



# Water Talk

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## Closed System Guidelines

Treatment Goals in Order of Importance	Range or Limit
1. pH	9.0-10.5 in logarithmic units
2. "P" Alkalinity	100-500 ppm
3. Boron	100-200 ppm Boron
4. Chemical Oxygen Demand (COD)	100 maximum ppm as oxygen
5. Corrosion inhibitor: Sodium Nitrite Molybdate Chromate Nitrite + Molybdate Chromate +Molybdate	1,000-1,500 200-300 200-300 100-200 each 50-100 each Ppm as indicated
6. Soluble Copper	0.20 ppm Maximum ppm as copper
7. Tolytriazole copper inhibitor	10 ppm minimum ppm
8. Total suspended solids	10 ppm maximum
9. Ammonia	20 ppm maximum ppm
10. "OH" or Free Caustic Alkalinity	20 ppm maximum
11. Microbial Limits Total Aerobic Plate Count Total Anaerobic Plate Count Nitrate Reducers Sulfate Reducing Bacteria Iron Bacteria	1,000 10 10 0 0 In colony forming units

pH is a measure of acid (hydrogen ion) concentration and indirectly caustic (hydroxyl ion) present in water. The pH scale runs from 0.0, which is strongly acidic to 14.0 which is strongly caustic. pH 7.0 corresponds to neutral water where acid and caustic concentrations are exactly equal. Declining pH, below 7.0, indicates increasingly corrosive conditions. Rising pH, above 7.0, indicates ever increasing potential for scale or sludge formation. Each unit change in pH equals a ten fold change in acidic or caustic content. In closed recirculating water systems, corrosion of steel is minimized when pH is held at from 9.0-10.5. Should pH fall below 8.0, corrosion of steel will increase, corrosion inhibitor concentration may fall due to low pH chemical change of the inhibitor, and over time, any glycol based anti-freeze present may begin to deteriorate. Should pH rise above 11.0, corrosion of copper and its alloys, especially yellow brass, may occur. Increase in soluble copper content typically accompanies excessively high pH. High pH, in excess of 11.0, may influence pump seal life.

"P" or "Reserve" Alkalinity includes all alkaline chemical species dissolved in water contributing to pH above 8.2. "P" Alkalinity is also termed Reserve Alkalinity by manufacturers of automotive grade anti-freeze. In closed recirculating water systems, "P" alkalinity measures buffering due to alkaline pH stabilizers such as borax, phosphate, or silicate. Buffering imparts moderate resistance to pH change should acidic or caustic contaminants enter or form in the water. Proper pH stabilization is absolutely essential for good control over steel, copper, or copper alloy corrosion, minimizing microbial activity, preservation of nitrite or Molybdate based corrosion inhibitors, and for avoiding acidic formation in glycol based anti-freeze. Holding "P" alkalinity limits insures desired treatment performance.

Borax (Sodium Tetraborate) is used to buffer pH in Aqua-Serv nitrite and Molybdate based closed system treatment formulations. Since buffering derived from

borax produces roughly fixed pH irrespective of how much borax is present, pH alone is not a reliable indicator of the amount of borax buffer present in treated water. "P" alkalinity increases in direct proportion to the amount of borax introduced and typically is used in field determination. Determination of elemental boron derived from borax cannot readily be accomplished in the field, but boron concentration data may be obtained with sample submission to the lab. Borax is used for buffering because it does not form insoluble precipitates.

COD is a laboratory test used to determine organic or carbon containing compounds in water. Organics are problematic in closed systems because they serve as principle nutrient for microbial activity. This in turn alters system water chemistry leading to increased corrosion as microbial activity converts organics to weak organic acids. The most common source of COD is ethylene glycol anti-freeze either not, or insufficiently, flushed from "winterized" chilled water coils prior to spring start-up. Trace glycol is microbiologically converted to acetic, formic, glycolic, oxalic, acid and other organic compounds, that act to reduce "P" Alkalinity and pH and to chelate iron and copper. If COD exceeds 100ppm, pH may fall below 6.0 substantially increasing corrosion. Trace glycol contamination is typically responsible for more corrosion than all other common causes of corrosion. For reference, one pound of ethylene glycol in a thousand gallons of water is equal to 120 ppm glycol and will theoretically increase COD by 155 ppm potentially lowering "P" Alkalinity by more than 100 ppm.

