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A synergistic effect between gluconate and molybdate on corrosion inhibition of recirculating cooling water systems

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ABSTRACT

A new corrosion inhibitor (NCI) consisting of gluconate along with a relatively low amount of molybdate and nitrite was developed. A synergistic effect between molybdate and gluconate on the corrosion inhibition of C-steel was investigated. The polarization measurement indicates that the corrosion of C-steel in the presence of gluconate is thermodynamically and kinetically unfavorable as compared to that with molybdate alone. According to FIB-SEM, FTIR, and XPS experiments, an inhibition mechanism is proposed whereby the gluconate could bridge the molybdate and iron, which is responsible for the formation of the protective film against the corrosion of C-steel.

1. Introduction

Cooling water systems provide a reliable method for industrial process temperature control. In general, heat produced during manufacturing processes is transferred to the recirculating water system by heat exchange equipment. As it is not easy to access and investigate the internal condition of the recirculating cooling water system, taking preventive measures can help ensure that the recirculating system is well-maintained. Generally, makeup water is supplied to the recirculating cooling water system only when water drainage is required for system management or repair [1,2]. In other words, the same water is used all the time in a recirculating system with negligible loss to the atmosphere. Therefore, water with high quality (low hardness) is usually used for the recirculating cooling water system to minimize the potential for scaling from mineral deposits and for biological fouling from slime and algae deposits.

The most important concern in industrial closed-loop cooling water systems, in part because of the significant economic repercussions, however, is corrosion. [3–5]. Several specialty chemicals such as chromates, heterocyclic organic compounds, rare-earth metal compounds, and phosphates have been proven to efficiently attenuate corrosion and deterioration of the metallic surfaces. [6]. Among these chemicals, chromate-based and nitrate-based corrosion inhibitors were commonly used for several years because of their high efficiency in aqueous media and their application for a wide range of metals and alloys [7]. Nowadays, due to new protective laws concerning the

environment, chemical reagents used as corrosion inhibitors must be non-toxic and biodegradable [3,4,8–10], thereby effectively prohibiting the use of chromates and nitrates [6,11,12].

Molybdate, having several similarities with chromate, is one of the most versatile corrosion inhibitors capable of controlling the corrosion [13–18]. However, the oxidation capability of molybdate is not as excellent as chromate. Furthermore, only in the presence of a primary passivation do molybdates inhibit corrosion as anodic inhibitors. Lizlovs indicated that in the aqueous system containing aggressive ions, molybdate acts as corrosion inhibitor only in the presence of oxygen [19]. Numerous researchers have also aimed to examine the synergistic effect between molybdate and other organic and inorganic compounds to achieve better inhibition efficiency in cooling water systems [20–24]. For example, the inhibition efficiency can be significantly improved when molybdate is formulated with nitrite [24]. However, the price of molybdenum fluctuates significantly depending on market conditions, resulting in a relatively high operation cost in managing the closed-loop cooling water system. Therefore, the development of an inhibitor formulation with a relatively low amount of molybdenum would greatly benefit the industry from a cost perspective.

Gluconate has been reported to be an attractive alternative corrosion inhibitor as it is effective and environmentally- and cost-friendly [24–30]. Sodium, calcium and zinc salts of gluconic acid, either as a single compound or in a mixture have been reported to be successful inhibitors against the corrosion of tin, iron, mild steel and carbon steel in different environments such as seawater, low chloride media, neutral

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aqueous environment, and the near neutral media [24,26–28,31–38]. Gluconate has also been considered an excellent material to inhibit the chloride pitting corrosion [38,39]. In addition, the combination of sodium gluconate (SG) and cetyltrimethylammonium bromide (CTAB) appears to effectively act as a corrosion-, scale- and microorganism-inhibitor [3,30].

This study attempts to explore the synergistic effect between molybdate and gluconate. A new corrosion inhibitor (NCI) consisting of gluconate along with a relatively low amount of molybdate and nitrite was developed for the recirculating cooling water system. The synergistic effect was investigated based on laboratory examinations using weight-loss measurements and electrochemical analysis. A suggested mechanism was also proposed based on the results obtained from focused ion beam scanning electron microscope (FIB-SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). A complementary biocide program was created to suppress any potential bacterial growth. In addition, a pilot test using carbon steel (C-steel) and admiralty brass coupons for corrosion assessments was also carried out to evaluate the performance of NCI and CCI for the further field test.

2. Experimental methods

2.1. Performance evaluation of corrosion inhibitors

Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and nitrite (NaNO_2) were formulated with sodium gluconate in a new corrosion inhibitor (NCI) to replace part of molybdate and nitrite in a commercial corrosion inhibitor (CCI). NCI contained 100 ppm of gluconate along with 50 ppm molybdate and 125 ppm nitrite, 20% and 50% of that which currently is found in CCI, respectively (250 ppm for both molybdate and nitrite). Both NCI and CCI contained similar concentrations of commercial scale inhibitor (Rohm and Haas Co.) and biocide (KATHON, DOW Chemical). The estimated cost of our specialty chemical NCI is reduced by 76% compared to that of CCI. A comprehensive evaluation approach used to evaluate the performance of the above corrosion inhibitors included weight-loss measurement, potentiodynamic polarization and a pilot test.

