Green Chemistry—Purified Tannin Molecules for the Protection of Low Carbon Steel Closed-Loop Systems

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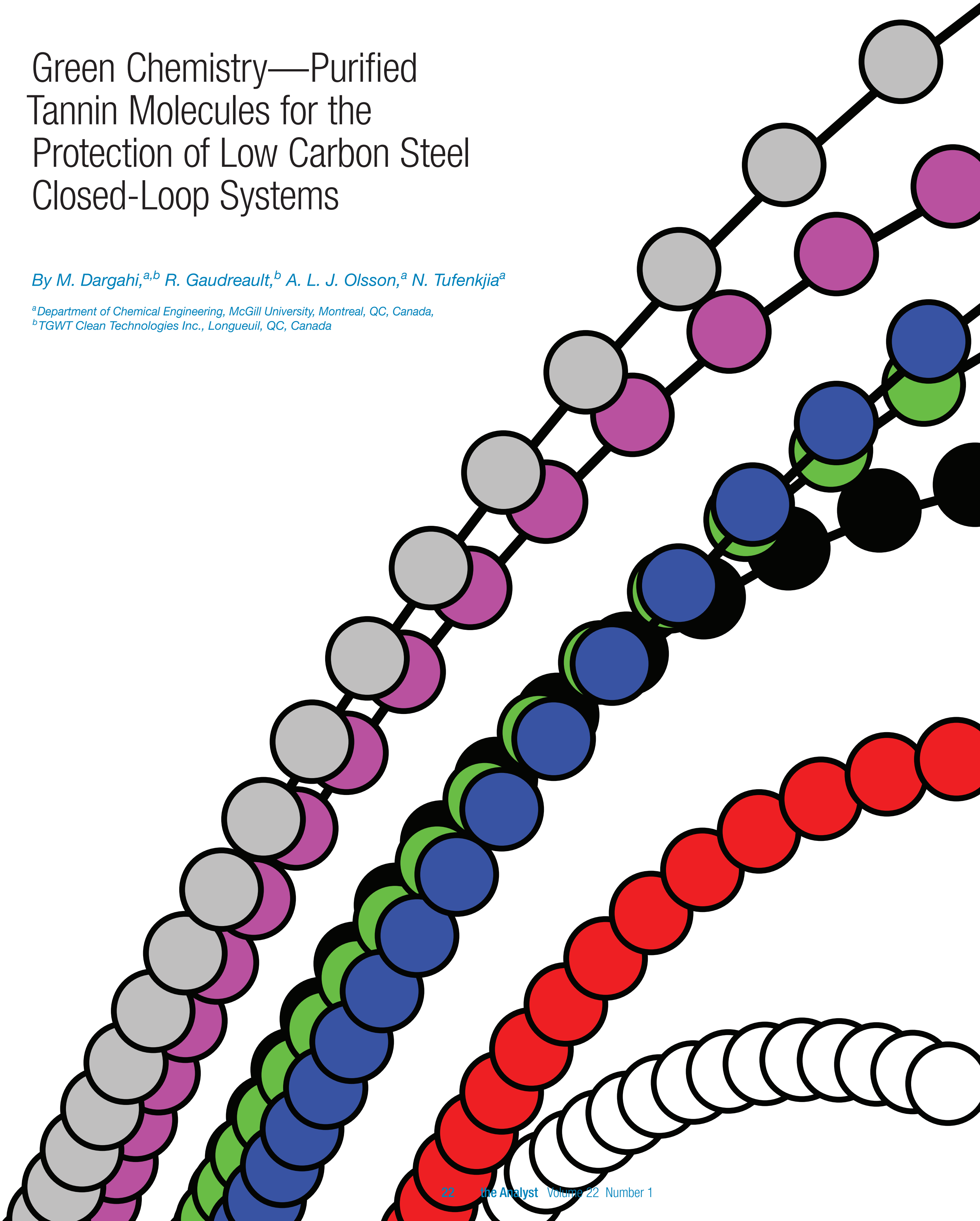


Abstract

Tannins extracted from renewable resources are green molecules that protect steam boilers much above ASME guidelines, for more than four decades. Using purified tannin-based corrosion inhibitors reduces water and energy consumption, greenhouse gas emissions, and effluent contamination, while reducing the environmental footprint of industry.