Borax buffering, sufficient to establish at least 100 ppm "P" Alkalinity, will help lower general corrosion in any closed system provided COD is kept below 100 ppm. To reduce corrosion to the lowest possible level, it is necessary to employ a corrosion inhibitor such as Nitrite, Molybdate, Chromate, or combinations of Nitrite and Molybdate or Molybdate and Chromate. With both pH control (buffering) and use of a corrosion inhibitor, steel corrosion in closed recirculating systems can typically be limited to less than 0.1 mil's per year as determined by corrosion test coupon. Nitrite and Molybdate may be used whether Ethylene Glycol anti-freeze is present or not. Chromate should not be used where Glycol anti-freeze is present or where C.O.D. is above 200 ppm. Corrosion inhibitors promote formation of an adherent oxide film on metals protecting against

corrosion. Chromate and nitrite are oxidizing inhibitors and as such do not require oxygen presence to function properly. Molybdate is essentially non-oxidizing and requires oxygen presence to function effectively. Where oxygen is diminished or absent, nitrite may become unstable.

The solubility of copper (compounds) in water having a pH ranging from 9.0 and 10.5 is normally less than 0.05 ppm. If soluble copper content rises above 0.05 ppm, ammonia or other copper-reactive containment may be present. If soluble copper exceeds 0.20 ppm, steps should be taken to determine the mechanism producing the increased solubility of copper. If a copper solubilizing contaminant is allowed to remain in the system, the protective oxide film normally found on copper may be removed leading to excessive corrosion. Yellow metal corrosion inhibitors such as Tolytriazole and Benzotriazole are designed to protect copper and its alloys against normal corrosion and the effects of low levels of copper reactive contaminants such as up to 20 ppm of ammonia. Extreme glycol decomposition, however can overcome this protection.

Sodium Nitrite and Molybdate are not considered to be effective corrosion inhibitors for copper or its common alloys. Tolytriazole inhibits corrosion by forming a very thin barrier film over copper containing metallic surfaces. For proper film maintenance, concentration of Tolytriazole in system water should not be allowed to fall below 10.0 ppm. Should soluble copper exceed 0.20 ppm, Tolytriazole is effective in controlling induced pitting corrosion of relatively more active metals than copper, such as steel or aluminum, due to copper "plating" on relatively more active metals. Tolytriazole in excess of 50 ppm should be avoided to control unnecessary elevation of COD.

Mill scale and corrosion debris, hard forms of magnetic iron oxide, typically erode from pipe over time due to mechanical forces such as thermal expansion and contraction and high water velocity. Coarse debris settles in dirt legs, is captured by side stream filtration, or is ground into fine abrasive matter difficult to remove by filtration. Abrasive action of almost microscopic sized particles causes pump seal and valve shaft packing along with other working surfaces to wear leading to premature failure of system components. Fine suspended solids should

be captured, if possible, using side stream filtration. Filters should be sized to process system volume 4-6 times every 24 hours. Filter porosity to be 30 microns the first 30-60 days after filter installation and 10 microns or less thereafter.

Ammonia in water will react with the protective copper oxide layer on metallic copper and its common alloys if the pH of the system water is above 7.0. This reaction produces a soluble copper-ammonia complex that becomes increasingly stable as pH rises above 7.5. If oxygen is also present, as is normally the case, removal of the protective film will lead to accelerated corrosion of the underlying metal. Tolytriazole will provide yellow metal corrosion inhibition provided ammonia content does not exceed roughly 20.0 ppm. Even in well treated water, if ammonia levels rise much above 20.0 ppm, both soluble copper content and copper corrosion will increase. Ammonia may form microbiologically if nitrogen containing compounds are present in chilled water and the water is totally anaerobic due to lack of dissolved oxygen.

