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An Introduction to Treatment of Closed Industrial Water Systems

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CONTENTS

- 1. INTRODUCTION**
- 2. WATER TREATMENT FOR CLOSED SYSTEMS**
- 3. WATER SAMPLING AND TESTING OF WATER SYSTEMS**

1. INTRODUCTION. The term “closed water system” refers to a water system that is used to provide heating, cooling, or both for industrial processes or facilities. The system is sealed (closed), sometimes under pressure, and is not open to the atmosphere. No evaporation takes place and, with good operation, water is lost only minimally from the system. In general, water treatment for closed systems is much easier than for open systems. Makeup water is needed only to replace seal leakage and other incidental leakage. Because of the small makeup water requirements of these systems, they require little chemical treatment, which can be added intermittently as needed. Once properly treated, the system water does not form scale and has little or no corrosion potential. Two main types of closed water systems are used at many installations: hot water closed heating systems and chilled water closed cooling systems.

1.1 HOT WATER HEATING SYSTEMS. Hot water heating systems are designed to produce hot water, and although they are often referred to as hot water boilers, they are actually hot water heaters rather than boilers. For new construction, hot water heating systems are preferred over steam systems. Hot water heating systems, also known as hydronic heating systems, recirculate water to distribute heat in facilities. They operate at three temperature ranges:

- High-temperature water systems (pressurized systems with water temperatures higher than 177 °C [350 °F]) – no steam, only very hot water.
- Medium-temperature water systems (pressurized systems with water temperatures from 121 to 177 °C (250 to 350 °F)) – no steam, only quite hot water.
- Low-temperature water systems (water temperatures lower than 121 °C [250 °F]) – no steam, only hot water.

1.1.1 HOT WATER BOILERS. Hot water boilers can be either direct-fired (heated by combustion of gas, oil, or coal) or unfired (heat supplied by steam from a steam boiler, heated by hot water from a higher-temperature hot water system, or heated by a solar energy system). For many applications, hot water boilers are preferred over steam boilers because there are essentially no makeup water requirements, and chemical treatment

programs are less complex and easier to maintain. They require less manpower for operation, less maintenance, and have fewer water-related problems than steam boiler systems. Figure 1 shows a hot water boiler.

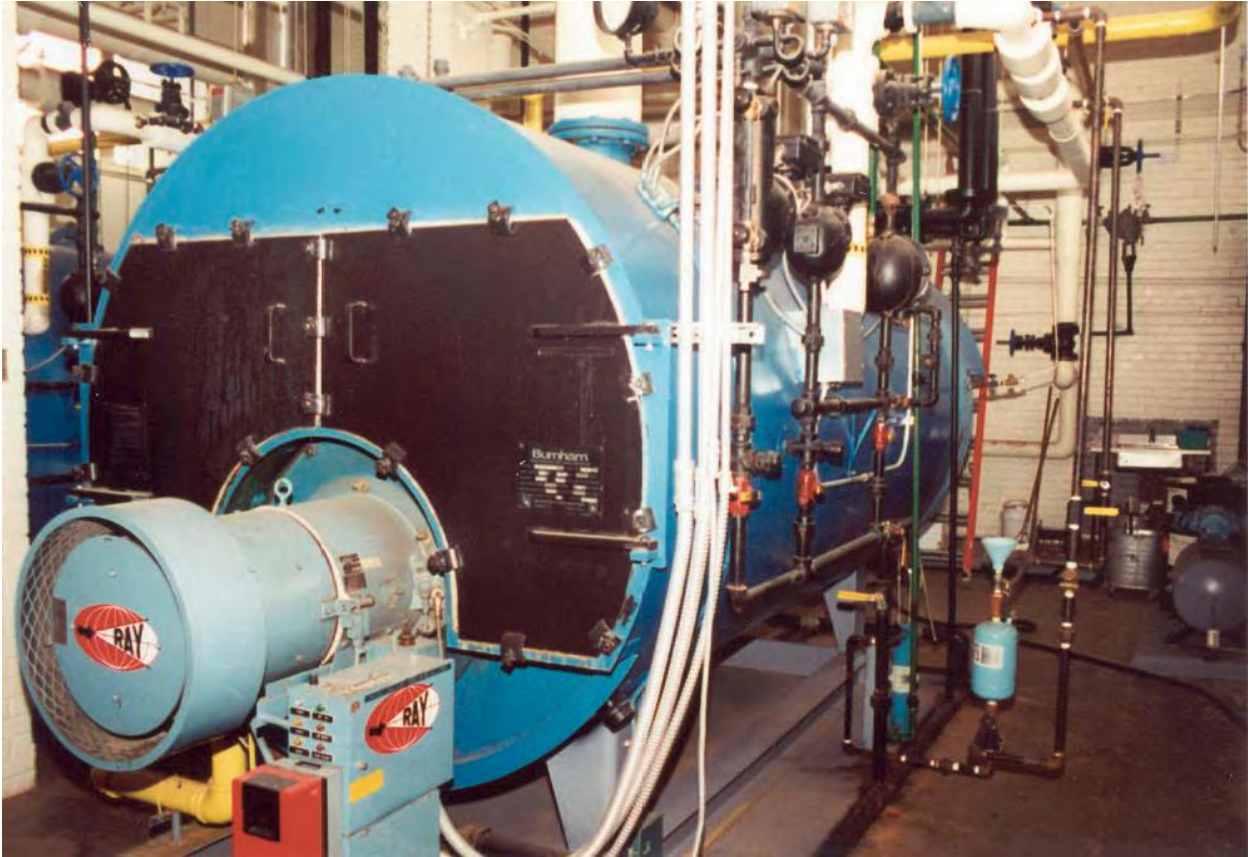


Figure 1
Hot Water Boiler

1.1.2 DESCRIPTION OF HOT WATER SYSTEMS. A typical hot water (hydronic) heating system is similar in composition to the closed cooling water system shown in Figure 2, except that a fired or non-fired heat exchanger is used rather than a chiller. Hot water boilers (fired and unfired) differ from steam boilers described in Chapter 3 because hot water boilers:

- Provide heated water but do not generate steam.

- Do not have deaerating heaters. (These are not required because there is essentially no makeup water requirement and thus very little air enters the system.)
- Require recirculating pumps to distribute the heated water to the processing equipment.
- Require expansion tanks that contain a cushion of steam or nitrogen.
- Do not contain a condensate return because there is no steam generated, but there is a return system.
- Are fabricated with mild steel components, but also may contain copper heat exchanger tubes, particularly in unfired systems.
- Do not require blowdown.

1.2 CLOSED CHILLED WATER SYSTEMS, BRINE SYSTEMS, AND GLYCOL SYSTEMS. Closed chilled water systems, brine systems, and glycol systems supply cold or chilled water for cooling processes and air conditioning. They are water systems designed for minimal loss of water. These systems contain mild steel piping, copper heat exchangers and, in some systems, aluminum piping, stainless steel piping, cold rolled steel piping, and potentially other metals.

1.2.1 CLOSED CHILLED WATER SYSTEMS. Closed chilled water systems circulate water that is cooled by refrigeration equipment. Water temperature ranges typically vary between 4 to 13 °C (40 to 55 °F). A typical chilled water system is depicted in Figure 2. Chilled water systems can have large storage capacity (3,785 cubic meters [1,000,000 gallons] or higher). Chillers are shown in Figure 3.

