

UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

COMPREHENSIVE ANALYSIS OF CORROSION IN OFFSHORE SYSTEMS IN GAS CONDENSATE PRODUCTION

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímica

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DEDICATION

To my family, my parents Mónica and Jairo, my brothers Jairo and Byron Paul and to my grandmother Fabiola for always supporting me in every step I take in my life and for their unconditional love.

All I am is thanks to you, you are my reason for life.

Karen Gissela Jaramillo Clerque

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Karen Gissela Jaramillo Clerque

RESUMEN

La corrosión en tuberías de gas natural se ha identificado como uno de los riesgos más importantes de la industria. Por tanto, un análisis de riesgos es uno de los factores críticos para el éxito de proyectos dentro de la industria. El objetivo de esta investigación se basa en realizar un análisis de riesgo comprensivo de las condiciones operacionales, las alternativas de control / mitigación de procesos de corrosión en los sistemas costa afuera de la producción de gas condensado. La metodología utilizada es basada en la aplicación del ciclo de vida de la gestión de riesgos aplicada dos casos de estudio como son: el uso de inhibidores para mitigar la corrosión interna en tuberías de gas natural; y estrategias de tratamiento de la formación de corrosión y polvo negro en tuberías de gas natural en las costas de África. El enfoque de este estudio es el uso de la gestión de riesgo, de manera que los datos para sus cálculos fueron estimados.

Para la evaluación de los riesgos se usaron los dos tipos de análisis como es el cualitativo basado en estimar puntuaciones de probabilidad e impacto para cada riesgo en diagramas (matriz de riesgo y Bow Tie). Para el análisis cuantitativo se usó la simulación probabilística de Montecarlo con una licencia de prueba del programa @RISK, para evaluar los costos de los riesgos y analizar cómo afecta su probabilidad e impacto al presupuesto general. Se encontró para los dos casos de estudio, una probabilidad menor del 10% para la cubrir los gastos de los riesgos con el presupuesto estimado. Además, se identificó los riesgos potenciales con probabilidad e impacto más significativos y que son los principales a controlar o mitigar. Esta investigación mostró el mecanismo de incorporar la gestión de riesgos por la corrosión en un proyecto, y los hallazgos permiten una mejor comprensión para desarrollar estrategias apropiadas de mitigación de riesgos.

Palabras clave: corrosión interna, gestión de riesgo, sistema offshore, gas natural, tubería, control y mitigación.

ABSTRACT

Corrosion in natural gas piping has been identified as one of the most significant hazards in the industry. Therefore, a sound risk analysis is one of the critical factors for the success of projects within the industry. The objective of this research is based on carrying out a comprehensive risk analysis of the operational conditions, the alternatives for the control/mitigation of corrosion processes in the offshore gas condensate production systems. The methodology used is based on the application of the risk management life cycle for the two case studies such as the use of inhibitors to mitigate internal corrosion in natural gas pipelines, and strategies for treating the formation of corrosion and black dust in natural gas pipelines off the Coast of Africa. The focus of this study is the use of risk management, in such a way that the data for its calculations were estimated.

For the evaluation of the risks, the two types of analysis were used, such as the qualitative one based on estimating probability and impact scores for each risk in diagrams (risk matrix and Bow Tie). For the quantitative analysis, the Monte Carlo probabilistic simulation was used with a trial license of the @RISK program, to evaluate the costs of risks and analyze how their probability and impact affect the overall budget. For the two case studies, a probability of less than 10% was found to cover the expenses of the risks with the estimated budget. In addition, the potential risks with the most significant probability and impact were identified and which are the main ones to be controlled or mitigated. This research showed the mechanism for incorporating corrosion risk management into a project, and the results allow a better understanding to develop risk mitigation strategies.

Keywords: internal corrosion, risk management, offshore system, natural gas, pipeline, control, and mitigation.

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CHAPTER I: PURPOSE AND SIGNIFICANCE OF THE STUDY

1. Introduction

The hydrocarbon industry has proven that pipelines are the most economical means of large-scale land and sea transmission of natural gas and oil. Its transmission is a continuous process and it has demonstrated the ability to adapt to different environments, including remote areas and harsh environments¹. Pipelines in offshore systems are the only efficient means of transmission fluids. These types of pipes are dimensioned to withstand high pressures, low temperatures, and conditions different from those found in a normal installation¹. At present, the problem that most affects industrial equipment, particularly pipelines, is corrosion. Corrosion is a natural phenomenon that appears as the deterioration of a material that is generally metal and, it is the result of a chemical or electrochemical reaction with its environment. Corrosion can cause dangerous and costly damage¹.

In the transmission of fluids by this type of pipeline, the presence of factors that contribute to internal corrosion, which can affect both design and operation, must be considered. The causes of incidents in pipelines for the year 2020 were determined, of which 15% are own to corrosion failures and 38% to equipment failures². Therefore, corrosion can be mitigated, prevented, and controlled to reduce or eliminate its impact on public safety, the economy and the environment². In general, the lack of control in this problem affects the profitability of production systems, as industries are forced to implement expensive repair methods. Corrosion has for many years been one of the greatest challenges for flow assurance in both, onshore and offshore production lines. Mechanical failures that occur in the production system because of these problems can lead to lengthy shutdowns for major repairs. In severe cases, the deterioration of pipes, production lines, and other elements of the system causes the leakage of hydrocarbons and other fluids that put the closest environment at risk². To ensure the uninterrupted fluid flow of natural gas in offshore systems, pipeline operators, engineers, and designers must be aware of the corrosion that can occur in pipelines and implement operational condition analysis, control alternatives, and mitigation. This study provides risk analysis of operating

conditions, alternatives to control and mitigate the corrosion process in offshore systems in the production of gas condensates.

This work is organized as follows: first, a bibliographic compilation is presented on the main problems in offshore gas condensate systems such as flow patterns, design problems, and formation of hydrocarbon components. Second, a bibliographic compilation of corrosion is developed in which internal degradation systems and internal corrosion mechanisms are identified. Third, the technologies for preventive measures and mitigation of internal corrosion are analyzed and identified, focusing the study on inhibitors. Fourth, the study methodology that is based on risk management is identified for application in the established cases of study. Finally, the case of study 1, focused on the use of inhibitors to mitigate internal corrosion and black powder treatment strategies in gas pipelines of the Coast of Africa. For which qualitative evaluations such as the risk matrix, Bow Tie diagram, and quantitative evaluation are carried out using Monte Carlo probabilistic simulation.

1.1.Problem Approach

The natural gas and oil industry continually seeks to reduce costs that have to do with pipeline failures own to corrosion, which cause structural and operational damage affecting the normal operation of a certain project. When it comes to controlling the corrosion failures present, it represents an attraction for the industry because it saves costs and time in the execution of a project.

That is why this work analyzes the corrosion risk management present in offshore natural gas systems, to verify that industries can reduce costs/times and ensure the well-being of their workers. Preventing, mitigating and controlling events with potential risks.

1.2.Objectives

1.2.1. General.

To analyze the operational conditions, control alternatives, and mitigation of the corrosion process in offshore systems in gas condensate production.

1.2.2. Specifics.

- ✓ To identify the main problems in offshore gas condensate systems such a flow patterns, design problems and the formation of hydrocarbon components.
- \checkmark To identify internal degradation systems and corrosion mechanisms.
- ✓ To study internal corrosion in natural gas pipes and identify their types of corrosion and the formation of black powder as a result of corroded systems.
- ✓ To identify the technologies for preventive measures and mitigation of internal corrosion. Focusing the study on inhibitors.
- ✓ To develop tools for decision-making through risk management for the study cases.
- ✓ To analyze the established case studies to develop risk management techniques, through qualitative evaluations such as the risk matrix, Bow Tie diagram, and quantitative evaluation through Monte Carlo probabilistic simulation.

CHAPTER II: BACKGROUND INFORMATION

2.1. Natural Gas Condensate

Natural gas condensates are found in deep tanks that predominantly contain gas but produce significant amounts of liquids when the gas reaches the surface. Liquids vaporize in the gas phase and condense on the surface own to the inability of the gas to retain those liquids when it reaches a surface pressure and a temperature below the pressure and temperature of the reservoir. Figure 1 represents a typical gas condensate phase diagram. Both the tank temperature and the separator conditions are within the two-phase envelope. Gas condensate reservoirs are either under-saturated (the initial reservoir pressure is higher than the dew point pressure) or saturated (the initial reservoir pressure equals the dew point pressure). The tank temperature is higher than the critical temperature. Above the dew point pressure, the liquid gas condensate has a constant composition³.

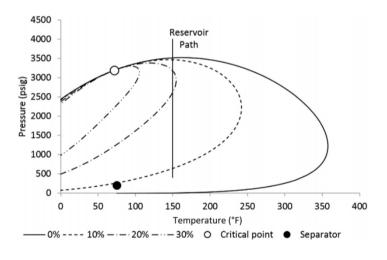


Figure 1. Typical phase diagram for gas condensate fluid³

2.1.1. Use importance of Natural Gas

Petrochemical processing plants through cracking processes allow the breaking of hydrocarbons, using hot steam to break the carbon-carbon bonds and use them for further processing. Natural gas liquids are versatile products that are used in various economic sectors such as residential, commercial, manufacturing, agriculture, transportation, and electricity generation. Table 1 below lists the chemical composition, uses, products, and main sectors of natural gas use⁴.

NGL	Chemical formula	Uses	Products	Sectors
Ethane	C₂H ₆	Power generation and petrochemical feedstock for ethylene production.	Antifreeze Plastics Detergents	Manufacturing Power generation
Propane	C3H8	Petrochemical feedstock and fuel for heating, cooking, drying and transportation.	Fuel (Cooking, heating, drying, etc.) Plastics	Manufacturing, agriculture, residential, commercial, and transportation. Power generation.
Butanes: normal butane and isobutane	C_4H_{10}	Petrochemical and petroleum refinery feedstock and motor gasoline blending	Motor gasoline Plastics Synthetic rubber Lighter fuel	Manufacturing and transportation
Natural gasoline (pentanes plus)	Mix of C_5H_{12} and heavier	Diluent for heavy crude oil, petrochemical feedstock and additive to motor gasoline.	Motor gasoline Solvents Ethanol denaturant	Manufacturing and transportation

Table 1. Natural gas liquid, uses, products and consumers⁴.

How main sectors use natural gas:

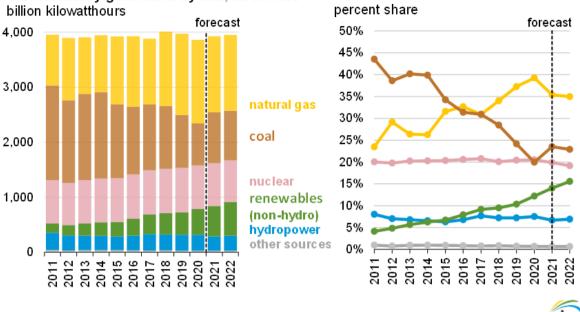
The manufacturing sector uses natural gas as a fuel for heating processes, in combined heat and power systems, as a raw material (feedstock) to produce chemicals, fertilizers and hydrogen, and as a lease and plant fuel⁵.

The residential sector uses natural gas to heat buildings and water, cook, and dry clothes⁶.

The commercial sector uses natural gas to heat buildings and water, operate refrigeration and cooling equipment, cook, dry clothes, and provide outdoor lighting. Some consumers in the commercial sector also use natural gas as a fuel in combined heat and power systems⁷.

The transportation sector uses natural gas as fuel to operate compressors that move natural gas through pipelines and as vehicle fuel in the form of compressed natural gas and liquefied natural gas. Almost all vehicles that use natural gas as a fuel are found in government and private vehicle fleets⁸.

The electric power sector uses natural gas to generate electricity and produce useful thermal production. (The manufacturing and commercial sectors also use natural gas to generate electricity, and they use almost all of this electricity). The important use of natural gas has a fundamental role in the transition to a lower carbon intensity economy, becoming a new natural alternative to carbon. The monetization of natural gas in the electricity sector is one of the current trends for the decarbonization of energy. The Energy Information Administration (EIA) expects the proportion of electrical energy generated from natural gas in the United States to average 35% in both 2021 and 2022, up from 39% in 2020. The projected share of natural gas as a generation fuel declines in response to an 85% increase in the average price of natural gas, the projected share of generation from an average of \$ 2.39 / MMBtu in 2020 to 24% this year and 23% the next. However, the percentage of natural gas is higher since 2017, stopping that of coal, which has remained with low percent, Figure 2⁹.



U.S. electricity generation by fuel, all sectors

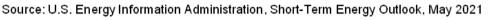


Figure 2. U.S electricity generation by fuel, all sectors ⁹

2.2. Offshore Systems

An offshore platform is a large structure used to house workers and machinery essential to drill and/or produce natural resources (i.e. oil, natural gas, minerals, etc.) through tunnels and wells¹⁰. Depending on the circumstances, the platform can be attached to the ocean floor, an artificial island¹¹, or float¹². The location is commonly on the continental shelf. The new trend is deeper water drilling and production. Primary goals are used for a variety of applications such as drilling, preparing water or gas for injection into the reservoir, oil and gas processing, cleaning produced water for removal at sea, and housing facilities¹³. The offshore platforms are self-sufficient in terms of energy and water needs, have electricity generation, water desalination plants, and all the necessary equipment to process oil and gas so that it can be delivered directly on land by pipeline to a Floating Storage Unit and/or tanker truck¹⁴. *Infrastructure:* main elements in the oil/gas production process for gas drying, gas compressors, water injection pumps, oil/gas export measurement, and mainline oil pumps¹⁴.

Offshore pipelines are predominantly made of carbon steel. The same installation methods and restrictions apply to all steel pipes. Steel pipes are invariably coated against

corrosion with a fiber bonded epoxy 4 inches thick. Concrete weight coating is often used to provide stability to the bottom of the pipe¹⁵.

The main problems in offshore gas production systems are in the design, flow assurance, presence of hydrocarbon components, and corrosion. Which are detailed below.

2.2.1. Design Issues

In the design of subsea production systems, the high and low pressures and temperatures in which the pipes can be considered. Its design uses a system-wide modeling approach to define hardware requirements and operational strategies. To optimize system design, software models are used for each component to understand the tradeoffs that result from balancing steady-state and transient operations with flow assurance management: steadystate hydraulic and thermal conditions, transient operations, heating, cooling, purging, hot oil heating, flow assurance management and remediation, hydrate prediction and inhibition, wax deposition, asphaltene deposition, scale prediction, internal corrosion, erosion, and corrosion¹⁶.

Methods of Pipeline Installation

The method of pipeline installation depends on a combination of factors such as the water depth, diameter, and the weight of the pipeline; the installation methods are divided into the following categories¹⁵.

S-Lay: In this shallow water installation method, the pipeline is configured in the shape of the letter "S" where the pipeline bends in a hogging mode as it exits the lay barge and in a sagging mode as it touches the seabed.

J-Lay: Useful to deep-water pipeline installation, the pipeline is assembled in a near-vertical plane which allows it to exit the vessel with little bending curvatures, thus eliminating the overbend that characterizes the S-lay configuration.

Reeled: In this method of installation, the pipe is spooled on a reel that is installed on the pipelay vessel. At the offshore installation site, the pipe is "unspooled" and deployed to the seabed. This method of installation is faster than both S-lay and J-lay since the pipe does not need to be welded on board the vessel.

Towing: Short pipelines or pipe bundles can be fabricated on land and launched into the water to be towed to the installation site using tugs¹⁵.

Diameter Selection

The selection of diameter is a process where the initial capital expenditure (capex) and operational expenditure (opex) are evaluated leading to an optimized design by minimizing total cost through the life of the project. The main criterion for the selection of pipeline diameter is the ability to carry fluids at the design flow rates, within the allowable pressure¹⁵.

Classification of materials

The selection of materials used in offshore production and structure depends on parameters such as material type, strength, fracture control, corrosion resistance, chemistry, microstructure, weldability, etc.