### **Explanation – Significance**

“OH” or Free Caustic Alkalinity should not be present in a properly treated closed system. If “OH” Alkalinity is found, pH will most likely be in excess of 10.5. Usually, “OH” Alkalinity results from the insufficient or depleted pH buffering combined with presence of a highly alkaline contaminant such as Sodium Hydroxide (Caustic Soda) or Potassium Hydroxide. A laboratory analysis should be performed prior to treatment introduction to determine if all contamination due to alkaline cleaners or acid forming organics, such as anti-freeze, has been fully purged from the system. Sometimes, sodium hydroxide is used to rapidly elevate pH, if anti-freeze deterioration has significantly lowered pH. If too much Caustic Soda is introduced, very high pH and an “OH” Alkalinity in excess of 20 ppm may result. Under no circumstances should pH be allowed to remain above 11.0 for an extended period of time. This could produce general damage to copper or its alloys and especially copper containing pump impellers exposed to very hot water in excess of 240 degrees Fahrenheit.

Microbial limits shown signify ideal conditions, typically difficult to achieve or maintain in most

systems. Microbiocides may be introduced and bacterial counts may be briefly suppressed, but, it is near impossible to totally sterilize any given system. Some bacterial re-inoculation always takes place, returning population to pretreatment levels within a few days or weeks. Additional microbiocide may be introduced to limit re-growth, but such efforts usually become ineffective as resistant bacterial strains predominate, eventually leading to unchecked growth. When this happens, it usually becomes necessary to employ a second or third microbiocide. Eventually, even alternate application of products proves ineffective. Where growth then spirals out of control even as more and more microbiocide is introduced, it is not the products fault but the strategy of using an organic, non-oxidizing microbiocide in the first place.

To be approved for use by the Federal EPA, any pesticide must quickly break down yielding “harmless” byproducts. Any organic non-biocidal decomposition product adds COD, effectively becoming a nutrient. For this reason, use of non-oxidizing microbiocides in closed systems is not recommended without specific reason. If oxygen is present and microbial activity is aerobic, control is best achieved by limiting COD.

If a closed system contains freeze preventing ethylene or propylene glycol, COD will exceed 200,000 ppm suggesting a possibility for extreme growth. Rich glycol solutions, above 20% by weight, actually inhibit microbial activity. Glycols become subject to attack as percentage falls. Total breakdown occurs below 1.0% by an uncontrollable fermentation-like process producing very acidic conditions.

### **When should anti-freeze be changed due to decomposition?**

*When the sum of reported glycol decomposition products; i.e. Acetate + Formate + Glycolate + Oxalate + Propionate exceeds 1,500 to 2,000 ppm*

Ethylene and Propylene Glycol slowly oxidize in any closed system by chemical and microbial processes. The rate of decomposition is inversely proportion to pH and glycol concentration, increasing as pH and glycol concentration fall. It is essential to keep pH

above 9.0, and maintain recommended anti-freeze level.

Anti-freeze can be kept in good condition for 10 years or more if properly maintained. Improperly maintained anti-freeze may become unusable in as little as a year or less. pH below 8.0 and/or concentration below 15% increases breakdown producing bad odor, rusty appearance and operational difficulty. Glycol breakdown produces carboxylic acids including but not limited to: acetic, formic, glycolic and oxalic acid.

Alkaline pH buffering converts these acids to their respective sodium or potassium salts. These salts are not themselves overtly troublesome, but for two reasons their continued presence is undesirable.

First, weak, complexes (chelates) of oxidized iron, copper and zinc signify weakening of protective metal oxide films slightly increasing system wide corrosion. Chelated metals can deposit on pump seal surfaces decreasing surface life.

