Preservation of Caisson Leg

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Article Info

Abstract

Sacrificial Anodes were used commercially to protect caisson legs against corrosion in seawater. However, there was a paradigm shift in 2000 after an explosion occurred in a caisson leg, which prompted an investigation to ascertain the cause.

Subsequently, NACE published a **Technical Paper No.4200** under "Protection of Offshore Platform Caisson Legs with a Vapor Corrosion Inhibitor- A Case Study" in 2014.

The abstract of the paper states "In November 2000, **gas build-up inside the confined compartment** around an offshore platform caisson leg led to an explosion. **The gas was found to be hydrogen generated by the depleted anodes inside the Caisson Leg**. An investigation of the fatal explosion made several recommendations, including removal of the anodes, biocide-treated water and blasting grit that had accumulated inside the caisson legs over two decades."

Based on the above Technical Paper, the Research Team from Magna International and UABC have been approached by ADMA-OPCO to use Vapour Corrosion Inhibitors to protect the Caisson Leg over a period of 5 years. The recommended proposal includes the use of VCI technology, VCI products and a monitoring system to ensure the integrity of the recommended preservation methodology.

FINDINGS FROM MAGNA INTERNATIONAL AND UABC

Magna International and UABC have been tasked to consider said preservation with reference to the Technical Paper No. 4200.
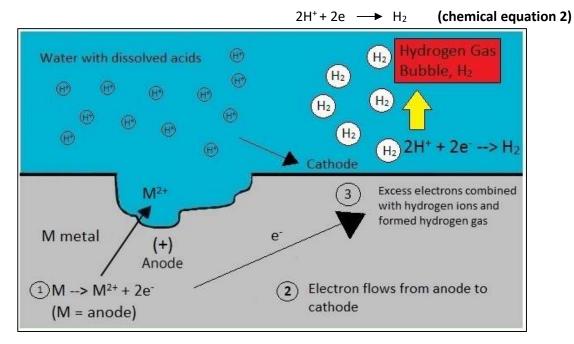
While studying the Technical Paper No. 4200, the research team discovered new findings and would like to highlight to all parties concerned that it is essential to include the

protection of the caisson leg against SRB when submitting the Technical Proposal.

The Research Team from Magna International and UABC found out that the likely cause of the explosion in the Caisson leg in 2000 was likely due to **hydrogen sulfide** rather than **hydrogen gas** as mentioned in Technical Paper No. 4200, because depleting of anodes will not result in significant presence of hydrogen gas unless the anodes were exposed to an **acidic environment** as shown in the **chemical equation 2.**

Anodic reactions involve oxidation of metal to its ions, e.g. for anode the following reaction occurs

$$M \longrightarrow M^{2+} + 2e \qquad \textbf{(chemical equation 1)}$$

whereas M equals to sacrificial anode.

For cathodic reaction where anode is exposed in an acidic condition, where hydrogen ion is predominant, the following chemical reaction will take place as mentioned below and in figure A.
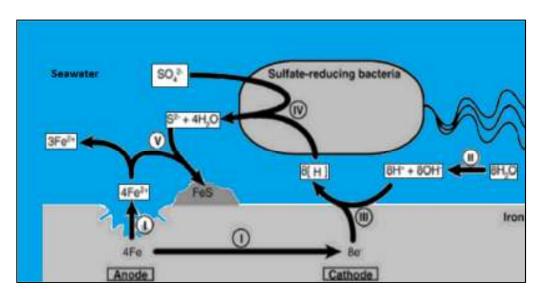
$$2H^+ + 2e \longrightarrow H_2 \qquad \textbf{(chemical equation 2)}$$

Figure A

It is imperative to note that the **Lower Explosion Limit (UEL) and the Upper Explosion Limit of hydrogen 18.3% and 59% respectively.**

Whereas the **LEL and UEL of H_2S is 4.5% and 45.5 % respectively, making it more prone to explosion than hydrogen.**

As seawater is alkaline and the hydrogen ion is not predominant, it is very unlikely that the

depleting anodes will generate enough hydrogen gas that led to said explosion.

in turn will promote Hydrogen Sulfide (H₂S), as shown in the figure B mechanism below.