The most used are presented below:

- 1. Structural steels: These are carbon and low-alloy steels that are used for structures and pipes.
- 2. Production Equipment Steel: These are carbon, low-alloy, and alloyed steels used for pipes, fittings, and production/process equipment.
- Corrosion-resistant alloys: these materials are used for the production and processing of equipment or pipes subjected to corrosive environments containing CO₂ and H₂S. (For example, stainless steels, nickel-based alloys, cobalt-based alloys, nickel-copper alloys, and titanium alloys)
- 4. Nonmetals These are elastomers, coatings, and plastics¹⁵.

2.2.2. Flow assurance

Flow assurance is an important design consideration for subsea wells. One of the most important design problems for deepwater offshore pipelines is the operational hazards associated with the transmission of multiphase fluids¹⁷. Wax, hydrates, and asphaltenes are the top three threats to flow assurance. Hydrate blockages are more common in gas and gas condensate systems.

In flow assurance, an important aspect is the flow patterns in gas production from the reservoir to the processing facility. The flow is transmitted through different channels from the extraction zone in the reservoir to the bottom of the well, then it is transmitted to the wellhead and finally to flow lines connected to the main platform. Transmission of fluid from the reservoir to the bottom of the well, in this section the operations are designed to work under conditions of pressures above the critical pressures of the reservoir, called bubble point and dew point pressures. In gas reservoirs, when the reservoir pressure drops below the critical dew point, the condensates will fall into the reservoir, reducing flow paths and production rates, leaving behind hydrocarbons that are not producible. Transmission of fluid from the bottom of the well to the wellhead, and the tree, the trees in the mud line are called wet trees and the trees above the waterline are called dry trees. Wellheads can be on the seabed or located on the platform. As a flow line, pipes can be insulated, buried, heated, or not insulated based on multiphase flow transmission and the phase equilibrium of fluids along the good path. Flow lines are sized to alleviate operational difficulties over the life of the well and fluid chemistry, well pressures and conditions will determine whether chemical injection is required to mitigate the appearance of hydrates, asphaltenes, paraffin, scale, or corrosion¹⁸. Export Pipeline Flow on a production platform, hydrocarbon fluids are separated into gas, oil, and water phases to meet pipeline export specifications on vapor pressure, water vapor, heating value, and other properties, and regulatory conditions on water discharge¹⁸.

One of the main challenges is the administration of chemical inhibitors in conditions of high pressures and depths. So it is administered continuously through metering pumps placed at different points along the pipeline. Operations must also extend well below the seafloor, where the back pressure can measure five to seven times as much as the pressure on the seafloor. To control flow assurance, technologies must allow safe fluid transmission. The field of study covers the hydraulic design of the piping system (multiphase flow) and all the phenomena that can compromise the efficiency and safety of the system (plugging, flow instability, erosion/corrosion)¹⁸.

2.2.3. Hydrocarbon components and corrosion

Waxes are complex mixtures of solid hydrocarbons, which freeze when the temperature is lower than the cloud point of crude oil. Without control, wax deposits can completely

block the flow path. Most operators consider scraping and the use of inhibitors to reduce the deposition rate as a preventive measure¹⁹.

Hydrates formed at low temperatures and high pressures occur when a gas molecule gets attached inside a cage of water molecules linked by hydrogen. Hydrates are the major problem for deepwater flow line designs. Hydrate blockages are more common in gas systems. Hydrates are mitigated by heat retention, dead oil displacement for shutdowns, and hydrate inhibitors such as methanol, glycols, or sodium chloride²⁰.

Asphaltenes are solid, dark-colored, friable, infusible hydrocarbons sometimes referred to as petroleum "cholesterol". Asphaltenes originate from complex molecules found in plants and animals that have only partially decomposed over geologic time. Asphaltenes are common in viscous heavy crude and are generally controlled by inhibitors²¹.

Corrosion in gas pipelines is the main problem because it is in an underwater offshore system, which contributes to the creation of a corrosive environment by water, salts, and pollutants. Natural gas from wells contains amounts of pollutants such as water, carbon dioxide, and hydrogen sulfide; which increases the probability of corrosion in pipes.

2.3. Corrosion Mechanisms

The main cause of oil and gas pipeline failures is corrosion degradation or corrosioninduced cracking. With the significant risk of corrosion damage to pipeline integrity on the one hand and its complexity on the other, a great deal of effort has gone into accurately modeling corrosion progress. Corrosion control strategies have been established and involve two facets²². The chemical or electrochemical reaction between a metal or alloy material is corrosion. An unfavorable environment can contribute to the deterioration of the metal and its properties. Depending on the characteristics of the environment, they are classified into chemical or electrochemical corrosive processes. Chemical corrosion processes occur when metal reacts with a non-electrolyte, while electrochemical corrosion processes occur when metal dissolves in an electrolyte, forming metal cations, involving the transfer of electricity through the metal interface or the environment²³. The fight against corrosion constitutes a significant source of expenses for the oil industry, the pipelines are the main means of transmission and the most affected by corrosion. Carbon steel pipeline material and low alloy steel are the friction materials for most metal pipes that are prone to corrosion. Material properties and environmental conditions determine the rate and type of reaction. Internal and external corrosion will be influenced by the geometry of the pipe, the environment of the pipe and corrosion control, and mitigation processes. According to its statistical data, only for 2020, indicate that significant failures in pipelines and equipment were 15% and 38%, respectively. These failures occur own to corrosion, as shown in Figure 3 below²⁴.

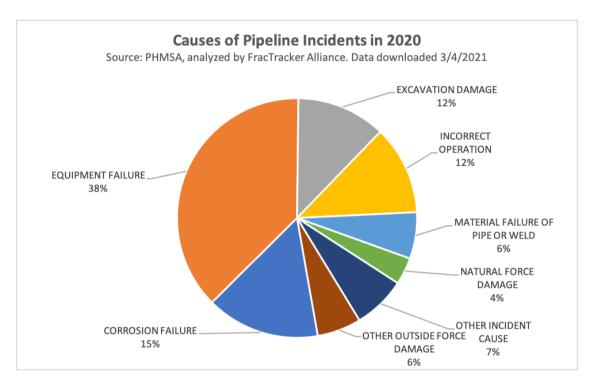


Figure 3. Causes of Pipeline Incidents in 2020. Source: PHMSA.²

2.3.1. External corrosion

External corrosion in offshore pipelines, although it is not the central theme of this study, it is important to contrast the problem of corrosion. Considering that the pipelines are buried and exposed to saltwater corrosion, and beign this type of corrosion a complex issue in comparison with the pipelines on land²⁵. Some ways to minimize external corrosion in offshore pipelines are reversal and cathodic protection.

Coating

The external coatings on the pipes are used to protect them from corrosion, the coating is placed along the pipe. There is a possibility that the coating could be damaged by handling the pipeline, either during shipping or during installation. There are two ways of singlelayer lining for pipes with a static and laterally stable condition found in soils such as clay or sand. The other way is the multilayer coating generally used in offshore systems, adding different layers generates weight to help the pipe remain laterally stable on the seabed, provide insulation, prevent the precipitation of microorganisms and prevent early wear of the saline environment. Desirable coatings for the deep-water pipeline are as follows: resistance to seawater, resistance to seawater absorption, resistance to chemicals in seawater, resistance to cathodic detachment, adhesion to the pipe surface, flexibility, resistance to impact and abrasion, weather resistance²⁶.

Cathodic protection

Another mitigation process is cathodic protection (CP) provided by sacrificial anodes to prevent corrosion of damaged areas. The main CP methods are galvanic anodes and impressed current systems. In offshore pipelines, the galvanic anode system is generally used. This is because the surface of the steel pipe consists of randomly distributed cathodic and anodic areas, and seawater is the electrolyte that completes the galvanic cell. This causes electrons to flow from one point to another resulting in corrosion. Then the cathodic protection connects a metal with higher potential to steel pipe, it is possible to create an electrochemical cell in which the metal with the lowest potential becomes a cathode and is protected. CP uses another metal that will lose electrons in preference to the steel. The main metals used as sacrificial anodes are aluminum and zinc alloys^{27, 26}.

2.3.2. Internal corrosion

Metal tubes are made primarily of carbon and low-alloy steel and are inherently prone to corroding from electrochemical reactions with the environment. The type and rate of corrosion are highly dependent on material properties and environmental conditions. The specific geometry of the pipe and the electrolytic insulation between the inner wall means that corrosion can $occur^{28}$.

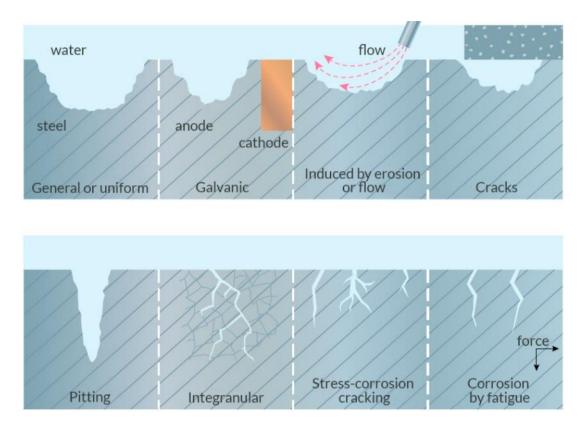


Figure 4. Corrosion generally leaves a visible rubric²⁹

Corrosion generally leaves a visible rubric that is characteristic of the agent and the mechanism that produced it, although they do not constitute an exhaustive list, corrosion usually corresponds to one or more of the following classes (Figure 4):

- *General or uniform*, it is observed in the roughness of the surface since the thickness of the metal is reduced as it corrodes. This type of corrosion is linked to surface exposure.
- *Located* in certain places in the pipeline, it is considered one of the most dangerous own to its potential for rapid development and unpredictable nature. It is subdivided into pitting corrosion, cracks or fissures, and corrosion under deposit.
- *Pitting*, generates holes in the metallic components, by cracks or fissures. It occurs in restricted areas where the metal in the crack appears anodic and the rest of the metal acts as a cathode.
- *Galvanic*, occurs in the presence of two metals in which the metal that has the least resistance to corrosion acts as an anode and the other as a cathode.
- *Induced by flow*, it takes place when the transmitted flow accelerates the corrosion, this type of corrosion can manifest itself as erosion in which the fluids

remove the protection film and as cavitation produced by the implosion of the bubbles, which take place when the pressure changes rapidly in circulating fluids.

- *Intergranular corrosion* is the result of corrosive attacks produced as cracks or fissures in the intergranular limits of the metal. These limits can become anodic concerning the surrounding cathodic surface.
- *Environmental cracking* occurs when corrosion coincides with tensile stress and can manifest itself as hydrogen embrittlement, stress corrosion cracking, or sulfur stress corrosion cracking²⁹.

Internal corrosion in pipelines is a major problem in the natural gas industry. This type of corrosion will be mainly influenced by the composition of the transmitted fluid, metallic tubes, mostly made of carbon steel and low-alloy steel, are inherently prone to be corroded by electrochemical reactions with the environment²⁸. The type and rate of corrosion are highly dependent on material properties and environmental conditions. The specific geometry of the pipe and the electrolytic insulation between the inner wall means that corrosion can occur. The severe impact is on pipeline operations, leading to unscheduled loss of production, maintenance, or downtime own to repair, and even catastrophic failures that affect operator's health, the environment, and safety²⁸.

2.3.2.1. Types of internal corrosion in natural gas pipes

The corrosion rate is measured in mils of penetration per year (mpy) of carbon steel shows pronounced differences when the steel is exposed to varying concentrations of O_2 , CO_2 , and H_2S . With a concentration of 5ppm. O_2 is almost three times more corrosive than H_2S and 30% more corrosive than CO_2 . As is known, corrosion occurs when a metallic material, oxygen, and a corrosive environment are in contact, an electrochemical effect occurs, so as seen in Figure 5, O_2 will be in the first place because of the general corrosion process. Second, CO_2 is found the same way and it is own to the presence of oxygen which generates a corrosive environment and finally H_2S which contributes to corrosion but at a lower corrosion rate compared to the other two compounds.

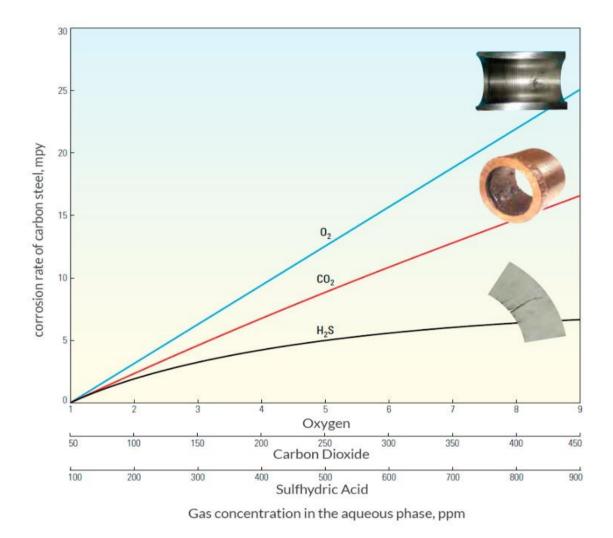


Figure 5. Corrosion rate vs gas concentration in the aqueous phase²⁹

Fighting corrosion requires an understanding of the main elements that cause and the quality of this phenomenon. The most common types of internal corrosion in natural gas pipelines are listed below:

Corrosion by oxygen or O₂ corrosion

Corrosion related to oxygen in oil and gas production environments is often much more aggressive than corrosion caused by CO_2 or H_2S . Corrosion by oxygen is directly proportional to the concentration of dissolved gas. If CO_2 or H_2S is present, the corrosion rate can increase significantly. Oxygen can induce corrosion at all production sites. Inhibition of corrosion by oxygen is difficult, and efforts to reduce corrosion in water treatment and production facilities, in general, have been directed at the exclusion of

oxygen with the use of oxygen scavengers, such as ammonium bisulfite [NH₄HSO₃], sodium sulfite [Na₂SO₃] and sodium bisulfite [NaHSO₃]. Vacuum buffers can also be used to control corrosive effects.

Sweet corrosion or CO₂ corrosion

 CO_2 corrosion can result in high corrosion rates. CO_2 as an acid gas is present in gas tanks, own to its solubility in water it causes corrosive environments for carbon steel. In the case of mild steel, the reaction of this type of corrosion, it can be written that CO_2 as iron (Fe) in the steel oxidizes to ferrous ions (Fe^{+2}) in the presence of CO_2 and water (H₂O), the Hydrogen gas (H₂) develops own to the reduction of hydrogen ions present in water, as presented by the following reaction:

$$Fe + CO_2 + H_2O \rightarrow Fe^{+2} + CO_3^{-2} + H_2$$
 (1)

The cost of pipeline failure own to internal CO_2 corrosion can be enormous considering pipeline repair or replacement costs, loss of production, and environmental impact. During the transmission of natural gas in pipelines, water vapor condenses as the gas cools, CO_2 is dissolved in water, and pH decreases to 4. Sometimes liquid water as a thin layer remains on the inner surface of the upper part of the pipeline, and severe localized corrosion occurs. Usually, this corrosion type occurs during wavy-stratified flow at a velocity of less than 3 m/s, and two phases exist: liquid and gas containing water vapor and CO_2 and there are no materials (e.g., corrosion inhibitors) that can protect the pipeline's upper inner surface²⁴.

Sour Corrosion or H₂S Corrosion.

