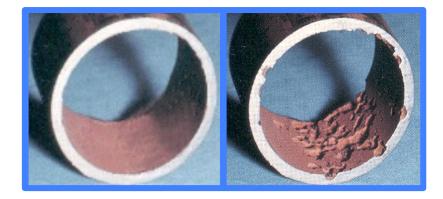
Closed System Protection

A HOW-TO HANDBOOK FOR PLANT MANAGERS AND FACILITIES ENGINEERS



Water chemistry determines corrosion rate. Corrosion rate determines system longevity. Therefore, water chemistry determines system longevity.

Myths Of System Failure

- It is *impossible* in airtight systems.
- It is *inevitable* because water is corrosive.
- It is *best avoided* by using treatment from specialty chemical companies.

Such misconceptions can be very expensive. Our mission is to provide objective guidance and leadership in the management and protection of closed water loops. This handbook is designed to help plant managers and facilities engineers make the transition to *protective monitoring*, which is essential to system efficiency, dependability and longevity.

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Introduction

In open water systems – such as cooling towers and evaporative coolers – problems such as corrosion, scaling and fouling are apparent to anyone who takes a moment to peek through the access door.

In closed water systems – such as heated, chilled and geothermal loops – the interiors of boilers and pipes are permanently hidden from view. Problems such as corrosion, scaling and fouling can proceed unabated, until systems rupture and fail.

Most plant managers know that systems are best protected when the chemistry of the circulating water is routinely monitored and corrected to prevent harmful chemical reactions from doing irreversible damage. In others words, they realize that *protective monitoring* must be applied if systems are to perform for many decades.

What many plant managers do not know is how to conduct *protective monitoring* themselves, or how to find someone who does. Most closed system water-side management services are really sales schemes. Expensive, brand-name treatments, accompanied by free test kits and log sheets, are marketed by specialty chemical companies. Their commissioned salesmen often have little knowledge of water chemistry and limited technical training. Their focus is product sales, not system science.

Protective monitoring is defined and described here, so it may be implemented in-house, or successfully sought and contracted to qualified professionals. Either way, responsible, lifelong system protection, which holds corrosion at negligible levels and eliminates scaling and fouling, can be accomplished for less than \$1 per day of system operation.

Problems With The Status Quo

A Typical Scenario

A new heating system is installed, and responsibility for its care is transferred to the plant manager. He is advised by the industry – the manufacturer, the mechanical engineer, the contractor, the boiler inspector, the insurance company – to contact a *water treatment professional*. The problem is there are very few qualified professionals – chemical engineers and water chemists – in the closed system protection business. Chemical sales companies have filled the void with expensive treatment products that are often 85% water. The plant manager may presume these companies will provide the guidance he seeks. Or, if he recognizes they are not an objective source of information, he may choose to do nothing.

Signs Of Trouble

- Water is not routinely analyzed.
- Corrosion rates are not measured.
- Water is cloudy, off-color or odiferous.
- Water has high conductivity or low pH.
- Zone-valves, pump-seals and boiler-tubes fail.
- Annual chemical costs exceed \$30 per system.
- Treatment, if used, is added on a time-schedule.
- Pipes show rusting, pitting, grooving, deposits or scale.

About Nitrite

Sodium nitrite, mixed with sodium borate, is a standard offering among chemical sales companies. But, nitrite treatment is a poor choice for closed systems for a number of reasons.

First, nitrite is an environmental toxin. Second, it is aggressive to copper and brass. Third, at levels above target concentrations, it hardens rubber gaskets and forms abrasive crystals at evaporation sites, wearing seals and valves. At levels below target concentrations, it accelerates corrosion rates, making it worse than having no treatment. Fourth, nitrite is a ready source of food for the microbes that cause fouling.¹

Destructive Processes: Causes & Preventives

Corrosion

Corrosion is the primary cause of failure in closed systems. Corrosion is the reversion of metal to its stable, oxidized, ore form. Iron, for example, reverts to various oxides we call "rust". Corrosion processes are complex electrochemical reactions, with results ranging from pinpoint penetration to generalized metal loss.