The authors investigated surface interactions of purified tannins (TG 3300) corrosion inhibitor with low carbon steel surfaces using Electrochemical Impedance Spectroscopy (EIS) and Quartz Crystal Microbalance with Dissipation (QCM-D) to characterize the performance of the tannin-based protective layer.

The results show the formation of an effective and stable tannin-based protective layer on mild steel within the first 5–15 minutes. High corrosion protection of low carbon steel by TG 3300 was also evidenced by the field results.

This study is a significant advancement in the field of tannin-based corrosion inhibition of low carbon steel because it links the laboratory results with four decades of industrial empirical optimization.

Introduction

Approximately 550 billion U.S. dollars of national income is spent on corrosion prevention and the maintenance or replacement of products lost or contaminated as a result of corrosion, which is far more than the annual budget of some countries.[1] One of the most common techniques for minimizing corrosion in the water industry is to apply corrosion inhibitors, which form a protective (blocking) layer on metal surfaces and minimize the access of corrosive electrolytes to the surface.[2] Unfortunately, conventional corrosion inhibitors (e.g., phosphates, sulfites) are neither renewable nor have reliable performance in highly conductive environments. Developing new, highly protective, and environmentally friendly corrosion inhibitors for steam boilers, hot-water closed-loop systems, pipelines, and tanks is critical. To address this problem, TGWT Clean Technologies Inc. has a portfolio of renewable/green corrosion inhibitors that function under much higher conductive/corrosive environments (8,000–10,000 µS/cm) than conventional chemistries (<3,000 µS/cm). Using purified tannin-based corrosion inhibitors reduces water and energy consumption, greenhouse gas emissions, and effluent contamination while reducing the environmental footprint of industry. Even though the physicochemical properties of tannin molecules have been studied widely,[3,4] the corrosion inhibition properties of these molecules are still poorly understood.

This study investigates the adsorptive and protective behavior of tannin-based corrosion inhibitors for low carbon steel (CS) hot-water closed-loop systems/boilers.

Materials and Methods

Chemicals and Solutions

The corrosion inhibitor solutions, purified tannins (TG 3300), were prepared by diluting concentrated TG 3300 to 1:1 using deionized water (DI) and then further diluting to desired concentration (dry basis of active ingredients) in tap water. Montreal city tap water was used as a corrosive liquid in the corrosion cell, in the absence (control) and presence of the TG 3300. For pH adjustment, aqueous 0.1 M sodium hydroxide and 0.1 M sulfuric acid were used.

Quartz Crystal Microbalance With Dissipation (QCM-D)

An E4 QCM-D unit (Q-Sense AB, Göteborg, Sweden) was used for the QCM-D experiments. C10200 steel (CS) coated AT-cut quartz crystals (QSX301) were used as model substrate. The crystals were cleaned by soaking and sonicating for at least 10 minutes in a 2% Hellmanex solution before being rinsed with DI water and dried with nitrogen gas. The crystals were exposed to ultraviolet light for 20 minutes before the experiment.

A flow rate of 50 µL min^{-1} was maintained through the QCM-D using a peristaltic pump. The temperature was controlled by the QCM-D at 72 °F.

The Sauerbrey equation was used to calculate the mass of adsorbed molecules on the QCM-D sensor surface.[5]

Electrochemical Cell and Equipment

A three-electrode electrochemical cell was used in the experiments. The counter electrode (CE) was a graphite rod. The reference electrode (RE) was a saturated calomel electrode (SCE). The working electrode (WE) was prepared from a CS rod and sealed with epoxy resin to give a two-dimensional surface exposed to the electrolyte.

Electrochemical measurements were performed using a Solartron 1287 Electrochemical Interface potentiostat/galvanostat and Solartron 1260 Impedance/Gain-Phase Analyzer. To ensure complete characterization of the interface and the surface processes, electrochemical impedance spectroscopy (EIS) measurements were made over a frequency range from 100 kHz to 100 mHz, with the alternating current (AC) voltage amplitude of ±10 mV.

Prior to each experiment, the WE surface was polished with 600-gradation sandpaper and then thoroughly rinsed with ethanol. After this, the electrode was kept in an ultrasonic bath for 5 minutes in ethanol and then rinsed with DI water. The electrode was then immersed in the test electrolyte and equilibrated for 3 hours at 158 °F at open-circuit potential (OCP), followed by the electrochemical measurements. All the solutions were mixed with a magnet stirrer. All data reported in this study represent mean values of four to six replicates.

