

Inhibition of Seawater Steel Corrosion Via Colloid Formation

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Abstract— The main purpose of this research was to establish the effectiveness of the V844* corrosion inhibitor for seawater on various metallic materials: carbon steel, aluminum and copper alloy at different concentrations via colloid formation. The changes in both physical and chemical properties of seawater, including pH, total hardness, alkalinity, total dissolved solids (TDS) and conductivity at different concentrations of V844 were assessed, too. The test procedure involves dissolving the V844 corrosion inhibitor (CI) powder provided by Magna International Private Limited in seawater to obtain a stock solution of 4% V844 in seawater, which was further diluted to obtain the remaining concentrations. The analysis of parameters begun when various metal species, polished beforehand, were placed into the solutions. The analysis was observed over a period of 26 days and a total of 9 sets of readings were obtained. From our observation and ear power stations burning fossil-fuels generating acidic rains, the pH can diminish to 6.

I. INTRODUCTION

Corrosion is a worldwide problem that strongly affects natural and industrial environments, in particular the oil and gas industry. All its numerous and diverse facilities, equipment and installations require products, methods and techniques to protect, mitigate and prevent the corrosion damage (Hummel, 2014; Raichev et al., 2009). Corrosion inhibitors (CI) are one of the modern technologies applied for the management of corrosion, for the benefit of the global economy (Garcia, 2013).

The world and Mexico in particular are undergoing an intense reformation process in the energy sector that is involving its oil, natural gas, and electricity industries. The abundant resources, such as deep-sea oil and shale gas, will be utilized; and additional refineries and pipelines will be built with the active participation of heavy foreign investments. The reform was recently approved by the Mexican parliament and is setting Petroleos Mexicanos (PEMEX), the national oil company, on the way to becoming a world oil enterprise (Layoza, 2014).

II. SEAWATER CORROSION

The sea is a dynamic system in permanent motion, with complex surface currents and winds blowing over its surface generating waves that reach the coast and its facilities and installations.

Seawater consists of a solution of many salts and numerous organic and inorganic particles in suspension. Its main characteristics are salinity and chlorinity and, from the corrosion point of view, dissolved oxygen (DO) content which ranges from 4 to 8 mg/L, depending on temperature and depth. Its minor components include dissolved gases – CO₂, NH₃ and H₂S – found in seawater contaminated by urban sewage. The oceans house algae, bacteria and phytoplankton that generate about half of the oxygen in the atmosphere.

Ocean surface salinity is determined by the balance between water lost by evaporation and water gained by precipitation. The salt concentration, particularly NaCl, varies from 2.0% to 3.5%, according to the sea location and the massive addition of fresh river water. For instance, in the Red Sea, an enclosed basin, salinity at high summer temperatures is 4.1%, but in the Baltic Sea it is about 2.0% since many rivers feed into it.

Seawater is slightly alkaline, with a pH about 8.0 but when it is contaminated by acids, such as in coastal regions near power stations burning fossil-fuels generating acidic rains, the pH can diminish to 6.

III. CORROSION INHIBITORS

In the last years the use of CI is rapidly expanding worldwide, for numerous technological and industrial applications; as cooling water systems (Schorr et al., 2012), steel reinforced concrete, protected storage of military and electronic equipment (Valdez et al., 2003), acid pickling and cleaning (Carrillo et al., 2012) oil and gas industry, as additives to coatings, paints and elastomers, for corrosion avoidance in oil pipelines (Hilleary et al., 2014; Murthy, 2014).

The importance and relevance of the CI technology are evident by the many patents gathered in published reviews (Inzunza et al., 2013; Bastidas et al., 2005).

To prevent atmospheric corrosion, vehicles are covered, during long periods of time, with plastic sheets impregnated with vapor phase corrosion inhibitors (VPCI), also called Volatile CI (VCI).

CI slows the rate of corrosion reactions when added in relatively small amounts to the treated system. They are classified into three groups:

- Anodic inhibitors, which retard the anodic corrosion reactions by forming passive films.
- Cathodic inhibitors, which repress the corrosion reaction such as reduction of DO.
- Adsorption inhibitors, such as amines, oils, and waxes, which are adsorbed on the steel surface to form a thin, protective film that prevents metal dissolution.

IV. A COLLOIDAL CORROSION INHIBITOR

This polymolecular CI is added to seawater as a powder; then it converts into a colloidal suspension with nanoparticles dispersed in the water. These particles are adsorbed on the steel wall, forming a thin protective film. The performance of this inhibitor depends on physical, biological and chemical factors. The factors under analysis for this study include hardness, alkalinity, conductivity and pH. Other factors such as dissolved oxygen, etc. contributes as well but is not within our scope of this investigation.

