

Closed Cooling Loop Corrosion Control: Case Studies of a Reliable, Robust, & Sustainable Treatment Program

Michael P. Weberski Jr.
Nalco Water, an Ecolab Company
1601 W. Diehl Rd.
Naperville, IL 60563
USA

Dan Meier
Nalco Water, an Ecolab Company
1601 W. Diehl Rd.
Naperville, IL 60563
USA

Bingzhi Chen
Nalco Water, an Ecolab Company
1601 W. Diehl Rd.
Naperville, IL 60563
USA

Claire Rayner
Nalco Water, an Ecolab Company
Oude Rhijnhofweg 17
2342BB, Oegstgeest
The Netherlands

Renate Ruitenber
Nalco Water, an Ecolab Company
Oude Rhijnhofweg 17
2342BB, Oegstgeest
The Netherlands

Sai Sudhakaran
Nalco Water, an Ecolab Company
KAUST Building 1030 Level 3, Room 3-3275,
Thuwal, 23955-6900
Saudi Arabia

Steeff Vrijhoeven
Nalco Water, an Ecolab Company
Oude Rhijnhofweg 17
2342BB, Oegstgeest
The Netherlands

ABSTRACT

Closed cooling loops are used to provide the required cooling to critical industrial equipment and processes that cannot tolerate the variability from open recirculating cooling towers. The key challenges in operating a closed loop are corrosion control and microbiological growth. A new non-toxic closed loop corrosion inhibitor program was developed that does not contain nitrite, heavy metal, P, B, or filming amine. This paper will present results from recent field trials using this new digitally-enabled, sustainable corrosion inhibitor program. The first field trial was conducted at a refinery in the Middle East that provided an opportunity to evaluate the new program in a hot loop (>90 °C) that experienced upsets and hydrocarbon ingress. A second field trial was conducted at a steel mill in Europe with a significantly more challenging makeup water that included moderate chloride and no hardness. Positive results from both

field trials will be presented that will include coupon weight loss measurements, dissolved Fe concentration, and product actives monitoring

Key words: Chemical treatment, corrosion inhibitors, corrosion management, water treatment

INTRODUCTION

An emerging market driver in industrial water treatment is the move to more sustainable chemistries. Corporate sustainability goals are becoming more common and more stringent. Customers are turning to water treatment companies for innovative solutions that can satisfy their sustainability goals and not sacrifice performance or asset integrity. Indeed, a major trend in evaporative open cooling water treatment is to move away from heavy metals such as zinc and other environmentally questionable materials such as phosphates. Another area of cooling water that is in need of a sustainability refresh is closed cooling loops. The most widespread closed cooling treatment programs are based on combinations of nitrite, molybdate, and borate. All three of these chemicals have regulatory, discharge and/or SH&E concerns.^{1,2}

Like open cooling towers, closed cooling loops provide cooling to critical operations, but with no cycling or evaporative losses. Key challenges in operating a closed loop are corrosion and microbiological growth. Scale is not typically a concern in closed loops since the makeup waters are usually softened. In addition to nitrite and molybdate, some treatment options exist that are based on phosphorus or filming amines,^{3,4} but nitrite and molybdate have been and remain the most widely used.⁵ Although scale is not a concern in closed loops, the chloride content in the loop has been shown to be the primary driver of corrosion. Chlorides can enter the closed loops either from the makeup water, or from leaks in seawater cooled heat exchangers. For example, refineries in the middle east are prone to such chloride ingress. Such spikes in chloride concentration can prove problematic for less robust closed cooling options such as molybdate and filming amines. As such, a market need has emerged for a reliable, robust, and sustainable closed cooling treatment program.

