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Next Generation Closed Loop Corrosion Inhibitors: Increasing Reliability & Decreasing Environmental Impact

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ABSTRACT

Closed hydronic loops are of critical importance in many applications including industrial process equipment as well as heating, ventilation, and air conditioning (HVAC) systems. In industrial applications, closed loops are typically used to cool essential processes or equipment that would not tolerate the variability typically observed in open cooling towers. The major challenges encountered when operating a closed loop are microbiological growth and corrosion. Molybdate and nitrite have been used for decades to control corrosion in closed loops, along with borate as the most widely used buffer. However, each chemical has its limitations. Molybdate is very costly and performance is highly dependent on chloride/sulfate levels and temperature; nitrite provides very robust performance but at high dose. Additionally, nitrite is known to promote biological growth. Borate compounds, though not banned yet, have been classified as Substances of Very High Concern (SVHC) under the EU REACH regulations. Because of these drawbacks and increasing environmental regulations, new non-toxic corrosion inhibitors are needed that can provide excellent corrosion inhibition, meet strict discharge regulations, and maintain performance in the presence of high microbiological growth. Here we present a next generation non-toxic closed loop corrosion inhibitor that contains no nitrite, heavy metal, P, B, or filming amine. Laboratory feasibility experiments based on jar testing, pilot closed loop testing, and electrochemical testing show excellent corrosion inhibition results (<0.2 mpy) on mild steel in highly corrosive water. Corrosion inhibition results are compared to incumbent corrosion inhibitors based on nitrite, molybdate, and filming amine. Additionally, the biostability of the new corrosion inhibitor is demonstrated through stability experiments in the presence of cooling water microorganisms.

Key words: Corrosion inhibitor, water treatment, chemical treatment, corrosion control, corrosion tests.

INTRODUCTION

Closed cooling loops are encountered across a variety of industries where cooling is critical to operations and operators cannot tolerate the variability typically seen in open cooling towers. The water inside a closed loop is ideally circulated for a long period of time without need for significant makeup water or deliberate blowdown of the loop. Most industrial plants will contain some amount of closed cooling loops; closed loops can be found in refineries, petrochemicals, steel making, and microelectronics. Because closed cooling loops can run with little maintenance for long periods of time, they can become a neglected part of a customer's water treatment system. This neglect can lead to significant issues that can negatively impact heat transfer efficiency in the cooling process. The most common issues in closed cooling loops are corrosion and microbial growth.^{1,2} Scaling in closed loops is not normally a concern as most operators fill their loops with relatively low hardness/alkalinity makeup water. In terms of water quality, the main driver for corrosion in closed loops is chloride concentration. Most closed loops have a chloride concentration less than 50ppm. Typical temperatures encountered in closed loops vary, but in general temperatures are 35 – 80 °C. Closed loops are constructed mostly with carbon steel, stainless steel, and copper alloys, however the use of aluminum alloys in closed loops is becoming more prevalent. Closed loop volumes can vary significantly; in HVAC applications volumes can be as low as 10 gallons, whereas some refineries have closed loop volumes of several million gallons.

Corrosion inhibition in closed loops is predominantly treated using nitrite and molybdate-based corrosion inhibitors,³ although organic-based closed loop corrosion inhibitors have been reported.^{4,5} Nitrite provides excellent corrosion inhibition performance over a wide range of temperatures and chloride content. Nitrite functions as an anodic corrosion inhibitor and functions without the need of dissolved oxygen. Despite excellent corrosion inhibition performance, nitrite does have several limitations. The biggest potential issue with nitrite in closed loops is its biodegradability in the presence of microbiological organisms. This biodegradability is an issue for two reasons; first, the nitrite is consumed by microbiological growth which increases the risk of loop corrosion, specifically pitting corrosion, if nitrite levels are decreased significantly. Second, microbial growth can easily get out of control since the nitrite is an excellent food source which can encourage even more microbial growth which can lead to microbiological induced corrosion (MIC). The potential for microbial growth in closed loops treated with nitrite can also lead to significant water costs. For example, closed loop operators standard operating procedure is to keep microbial content below a certain threshold. Because nitrite is not compatible with oxidizing biocides, non-oxidizing biocides are used as one measure to control microbiological growth. When/if the non-oxidizing biocides are ineffective at reducing microbial counts, the loop must be drained and refilled with clean makeup water. Depending on the extent of microbial problem in the loop, this makeup water cost can be quite significant. Nitrite is also toxic, so any nitrite-based corrosion inhibitor suffers from a safety, health, and environment (SH&E) perspective. Molybdate is also used as a corrosion inhibitor in closed loops. Molybdate does not have the large application window that nitrite has; molybdate struggles to inhibit corrosion when chloride levels are >15ppm. Molybdate is also much more expensive than nitrite. Additionally, in some regions there are very strict discharge limits on Mo, which limits where MoO_4 can be used as corrosion inhibitor. An advantage of molybdate closed loop corrosion inhibitors is that microbiological growth does not consume molybdate.

Closed loop corrosion inhibitor formulations must also include a buffer to keep loop pH high in case of process leakage into the loop. Historically, borates have been formulated into closed loop corrosion inhibitors due to their low cost and appropriate buffering range (pKa). Currently, however, borates are classified as a substance of very high concern (SVHC) by the European Union. Borates have been classified as a toxin for human reproduction. As such, water treatment companies are removing borate from their product lines due to these SH&E concerns around borate.