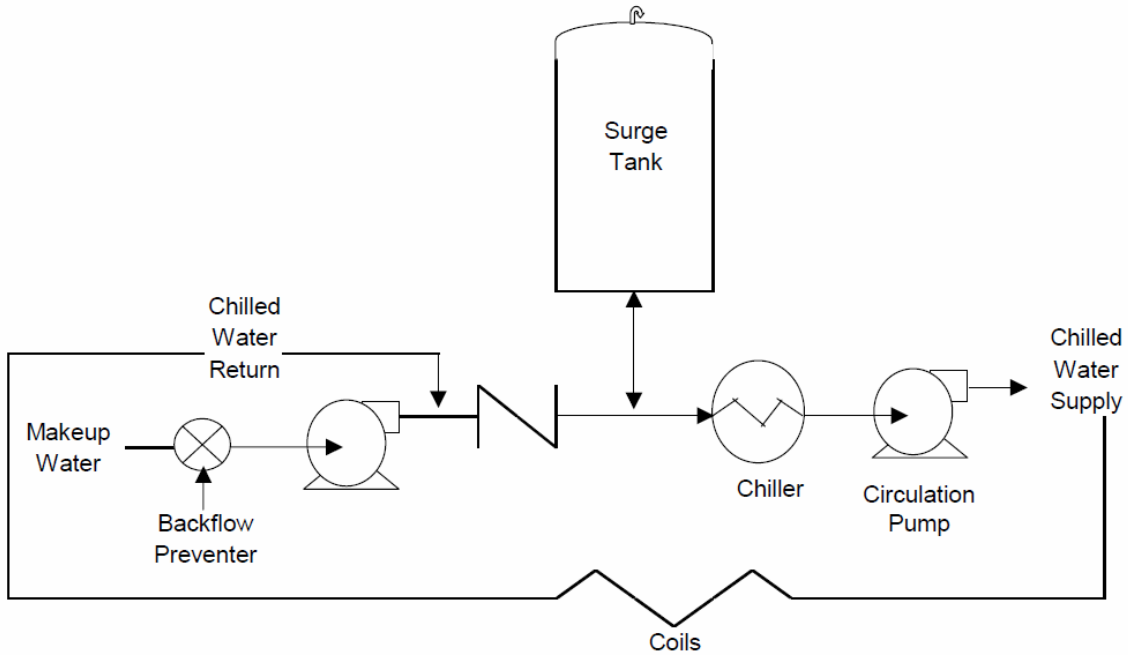


Figure 2

Typical Closed Chilled Water System Schematic



Figure 3

Chillers

1.2.2 CLOSED BRINE SYSTEMS. Closed brine systems are chilled water systems in which calcium chloride, sodium chloride, or a mixture of sodium chloride and calcium chloride has been added to the water to lower its freezing point sufficiently to maintain it as a liquid (ice-free) at temperatures of -1 to 10 °C (30 to 50 °F). Brine systems have been largely replaced by glycol systems.

1.2.3 CLOSED GLYCOL SYSTEMS. Closed glycol systems are chilled water systems that contain a mixture of water and glycol (ethylene or propylene) that will not freeze at the system operating temperature of -7 to 2 °C (20 to 35 °F).

1.3 COMBINED HOT AND CHILLED WATER SYSTEMS. Some closed systems serve the dual purpose of producing circulating hot water during the cold season and chilled water during the hot season.

1.4 DIESEL ENGINE JACKET COOLING SYSTEMS. Diesel engine cooling systems are considered closed systems, even when surge tanks are open to the atmosphere. The heat transfer from the circulating water is usually accomplished using a heat exchanger, not by evaporation. These systems have low water losses. Several of the metals used in these systems require good corrosion control. The three basic types of diesel engine cooling systems are described below.

1.4.1 AIR-COOLED DIESEL COOLING SYSTEMS. Air-cooled diesel cooling systems are used on most small engines as well as some large engines. The jacket water is circulated through an air-cooled radiator. Antifreeze must be used in these systems when radiators are exposed to low-temperature atmospheric air or when the water temperature exceeds the boiling point (100 °C [212 °F]).

1.4.2 WATER-COOLED DIESEL ENGINE COOLING SYSTEMS. Water-cooled diesel engine cooling systems are used mainly on large engines. The jacket cooling water passes through a heat exchanger, rather than a radiator, where a separate cooling water

loop removes the heat from the jacket cooling water. These systems commonly use antifreeze.

1.4.3 VAPOR-PHASE DIESEL ENGINE COOLING SYSTEMS. Vapor-phase diesel engine cooling systems, also called ebullient systems, use water that is heated to a temperature at the boiling point or above the boiling point for pressurized systems. Steam is formed from the cooling water as it removes heat from the system. The steam produced in this way can be recovered and used for space heating. This type of system requires significant amounts of makeup water and chemical treatment.

2. WATER TREATMENT FOR CLOSED SYSTEMS. Water treatment programs for both closed hot water and closed chilled water systems are developed primarily to control corrosion, although the programs may also control deposition of microbiological organisms. If needed, scale deposition can be prevented by external treatment (i.e., ion exchange softening) or can be controlled with inhibitors as described in Chapter 4. Corrosion must be completely controlled by water treatment programs. If corrosion occurs, corrosion products will eventually plug the system, resulting in decreased operational efficiency and the need for cleaning. Microbiological growth is not a concern in hot water systems, but can occur in chilled water systems and should be controlled (see Paragraph 2.3).

2.1 MAKEUP WATER REQUIREMENTS. Makeup water requirements for closed systems are very small unless there are leaks in the system (see Paragraph 2.4). Closed systems should not be drained or purged unless there is evidence that indicates the need to remove dirty water or sludge. For proper operation, makeup water in high-temperature and medium-temperature water systems is deaerated (de-oxygenated), using both mechanical and chemical methods, and is also softened. Oxygen can be removed from low-temperature water systems either chemically or mechanically to prevent oxygen-induced corrosion. Chilled water systems can require partial softening if the makeup water exceeds 250 ppm total hardness (as CaCO). The makeup water requirements are monitored carefully in systems of all types (see Table 1). If there is an increase in the quantity of makeup water required, the leak should be found and repaired quickly. After the repair, water treatment chemicals should be replenished immediately.

System Type	Requirement
High-temperature hot water	Softened and deaerated
Medium-temperature hot water	Softened and deaerated
Low-temperature hot water	Less than 100 ppm total hardness as CaCO ₃
Chilled, brine, glycol	Less than 250 ppm total hardness as CaCO ₃
Diesel engine jacket	1. Less than 50 ppm hardness as CaCO ₃ 2. Demineralization when brackish water is used

Table 1
Makeup Water Requirements for Closed Systems

2.2 CORROSION CONTROL PROGRAMS. Five basic water treatment programs are used in closed systems:

- Sulfite-caustic soda
- Nitrite-azole
- Molybdate-azole
- Nitrite-molybdate-azole blend
- Polysilicate-azole

The choice of which chemical treatment system to use should be based primarily on the water temperature and the metals in the system as well as the relative cost of the treatment program at the specific installation. The various water treatment programs are listed in Table 2 for each type of closed water system. Table 3 provides microbiological control monitoring guidelines for closed water systems.

System Type	Treatment Program
High-temperature hot water	Sulfite-caustic (1)
Medium-temperature hot water	Sulfite-caustic (1)
Low-temperature hot water	1. Sulfite-caustic (1) 2. Nitrite-azole 3. Molybdate-azole 4. Nitrite-molybdate-azole
Chilled, brine, glycol	1. Nitrite-azole 2. Molybdate-azole 3. Nitrite-molybdate-azole
Diesel engine jacket	Polysilicate-azole

NOTES: (1) Or other oxygen scavenger-caustic.

Table 2
Selection Guidelines for Closed System Treatment

Bacterium Type	Colony-Forming Units/ml
Total aerobic bacteria	< 10 ³
Sulfate-reducing bacteria	Undetectable
Surface microbiological	< 10 ⁶ - Undetectable

Table 3
Microbiological Control Guidelines for Closed Water Systems

2.2.1 SULFITE-CAUSTIC (OR OTHER OXYGEN SCAVENGER-CAUSTIC) TREATMENT PROGRAM. This program is required for high- and medium-temperature closed hot water systems. It is optional for low-temperature water systems. The water is treated with sodium hydroxide (caustic soda) and with sodium sulfite. This program is suitable for water systems having temperatures up to 288 °C (550 °F). This chemical program is not compatible with ethylene glycol nor propylene glycol. A recommended procedure for maintenance is described below:

1. Soften makeup water unless the total hardness in the makeup water supply is less than 10 ppm. The makeup water should be dealkalized if the makeup's total alkalinity is more than 200 ppm, as CaCO₃.
2. Add sodium sulfite to maintain 50 to 100 ppm sulfite (as SO₃).
3. Add the appropriate chemical to maintain a pH of 9.0 to 10.0. A pH lower than 9.0 can be raised by adding sodium hydroxide (caustic soda). A pH higher than 10.0 can be lowered by adding sodium bisulfite.
4. Test daily to maintain pH and sulfite levels within range.
5. Deaerator can be used to help reduce incoming oxygen in high make-up systems.

