Inhibition of Seawater Steel Corrosion via Colloid Formation

N. Cheng and J. Cheng, *Magna International Pte., Ltd., Singapore and Canada*
B. Valdez and M. Schorr, *University of Baja California, Mexico*
J.M. Bastidas, *National Center for Metallurgical Research, CSIC, Spain*

The performance of a volatile corrosion inhibitor (VCI) on steel via colloid formation through its reaction with Ca and Mg ions in seawater was studied. The physical and chemical properties of seawater, with and without the VCI at different concentrations, were determined. The VCI's efficiency was assessed, and its suitability for the steel system in seawater was indicated at an optimal concentration of 0.05%.

Corrosion and degradation of materials are pernicious problems that affect environment quality, industry efficiency, and infrastructure assets.[1-2] All of these diverse facilities and installations require products, methods, and techniques to protect against, mitigate, and prevent corrosion damage. Volatile corrosion inhibitors (VCIs) are one of the modern technologies used to manage corrosion for the benefit of the global economy.[3]

Seawater Corrosion

The sea is a dynamic system in permanent motion. Complex surface currents and winds blowing over its surface generate waves that reach the coast and its industrial facilities located there.

Seawater is a solution consisting 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 that ranges from 4 to 8 mg/L depending on temperature and depth. Seawater's minor components include dissolved gases—carbon dioxide (CO_2), ammonia (NH_3), and hydrogen sulfide (H_2S)—from urban sewage contamination. 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 from evaporation and water gained through precipitation. The salt concentration, particularly sodium chloride (NaCl), varies from 2.0 to 3.5% according to the sea location and added amounts of fresh river water. For instance, salinity of the Red Sea (an enclosed basin) at high summer temperatures is 4.1%, but salinity of the Baltic Sea is ~2.0% since many rivers feed into it.

Seawater is slightly alkaline, with a pH of ~8.0. When it is contaminated by acids (i.e., in coastal regions near power stations burning fossil fuels and generating acidic rains), the pH can drop to 6.0.

Corrosion Inhibitors

In recent years, the use of VCIs has rapidly expanded worldwide for numerous technological and industrial applications such as cooling water systems;[4] steel-reinforced concrete; protected storage of military and electronic equipment;[5] acid pickling and cleaning;[6] the oil and gas industry; as additives to coatings, paints, and elastomers; and for corrosion avoidance in oil pipelines.[7-8] The importance and relevance of VCI technologies are evident by the many patents gathered in a recently published review.[9]

VCIs slow the rate of corrosion reactions when added in relatively small amounts to water. 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 (e.g., by reducing 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

A Colloidal Corrosion Inhibitor

A polymolecular VCI, VAPPRO 844†, was studied, which is added to seawater as a powder, and then it converts into a colloidal suspension with nanoparticles dispersed in the water. These nanoparticles are adsorbed on the steel surfaces and a thin, protective film is formed. The performance of this inhibitor depends on physical, biological, and chemical factors. The factors under analysis for this study included solution hardness, alkalinity, conductivity, and pH. Other factors, such as DO, contribute as well but were not within the scope of this investigation.

It is proposed that the mechanism of colloidal formation functions by combining the inhibitor (CI) with Ca^{2+} ions present in seawater to form an inert colloidal particle that is cationic in nature, as shown in Equation (1):

$$Ca^{2+} + CI \rightarrow Ca^{2+}\text{-}CI \text{ complex} \quad (1)$$

The formed colloidal particles 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 VCI 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 VCI was tested to establish its effectiveness and to determine the changes in both physical and chemical properties of the seawater, which include pH, total hardness, alkalinity, and total dissolved solids/conductivity, at different VCI concentrations. The purpose was to find the optimum VCI concentration and provide recommendations on how the effectiveness of the inhibitor could be improved to reduce corrosion.

†Trade name.

Results and Discussion

Weight Loss

The practices recommended in ASTM G31[10] and NACE TM0169[11] were followed for evaluating the steel corrosion resistance. The measured weights for mild 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 without inhibitor had lost 0.58 g, while those specimens in seawater with inhibitor had reduced metal loss—~0.10 g on average. This was even lower than the tap water control of 0.15-g metal loss. The most effective VCI concentration was 0.05%, as the metal loss was only 0.03 g (Table 1).

The inhibition efficiency (IE) was determined using Equation (2):

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

where M_u and M_i are the weight loss of the steel in uninhibited and inhibited solutions, respectively.

