Slow Release Corrosion Inhibiting Block

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Abstract

Corrosion Inhibitor Releasing Block (IRB) is formulated using renewable soybean-based wax and proven Vapor phase Corrosion Inhibitor (VCI) technology. Bench test and pilot cooling tower test show that when immersed in water, IRB slowly dissolves and releases a calculated amount of inhibitors required for corrosion protection of a system. The inhibitors in IRB provide corrosion protection to multi-metals, including carbon and galvanized steels, aluminum and yellow metals. IRB can be used as a corrosion inhibitor additive in most water treatment programs, including open, re-circulating cooling systems and waste water systems. It is also compatible with the majority of commercially available biocides and anti-scalants. IRB can be placed in make-up water, cooling tower basins, return water circuits or waste water systems, providing a safe and easy method to deliver time-release corrosion inhibitors.

Introduction

Water treatment systems are an ideal environment for the destructive attack on metals to occur. Slow-release corrosion inhibiting product provides an easy way to combat corrosion in water treatment systems and avoid expensive repairs and disruptions.

Products which slowly release their active ingredients are employed by many industries, including water treatment industries. Generally a slow-release product incorporates relatively large amount of active ingredients with an appropriate delivery system to provide a steady concentration of the active components over a specified period of time.

This study includes:

- Selecting the corrosion inhibitors
- Selecting a biodegradable inactive carrier that is based on renewable source
- Evaluating the compatibility of the inhibitors and the carrier
- Determining the weight ratio of the inhibitor/carrier and the size of the block
- Adjusting the manufacturing technology
- Evaluating the product in bench test
- Evaluating the product in pilot cooling tower

Experimental Work

Corrosion Inhibitors Selection

The corrosion inhibitor selected as the active ingredients for the Corrosion Inhibitor Releasing Block (IRB) is the Cortec Building Block (BB). BB is a blend of contact and vapor corrosion inhibitors and alkalinity builders. Previous studies and field experience [1] show that BB provides effective protection in water treatment at low dosage level (starting dosage is 7 ppm) when continuously added to makeup water. In addition, BB is very low in toxicity; below are its toxicity test results (Table 1) conducted by EPA test lab [2].

Table 1. Acute 48-hr Static-renewal Toxicity Test on the Selected Inhibitor BB

Sample	NOEC/ LOEC*, ppm D.pulex	NOEC/ LOEC, ppm P.promelas
BB (test # E-17766-01)	10,000/>10,000	10,000/>10,000

* NOEC – no observable effect concentration; LOEC – lowest observable effect concentration

The results showed that BB had very low impact on the fresh water aquatic life, and the discharge of BB would not be a concern for environment regulations.

All these data make BB an ideal candidate as the active ingredients in a slow-release format. The IRB provides easy application of a field-proven water treatment protection.

<u>Inactive Carrier Selection</u>

Several samples of slow release carriers were prepared and evaluated.

For the preliminary evaluation, a blend of sodium sulfonates and cocoamides was used as the carrier for the corrosion inhibitor, and the blocks were manufactured by extrusion. Laboratory and pilot cooling tower tests confirmed that the selected corrosion inhibitors can be incorporated in, and later released from, the blocks. Tests in pilot cooling tower, however, showed that such a carrier was very foamy and dissolved faster than the desirable rate for a slow release product.

In the second round of the tests, soybean-based waxes were utilized as carrier. In addition to being bio-based and bio-degradable, soybean-based waxes were chosen because of their melting points and their tendency to form micro-emulsion with water in the presence of specific surfactants. Those waxes together with sufficient nonionic surfactants and amide-based lubricating components constitute the inactive carrier of IRB. The IRB was molded.

Evaluating IRB Performance

IRB was evaluated in stagnant water conditions in bench test, and in fast-flowing water conditions in a pilot open re-circulating cooling water system. Vapor phase protection of IRB was evaluated using the Vapor Inhibiting Ability (VIA) test (see Test Procedures).