2.2.2. NITRITE-AZOLE TREATMENT PROGRAM. This program is not recommended for systems having water temperatures exceeding 121 °C (250 °F), or for (CL + SO₄) concentrations greater than 800 ppm. Also, avoid nitrate-based programs if (CL + SO₄) concentrations are greater than 800 ppm. It can be used in low-temperature water and chilled water systems. Water is treated with a nitrite-borax compound to a nitrite level of 1000 ppm (as NO₂). This level will require about 0.77 to 0.81 kilogram (1.7 to 1.8 pounds) nitrite-borax per 0.38 cubic meters (100 gallons) of water in the system. Most water treatment service companies offer this treatment as a formulated product. There is also a generic nitrite-borax compound product that is a premixed blend containing approximately 68% sodium nitrite, 10% borax, 17% sodium carbonate (soda ash) and 5% copper corrosion inhibitor. Adjust to a pH of 9.0 to 9.5 with sodium carbonate (soda ash), if necessary. This chemical treatment program is compatible with ethylene glycol water mixtures used for freeze protection. A recommended procedure for maintenance is described below:

1. Soften makeup water if the hardness is over 250 ppm as CaCO₃.
2. Add sodium nitrite-borax-azole blend to maintain a nitrite level of 600 to 1000 ppm (as NO₂) in the system.
3. Add sodium carbonate, if necessary, to maintain a pH range of 8.5 to 9.5.
4. If copper is present, maintain a minimum of 10 ppm of tolyltriazole.
5. Test after chemical addition and then monthly for pH and nitrite levels.

2.2.3 MOLYBDATE-AZOLE TREATMENT PROGRAM. This program is not recommended for systems where water temperatures exceed 121 °C (250 °F). Most water treatment service companies offer this as a formulated product. There is also a generic molybdate-azole compound product that is a pre-mixed liquid containing approximately 10% sodium molybdate, 3% caustic soda, and 3% azole (copper corrosion inhibitor). Maintain a molybdate level of 125 ppm (as Mo) and adjust pH to the range of 8.5 to 9.5 with sodium hydroxide (caustic soda). (NOTE: Some restrictions may pertain to discharge of water containing molybdate). This chemical treatment program is compatible with ethylene glycol or propylene glycol. A recommended procedure for maintenance of the system consists of five steps:

1. Soften makeup water if hardness is over 250 ppm as CaCO₃ (calcium carbonate).
2. Control the molybdate-azole compound to maintain a molybdate level of 100 to 125 ppm (as Mo).
3. Add sodium hydroxide (caustic soda) to maintain a pH of 8.5 to 9.5. It is likely that a buffer will be needed for pH control in this range.
4. If copper is present, maintain a minimum of 10 ppm of tolyltriazole.
5. Test monthly for proper pH and molybdate levels.

2.2.4 MOLYBDATE-NITRITE-AZOLE TREATMENT PROGRAM. This program is not recommended for use in systems in which water temperatures exceed 121 °C (250 °F). An effective approach for corrosion control in these systems involves a program that combines elements of the molybdate program and the nitrite program. The targeted maintenance level for the combined addition of molybdate and nitrite is about half of what either would be for individual addition. Most water treatment service companies offer this chemical combination as a formulated product. This chemical treatment program is also compatible with ethylene glycol or propylene glycol. A recommended procedure for maintenance of the system consists of five steps:

1. Soften makeup water if hardness is over 250 ppm as CaCO₃ (calcium carbonate).

2. Control the nitrite-molybdate-azole compound to maintain a nitrite level of 300 to 400 ppm (as NO₂), a molybdate level of 50 to 75 ppm (as Mo). Avoid this program if (CL + SO₄) concentration exceeds [(NO₂ + MO)-100] ppm.
3. Add sodium hydroxide (caustic soda) to maintain a pH of 8.5 to 9.5. It is likely that a buffer will be needed for pH control in this range.
4. If copper is present, maintain a minimum of 10 ppm of tolyltriazole.
5. Test monthly for proper pH and treatment levels.

2.2.5 POLYSILICATE-AZOLE TREATMENT PROGRAM. This program is not recommended for systems where water temperatures exceed 121 °C. This program is especially beneficial when aluminum metal is present. Aluminum is rarely found in comfort heating and cooling systems, but is sometimes found in closed process cooling water loops or diesel engine jacket systems. Aluminum will corrode at high pH, so the pH of the system water must be closely monitored if aluminum is present. This chemical treatment program is also compatible with ethylene glycol or propylene glycol. A recommended procedure for maintenance of the system consists of five steps:

1. Soften makeup water if hardness is over 250 ppm as CaCO₃ (calcium carbonate).
2. Control the treatment to maintain a polysilicate level of 80 to 100 ppm (as SiO₂).
3. Maintain a pH of 7.5 to 8.9. Adjust with dilute hydrochloric or caustic as necessary.
4. If copper is present, maintain a minimum of 10 ppm of tolyltriazole.
5. Test monthly for proper pH and treatment levels.

2.3 TREATMENT AND CONTROL OF MICROBIOLOGICAL GROWTH. Treatment and control of microbiological growth is a concern in chilled or closed cooling water systems. It is a particular concern if a nitrite-based corrosion inhibitor is used. Nitrite can serve as a nutrient for some bacteria. Microbiocide selection must be compatible with the corrosion inhibitor program and the pH levels in the system water. Glutaraldehyde and isothiazolone are commonly used in chilled water systems. Oxidizing biocides should not be used since they are not compatible with nitrite water treatment.

2.4 IDENTIFYING WATER LEAKS. The best way to check for leaks in a closed water system is to periodically read and record the water usage displayed by a totalizing water meter installed in the makeup water line or to use an inert, fluorescent material to indicate a leak. The fluorescent material can also be used to help pinpoint leaks or do leak studies. If the system does not have a water meter, the existence of leaks can be checked by testing the inhibitor concentration in the circulating water. The inhibitor concentration should be measured once per month using molybdate, polysilicate, or azole, but not nitrite. Do not depend upon the nitrite test; nitrite can be lost due to bacteria action. If nitrite is measured and its concentration has decreased while the conductivity has remained constant, biological contamination is present. If the measured values for both parameters decrease, there is a leak in the system. Borate concentration would be the best indicator of leak detection. When the inhibitor concentration has dropped to 98% of the original value, about 2% of the system water will have been lost. If the lapsed time for this 2% loss is less than 4 months, the system's loss of water is excessive and any leaks should be found and eliminated. Another convenient indication of water loss is the measurement over time of a drop in conductivity. If the system water conductivity equals that of the makeup, the treatment chemical is totally absent. Inert fluorescent material can be added to the system and used to help pinpoint leaks, or perform leak studies. Loss of the fluorescent material can be monitored in real time; such loss indicates a leak. (NOTE: A 2% loss over 4 months equals 0.5% loss per month. The accuracy of this test is limited, so if the loss for any month exceeds 1%, the test should be repeated. If retesting confirms the water loss, the leaks should be found and eliminated.)

EXAMPLE 1:

- a) The initial recommended molybdate concentration in chilled water systems is 125 ppm. After 4 months, the concentration is 123 ppm. Is the water loss excessive?

EQUATION | $\text{Loss} = ([\text{initial} - \text{final}] / \text{initial}) \times 100$

$$| = ([125 - 123]/125) \times 100 = 1.6\% \text{ after 4 months}$$

b) The monthly loss based on the 4-month result is calculated:

$$\text{EQUATION } | \quad 1.6\% \text{ over 4 months} = 0.4\% \text{ per month}$$

This loss is less than 1% per month and not excessive.

c) If the concentration had dropped to 123 ppm after 1 month, the loss would be:

$$\text{EQUATION } | \quad \begin{aligned} \text{Loss} &= ([125 - 123]/125) \times 100 \\ &= 1.6\% \text{ after 1 month} \end{aligned}$$

d) The monthly loss is calculated:

$$\text{EQUATION } | \quad 1.6\% \text{ over 1 month} = 1.6\% \text{ per month}$$

This loss is greater than 1% per month, and the system should be inspected for leaks.