The H₂S corrosion occurs in an aqueous medium, as observed in reactions (2) to (4) wherein the gas phase can dissolve, as a weak acid, H₂S is only partially dissociated in the aqueous phase, forming a chemical equilibrium in the system. Influencing the corrosion process both its electrochemical tendencies and its contribution to the formation of a layer of localized corrosion and corrosion product³⁰.

$$H_2 S_{(g)} \leftrightarrow H_2 S_{(aq)} \quad (2)$$

$$H_2 S_{(aq)} \leftrightarrow HS^-_{(aq)} + H^+_{(aq)} \quad (3)$$

$$HS^-_{(aq)} \leftrightarrow S^{2-}_{(aq)} + H^+_{(aq)} \quad (4)$$

Sulfihidric acid is found in the fluids produced, it becomes corrosive in the presence of water. The effect of internal corrosion can affect the internal parts of the well and the collecting networks. It is considered acidic if the gas produced contains more than 5.7 mg of H₂S. The product of reaction (4), the anode S^{2-} is free to bind with iron to form different variants of iron sulfide [Fe_xS]. Corrosion cells formed during acid corrosion can form environmental cracking of carbon steel pipes caused by the generation of atomic hydrogen as a by-product of the corrosion reaction. The diffusion of atomic hydrogen in the steel causes different types of damage to the steel. Atomic hydrogen is small in size to migrate into the steel structure. By recombining atomic hydrogen within the metal, hydrogen gas is produced as a potentially damaging agent. As atomic hydrogen diffuses through solid steel at rates of several cubic centimeters per square centimeter per day²⁸. This high concentration of atomic hydrogen can affect steel in several ways:

Hydrogen-induced cracking (HIC), this cracking is without stress is a stepwise cracking caused by hydrogen diffusion into the steel and entrapment in voids and inclusions³¹.

Sulfide Stress Cracking (SSC), this cracking is with stress, usually occurs in welds because it needs high stress and high yield strength/hardness. This type of cracking can be mitigated with residual stress techniques to release stress³².

Stress-Oriented hydrogen induced cracking (SOHIC), this cracking is with stress, is staggered small crack formed nearly perpendicular to the principal stress³³.

Microbial Corrosion (MIC).

This type of corrosion is considered a major threat of internal corrosion in oil and produced or injected water pipes. The parameters that influence this type of corrosion are sulfate, nutrients, type of bacteria, pH, flow rate, salinity, and temperature. In the pipelines, they are affected as pockets of water in the lower sections of the pipeline. There are two mechanisms for MIC corrosion: the classic and the modern³⁴. The classical mechanism considers that microbial activity generates chemical reactions that accelerate the corrosion process. The main microbial species present are sulfate reducing bacteria (SRB), acid producing bacteria (APB), iron reducing bacteria (IRB), and iron oxidizing bacteria (IOB)³⁵. On the other hand, the modern mechanism considers that it begins with the formation of a biofilm where the oxygen content decreases because of bacterial activity. Resulting in an isolated area for bacterial growth and corrosion. MIC corrosion generally occurs in stagnant flows with water retention, a stratified flow regime providing

conditions prone to deposition and bacterial growth that consequently generates pits in the bottom of the pipe with a localized pattern²⁴.

Top of Line Corrosion (TOLC).

Corrosion in the upper part of the line is caused by the condensation of water on the upper surface of the interior of the pipe, it occurs mainly in wet gas pipes with a sweet hydrocarbon that contains 500-3000 ppm of organic acids (formic acid, propionic acid, and anodic acid) in a stratified flow regime²⁴. In addition, a potential location for corrosion is placed where the temperature drops below the dew point (loss of thermal insulation and concrete lining, river section, and submerged, buried, or above ground pipeline exposed to low temperature). This type of corrosion occurs mainly in stratified flow regimes is shown as a chemical pattern of TOLC in a typical multiphase pipe³⁶.

Under Deposit Corrosion.

Under-deposit corrosion (UDC) is when localized corrosion in the form of pits or cracks can develop under or around components deposited in horizontal pipes, where the flow rate is not sufficient to agitate the deposits and disperse them in solution. One of the possible deposits is organic, which can precipitate from crude oil (eg asphalt, wax) or form on the surface because to microbiological activity (eg biofilms). No theory indicates its appearance but it is believed that it has a close relationship and similarity with other corrosion mechanisms such as H₂S, CO₂ corrosion, MIC, etc. The deposits generated by sour gas pipelines are the products of iron sulfide corrosion, considering that the risk of UDC is low if an effective corrosion inhibitor is applied that controls the level of iron sulfide corrosion products³⁷.

Preferential Weld Corrosion (PWC).

Preferential Weld Corrosion is selective corrosion of the weld metal and the heat affected zone (HAZ) that are more active than the base metal of the pipe to be corroded. It is one of the most challenging threats to the integrity of the pipeline resulting in premature failure. Its corrosion rate prediction, location, and effectiveness are impossible to calculate because of the complexity of the phenomena involved. PWC occurs in welding areas that are exposed to corrosive environments, high temperatures, and high flow rates. It generally occurs when there are high flow rates in the pipes and the change in flow direction affects areas of seam welds in elbows, reducers, or expansors³⁸.

Hygroscopic corrosion

In offshore pipeline systems, draining seawater can leave hygroscopic salt residue on the pipe walls, this salt residue can accumulate water from a gas stream³⁹. Hygroscopic salts and their potential to lead to corrosion have been examined in atmospheric corrosion studies where the deposition of salt aerosols on metals can lead to corrosion in oxic conditions²⁴. The corrosive effect of hygroscopic NaCl particles on mild steel in atmospheric environments was investigated by Schindelholz, et al ³⁹. NaCl was deposited on mild steel samples and subjected to air with relative humidity ranging from 1.5% to 90% relative humidity for up to 300 days, which shows that water adsorbed on NaCl particles and steel can initiate corrosion at relative humidities as low as 33%. Figure 6 shows the optical images of the surfaces exposed for 14 days to gas with 15 psig H₂S and 57 psig CO₂. General and localized corrosion rates were measured for NaCl⁴⁰.

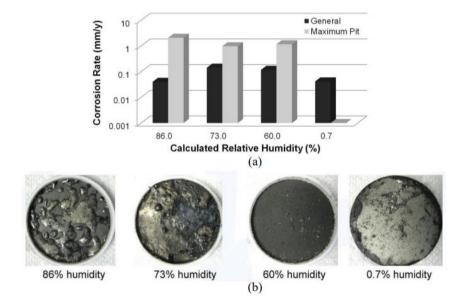


Figure 6. (a) Corrosion rates and (b) optical images taken after extraction of specimens with NaCl deposits exposed to CO₂/H₂S gas mixtures with the indicated relative humidity ⁴⁰.

2.3.2.2. Corrosion depositions / Black Powder

The "black powder" is a material that forms in the gas pipes, causing wear and obstruction of the pipes, reducing the efficiency since it causes flow losses. The appearance of this powder is of a fine powder sometimes mistaken as smoke, it can be wet or dry. Its composition from chemical analysis concludes that it has various forms of iron sulfide or iron oxide, it can be chemically mixed with any pollutant such as water, liquid hydrocarbons, chlorides, salts, dirt, or sand. Iron sulfides and oxides are created within the natural gas and other similar wells and pipelines⁴¹.

Black Powder formation is mainly of iron carbonates, iron sulfides, and iron oxides that are formed by an internal corrosion reaction of acid corrosive gases (Eg., carbon dioxide and hydrogen sulfide) with the internal wall of the pipe. This reaction occurs in a wet environment as these gases are benign in a dry environment. The chemical reactions form iron sulfides, iron carbonates (siderite), and iron oxides. H_2S and CO_2 are naturally occurring constituents of natural gas⁴².

H₂S in gas reacts with condensed water and pipe steel by the following reaction equations:

$$H_2 O + H_2 S \rightarrow H_3 O^{+3} + HS^-$$
(5)
$$HS^- + Fe \rightarrow FeS + H_2$$
(6)

 CO_2 in natural gas reacts with condensed water to produce siderite (FeCO₃) in the following equation:

$$H_2O + CO_2 \rightarrow H_2CO_3 \tag{7}$$
$$H_2CO_3 + Fe \rightarrow FeCO_3 + H_2 \tag{8}$$

Complete mitigation of black powder is the removal of H_2S and CO_2 , but it is generally known to be a highly expensive treatment⁴². There are chemical or physical methods that companies take as preventive measures to minimize corrosion and the formation of unwanted products. For correct mitigation, prevention must be done from the early design stages, either in the medium or long term, as presented in Figure 7, below⁴¹.

Mitigation Plans	of Black Powder
Short Term	Medium and long term
Corrosion prevention methods	Water treatment from sources
Injection of inhibitors	Injection of monoethylene Glycol (MEG)

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2.4.Technological solutions for preventive measures and mitigation of internal corrosion.

The problem of internal corrosion entails a necessary implementation of mitigation and prevention measures. The most commonly used for internal corrosion in offshore natural gas pipelines are the following:

- Dehydrates
- Coatings
- Buffering
- Cleaning pigs
- Preventive measures for weld corrosion.
- Preventive measures for microbial corrosion (MIC)
- Injection of mono ethylene glycol (MEG)
- Inhibitors

All these technologies can be combined to improve the control results. Table 2, shows which technologies can be used with each other and their priority levels, respectively. Where it can be seen that the injection of inhibitors can be combined with more technologies, so it will be the most studied technology in this work.

Table 2. Priority levels of preventive and mitigation measures for internal corrosion

PRIORITY COLOR SCALE	1°	2°	3°	4°	5°	6°		
PREVENTIVE MEASURES AND MITIGATION	Dehydration	Coatings	Buffering	Cleaning pigs	Weld corrosion mitigation	(MIC) mitigation	(MEG)	Inhibitors
Dehydration								
Coatings								
Buffering								
Cleaning pigs								
Weld corrosion mitigation								
Microbial corrosion (MIC) mitigation								
Injection of mono ethylene glycol (MEG)								
Inhibitors								

Natural gas from wells contains amounts of pollutants such as water, carbon dioxide, and hydrogen sulfide. So if the water condenses, it can react with carbon dioxide or hydrogen sulfide to form an acid that could build up at a low point and cause internal corrosion. So there are preventive/mitigating measures for internal corrosion, which are presented below.

2.4.1. Dehydration

Gas dehydration is an important process in offshore gas processing, it involves the removal of water vapor from the gas stream. It is considered one of the most applied measures to mitigate the risk of condensed water that leads to flow capacity problems, hydration, formation problems, and/or corrosion. The main reasons for removing water vapor from natural gas are the following⁴³:

- Liquid water and natural gas can form hydrates that plug equipment and pipes.
- Liquid water in natural gas is corrosive mainly if it contains CO₂ and H₂S.
- Water vapor in natural gas can condense in the lines causing clogging.
- To optimize the operation of compressors
- To meet the quality required for transmission in pipes and commercialization.

This ensures smooth operation in downstream systems, which can be subsequent liquefaction or another processing package, of the gas pipe⁴³.

2.4.1.1. Gas permeation

Gas permeation is based on the principle of mass transfer by diffusion of gas through a membrane⁴⁴. A membrane is a semi-permeable barrier between two phases, which allows the passage of various solutes through it at different rates and, it also allows selective components to penetrate while retaining other components at the feed inlet⁴⁵. Solutes consist of molecules or particles that are transmitted through the membrane own to forces acting on those molecules or particles. The extent of these forces is determined by the potential gradient across the membrane. The membranes are used in the natural gas industry mainly to remove CO₂, water, and hydrogen sulfide H₂S⁴⁴.

For example, as shown in Figure 8 below, in gas separation a feed mixture of gases enters the membrane module through the inlet port to the tube side and flows through the inside

of the hollow fibers. The gas species in the mixture with higher permeability will transfer at a greater rate across the walls of hollow fibers leaving behind the less permeable species. The transferred gas is referred to as the permeate. On the shell side, a vacuum can be applied or a sweep gas (or liquid) can flow therein to carry away the permeate. Exiting the outlet of the tube side is the retentive which constitutes a gas mixture with a higher concentration of the less permeable gas species⁴⁵.

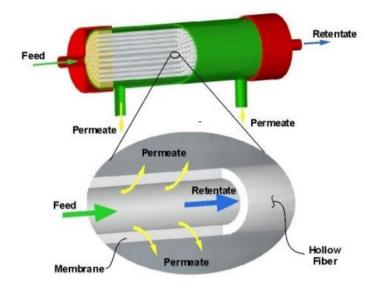


Figure 8. Scheme of gas permeability⁴⁵.

2.4.1.2. Twister Technology

It is very attractive in offshore applications own to its simplicity Figure 9 (it has no moving parts), its little size, and low weight. A Twister tube designed for 100 bar is approximately 2 m long. The simplicity and reliability of this static device without rotating parts, which operates without chemicals, ensures a simple installation, friendly to the environment, with high availability, suitable for operation automated. The supersonic twister separator is a unique combination of known physical processes, such as expansion, gas / liquid cyclonic separation, and steps in the recompression process, on one device compact and tubular to condense and separate water and heavy hydrocarbons from Natural Gas. Condensation and separation at supersonic speed are key to achieving reductions in one step both in capital and in maintenance costs⁴⁶. The residence time within the twister separator supersonic is only thousandths of a second, which does not allow the deposit of solids or the formation of hydrates, thus avoiding the application of chemical inhibitors⁴⁷.

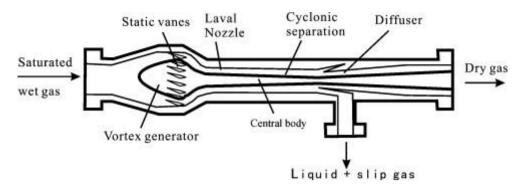


Figure 9. Cross-section of Twister Tube⁴⁷

2.4.2. Coatings

Tenaris⁴⁸, a world leader in the production of steel pipes, offers a variety of coating options that protect the internal surfaces of the pipe from the effects of corrosion and erosion and reduce friction and turbulence to increase flow efficiency. The liner also acts as protection during storage and transmission. Tenaris supplies liquid epoxy, internal fusion bonded epoxy (FBE), and special anti-corrosion paint for corrosion protection, they are recommended for production and injection pipes, flow lines, line pipe products, and drill pipes.

These options are:

- Suitable for immersion in fresh and saltwater
- Cash to speed up production
- Suitable for corrosive environments
- Resistant to many solvents and chemicals
- Resistant to cathodic detachment
- They are thermosetting coatings that comen epoxy powder form.⁴⁸

Another leading company in the production of pipes, such as EUROPIPE GmbH⁴⁹, was the supplier in charge to provide pipes for the construction of the Baltic Pipe maritime pipeline. For which its pipes include all the protective coatings specified by the design that, on the one hand, will protect the gas pipeline and, on the other, will minimize its impact on the environment. The wall thickness of the pipe is approximately 23 mm. The pipe is covered with a special 4.2 mm thick anti-corrosion coating to protect it during its operation on the seabed. All offshore pipelines it is protected with a 60-110mm thick concrete liner⁴⁹.

2.4.3. Buffering

It is based on changing the chemical composition of the pipe to prevent internal corrosion, its mechanism is based on the introduction of a buffering agent, such as a mild or diluted alkaline mixture, it can significantly reduce the corrosively of any liquid at rest, mainly increased its pH value above seven (neutral), and change from acid to alkaline. By obtaining alkalis inside the pipe, they will not damage the steel²⁵.

2.4.4. Cleaning pigs

The mechanical cleaning of internal surfaces has the function of displacing the solids and eliminating them from the pipe through the hog trap at the end and also be a mechanism for preventing the formation of corrosion⁵⁰. The pigs are repeatedly sent through the pipeline to exchange the tanks in that pipeline until almost no deposits can be found at the receiving station for the pigs. However, it is difficult to determine if this implies that the pipe is clean. When a pig moves through a pipe, it will exhibit a deposit material drag, as shown in Figure 10. Additional mechanical scraping will compact this deposited layer and grind the deposit particles into submicroparticles. This, not only will cause downstream nuisance, but it can also initiate a corrosion mechanism if harmful material gets trapped underneath the tight layer of the reservoir (e.g., CO₂ corrosion under the reservoir). There are several types of cleaning pigs and the choice will depend on the product to be transmitted and the contaminants to be removed⁵⁰. Its application may exclude the use of Direct Internal Corrosion Assessment (ICDA) models, cleaning pigs transmit corrosive liquids and solids to pig traps to remove them from the pipeline. Modern technologies in intelligent pigging, such as Magnetic Flux Leakage (MFL) ⁵¹ and the new optical inspection (Opto-Pig)⁵², produce superior readings, some of which allow a three-dimensional and almost visual inspection of the entire interior of the pipe. The readings of these modern smart pigs are even more accurate and the results are easier to interpret⁵⁰.