The main objectives of evaluating in stagnant condition were:

- Average time for complete dissolution of the IRB
- Effect of the IRB on bio-growth
- Effectiveness of the corrosion inhibitors released from the IRB versus the BB

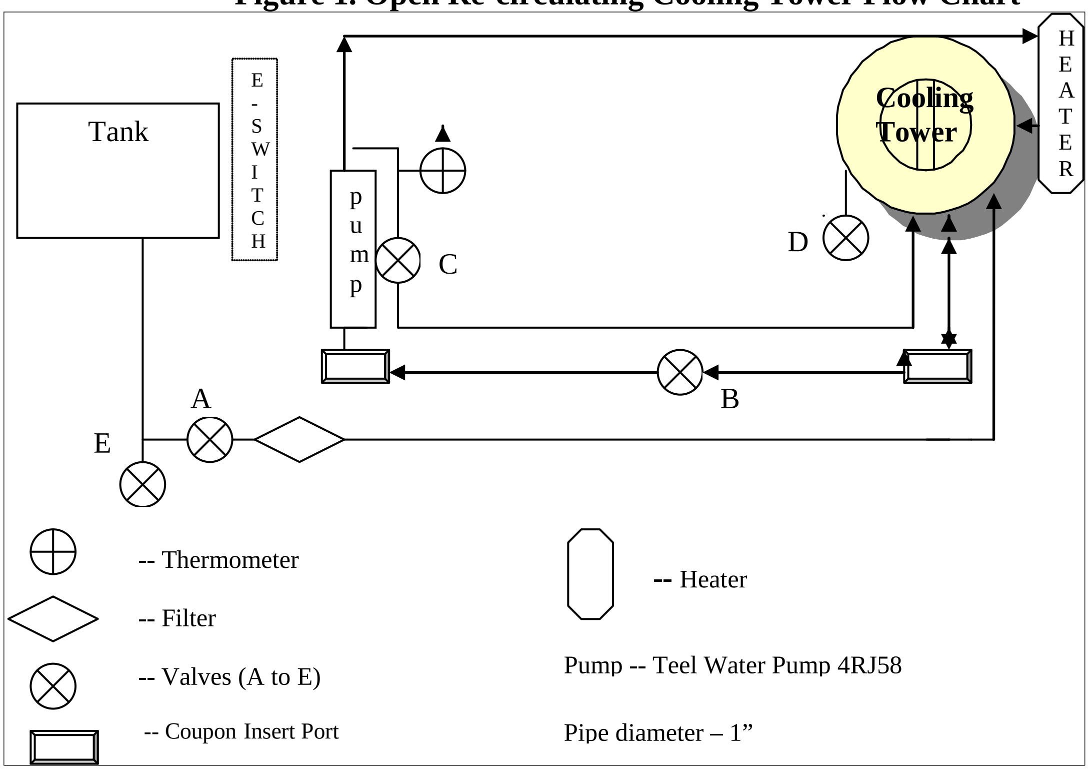
The main objectives of evaluating in open re-circulating cooling tower were:

- Lifespan of an IRB in Open Re-circulating Cooling Tower
- Bio growth impact
- Effectiveness in corrosion prevention

Instruments and Materials Used

- Metal Coupons
  Carbon Steel Coupon (SAE1010) was used in stagnant water testing and in pilot cooling tower testing. Galvanized Steel Coupon (Hot Dip, ASTM A-525 (G90) [3]), and Copper Coupon (CA110, QQ-C576) were used in the pilot cooling tower testing. Corrosion rate was determined by coupon weight loss. Coupons were cleaned with laboratory grade methanol prior to testing. Corrosion products after testing were removed according to the cleaning procedure of ASTM G1 [4].
- Molybdate Test Kit, MO-2 test kit (HACH), was used to measure the amount of a Molybdenum-based tracer to determine the inhibitor concentration released from the IRB.
- TDS Meter (OakTon, EC/TDA/Salt Testr)
- pH Meter (IQ Scientific Instruments)
- Duo Bio Dip Slides BTM-2 (WET International, Inc.) was used to check bio growth in water.
- Pilot Cooling Tower (RSD–005) with a ½ hp pump and flow rate approx 30 GPM. Water velocity inside circulating pipe was approx 298 m/min (Figure 1)
- VIA Test Kit (see Test Procedures, Evaluating Vapor Inhibiting Ability)

Figure 1. Open Re-circulating Cooling Tower Flow Chart



Test Procedures

Evaluating Vapor Inhibiting Ability (VIA)

VIA Test evaluates a product's ability to protect metal from corrosion without being in direct contact. The method used is based on the Federal Standard MIL-STD 3010B, Method 4031. An illustration of the VIA test assembly is shown in Figure 2. A sample of IRB material was placed in a dish inside a capped quart-sized jar with a freshly polished and cleaned carbon steel plug (SAE 1010) for 20 hours at ambient temperature. A relative humidity of nearly 100% was then created in the jar (via addition of 3% glycerol in water) for 2 hours at ambient temperature, followed by another 2 hours at 40°C. After being removed from the oven, the plugs were inspected and rated on a scale of 0 to 3, where 0 is heavily corroded (no corrosion inhibition), and 3 means no visible corrosion and good inhibiting effects (see VIA Grading Chart, Figure 3). The test was run in triplicate. The control was a plug exposed in a jar without inhibitor.

