Microbiological Induced Corrosion (Sulphate-Reducing bacteria) Attack in Oil/Gas Refining Industries: An Overview

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Abstract

Several critical equipment in Oil and Gas refining facilitates experiencing an accelerated corrosion attack when microbes or bacterial species reacts with the metallic surface typically referred as Microbiological induced corrosion. MIC is an electrochemical mode of corrosion where the type of material and the chemical medium plays major role with the microbes and resulted in surfaces that are covered with a thin film called (biofilm). This type of corrosion has been known as a costly phenomenon as they reported to cost 20% of the total reported corrosion cost. In this paper the MIC phenomenon has been described in detail with a special reference to oil and gas applications, also the current and most effective inspection and monitoring methodologies and programs have been discussed and compared with several reported literatures. The Paper showed that the monitoring systems and current inspection methodologies are considered complex in term of implementations, cost and reliability and there are plenty room of improvements.

Keywords: MIC; Inspection Programs; Qualtiy Control; Oil and Gas Sector.

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1. Introduction

According to recent technical reports and published studies, the cost of the damage due to microbiologically influenced corrosion (MIC) in the United States is estimated to be 250 $ billion US annually. Similar surveys in the United Kingdom, Japan, Australia, and Germany estimated the cost of corrosion to be 1-5% of the gross national product, and the (MIC) is reported to account for 20% of the total cost of corrosion. The most impacted industries are oil production, water distributions, and power generations [12].

Despite the above-highlighted facts, there are nothing more significant and expensive than a human being lives. On Saturday, August 19, 2000, at 5:26 a.m., a 30-inch diameter gas transmission pipe-line ruptured adjacent to the Pecos River near Carlsbad, New Mexico. The released gas ignited and burned for 55 minutes and caused twelve fatalities of people who were camping around the pipeline area addition to the unfortunate loss to the Natural Gas Company total damages were found to be $998,296 [16]. The major cause of the incident was "microbiologically influenced corrosion" (hereafter called MIC).

This paper devoted to the general understanding of microbiologically influenced corrosion Specifically the Sulfate-reducing bacteria (SRB) and the effects on material commonly used in oil, gas and refining industries. This paper will provide a general Failure mechanism, metallurgical and microstructural impact, mitigation, and inspection aspects.

2. What is Microbiological Induced Corrosion

### 2.1   *Historical Research Background*

Going back into the history of understating MIC, the first research to electrochemically interpret MIC goes back into the twentieth century. Specifically to the pioneering work of von Wolzogen Kuhr and van der Flugt, in 1934. Between the 1960s-1970, the publications on MIC was mainly related to either objecting to the anaerobic corrosion theory of iron via SRB. However, in the 1980s, MIC attracted the attention in response to several industrial needs that helped the understanding of MIC behaviors and its complexity significantly. By the end of the 1990s, and at the beginning of the new century, new technologies such as surface analysis techniques, electrochemical experiments, and microscopy findings were utilized to clarify the role of sulfide films on the corrosion behavior of steel [8].

2.2   *Definition*

MIC is an electrochemical mode of corrosion that will result from microbes that react with the surface and lead to corrosion or influence other corrosion processes of metallic materials. MIC is a form of corrosion produced by living organisms such as bacteria, algae or fungi, those organisms cannot be seen with the unaided human eye, and they are often associated with the presence of tubercles organic substances [1]. MIC encourages the increase in the corrosion rates of a preexisting surface corrosion due to the presence of bacteria that accelerate the rates of the anodic and cathodic corrosion reaction. MIC- specifically Sulfate-reducing bacteria (SRB) has been found one of the major corrosion reported cases in oil, gas, and refineries industries [13].

Sulfate-reducing bacteria (SRB) is deriving their energy from organic nutrients by oxidizing it or molecular hydrogen (H2) reducing (SO2−4) to (H2S). SRB's fundamentally are anaerobic which mean that they do not require oxygen for growth and activity, as a result as an alternative to oxygen, and these bacteria use Sulfate. SRB will usually grow in the pH range between 4 and 9.5. Sulfate-reducing bacteria (SRB) are most well-known as the bacteria that are associated with high bacterial corrosion rates [11].