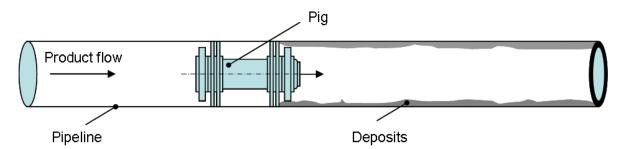


Figure 10. Deposit carry-over of mechanical pigs⁵⁰.

2.4.5. Preventive measures for weld corrosion.

Selective attack on weld or heat affected zones in which uninterrupted high velocity flow contributes to faster wear and corrosion⁵³. This form of corrosion is controlled by adding a chemical inhibitor, which adsorbs on the metal surface to form a protective film.

Another form of preventive measure used in the United States is to construct the pipes with the longitudinal seam welded in the upper half of the pipe to prevent water from coming into contact with the seam inside the pipe⁵⁴.

2.4.6. Preventive measures for microbial corrosion (MIC)

The control of this type of corrosion can be treated in different ways as presented in the following section:

Physical methods, the attenuation of MIC, through physical treatments, undo the biofilm formed through the use of pigging, ultraviolet radiation and ultrasound can also be used³⁴.

Chemical methods, with biocides that are effective chemicals to combat this type of corrosion. They are injected into the pipeline in the current of an electrolytic carrier. Generally, only one addition of chemical method is needed to the capping agent, other active agents could also be added, such as film formers and agents that promote electrolyte evaporation⁵⁵.

Electrochemical methods, one of the most commonly used methods is the application of negative potential (cathodic protection) to structural materials. It can reduce/prevent corrosion of any metal/alloy electrolyte combination in industry⁵⁶.

Biological Treatments, use of different types of bacteria against the primary bacteria responsible for MIC in a specific industrial environment³⁴.

Technological methods, must start from the engineering design where it is sought to control the process conditions (temperature, pressure, flow)²⁵.

2.4.7. Injection of mono ethylene glycol (MEG)

Another method of prevention of hydrate corrosion and suppression is the application of mono ethylene glycol (MEG) in submerged natural gas transfer lines⁵⁷. This type of technology requires the installation of MEG regeneration plants at the production facilities, and then the MEG is returned to the offshore production platforms.

In gas-producing fields, there is a risk of gas hydrate formation within flow lines, when certain conditions are met. Hydrate build-up needs to be avoided because they can clog pipes, which can cause operational problems and disrupt production, and in the worst case, it can cause flow lines to rupture. To prevent the formation of gas hydrates, liquid mono ethylene glycol (MEG) is injected into the inlet to bind the water⁵⁸.

A study carried out by Ehsani⁵⁷, analyzes the influence of mono ethylene glycol on the CO_2 corrosion behavior of carbon steel. Evaluating the effect of MEG concentration, acetic acid concentration, temperature, and immersion time on mild steel corrosion rates in CO_2 environments by electrochemical measurements and surface analysis. The results showed a decrease in corrosion rates with increasing MEG concentrations. Both the anodic and cathodic reactions are retarded in the presence of MEG. The conductivity with high concentrations of MEG decreases (Table 3)⁵⁷.

C _{MEG} (vol%)		0	10	50 80				
Conductivity	24 °C	53	33.9	7.1	1.1			
(mS/cm)	60 °C	55.5	33.9	9.3	1.9			

Table 3. conductivity of the MEG solutions in different concentrations at 24 °C and 60 °C⁵⁷.

It has been shown that the higher the concentration of MEG, the lower the corrosion rate. In addition, as can be seen in Figure 11, the increase in temperature contributes to the corrosion rate⁵⁸.

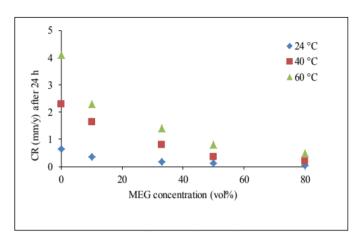


Figure 11. Temperature effect on carbon steel corrosion in CO₂ saturated solutions in the absence and presence of 10% to 80% MEG at 24 °C, 40 °C, and 60 °C⁵⁷.

The condensation rate is the main factor influencing the corrosion rate at the top of the line and controlling the condensation of water is the most reasonable way to control the internal corrosion rate of wet gas pipes. In that study, the effect of the presence of MEG in the liquid phase on the condensation rate is investigated. The measurement of MEG content in the condensation liquid is based on the analysis of the condensation liquid using Fourier transform infrared spectroscopy (FTIR) to obtain quantitative data on the mass transmit of MEG from the liquid water / MEG phase to the condensation liquid on the surface of the sample. The results in Figure 12 indicate that MEG effectively reduces the condensation rate by increasing the concentration of MEG in the aqueous phase. Furthermore, significant amounts of MEG are present in the condensation liquid at higher temperatures, which could effectively control top-of-the-line corrosion⁵⁷.

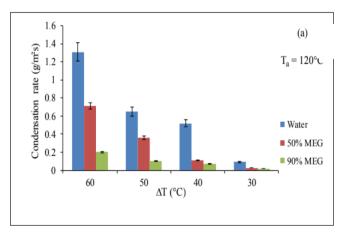


Figure 12. Condensation rate as a function of cooling temperature at different MEG/water mixtures at 120°C, bulk liquid temperatures, 20 bar CO₂⁵⁷.

2.4.8. Inhibitors

They are chemical products to reduce the rate of corrosion in pipes. Inhibitors are absorbed into the metal surface or react on it to produce a protective film, or they can react with pre-corroded pipes to make them less corrosive. There are a wide variety of inhibitors so the choice will depend on the types of product in the pipe, the type of corrosion, the cost, availability, toxicity, and respect for the environment. Inhibitors are substances or mixtures that in low concentration and aggressive environments inhibit, prevent or minimize the corrosion⁵⁹. Generally, the functioning of inhibitors can be:

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by a combination between inhibitor ions and metallic surface.
- the inhibitor leads to a formation of a film by oxide protection of the base metal.
- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex⁶⁰.

2.5. Inhibitors classification

Inhibitors are chemicals that react with a metal surface, or with the environment to which it is exposed, giving to the surface a certain level of protection. Inhibitors slow down the corrosion processes own to an increase in the behavior of anodic or catholic polarization, reduce the movement or diffusion of ions to the metallic surface and increase the electrical resistance of the metallic surface⁵⁹. Figure 13 a clear structure of the types of inhibitors, defining what type of inhibitor should be used will depend on the factors that arise in each situation in the following section the selection criteria are explained in more detail.

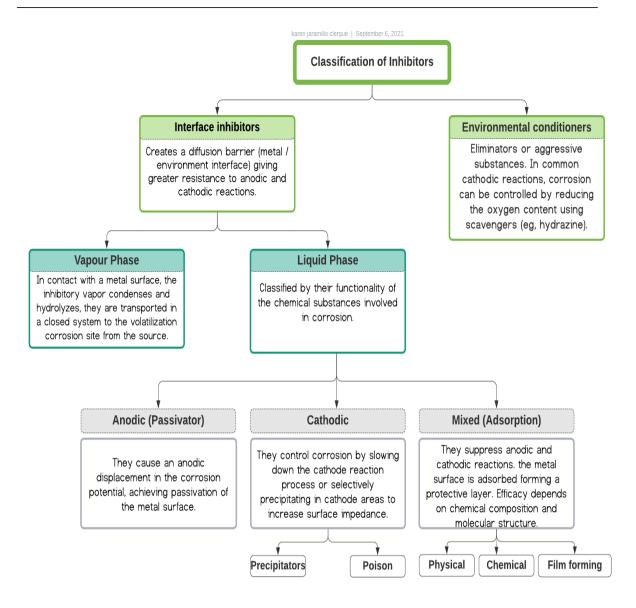


Figure 13. Classification of inhibitor⁵⁹.

2.5.1. Criteria for the selection of an inhibitor in oilfields.

Inhibitor solubility

Typically, water-soluble inhibitors are used in water systems, although water-dispersible inhibitors often offer better protection than soluble inhibitors. However, there is concern about the possibility of line plugging from the use of these types of inhibitors⁶¹.

Dissolved oxygen

Normal organic corrosion inhibitors do not effectively inhibit corrosion caused by dissolved oxygen. Common organic inhibitors are rarely effective in the presence of dissolved oxygen, so oxygen must be removed or minimized to a value of 20 ppb to use this type of inhibitor⁶².

Incompatibility

If other chemicals are injected into the system such as scale inhibitors, biocides, or oxygen scavengers, compatibility with these should be checked. If they react with each other, the effectiveness of the inhibitor may be reduced or destroyed⁶³.

Cost of inhibitor

The selection of an inhibitor should be based on the inhibitor that generates the lowest cost of chemical treatment per barrel of injected water, maintaining the lowest corrosion rate⁶⁴.

Inhibitor application.

Organic inhibitors are provided in liquid form and injected with chemical pumps. The chemical is often diluted to facilitate application. In cold climates, the chemical must be conditioned to this condition (often with alcohol) or it must be kept in a heated facility. If conditioned for cold, the chemical must be compatible with alcohol as it can cause precipitates⁶⁴.

Inhibitor detergency

Some corrosion inhibitors contain detergents that help keep the system clean and allow it to reach the metal surface to do its job. The correct amount of inhibitor must be placed, or else inhibitor interference, plugging problems, and metal surfaces may adsorb⁶⁵. Once the surfactant has been adsorbed to the available interfaces, its monomolecular concentration begins to increase, until the molecules associate and form structures called micelles, reaching the critical micellar concentration (cmc)⁶⁶.

The critical micellar concentration will indicate the effective dose of the inhibitor to be injected into the pipeline, the correct concentration must be analyzed for the dose to be effective, this can be studied by the electrical conductivity method where the breaking point represents the correct amount of cmc⁶⁷. The simplest approach is to plot the specific conductivity (k) versus the concentration of compounds to obtain two nearly straight lines whose intersection is the cmc. Eventually, the data corresponding to each straight line can be summarized by equations and the analytically obtained cmc⁶⁸. Figure 14 illustrates how the cmc value is determined as the discontinuity point⁶⁹.

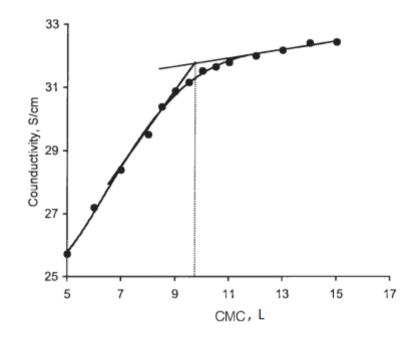


Figure 14. Scheme of CMC using the conductivity method. The dotted line represents the CMC⁶⁹.

Micelle and microemulsion solutions may be advantageous in minimizing corrosion problems, depending on the concentration of the inhibitor and the duration of contact of the surfactant with the surface. However, more recent theories indicate that complete micelles and other more complex self-assembling structures can also adsorb metal surfaces⁷⁰. As a result, some exposed gaps may appear on the surface of the metal. Especially in pre-corroded surface layers with the presence of iron carbonate and iron sulfide. So to avoid corrosion, film inhibitors are injected without detergency effect.

2.5.2. Mechanical effects

Inhibition of CO₂ Corrosion of Mild Steel – Study of Mechanical Effects of Highly Turbulent Disturbed Flow

The study by Li, Pots, Zhong and Nesic⁷¹, deals with corrosion experiments on X65 pipe steel that were performed with an imidazoline-based corrosion inhibitor using a high-shear turbulent channel flow cell, which included a disturbance of the flow in the form of a small bump as seen in Figure **15**, bellow⁷¹.

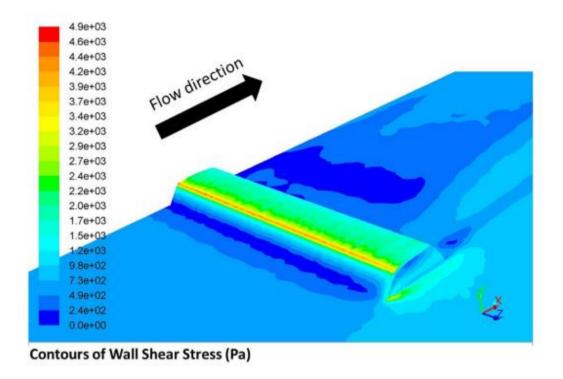


Figure 15. A 3-D image of wall shear stress distribution at the bottom⁷¹.

First, in the experiment, the inhibitor of imidazolinium chloride TOFA / DETA was added, but once the scanning electron microscope (SEM) studies were carried out, the presence of localized corrosion was observed (Figure 16).

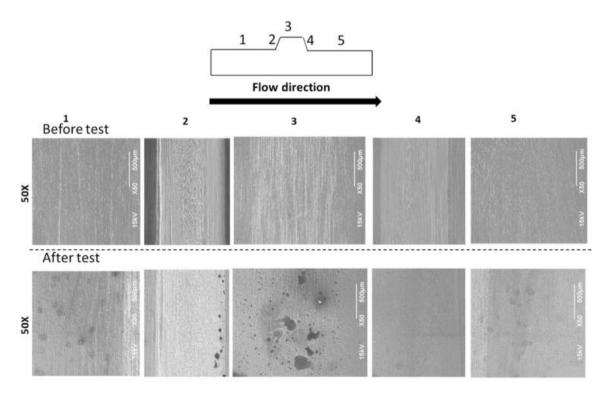


Figure 16. SEM images when adding inhibitors the corrosion rate decreases but with the studies, the presence of localized corrosion can be observed⁷¹.

This localized corrosion is own to the presence of cavitation in the area of the small bump, concluding that because of the small bump there is a sudden increase in flow velocity, and pressure is reduced at this location. The total pressure distribution across the plane of symmetry is shown in Figure 17, which clearly illustrates the sudden pressure drop at the leading edge of the bulge forming a zone where zero total absolute pressure approaches. In reality, it is expected that the pressure in that place reached at least the saturation pressure water vapor (0.032 bar at 25 °C) and vapor bubbles formed causing the cavitation and therefore localized corrosion in the downstream zone of the protrusion (Figure 18)⁷¹.

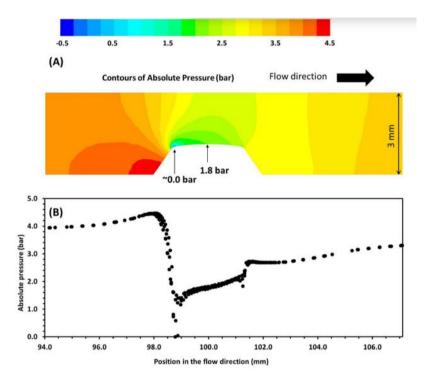


Figure 17. Absolute (total) pressure distribution⁷¹.

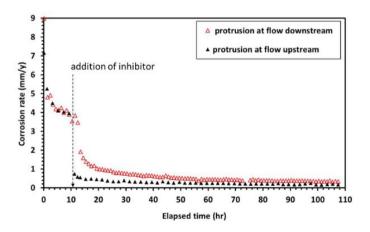


Figure 18. LPR Corrosion Rates for Experiments with Varied Levels of Dissolved O2 Concentration of protrusion at flow downstream and flow upstream ⁷¹.

To reduce this localized corrosion, a greater amount of the imidazolinium chloride inhibitor TOFA / DETA was used at a concentration of 72 ppmv. The surface is shown to be uniformly corroded, as exemplified in Figure 19. Therefore, the results support the hypothesis that cavitation is the most likely cause of the localized corrosion observed in previous experiments. The flow acceleration at the leading edge of the protrusion caused a drop in pressure and led to cavitation, with bubble collapse further downstream. This was the main cause of inhibitor failure and localized corrosion⁷¹.

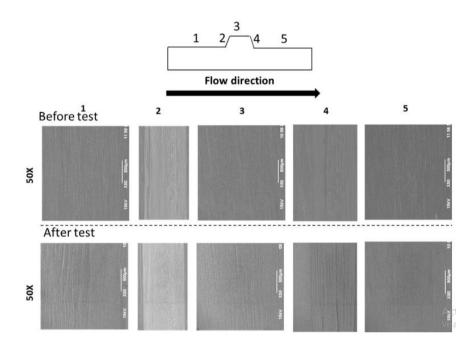


Figure 19. SEM images of the protrusion before and after test with TOFA/DETA imidazolinium chloride inhibitor were used at a concentration of 72 $ppmv^{71}$.

