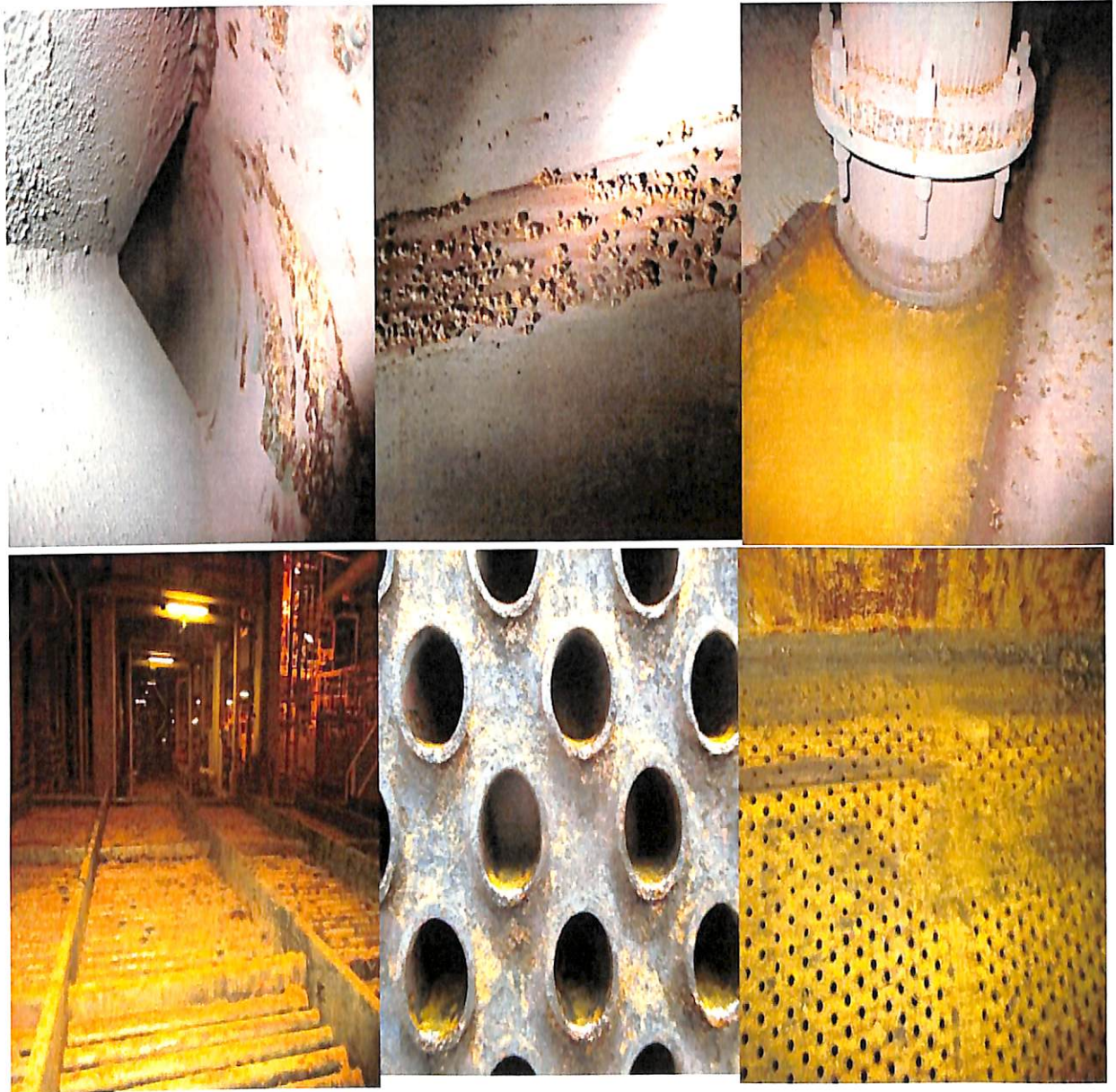
**4.2.2: Reported acid etching / pit initiation:**

**Reported acid etching / pit initiation at the bottom of Off-Gas Compressor 1<sup>st</sup> stage suction drum reviewed in detail with below findings:**

- 1) Bottoms of 1<sup>st</sup> Stage OG Suction Drums have been subject to accumulation of salty deposits with unexpectedly high Sulfates + Chloride contents > 50,000 wt ppm / pH < 3.5.

- 2) Significantly high amounts of Silica (+Sulfates/ Chlorides) in deposits indicate an unexpected “liquid + solids” carryover downstream Stabilizer Column.
- 3) New KRANJI internals, with higher coalescing efficiency, is expected to aggravate solids accumulation at the drum bottom.
- 4) Deposits are significantly sticky / muddy and are highly concentrated in salt content. CRAs (except Alloy 625) would be prone to under-deposit corrosion in presence of such concentrated salt deposits.
- 5) Evidently, this situation has resulted in acid etching / pitting initiation on Alloy 825 surface at the drum bottom.
- The above situation needs to be addressed / mitigated urgently since higher quantities of acid salts / muddy deposits are expected to be all accumulating in the drum during future well work-overs (RMOP).
- Belzona 1391/1591 coating recommended as mitigation for Off-Gas Compressor 1<sup>st</sup> stage suction drum under deposit corrosion.