Sulfate occurs widely in seawater, which is a nutrient for Sulfate Reducing Bacteria, hence seawater will promote the growth of SRB and

Figure B: Mechanism behind the formation of Hydrogen

I. Dissociation of Iron (Fe) due to Anode and Cathode arrangement.
$$4Fe \longrightarrow 4Fe^{2+} + 8e^-$$

II. Dissociation of water in Seawater.
$$8H_2O \longrightarrow 8H^+ + 8OH^-$$

III. Electrons that transferred from anode to cathode combine with hydrogen ions and formed hydrogen atom.
$$8H^+ + 8e^- \longrightarrow 8[H]$$

IV. Sulfate-reducing bacteria (SRB) used the hydrogen atom in its respiratory process to reduce sulfate (SO_4^{2-}) in the seawater. Hydrogen sulfide is produced.
$$SO_4^{2-} + 4[H] \longrightarrow H_2S + 2H_2O + 2OH^-$$

V. The newly-formed hydrogen sulfide reacted with Iron ions (Fe^{2+}) and caused sulfuric corrosion (FeS).
$$Fe^{2+} + H_2S \longrightarrow FeS + 2H^+$$

COMMON PROBLEMS IN CAISSON LEG

Element	Description

High chloride content in seawater	Promotes high electrochemical activity in Caisson Leg causing excessive flow of electrons from the anodic to cathodic points, resulting in severe corrosion.
Presence of Sulfate Reducing Bacteria (SRB)	Promotes the presence of Hydrogen Sulfide (H_2S), resulting in Sulfide Stress Cracking Corrosion (SSC).

CORROSION IN MARINE ENVIRONMENT

Corrosion occurs when a substrate is in contact with an environment that produces a potential difference between the metal and its environment or within the metal itself. The metal then reacts with its environment – usually oxygen in air– to return to its natural occurring state, usually its oxides.

In the marine industry, the environment that causes corrosion is seawater. Seawater is a complex matrix which **contains ions like sulfates, chlorides, calcium ions etc, which are charged in nature (either positively or negatively).** As such, it was reported that a solution full of charges promotes corrosion as it widens the potential difference between substrate and environment and within the substrate itself. It is especially notable that chlorides play the main role in the accelerating corrosion, as they are present as a majority as compared to other ionic species. Hydrogen Sulfide is another cause of concern due the reduction of sulfate presence in seawater by the Sulfate Reducing Bacteria.

As the marine industry seeks pre-emptive and preventive measures toward corrosion, corrosion inhibitors – cathodic inhibitors such as sacrificial anodes in this case – is one of the methodologies that were used.

NEEDS STATEMENT

The inherent problem of H_2S in the Caisson Leg is a cause for concern and need to be arrested.

Vappro 849 does not contain any biocides, as such, it does not contain any biocidal efficacy to combat Sulfate Reducing Bacteria (SRB).

The Research Team from Magna International and UABC would like to propose the use Vappro SRB-X which is based Glutaraldehyde CH_2 (CH_2 $CHO)_2$ chemistry in conjunction with the usage of Vappro 849.

Vappro SRB-X is the preferred biocide as its biocidal efficacy is not affected by the presence of H_2S, a paramount importance for combating SRB. It addition, it has lasting lingering biocidal effect.

OBJECTIVE

The objective of this proposal is to provide a comprehensible proven preservation methodology and using pragmatic scientific monitoring system that will ensure the integrity of the preservation methodology over a period of 5 years.

PRESERVATION PROPOSAL

Taking into consideration the findings above and since VCI Technology is the preferred technology by the client, the Research Team from Magna International and UABC would like to recommend the use Vappro 849, Vappro VCI Pouch and Vappro SRB-X for said preservation.