Due to the limitations described above in performance (molybdate) and SH&E (nitrite and borate), a next generation closed loop corrosion inhibitor is needed. Previous literature has described the desired characteristics of new closed loop programs including:

New Closed Loop Program Desired Characteristics	Reference
- Low environmental impact, with good long-term biodegradability in the environment, but not readily biodegradable in application. - Mild steel corrosion rates <0.5mpy, and copper corrosion rates <0.1mpy. - Ability to measure product actives by field personnel.	6
- Cost effective in most applications regardless of system volume. - Robust performance over a wide range of conditions, including high chloride/sulfate water.	7

We present here a novel **A**nchoring **C**orrosion Inhibitor **D**erived from **C**arboxylate (AC/DC) for carbon steel that does not contain nitrite, heavy metal, boron, phosphorus, or filming amine. An inert fluorescent tracer was blended into the formula for advanced product monitoring and control. The AC/DC based corrosion inhibitor package meets the characteristics described above as well as additional features outlined below.

AC/DC

- No aquatic toxicity: non-NO₂, non-Phosphorus, non-Molybdate, non-Borate; potentially enabling direct discharge to sea or wastewater treatment plant (WWTP)
- Safer materials handling: Improved safety over current treatment chemistry
- Robust treatment: Superior performance by protecting the surface of the metal under high stress conditions, such as high skin temperature, high chloride/sulfate concentration
- Highly stable treatment: Improved resistance of the treatment against biological and chemical oxidation, such as oxidizing biocide
- Optimal cost/performance ratio: Robust performance at reasonable cost to replace molybdate at applications that other inhibitors are precluded

This rest of this paper will present experimental data to support the key claims and requirements of AC/DC that are listed above. These experiments involve jar testing, pilot closed loop testing, electrochemical corrosion testing, and biostability experiments. Throughout the paper general corrosion rates will be given written descriptions based on previous literature (Table 1).

Table 1. Quantitative Classification of Corrosion Rates for Closed Cooling Loops, Corrosion Rates in mpy.⁸

Description	Carbon Steel	Copper Alloys
Excellent	Less than or equal to 0.2	Less than or equal to 0.1
Very Good	0.2 – 0.3	0.10 to 0.15
Good	0.3 – 0.5	0.15 – 0.20
Moderate to Fair	0.5 – 0.8	0.2 – 0.3
Poor	0.8 – 1.0	0.3 – 0.5
Very Poor to Severe	Greater than or equal to 1	Greater than or equal to 0.5

EXPERIMENTAL PROCEDURE

Synthetic Cooling Water Chemistry

Two water matrices were used for the tests described in this paper. Naperville, IL USA tapwater (Table 2, W1) is a low corrosion stress water due to relatively high calcium and alkalinity, and low

concentration of corrosive ions such as chloride and sulfate. To increase the corrosivity of the water, and stress the corrosion inhibitors, additional chloride (sodium chloride) and sulfate (sodium sulfate) were added into Naperville tap water to reach 150 ppm chloride and 200 ppm sulfate (Table 2, W2). Typically, a test was performed at 60°C with W2 to test the performance of a newly developed formula for its performance robustness. A chloride concentration of 150 ppm, and a sulfate concentration of 200 ppm, would represent 80% of the make-up water in the United States. A third water matrix was used to simulate the makeup water typically used for closed loop cooling water applications (Table 2, W3).

Table 2. Water Matrices Used in Corrosion Inhibitor Experiments

Component	W1	W2	W3
Ca (ppm as CaCO ₃)	88	88	42
Mg (ppm as CaCO ₃)	44	44	5.5
Cl, ppm	15	150	30
SO ₄ , ppm	26	200	5
Alkalinity, ppm CaCO ₃	110	110	32

Jar Tests

Corrosion inhibition performance was evaluated using stirred jar tests at 40 °C and 60 °C. Glass jars were filled with water and were then dosed with the corrosion inhibitor to be tested. Total mass in each jar was 400g. Fresh mild steel coupons were submerged under the liquid level and were suspended using PTFE tape. The jars were sealed and placed in a heater shaker water bath that was temperature-controlled. The jars were heated and shaken at 60rpm for 17d after which the coupons were removed and analyzed. General corrosion rates were calculated gravimetrically; coupons were also inspected for signs of localized corrosion.

Pilot Closed Loop Testing

The pilot closed loop testing apparatus is shown in Figure 1. A coupon rack was built on a recirculating water bath. The bath had an operating temperature from -30°C to 100°C depending on the circulating media used. Typically, the testing temperatures were 10°C, 60°C, and 80°C to mimic both cooling and heating loops. Water flow could also be adjusted based on the design of the water bath. Experiment times were dependant on coupon metallurgy tested. Carbon steel runtimes were at least 30d. After the desired runtime, coupons were removed and general corrosion rates were calculated gravimetrically; coupons were also inspected for signs of localized corrosion. Instantaneous corrosion rates in the pilot closed loops were also monitored using inline carbon steel LPR probes (Nalco Corrosion Monitor). The LPR probe measured the linear polarization resistance of the coupon and calculated a corrosion rate through this electrochemical measurement.

Pilot closed loop tests were also performed using a filming amine, in particular oleylpropyldiamine (OPDA). The OPDA-based formulation also contained tertiary amine, azole, and an organic surfactant to increase OPDA solubility. The pH of the OPDA pilot closed loop experiment was 8.8. The OPDA concentration investigated (64ppm actives) was greater than the typical dose of OPDA in closed cooling applications. A high dose of OPDA was chosen to thoroughly evaluate the comparative performance of OPDA vs AC/DC. The AC/DC dose was 2500ppm as product, which is consistent with typical dosage of conventional closed cooling corrosion inhibitors.