Mild Steel Corrosion Reactions

A drop in solution hardness was observed; however, this was not reflected in the conductivity. This means that ions other than Ca^{2+} and Mg^{2+} had interacted in the seawater. The proposed reactions are shown in Equations (3) and (4):

$$CI + Ca^{2+}/Mg^{2+} \rightarrow \text{Gelatinous white precipitate} \quad (3)$$

$$CI + Ca^{2+}/Mg^{2+} + Fe^{2+}/Fe^{3+} \rightarrow \text{Insoluble complex} \quad (4)$$

TABLE 1. INHIBITION EFFICIENCY OF VCI IN SEAWATER

Inhibitor Concentration (%)	Metal Loss (g)	Inhibition 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

As iron underwent the anodic reaction in Equation (5), the cathodic reaction expressed the oxygen reduction reaction under acidic conditions shown in Equation (6) and under neutral alkaline conditions in Equation (7):

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (5)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (6)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (7)$$

In all of these reactions, the reduction of the hydrogen ions or the production of hydroxyl ions raised the pH of the electrolyte in fresh water. However, in seawater, the cathodic reduction observed by Equations (8) and (9) produced a slightly alkaline surface condition, which precipitated calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$]:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow H_2O + CaCO_3 \quad (8)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (9)$$

On mild steel pieces in seawater with 0.25 and 0.10% VCI and a pH range of 5 to 6, dark pits were observed on the metal toward the end of the analysis. These pits were much more likely to be formed at the anodic area due to the formation of the precipitate layer.

Steel pieces in seawater with 0.025% or less VCI and a pH of 7.5 to 8.0 started to corrode. Thus, the inhibitor was not beneficial at such low concentrations.

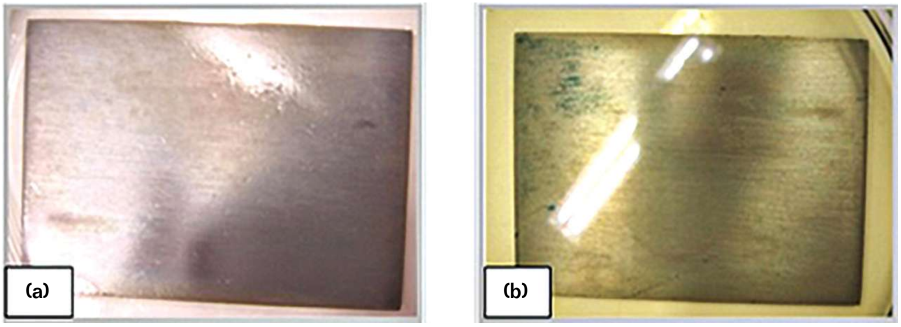

FIGURE 1 Mild steel samples exposed to seawater and 0.05% VCI 844 before (a) and after (b) immersion in ferroxyl indicator.

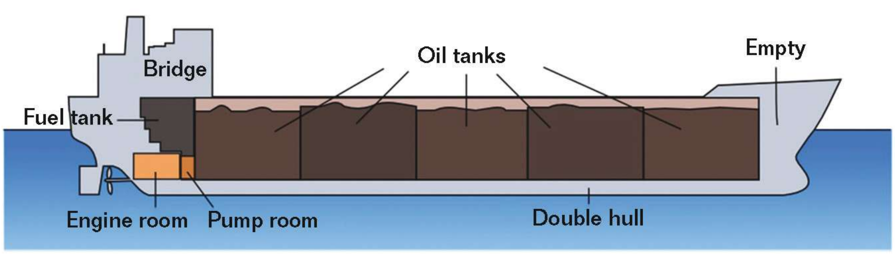

FIGURE 2 Petroleum transportation tanker showing holds.

With 0.05% VCI in seawater, the pH range was ~7.0. Immersion in a ferroxyl indicator and weight loss tests demonstrated that there was optimum corrosion inhibition at this concentration, although the metal had some staining (Figure 1).

Applications

About 4,400 petroleum transportation tankers from oil-producing countries cross the oceans and seas of the world to energy-consuming countries. If, on average, each tanker has 10 holds, it means 44,000 holds require a VCI for their ballast seawater.

Petroleum steel tankers (Figure 2) are cheaper and more efficient than submarine pipelines installed on the seabed for oil transportation. For their trip back, the tanker holds are filled with seawater to provide adequate stability (Figure 3). A VCI is added to this ballast water. Pipes, storage tanks (Figure 4), and pumps using water for hydrotesting also can be dosed with the same VCI.

Conclusions

From the experimental observations, mild steel was well protected with a VCI concentration of 0.05%, showing only slight staining after a period of 26 days.

Changes in seawater parameters were observed when the VCI powder was introduced. It contributed to the increase of conductivity when introduced into the solution; however, when it reacted with the ions in seawater to form colloids, the conductivity dropped. The introduction of the VCI made the solution more acidic due to the mild acidic properties of this particular VCI.

Higher concentrations of inhibitor reduced the alkalinity of the seawater. For solution hardness, the calcium and magnesium ions were consumed in the reaction. This confirmed that the VCI powder followed the proposed reaction mechanism to form colloids.