Propose the said preservation as follows:

i. Empty Caisson Leg of seawater.

ii. By means of a pressurized spray gun, spray Vappro SRB-X into the Caisson Leg to remove remnant of Sulfate Reducing Bacteria.

iii. Sulfate Reducing Bacteria (SRB) is anaerobic in nature, it will die when exposed to air, by means of an industrial air blower introduce voluminous of air into the Caisson Leg to speed up the drying process of Vappro SRB-X and enhance the killing rate of SRB.

iv. Then fog **Vappro 849** into the Caisson Leg by means of a blasting pot, just like fogging any powder, please ensure no naked flame is allowed near Caisson Leg.

v. The dosage for **Vappro 849 is 10 grams per 28 litres**, therefore the required amount of Vappro 849 for Caisson Leg with the volume of 112,000 litres is equal to 10grms x 112,000 litres divide by 28 litres= **40,000 grams or 40 kilos of Vappro 849.**

vi. To reinforce the protection of the Caisson Leg over the period of 5 years, the use Vappro Pouch is recommended as it is a slow release vapor corrosion inhibitor with lower vapor pressure than Vappro 849.

vii. One Vappro pouch is effective to protect up to 1410 litres of volume space, therefore 112,000 litres of volume space in Caisson Leg requires 112,000 divided by 1410 equal to 79.4 Vappro Pouches.

viii. About 80 Vappro Pouches will be held in suspension uniformly by means of nets on the cross bar.

ix. Please see figure C on how to install Vappro Pouches in the Caisson Leg.

x. Corrosion Coupons are held in suspension uniformly on the cross bar to monitor the effectiveness of VCI products used and to measure the electrochemical activity of the preserved structures. Please see Figure D on how to install Corrosion Coupons.
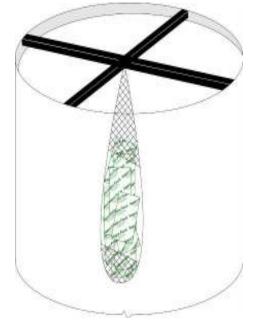

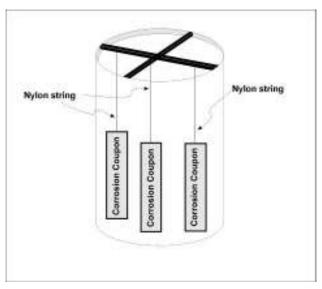**Figure C Install Vappro Pouches in the Caisson Leg**

Figure D How to Install Corrosion Coupons.

ANNUAL CORROSION MONITORING SYSTEM OF CORROSON COUPONS

Corrosion rate is the speed at which any metal in a specific environment deteriorates. It also can be defined as the amount of corrosion loss per year mm in thickness (mmPy). The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under reference.

It is found by: R = d/t expressed in µm/y but can also be expressed in terms of weight loss g/m2, mg/dm2.day, oz/ft2, among others. The total amount of lost thickness in micrometers is d = total. Loss occurrence is t = time in years.

Several pieces of data must be collected when calculating the corrosion rate of any given metal. Required data includes:

- Weight lost (the decrease in weight of the metal during the period of reference)
- Density of the metal
- Total surface area initially present
- Length of time taken

Corrosion rate is best expressed in terms of thickness or weight loss where the surface of

A = the surface area of the exposed metal

the metal corrodes uniformly across the area that has been exposed.

This rate may vary if the rate expressed by the function above is used to compare corrosion rates for a period not less than one year with rates calculated over short periods. This is because the short time rates are prone to fluctuating environmental changes from season to season and from day to day. This method involves the exposure of a weighed piece of test metal or alloy to the specific environment for a specific time. This is followed by thorough cleaning to remove the corrosion products and then determining the weight of the lost metal due to corrosion.

The rate can also be calculated as follows:

R = KW/ (AT)

K = constant

W = total weight lost

T = time taken for the loss of metal

MECHANISM OF VAPPRO 849 AND VAPPRO POUCH

Vappro 849 is an anodic inhibitor which is a passivation inhibitor. It acts by a reducing anodic reaction, blocking the anode reaction and supporting the natural reaction of passivation metal surface, also forming an absorbed cohesive and insoluble layer on the metal.

The Vappro 849 anodic inhibitors reacts with metallic ions Me^+ produced on the anode, forming generally insoluble hydroxides, which are deposited on the metal surface as insoluble film and impermeable to metallic ions. From the hydrolysis of inhibitors results in OH- ions, Figure E shows the mechanism of the anodic inhibitor effect. It is very important

that the Vappro 849 inhibitor concentration should be high enough as under-dosage of Vappro 849 affects the integrity of formation film protection.

In summary, The Research Team from Magna International and UABC wish to bring to the attention of ADMA-OPCO that our Technical Preservation Proposal is more comprehensive than the said recommendation mentioned in Technical Paper No.4200.

