

PHORGOTTEN PHENOMENA

Green Corrosion Inhibitors for Water Systems

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Corrosion affects the durability of civil infrastructure assets, including water production, supply, and storage systems. "Green" corrosion inhibitors will extend the life of industrial equipment for water systems. Special green inhibitors are obtained from plants growing in desert regions of the State of Baja California, Mexico, by ethanolic and aqueous extraction.

Environmental quality, worldwide water scarcity, and clean energy have been established today as central disciplines in modern science, engineering, and technology. They are already being linked to the critical problems of climate change, global warming, and greenhouse gas emissions, all interrelated phenomena.¹⁻² Furthermore, it is now generally accepted that corrosion and pollution are harmful processes that are interrelated, since many pollutants accelerate corrosion, and corrosion products such as rust also pollute bodies of water. Both are pernicious processes that impair the quality of the environment, the efficiency of industry, and the durability of the water infrastructure. In this time of energy crisis and economic turmoil, it is essential to develop and apply safe, "green" (environmentally friendly) corrosion inhibitors.³

Water Systems

Fresh water comes from rain and snow; it accumulates in rivers and lakes and generally contains <1,000 mg of dissolved solids per liter (mg/L). Potable and building water include low levels of total dissolved solids (TDS), and some chemicals (e.g., chlorine) are added for health reasons.

Many types of water are produced, transported, and used: potable for municipal systems, irrigation for agricultural crops, and cooling for industrial facilities, facilities using fossil fuels, and nuclear energy. Figure 1 depicts a plant for treatment and clarification of water for human consumption.

Water is conveyed by a pipeline system, which consists of a large number of pipes, pump stations, and valves, that moves the water from a source to the consumption location. Pumps are essential components of water supply systems (Figure 2). Usually water pipelines are fabricated from ductile iron (DI) and from

carbon steel (CS) based on the American Petroleum Institute (API) standards, but they may also be constructed from concrete or plastics, including reinforced plastics.⁴ A system of painted steel water pipelines is shown in Figure 3.

Water pipes have an inner diameter between 0.10 and 2.0 m, and the water flows at speeds of 1 to 6 m/s. Modern water pipelines are operated remotely from computerized control rooms and satellite surveillance is used to detect leaks or mechanical failures. The water quality and its influence on human health depends on the pipeline performance and whether it is free from corrosion, scaling, and fouling.

Steel corrosion is an electrochemical process that occurs on a pipe surface upon reaction with the water components, mainly dissolved oxygen (DO) and salts. Waters with a high concentration of dissolved and suspended solids, such as carbonates, silicates, phosphates, and hydroxides, form thick scales that might plug the pipes and interfere with water flow. Sometimes macro- and microorganisms thrive in water and cause corrosion.

The water corrosivity is determined by laboratory corrosion tests, simulating industrial conditions, and applying ASTM standards⁵ and NACE TM0169.⁶

Corrosion Protection and Control

The water infrastructure requires the application of corrosion control methods and techniques from the early stages of design through the construction and operation of the equipment. Practical methods that minimize or eliminate corrosion include the selection of corrosion-resistant construction materials, application of coatings and linings, cathodic protection (CP), and use of corrosion inhibitors. The most direct means of preventing corrosion is the choice of suitable materials. The final selection, par-

FIGURE 1



A plant for water treatment and clarification.

FIGURE 2



Pumps for water transportation.

ticularly for water pumps, must be a compromise between technological and economic factors.⁷

The purpose of a coating or lining is to act as a nonreactive barrier between the water and the material to be protected, generally steel (Figure 4). Coatings fall into three main groups based on their chemical nature: metallic, organic (in-

cluding paints), and inorganic. CP is based on the electrical nature of corrosion and is usually applied to water pipelines.

Corrosion Inhibitors

Corrosion can be controlled by modifying the water environment and by neutralizing or removing corrosive agents (e.g., DO). Corrosion inhibitors slow the

FIGURE 3



Painted steel water pipelines.

FIGURE 4



Coatings for protection against corrosion pipelines.

rate of corrosion reactions when added in relatively small amounts to the water. They are divided into three groups:

- Anodic inhibitors, which retard the anodic corrosion reactions by forming passive films.
- Cathodic inhibitors, which repress the corrosion reaction such as 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.

These conventional inhibitors are applied in many sectors of the water and energy industries—cooling water systems,^{3,8-9} desalination plants,¹⁰⁻¹² coal-

water slurries,³ acid pickling of metals,³ on reinforcing steel in concrete, and for control of galvanic corrosion in heat exchangers exposed to reverse osmosis water (Table 1).¹²

In the last decade, a new family of inhibitors has emerged, called green corrosion inhibitors, which are relevant in this crucial time of energy problems and economic havoc since they will extend the life of the water infrastructure and save large expenses in materials, equipment, and structures. They belong to the advanced field of green chemistry, also known as sustainable chemistry, which involves the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

In one example, R. Garcia¹³ evaluated the inhibitive action of an ethanol extract derived from a desert plant on the corrosion of CS in hydrochloric acid (HCl) and found it to be effective. HCl is employed at times to remove carbonate scales from steel surfaces.¹³⁻¹⁴

Conclusions

Corrosion is a damaging process that affects the water infrastructure including pipelines, pumps, valves, and auxiliary equipment. Economic considerations are of the utmost importance when evaluating anticorrosion methods involving inhibitors. The use of an inhibitor under operating conditions is determined largely by both its chemical stability and its corrosion-prevention efficiency. Conventional corrosion inhibitors, especially green corrosion inhibitors, will contribute to maintain effective water systems and their related natural and man-made environments.

