



US006998092B2

(12) **United States Patent**
Duke et al.

(10) **Patent No.:** **US 6,998,092 B2**
(45) **Date of Patent:** ***Feb. 14, 2006**

(54) **COOLING WATER SCALE AND CORROSION INHIBITION**
(75) Inventors: **Dan A. Duke**, Temecula, CA (US);
John L. Kubis, Mission Viejo, CA (US)

6,334,955 B1 * 1/2002 Kawashima et al. 210/636
6,402,957 B1 * 6/2002 Boyce 210/652
6,468,470 B1 * 10/2002 Oldsberg et al. 422/15
6,537,456 B1 * 3/2003 Mukhopadhyay 210/652
6,733,636 B1 * 5/2004 Heins 203/1

(73) Assignee: **Water Conservation Technologies International**, Temecula, FL (US)
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

OTHER PUBLICATIONS

Strumm, et al.; "Formation of Polysilicates as Determined by Coagulation Effects"; Environmental Science and Technology; 1967; vol. 1, 221-227.
Rozenfeld, I.L.; "Corrosion Inhibitors"; 1981; McGraw Hill; 171-174.
The NALCO Water Handbook; 1979; Chapter 3, p. 14 and 16.
Drew; Principles of Industrial Water Treatment; Sixth Edition; 1983; Chapter 3, pp. 43 and 64.
Boffardi, Bennett P., PhD; Calgon Internal Publication; 1988; Chapter 4; pp. 30-31.

(21) Appl. No.: **11/018,732**

* cited by examiner

(22) Filed: **Dec. 21, 2004**

(65) **Prior Publication Data**

Primary Examiner—Peter A. Hruskoci
(74) *Attorney, Agent, or Firm*—Stetina Brunda Garred & Brucker

US 2005/0218080 A1 Oct. 6, 2005

Related U.S. Application Data

(57) **ABSTRACT**

(60) Division of application No. 10/814,324, filed on Mar. 31, 2004, now Pat. No. 6,949,193, which is a continuation-in-part of application No. 10/754,797, filed on Jan. 9, 2004, now Pat. No. 6,929,749.

A methods for inhibiting silica scale formation and corrosion in aqueous systems where soluble silica (SiO₂) can be maintained at residuals below 200 mg/L, but more preferably maintained at greater than 200 mg/L as SiO₂, without silica scale and with control of deposition of source water silica accumulations as high as 4000 mg/L (cycled accumulation) from evaporation and concentration of source water. The methods of the present invention also provide highly effective inhibition of corrosion for carbon steel, copper, copper alloy, and stainless steel alloys. The methods of the present invention comprise pretreatment removal of hardness ions from the makeup source water, maintenance of electrical conductivity, and elevating the pH level of the aqueous environment. Thereafter, specified water chemistry residual ranges are maintained in the aqueous system to achieve inhibition of scale and corrosion.

(51) **Int. Cl.**
C23F 11/06 (2006.01)

(52) **U.S. Cl.** **422/3**; 159/47.1; 203/10; 210/652; 210/687; 210/696; 422/13; 422/14

(58) **Field of Classification Search** 159/47.1, 159/47.3; 203/10; 210/652, 687, 696-702, 210/743, 746, 748, 96.1; 422/3, 13, 14
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,277,823 A 1/1994 Hann et al.
5,403,521 A * 4/1995 Takahashi 261/26
6,315,909 B1 * 11/2001 Hoots et al. 210/745

15 Claims, No Drawings

1

COOLING WATER SCALE AND CORROSION INHIBITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of Ser. No. 10/814,324, filed Jan. 9, 2004, now U.S. Pat. No. 6,949,193.

The present application is a continuation-in-part of U.S. patent application Ser. No. 10/754,797 filed on Jan. 9, 2004, now U.S. Pat. No. 6,929,749 entitled Cooling Water Scale and Corrosion Inhibition.

STATEMENT RE: FEDERALLY SPONSORED RESEARCH/DEVELOPMENT

Not Applicable

BACKGROUND OF THE INVENTION

Silica is one of the major scale and fouling problems in many processes using water. Silica is difficult to deal with because it can assume many low solubility chemical forms depending on the water chemistry and metal surface temperature conditions. Below about pH 9.0, monomeric silica has limited solubility (125–180 mg/L as SiO₂) and tends to polymerize as these concentrations are exceeded to form insoluble (amorphous) oligomeric or colloidal silica. At higher pH, particularly above about pH 9.0, silica is soluble at increased concentrations of the monomeric silicate ion or in the multimeric forms of silica. Since conversion can be slow, all of these forms may exist at any one time. The silicate ion can react with polyvalent cations like magnesium and calcium commonly present in process waters to produce salts with very limited solubility. Thus it is common for a mixture of many forms to be present: monomeric, oligomeric and colloidal silica; magnesium silicate, calcium silicate and other silicate salts. In describing this complex system, it is common practice to refer to the mixture merely as silica or as silica and silicate. Herein these terms are used interchangeably.