Results and Discussion

Kinetics of Purified Tannins (TG 3300) Adsorption on CS Surface

It is interesting to investigate the kinetics of corrosion inhibitor adsorption to find the time scale within which the equipment surface will be covered by the inhibitors. Figure 1 shows that at a constant inhibitor bulk concentration of 275 mg/L (i.e., the common operating condition), the surface concentration of adsorbed inhibitor increases rapidly within approximately 5–15 minutes and then gradually levels off to a plateau at about 4.25 mg/m^2. From practical perspective, this timeframe is considered extremely short with respect to a hot water closed-loop system application and highly suitable to regenerate the tannin protective layer during a startup.

Open-Circuit Potential (OCP) Measurements

Figure 2 shows that when TG 3300 bulk concentration increases, the OCP value also increases to more noble values, indicating the adsorption of TG 3300 and its protective influence on CS surface.[6]

Electrochemical Impedance Spectroscopy Measurements

Electrochemical impedance spectroscopy (EIS) was applied to investigate the electrode/electrolyte interface and processes that occur on a low carbon steel surface at OCP in the presence and absence of TG 3300 in the solution, most notably the general corrosion resistance of CS. Figure 3 shows that the diameter of the EIS spectra semicircle increases with the increase in inhibitor bulk concentration, indicating an increase in corrosion resistance of the material.[6]

Figure 1: Purified tannins (TG 3300) surface concentration on CS as a function of time at the inhibitor bulk concentration of 275 mg/L at pH 10.5 and room temperature, obtained from QCM-D

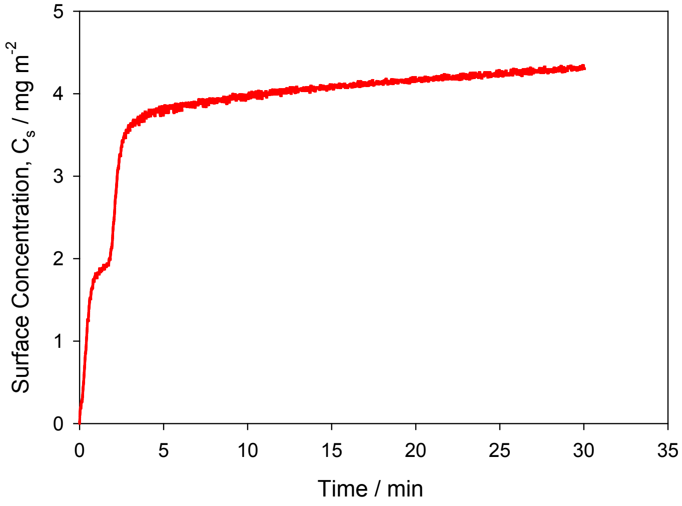


Figure 2: Open-circuit potential (OCP) of CS as a function of purified tannins (TG 3300) bulk concentration, recorded after 3 hours incubation at pH 10.5 and 158 °F