2.5 PROCEDURES FOR LAYUP OF HOT AND CHILLED WATER SYSTEMS. Follow the procedure for wet layup of operational boilers. Note these additional recommendations:

- For hot water systems, completely fill the hot water generator and expansion tank. Where nitrogen pressurization is used for the system, the expansion tank should not be filled.
- For all steel systems using the sulfite-caustic soda program, increase the pH to 11.7 with sodium hydroxide (caustic soda). Add sodium sulfite to a level of 100 ppm (as SO₃).
- Treat chilled water systems using the nitrite-borax or molybdate-caustic soda treatments with appropriate chemicals to maintain levels required for normal operation.
- Test monthly for treatment chemicals and check water levels.

3. WATER SAMPLING AND TESTING OF WATER SYSTEMS

3.1 WATER SAMPLING AND TESTING. Water sampling and testing procedures provide information that can be used for the following purposes: to ensure the protection of the water system equipment; to prevent unexpected system failure; to provide information used to control water quality; and to verify that water treatment chemicals are maintained at the proper concentration within the system or, if not, to allow for adjustment of their concentration. Adequate chemical treatment of water systems requires that specific levels of specific chemicals be maintained in the water to provide the system with protection from corrosion and deposits. This requirement applies to both cooling and boiler water systems. The purpose of a sampling and analysis program for industrial water is to ensure and verify that the required levels of treatment chemicals are being maintained and that the water quality parameters are within the specified control ranges. The sampling and analysis program incorporates two levels of testing: in-plant routine testing used for operational purposes, and periodic independent (third-party) QA testing used for verification and oversight. When an analytical test indicates that the concentration of a given chemical is not within the limits required, the testing process must be evaluated to determine that the sampling and testing were performed properly and that the test result is valid. As part of an adequate QA/QC program, test methods, including the chemical reagents, must be checked on a routine basis. A properly applied industrial water treatment program incorporates procedures that ensure that representative samples, which are samples that are representative of actual water system conditions, have been collected and analyzed. Safety considerations must be a priority when sampling any industrial water system (particularly boilers) and when conducting laboratory tests.

3.1.1 IN-PLANT TESTING. In-plant testing is used by water system operators to monitor and ensure both the proper operation of system equipment and the proper quality of the water in the equipment. Routine, appropriate, in-plant operational testing of the system water is an essential component of a water treatment program. Routine testing of specific operational parameters and water quality criteria allows the operator to verify the adequacy of the water treatment program and to make necessary adjustments to avoid

and prevent operational problems. When an analytical test indicates that the concentration of a given chemical is not within the limits required, the testing process must be evaluated to determine that the sampling and testing were performed properly and that the test result is valid. If testing data for the water quality analyses are inconsistent with that expected for the treatment method being used, the reasons must be determined. This determination can involve reanalysis and checking of the test reagents, as well as checking the accuracy of the in-plant testing results through independent QA analysis. Test procedures is furnished with the test kits.

3.1.2 INDEPENDENT QA ANALYSIS. To verify the accuracy of the in-plant testing, as well as to provide supplemental or additional analyses, independent (third-party) QA analytical services are incorporated as part of the plant's QA program. These services can be more complete than routine in-plant testing and can provide a more detailed analysis of the system conditions. Independent QA analysis is a useful tool for plant managers and operators to verify that their systems are being maintained properly, and is an especially important tool for government managers at sites where plant operations have been contracted out (outsourced).

3.2 COOLING TOWER WATER SAMPLING AND TESTING

3.2.1 COOLING WATER TESTING REQUIREMENTS. Water samples from the recirculating cooling water systems should be tested for pH, conductivity, and inhibitor content. Calcium hardness and methyl orange (M) alkalinity may also be tested. In addition, follow the water testing requirements established by the supplier of the water treatment chemicals where appropriate. Testing parameters for the makeup water include, as a minimum, M alkalinity, conductivity, and calcium hardness. Appropriate water testing requirements and sampling frequency are summarized in Table 4. Periodic testing for chlorides in the recirculating water and makeup water may be required to calculate the most accurate COC in an operating system.

Water Tested	pH	M Alkalinity	Conductivity (or TDS)	Calcium Hardness	Inhibitor
Makeup water	--	1/W	1/W	1/W	--
Small CT < 88 kW (25 tons) water*	1/W	1/W	1/W	1/W	1/W
Medium CT 88-352 kW (25-100 tons) water*	2/W	2/W	2/W	2/W	2/W
Large CT > 352 kW (100 tons) water	1/D	1/D	1/D	1/D	1/D

Table 4
Recommended Water Sample Frequency and Testing Requirements for Cooling Tower Systems

NOTES:

C = Cooling tower.

W = Week (for example, 1/W = once per week).

D = Day (for example, 1/D = once per day).

* = Slowly soluble polyphosphate chemicals used in treatment of small and medium cooling towers should be checked at least weekly and replaced as necessary.

3.2.2 FREQUENCY OF COOLING WATER SAMPLING AND TESTING. Water samples of the recirculating water in small towers (less than 88 kilowatts [25 tons]) should be sampled and tested at least once per week, those of medium-sized towers (88 to 352 kilowatts [25 to 100 tons]) at least 2 times per week, and those of large towers (more than 352 kilowatts [100 tons]) daily. You can establish a routine schedule that is designed to meet these goals for sampling and testing. For many cooling towers, the makeup water quality is quite consistent over time. Collection and analysis of 1 sample per week of the makeup source is usually an adequate frequency. If makeup water quality varies, increase the frequency to allow for sampling of makeup water at the same time as cooling water sampling. Always flush the water sample line prior to sampling.

3.2.3 COOLING WATER SAMPLING. Cooling tower water samples are collected in clean, 1-liter (1-quart) glass or plastic bottles. The bottle is capped (sealed) immediately and tested without delay (i.e., within 1 hour since some water quality will gradually change). The sample is not collected immediately after the addition of treatment chemicals but is collected after the chemicals have been allowed to mix thoroughly with the system water. Samples of the recirculating cooling water can be collected by dipping from the cold well, or can be collected from the recirculating pump discharge after the line has been flushed for 10 seconds or until no sediment remains. If these locations are inaccessible, another location may be used. Typical sampling points for an open recirculating system are shown in Figure 4. It is best to always collect the sample for each system in the same manner and from the same location for consistent results.