To address such problem, methods for controlling deposition and fouling of silica or silicate salts on surfaces in an aqueous process have been derived and include: 1) inhibiting precipitation of the material from the process water; 2) dispersing precipitated material after it has formed in the bulk water; 3) maintaining an aqueous chemical environment that supports formation of increased residuals of soluble silica species; and 4) producing a non-adherent form of silica precipitants in the bulk water. The exact mechanism by which specific scale inhibition methods of the present inventions function is not well understood.

In industrial application, most scale and corrosion control methods used in aqueous systems typically rely on the addition of a scale and corrosion inhibitor in combination with controlled wastage of system water to prevent scale and corrosion problems. In this regard, the major scale formation potentials are contributed by the quantity of hardness (calcium and magnesium) and silica ions contributed by the source water, while the major corrosive potential results from the ionic or electrolytic strength in the system water.

Treatment methods to minimize corrosion have further generally relied on the addition of chemical additives that inhibit corrosion through suppression of corrosive reactions occurring at either the anode or the cathode present on the metal surface, or combinations of chemical additives that inhibit reactions at both the anode and cathode. The most

2

commonly applied anodic inhibitors include chromate, molybdate, orthophosphate, nitrite and silicate whereas the most commonly applied cathodic inhibitors include polyphosphate, zinc, organic phosphates and calcium carbonate.

In view of toxicity and environmental concerns, the use of highly effective heavy metal corrosion inhibitors, such as chromate, have been strictly prohibited and most methods now rely on a balance of the scale formation and corrosive tendencies of the system water and are referred to in the art as alkaline treatment approaches. This balance, as applied in such treatment approaches, is defined by control of system water chemistry with indices such as LSI or Ryznar, and is used in conjunction with combinations of scale and corrosion inhibitor additives to inhibit scale formation and optimize corrosion protection at maximum concentration of dissolved solids in the source water. These methods, however, are still limited by the maximum concentration of silica and potential for silicate scale formation. Moreover, corrosion rates are also significantly higher than those available with use of heavy metals such as chromate. Along these lines, since the use of chromate and other toxic heavy metals has been restricted, as discussed above, corrosion protection has generally been limited to optimum ranges of 2 to 5 mils per year (mpy) for carbon steel when treating typical source water qualities with current corrosion control methods. Source waters that are high in dissolved solids or are naturally soft are even more difficult to treat, and typically have even higher corrosion rates.

In an alternative approach, a significant number of methods for controlling scale rely on addition of acid to treated systems to control pH and reduce scaling potentials at higher concentrations of source water chemistry. Such method allows conservation of water through modification of the concentrated source water, while maintaining balance of the scale formation and corrosive tendencies of the water. Despite such advantages, these methods have the drawback of being prone to greater risk of scale and/or corrosion consequences with excursions with the acid/pH control system. Moreover, there is an overall increase in corrosion potential due to the higher ionic or electrolytic strength of the water that results from addition of acid ions that are concentrated along with ions in the source water. Lower pH corrosion control methods further rely on significantly higher chemical additive residuals to offset corrosive tendencies, but are limited in effectiveness without the use of heavy metals. Silica concentration must still be controlled at maximum residuals by system water wastage to avoid potential silica scaling.

In a further approach, source water is pretreated to remove hardness ions in a small proportion of systems to control calcium and magnesium scale potentials. These applications, however, have still relied on control of silica residuals at previous maximum guideline levels through water wastage to prevent silica scale deposits. Corrosion protection is also less effective with softened water due to elimination of the balance of scale and corrosion tendency provided by the natural hardness in the source water.