Causes Of Acidic (Etching) Corrosion

Carbon dioxide dissolves in water, forming hydrogen ions and bicarbonate ions. $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$ Oxygen dissolves in water and reacts with glycol, forming organic acids. $O_2 + H_2O + RCOH \rightarrow RCOO^- + H^+$ Then, hydrogen ions accept electrons from metal, forming dissolved metal and hydrogen gas. $H^+ + M \rightarrow M^+ + H_2$

Preventives¹

Buffering agents provide hydroxide ions that combine with hydrogen ions, forming harmless water. $OH^- + H^+ \rightarrow H_2O$ Reducing agents provide ions that combine with dissolved oxygen, forming harmless compounds. $RO_3^- + O_2 \rightarrow RO_4$

Causes Of Bimetal (Galvanic) Corrosion

An electrical potential exists between two dissimilar metals in a conductive solution. The relatively-active metal donates electrons to the relatively-inert metal, dissolving the former. Fe + Cu \rightarrow Fe⁺⁺ + Cu⁻⁻

Preventives¹

System-flushing decreases conductivity. Film-forming agents provide electrochemical insulation for metal surfaces. Fe + Cu \rightarrow Fe + Cu

Cause Of Oxidative (Rusting) Corrosion

Oxygen dissolves in water and accepts electrons from iron, forming rust. $O_2 + H_2O + Fe \rightarrow Fe^{++}(OH^{-})_2$

Preventives¹

Reducing agents provide ions that combine with dissolved oxygen, forming harmless compounds. RO_{3} + $O_2 \rightarrow RO_4$

Scaling

Water lost from leaky seals, faulty valves, and plumbing work requires systems to draw make-up water, which may contain scale-forming minerals. The deposits they form on interior surfaces can accelerate wear on pumps and valves, and reduce operational efficiency.

Cause Of Scaling

Hardness ions in water react with bicarbonate, phosphate and silicate ions, forming precipitates. $Ca^{++} + Mg^{++} + HCO_3^- + PO_4^{--} + SiO_2^{--} \rightarrow CaCO_3 + Ca_3PO_4 + MgHPO_4 + MgSiO_3$

Preventives

Softening make-up water lowers concentration of hardness ions. Capping make-up rates at 10% of system volume per year lowers concentration of hardness ions.

Fouling

Fouling is relatively rare in closed systems. When it occurs, it leads to operational inefficiency and down-time, making it more of an inconvenience than a catastrophe. Fouling does not occur in heated loops where temperatures exceed 140 °F, and is unusual in chilled loops where glycol concentrations exceed 30%. If system temperature and glycol concentration are routinely below these levels, microbes may flourish.

Cause Of Fouling

Bacteria consumes organic compounds (nitrites and dilute glycols) and proliferate.

Preventives

Avoiding nitrite treatment eliminates a food source. System-flushing to decrease nitrite levels to < 50 ppm reduces availability. Maintaining glycol concentrations above 30% creates an unfavorable osmotic environment.

Intelligent Application Of Preventives

Understanding Safe Zones

Safe zones are the optimal ranges for protective chemistries in closed systems². Practicing safe-zone chemistry minimizes the occurrence of destructive processes, and defines and standardizes the responses to causal chemistries.

Destructive Process	Cause	Preventive	Safe Zone
acidic corrosion	low pH	add Dipotassium Phosphate*	pH 8.0*** or pH 9-10****
		or Sodium Tetraborate**	
oxidative corrosion	dissolved oxygen	add Sodium Sulfite	30-50 ppm
bi-metal corrosion	no protective film	add Sodium Lauroyl Sarcosinate	30-100 ppm
bi-metal corrosion	high conductivity	flush loop	< 4000 µmhos / cm
scaling deposits	hard make-up water	soften make-up water	< 10% make-up / year
			< 100 ppm hardness
microbial fouling	low glycol / nitrite	increase % glycol / use no nitrite	> 30% glycol / < 50 ppm nitrite

*pH buffer for glycol loops. **pH buffer for water loops. ***For loops with aluminum. ****For loops without aluminum.

Implementing Safe Zones

Safe-zone chemistry is the cornerstone of *protective monitoring*. A protective monitoring program consists of periodic water sampling and analysis, followed by a comparison of results to safe-zone standards. If any parameter lies outside its safe zone, the appropriate preventive action is taken to bring it into specification.

Do-It-Yourself Protective Monitoring

In-house protective monitoring requires a small initial investment and a few hours of labor each year. The requisite tools^{3,4,5} and techniques are within everyone's reach. Following are step-bystep instructions for a successful program.

Drawing Samples

A sample should be drawn every three months during the period the system operates. If a system runs just part of the year, sample again right before shut-down to ensure it is protected before it sits idle. System water may be analyzed right at the valve, or collected³ and returned to a work area for analysis. A one-ounce sample is needed.

- Select a faucet not used to feed chemical into system.
- Open valve and allow fluid to run until its appearance stabilizes.
- Fill sample bottle all the way to the top, cap tightly and close valve.