Our Proposal covers the usage of VCI technology and arrests the concern of Sulfate Reducing Bacteria, thereby eliminating the presence of H$_2$S and Sulfide Stress Corrosion (SSC) in the Caisson Leg.
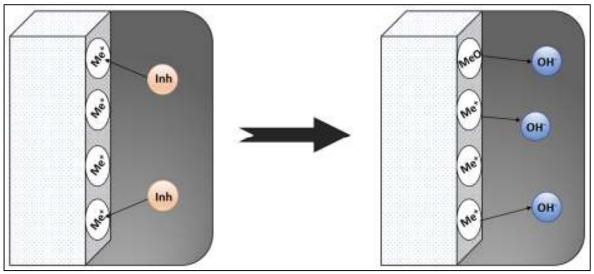

Figure E Mechanism of the Anodic Inhibitor

SULFATE REDUCING BACTERIA AND HYDROGEN SULFIDE PRODUCTIONS

Sulfate Reducing Bacteria (SRB) are non-fermentative anaerobes that obtain their energy for growth from the oxidation of organic substances using inorganic sulfur oxy-acids or nitrate as terminal electron acceptors whereby sulfate is reduced to sulfide. Biogenic sulfide may result in the corrosion of mild steel in an anaerobic environment. For sulfate-reducing bacteria to produce hydrogen sulfide at such high concentrations a number of conditions must be met. They include a **sufficiently** high sulfate concentration, the presence of sufficient biodegradable organic materials and nutrients, time, absence of oxygen (anaerobic), and reducing conditions for the microbial production of hydrogen sulfide gas.

The factors affecting **SRB growth rates** are as follows:

- **Temperature** – general range: 20°C to 45°C. Optimum: 25°C to 38°C

- **pH** – general range: 6 to 9. Optimum: $7 \leq pH < 8$

- **Salinity requirements**: SRB can survive and grow over a range of salinities. In addition, some SRB have a definite requirement for saline solutions. They are usually non-occurring in fresh waters.

- **Nutrients:** In addition to the main metabolic requirement many nutrients are also required. The common ones are phosphorus (dissolved phosphate ion), nitrogen (in the form of ammonia), calcium and magnesium (found as dissolved salts).

- Sulfide inhibition and adhesion of cells to the metal

- **Limiting reactant** is generally carbon source. However, in this case, **sulfate ions** could be the limiting reactant as well. It was found that the initiation of biocorrosion due to SRB only occurred in the presence of sulfate species tested on the corrosion of mild steel under different media both with and without sulfate ions. Additionally, it can be said that **too high** an initial concentration of sulfate ions may inhibit the sulfate reduction rate of SRB, thus lowering the production rate of H_2S.

H_2S, instead of hydrogen ion could act as cathodic reactant,

$$\text{i.e. } 2H_2S + 2e^- \longrightarrow 2HS^- + H_2$$

Adsorbed H_2 is removed to facilitate reduction of sulfate to sulfide by the bacteria, hydrogenase. The activity of hydrogenase of SRB combines the adsorbed hydrogen atoms to produce H_2 gas first and then regenerates protons (H^+ ions). The produced sulfide would react with available proton to form H_2S.

VAPPRO SRB-X

Sulfate reducing bacteria (SRB) are found in most oilfield systems posing a serious challenge for effective control of microbial contamination in a production system. In view of the above, Vappro SRB-X was developed to combat said problem.

Vappro SRB-X is chemically stable in the presence of sulfides and organic acids making it very effective to combat sulfate reducing bacteria and acid producing bacteria. It does not react with and is not deactivated by H_2S or other organic acids. The said chemical properties ensure that Vappro SRB-X when added into the oilfield systems will be fully available to act as biocide.

Some common applications of the product are described below:

- *Water Flood Injection Water*

Vappro SRB-X exhibits excellent stability in oilfield injection waters, which ensures that its antimicrobial activity will not be diminished in long pipelines. Hard waters and brines do not adversely affect its biocidal efficacy, and Vappro SRB-X is non-ionic, so it won't interfere with the action of demulsifiers, corrosion inhibitors, or surfactants. Vappro SRB-X is typically slug dosed into the injection water on a daily or weekly basis at 50 to 2500 ppm active up to 4 hours, although the exact treatment regimen will depend on the condition of the system and the amount of water being treated.