2.5.3. Inhibition in pre-corroded pipes

In pre-corroded pipes, deterioration own to corrosion is observed in areas with the presence of previous gas or hydrocarbon films, in these cases, it is recommended to apply corrosion inhibitors that are soluble in the presence of hydrocarbons, have no detergent effect, and can be easily dispersed by water. A study carried out in this type of pipes⁷² Figure 20 showed that the influence of corrosion against the effectiveness of the inhibitors, obtaining the results that at 25 °C the inhibitor significantly reduces the corrosion rate to levels lower than 2 mm/year. At 90 °C, the addition of the same corrosion inhibitor exerts a detergency effect on the corrosion products, increasing the corrosion rate to values higher than 6 mm/year⁷².

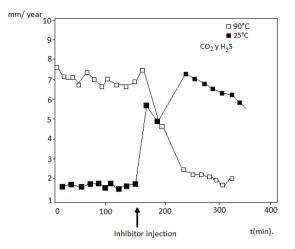


Figure 20. Corrosion inhibitors on pre-corroded surfaces⁷².

2.6. Risk management

2.6.1. Identify the risk.

The first phase of the risk management process is to identify and define potential project risks with teamwork. After all, only the work team can manage risks if they know what they are.

2.6.2. Analyze the risk.

This stage of the process is generally divided into two sub-stages: a quantitative analysis that focuses on an objective assessment of risk and a qualitative analysis that focuses on the identification and subjective assessment of risk⁷³.

2.6.2.1. Qualitative analysis

An initial qualitative analysis is essential since it allows identifying the main sources of risk factors, through an evaluation of each risk and subjectively labeling each risk (high/low) in terms of its probability of occurrence. Furthermore, this analysis provides considerable benefit in terms of understanding the project and its analysis of the problem. In the oil and gas industry, they are commonly used, in the Tabla 4 shows different

qualitative evaluation models. The evaluation models used in this thesis work are the risk matrix and the Bow Tie since they show the risk analysis through clear and easy-to-understand diagrams of structures⁷³.

Hazard identification (HAZID)	Structured brainstorming technique to identify all major hazards. Generally carried out at the beginning of a project, it is the starting point for a qualitative assessment of the risks of serious accidents ⁷⁴ .
Risk and operability (HAZOP)	A systematic approach to identify hazards and operability problems in design and operations that occur as a result of deviations from the intended range of process conditions ⁷⁵ .
Job Hazard Analysis (JHA)	Hazard analysis of a complete procedure to identify additional hazards to people or the process before putting it in the field. In some cases, JHA is a general job-related safety analysis ⁷⁶ .
Bow Tie Analysis	Bow Tie are a visual risk assessment method focused on a single event and the threats (cause) and consequences (effect). They are more commonly used to analyze major accident events such as loss of containment, facility explosion, fire, etc. Bow Tie can illustrate relationships between hazards, controls, and an organization's safety management systems, otherwise known as "barriers" ⁷⁷ .
Matrix Risk	A risk matrix (also called a risk diagram) visualizes risks in a diagram. In the diagram, the risks are divided depending on their likelihood and their effects or the extent of damage, so that the worst-case scenario can be determined at a glance. In this sense, the risk matrix should be seen as a result of the risk analysis and risk evaluation and is, therefore, an important component of a project and risk management ⁷⁸ .

Table 4.	Qualitative	evaluation	models
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2.6.2.2. Quantitative analysis.

This type of analysis involves assigning numerical values supported by data in the evaluation of probability and consequence⁷⁹. It is generally based on the initial qualitative assessment and focuses on the risks identified with the highest priority. Quantitative assessments can provide additional information when the operation or technology is more complex; decisions about the effectiveness of risk controls and the possible consequences depend on many variables⁷⁹. Ultimately, choosing the right risk assessment method also involves proper risk communication between the operator, the regulator, and other

stakeholders⁸⁰. Table 5 shows some of the methods to perform quantitative risk assessments, this thesis will carry out a study with the Monte Carlo simulation of the @RISK program.

Table 5. Quantitative evaluation models

Kent analysis method	W. Kent Muhlbauer's quantitative model for risk assessment, based on an indexing model, this technique is generally used for pipes. In this approach, numerical values (scores) are assigned to important conditions and activities in the piping system that contribute to the risk image. Its disadvantage is that the risk assessment becomes a subjective analysis in a way that does not allow a clear study ⁸¹ .
Event &Fault Tree Analysis	The graphical model represents the various event chains that can occur as a result of an initiating event. Used quantitatively to determine the probability or frequency of different consequences arising from the hazardous event ⁸² .
Quantitative Risk Assessment (QRA) - Monte Carlo simulation	The systematic development of numerical estimates of the expected frequency and severity of potential incidents associated with a facility or operation based on evaluation of engineering and mathematical techniques. Monte Carlo simulation performs risk analysis by building models of possible results by substituting a range of values a probability distribution for any factor that has inherent uncertainty. It then calculates results over and over, each time using a different set of random values from the probability functions ⁷⁹ .

2.6.3. Evaluate the risk.

Next, use the results of your risk analysis to determine which risks to prioritize. By two risk assessment methods such as risk matrix and Bow Tie analysis.

2.6.3.1. Matrix Risk (Qualitative)

The Risk Matrix (RM) is a widely adopted approach to assessing and analyzing risks in the oil and gas industry⁸⁰. RM have been implemented throughout that industry and are widely used in risk management contexts. An RM is a graphical presentation of the study of the probability of the risk and the consequence or failure. Figure 21, is a graphic representation of colors ranging from red as a very serious risk, an orange color as a

significant risk, a yellow color for an appreciable risk, and a green color for a marginal risk. The objective of the RM is to prioritize risks and risk mitigation actions⁷⁸.

ure	People (P)		Slight Injury	Minor Injury	Major	Single Fatality	Multiple Fatalities
of fail)	Asset (A)		Slight Damage	Minor Damage	Local Damage	Major Damage	Extensive Damage
ence (COF)	Environment ((E)	Slight Effect	Minor Effect	Localized Effect	Major Effect	Massive Effect
Probability of failure Probability of failure (POF) Consequence of failu (POF) Consequence of failu (COF) COF) Consequence of failu (COF) Asset Asset Asset Consequence of failu (COF) Asset	Reputation (R))	Slight Impact			National Impact	International Impact
O	Severity rating		1	2	3	4	5
0	Severity rating		Negligible	Minor	Moderate	Major	Catastrophic
Probability of failure (POF) and (POF) Por nul nul nul	E Very likely to happened	Happens several times per year at location	Moderate	High	High	Very High	Very High
ilure	D Likely to happened	Happens several times per year in company	Low	Moderate	High	High	Very High
ility of fa (POF)	C Possible to happened	Incident has occurred in company	Low	Low	Moderate	High	High
Probat	B Unlikely to happened	Heard of incident in industry	Very Low	Low	Low	Moderate	High
	A Very unlikely to happened	Never heard of in industry	Very Low	Very Low	Low	Low	Moderate

Figure 21. Scheme of a Matrix Risk⁷⁸

2.6.3.2. Bow Tie analysis (Qualitative)

The Bow Tie analysis Figure 22 is a qualitative risk assessment methodology that provides a way to effectively communicate complex risk scenarios in an easy-tounderstand graphical format and shows the relationship between the causes of unwanted events and escalation potential for loss and damage. Bow Tie can display the commands, which prevent the top event from happening first, specific to each threat, and also the recovery measures, which are ready to limit the possible effects once the event top has been achieved, specific for each credible result. The advantages of the approach to adopting Bowtie in the risk analysis are: provides a solid technique of comprehensive identification of all risk events and promote an understanding of their reciprocal relations; uses a format in the form of an easy-to-understand scheme to communicate the cause and effect relationships underlying more complex risk scenarios for a wide range of stakeholders; it helps to demonstrate the level of control that exists on the risks and therefore provides a way of identifying weaknesses, gaps, and opportunities for a continuous reduction of risks; allows verification and connection to relevant sections of the management system⁷⁷.



Figure 22. Scheme of Bow Tie analysis⁸³.

2.6.3.3. Monte Carlo simulation with @RISK program (Quantitative)

The risk analysis with the Monte Carlo simulation of the @RISK for excel program with a free trial license allows to see the possible results of the decisions and evaluate the impact of risk, which allows better decision-making under conditions of uncertainty. This simulation is based on a computerized mathematical technique that performs risk analysis by modeling possible outcomes by substituting a range of values (a probability distribution) for any factor that has inherent uncertainty. Using random values of the probability functions, in this work, the cost risk analysis will be carried out, for which the following probability distributions are used:

- *Triangular* it is used to generate values closer to the most probable between the scale of the minimum, most probable, and maximum values.
- *Poisson was* used to modeling the number of independent events in a fixed interval of time.
- *Compound* used for combining multiple samples from a "severity" distribution together, controlled by a "frequency" distribution. Commonly used in operational risk and current analysis⁸⁴.

2.6.4. Treat the risk and mitigate

During this phase, make a plan for how to treat and manage each risk. It might choose to ignore minor risks, but serious risks need detailed mitigation plans as presented in Figure 23.



Figure 23. The four types of risk mitigation⁷³

Avoid: when a risk has an unintended negative consequence, it is possible to avoid those consequences altogether. By moving away from the causes of the risk, you can successfully prevent the undesired events from occurring.

Minimize: mitigating risk involves trying to minimize the catastrophic effects that it could have on the project. The key to minimizing risk starts with realizing that the risk exists.

Transfer: this strategy is to shift the burden of the risk consequence to another party. This may include giving up some control, yet when something goes wrong your organization is not responsible. A conventional means to transfer risk to another organization is with the purchase of insurance.

Accept: every product produced has a finite chance of failing in the hands of your customer. When that risk is at an acceptable level, sufficiently low estimated field failure rate, then ship the product to accept the risk⁷³.

2.6.5. Monitor and control the risk.

Finally, assign team members to monitor, track, and mitigate risks if the need arises.

CHAPTER III: DESIGN METHODOLOGY AND STUDIES CASES

3.1. Risk Management Methodology

The methodology used in this degree work is the use of risk-based integrity management systems with established case studies, based on questions Figure 24 that allows to have an order for the solution of each case study and learn about risk assessments in high consequence areas.

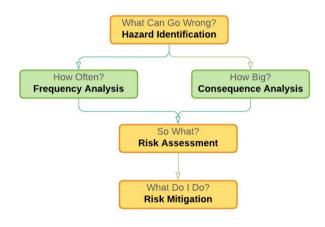


Figure 24. Risk assessment scheme based on questions

The methodologies used range from qualitative scoring schemes to detailed quantified systems requiring structural reliability analysis, with a risk management life cycle (Figure 25) baseline analysis presented below.



Figure 25. Risk management life cycle

The case studies in this degree work include estimated values, the objective of this methodology is to show the operation of the risk management analysis. So that this work allows experts in the field to have a basis for development with real values.

3.2.■ Study case 1: Use of inhibitors to mitigate internal corrosion in natural gas pipelines.

The application of this study methodology for the case use of inhibitors in offshore systems in the hydrocarbon industry of Ecuador, can be applied in "Campo Amistad" in the Gulf of Guayaquil. It has an offshore system made up of four platforms and a 12 "and 72 Km gas pipeline. The importance of the gas produced in Campo Amistad is own to it is distribution in Thermogas Machala, Petroecuador and for domestic use in towns near Campo Amistad⁸⁵.

3. **2**. **1**. ■ Identify the risk

Accidents at the offshore platform are unavoidable own to unexpected reasons. The nature of its operations involves unstable materials sometimes under extreme pressure in aggressive environments leading to an increase in risk, thus accidents and tragedies can cause higher severity to platform's workers. Risk assessment in the oil and gas industry is essential to protect humans and the ecosystem from damages as it helps to create awareness and identify if existing control measures are adequate or viceversa for hazards and risks before an accident happens. The consequence of failure is a part of the risk assessment process, it consists of four categories which are people loss, asset loss, environmental loss, and reputation loss.

3.2.2. ■ Analyze the risk

In natural gas pipelines, one of the main problems is internal corrosion for which inhibitors are used for mitigation.

The main consequence of this problem is the rupture of pipes, product contamination, decrease in quality and production. Corrosion affects the microstructure, mechanical properties, and physical appearance of the metal. Rust and other types of deterioration

drastically reduce equipment capacity, resulting in lost production as well as loss of equipment, or even life.

In the risk assessment is the poor selection of inhibitors or the misuse of inhibitors, many corrosion inhibitors have some health and/or environmental problems own to their toxicity. Thus, a correct selection of inhibitors must be had, based on their properties such as considering that they do not have a detergent effect, since by dissolving the precorroded layer, the inhibitor will strip the pipe again and expose it to corrosion again. Then the selection should be of a more neutralizing film that does not have detergency effects. Consideration of all viable threats:

External corrosion: affectation of the pipe causing fractures Internal corrosion: incorrect use of inhibitors without prior study Third Party Damage: operational or personnel damage Manufacturing: low quality inhibitors

Types of consequences:

- Safety: Employee health when using highly toxic inhibitors and damage to infrastructure caused by inhibitors.
- Economic: Economic losses own to poor selection of inhibitors.
- Environmental: Incorrect treatment of inhibitors causing environmental pollution own to their high toxicity.
- Regulator: Incorrect regulation of the amount of inhibitor placed in the pipe
- Corporate image: erroneous business reputation for use of inappropriate inhibitors

3. **2**. **3**. ■ Evaluate the risk

In the risk evaluation, the risk matrix and Bow Tie were qualitatively analyzed, the quantitative analysis was done by Monte Carlo probability simulation with the @RISK program.

The risk matrix in Table 6 presents different risks and estimated values of probability and gravity are shown. These allow to obtain the value of the risk and its level of risk and then, transfer these results to the matrix that is observed in the results section.

RISK MATRIX									
RISK	Probability (occurrence)	Gravity (Impact)	Risk Value	Risk level					
Misuse of inhibitors	3	4	12	Important					
Incorrect selection of inhibitors	5	3	15	Very serious					
Consider inhibitors with detergent	3	5	15	Very serious					
Damage to pipes due to inhibitor selection failure	3	5	15	Very serious					
Economic losses when seeing that the applied inhibitor did not work	3	5	15	Very serious					
Employee poisoning by highly toxic inhibitors	4	4	16	Very serious					
Environmental damage from toxic inhibitors	3	3	9	Important					
Incorrect amount of inhibitor placed	5	2	10	Important					
Disrepute of corporate image due to use of bad inhibitors	4	3	12	Important					
Using expired inhibitors	1	5	5	Apreciable					
Use of low-quality inhibitors	2	4	8	Apreciable					
Use of contaminated inhibitors	2	5	10	Important					
Inappropriate use of inhibitors in pre- corroded pipes	4	5	20	Very serious					
Inject inhibitors into very long battery	5	4	20	Very serious					
Fire near the pipe	2	5	10	Important					
Pipeline colaps by corrosión	5	5	25	Very serious					

Table 6. Risks of using inhibitors to mitigate internal corrosion in gas pipelines

Bow Tie was carried out for the following evaluation that allows identifying important aspects such as causes, consequences, and control. Subsequently, its diagram was elaborated, which is presented in the results section.

- *Identify the Bow Tie hazard:* the hazard in this case of study is the inappropriate use of inhibitors and the event of the collapse of natural gas pipes by internal corrosion.
- *Assess the threats:* the first threats will be chemical, environment, quality, safe, knowledge, external factors.
- Assess the Consequences: pipeline corrosion, low gas quality, environmental pollution, fire and explosion of pipelines, bad company reputation, worker health problems.
- *The control:* adequate use of inhibitors, use green inhibitors to produce less contamination, studies on the probability of the presence of fire, study the correct

inhibitor for each situation, care the human lives to work with inhibitors, study plan of the inhibitor products to be used, socialize its risks and dangers, control the correct use of inhibitors.