SRB is the most troublesome groups of organisms among all other bacteria involved in MIC of steels, copper, and other metals in oil and gas industries. SRB-MIC is known to be Black in color, smelly Iron Sulfate corrosion products. Figure (1) shows the appearance of mild steel before and after two months of exposure to SRB Culture [10]. There are several factors that could affect SRB behavior, and the resultant corrosion of mild steel includes but not limited to nutrient availability, temperature, PH and adhesion of cells to the metal surfaces [17].
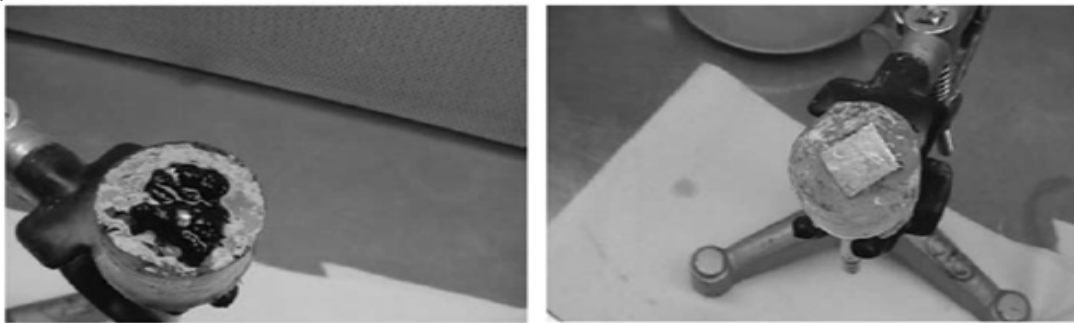
Figure 1: Appearance of mild steel before and after two months of exposure [10].

3. General Failure Mechanism and surface effects

The typical electrochemical corrosion depends only on the material, and its chemical medium, however, in SRB MIC a third element that is the microorganisms in the biofilm should be considered. Figure 2 shows the basic factors that lead to SRB MIC [3].
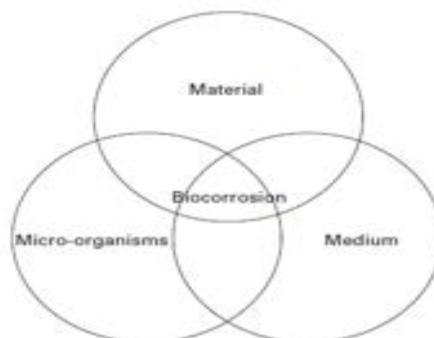
Figure 2: Factor involved in SRB-MIC corrosion [3].

The mechanism stars When SRB attach themselves to metallic surfaces, and they start to form a thin film known

as "biofilm" that consists of cells immobilized at a substratum, frequently embedded in an organic matrix of microbial origin. The Biofilms are believed to contain typically about 95% water [10]. The importance of Biofilms driven from the fact that it represents the predominant form of life of bacteria in natural environments. In other words, the biofilm is the consequence of the development of microbial communities on submerged surfaces in aqueous environments. They usually grow as a general phenomenon that can be observed in almost all media, and at a temperature range between -12 °C to 115°C and in almost all ranges of PH (from 0 to 13) [3]. Upon formation of biofilm, the cathodic polarization theory as postulated by Kuhr and Vlugt, are the most applicable explanation whereby protons may act as an electron acceptor at the cathode in the absence of oxygen, the typical reactions of this theory are provided below:

- Metal: Anodic reaction $4Fe \rightarrow 4Fe2+ + 8e-$ Electrochemical Cell.
- Solution: Cathodic reaction $8H+ + 8e- \rightarrow 8H(ad)$
- Cathodic Reaction $8H2O \rightarrow 8H+ + 8OH-$ Electrolyte
- Micro-Organism: $SO42- + 8H (ad) \rightarrow S2- + 4H2O$ Microbial Depolarization.
- $Fe2+ + S2- \rightarrow FeS$ (Corrosion Products)
- $3Fe2+ + 6OH- \rightarrow 3Fe(OH)2$ (Corrosion Products)
- $4Fe + SO42- + 4H20- \rightarrow 3Fe (OH)2 + FeS + 2OH-$ (Overall Reaction).

At the absence of oxygen, the cathodic areas of the metal surface quickly become polarized by hydrogen atomic [10]. It has been assumed that main probable effect of SRB on corroding metal is the removal of hydrogen from the metal surface utilizing hydrogenase and catalyzing the reversible activation of hydrogen. Then again, Costello 1974 postulated that hydrogen sulfide, H2S, instead of hydrogen ion could act as a cathodic reactant. It is more probable that under anaerobic conditions corrosion rates are increased due to [5]:

- Cathodic reduction of H2S:$H2S + 2e- \rightarrow H2+ S2-$
- Accelerate of the anodic reaction due to the formation of iron sulfide: $Fe+S2- \rightarrow FeS+2e-$.