Figure 2. Illustration of VIA Test Assembly

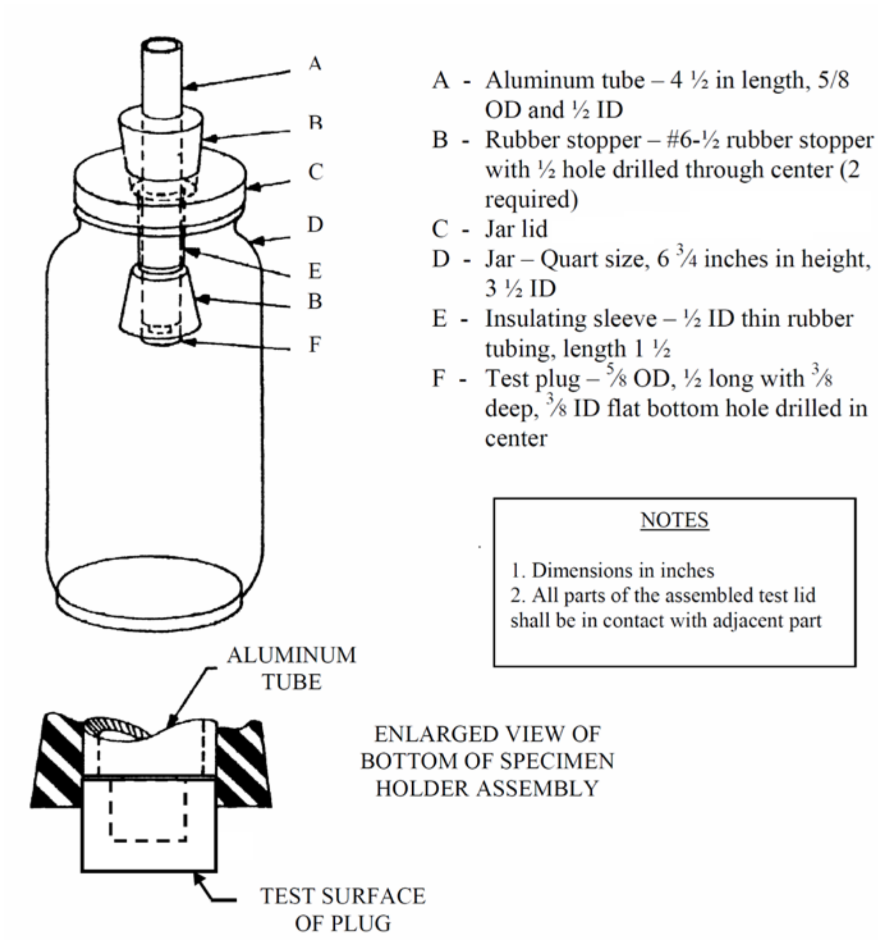
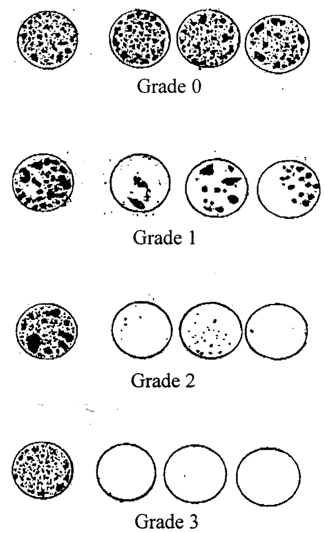


Figure 3. VIA Test Grading Chart (Grade 2 or 3 are passing)

Grade 0:	Blind test No corrosion inhibiting effect
Grade 1:	Blind test Minute corrosion inhibiting effect
Grade 2:	Blind test Medium corrosion inhibiting effect
Grade 3:	Blind test Good corrosion inhibiting effect



A. Test in stagnant conditions was performed as follows:

1. An IRB was weighed, and immersed in 1L of tap water. After 10 days the concentration of inhibitor was determined using the Molybdenum Test Kit; a carbon steel immersion test was set up in this water.
2. Time lapsed before the IRB was dissolved (fell apart) was recorded.
3. A solution of 1200ppm $CaCO_3$ in water was made, and used as a blank. Solutions of 0.7% IRB and 0.28%BB in this water was each made. Immersion of carbon steel was carried out again in the above 3 solutions.