• *The recovery control: systems to detect and abate incidents (gas, fire & smoke alarms); systems intended to protect the safeguards (fire & blast walls, protective coatings, drain systems).*

The quantitative risk assessment with Monte Carlo probability simulation focused on a study of the costs of each risk. The simulation model was developed based on the risks previously validated in the risk matrix. To carry out the simulation, the following steps were followed: 1) Develop the estimate of the maximum, most probable, and minimum costs, 2) Enter the identified risks, 3) Establish the criteria for evaluating probability and impact, 4) Determine the probability and the value of the impact. The evaluation is observed in Table 7, the values and calculations used in each column are described below:

- *Risks* previously identified in the first section.
- *Probability estimation* based on the qualitative evaluation of the risk matrix.
- *Medium probability* which is calculated by dividing the number of occurrences by the time in which the project is developed. The values assigned for this case study are estimated.
- *Poisson probability* is calculated with the Poisson probability distribution that allows modeling events in a fixed time interval. For this study, the established time was 3 years, the values calculated in the mean probability were taken.
- *Impact* calculated with the triangular probability distribution generating values closer to the most probable, this study occupies minimum, most probable, and maximum cost values that are observed in Table 7, these values for this case study are estimated.
- *Risk* is calculated with the composite probability distribution that allows combining several samples of a "severity" distribution, controlled by a "frequency" distribution allowing to obtain risk values to later analyze them.
- *Total impact of the risk* is obtained with the output function and presents the results graphically of the risks present in this case study, the graph and its analysis are shown in the results section.

		5	Study ir	n thousands	of dollars \$0	,000					
Risk	Probability estimation	Medium poability	Poisson Probability	Impact (S)	Risk= P * I (S)	Minimal impact (S)	Most likely impact (S)	Maximum impact (S)	(10) N occurrences	Period (years)	Medium poability
Misuse of inhibitors	50%	1.67	1.7	39.0	64.9	35	40	42	5.00	3.00	1.67
Incorrect selection of inhibitors	80%	2.67	2.7	30.0	79.8	28	30	32	8.00	3.00	2.67
Consider inhibitors with detergent effect	30%	1.00	1.0	45.3	45.2	43	45	48	3.00	3.00	1.00
Damage to pipes due to inhibitor selection failure	40%	1.33	1.4	40.0	53.3	35	40	45	4.00	3.00	1.33
Economic losses when seeing that the applied inhibitor did not work	60%	2.00	2.0	47.7	95.3	44	48	51	6.00	3.00	2.00
Employee poisoning by highly toxic inhibitors	50%	1.67	1.7	33.7	56.1	28	35	38	5.00	3.00	1.67
Environmental damage from toxic inhibitors	60%	2.00	2.0	23.7	47.3	20	23	28	6.00	3.00	2.00
Incorrect amount of inhibitor placed	75%	2.50	2.5	20.0	50.0	15	20	25	7.50	3.00	2.50
Disrepute of corporate image due to use of bad inhibitors	50%	1.67	1.7	24.7	41.1	19	25	30	5.00	3.00	1.67
Using expired inhibitors	20%	0.67	0.7	44.0	29.3	38	45	49	2.00	3.00	0.67
Use of low-quality inhibitors	25%	0.83	0.8	41.0	34.2	38	40	45	2.50	3.00	0.83
Use of contaminated inhibitors	30%	1.00	1.0	45.3	45.2	40	46	50	3.00	3.00	1.00
Inappropriate use of inhibitors in pre-corroded pipes	75%	2.50	2.5	40.0	99.9	35	40	45	7.50	3.00	2.50
Inject inhibitors into very long battery limits	60%	2.00	2.0	43.3	86.7	35	45	50	6.00	3.00	2.00
Fire near the pipe	20%	0.67	0.7	48.7	32.4	42	50	54	2.00	3.00	0.67
Pipeline colaps by corrosión	70%	2.33	2.3	55.3	129.0	52	55	59	7.00	3.00	2.33
SUM					\$989.62						
TOTAL IMPACT RISK	\$989.62	1									
TOTAL INITACT KISK	3707.02										

Table 7. Qualitative risk analysis for study case 1

Study case 1: Use of inhibitors to mitigate internal corrosion in natural gas pipelines

TOTAL IMPACT RISK

Own estimation based on qualitative analysis and estimate data the @RISK formulas Analysis result

3. 2. 4. ■Treat the risk and mitigate

Correct selection of inhibitors will allow the reduction of internal corrosion and improvements in production. The segments that require risk reduction will be those that have been mitigated with inhibitors seeking only to control and maintain. Also, analyze the properties of the inhibitors before being used.

Risk mitigation

Risk mitigation is the process of planning for disasters and having a way to lessen negative impacts. Risk mitigation focuses on the inevitability of some disasters and is used for those situations where a threat cannot be avoided entirely⁸⁶. Rather than planning to avoid risk, mitigation deals with the aftermath of a disaster and the steps that can be taken before the event occurrs to reduce adverse and, potentially, long-term effects. Ideally, an organization would be prepared for all risks and threats and avoid them entirely. However, having a risk mitigation plan can help an organization prepare for the

worst, acknowledging that some degree of damage will occur and having systems in place to confront that.

The mitigation of risks in the use of inhibitors for internal corrosion in natural gas pipelines is based on studying the risk curve of the probability of damage vs. consequence in which its mitigation will focus on seeking to displace the risk to a low probability, that is, its occurrence is low and in turn the consequence is low. The mitigation for the different risks is presented below⁸⁶.

• The wrong amount of inhibitor was placed.

Monitor the amount of inhibitor entering the pipes using a schematic record. Train employees on the amounts to be placed. Keep a record of the inhibitors used and the amounts to be added. In addition, periodically control the proper compliance with these records.

• *Fire near the pipe.*

Keep the land near the pipeline clean without plants or waste, have a cleaning schedule with periods of approximately 2 months, in addition to considering the growth of the plant according to the time of year and the sea, summer or winter. Before laying the pipes, carry out studies on the probability of the presence of fire because of external factors such as the growth of vegetation or areas of high fire risk.

• Dishonor of the corporate image by the use of bad inhibitors.

Have a study plan of the inhibitor products to be used, carry out tests, and different tests on different equipment at different conditions considering their characteristics and mechanical effects. In such a way as to avoid large-scale damage that causes a bad corporate image. Study what are the weaknesses of the company concerning the inhibitors that are going to be used and what problems can be faced, and inventory them for their subsequent mitigation and avoid a bad corporate image.

• Misuse of inhibitors

Train workers in the proper use of inhibitors to create a preventive culture of maintenance, supervision of their use. Create user manuals in which it indicates the steps to follow before using an inhibitor properly.

• Inappropriate use of inhibitors in pre-corroded pipes

Evaluate the physical and chemical properties of the inhibitors to be used and avoid the use of inhibitors with detergency provoking properties since exposed spaces may appear on the metal surface and generate corrosion again. Carry out a preliminary study of the inhibitor to be used and study the pre-corroded pipe for corroded areas.

• Poisoning of employees by highly toxic inhibitors.

Put the products in the appropriate places previously labeled. Before workers interact with the product, socialize its risks and dangers. Far more important than any loss of revenue or cost to the business is the increased risk to human life. The pipelines, facilities, and assets can be replaced in the event of explosions or disasters, but human life sadly cannot.

• Damage or collapse to pipes own to failure of inhibitor selection.

A previous study of the corrosion problem for the correct choice of an inhibitor that meets the requirements or prevents corrosion. Consider an evacuation program in case the plant needs to be evacuated. Train and introduce employees to the evacuation program.

• Inject inhibitors into very long battery limits.

For very long battery limits, consideration should be given to having powder service points and monitoring points where the dosing tanks are located. In addition, control the monitoring points with greater security since there are generally thefts of the facilities.

3.2.5. ■Monitor and control the risk

Once the prevention and mitigation measures are established, it will be sought that the mitigation measures are controlled and monitored so that the probability/consequence of the risks decreases.

3.3.⇒ Study case 2: Corrosion and black powder treatment strategies in gas pipelines of the Coast of Africa.

3. **3**. **1**. \Rightarrow **Identify the risk**

It is proposed to carry out a state of the art on the formation and treatment strategies of corrosion and black powder that is formed in the natural gas production streams. The study is carried out off the coast of Africa.

Fields that produce natural gas are associated with crude oil and natural gas. At the outlet of the high-pressure separator, the associated natural gas and dry natural gas are combined, treated, and transmitted through a pipeline 14 in diameter for 103 Km. The nature, composition, and formation of black powder as a product of corrosion are present in the supply pipes. Specifically, on the internal surface of gas pipelines. Without proper prevention and mitigation plans, the black powder can gradually wear downpipes and equipment, which can fracture and cause material, economic and human damage.

The main causes of corrosion can be:

- The presence of natural gas by-products such as O₂, CO₂, and H₂S, cause different types of corrosion.
- Microbiologically influenced corrosion (MIC) caused by microbial activities in areas that provide their required habitat.
- The formation of black powder is produced by the precipitation of waxes and asphalts associated with the dragging of liquid hydrocarbons and subsequent precipitation in the lines causing corrosion under deposits or by general and localized corrosion because of the presence of liquid water and CO₂ and H₂S dissolved in the aqueous phase.
- Metallic pipes made primarily of carbon steel and low-alloy steel, inherently corroded by electrochemical reactions with the environment.
- The type and rate of corrosion are highly dependent on material properties and environmental conditions.
- The specific geometry of the pipe and the electrolytic insulation between the inner wall and the outer wall implies that corrosion can occur, develop internally and externally depending on the conditions.

3. **3**. **2** \Rightarrow **Analyze the risk.**

Once the case study has been defined, a risk study is carried out that includes: a general description of the case, risk assessment, the study of the probability of failure, and consequences. To finally establish the risk matrix and the Bow Tie analysis for this case study.

The risks identified in this study case are:

- An inefficient gas-liquid multiphase separation, causing the entrainment of liquids forming aqueous hydrocarbon phases that generate corrosive environments.
- Accumulation of natural gas liquids in the gas transfer pipeline, significantly reducing the calorific capacity of the gas to be extracted by obtaining LPG (liquefied petroleum gas) and, therefore, strongly impacting on the performance of this product, as well as its interchangeability in national and international markets.
- The quality of transmitted gas decreases.
- Potentially contaminating factors of the upstream production facilities of a liquefied petroleum gas plant can seriously compromise the quality of LPG.
- Corrosion by O₂, CO₂, and H₂S causes deterioration of the metal of the pipe and severe effects on the localized corrosion. H₂S produces different types of fragmentation.
- Clogging in offshore transfer pipelines causes the capacity of gas transmission to be significantly reduced. This creates a sealed liquid phase in the pipe, together with the phenomenon of condensation of the liquid promoted by the low temperatures of the seabed.
- Accumulation of black Powder, waxes, and asphalt inside gas pipes, causes equipment damage and affects the production system.
- The flow assurance is affected in thermodynamic parameters, operational and other variables of high sensitivity.
- Severe microbial corrosion (MIC) can produce black powder or iron sulfide.
- During cleanup, clogging and damage to processing plant equipment, especially expanders and compressors, can occur.
- Excessive annual costs related to corrosion were estimated at 7 MMMUSD to monitor, replace and maintain these assets.
- Placing corrosion coupons in the pipe, in welding areas can cause hot Tappin and cause leaks, combustion explosion, and thermochemical reactions inside the pipe.
- The use of external jackets can lead to damage such as extensive mechanical damage or leakage, corrosion, punctures, and cracks.
- Erosion corrosion associated with black powder, black powder particles can pose a risk of possible erosion or abrasion in the pipeline. When formed, iron sulfide particles can be 0.09906 mm in size, creating abrasion inside the pipelines.

 Hygroscopic corrosion in acidic environments, the effect of relative humidity associated with hygroscopicity on corrosion, given between the mass of the corrosion product and the potential for black powder formation. Based on the obtained it is obvious that the corrosion occurs below the relative humidity deliquescence, but the corrosion products are not easily observed if the deliquescence occurred. Soluble materials with a high affinity for water can dissolve if the availability of water is high enough through a process called deliquescence.

3. **3**. **3**. \Rightarrow Evaluate the risk

In the risk evaluation, the risk matrix and Bow Tie were qualitatively analyzed, the quantitative analysis with the Monte Carlo probability simulation with the @RISK program.

In the risk matrix, Table 8 different risks and estimated values of probability and gravity are shown that allow obtaining the value of the risk and its level of risk and then transferring these results to the matrix that is observed in the results section.

RISK MATRIX								
RISK	Probability (occurrence)	Gravity (Impact)	Risk Value	Risk løvel				
An inefficient gas-liquid multiphase separation	3	4	12	Important				
Accumulation of natural gas liquids	4	4	16	Very serious				
The quality of transported gas decreases	3	5	15	Very serious				
Potentially contaminating factors	5	4	20	Very serious				
Corrosion by O2, CO2 and H2S causing	4	4	16	Very serious				
Fragmentation by H2S	2	5	10	Important				
Hold-up in offshore transfer pipelines	3	4	12	Important				
Accumulation of black powder, waxes and asphalt inside gas pipes	4	5	20	Very serious				
The flow assurance is affected in thermodynamic parameters, operational and other variables of high sensitivity	2	5	10	Important				
Severe microbial corrosion (MIC)	2	4	8	Apreciable				
During cleanup, clogging and damage to processing plant equipment	4	3	12	Important				
Excessive annual costs related to corrosion	3	5	15	Very serious				
Placement of corrosion coupons can cause burning explosion, thermochemical reaction	5	2	10	Important				
The use of external sleeves can cause mechanical damage or leakage, corrosion, punctures and cracks	3	3	9	Important				
Hygroscopic corrosion in acidic environments, the effect of relative humidity	2	4	8	Apreciable				
Erosion corrosion can cause abrasion when transported through pipelines.	5	3	15	Very serious				
Pipeline colaps by corrosión and black powder	5	5	25	Very serious				

Table 8. Risks of corrosion and black powder in the gas pipelines of Africa coast

Bow Tie was carried out and the following evaluation allows identifying important aspects such as causes, consequences, and control. Subsequently, its diagram was elaborated, which is presented in the results section.

- Identify the Bow Tie hazard: Hazard is the formation of corrosion and black powder and the event is the collapse of natural gas pipes on the coast of Africa.
- Assess the Threats: the first threats will be the presence of CO₂, O₂, and H₂S, accumulation of black powder, waxes, and asphalt, accumulation of natural gas liquids, material properties, and conditions of pipelines, potentially contaminating factors and microbial, erosion, and hygroscopic corrosion.
- Assess the Consequences: corrosion by CO₂, O₂ and H₂S, equipment damage and affecting the production system like clogging in offshore transfer pipelines,

reducing the calorific the capacity and quality production, capacity of gas transmission is significantly reduced, flow assurance is affected in thermodynamic parameters and operational and excessive annual cost related to corrosion.

- The control: accurate prediction and modeling of corrosion rates, elimination of black powder and clean the pipeline, injection of inhibitor MEG, separation water by slug catcher and super cyclone, correct selection of materials by testing and modeling, use of mitigation plan and clean the pipes and use of mitigation plan depending on the case.
- The recovery control: control of the infrastructure necessary for inhibitor injection like pumps, corrosion monitoring through massive loss coupons, pipeline cleaning and maintained control system, gas quality control, systems to detect a reduce fires, constant monitoring by flow assurance systems, and establish a relationship between mitigation plan and cost analysis.

The quantitative risk assessment with Monte Carlo probability simulation focused on a study of the costs of each risk. The simulation model was based on the risks previously validated in the risk matrix. To carry out the simulation, the following steps were followed: 1) Develop the estimate of the maximum, most probable, and minimum costs, 2) Enter the identified risks, 3) Establish the criteria for evaluating probability and impact, 4) Determine the probability and the value of the impact. The evaluation is observed in Table 9 where values and calculations used in each column apply the same procedure for case 1.

Table 9. Oualitative risk analysis for study case 2.