The schematic process of corrosion of ferrous metal due to SRB by the cathodic depolarization theory is shown in Figures 3 [15].
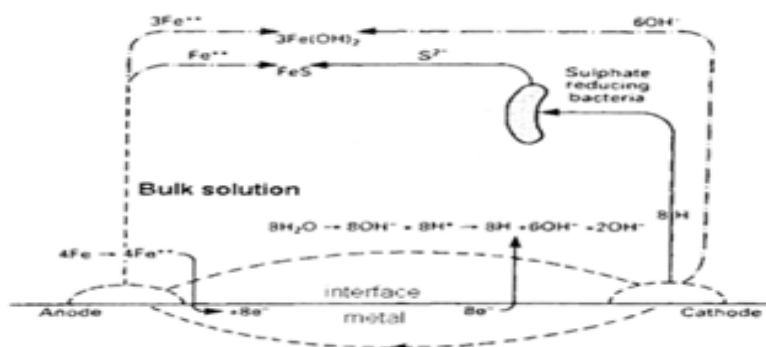

Figure 3: Schematic process of corrosion of ferrous metal [15].

The SRB – MIC corrosion is usually observed as localized pitting under deposits or tubercles that shield the organisms. The Damage is often characterized by cup-shaped pits within pits in carbon steel or subsurface cavities in stainless steel (Figures 4 and 5) [1]. Furthermore, pitting can act as an SCC initiator; because the "roots" of pits act as "stress magnifies" so that the applied stress becomes multiplied several times, resulting in stresses far more than the tensile yield strength, thus producing failure [10].
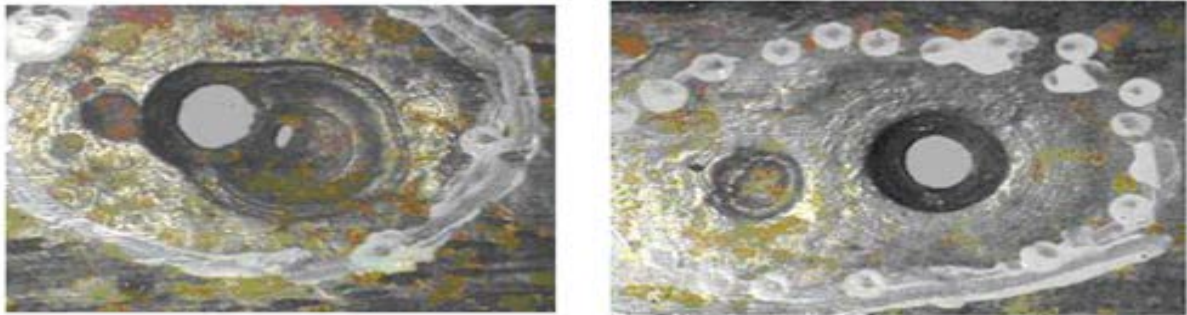
Figure 4: Pitting corrosion on the I.D of 6'' Carbon Steel sour after 2.5 years in operation. Pits are about 1-2 inches [1].
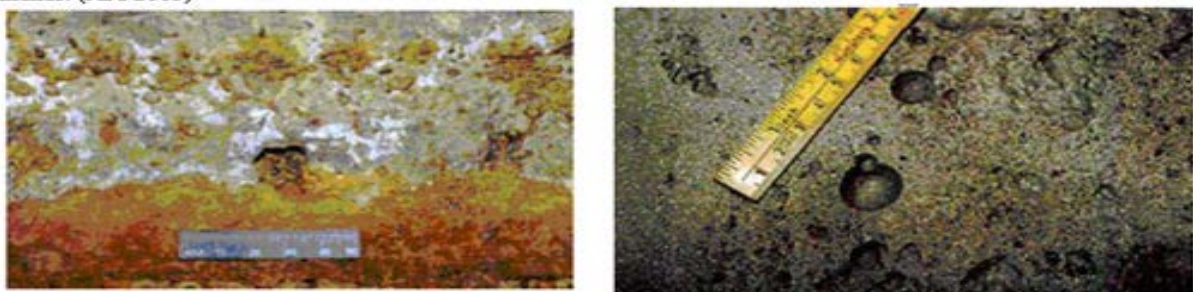
Figure 5: Carbon Steel oil line with MIC damage beneath tubercles before grit blasting and after [1].

4. Vulnerable Oil and Gas Units/Equipment

The below listed equipment/ unit have been considered the most vulnerable to MIC-SRB [1]:

- Heat exchangers and piping with a stagnant or low flow liquid.