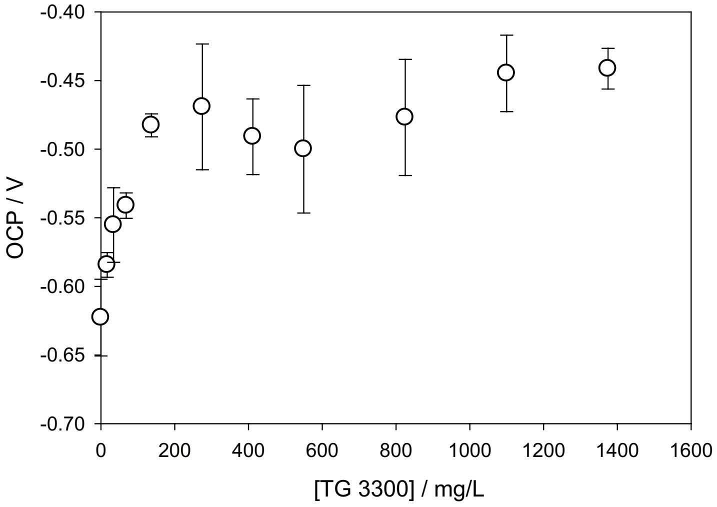
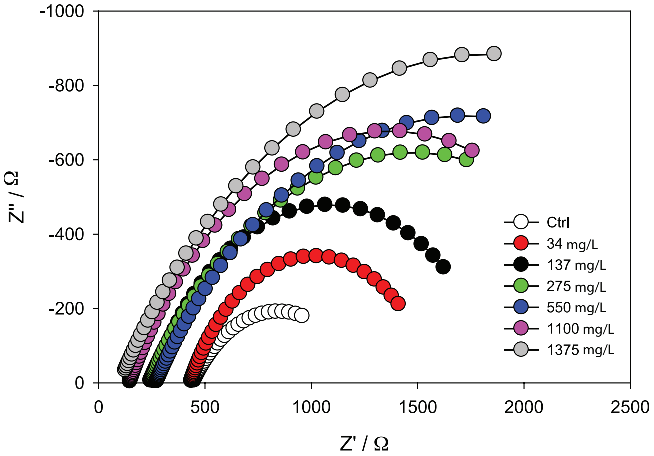
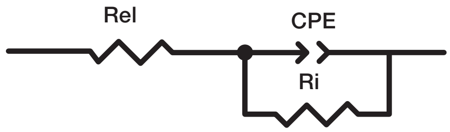


Figure 3: Nyquist plot of CS substrate recorded at different bulk concentrations of purified tannins (TG 3300) at 158°F and pH 10.5 after 3 hours of incubation at OCP. Circles are experimental data and solid lines represent the simulated spectra.



To extract qualitative information, a nonlinear least squares (NLLS) fit analysis was used to model the spectra, employing electrical equivalent circuits (EECs) presented in Figure 4.[6] In these EECs, represents the ohmic resistance between the WE and RE; R_i is the charge transfer resistance related to the corrosion reaction at OCP, while CPE is the capacitance of the electric double-layer at the electrode/electrolyte interface. The EEC in Figure 4 was used to fit the spectra recorded in the absence and presence of TG 3300 in the solution.

Figure 4: EEC model used to fit EIS data recorded CS in absence and presence of the inhibitor.

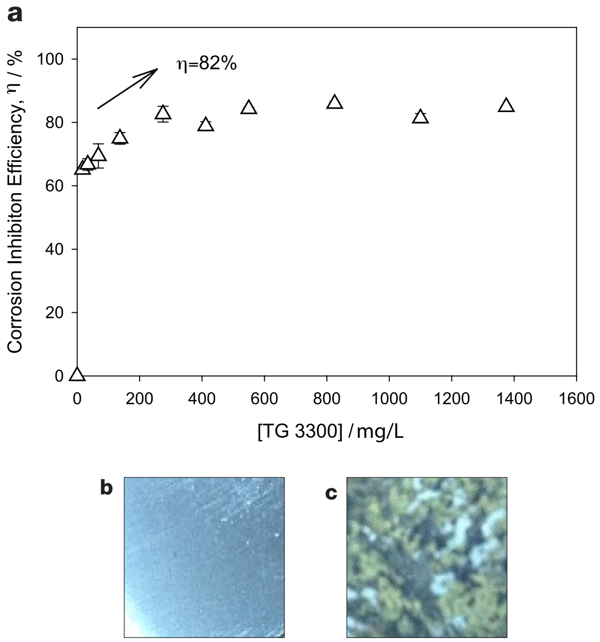


Taking into account the physical meaning of the EEC parameters of the circuits in Figure 4, the corrosion resistance of the bare (control) and covered CS surface is equivalent to the charge-transfer resistance, R_i; consequently, the corrosion inhibition efficiency of TG 3300 (η_i), was calculated by comparing the total resistance value, R_i, recorded at various concentrations of TG 3300, and the R_0 value recorded in the absence of TG 3300 (control sample):

$$\eta_i = 100 \times \left(1 - \frac{R_0}{R_i} \right)$$

Figure 5a shows that by increasing TG 3300 inhibitor bulk concentration, the corrosion inhibition efficiency also increases and reaches a maximum value of ca. 82%, indicating high surface corrosion protection of CS. Figure 5b shows that in the absence of the corrosion inhibitor, the electrode is fully corroded. However, in the presence of 275 mg/L of TG 3300, the sample is highly protected and there is no corrosion mark on the electrode, Figure 5c. Interestingly, this bulk concentration converges toward the optimum value observed after four decades of empirical optimization in industrial CS boilers treated with tannin-based chemistries.