References

- 1 B. Valdez, M. Schorr, et al., "Effect of Climate Change on the Durability of Engineering Materials in Hydraulic Infrastructure: An Overview," *Corr. Eng. Sci. and Technol.* 45, 1 (2010): pp. 34-41.

TABLE 1

Applied corrosion inhibitors for water systems^(A)

System	Corrosion Inhibitors
Engine coolants	• Molybdate • Molybdate with nitrite; molybdate, arsenite, or arsenate and benzotriazole along with borate/phosphate/amine • Nitrite, nitrate, phosphate, borate, silicate, benzoate, aminophosphonate, phosphinopolycarboxylate, polyacrylate, hydroxybenzoate, phthalate, adipate, benzotriazole, tolytriazole, mercapto-benzothiazole, and triethanolamine are combined with molybdate. In glycol, 0.1 to 0.6 wt% of molybdate is used.
Closed recirculating cooling water	• 200 ppm sodium molybdate with 100 ppm of sodium nitrite • 50 ppm molybdate, 50 ppm phosphate, 2 ppm Zn²⁺ • 40 ppm sodium molybdate + 40 ppm sodium silicate • 2-phosphonobutane-1,2,4-tricarboxylic acid and polyvinylpyrrolidone
Cooling water of steam plant boiler waters	• Molybdate with an aluminum salt and thiourea • Mild steel corrosion inhibition in boilers by a mixture of sodium molybdate, sodium citrate, manganese sulfate, polymaleic acid, and morpholine • Protection of mild steel in hard water boilers by sodium molybdate and sodium nitrite

^(A)Source: V.S. Sastri, *Green Corrosion Inhibitors: Theory and Practice*, Wiley and Sons (2011).

- 2 B. Valdez, M Schorr, eds., "Special Issue: Relationship of Corrosion with Climate Change," *Corr. Eng. Sci. Technol.* 45 (2010).
- 3 V.S. Sastri, *Green Corrosion Inhibitors: Theory and Practice* (Hoboken, NJ: John Wiley and Sons, 2011), pp. 212, 216, 223.
- 4 W. Sung, "Corrosion in Potable Water Distribution and Building Systems," S.D. Cramer, B.S. Covino, Jr., eds., *Corrosion: Environments and Industries*, ASM Handbook, Vol. 13C, (Materials Park, OH: ASM International, 2006), pp. 8-11.
- 5 *Corrosion of Metals, Wear and Erosion*, Annual Book of ASTM Standards, Vol. 03.02 (West Conshohocken, PA: ASTM, 2012).
- 6 NACE TM0169-2000, "Laboratory Corrosion Testing of Metals" (Houston, TX: NACE International, 2012).
- 7 P. Dupont, J.P. Peri, "World-Class Water Pumps," *Sulzer Technical Review* 3 (2011): pp. 12-15.
- 8 B.P. Boffardi, "Corrosion Inhibitors in the Water Treatment Industry," S.D. Cramer, B.S. Covino Jr., eds., *Corrosion: Fundamentals, Testing and Protection*, ASM Handbook, Volume 13A (Materials Park, OH: ASM International, 2003).
- 9 A. Abulkibash, et al., "Corrosion Inhibition of Steel in Cooling Water System by 2-Phosphonobutane-1,2,4-Tricarboxylic Acid and Polyvinylpyrrolidone," *The Arabian J. for Sci. and Eng.* 33 (1A), 1 (2008): pp. 29-40.
- 10 M. Schorr, B. Valdez, J. Ocampo, A. Eliezer, "Corrosion Control in the Desalination Industry," M. Schorr, ed., *Desalination, Trends and Technologies* (New York, NY: Intech, 2011).
- 11 M. Schorr, B. Valdez, J. Ocampo, A. Eliezer, "Materials and Corrosion Control in Desalination Plants," *MP* 51, 5 (2012): pp. 56-60.
- 12 I. Carrillo, B. Valdez, M. Schorr, R. Zlatev, "Inorganic Inhibitors Mixture for Control of Galvanic Corrosion of Metals Cleaning Process Industry," *CORROSION* 2012 (Houston, TX: NACE, 2012).
- 13 R. Garcia, B. Valdez, R. Kharshan, A. Furman, M. Schorr, "Interesting Behaviour of Pachycormus Discolor Leaves Ethanol Extract as a Corrosion Inhibitor of Steel in 1 M HCl: A Preliminary Study," *Intl. J. of Corrosion* (2012).

- 14 C. Chandler, M. Kharshan, A. Furman, "Sugar Beets Against Corrosion," *Corrosion Reviews* 20, 4-5 (2002): pp. 379-390.

This article is based on CORROSION 2013 paper no. 132814, presented in Orlando, Florida.

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