The apparatus for the weight-loss measurement was developed from jar-testing equipment modified such that the nitrogen gas (99.7%) purge tube and hotplate adjusted the concentration of dissolved oxygen (DO) and the temperature in the test solution (0.2 M HCl), respectively. The DO concentration was monitored with an oxygen probe (HACH sension) and controlled at approximate 4 ppm for the condition of the recirculating cooling water system. Test coupons were made of carbon steel with the following chemical composition (wt%): C: 0.24; Si: 0.41; Mn: 2.3; P: 0.04; S: 0.04; Fe: balance. Test coupons were prepared by polishing with 240-grit papers followed by the finer grades with grit sizes of 500 and 1000. A household cleaning reagent was used to clean the test coupons before weighing by an electronic balance with a sensitivity of 0.1 mg. The pretreated coupons were subsequently fixed on paddle stirrers with specific acrylic clamps. The test solutions with NCI and CCI, respectively, were stirred at 100 rpm for 7 days at 37 °C with a glass lid to prevent the evaporation of test solution. After 7 days, the coupons were roughly brushed with a plastic brush to remove the loose iron oxide and subsequently immersed in a homemade acid reagent consisting of 70 wt% of HCl (36.5 wt%), 20 wt% pure water and 10 wt% formaldehyde for 30 s, followed by immersion in a saturated NaHCO_3 solution 30 s. The coupons were then washed with DI water to remove any residual chemicals, followed by acetone to remove facilitate drying. The treated coupons were further dried in an oven at 60 °C for 10 min before weighing on the 5-digit weighting balance. The measured weight was subtracted from the original coupon weight to calculate the weight loss as a result of corrosion. All coupons used in the weight loss measurement study were subject to the same procedure, and the error due to the cleaning procedure was minimized.

The electrochemical analysis was conducted using a conventional three-electrode cell assembly. The cell consisted of a Pt electrode and a Hg/HgCl₂ electrode as counter and reference electrode, respectively. The C-steel electrode with an exposed area of 1 cm² was used as a working electrode. All the tests were performed under an unstirred condition with no aeration. The working electrode was immersed for 60 min before the start of the scan to attain a stable state. The polarization studies were carried out over a potential of –1 to 0 V span versus open circuit potential at a scan rate of 0.5 mVs⁻¹.

2.2. Determination of bacterial populations

Since gluconate may support microorganism growth, the number of bacteria in the test solution was determined by the Cult Dip Combi[®] method (Merck). The slide was unscrewed from the tube without touching the agar surface and subsequently dipped into the fluid tank. The slide was in contact with the solution for c.a. 5–10 s before excess fluid was drained off the slide. The slide was then screwed tightly back into the tube, and the tube was placed upright in an incubator. The incubation time and temperature were 48 h and 30 °C, respectively. After the 48-h incubation period, the bacterial population in the solution was quantified. The total bacterial count was obtained by comparing the density of the colonies appearing on the slide with densities shown on a model chart provided by Merck.

2.3. Characterization of C-steel after immersed in CCI and NCI

FTIR spectra (Nicolet 6700, Thermo Inc.) of the C-steel coupons after immersion in the inhibitors were performed in the transmission mode ranging from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹ and accumulation of 128 scans. The specimen for FTIR characterization was assumed to be the complex film formed on the C-steel surface after immersion in 0.2 M HCl for 24 h. A focused ion beam scanning electron microscope (FIB-SEM, 1540XB-cross beam, Zeiss Inc.) was employed to observe the surface morphology of C-steel with and without the presence of the inhibitor in an acidic medium. The images were taken after immersing the samples for 24 h in 0.2 M HCl with and without the corrosion inhibitor. XPS measurements (PHI Quantera SXM) were performed with monochromatic X-ray radiation. High resolution scans with a 0.1 eV step were conducted over the regions of interest, including Fe 2p, O 1s, N 1s, and C 1s. Broad scan spectra were obtained with a pass energy of 150 eV, while narrow scans of Fe 2p, O 1s, N 1s, and C 1s used a pass energy of 15 eV. All XPS spectra were referenced to the Fe 2p_{3/2} line of the C-steel coupon (710.6 eV) without the presence of inhibitor.

2.4. Pilot test

Pilot-scale cooling water systems were also used to compare the performances of corrosion inhibitors formulated by CCI and NCI. For simultaneous evaluation of two corrosion control programs, two pilot systems were operated side by side to eliminate the possible effect of contaminants from the surrounding environment. The heat load for the pilot system was applied through a heat exchanger which allowed the water temperature to reach up to 45 °C at maximum across the pilot system. Pilot systems were also equipped with automatic safety shutoffs in the event of loss of cooling water or a high temperature alarm. The chemical feed system incorporated four mini pumps and storage tanks. All the pumps were timer-controlled to ensure proper dosing of the corrosion inhibitors and biocide. System pH was controlled at 9.5 ± 0.2 and standard pH controllers were used to control pH via acid and alkali feed. The pilot tests were run with water at 38 °C. The temperature difference between inlet and outlet was normally in the range of 6–9 °C, making the efficiency of the cooling tower approximately 66–75%.

Before the startup of the pilot test, the towers were cleaned with

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