			Study i	n thousand	is of dollars	\$0,000					
Risk	Probability estimation	Medium poability	Poisson Probability	Impact (S)	Risk= P*I (S)	Minimal impact(S)	Most likely impact(S)	Maximum impact (S)	(10) N occurrences	Period (years)	Medium poability
An inefficient gas-liquid multiphase separation	30%	1.00	1.0	24.3	24.3	20.0	25.0	28.0	3	3.00	1.00
Accumulation of natural gas liquids	40%	1.33	1.3	36.0	47.9	33.0	35.0	40.0	4.00	3.00	1.33
The quality of transported gas decreases	30%	1.00	1.0	50.0	49.9	46.0	49.0	60.0	3.00	3.00	1.00
Potentially contaminating factors	80%	2.67	2.7	35.0	93.1	30.0	35.0	40.0	8.00	3.00	2.67
Corrosion by O2, CO2 and H2S causing deterioration of the metal and corrosion	70%	2.33	2.3	35.3	82.4	33.0	35.0	38.0	7.00	3.00	2.33
Fragmentation by H2S	20%	0.67	0.7	42.7	28.4	40.0	43.0	45.0	2.00	3.00	0.67
Hold-up in offshore transfer pipelines	40%	1.33	1.3	34.7	46.1	32.0	35.0	37.0	4.00	3.00	1.33
Accumulation of black powder, waxes and asphalt inside gas pipes	45%	1.33	1.3	28.3	37.7	25.0	28.0	32.0	4.00	3.00	1.33
The flow assurance is affected in thermodynamic parameters, operational and other variables of high sensitivity	35%	1.00	1.0	49.0	48.9	45.0	50.0	60.0	3.00	3.00	1.00
Severe microbial corrosion (MIC)	35%	1.00	1.0	35.0	34.9	32.0	35.0	38.0	3.00	3.00	1.00
During cleanup, clogging and damage to processing plant equipment	65%	2.00	2.0	20.0	40.0	15.0	20.0	29.0	6.00	3.00	2.00
Excessive annual costs related to corrosion	40%	1.33	1.3	60.0	79.9	55.0	60.0	65.0	4.00	3.00	1.33
Placement of corrosion coupons can cause burning explosion, thermochemical reaction	85%	1.67	1.7	25.0	41.7	20.0	25.0	30.0	5.00	3.00	1.67
The use of external sleeves can cause mechanical damage or leakage, corrosion, punctures and cracks.	40%	1.33	1.3	30.0	39.9	25.0	30.0	35.0	4.00	3.00	1.33
Hygroscopic corrosion in acidic environments, the effect of relative humidity	25%	0.67	0.7	42.3	28.2	40.0	42.0	49.0	2.00	3.00	0.67
Erosion corrosion can cause abrasion when transported through pipelines	85%	2.83	2.8	31.3	88.6	28.0	31.0	35.0	8.50	3.00	2.83
Pipeline colaps by corrosión and black powder	70%	2.33	2.3	50.0	116.6	45.0	50.0	55.0	7.00	3.00	2.33
SUM					\$928.5						
TOTAL IMPACT OF RISK	\$928.54					-					

Study case 2: Corrosion and gunpowder treatment strategies in gas pipelines of the coast of Africa. ands of dollars \$0,000 Chudu in the

Own estimation based on qualitative analysis and estimate data the @RISK formulas

Analysis result

3.3.4. \Rightarrow Treat the risk and mitigate

- Accurate prediction and modeling of CO₂ corrosion rates for carbon and alloy • steel pipes are vital tasks in the basic design phase of oil and gas projects to determine whether to consider additional wall thickness for pipeline valves. defined as "corrosion tolerance."
- Separation of water in Lion LPG production platforms by filtration or by • separators with a correct and appropriate design of the separators is of great because they are generally the initial equipment in many processes. The need to remove water to enable profitable gas transmission also adds complexity, cost, and safety implications for gas separation projects. The recommended

technologies (some already installed) for the efficient management of fluid separation such as slug catcher and supersonic cyclone

- Mitigation plans to be implemented in the short term such as injection of chemical treatments in production platform. These can be spill corrosion inhibitors in the gas transfer lines to the LPG plant through injection systems or pumps.
- Elimination of black powder and clean the pipes before carrying out an internal inspection of the pipe walls using instrumented scrapers (pigs), to know the current state of the pipes.
- Injection of mono ethylene glycol (MEG) in offshore production platforms is a method for corrosion control. In addition, it allows the suppression of hydrate formation), in submerged natural gas transfer lines for onshore production facilities.
- Correct selection of pipeline materials by testing and modeling.
- If the corrosion greatly affects the operational performance of the pipeline, the pipes should be replaced.
- Composite interior linings for pipes to create waterproof barriers to reduce or eliminate carbonic acid corrosion of steel

3. **3**. **5**. \Rightarrow **Monitor and control the risk**

Corrosion monitoring through massive loss coupons determined by coupon inserted in an area of interest over several weeks or months. Standardized coupons and related calculations are carried out according to the standards.

Coupons can be in the form of a strip, rod, or recessed disk. Recessed coupons are highly recommended when performing cleaning operations as they do not need to be removed during internal pipe cleaning operations.

Control of the infrastructure necessary for injection (pumps and injection systems), with systems of continuous injection of corrosion inhibitors. Constant monitoring by SCADA systems is essential.

CHAPTER IV: RESULTS AND ANALYSIS

Once risk management has been applied in the two established case studies, it allows us to have both qualitative and quantitative results. In the case of qualitative studies, a study was carried out through two diagrams such as the risk matrix and the Bow Tie analysis. The risk matrix allows us to analyze the probability and the consequences present, obtaining the risk levels and sectioned by colors such as red \rightarrow serious risk, orange \rightarrow significant risk, yellow \rightarrow appreciable risk, and green \rightarrow marginal risk. The Bow Tie analysis, which allowed us to make a visual assessment of the risks through its diagram structure, which focuses on a single event and the threats (cause) and consequences (effect). Its diagram illustrates the relationships between hazards, controls, and an organization's safety management systems, also known as "barriers." The quantitative analysis was assigned numerical values of the risk costs and through the Monte Carlo simulation with the @RISK program that allows an evaluation with probabilistic distributions, the risk analysis focused on its costs was obtained. The analyzes carried out for each case study are detailed below.

4.1. Results of study case 1

■ Use of inhibitors to mitigate internal corrosion in natural gas pipelines.

Once the risk management methodology was applied, the risk matrix and the Bow Tie analysis were obtained for qualitative analysis. The results obtained in the risk matrix as shown in Figure 26, indicate the risks with the highest probability and impact in red, for which the following risks were identified: the collapse of the pipe own to corrosion, inappropriate use inhibitors in pre-corroded pipes, injection of inhibitors into very long battery limits, poisoning of an employee from high inhibitor toxicity, incorrect selection of inhibitors, damage to pipes because to the faulty selection of inhibitors and the financial loss of using inhibitors that do not work⁸⁷. They are considered risks that require an urgent application of preventive measures, the project or work cannot start or continue without an urgent application of preventive measures²².

The risks with a medium level of probability and impact represented with the color orange are the following: misuse of inhibitors, dishonor of the corporate image own to the use of bad inhibitors, fire near the pipe, use of contaminated inhibitors, the incorrect amount of inhibitor placed and environmental damage from toxic inhibitors. These risks are considered important, so mandatory preventive measures must be applied where the risk variables must be strictly controlled during the project⁷⁸.

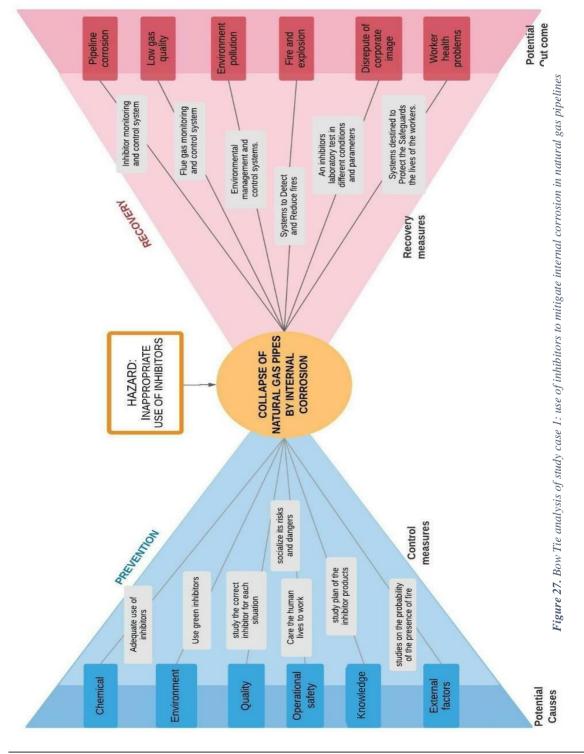
The risks with an appreciable level of probability and impact represented by the color yellow are the following: use of low-quality inhibitors and using expired inhibitors⁸⁸. Its appreciable level of risk indicates that it should be studied whether it is possible to introduce preventive measures to reduce the level of risk and keep the variables under control⁷⁸.

			GRAVITY (IMPACT)						
			NEGLIGIBLE 1	MINOR 2	MODERATE 3	MAJOR 4	CATASTROPHIC 5		
PROBABILITY	VERY HIGH	5		Incorrect amount of inhibitor placed	Incorrect selection of inhibitors	Inject inhibitors into very long battery limits	Pipeline colaps by corrosión		
	HIGH	4			Disrepute of corporate image due to use of bad inhibitors.	Employee poisoning by highly toxic inhibitors	Inappropriate use of inhibitors in pre-corroded pipes		
	HALF	3			Environmental damage from toxic inhibitors	Misuse of inhibitors	Damage to pipes due to inhibitor selection failure and economic losses when seeing that the applied inhibitor did not work		
	LOW	2				Use of low-quality inhibitors.	Fire near the pipe and use of contaminated inhibitors		
	VERY LOW	1					Using expired inhibitors.		

Figure 26. Matrix risk of study case 1: use of inhibitors to mitigate internal corrosion in natural gas pipelines.

The results of the Bow Tie analysis are presented in Figure 27, which details the danger of improper use of corrosion inhibitors, the event of the collapse of the natural gas pipeline own to internal corrosion. In addition, its potential causes are detailed with their respective control measures such as⁸⁷ in the chemical aspect, inhibitors should be used appropriately, in the environmental aspect, organic inhibitors that are not aggressive to the environment should be used, in the quality should be studied the correct inhibitor for each situation, operational safety must be controlled by socializing the existing risks and dangers, the knowledge aspect must be studied the probability of the presence of fire near

the pipes. The potential results with their respective recovery measures such as corrosion in the pipeline, inhibitor monitoring, and control systems must be added, low quality gas, gas control, and monitoring systems must be implemented, environmental pollution must be implemented, environmental management, in the case of fire and explosions, fire detector systems must be implemented, the disgrace of the corporate image must be tested in different conditions and parameters to the inhibitors and health problems with the workers must be implemented protection that allows safeguarding the lives of workers⁸³.



The quantitative risk assessment with Monte Carlo probability simulation focused on a study of the costs of each risk, which allows identifying the risks with a potential level of probability and impact and treating them with priority⁷⁹. The simulation model was developed based on the risks previously validated in the risk matrix. Figure 28, shows the histogram of the distribution of risk cost impacts versus the project probability estimate after undergoing 1000 iterations⁸⁴. The graph has three axes, the X-axis shows the impact of risk costs, the Y-axis at the top shows the estimated probability, and the percentage of the impact of the study. Considering the initially estimated budget of costs for risks as shown in Figure 28 the estimated budget, of a minimum value of \$ 547,000 and a value of \$ 691,000. Once the evaluation has been carried out, it is obtained that this cost estimation only allows covering 3.8% of the total costs of risks. In Figure 29, it is observed the real budget that to cover all risks costs a 90%, between \$ 666,000 - \$ 1,328,000 are needed, values that are out of the initial budget. Therefore, it is observed that it is necessary to implement control and mitigation measures to reduce costs⁷⁴.

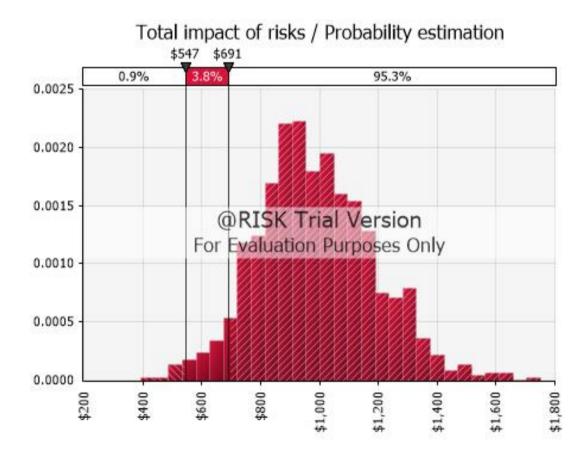


Figure 28. The histogram of the distribution of risk for the estimated budget case study 1

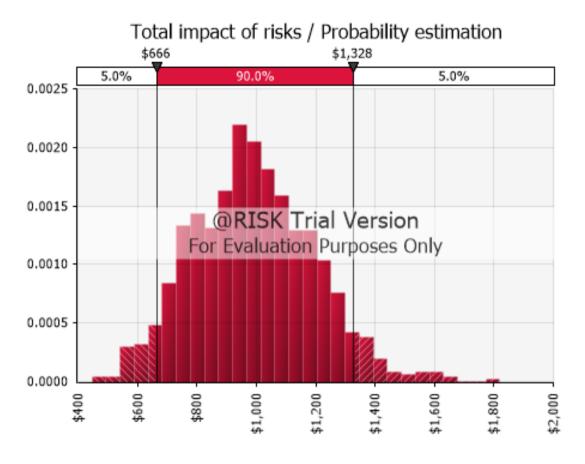
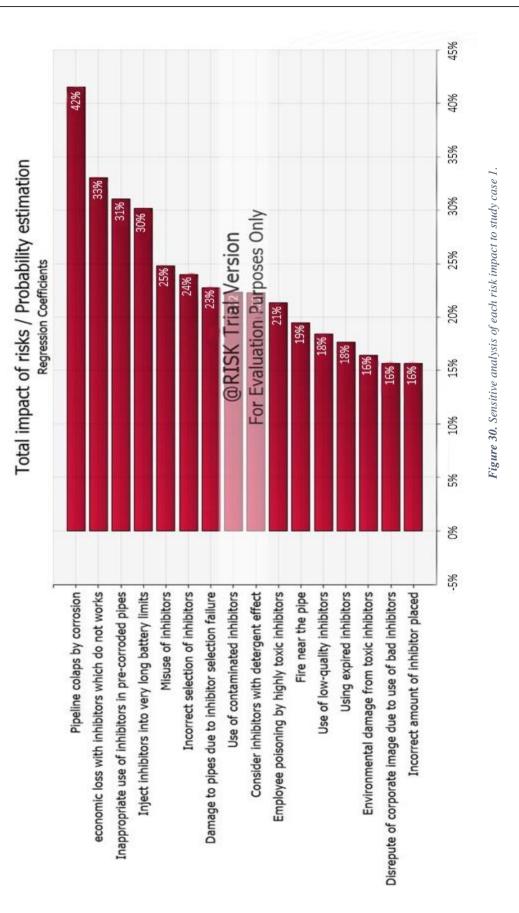


Figure 29. The histogram of the distribution of risk for the real budget case study 1

Sensitivity analysis

The sensitivity analysis indicates the probability of impact of each risk⁸⁴. As can be seen in Figure 30 the events with the highest risk are the collapse of the pipe because to corrosion 42%, economic losses when using inhibitors that do not work 33%, the inappropriate use of inhibitors in pre-corroded pipes 31%, injection of inhibitors in very long battery limits 30%, misuse of inhibitors 25%, incorrect selection of inhibitors 24%, damage to pipes own to failure of inhibitor selection 23% and use of contaminated inhibitors 22%. The aforementioned events obtained a higher level of risk so that the implementation of a risk response plan is aimed to minimize and mitigate the potential risk that may affect the project in terms of costs.