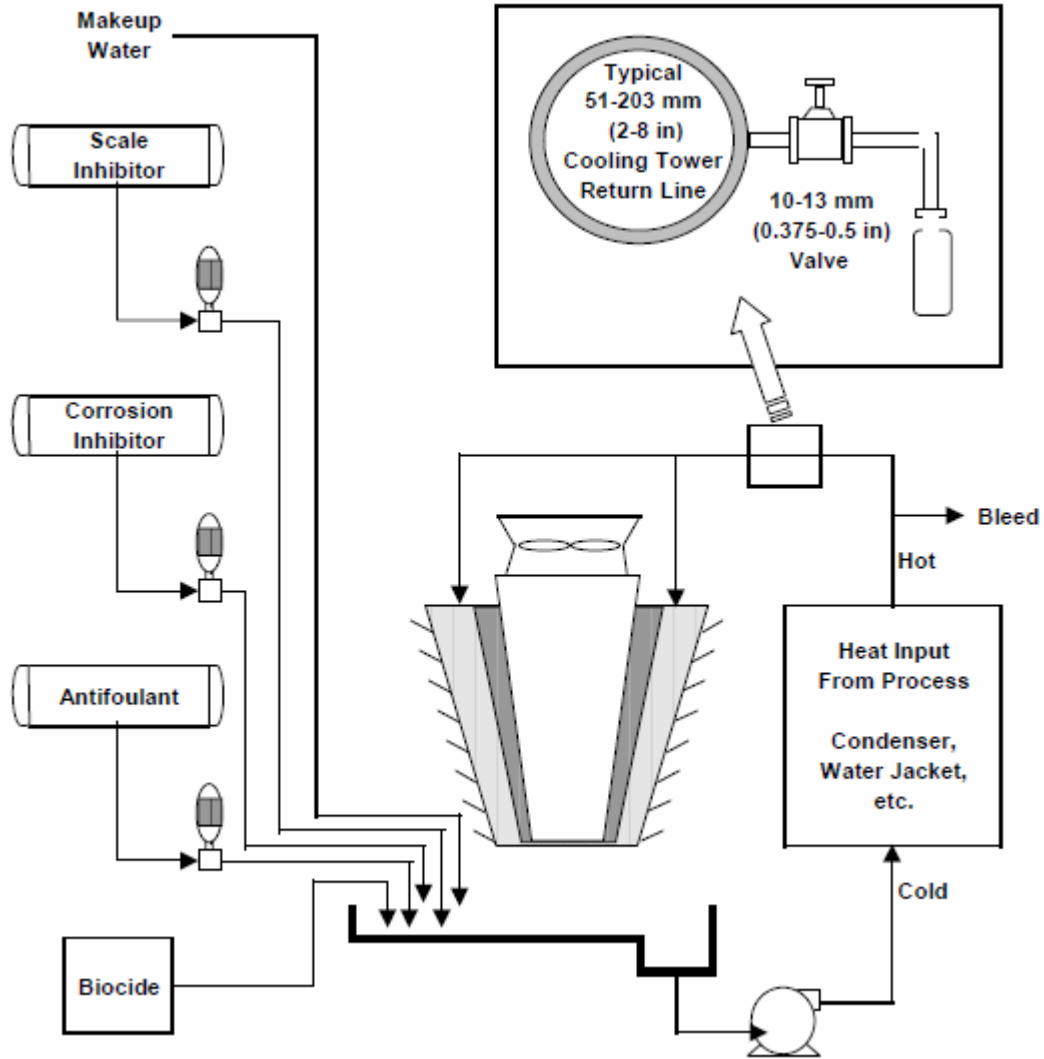


Figure 4
Typical Water Sampling Points for an Open
Recirculating Cooling Water System

3.3 ROUTINE BOILER WATER SAMPLING AND TESTING. Boiler water is very hot and under pressure. Caution should be exercised and appropriate safety procedures followed when collecting samples. If the boiler water is not cooled as it is sampled, part of the water will flash off as steam during the sampling process and the remaining sample will not be truly representative of the boiler water. The sample could contain a lower level of oxygen or carbon dioxide than the actual levels in the boiler water. Values of other sample constituents would be higher because less water would be present, as described in

Paragraph 3.1, which will greatly reduce the chance of the operator getting burned, and will allow a representative boiler water sample to be collected.

3.1 BOILER WATER SAMPLING COOLER. A commercially available boiler water sample cooler can be used when collecting a boiler water sample. If one is not available, then a 4.6- to 6.1-meter long (15- to 20-foot) coil of copper or stainless steel tubing (60 millimeters [0.25 inch]) may be used to cool the sample. The coil can be immersed in a permanent cooling jacket as shown in Figure 5, or it may be immersed in a bucket of cold water, if this does not interfere with operation of the system or create a hazard. The flow of the boiler water sample through the coil must be slow enough so that the cooled boiler water sample is no more than just warm to the hand (approximately 38 °C [100 °F]).

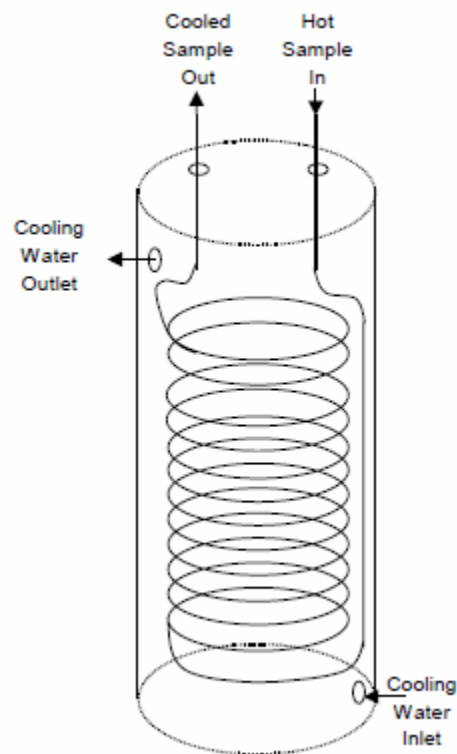


Figure 5

Boiler or Condensate Water Sample Cooling Coil

3.3.2 BOILER WATER SAMPLING PROCEDURES. The cooling water to the jacket cooling coil is turned on before taking the boiler water sample and turned off after the sample has been collected. The coil with boiler water is flushed with several times its volume before collecting the sample to be tested. The cooled end of the boiler water sample coil is then extended to the bottom of the sample bottle and at least 1 volume of the bottle is allowed to overflow the container during the collection process. The sample collection bottle can be plastic or glass. Glass bottles are not used if the boiler is silica limited or if high silica is suspected.

3.3.3 SAMPLING LOCATIONS. Typical locations for water sampling points in a steam boiler system are shown in Figure 6. Each sampling point has a separate cooling coil. Two or more sampling points are not connected by a single manifold to the same cooling coil because it is almost impossible to determine if one of the valves has a leak that might contaminate the sample being taken. Guidelines for sample collection are provided below.

- The makeup water sample does not have to be cooled. The sample location typically will be the output of an ion exchange unit or some other water-softening unit.
- The boiler feedwater sample is a combination of makeup and condensate return. An appropriate location for sample collection is from the discharge of the boiler feed pump. This will be a hot sample, so a cooling coil is used. Alternatively, sample collection for feedwater can be from the low-pressure deaerator outlet.
- The boiler water is very hot. Collect this sample from the continuous blowdown line between the boiler and the regulating valve if possible. You may collect it from a gauge-glass connection, if necessary. Use of a cooling coil is recommended.
- The steam condensate is hot. For small systems, collect this sample from a line that enters the deaerating heater if possible. For medium and large systems, you may need to collect condensate samples at two or more locations in the system to obtain sufficient data for calculation of the proper treatment level. When attempting to find a leak, you may need to collect condensate samples from various locations in the system. Use of a cooling coil is recommended.

- Steam is collected regularly for systems with high-quality steam requirements like those with turbines and those meeting NAVSEA steam quality requirements. Otherwise, steam samples are rarely collected. Refer to the ASME Performance Test Code (ASME PTC 19.11, Steam and Water Sampling, Conditioning and Analysis in the Power Cycle) for sampling procedures.

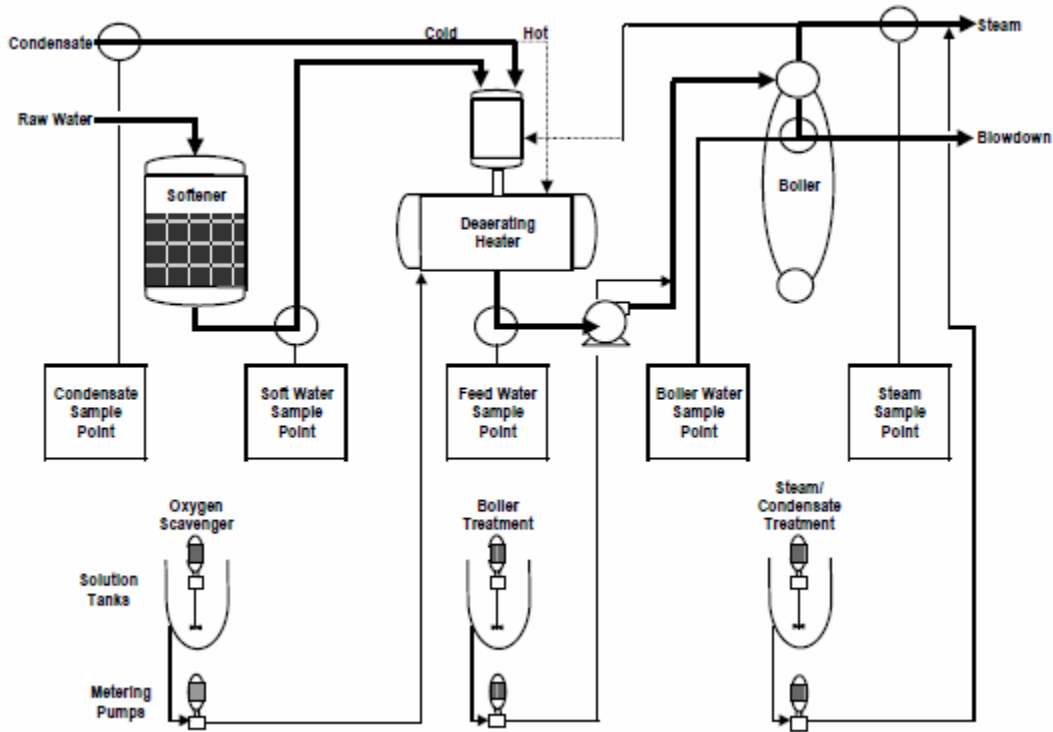


Figure 6

Typical Locations for Water Sampling in a Steam Boiler Water System

3.3.4 FREQUENCY OF SAMPLING AND TESTING. The recommended sampling and testing frequency for steam boiler systems is summarized in Table 5.