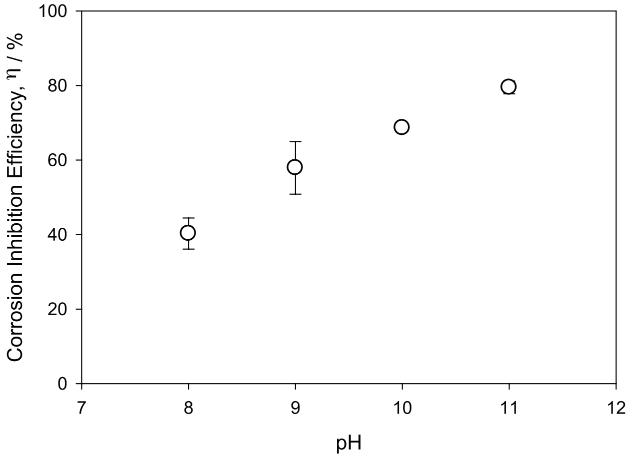
Figure 5: (a) Corrosion inhibition efficiency of purified tannins (TG 3300) as a function of inhibitor bulk concentration for CS after 3 hours of incubation at 158 °F and pH 10.5. Images of CS electrodes after incubation in the absence (b) and presence (c) of 275 mg/L of TG 3300.



Effect of pH on Purified Tannins (TG 3300) Corrosion Protection of CS Surface

The influence of pH on the CS corrosion inhibition efficiency was studied in a pH range from 8 to 11 in the absence and presence of 275 mg/L of TG 3300. Figure 6 shows that corrosion inhibition increases with pH and give the highest efficiency at pH 11 (i.e., ~80%). Low corrosion inhibition efficiencies at lower pH are likely due to the low carbon steel dissolution in lower alkalinity environment.[6] The author in previous studies observed similar behavior.[7]

Figure 6: Low carbon steel corrosion inhibition efficiency as a function of pH. The EIS data were recorded in the absence and presence of 275 mg/L of purified tannins (TG 3300) at 158 °F and 3 hours.



Practical Results From the Field

Table 1 shows corrosion coupon results from the field for heating and cooling water closed-loop CS systems treated with TG 3300. Measurements from different locations showed very low corrosion rates (overall average of 0.157 ± 0.276 mpy for 173 days). Consequently, this study highlights that our laboratory method (ca. 80% corrosion inhibition efficiency, Figure 5) underestimates the performance of the field observations (Excellent, Table 1). Thus, more laboratory work is needed to develop a method that accurately predicts the performance of tannin-based corrosion inhibitor for the field applications.

Table 1: Low carbon steel water closed-loop systems treated with purified tannins (TG 3300)

Location	Type	Ave. # Days	pH	Conductivity / µS cm^{-2}	Ave. Corr. Rate* / mpy	QC
PACCAR Canada	Heating (158 °F)	120	8.9 ±0.3	407 ±78	0.154 ±0.112	Excellent
Sherbrooke University / Sherbrooke campus	Cooling (40 °F)	203	9.0 ±0.3	388 ±72	0.183 ±0.344	Excellent
Sherbrooke University / Longueuil campus	Heating (158 °F)	132	9.6 ±0.2	407 ±30	0.033 ±0.020	Excellent

NB:* Average ± standard deviation expressed in absolute values.

Conclusion

The QCM-D method was used to investigate the adsorption kinetics of purified tannins (TG 3300) corrosion inhibitor on low carbon steel (CS), which showed TG 3300 adsorption reaches equilibrium after 5–15 minutes. Electrochemical impedance spectroscopy (EIS) showed that high CS corrosion inhibition efficiency (i.e., ~80%) is achieved within 3 hours in a TG 3300 solution. Laboratory results showed that by increasing the pH, CS surface protection increases. High corrosion protection of CS by TG 3300 was also evidenced by the field results (e.g., corrosion coupons) (overall average corrosion rates of 0.157 ± 0.276 mpy in 173 days). Finally, the optimum dosage of tannins (~275 mg/L) and corrosion inhibition efficiency in laboratory experiments converges toward the optimum value observed after four decades of industrial empirical optimization for low carbon steel boilers.

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