B. Test in pilot cooling tower was performed as follows:

An IRB was weighed and placed in basin of cooling tower.

1. pH, TDS, and the inhibitor concentration in the circulating water were monitored daily. pH and TDS of the makeup water (Tap) was also measured.
2. Based on a control run (without the IRB in the tower basin), the blowdown schedule was set at every seven days using the measured Cycle of Concentration data (within the range of 4-6). Bacterial count and weight of IRB was measured at each blowdown.
3. Corrosion tests were performed by inserting coupons of galvanized steel, steel, and copper into circulating pipe to study the protection during the lifespan of an IRB. The control was circulating water from a cooling tower operated without IRB.

Corrosion rate and percent of corrosion protection were calculated using formula:

Corrosion rate (mpy) $= (3.45 \times 10^6 \times W)/(A \times T \times D)$

Where:

T=Time exposure in hours to the nearest 0.1 h

A=surface area of the coupon in cm^2 to the nearest 0.1 cm^2

W=mass change in g, to the nearest 1 mg

D=density of metal in g/cm^3 (steel=7.85 g/cm^3; copper=8.94 g/cm^3)

Corrosion Protection (%) $Z = \frac{(C_c - C_i) \times 100}{C_c}$

Where:
C_c = the corrosion rate without inhibitor
C_i = corrosion rate with inhibitor

Results

VIA Test

IRB showed protection in vapor phase in VIA test, Table 2 and Figure 4.

Table 2. Vapor Inhibition Ability of IRB

Sample	Plug 1	Plug 2	Plug3
10g IRB	3	3	3
Control	0	--	--

Figure 4. Carbon Steel Plug after VIA Test in IRB

Plug1 Plug2 Plug3 Control

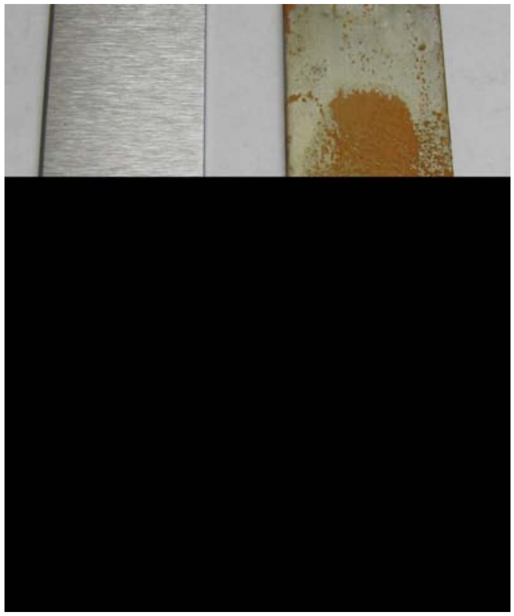
Tests in stagnant water (bench results)

1. It took approximately 4 months for one IRB to be mostly dissolved in 1L of stagnant tap water (several small pieces remained).
2. After an IRB had been immersed in 1L of tap water for 10 days, the concentration of the corrosion inhibitor was found to be 4300ppm.
3. The carbon steel coupon showed no signs of corrosion for 90 days when immersed in the above IRB containing water. The control (in tap water) showed signs of corrosion within 2 hours (Table 3, and Figure 5).

Table 3. Results in Stagnant Water Test (10 days)

Medium	Molybdate Concentration / Corrosion inhibitor concentration (ppm)	Time before corrosion starts
Tap Water with IRB	90/4300	>90 days
Tap water only	<0.1	<2 hours

Figure 5. Immersion of Carbon Steel in IRB treated water (L) vs. untreated water (R)



>90 days **<2 hours**

4. Corrosion protection provided by IRB versus BB was evaluated by immersion in solutions containing elevated calcium ion content, to simulate the conditions of cooling tower operation (Table 4). It showed that the process of incorporating BB into IRB did not affect the protection effectiveness. The data also suggested that the carrier materials did not provide extra protection.