Source of Sample	pH	Total Alkalinity* (M)	Hydroxyl Alkalinity (Causticity)	Calcium Hardness	TDS	Copper and Iron	Ortho-phosphate	Sulfite
Makeup water	--	1/W	--	1/W	1/W	--	--	--
Feedwater, small boilers (< 245 kW [25 hp])	--	1/W	--	1/W	1/W	--	--	--
Feedwater, medium boilers (245–1470 kW [25–150 hp])	--	2/W	--	2/W	2/W	--	--	--
Feedwater, large boilers (> 1470 kW [150 hp])	--	1/D	--	1/D	1/D	--	--	--
Boiler water, small boilers	1/W	--	1/W	--	1/W	--	1/W	1/W
Boiler water, medium boilers	2/W	--	2/W	--	2/W	--	2/W	2/W
Boiler water, large boilers	1/D	--	1/D	--	1/D	--	1/D	1/D
Condensate return (small boilers)	1/W	--	--	As needed	1/W	1/Q	--	--
Condensate return (medium boilers)	2/W	--	--	As needed	2/W	1/Q	--	--
Condensate return (large boilers)	1/D	--	--	As needed	1/D	1/Q	--	--

NOTES:

W = Week (for example, 1/W = once per week).
 D = Day (for example, 1/D = once per day).

Q = Quarter (for example, 1/Q = once per 3 months).
 * = Feedwater alkalinity only for boilers that use dealcalizers.

Table 5

Water Sampling Frequency and Testing Requirements for Boiler Water Systems

3.3.5 BOILER FEEDWATER SAMPLE. Boiler feedwater samples should be collected once per week for small boilers (less than 245 kilowatts [25 horsepower]), at least 2 times per week for medium boilers (245 to 1470 kilowatts [25 to 150 horsepower]), and daily for large boilers (greater than 1470 kilowatts [150 horsepower]). The samples should be tested for M alkalinity, conductivity, and calcium hardness.

3.3.6 CONDENSATE WATER SAMPLE. Condensate water samples should be collected once per week for small boilers (less than 245 kilowatts [25 horsepower]), at least 2 times a week for medium boilers (245 to 1470 kilowatts [25 to 150 horsepower]), and daily for large boilers (greater than 1470 kilowatts [150 horsepower]). The samples should be tested for pH and conductivity. If the conductivity is greater than 35 micromhos, the sample should be tested for calcium hardness. If applicable based on the metallurgy of the system, the condensate samples should be tested for iron and copper on a quarterly basis.

3.3.7 BOILER BLOWDOWN WATER SAMPLE. Boiler blowdown water samples should be collected for small boilers (less than 245 kilowatts [25 horsepower]) once per week, for medium boilers (245 to 1470 kilowatts [25 to 150 horsepower]) at least 2 times per week, and for large boilers (greater than 1470 kilowatts [150 horsepower]) daily. The samples should be tested for hydroxyl (OH) alkalinity (causticity), neutralized conductivity, scale treatment chemicals (e.g., orthophosphate), and sulfite.

3.3.8 BOILER WATER QA ANALYSIS. The components of a boiler water QA program are described. Appropriate boiler water sampling requirements are described below.

- Each operating boiler plant equipped with hot water or steam boilers and having one or more boilers of 980 kilowatts (3.3 million BTU per hour or 100 horsepower) or greater capacity may submit a boiler water sample for QA once per month to an independent QA laboratory or to the contractor providing the service. These QA contractors are independent experts in the field of boiler and cooling water treatment as well as interpretation of sample analysis data.

- Each operating boiler plant equipped with hot water or steam boilers of less than 980 kilowatts (100 horsepower) capacity submits a boiler water sample for QA once every 3 months to an independent QA laboratory or to the contractor providing the service to the customer.
- For all high-pressure (greater than 103 kilopascals [15 pounds per square inch gauge]) boilers and for low-pressure boilers treated with caustic, phosphate, tannin, and sodium sulfite, the boiler water sample size is a 1-liter plastic bottle, or as required by the QA laboratory.
- For low-pressure boilers (less than 103 kilopascals [15 pounds per square inch gauge]) treated only with caustic, the boiler water sample size is a 0.12-liter (4-ounce) plastic bottle, although a 1-liter plastic bottle may be used.
- For hot water boilers, the boiler water sample size is a 1-liter plastic bottle, or as required by the contract laboratory.
- Boiler water sample shipping containers and bottles used for submitting boiler water check samples can be obtained by request to the contract laboratory. Shipping containers for high-pressure boiler water samples are designed for shipping a 1-liter plastic bottle. Shipping containers for water samples from low-pressure boilers treated with caustic soda are designed for shipping a 0.12-liter plastic bottle. Pack the bottle carefully so it will not leak during shipping. A completed information data sheet must be enclosed in each sample shipping container shipped to the laboratory.

3.4 WATER SAMPLING AND TESTING FOR CLOSED HOT AND CHILLED CIRCULATING WATER SYSTEMS. The recommended testing frequency for these systems is summarized in Table 6, with additional information provided below.

System	pH	Sulfite	Nitrite	Molybdate	Total Hardness	Total Alkalinity
HTW with caustic-sulfite treatment	1/day	1/day	--	--	--	--
Closed MTW & LTW hot water w/nitrite-borax treatment	1/mo	--	1/mo	--	--	--
Closed MTW & LTW hot water w/molybdate treatment	1/mo	--	--	1/mo	--	--
Chilled water & brine; w/molybdate treatment	1/mo	--	--	1/mo	--	--
Chilled water & brine w/nitrite-borax treatment	1/mo	--	1/mo	--	--	--
Diesel jackets w/molybdate treatment	1/mo	--	--	1/mo	--	--
Diesel jackets nitrite-borax	1/mo	--	1/mo	--	--	--
Ion exchange feedwater	--	--	--	--	1/week	--
Ion exchange outlet	--	--	--	--	3x/day	--
Dealkalizer feedwater	--	--	--	--	--	1/week
Dealkalizer outlet	--	--	--	--	--	3x/day

Table 6

Water Sampling and Testing Requirements for Closed Hot and Chilled Circulating Water Systems

3.4.1 SAMPLING AND TESTING OF MAKEUP WATER. The makeup water for boiler systems, chilled water systems, and diesel engine jacket water systems usually comes from an ion exchange unit or a dealkalizer. The recirculating water from high-temperature water systems and from systems that use the sulfite-caustic soda treatment program is tested once per day for pH and sulfite. Recirculating chilled water and hot water treated with the nitrite-borax or molybdate programs is tested once per month for either molybdate or nitrite, depending upon the chemical in use. The system pH is tested once per month and on the day following chemical additions.

3.4.2 ION EXCHANGERS AND DEALKALIZER WATER. The recommended water testing frequencies for these systems are summarized in Table 6, with additional information provided below.

3.4.2.1 INFLUENT WATER TESTING. Ion exchange influent water is tested once per week for total hardness. Dealkalizer influent water is tested once per week for total (M) alkalinity.