- Product storage and water Tanks.

- Firewater systems.

- All equipment where the hydro-test water has not been removed.

5. How does equipment or system Become Vulnerable to MIC?

There are major factors, procedures and design practices that make materials more vulnerable to SRB-MIC

corrosion; however in this paper limited number of factors will be discussed:

5.1. Welding

Produces an altered microstructure, in size, shape, amount, and composition at Fusion and Heat Affected Zones, which makes the material more susceptible to MIC-SRB [5]. Figure 6. Shows a sample of extensive corrosion on the weld metal and fusion line [18].
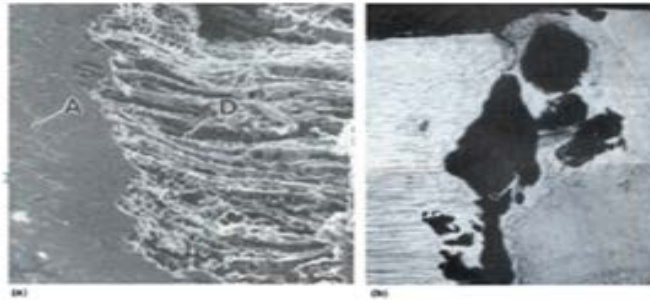
Figure 6: in (a) SRB-MIC showing a surface view of interdentritic attach at the fusion line of a stainless steel weldment (A) nondenritic and (D) Dendrite and (b) corrosion cross section [18].

5.2. Hydrotesting

Many historical cases of SRB-MIC are directly related to the stagnancy of microbiologically active waters [5]. An example of SRB attack resulted in severe pitting is shown the in figure.7 [10].
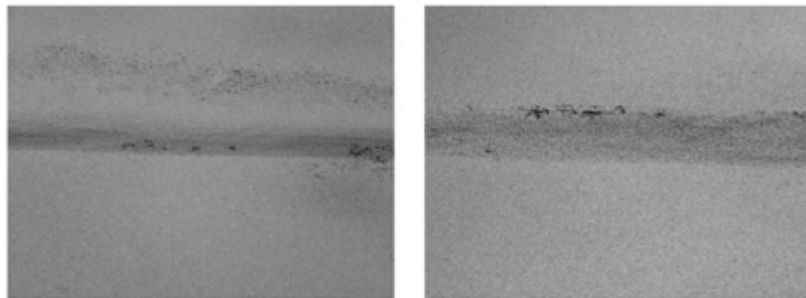
Figure 7: Sever pitting resulted from water left in the vessel after hydro testing [10].

5.3. Material Selection

Most common materials used to construct wide range industries are susceptible to MIC with varying degrees and probabilities including carbon and low alloy steels, 300 Series SS and 400 Series, aluminum, copper and some nickel base alloys, previous oil and gas refining plants cases will be presented [1].

- Carbon Steel: SRB is the main bacteria considered responsible for the microbial corrosion of carbon steel. It has a corrosion rate of between (0.7-7.4) mm/year [3].However, other study shows that the

corrosion rate to be (0.2-0.7) mm/year [5] and all scenario observed depends on the concentration of FeS involved.

- Stainless Steel: SRB-MIC in SS leads to pitting and crevice corrosion and as a percentage of total corrosion failures for stainless steel systems due to SRB-MIC may be as high as 20% [18].
- Copper: SRB-MIC leads to pitting and in the presence of high chloride concentrations, the copper chloride gets deposited between the copper metal and the cupper film resulted in pitting corrosion leads to the final pin-hole failure [7]. Copper is the most widely used in oil/gas industries equipment due to their availability and low prices [18].

6. Incubation time

The incubation time is estimated as short as few hours or can extend to several years. The length of this period is sensitive to operating temperature, pressure, PH value and steel metallurgy [1]. Carbon steel as example was investigated in the presence of SRB at different incubation time to study the material Weight, and it has been noticed that 0.003 g/cm2 was lost within 21 days only as shown in the figures from 8-11 [9]:
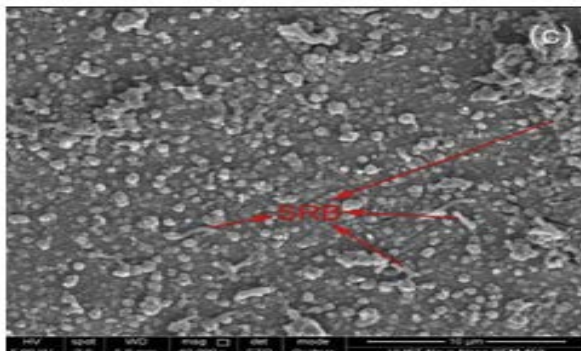