We have previously communicated the laboratory feasible experiments for a closed loop corrosion inhibitor package that does not contain nitrite, molybdate, borate, phosphorus, or filming amine.⁶ The new formulation, EXP2083, displays excellent corrosion inhibition performance even at high temperatures (60 °C) and high chloride (150 ppm). Following the excellent performance in the laboratory, two technical field trials were conducted to continue validation of the new sustainable chemistry EXP2083. This paper will summarize the results of these field trials. Field Trial #1 was conducted at a French steel mill on one of the closed loops of the blast furnace. Field Trial #2 was conducted on a closed loop in a refinery in Saudi Arabia. It will be shown that EXP2083 displayed excellent results during these field trials.

The paper will conclude with some biocide compatibility experiments. As previously mentioned, microbiological growth is one of the key challenges in operating closed loops. Any new closed loop treatment must be compatible with the conventional biocides that are used in closed loops. Most commonly non-oxidizing biocides are used. Our testing showed that EXP2083 is compatible with commonly used non-oxidizing biocides.

EXPERIMENTAL PROCEDURE

Corrosion inhibition performance was evaluated using beaker tests at 40 °C, 60 °C, and 80 °C. 1 L duran bottles were filled with 1100 mL of either synthetic or site-specific makeup water and dosed with the desired corrosion inhibitor treatment. Coupons were submerged into the water, below the liquid surface, and secured in place by means of a cable tie. Two coupons were inserted in each beaker, with a plastic spacer in between the coupons; the average corrosion result for each test is reported. Temperature was controlled to a set point, via a thermocouple immersed into the liquid and heat was provided by a hotplate. The samples were agitated at 400 rpm using a 10 x 50 mm magnetic stirrer and testing was typically carried out for 14 days.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

RESULTS

Field Trial #1: French Steel Mill

A new non-toxic closed loop corrosion inhibitor program (EXP2083) was developed, that is borate, nitrite, molybdate and phosphorus free. The previously reported laboratory results,⁶ indicate that the new closed loop corrosion inhibitor program is a robust treatment; in that it is able to tolerate higher chloride levels than conventional molybdate and organic based treatments. The program also offers superior buffer capacity and favorable biostability (in comparison to conventional nitrite-based treatments). These key attributes make this new offering very attractive for potential application in the primary metals sector in Europe, where regulations around the use of some of the traditional closed loop chemistries may restrict treatment options. Furthermore, the challenging conditions encountered in such applications often leads to performance related issues, predominantly, corrosion and microbiological growth, which can directly impact steel mill production.

A field trial was performed at a steel mill in France on one of the closed loops of the blast furnace. The makeup water of this closed loop was lime softened and basic ion-exchanged and considered to be inherently corrosive in nature due to the high chloride and sulfate content (50 ppm chloride and 110 ppm sulfate (as shown in Table 5 below). The incumbent treatment was a molybdate based product in combination withazole for yellow metal protection. Caustic was also dosed to maintain pH to a target of between 9.5 to 10. The site was suffering from localized and general corrosion, exceeding the site KPI $<20 \mu\text{m}/\text{year}$ (0.8 mpy) for mild steel, as well as dissolved iron levels at 2-10 ppm (see Figure 2 below) despite sockets and magnetic filters being in place. Furthermore, the high level of total iron in the system resulted in frequent blow down increasing water consumption.

Prior to the field trial, laboratory beaker screening tests were completed to evaluate the performance of the new treatment program in makeup water collected from the site. The purpose of the beaker testing was to evaluate the performance of the new program against the incumbent chemistry, as well as establish the dose rate required for adequate corrosion protection in this specific makeup water.

The beaker testing was carried out for a period of 14 days at a temperature of 40 °C and 80 °C under agitation (400 rpm). The makeup water was dosed with the desired chemistry and mild steel coupons were inserted into the beakers to evaluate the performance of the corrosion inhibitor (by determining the weight loss per surface area over the duration of exposure). A 48-hour stagnant period was also incorporated into the test to allow initial rusting and to evaluate program response (in order to obtain better differentiation and more realistic performance indication) as shown in Table 1.