3.4.2.2 EFFLUENT WATER TESTING. Effluent water from these systems is tested for total hardness either once per day or once per shift (3 times a day) depending on the frequency of regeneration; more frequently if the frequency of regeneration is excessive. The appropriate frequency (cycle length) will depend upon feedwater hardness, bed size, resin type, strength of regenerant, and flow rate.

3.4.2.3 SAMPLING LOCATION. The location of the water sample point is an important consideration for ensuring that a representative water sample is obtained. Care must be taken to avoid collecting a sample that is a mixture of influent and effluent water on ion exchange units that use automatic regeneration and multi-port valves.

3.4.2.4 BRINE TESTING. The brine used for regeneration is sampled periodically and tested with a hydrometer to measure its strength. The sodium chloride brine should be as near 100% saturation as possible (approximately 28% by weight) for efficient softener regeneration.

3.5 WATER TESTING. Routine and appropriate testing of the system water is an essential component of a water treatment program. Water testing provides information that can be used: to ensure the protection of the water system equipment; to prevent unexpected system failure; to provide information used to control water quality; and to verify that water treatment chemicals are maintained at the proper concentrations within the system or, if not, to allow for adjustment of their concentrations. An adequate testing program requires proper recordkeeping of the data that are used for assessing the

effectiveness of the water treatment program. If testing data for the water quality analyses are inconsistent with that expected for the treatment method being used, determine the reasons. This determination can involve reanalysis and checking of the test reagents. If the test results are correct, the water quality and water treatment program must be re-evaluated and modified, if necessary. Paragraph 3.6 describes the interpretation of water test results.

3.5.1 WATER SAMPLE TESTING METHODS. Water tests are usually performed with test kits obtained from commercial sources. Test kits can be used to test for: alkalinity-phenolphthalein (P); alkalinity-methyl orange (M or total); alkalinity-hydroxyl (OH) or “causticity”; conductivity; tannin; pH; hardness (total and calcium, magnesium by difference); phosphate (ortho and total); sulfite; nitrite; chloride; molybdate; phosphonate; chlorine or bromine (total and free); total iron; and total copper.

3.5.2 CORROSION TESTING. Corrosion test specimens or corrosion testing instruments can be used to monitor the rate of corrosion. Corrosion test information can also be used to evaluate how well equipment is being protected from corrosion by the water treatment program. The degree of corrosion (if any) that is occurring in large or critical heating and cooling systems should be determined. Consider the following information when developing a program of corrosion testing:

3.5.2.1 CORROSION TEST COUPONS. Corrosion test coupons are usually used as corrosion test specimens for open and closed cooling systems, closed hot water systems, and domestic water systems.

3.5.2.2 CORROSION PIPE INSERTS. Corrosion pipe inserts are often used as corrosion test specimens in steam condensate return systems.

3.5.2.3 COMMERCIAL RESOURCES FOR TESTING. Corrosion test coupons and testing analysis services can be obtained from commercial sources. Corrosion pipe insert

assemblies for steam condensate systems and analytical evaluation of the test inserts should be obtained from a QA laboratory or contractor under contract with the customer.

3.5.2.4 CORROSION TEST RESULTS. Corrosion test results are usually determined as a rate of corrosion penetration into the metal and reported in mils metal loss per year (mpy). A mil is 2.5-thousandths of a centimeter (one-thousandth [0.001] of an inch); thus, the corrosion rate of 10 mpy means that the thickness of a piece of metal is reduced by $10 \times 0.0025 = 0.025$ centimeter per year (0.01 inch per year). If the metal coupon being studied is 0.1588 centimeter (0.0625 inch) thick, this means that it will be completely dissolved or corroded in just over 6 years. Corrosion rates may also be expressed in millimeters per year (mmpy) corrosion. The relationship between mpy and mmpy is: 1 mpy = 0.0254 mmpy; 1 mmpy = 39.4 mpy. Corrosion also may be given as a weight loss in milligrams per square decimeter per day (mdd). For mild steel, the relationship is: 1 mdd = 0.2 mpy or 1 mpy = 5 mdd.

3.5.2.5 TESTING INSTRUMENTS. A variety of electronic instruments are available to monitor and record corrosion rates. These instruments are installed and maintained by individuals who have been adequately trained for these activities. The most commonly used instrument of this type is a linear polarization corrosion instrument that provides instantaneous corrosion measurement and is often used for troubleshooting.

3.5.2.6 HEAT TRANSFER CORROSION TEST EQUIPMENT. Heat transfer corrosion test equipment is used to determine the corrosion rate under heat transfer conditions. This type of equipment can more accurately determine corrosion in chillers.

3.6 INTERPRETATION OF RESULTS FROM WATER TESTS. Adequate chemical treatment of water systems requires that specific levels of specific chemicals be maintained in the water to provide the system with protection from corrosion and deposits. This requirement applies to both cooling and boiler water systems. When an analytical test indicates that the concentration of a given chemical is not within the required limits, the testing process must be evaluated to determine whether sampling and testing were

performed properly and the test result is valid. As part of an adequate QA/QC program, test methods, including the chemical reagents, must be checked on a routine basis. Consider these guidelines when evaluating test results:

- When the (valid) test results indicate a treatment level that is too low, the chemical addition program should be evaluated and the appropriate adjustment made; this normally means increasing the chemical feed rate by 10% or less. If adjustments to the treatment program do not correct the situation, then the entire water system may need to be evaluated to determine the nature of the problem.
- When the (valid) test results indicate that a given level of treatment chemical is too high, the chemical addition program should be evaluated. Exercise caution when reducing chemical feed rates to adjust the level of a treatment chemical that exceeds the required limits. The chemical feed rate should not be reduced more than 5 to 10% at any one time.
- When the test results indicate that the level of hardness in the water is higher than the required level, the makeup water treatment system should be investigated and problems identified, including other possible incoming sources of water hardness into the system.

3.6.1 ALKALINITY TEST RELATIONSHIPS

3.6.1.1 SOURCES OF ALKALINITY. The three basic sources of alkalinity in water result from the bicarbonate ion (HCO_3^-), the carbonate ion (CO_3^{2-}), and the hydroxyl ion (OH^-). The amount of each of these ions in water can be determined by titration with an acid to specific pH levels (end points) using phenolphthalein (P alkalinity) or methyl orange (M alkalinity) indicators to their particular titration end-points. The relationship between pH and the various types of alkalinity is shown in Figure 7.

