

A Robust Non-Phosphorus Cooling Water Treatment Program That Reduces the Biological Control Challenge - Case Studies

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ABSTRACT

In open cooling water systems, phosphorus-based (P-based) programs are the most widely used treatment program for corrosion and scale control. Excellent performance of P-based programs has been long proved in many institutional and industrial applications. Despite this high performance, phosphorus is one of the limiting nutrients to bacteria and may accelerate microbial growth if with excess concentration. A recently developed and innovative non-phosphorus (non-P) program has been deployed globally, not only to comply with discharge regulations, but also to provide additional benefits/value to our customers. One feature of the non-P program is to eliminate/reduce phosphorous feed that enhances biological control. First case study of a non-P program is in a microelectronics plant. The new non-P program showed excellent corrosion, scale, and microbiol control performance. Superior performance of corrosion and scale control was demonstrated and is fully understood from a mechanistic perspective. For microbiol control, the bacteria count dropped two orders of magnitude after switching from an incumbent phosphorus-based program to the innovative non-P program. In the 2nd case study, an ethanol production plant recently switched from P-based program to the non-P program to improve the algae control in the discharge pond. After 10+ years suffering from algal bloom at summertime, very positive results have been observed. Moreover, corrosion control was further improved as reported.

Keywords: non-phosphorous program, microbiol control, algae control, open cooling water system

INTRODUCTION

Cooling water systems are commonly used to cool a process, either steam, gas or liquid, through heat exchangers or condensers in various plants. The heat exchangers or condensers can be corroded easily or have scale and biofilm growth due to the poor water treatment program. The corrosion, scale, and biofilm growth on heat exchangers can lead to significant reduction in heat exchanger efficiency and lifetime. The repair expense or loss of production often costs plants a few hundred thousand or millions of dollars per day for heavy industries, such as chemical and power plants, refineries, and steel mills. Thus, cooling water treatment is critical to maintain the integrity and efficiency of heat exchangers.

Since the use of chromate was banned in the 1980s, phosphate became one of the most common corrosion inhibitors in cooling water treatment programs.¹ For effective corrosion control, the phosphate concentration needs to be adjusted based on pH, chloride, sulfate and calcium concentration and heat exchanger skin temperature. Typically, the phosphate requirement increases with decreasing pH and calcium concentration and increasing temperature and chloride/sulfate concentration. Polymeric scale inhibitor is needed to prevent calcium phosphate scale. In general, higher scale inhibitor dosage is needed at higher pH, phosphate, and calcium concentration. Precise control of polymer concentration is required in the stabilized phosphate programs. Changes in makeup water matrixes can lead to serious scale or corrosion events if stabilized phosphate program is not adjusted appropriately.²

Apart from precise dosage control requirements, phosphorus by itself is an undesirable aquatic nutrient. Phosphorus, like nitrogen, is a critical nutrient required for all life. The most common form of phosphorus used by biological organisms is phosphate (PO_4), which plays major roles in the formation of DNA, cellular energy, and cell membranes (and plant cell walls).³ As early as 1972, phosphorus was globally recognized as the primary limiting nutrient for algae growth in lakes and other bodies of fresh water.^{1,2} High concentrations of phosphorus may result from poor agricultural practices, runoff from urban areas and lawns, leaking septic systems or discharges from sewage treatment plants. A significant portion of water effluent is coming from cooling water effluent which contained varying amounts of phosphorus. Too much phosphorus can cause increased growth of algae and large aquatic plants, which can result in decreased levels of dissolved oxygen – a process called eutrophication.³ High levels of phosphorus can also lead to algae blooms that produce algal toxins which can be harmful to human and animal health. Phosphorus discharge restriction from cooling systems is a steady trend worldwide.¹⁻⁴

Nalco Water has developed a novel, non-phosphorus treatment program, which includes a proprietary dual function organic corrosion and scale inhibitor, along with an inorganic-based cathodic corrosion inhibitor. This response to the challenges of conventional non-phosphorus treatment programs. Based on the testing results presented in previously published paper^{1,4}, the newly developed non-phosphorus program brings the following advantages compared to conventional non-phosphorus programs

- Extended application window from medium to high Ca/Alk water to soft water, and high conductivity water with high chloride
- Tolerant to both fluctuating make-up water and the tower water
- Robust performance at varying pH
- Operational flexibility without the need of dosage tuning with a varying water matrix
- Adaptable to high cycles and long Holding Time Index (HTI) (200 hours) application
- Fluorescence based tracing and tagging technology for monitoring and dosage control of both inhibitors.