We propose that the mechanism of colloidal formation functions by combining of VAPPRO 844 with Ca^{2+} ions present in seawater to form an inert colloidal particle which is cationic in nature.



The colloidal particles formed adhere to the metal and prevent the onset of corrosion by preventing the loss of electrons. This causes the electrochemical cell to be incomplete and corrosion cannot occur.

The CI VAPPRO 844 powder was specially developed to combat corrosion on mild-steel and iron structures in stagnant seawater found in ballast tanks of ships and rigs.

In this study the CI was tested to establish its effectiveness, the changes in both physical and chemical properties of seawater which include pH, total hardness, alkalinity and total dissolved solids/conductivity at different concentrations, with the purpose to find the optimum CI concentration and to provide recommendations on how the effectiveness of the inhibitor can be improved to reduce corrosion.

V. RESULTS AND DISCUSSION

The practices recommended in the ASTM (ASTM, 2013) and NACE (NACE, 2000) standards were followed for evaluating the steel corrosion resistance. The measured weights for carbon steel show that at 0.05% concentration, there was the least weight loss, indicating the least corrosion. Over the period of 26 days, the steel control specimen in seawater had lost 0.58g, while those with inhibitor on the average had reduced the metal loss to about 0.10g. This was even lower than the tap-water control of 0.15g metal loss. The most effective CI concentration was 0.05% as the metal loss was only 0.03g (Table 1).

TABLE I
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Inhibitor Concentration, %	Corrosion Extent, g	Inhibitor Efficiency, %
-	0.58	-
0.0125	0.19	22.6
0.025	0.11	81.0
0.05	0.03	94.8
0.10	0.05	91.3
0.25	0.09	84.4

The inhibition efficiency (IE) was determined using the equation:

$$IE\% = \frac{M_u - M_i}{M_u} \times 100 \quad (2)$$

Where M_u and M_i are the weight loss of the steel in uninhibited and in inhibited solutions.

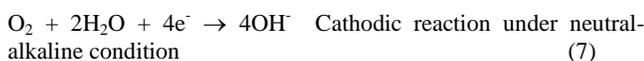
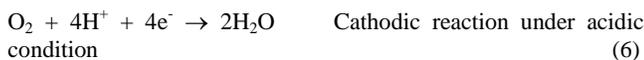
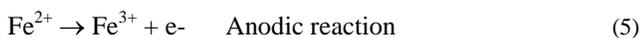
VI. CARBON STEEL CORROSION REACTIONS

A drop in water hardness was observed, however, this was not reflected in the conductivity. This means that other ions present in seawater had interacted other than Ca^{2+} and Mg^{2+} ions. The proposed reactions include:

Vapro 844 + Ca²⁺/ Mg²⁺ → Gelatinous white precipitate (3)

Vapro 844 + Ca²⁺/ Mg²⁺ + Fe²⁺/Fe³⁺ → Insoluble complex (4)

As iron underwent the anodic reaction, the cathodic reaction express the oxygen reduction reaction:



In all the above reactions, the reduction of the hydrogen ions or the production of hydroxyl ions raised the pH of the electrolyte in fresh water. Whereas, in seawater, the cathodic reduction observed by equations 8 and 9 produced a slightly alkaline surface condition which precipitated CaCO₃ and Mg(OH)₂.

In both mild steel pieces at 0.25% and 0.1% Vapro 844 in seawater, with pH range 5-6, dark pits were visually observed on the metal towards the end of the analysis. These pits were much likely to be formed at the anodic area, due to the formation of the precipitate layer.

At 0.025% Vapro 844 in seawater and below, at pH 7.5-8.0, the steel pieces started to corrode. Thus, the inhibitor was not useful at such low concentrations.

At 0.05% Vapro 844 in seawater, the pH range was about 7.0. With support from ferroxyl indicator test and weight loss test, it proved that there was optimum corrosion inhibition at this concentration of Vapro 844 in seawater, though with some staining of the metal (Figure 1).

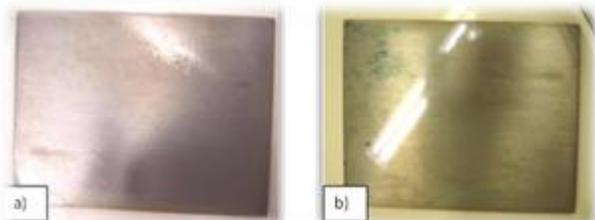


Figure 1: Carbon steel samples exposed to seawater and 0.05% Vapro 844 before (a) and after (b) immersion in ferroxyl indicator.

VII. APPLICATIONS

Oil tankers, also called petroleum tankers, are ships specially designed and constructed at American and Asian shipyards, for the bulk transportation of crude oil from the extraction sites (onshore and offshore) to the refineries. Smaller tankers are used to move refined products: fuel derivatives to the market. Since oil tankers were involved in damaging oil spills in the last years they are strictly regulated and controlled (Heiderbach, 2011; Chilingar, 2008).