Once the potential risks had been identified, the following preventive measures were established in the risk treatment and control section²⁸:



- For pipeline collapse own to corrosion or black powder, the prediction and modeling of corrosion rates should be established and whether additional valve wall thickness or application of inhibitors should be considered.
- For economic losses from the use of inhibitors that do not work, a connection must be made between the mitigation plan and the cost analysis. Inhibitors should be studied in advance to utilize both their physical and chemical properties.
- For pipe injection with very long pipe limits, more points should be established with metering pumps along the pipe for the injection of inhibitors.
- For the inappropriate use of inhibitors in pre-corroded areas, the inhibitors must be studied for both their physical and chemical properties, in addition to studying where the pre-corroded areas are located and avoiding the use of inhibitors with a detergent effect as they accelerate the corrosive process.
- Own to the misuse of inhibitors, it must be previously studied which ones will be appropriate depending on the conditions.

Control and monitoring measures must be applied in order of priority.

4.2.Results of study case 2

\Rightarrow Corrosion and black powder treatment strategies in gas pipelines of the coast of Africa.

The results obtained in the risk matrix as shown in Figures 31 indicate the risks with the highest probability and impact in red color that require an urgent application of preventive measures are: pipeline collapse by corrosion and black power, potentially contaminating factors, accumulation of black powder, waxes and asphalt inside gas pipes, corrosion by O₂, CO₂ and H₂S causing deterioration of the metal, excessive annual costs related to corrosion, quality of transmitted gas decreases and erosion corrosion.

Risks with a medium level of probability and impact represented by the color orange are **considered risks that are identified important, so mandatory preventive measures must be applied**⁸⁰. In the case of the study, the following risks were identified: an inefficient gas-liquid multiphase separation and hold-up in offshore transfer pipelines, during cleanup there are clogging and damage to processing plant equipment, placement of corrosion coupons, fragmentation by H₂S and flow assurance is affected, the use of external sleeves can cause mechanical damage or leakage, corrosion, punctures, and

cracks²². The risks with an appreciable level of probability and impact represented by the color yellow are the following: Hygroscopic corrosion in acidic environments and the effect of relative humidity. In these risks, it should be studied whether it is possible to introduce preventive measures to reduce the level of impact and keep the variables under control²².

			GRAVITY (IMPACT)						
			NEGLIGIBLE 1	MINOR 2	MODERATE 3	MAJOR 4	CATASTROPHIC 5		
	VERY HIGH			Placement of corrosion coupons	Erosion corrosion	Potentially contaminating factors	Pipeline colaps by corrosión and black powder		
	HIGH	4			During cleanup, clogging and damage to processing plant equipment	Corrosion by O2, CO2 and H2S causing deterioration of the metal and corrosion.	Accumulation of black powder, waxes and asphalt inside gas pipes		
PROBABILITY	HALF	3			The use of external sleeves can cause mechanical damage or leakage, corrosion, punctures and cracks	An inefficient gas- liquid multiphase separation and hold-up in offshore transfer pipelines	Excessive annual costs related to corrosion and quality of transported gas decreases		
	NOT	2				Hygroscopic corrosion in acidic environments, the effect of relative humidity	Fragmentation by H2S and flow assurance is affected.		
	VERY LOW	1							

Figure 31. Matrix risk of study case 2: Corrosion and black powder treatment strategies in gas pipelines of the coast of Africa

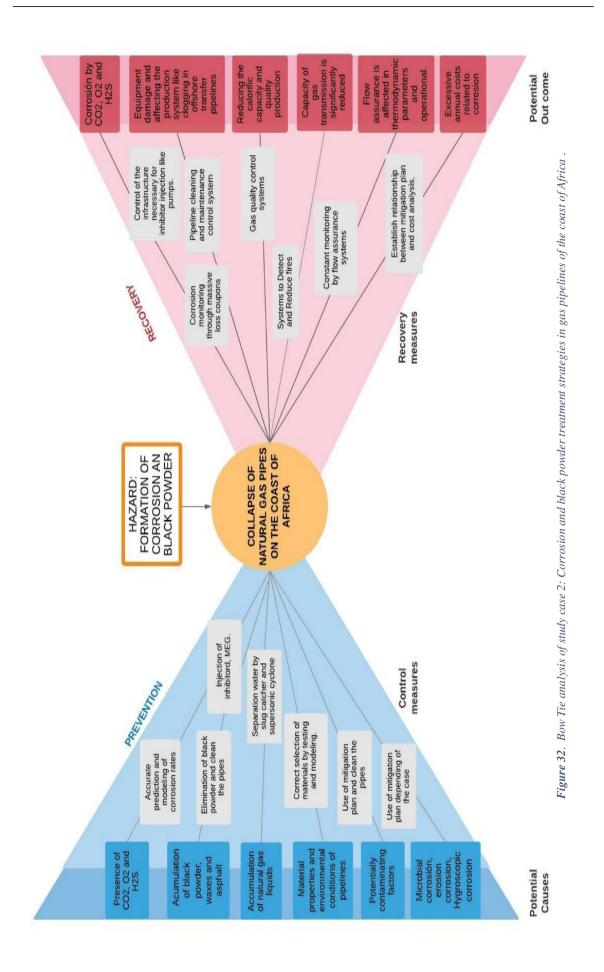
The results of the Bow Tie analysis are presented in Figure 32, which details that the main event will be the collapse of the natural gas pipelines on the coast of Africa own to the danger of the formation of corrosion and black powder. The causes of this event and the control measures are as follows⁸³:

- Presence of CO₂, O₂, and H₂S must be controlled with an adequate prediction and modeling of the corrosion rate and the injection of inhibitors or MEG.
- The accumulation of black powder, waxes, and asphalt must be controlled by cleaning pipes for their elimination and the injection of inhibitors or MEG.
- The accumulation of natural gas liquids should be controlled with the separation of water either by slug catcher or dehydration.
- The property of the materials and the environmental conditions of the pipes must be controlled with a correct selection by testing and modeling the materials.

- Potential polluting factors should be controlled using pipeline cleaning and mitigation plans.
- Microbial, erosion, and hygroscopic corrosion should be controlled using mitigation plans for each case.

The consequences or potential results with their respective recovery measures such as:

- Corrosion by CO₂, O₂, and H₂S, control of the infrastructure necessary for the injection of inhibitors such as pumps, and corrosion monitoring must be implemented.
- Damage to equipment and damage to the production system own to clogging, a control and monitoring system for pipeline cleaning must be implemented.
- To reduce heat capacity and product quality, gas quality control systems must be implemented.
- To significantly reduce the gas transmission capacity, a flow control system must be implemented.
- To ensure a flow that is affected by thermodynamic and operational parameters, the flow control system must be constantly monitored. For excess costs related to corrosion, a relationship must be established between the mitigation plan and cost analyzes.



The results obtained in the Monte Carlo simulation focused on a study of the costs of each risk, to identify which are the risks with potentials⁸⁴. The simulation model was developed based on the risks studied in the risk matrix. Figure 33, shows the histogram of the distribution of risk cost impacts versus the project probability estimate after undergoing 1000 iterations⁸⁴. The graph has three axes, the X-axis shows the impact of risk costs, the y-axis on the left shows the estimated probability, and the top Y-axis shows the percentage of the impact of the study⁸⁴. Considering the initially estimated budget of costs for risks as shown in Figure 33, of a minimum value of \$ 584,000 and a maximum value of \$ 716,000, once the evaluation has been carried out, it is obtained that with these costs estimate it only allows to cover 9.6% the total costs of the risks. In Figure 34, it is observed the real budget that to cover 80% of the total risk costs, between \$ 705,000 - \$ 1,176,000 is needed, values that are out of the initial budget. Therefore, it is observed that it is necessary to implement control and mitigation measures to reduce costs⁸⁴.

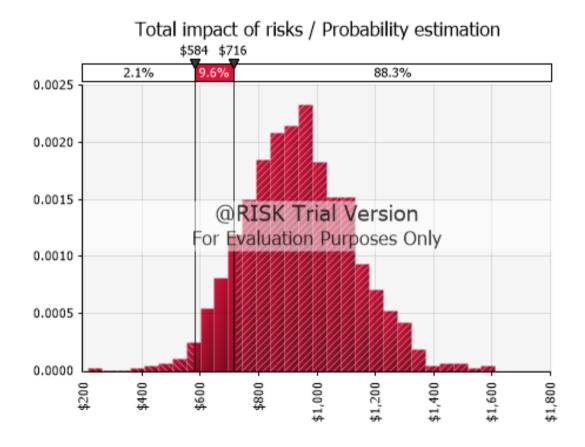


Figure 33. The histogram of the distribution of risk for the estimated budget case study 2

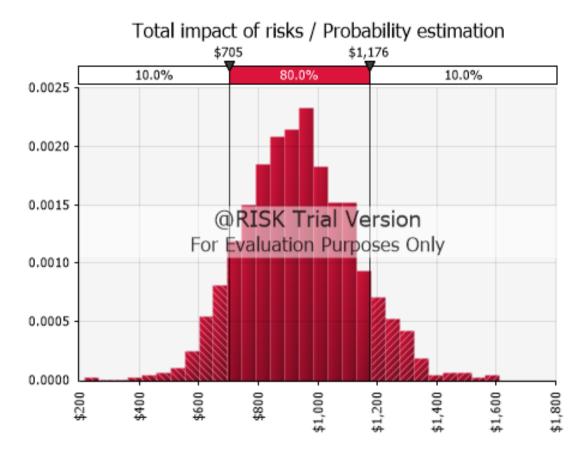
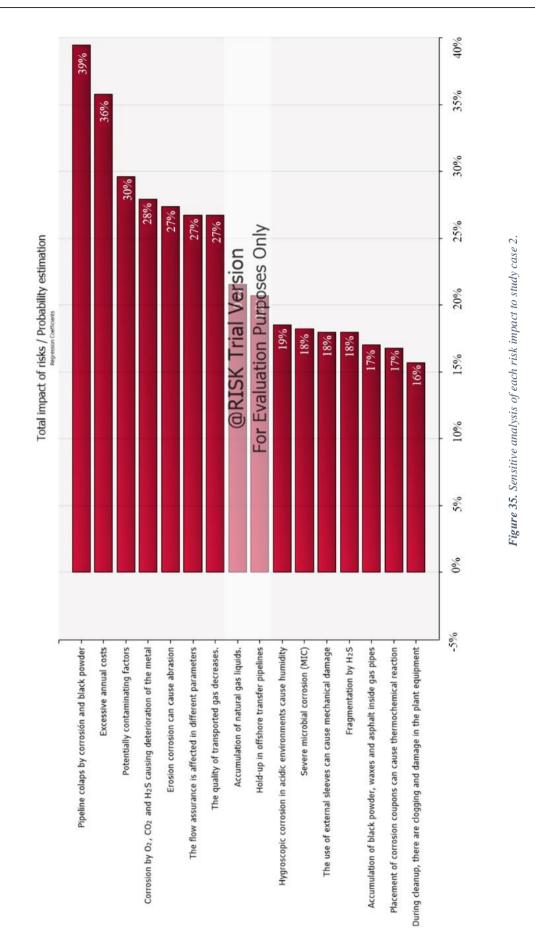


Figure 34. The histogram of the distribution of risk for the real budget case study 2

Sensitivity analysis

The sensitivity analysis indicates the probability of impact of each risk⁸⁴. As can be seen in Figure 35 the events with the highest risk are pipeline collapse by corrosion and black powder 39%, excessive annual cost 36%, potentially contaminating factors 28%, erosion corrosion can cause abrasion 27%, the flow assurance is affected in different parameters 27% and the quality of transmitted gas decreases 27%⁷⁹. The aforementioned events obtained a higher level of risk so that the implementation of a risk response plan is identified and aimed at minimizing and mitigating the potential risk that may affect the project in terms of costs.



Once the potential risks had been identified, the following preventive measures were established in the risk treatment and control section⁷⁹:

- For pipeline collapse owned to corrosion or black powder, the prediction and modeling of corrosion rates should be established and whether additional valve wall thickness or application of inhibitors should be considered.
- For the excessive annual cost, a relationship must be established between the mitigation plan and the cost analyzes to control these two variables.
- For potentially polluting factors for the environment. An environmental management must be implemented in the company, which controls the levels of contamination when applying chemical treatments.
- For corrosion by erosion that can cause abrasion, a preliminary study of the design of the pipes must be implemented.
- To ensure the flow that is affected in different parameters, flow control systems must be established and the pipes cleaned before carrying out an internal inspection of the pipe walls using instrumented scrapers (pigs), to know the current state of the pipes.
- To reduce the quality of the gas transmitted, control systems will be implemented through quality tests and avoid the formation of hydrocarbon components that affect the quality of the gas transmitted.

Control and monitoring measures must be applied in order of priority.

CHAPTER V: CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this thesis, the risks present in operational conditions of the corrosion process in offshore natural gas production systems were analyzed. Corrosion in natural gas pipelines is one of the common problems encountered in the oil and natural gas industry. The implementation of control and mitigation alternatives through the risk management methodology is essential to solve this problem.

The main problems in offshore gas condensate production systems were identified where design problems were studied for which it is established that software models are used to establish the operations and conditions in the pipeline before its design. Another present problem is the assurance of flow in which the hydraulic design of the piping system and the phenomena or hydrocarbon components such as waxes, asphalt, hydrates, and corrosion must be studied because they can compromise the efficiency and safety of the system so that a flow is guaranteed safely and economically.

The degradation systems and internal corrosion mechanisms in natural gas pipelines were identified for which corrosion by O_2 , CO_2 , H_2S , top of line corrosion, weld corrosion, microbial corrosion, and hygroscopic corrosion were determined. In addition, it was determined that the by-product of corrosion in these pipes is the formation of black dust that originated as a result of a previous corrosion process of iron carbonates, iron sulfides, and iron oxides that are formed by an internal corrosion reaction of acid corrosive gases. Which can be mitigated with the injection of inhibitors, the separation of liquids, or the application of MEG.

Solution technologies for the prevention and mitigation of internal corrosion were identified, for which dehydration, coatings, buffering, pig cleaning, preventive measures for microbial and welding corrosion, and the application of inhibitors were determined. The study focus was deepened in the use of inhibitors because it is the method commonly used own to its easy application and lower cost. Inhibitor classification, selection criteria, mechanical effects, and inhibition in pre-corroded pipes were studied.

Tools were developed for decision making with risk management, which allows to identify, analyze, evaluate, treat and control each event that represents a threat or risk

within the analysis of internal corrosion problems. In the risk assessment aspect, qualitative studies (risk matrix and Bow Tie analysis) and quantitative studies (Monte Carlo probability simulation) were carried out, so that it allowed to establish and identify the correct treatments and control measures.

Two case studies were established to develop the application of risk management so that the values recorded in the studies were estimated. Case study 1 focused on the use of inhibitors to mitigate internal corrosion in natural gas pipelines, for which qualitative and quantitative results were obtained that allow the main risks to be identified and controlled. For case study 2. Corrosion and black powder treatment strategies in gas pipelines of the coast of Africa, in the same way, qualitative and quantitative results were obtained, obtaining the most potential risks and their mitigation proposal.

Once the case studies have been applied, it is concluded that comprehensive risk-based management is important allowing companies to recognize the risks with higher priority and treat them. The use of quantitative and qualitative risk assessment through diagrams allows the method to have a creative approach, attractive and easy to understand for company employees.

5.2. Recommendations

Based on the work carried out, it is recommended that the application of the risk management methodology in the oil and gas industry be with real data on risk events presented in a specific project. Thus, the results of risk matrix analysis, Bow Tie analysis, and Monte Carlo probabilistic simulation can be appreciated with a more realistic approach. For future experimentation, it is recommended to control the risks periodically, either annually or semi-annually, allowing us to know the progress of the control and mitigation of the risks. In addition, to update the qualitative and quantitative analyzes.

As it was a test focused on showing the operation of the application of risk assessment qualitative and quantitative, in the qualitative analysis in which the costs of the risks are evaluated, it is recommended to implement the evaluation of the estimated time of each risk based on the project schedule, to analyze how the risks can affect creating delay in the project. Finally, an important recommendation is once the risk management study is completed, implement a mitigation and control manual, to deliver it to the workers of a certain project.

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