The following lab and field evaluations are presented to illustrate additional advantage, namely, improved microbiol and algae control.

EXPERIMENTAL PROCEDURE

Benchtop Corrosion/Scaling/Bio Tests

Benchtop microbial tests were designed and carried out to compare P-based and non-P program effect on microbial growth. Representative P-based (dispersant + zinc + phosphate + organic phosphonate) and non-P based (dispersant + organic dual functional inhibitor + metal-based inhibitor + azole) water treatment chemicals were dosed into tap water. Tap water matrix is listed in Table 1. Additional glucose nutrient was also added to all test samples for microbial growth. Samples were placed in 30°C incubator for up to 60 hours and taken off for standard plate count (SPC) test periodically for bacterial count.

Table 1
Water Chemistry of Benchtop Test

	Tap Water
Ca (ppm as CaCO ₃)	100
Mg (ppm as CaCO ₃)	40
M-Alk (ppm as CaCO ₃)	100
Cl (ppm as ion)	33
SO ₄ (ppm as ion)	40
pH	7.9
Conductivity (μS/cm)	300

RESULTS

Benchtop Bio Test Results

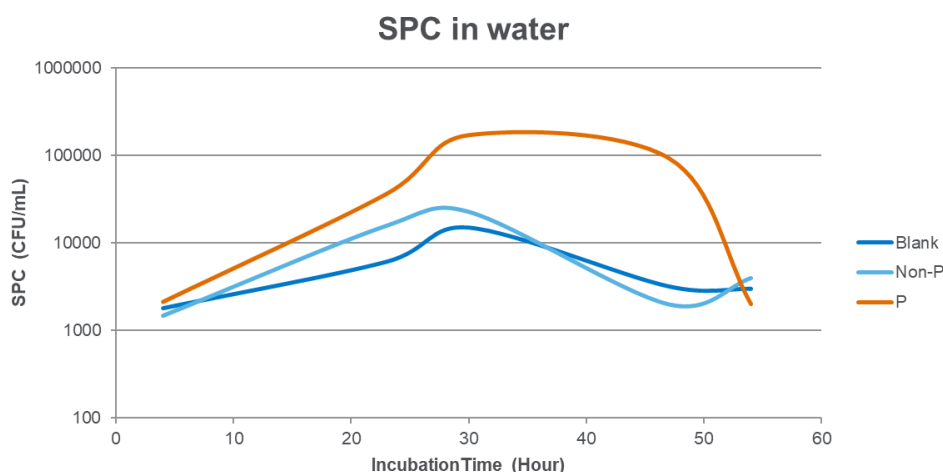


Figure 1: Aerobic bacteria by standard plate count SPC in tap water with glucose.

Tap water sample with glucose nutrients and without additional chemical treatment was used as a blank sample. For blank sample, microbial growth can be identified by a bacterial count increase to 10^4 CFU/mL in the first 30 hour of incubation and then drop to a lower level due to complete consumption of glucose nutrients. For sample with additional P-based program, a significant increase in bacterial count to $>10^5$ CFU/mL was observed in the first 30 hour. While for non-P program under same incubation time, the bacterial count is only $>10^4$ CFU/mL, slightly higher than blank sample. As phosphorous is a key nutrient for life, a slower microbial growth is expected in the absence of phosphorous element. We also observed that the bacterial count remained at a high level even after 50 hours of incubation for P-based program due to introduction of phosphorous nutrient. While for non-P program without additional phosphorous

nutrient, decay in bacterial count occurred shortly after 30 hours of incubation as running out of glucose nutrients.