Analyzing Samples

Seven parameters must be measured, one of which is particular to chilled loops. Portable probes and field test kits⁴ are available for five of the parameters. The remaining two are gauged by sight.

Opacity / Color: An indication of corrosion products, organic matter and particulates present.

- Examine sample under good lighting, against a white background.
- Note opacity ("clear" or "cloudy"). Note color ("colorless", "yellow", "pink", "rusty", "brown", etc.)
- Record values. Example: "clear/colorless"

pH: A measure of acidic or basic conditions.

- Make sure probe is properly calibrated (see manufacturer instructions).
- Remove cap, turn on probe and submerge tip in sample.
- Swirl gently until reading stabilizes.
- Record value as pH. Example: "pH 9.4"

Sulfite: A measure of Sodium Sulfite in ppm.

- Fill reaction tube with 25 ml of sample.
- Add one drop of phenolphthalein indicator and swirl (sample may turn red).
- While swirling sample, add acid-starch indicator one dipper-at-a-time until sample turns clear.
- Add two more dippers of acid-starch indicator and swirl to dissolve.
- Add iodide-iodate reagent one drop-at-a-time until sample turns blue.
- Multiply number of iodide-iodate drops used by ten.
- Record value as ppm. Example: 8 drops x 10 = "80 ppm"

Sarcosinate: A measure of Sodium Lauroyl Sarcosinate in ppm.

- Fill sample bottle about half-full and recap.
- Vigorously shake sample up and down for three seconds.
- Immediately remove cap and count seconds as you watch foam dissipate.
- Stop counting when clearing appears in the middle of foam.
- Multiply number of seconds counted by ten.
- Record value as ppm. Example: 3 seconds x 10 = "30 ppm"

Conductivity: A measure of dissolved inorganic salts in umhos/cm.

- Make sure probe is properly calibrated (see manufacturer instructions).
- Remove cap, turn on probe and submerge tip in sample.
- Swirl gently until reading stabilizes.
- Record value as µmhos/cm. Example: "480 µmhos/cm"

Freeze Point: Temperature at which fluid freezes in °F (for glycol systems).

- Make sure refractometer is properly calibrated (see manufacturer instructions).
- Make sure the prism surface is clean and dry.
- Use pipette to deposit two or three drops of sample onto surface.
- Close cover and make sure no bubbles are trapped and entire surface is wetted.
- Wait thirty seconds before taking reading.
- Read value at junction of blue and white fields.
- Record value as degrees Fahrenheit. Example: "-16 °F"

Hardness: A measure of calcium carbonate in ppm.

- Dip strip into sample and hold for 1 second, then remove and shake off excess water.
- Hold strip level, with test pad facing up, for 15 seconds.
- Compare test pad color to color chart printed on bottle.
- Estimate value if test pad color falls between chart colors.
- Record value as ppm. Example: "13 ppm"

Correcting Chemistry

Record test results and compare each to its safe zone. If a value lies outside the safe zone, follow the action recommended for that parameter in the legend on page 5. This completes the *protective monitoring* cycle. Repeat the process every three months. Examples of safe-zone reports are given below.

Safe	Opacity / Color	рН	Sulfite	Sarcosinate	Conductivity	Action Taken
Zones	clear / colorless	9-10	30-50	30-100	<4000	OK; no action necessary.
Heated Water System, 2000 gallons: 2016 REPORT						
Jan	cloudy / rusty	7.5	0	0	2400	Flushed system. Added: 20# Borate, 2# Sulfite, 2# Sarcosinate.
Apr	clear / colorless	8.4	60	40	420	Added: 5# Borate.
Jul	clear / colorless	8.9	50	30	450	OK; no action necessary.
Oct	clear / colorless	9.0	40	30	440	OK; no action necessary.

Safe	Opacity / Color	рН	Sulfite	Sarcosinate	Conductivity	Freeze Point	Action Taken
Zones	clear / colored	9-10	30-50	30-100	<4000	< winter lows	OK; no action necessary.
Chille	Chilled Glycol System, 1000 gallons: 2016 REPORT						
Jan	clear / pink	8.4	10	30	2340	+16	Added: 10# Phosphate, 1# Sulfite.
Apr	clear / pink	9.5	70	30	3210	+16	OK; no action necessary.
Jul	clear / pink	9.4	20	30	2980	+16	Added: 1# Sulfite.
Oct	clear / pink	9.4	80	30	3100	+17	OK; no action necessary.