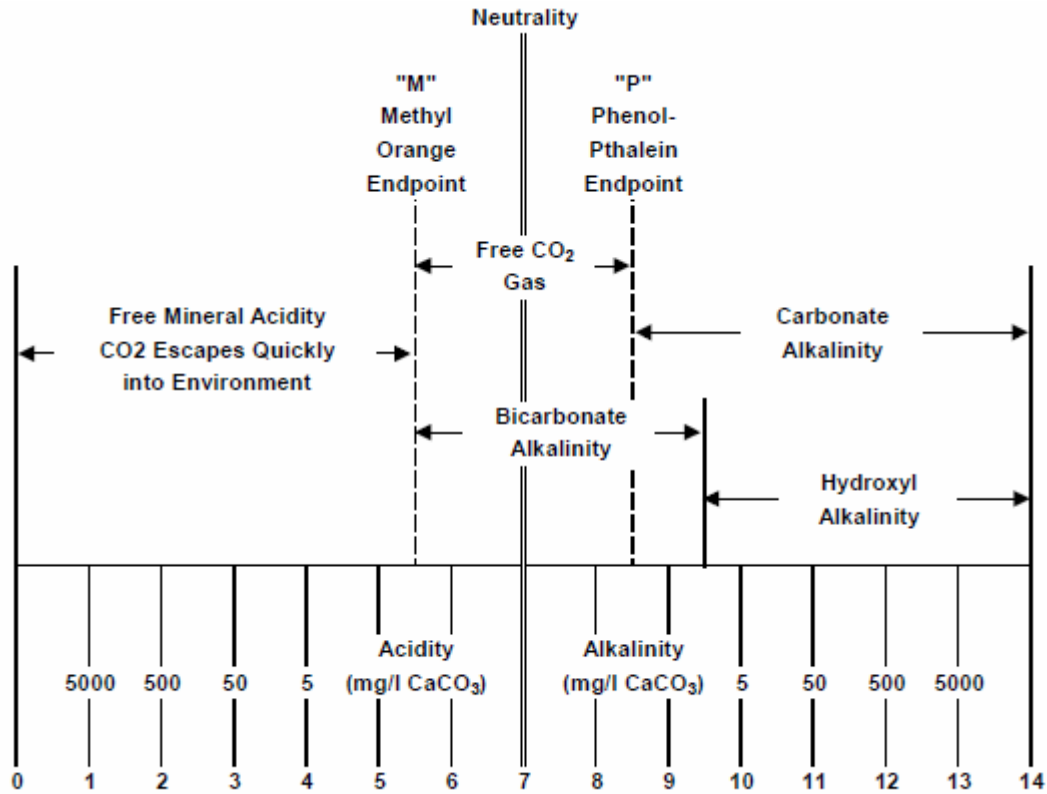


Figure 7
Acidity, Alkalinity, and pH Ranges

3.6.1.2 RELATIONSHIP OF P, M, AND OH ALKALINITIES. Test procedures for determining P and M alkalinities are included in commercially available test kits. The OH-alkalinity can be determined by a specific test or it can be estimated by knowing the P and M alkalinity values. The OH- alkalinity is contributed by the hydroxyl ions (OH-) in the water, and is also known as "caustic alkalinity" or "causticity." The relationship between the measured P and M alkalinity values and the level of hydroxyl, carbonate, and bicarbonate forms of alkalinity are shown in Table 7 and described below.

Situation	Hydroxyl	Level of Alkalinity Contributed by Carbonate	Bicarbonate
$P = M$	M	0	0
$P > \frac{1}{2}M$	$2P - M$	$2(M - P)$	0
$P = \frac{1}{2}M$	0	M	0
$P < \frac{1}{2}M$	0	$2P$	$M - 2P$
$P = 0$	0	0	M

Table 7

Alkalinity Relationship Based on P and M Tests

EXAMPLE:

If $P = 86$ ppm as CaCO_3 , and if $M = 118$ ppm as CaCO_3
 Then, situation 2 (from Table 6-4) exists ($P > \frac{1}{2}M$)
 or P is greater than $\frac{1}{2}$ of M);

Hydroxyl = $2P - M = (2 \times 86) - 118 = 54$ ppm as CaCO_3
 Causticity = hydroxyl alkalinity as $\text{CaCO}_3 \div 3$
 = $54 \div 3 = 18$ ppm as OH^-

Carbonate = $2(M - P) = 2 \times (118 - 86)$
 = 64 ppm as CaCO_3

Bicarbonate = 0 ppm as CaCO_3

Check: Total = $54 + 64 + 0 = 118$ ppm M alkalinity as CaCO_3

Review of each situation in Table 6-4 provides this information, with situation:

1. The tests for P alkalinity and M alkalinity are equal. This means that all of the alkalinity is due to hydroxyl ions. There is no carbonate or bicarbonate present. (This is rare but occurs when a caustic solution is not exposed to air.)
2. The P alkalinity is greater than one-half of the M alkalinity. This indicates that there is hydroxyl and carbonate alkalinity, but no bicarbonate alkalinity.
3. The P alkalinity is equal to one-half of the M alkalinity. This indicates that all the alkalinity is due to carbonate. There is no bicarbonate alkalinity, and the hydroxyl alkalinity is insignificant.
4. The P alkalinity is less than one-half of the M alkalinity. This indicates that carbonates and bicarbonates are present.

5. The P alkalinity is zero. The M alkalinity is due to bicarbonates only. No hydroxyl or carbonate alkalinity are present.

3.6.2 PH (HYDROGEN ION CONCENTRATION)

3.6.2.1 MEANING OF PH. The pH (value) is a measure of the acidity or alkalinity of water. The test specifically measures the concentration of hydrogen ions in the water. Neutral water will have a pH of 7. Water with a value of less than pH 7 is considered acidic, while water with a value greater than pH 7 is considered alkaline. Examples are shown below.

- Common pH values for materials on the acid side include: spinach with a pH of approximately 5.5; orange juice and most soft drinks with a pH of approximately 3.5; lemon juice with a pH of approximately 2.2; and 0.1 normality (N) sulfuric acid with a pH of 1.2.
- Common pH values of materials on the alkaline side include: sodium bicarbonate with a pH of approximately 8.4; milk of magnesia with a pH of approximately 10.5; household ammonia with a pH of approximately 11.5; and 0.1 N sodium hydroxide with a pH of 13.0.

The pH scale is logarithmic. A pH of 4 is 10 times as acidic as a pH of 5 and 100 times as acidic as a pH of 6. This is important to consider when adding a strong acid to a system, because 0.1 N sulfuric acid will have more than 1 million times the acidity of neutral water.

3.6.2.2 RELATIONSHIP TO CAUSTICITY. When the pH of water exceeds a value of 9.6 to 9.8, a measurable concentration of hydroxyl ions (OH⁻) is present in the water. As the hydroxyl alkalinity (causticity) increases, the pH of the solution also increases. The relationship between causticity and pH is shown in Table 8.

pH	Hydroxyl Alkalinity (ppm)	
	as CaCO ₃	as OH
9.0	0.5	0.17
9.5	1.6	0.54
10.0	5	1.70
10.2	8	2.72
10.5	16	5.44
10.6	20	6.80
10.7	25	8.50
10.8	33	11.2
10.9	40	13.6
11.0	50	17.0
11.1	63	21.4
11.2	79	26.9
11.3	100	34.0
11.4	126	42.8
11.5	158	53.7
11.6	199	67.7
11.7	250	85.0
11.8	315	107
11.9	397	135
12.0	500	170

Table 8
Relationship between Causticity and Ph

3.6.3 CONDUCTIVITY AND TDS. Each of these water quality parameters is a measure of the amount of soluble minerals present in the water. Conductivity is measured with an electronic instrument based on the flow of an electrical current through the water sample. The measurement of TDS requires evaporation of a fixed amount of water to determine the weight of the remaining minerals (i.e., the TDS in the water). The conductivity instrument may report the mineral content as micromohs or as dissolved solids. In neutral or alkaline waters, there is no consistent relationship between conductivity and TDS since each ion has its own specific conductivity. The hydroxyl ion has the highest conductivity of all the common ions found in boiler water. If alkaline boiler water is acidified to the phenolphthalein end-point with an organic acid (such as gallic acid), which neutralizes

causticity but does not contribute to conductivity, the TDS is approximately equal to two-thirds of the neutralized conductivity in micromhos. This is known as “neutralized conductivity.” In boiler water, a factor of 0.7 can be used for water treated with synthetic polymers as a sludge dispersant, and from 0.7 to 1.0 for water treated with Quebracho tannin, depending on the amount of tannin in the water. Conductivity and TDS are used to determine the COC and the potential for scale formation.

3.7 IN-PLANT LABORATORY WATER TESTING REQUIREMENTS. The water tester should be provided with a separate working space to perform the required routine water control tests. This space can be a separate room having a suitable work bench, a sink and cabinet, a distilled or deionized water source, and adequate ventilation, heating, and cooling. Standard white fluorescent lighting at reading intensity can be provided. A record file for test results and references can be located in the test area.

3.7.1 RECOMMENDED LABORATORY EQUIPMENT. At each location, laboratory equipment should be selected so that all routine water tests can be performed. The equipment list can include standard glassware such as beakers, test tubes, graduated cylinders, and casseroles so the tests can be performed efficiently. The equipment required for each test can be included with the appropriate test kit.

3.7.2 CHEMICAL REAGENTS. A master list of chemical reagents can be maintained. The list includes testing reagents that are stocked, their reference number, the quantity of stock, and the test for which the reagent is used. The minimum stock level should be defined and the reagent ordered when that level is reached. The chemical reagents required for field tests will be included with the appropriate test kit. The supplier provides an MSDS for each of the chemical reagents, and it should be kept in the vicinity of the test area in case of an emergency.