Second, buffering a lower pH than borax occurs. If buildup exceeds about 500 ppm, borax buffering may be overwhelmed lowering pH to 8.0, or less. Because pH is then buffered in this range, it may be very difficult to return pH to 9.0 or higher.

Experience has shown that when the sum of the four organic acids reported exceeds roughly 1500 to 2000 ppm, metal chelation has reached a point where general corrosion becomes significant and pH can't be stabilized above 9.0 Glycol based anti-freeze should be replaced at this point. Corrosion coupon data, if available, is a good aid in the decision process. In addition, rare elevated oxalate content may produce increased copper corrosion prompting a separate evaluation of anti-freeze retention.

Where badly deteriorated glycol is removed and remedial action is subsequently taken to clean and passivate a system, it is good practice to allow the system to stabilize before reintroducing new glycol. If possible, glycol removed in the spring should not be replaced until needed in the fall.

## **When Should a Closed System Be Cleaned?**

*When a condition such as new system, oil contamination, serious glycol breakdown, MIC activity, or extended poor history is encountered.*

Before introducing chemical treatment or anti-freeze, a closed loop system should be free of oil, loose mill scale, dirt, trace glycol, and cleaner residue.

Before resuming service after cleaning observe the following:

1. Total (M) alkalinity no more than 50 ppm over raw water.
2. Chemical Oxygen Demand less than 100 ppm.
3. Dissolved Solids less than 100 ppm over raw water.
4. Suspended solids less than 10 ppm.

Any detectable oil or knowledge of oil contamination is sufficient grounds for cleaning. If oil film remains in a system, significant microbiologically influenced corrosion may result. An alkaline detergent should be used. Such cleaners elevate total (M) alkalinity of system water by 4,000 to 6,000 ppm.

Serious glycol breakdown, with prolonged pH below 6.0, and iron content in excess of 100 ppm, warrants cleaning. It is generally best to first drain and refill prior to introducing an alkaline cleaner, alternately purge flushing may be used.

“Free cooling” systems, are prone to debris accumulation and excessive microbial activity. Systems of this type should be cleaned annually or on a set schedule to prevent formation of deposits that eventually become troublesome.

Any system poorly treated over a long period of time may have substantial accumulation of both adherent and loose iron oxide corrosion debris restricting water flow and necessitating deposit removal. Cleaning

under such difficult circumstances is generally conducted after detailed evaluation. Cleaning typically involves use of complex compounds such as ammoniated citric acid or other chelating agent and may require heating of system water.

Oil and grease may be removed from new or existing closed loop system without using an alkaline cleaner.

**Properties of Ethylene Glycol**

Taken from the “Merck Index”, 8<sup>th</sup> Edition, 1968

<u>Percent by Weight</u>	<u>Percent by Volume</u>	<u>Specific Gravity</u>	<u>Freeze Point °F</u>	<u>Freeze Point °C</u>
10	9	1.0130	+26	-3
20	18	1.0270	+17	-8
26	24	1.0350	+10	-12
31	28	1.0410	+5	-15
34	32	1.0450	-1	-18
42	40	1.0563	-15	-26
50	48	1.0670	-32	-36
58	56	1.0769	-54	-48

**Properties of Propylene Glycol**

Taken from the “Merck Index”, 8<sup>th</sup> Edition, 1968

<u>Percent by Weight</u>	<u>Percent by Volume</u>	<u>Specific Gravity</u>	<u>Freeze Point °F</u>	<u>Freeze Point °C</u>
7	10	1.006	+28	-2.2
17	20	1.017	+20	-6.7
21	25	1.020	+16	-8.9
26	30	1.024	+9	-12.8
31	35	1.028	+3	-16.1
37	40	1.032	-5	-20.6
42	45	1.037	-16	-26.7
45	50	1.040	-54	-28.0