Table 4. Comparison of Corrosion Protection Provided by IRB versus similar amount of BB (70 °C for 72 hrs)*

Sample	Initial weight, g	Final weight, g	Weight loss, g	Z, % of Protection
Control (tap water with 1200 ppm of $CaCO_{3)}$	24.7601	24.4162	0.0401	-
0.28% BB	22.7601	22.7612	-0.0011	97.2
0.7% IRB	23.1848	23.1871	-0.0023	94.3.

*1200ppm $CaCO_3$ in water

B. Test in Pilot Open Re-circulating Cooling Tower

The test results show that IRB dissolved in an even and linear fashion (Figure 6). Figure 7 is a daily monitoring chart of TDS and pH in the circulating water, with or without the presence of IRB. It shows that pH in the circulating water was not affected by IRB, while the Total Dissolved Solids (TDS) increased when IRB was added to the cooling tower basin, as expected. Furthermore, IRB released inhibitor slowly into the circulating water. During the lifespan of an IRB in one pilot test, the inhibitor concentrations in the circulating water were in the range of 150-440 ppm, Figure 8.

Figure 6. Weight Change of IRB in Pilot Test

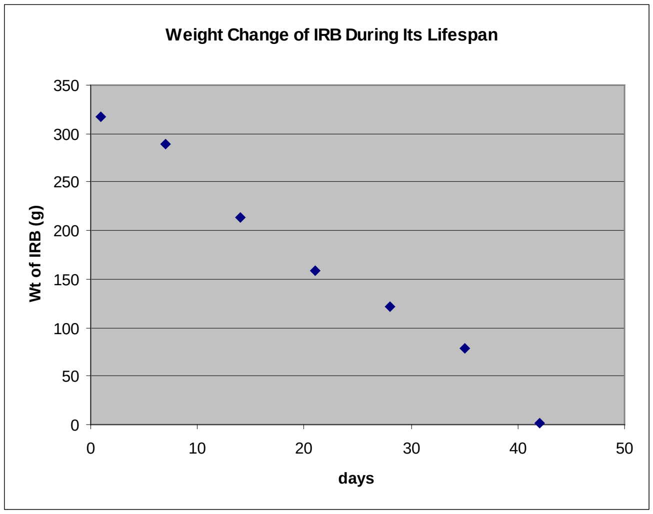


Figure 7. Comparison of pH, TDS in Circulating Water-- with or without IRB

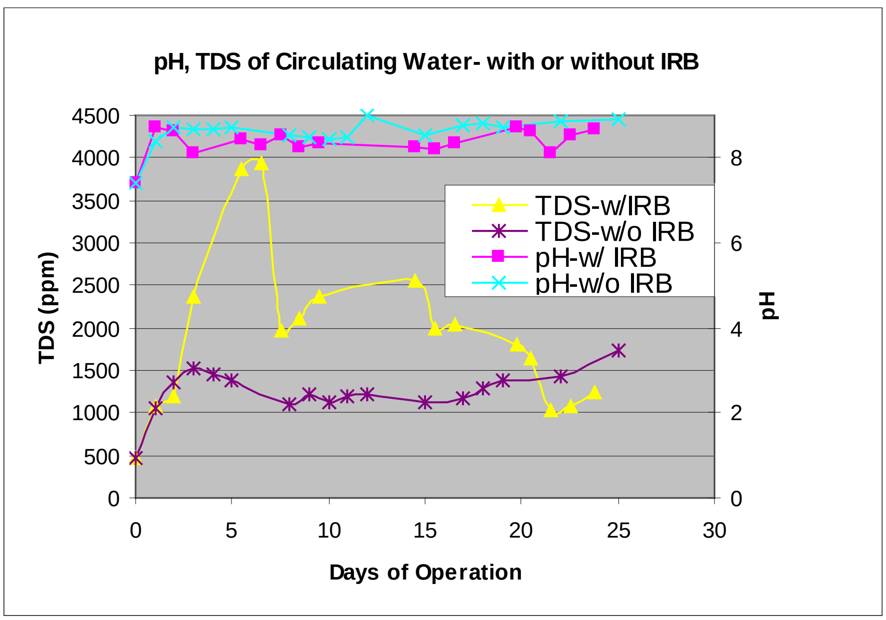
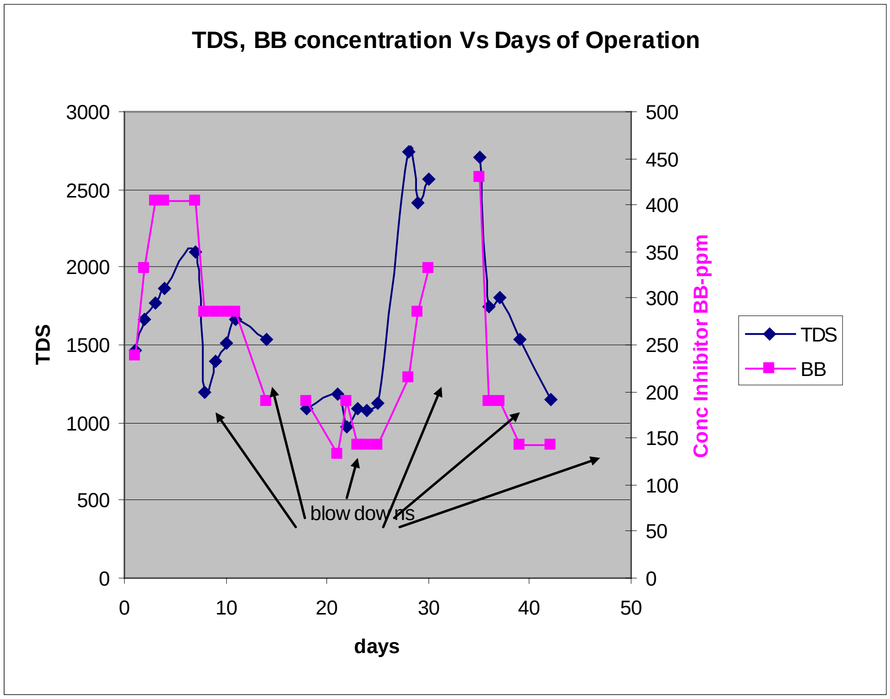


Figure 8. Release of Inhibitor BB



The circulating water treated with IRB provided 70% protection for Galvanized Steel (Table 5). It also provided 45% protection for Carbon Steel and 6.38% protection for copper. In addition, it showed a slightly reduced bio-growth (Table 6).

Table 5. Protection by IRB in circulating water in Pilot Cooling Tower Testing

	Galvanized Steel	
Condition	**Corrosion Rate (mpy)**	**Z (%)**
CorrBlock in Cooling Tower Basin	3.06	70.6%