**4.3:Pitting Corrosion inside the Claus Reactor Reheater:**



**Figure 4.3: Anomaly Snapshot: Claus Reactor Reheater:**

#### 4.3.1: Findings:

- Severe pitting corrosion was observed on both channel head baffle plate and internal surface of tubes (Steam side),
- Carried out Borescope inside the tubes confirmed pitting corrosion is taking place inside the tubes,
- Carried out hydro-test (shell side),
- IRIS not carried out yet as internal flushing of the tubes was not appropriate,
- The cited re-heater was successfully inspected in shutdown without any reported anomaly, (see attached previous report)

#### 4.3.2: Casual Factor:

- Phosphate injection rate,
- Uncontrolled O<sub>2</sub> in BFW,
- BB rate
- Steam load inside the re-heater
- Damage Mechanisms are
  - Boiler Water Condensate Corrosion (API 571 – Clause 4.3.5)
  - Caustic Corrosion (API 571 – Clause 4.3.10)



#### 4.3.3: Action(s):

- IRIS to be carried out immediately to identify severely defected tubes,
- IWL to be issued for plugging identified tubes for long term safe operation,
- Claus Reactor Reheater to be isolated and offered immediately for detailed inspection (CVI / IRIS),
- OSI (UTS) on several locations for Steam Drums and Interconnecting Piping,
- Fresh sample to be collected from upstream / down-stream identified locations / tags - Chemical analysis for collected sample of all systems.
- Above casual factor to be investigated for permanent solution to eliminate On-Stream failure.
- Plan for re-tubing during next outage (next outage to be confirmed based on IRIS result and AI assessment).

## 5: Conclusion and Scope of Future Work:

Non-destructive testing and corrosion monitoring are important measures in detection, prediction and prevention of corrosion in natural gas systems. We should distinguish between corrosion monitoring, inspection, and survey. Inspection and survey operations are planned and carried out periodically. Corrosion monitoring is carried out continuously to obtain real time information. Nondestructive testing and corrosion monitoring are interdisciplinary issues encompassing wide areas including different techniques, sensors, instruments, data analysis, and use of standards. The more we use various methods and means the more we get complete and up to date picture of corrosion situation. A selection of corrosion monitoring methods depends on the type of equipment or structure, conditions, and objectives. Therefore, there is no absolute and ready proposal for all systems and all cases. It is necessary to use corrosion monitoring methods as much as possible. Using of NDT and corrosion monitoring can reduce the risk of failures almost to zero. Sometimes visual inspection gives no warning to significant failure that requires high cost of repairs in a short time. Therefore, we need continuous monitoring in real time. There is no technology that can detect and immediately inform all kinds of corrosive failures. It is necessary to design and implement NDT and corrosion monitoring methods at the stage of a project design. It is very important to select points of inspection, testing and installation of sensors and coupons. It is recommended to measure the thickness using ultrasonic methods in places where

corrosion sensors are installed. Corrosion rates (even uniform corrosion) can vary at different distances and places of equipment and structures. The more locations will be covered by corrosion sensors the more we define and know real corrosion situation.

We should not talk about the cost of corrosion monitoring techniques. This cost is approximately 0.05% of the overall losses of corrosion damage. When corrosion failure occurs the cost of failure (corrosion loss) can be thousands of times higher than the cost of corrosion monitoring methods. Data of NDT methods and corrosion monitoring (thickness and

corrosion rates) enter and appear on a computer screen as other technological parameters: temperature, pressure, flow rate, and concentrations of chemicals.

There is a similarity between the corrosion rates and the behavior of the stock market: data in the past do not give guarantee for the future. Any change in the process (temperature, installation of an additional pump, changing the diameter of the pipe, adding a heat exchanger, flow regime, type of environment, inhibitors, neutralizers, and other chemicals) can cause sudden corrosion. Therefore, it is necessary to analyze all the changes in the system and how they affect corrosion. In light of this, corrosion monitoring and NDT methods represent an important role in preserving of metal equipment and structures in good condition and preventing damage to humans and the environment.

### **Bibliography:**

- [https://en.wikipedia.org/wiki/Sour\\_gas](https://en.wikipedia.org/wiki/Sour_gas)
- <https://www.yokogawa.com/us/library/resources/application-notes/sour-water-stripper-process>
- <http://www.electrochemsci.org/>
- [http://www.oilfieldwiki.com/wiki/Main\\_Page](http://www.oilfieldwiki.com/wiki/Main_Page)
- <https://www.sciencedirect.com/topics/engineering/sour-gas>

## References:

- R. Nyborg and A. Dugstad, "Top of Line Corrosion and Water Condensation Rates in Wet Gas Pipelines," *NACE International*, Paper No: 07555, 2007.
- Z. Zhang, D. Hinkson, M. Singer, H. Wang, and S. Nestic, "A Mechanistic Model of Top-of-the-Line Corrosion," *CORROSION*, vol. 63, no. 11, pp. 1051–1062, 2007.
- F. Vitse, S. Nestic, and Y. Gunaltun, "Mechanistic Model for the Prediction of Top-of-the-Line Corrosion Risk," *NACE International*, Paper No: 03633, 2003.
- F. Vitse and S. Nestic, "Mechanistic Model for the Prediction of Top-of-the-Line Corrosion Risk," *CORROSION*, vol. 59, no. 12, pp. 1075–1084, 2003.
- I. Jevremovic, A. Debeljkovic, M. Singer, M. Achour, S. Nestic, and V. Miskovic-Stankovic, "A Mixture of Dicyclohexylamine and Oleylamine as Corrosion Inhibitor for Mild Steel in NaCl Solution Saturated with CO<sub>2</sub> Under Both Continual Immersion and Top of the Line Corrosion," *J. Serbian Chem. Soc.*, vol. 77, no. 8, pp. 1047–1061, 2012.
- S. Nestic, J. Postlethwaite, and S. Olsen, "An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions," *CORROSION*, pp. 280–294, 2007.
- F. Vitse, K. Alam, and Y. Gunaltun, "Semi-Empirical Model for Prediction of the Top-Of-the-Line Corrosion Risk," *NACE International*, Paper No: 02245, 2002.