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N. CHENG is the founder and chairman of Magna Group, consisting of Magna International; Magna F.E. Chemical Pte., Ltd.; Magna Chemical Canada, Ltd.; Magna Australia Pvt., Ltd.; and Lupromax International Pte., Ltd. He graduated as a marine engineer under the United Nations Development Program (UNDP) Scholarship. He is recognized as Singapore's leading inventor and the Singaporean with the highest number of patents from the Intellectual Property of Singapore. He is an inventor of several technologies for corrosion protection such as vapor corrosion inhibitors,

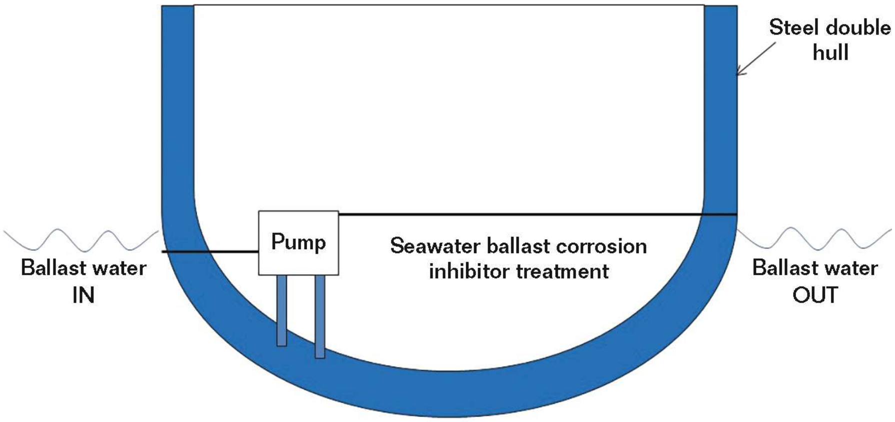

FIGURE 3 Ballast water tank.

FIGURE 4 Fire protection water storage tank.

heat-activated technology lubricants, molecular reaction surfaces, concrete rebar inhibitors, vapor biocorrosion inhibitors, and colloidal corrosion inhibitors.

J. CHENG is the president and CEO of Magna Chemical Canada, Inc. and Lupromax USA, LLC. He graduated with a bachelor's degree in education. Cheng oversees the activities of the Magna Chemical Group in the NAFTA Region. He contributed to the NAVSEA Warfare Research Center—Dahlgren Division by providing technical information for the development of a gelled fuel used for forest firefighting applications. Cheng is also the inventor of formulations for vapor corrosion inhibitors in cohesive paper and electro-spray, and designed master batch additives along with several VCI products that are being applied worldwide.

B. VALDEZ was the director of the Institute of Engineering during 2006-2013, Universidad Autonoma de Baja California, Blvd. Benito Juarez y calle de la Normal s/n, Colonia Insurgentes Este, 21280 Mexicali, Baja California, Mexico, benval@uabc.edu.mx. He has a B.Sc. in chemical engineering, a M.Sc. and Ph.D. in chemistry, and is a member of the Mexican Academy of Science and the National System of Researchers in Mexico. He was the guest editor of *Corrosion Reviews,* in which he produced two special issues on corrosion control in geothermal plants and the electronics industry. Valdez is a full professor at the University of Baja California. His activities include corrosion research, consultancy, and control in industrial plants and environments. During the IMRS Congress in August 2013, he received a "Distinguished Service Award" from NACE International and the NACE Central Mexico Section. He has been a NACE International member for 26 years.

M. SCHORR is a professor (Dr. Honoris Causa) at the Institute of Engineering, Universidad Autonoma de Baja California, mschorr2000@yahoo.com. He has a B.Sc. in chemistry and a M.Sc. in materials engineering from the Technion-Israel Institute of Technology, with 50 years of experience in industrial corrosion control. From 1986 to 2004, he was the editor of *Corrosion Reviews.* He has published 360 scientific and technical articles on materials and corrosion in English, Spanish, and Hebrew. He has worked as a corrosion consultant and professor in Israel, the United States, Latin America, Spain, South Africa, and Europe. During the IMRS Congress in August 2010, he received a "Distinguished Service Award" from NACE and the NACE Central Mexico Section. He is a member of the National System of Researchers in Mexico. He has been a NACE member for 23 years.

J.M. BASTIDAS has a Ph.D. in chemistry and is a full professor at the National Centre for Metallurgical Research (CENIM) belonging to the Spanish National Research Council (CSIC), bastidas@cenim.csic.es. He has been involved as leader in the development of over 45 research projects on corrosion. He has authored 240 original peer-reviewed journal articles, including book chapters; has presented 115 communications in congresses; and has supervised 30 Ph.D. theses and M.Sc. degrees. He was a winner in the Joint Global Call for Research 2005 project financed by the International Copper Association, USA. During the IMRS Congress in 2011, he received a "Meritorious Award to the International Trajectory" from NACE and the NACE Mexico Section. He is a member of the editorial board of five international journals: *Journal of Applied Electrochemistry, Corrosion Engineering Science and Technology, International Journal of Corrosion, Advances in Chemical Engineering,* and *Advances in Chemical Engineering and Science.* MP