Customer Field Trial Results

Case Study 1 – Microelectronic Manufacture Plant

Regulation on phosphorous discharge is getting progressively more stringent in China. A microelectronic manufacturing plant located in Yangtze River delta zone was faced with strict regulation and law enforcement on phosphorous discharge for their cooling water system. They were using a phosphate-based program and needed a solution for a non-phosphorous program. In addition to regulatory compliance concerns, the customer was also facing total plant water consumption challenges. They have a water quotation limit which became increasingly difficult to manage in the high-water demanding summer months. To comply, the customer would adjust operational parameters. This included increasing cycles of concentration for their cooling water system, leading to water chemistry fluctuation and a higher scaling tendency in their cooling water system. A high cycle of concentration also means longer holding time index (HTI) which may result in potential microbial control issue.

The cooling water system treated has about 100 m³ in volume and 500 m³/h in recirculation rate. Under 5 cycles of concentration and a delta T of ~5 °C, the estimated blowdown is 1 m³/h. The cooling water system contains both mild steel and copper. The cooling water is supplied to cool down chiller systems to remove heat from their manufacturing process.

Before kicking off customer field trials, both makeup water samples and cooling water samples were collected and analyzed. The representative water quality is summarized in Table 2. Detailed water chemistry including pH, conductivity, hardness, alkalinity, chloride and sulfate concentration, were provided. From water chemistry analysis results, the cooling water system was operated at a 4X cycles of concentration before conversion. Water chemistry started to fluctuate during trial phase with cycles of concentration ranges from 4X to 8X (Figure 2). Meanwhile, holding time index (HTI) also increased two-fold from 54 hours to 126 hours. As a result, the cooling water system was facing strong challenges in both scaling and microbial control. In order to keep tracking of microbial control, fresh samples were also collected and sent to standard plate count SPC test @ 35 °C for bacterial count.

Table 2
Water Chemistry During Baseline and Trial

	Makeup	Tower water baseline	Tower water trial
Conductivity (µS/cm)	360	1300	1300~2200
pH	7.95	8.73	8.65~9.05
Ca as CaCO ₃ (ppm)	78	325	300~740
Mg as CaCO ₃ (ppm)	32	125	100~270
M-A as CaCO ₃ (ppm)	110	430	320~960
Cl ⁻ (ppm)	24	110	110~240
SO ₄ ²⁻ (ppm)	33	140	130~300

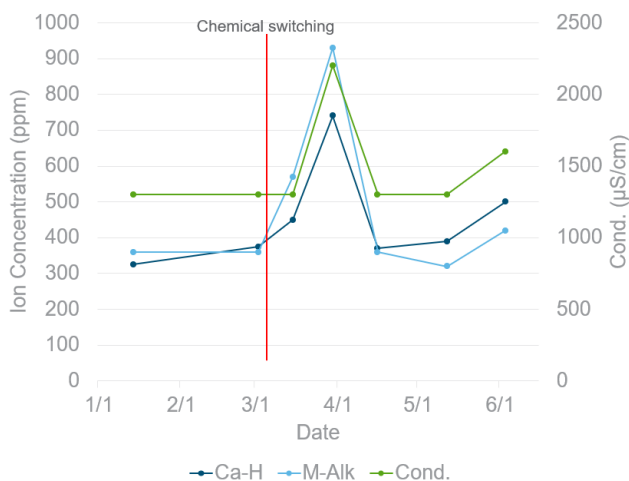


Figure 2: Water chemistry fluctuation during trial.

The corrosion inhibition performance was monitored both by a 30-day coupon and metal ion concentration from water chemistry analysis. As shown in Table 3, the 30-day mild steel coupon treated with phosphate-based program before trial was reported at 0.94 mpy in corrosion rate vs. 0.71 mpy for non-P program. An improved coupon appearance was also clearly demonstrated after the conversion from P-based program to a non-P program. Besides coupon data, water chemistry data (Figure 3) also indicated an improvement in corrosion control. Iron concentration dropped from 0.21 ppm to 0.07 ppm with >60% reduction. Copper concentration in water and coupon corrosion rate remain unchanged after conversion to non-P program due to similar azole dosage.

Table 3

30 Days Mild Steel and Copper Coupon with Pictures and Corrosion Rate

		Baseline with P-based program	Trial with non-P program
Mildsteel	Picture		
	Corrosion rate (mpy)	0.94	0.71
Copper	Picture		
	Corrosion rate (mpy)	<0.1	<0.1