Petroleum steel tanker (Figure 2) are cheaper and more efficient for oil transportation than submarine pipelines installed on the seabed, for instance to deliver oil from North Africa to south Europa. In its way back, the tanker holds are full of seawater to provide adequate stability to the tanker (Figure 3). The CI is added to this ballast water. Pipes, storage tanks (Figure 4) and pumps, using water for hydro test are dosed with the same CI (Schorr et al., 2015).



Figure 2: Petroleum transportation tanker showing holds.

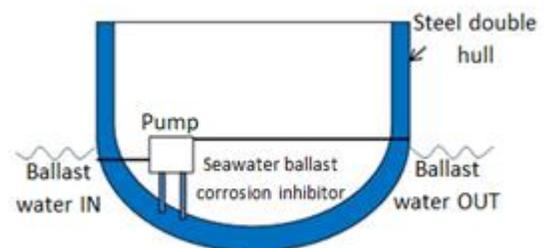


Figure 3: Ballast water tank.



Figure 4: Fire protection water storage tank.

VIII. CONCLUSIONS

From the experimental observations, mild steel was protected with Vapro 844 corrosion inhibitor at 0.05% inhibitor concentration, having only slight stains after a period of 26 days.

Changes in seawater parameters were observed when the powder CI was introduced.

Vapro 844 powder contributed to the increase of conductivity when it was introduced into the solution, however, when it reacted with the ions in seawater to form colloids, the conductivity dropped. The introduction of CI made the solution more acidic due to the mild acidic properties of Vapro 844.

The higher concentration of inhibitor added, the lower the alkalinity. For hardness, it showed that the calcium and magnesium ions were indeed used up in the reaction. This proved that the Vapro 844 powder followed the proposed reaction mechanism to form colloids.

REFERENCES

[1] ASTM G31-13, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (West Conshocken, PA: ASTM International).

- [2] Bastidas D. M., Cano E., Mora E. M., Volatile Corrosion Inhibitors: A Review, *Anti-Corrosion Methods and Materials*, Vol 52, No. 7, pp. 71-77, 2005.
- [3] Carrillo I., Valdez B., Schorr M., Zlatev R., Inorganic inhibitors mixture for control of galvanic corrosion of metals cleaning processes in industry, NACE Conference, 2012, USA.
- [4] Chilingar G. V., et al., *The Fundamentals of Corrosion and Scaling for Petroleum and Environmental Engineers* (Houston, TX: Gulf Publishing Co., 2008).
- [5] Garcia R., Valdez B., Schorr M., Eliezer A., Green Corrosion Inhibitor for Water Systems, *MP 52*, 6 (2013): pp.48-51.
- [6] Heidersbach R., *Metallurgy and Corrosion Control in Oil and Gas Production* (Hoboken, NJ: John Wiley and Sons, 2011).
- [7] Hilleary J., Dewitt J., Corrosion Rate Monitoring in Pipeline Casings, *MP 53*, 3(2014): pp. 28
- [8] Hummel R., *Alternative Futures for Corrosion and Degradation Research*, Potomac Institute Press, 2014, pp. 2-13
- [9] Inzunza R. G., Valdez B., Schorr M., Corrosion inhibitors patents for industrial applications. A review, *Recent Patents on Corrosion Science* 3, 2 (2013): pp. 71-78.
- [10] Layoza E., Building the PEMEX of tomorrow, Mexico oil and gas review, *New Energy Connections*, pp. 6-7, 2014.
- [11] Murthy T., Monitoring of Chemical Treatment is Essential to Prevent Internal Corrosion, *MP 53*, 9(2014): pp. 54
- [12] NACE TM0169-2000, "Laboratory Corrosion Testing of Metals" (Houston, TX: NACE International, 2012).
- [13] Raichev R., Veleva L., Valdez B., "Corrosión de Metales y Degradación de Materiales," Editor: M. Schorr, Universidad Autónoma de Baja California (2009), p. 281-284. (Spanish).
- [14] Schorr M., Valdez B., Ocampo J., So A., Eliezer A., Materials and corrosion control in desalination plants, *MP 51*, 5 (2012): pp 56-61.
- [15] Schorr M., Valdez B., Salinas R., Ramos R., Nedev N., Curiel M., Corrosion Control in Military Assets, International Material Research Congress 2015, Symposium 6J NACE: Corrosion and Metallurgy, Cancun, Mexico.
- [16] Valdez B., Flores J., Cheng J., Schorr M., Veleva L., Application of vapour phase corrosion inhibitors for silver corrosion control in the electronic industry, *Corrosion Reviews* 21, 5-6 (2003): pp 445- 457.