Verifying Protection

Even if safe-zone chemistry is consistently maintained, it is wise to directly measure system protection. A *system monitor* consists of mild steel and copper, the most common metals in water systems. It is submerged in system water for one year. During this time, the monitor experiences corrosion, scaling and fouling at the same rate and to the same degree as the system. After this period, the monitor is returned to the laboratory, where it is examined and assigned a corrosion rate. A corrosion rate lower than 0.1 mil per year is ideal.

Professional Protective Monitoring

Performance Standards

If you decide to contract closed system care, set standards for performance. Keep in mind that treatment chemicals are not inherently costly; they should be the *least* expensive part of a program. Any company asking for a chunk of your budget should meet a few basic criteria.

- Monitoring is emphasized, not chemicals.
- Objective protective standards are met.
- Corrosion rates are directly-measured.
- Treatment costs are minimized.
- Nitrites are not used.

Participating Laboratories

The following labs offer monitoring programs that meet the above criteria. About \$1 a day retains an HVAC chemist and covers all program costs, including sampling kits, system monitors, laboratory analyses, and preventive treatment. For more information about their services, or for assistance with an in-house endeavor, contact the lab nearest you.

Closed System Laboratories, Inc.

6602 Sutton Road Madison WI 53711 ask@closedsystemlabs.com <u>closedsystemlabs.com</u> (608) 213-9328

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1816 North Cascade Avenue Colorado Springs CO 80907 richard_kunz@msn.com rkchemist.com (719) 635-1325

closedsystemlabs.com

References

¹ ASHRAE has evaluated agents used to control water chemistry in heated and chilled systems: "Water Treatment In Closed Systems", Darrell Hartwick (<u>ashraejournal.org</u>).

² Richard Kunz was an HVAC chemist who made a life-long study of water chemistry in open and closed systems: "Maintaining Engineered Water Chemistries Assures Long Closed System Life", Richard Kunz (rkchemist.com).

Do-It-Yourself Supplies

³ Sampling Supplies: ~\$40

System water may be analyzed right at the valve, or collected and returned to a work area for analysis. If you choose the latter, we recommend having a few dozen sample bottles on-hand. These are tough enough to be re-useable, and affordable enough to be disposable. The caddy makes for easy toting of bottles as you make the rounds.

- 1-oz Boston Round Bottle: freundcontainer.com #35001 (32¢/bottle x 100 bottles = \$32)
- Rubbermaid® Carry Caddy: officedepot.com #948315 (\$9)

⁴ Probes & Test Kits: ~\$290

These are sturdy, accurate, easy-to-use portable probes and field test kits.

• Oakton PCTestr 35 pH / Conductivity Meter: <u>amazon.com</u> #WD35425-00 = \$110

- K-1529 Sulfite Test Kit: <u>taylortechnologies.com</u> = \$50
- RHA-200ATC Refractometer (for glycol systems): <u>amazon.com</u> = \$25
- Conductivity Calibration Solution: <u>hach.com</u> #1440042 = \$17
- pH 4 Calibration Solution: <u>hach.com</u> #2283449 = \$12
- pH 7 Calibration Solution: <u>hach.com</u> #2283549 = \$12
- pH 10 Calibration Solution: <u>hach.com</u> #2283649 = \$12
- Total Hardness Test Strips: <u>hach.com</u> #2745250 = \$12
- Total Dissolved Iron Test Strips: <u>hach.com</u> #2745325 = \$22
- Total Copper Test Strips: <u>hach.com</u> #2745125 = \$22

⁵ Preventive Treatment: ~\$20 / kgal system fluid

These are undiluted active ingredients, so a little goes a long way. Quantities shown are the smallest available from the manufacturer.

- Taylor Digital Scale With Bowl: <u>walmart.com</u> #380444, \$33
- Dipotassium Phosphate (15# treats 1 kgal): univarusa.com #683518, 50# bag = \$250
- Sodium Lauroyl Sarcosinate (1# treats 1 kgal): univarusa.com Hamposyl L-30, 450# drum = \$900
- Sodium Sulfite (1# treats 1 kgal): univarusa.com #353150, 50# bag = \$50
- Sodium Tetraborate (10# treats 1 kgal): <u>amazon.com</u> 20 Mule Team Borax, 4# box = \$6

Smaller quantities of undiluted chemicals can be purchased from Closed System Labs at (608) 213-9328.

- Sodium Lauroyl Sarcosinate (1 bottle treats 1 kgal): 34 bottles / case = \$95
- Sodium Sulfite (1 bottle treats 1 kgal): 34 bottles / case = \$95