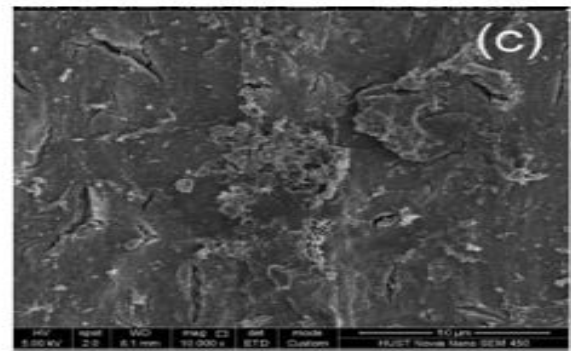Figure 8. SEM analysis of biofilm on coupons after 10-day incubation

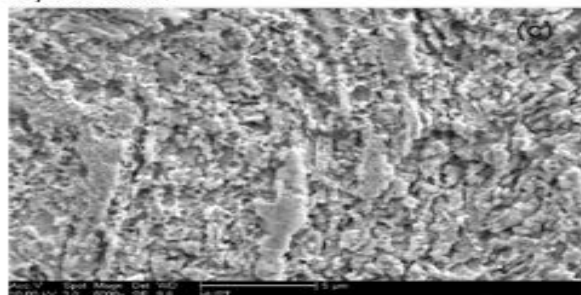Figure 9. SEM analysis of corrosion products on coupons after 21-day incubation

Figure 10. SEM analysis of coupon surfaces (corrosion products removed) after 21-day incubation
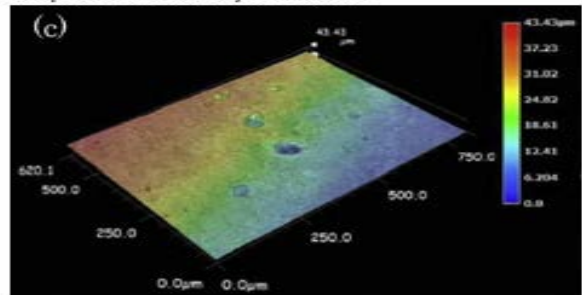
Figure 11. Morphologies of coupon surfaces after 21-day incubation (removed corrosion Product)

7. SRB-MIC Detection and Monitoring Methods

Testing to deduct for SRB is expensive and time-consuming, and considerable effort has been devoted to improving testing methods. Guidance for tests relating to oilfield practice is given in API* RP-38 and by the Institute of Corrosion [14]. Also, SRB testing should be conducted in association with other analyzes, such as pH, redox potential, oxygen content, total dissolved solids, and whenever possible, sulfide and sulfate content,

The below list of most common methods and techniques used in oil and gas production facilities to detect SRB-MIC:

7.1. Direct detection methods

These methods may have limitations such as minimum detection limit of SRB's and interference of inaccurate debris determinations of SRB numbers in turbid samples [4]

- **Quick (or rapid) Check Test:** The is a field test and may call as "acid test," a few droplets of diluted hydrochloric acid are added to the corrosion products and the if this is resulted in a smell of "rotten egg" then the corrosion products do contain sulfides [14].
- **Antibody Test:** commercially available only for SRB; it takes 20 min to an hour time for the result, and it's inexpensive (provided that there is microscopy available)
- **Radiorespirometry**:   Quantify SRB in the field and for testing biocide efficiency in the laboratory. It is a highly specialized method involving expensive laboratory equipment. Also, the handling of radioactive substances is highly regulated [14].
- **Fluorescent Antibody Microscopy**: This method counts the total number of bacteria in a sample can. The major advantage is speed, and the major limitation is they are specific only to the type of SRB used in their manufacture and a high degree of training required [4].