Control (No inhibitor)	10.41	--

Table 6. Bio Growth in Circulating Water

	Days of Operation	Bio Dipslide Test
Circulating water without the IRB	5th	10^5CFU/ml, moderate growth
	12th	10^4CFU/ml, slight growth
	19th	10^4CFU/ml, slight growth
Circulating water with the IRB	6.5th	10^3CFU/ml, very slight growth
	14.5th	10^3CFU/ml, very slight growth
	20.5th	10^3CFU/ml, very slight growth

Summary and Discussion

1. Based on the bench test data:

- IRB protected in vapor phase.

- IRB released corrosion inhibitors from the carrier. Steel panel was corrosion free after 90+ days in the IRB treated water.
- Immersion corrosion test showed that the manufacturing process of IRB did not affect the protection effectiveness of the corrosion inhibitors.

2. Based on pilot cooling tower experiments:

- IRB dissolved slowly and evenly in a linear fashion. The lifespan of an IRB was about 5 weeks in cooling tower basin. To maintain an effective inhibitor concentration level, the useful life of an IRB is probably 4 weeks.
- IRB released corrosion inhibitor.
- One IRB treated approx 4200L (1904 gal) of water.
- IRB provided good protection to carbon and galvanized steel.
- IRB doesn't promote bio-growth in cooling tower.
- IRB can be easily placed in make-up water, cooling tower basins, return water circuits, or waste water systems to provide time-release of corrosion inhibitors.

Reference

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2. Environmental Enterprises USA, 48-hour Static-Renewal Daphnia Pulex and Pimephales Promelas Toxicity Test Results, (2001)
3. ASTM A-525 (G90) Specification for General Requirements for Steel Sheet, Zinc-Coated (Galvanized) by the Hot-Dip Process
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