- *Drilling, Completion, Workover, and Fracturing Fluids*

Vappro SRB-X functions as a biocide over a board pH range and its efficacy I much faster at neutral to alkaline pH than at acidic pH. It is an excellent choice for use in preserving drilling muds and other oilfield fluids that are typically alkaline in pH. The combination of rapid alkaline efficacy at the typical use rate of 25 to 500 ppm as active and proven stability and effectiveness in high salinity matrices, ensures microbial protection of these important fluids.

- *Produced Waters*

Unlike some other biocides, Vappro SRB-X does not react and is not deactivated by H_2S or other organic acids. It is stable in the presence of sulfides and other organic acids commonly found in waterflood injection system. Vappro SRB-X is typically added in slug doses on daily to weekly basis at a concentration of 50 to 2500 ppm as active.
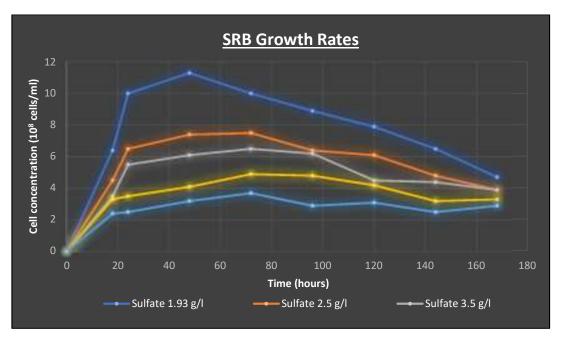
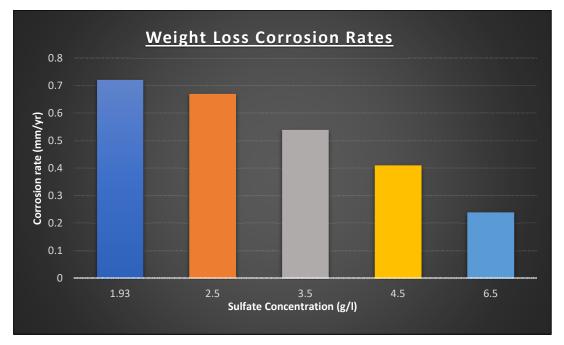**Figure F: SRB cell growth rates at different initial sulfate concentrations in the medium**

Figure G: Weight loss corrosion rates with different initial sulfate concentrations in the medium at 37°C, one week after inoculation.

From Figure F (above) sulfate concentration of 1.93 g/l peaked above the rest significantly after 48 hours, which translates to the highest corrosion rate (seen in Figure F).

We can understand from Figure F that SRB concentration was decreased as the initial sulfate concentration increases from 1.93 g/l to 6.5 g/l. Subsequently, as observed from Figure G, a lower corrosion rate was obtained when the SRB growth was hindered.

Similarly, sulfate concentration of 6.5 g/l tends to inhibit SRB growths much better than the rest for the whole duration of the testing (Figure F), hence giving rise to the lowest corrosion rates, as seen in Figure G.

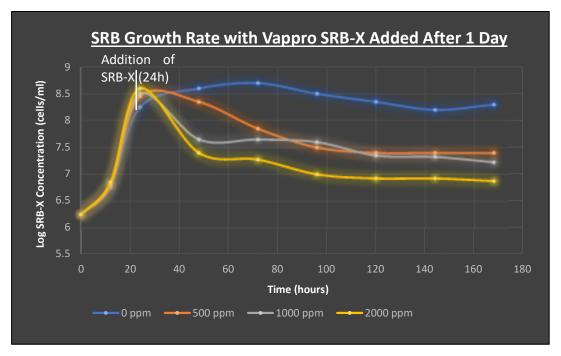This behaviour can be attributed to the increasing toxicity of sulfates towards SRB metabolism or sulfate reduction.

Figure H: SRB cell growth rates in a medium with SRB-X added after 1

One day after inoculation, the culture was already found to have a good growth with an SRB cell count of 1.8×10^8 cells/ml. Therefore, a high Vappro SRB-X concentration was needed to achieve the inhibitory effect of SRB cell growth as seen in figure H.

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