The testing indicated that corrosion control of the current molybdate treatment is weak (at 40 °C) to poor (at 80 °C) on pre-corroded surfaces as rusting of the coupon surface was observed during stagnancy and corrosion continued to be high once flow was resumed. The results (Table 2) showed that 2800 ppm EXP2083 (Treatment 3 and 4) was able to outperform the existing molybdate treatment (Treatment 1 and 2), achieving corrosion rates below 1 mpy in comparison to 3.96 (40 °C) and 15.75 (80 °C) mpy with the molybdate based treatment. EXP2083 was also able maintain corrosion protection after the 48-hour stagnancy period (under the conditions tested), noted by the visual appearance of the water after the 48-hour stagnancy period.

Further dose rate screening was carried out to establish a suitable starting dose rate for the trial. Similar beaker tests were performed at 40 °C for 14 days. The 48 hour stagnancy period (after 7 days) was also incorporated into the test. The EXP2083 dose rate screening test clearly indicated that higher dose rates ($\geq 2000 \text{ ppm}$) are required to maintain low iron levels and corrosion rates ($<0.7 \text{ mpy}$, $<0.4 \text{ ppm Fe}$) for this type of water chemistry.

Table 1
Results of the Beaker Screening Test Comparing EXP2083 to the Molybdate Based Treatment
Using Makeup Water Collected from a Steel Mill in France (Water quality: chloride = 50 ppm and
sulfate = 110 ppm).

Test Conditions	1	2	3	4
Temperature (°C)	40°C	80°C	40°C	80°C
Treatment (ppm)	200 ppm MoO ₄ 3.4 ppm azole 120 ppm 50 % NaOH	200 ppm MoO ₄ 3.4 ppm azole 120 ppm 50 % NaOH	2800 ppm EXP2083	2800 pm EXP2083
T= 7 days (Stirring stopped)				
pH (initial)	10.95	10.95	10.95	10.91
Conductivity (initial)	995 µS/cm	971 µS/cm	1520 µS/cm	1521 µS/cm
T= 7+ 2 days (Stirring resumed)				
T = 14 days				
pH (final)	9.58	9.44	10.05	9.74
Conductivity (final)	879 µS/cm	878 µS/cm	1421 µS/cm	1437 µS/cm

Table 2
Coupon Results of the Beaker Screening Test Comparing EXP2083 to the Molybdate Based Treatment Using Makeup Water Collected from a Steel Mill in France (Water quality; chloride = 50 ppm and sulfate = 110 ppm).

Test Conditions	1	2	3	4
Temperature (°C)	40°C	80°C	40°C	80°C
Treatment (ppm)	200 ppm MoO ₄ 3.4 ppm azole 120 ppm 50 % NaOH	200 ppm MoO ₄ 3.4 ppm azole 120 ppm 50 % NaOH	2800 ppm EXP2083	2800 pm EXP2083
Coupons after 14 days (Before acid cleaning)				
Average (mpy)	3.96	15.75	0.66	0.84

Table 3
Dose Rate Screening Test Evaluating the Performance of EXP2083 Using Makeup Water Collected From a Steel Mill in France (Water Quality: chloride = 50 ppm and sulfate = 110 ppm) at 40 °C.

Treatment	Dose Rate EXP2083 (ppm)	Temperature (°C)	Average corrosion rate after 14 days (mpy)	Fe (ppm) after 14 days	
				Filtered	Total
1	2000	40	0.64	0.29	0.36
2	1500	40	1.32	4.00	4.60
3	1000	40	2.63	16.00	17.00

Field Trial Objectives

Following the promising results of the lab testing, the objectives of the field trial were to reduce corrosion rates in line with key performance indicators (KPIs) specified by the site, namely:

- Mild steel Corrosion coupons: <20 µm/y (<0.8 mpy)
- Copper Corrosion coupons: <5 µm/y (<0.2 mpy)
- Total Iron levels (<5 ppm)