7.2. Culturing Bacteria

culturing in artificial growth media is accepted as the standard technique for the estimation of bacteria numbers. However, the limitations of this technique are time-consuming and not practical for daily operational use. [4]

7.3. The Molecular Biology Technique

 Is becoming more and more popular Genetic techniques and it mainly analyzes the DNA extracted from cultures samples. It's required specialized skills and laboratory facilities, and it's still in the development stages.[4]

8. Inspection and Monitoring

Currently, there is a wide variance in the in-service inspection techniques utilized by different oil and gas industries, this is because this type of corrosion may impact any process equipment, and each equipment should have a dedicated SRB MIC inspection program that may as well have different inspection methods. As a result, there are no sole recommended inspection methods can be standardized [1]. However recommends that inspection should be done using more than one methods. The most effective inspection methods are Visual Inspection, Magnetic Particle, Dye penetration testing and Ultrasonic test (including the advanced techniques such as TOFD and phase array) [1]. The new inspection practices show that above NDT methods are costly and time-consuming as the inspection method should cover a wide range of areas, and most recommended inspection methods are the long range ultrasonic, pulsed eddy current techniques and saturated low-frequency eddy current techniques[6].

All the above inspection methods are essential to identify the thickness reduction, thinning and to assess the impact of the pitting corrosion and ensure the current set up are safe for normal operation. As a result, it's highly recommended that inspection program should be established by the inspection frequency, critical location, Shape, inspection point design and the expected inspection coverage and specify the most effective method per application.

In oil and gas industry the most general practical method to monitor material degradation and corrosion is the On/Off-line corrosion monitoring systems that depend on basically coupons. This method is not always a reliable to monitor MIC-SRB corrosion in which there are deposits or stagnant areas. As a result, direct monitoring and control of the microorganisms are recommended [2].There are several early deduction operational performance indication that help to monitor SRB-MIC which are[1,2,6]:

- Reduction in the pumping performances.
- An increase in the loss of duty of a heat exchanger.
- Foul smelling water may be a sign of trouble.

9. Prevention and Mitigation

Prevention of SRB-MIC is considered one of the critical parts to ensure system reliability and safety. There are several factors that can be classified into three categories, treatment (biocides), cleaning and operational control [2]. Examples of these factors are:

- The effectiveness of biocides treatment is monitored by measuring biocide residual, microbe counts and visual appearance.
- Drain the equipment during shutdown or treating with biocides before layup.
- Maintain and monitor the flow velocities above minimum levels to avoid low flow and stagnant zones.
- Design the Systems to ensure sure they are clean and dry
- Protect underground structures utilizing cathodic protection, and monitoring programs.
- Apply and maintain coatings on the interior of pressure vessels and tanks.

Mitigation is considered the most important part to avoid the SRB-MIC corrosion failures, mitigation should be designed on the basis to set an effective microbiological control system. An effective program should be on the basis of:

- Keeping metal surfaces free from deposits.
- Incorporating corrosion inhibitors into the treatment program and ensure its effectiveness. Pre-passivating new and recently cleaned equipment.
- Using demineralized water, drain and dry as soon as possible after hydro-testing.
- Avoiding dead leg on the piping designs [5].

A sample of effective control plan as highlighted by should contain Four vital steps to be effective figure12. [10]

Steps	Factors to be considered
Confirmation	Vulnerability of material to MIC; physical, chemical, and biological vulnerability of the system and working conditions to MIC, including factors such as pH, temperature, the availability of nutrients, and required chemical species such as carbon and nitrogen; the availability of energy source, low-flow or stagnant water, existence of too many branches, or dead corners (in piping systems); existence of corrosion-enhancing bacteria in the system, finding corrosion by products unique to corrosion-enhancing micro-organisms (such as FeS for SRB), in some cases with high care, pit morphology (pit-within-pit) ...
Mitigation	Physical mitigation such as pigging for pipelines, chemical mitigation such as use of inhibitors and/or biocides, improving working conditions such as avoiding water stagnation, adjusting pH so that it will not help micro-organisms to grow and act, design modifications of the system, applying corrosion management ...
Control	Comparing corrosion rates before and after applying mitigation, comparing performance of the system before and after, cost-effectiveness of the mitigation program ...
Feedback	Documentation of working conditions before and after applying mitigation, documentation of the mitigation method(s) for later use ...

Figure 12: Four major factor for effective mitigation plan [10].

10. Recommendations

Based on the above literature reviews it would be recommended that a unified inspection programs is to be established for each critical equipment to suit the application with the most recommended inspection methods starting from the construction phase of the equipment to the commissioning phase. Furthermore, it would be also highly beneficial if a monitoring system and program is being published and addressed all common best practices with lesson learned to mitigate and control this type of corrosion phenomenon.

11. Conclusion

SRB-MIC is a very exciting subject for research, rather, complex and complicated damage mechanism. It has been causing several incidents, injuries, equipment failures and loss of production over the years. Based on the current researches and literatures the development of testing mechanism and unified inspection programs are in progress to reach effective mitigation plans and bacteria free environments.

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