Accordingly, there is a substantial need in the art for methods that are efficiently operative to inhibit corrosion and scale formation that do not rely upon the use of heavy metals, extensive acidification and/or water wastage that are known and practiced in the prior art. There is additionally a need in the art for such processes that, in addition to being efficient, are extremely cost-effective and environmentally safe. Exemplary of those processes that would likely benefit from such methods would include cooling water processes, cooling tower systems, evaporative coolers, cooling lakes or

ponds, and closed or secondary cooling and heating loops. In each of these processes, heat is transferred to or from the water. In evaporative cooling water processes, heat is added to the water and evaporation of some of the water takes place. As the water is evaporated, the silica (or silicates) will concentrate and if the silica concentration exceeds its solubility, it can deposit to form either a vitreous coating or an adherent scale that can normally be removed only by laborious mechanical or chemical cleaning. Along these lines, at some point in the above processes, heat is extracted from the water, making any dissolved silicate less soluble and thus further likely to deposit on surfaces, thus requiring removal. Accordingly, a method for preventing fouling of surfaces with silica or silicates, that further allows the use of higher levels of silica/silicates for corrosion control would be exceptionally advantageous. In this respect for cooling water, an inhibition method has long been sought after that would enable silica to be used as a non-toxic and environmentally friendly corrosion inhibitor.

To address these specific concerns, the current practice in these particular processes is to limit the silica or silicate concentration in the water so that deposition from these compounds does not occur. For example in cooling water, the accepted practice is to limit the amount of silica or silicates to about 150 mg/L, expressed as SiO₂. Reportedly, the best technology currently available for control of silica or silicates in cooling water is either various low molecular weight polymers, various organic phosphate chemistries, and combinations thereof. Even with use of these chemical additives, however, silica is still limited to 180 mg/L in most system applications. Because in many arid areas of the U.S. and other parts of the world make-up water may contain from 50–90 mg/L silica, cooling water can only be concentrated 2 to 3 times such levels before the risk of silica or silicate deposition becomes too great. A method that would enable greater re-use or cycling of this silica-limited cooling water would be a great benefit to these areas.

SUMMARY OF THE INVENTION

The present invention specifically addresses and alleviates the above-identified deficiencies in the art. In this regard, the invention relates to methods for controlling silica and silicate fouling problems, as well as corrosion of system metallurgy (i.e. metal substrates) in aqueous systems with high concentrations of dissolved solids. More particularly, the invention is directed to the removal of hardness ions from the source water and control of specified chemistry residuals in the aqueous system to inhibit deposition of magnesium silicate and other silicate and silica scales on system surfaces, and to inhibit corrosion of system metallurgy. To that end, we have unexpectedly discovered that the difficult silica and silicate scaling problems that occur in aqueous systems when silica residuals exceed 125 mg/L, and more preferably are approaching or greater than 200 mg/L as SiO₂, to as high as 4000 mg/L of silica accumulation (cycled accumulation from source water), can be controlled by initially removing hardness ions (calcium and magnesium) from the makeup source water (i.e., water fed to the aqueous system) using pretreatment methods of the present inventions known in the art, such as through the use of ion exchange resins, selective ion removal with reverse osmosis, reverse osmosis, electrochemical removal, chemical precipitation, or evaporation/distillation. Preferably, the pretreatment methods of the present invention will maintain the total hardness in the makeup water at less than 20% of the makeup silica residual (mg/L SiO₂), as determined from

an initial assessment of the source water. In some embodiments, the total hardness ions will be maintained at less than 5% of the makeup silica residual. When source makeup water is naturally soft, with less than 10 mg/L hardness as CaCO₃, pretreatment removal of hardness ions may be bypassed in some systems. Thereafter, the conductivity (non-neutralized) in the aqueous system is controlled such that the same is maintained at some measurable level (i.e., at least 1 μmhos and the pH of the source water elevated to a pH of approximately 9.0, and preferably 9.6, or higher. With respect to the latter, the pH may be adjusted by the addition of an alkaline agent, such as sodium hydroxide, or by simply removing a portion of the aqueous system water through such well known techniques or processes as evaporation and/or distillation.

In a related application, we have unexpectedly discovered that the excessive corrosion of carbon steel, copper, copper alloys, and stainless steel alloys in aqueous systems due to high ionic strength (electrolytic potential) contributed by dissolved solids source water or highly cycled systems can likewise be controlled by the methods of the present inventions of the present invention. In such context, the methods of the present invention comprises removing hardness ions (calcium and magnesium) from the makeup source water using known pretreatment methods of the present inventions, such as ion exchange resins, selective ion removal with reverse osmosis, reverse osmosis, electrochemical removal, chemical precipitation, or evaporation/distillation. The pretreatment methods of the present invention will preferably maintain the total hardness ratio in the makeup water at less than 20%, and preferably at least less than 5%, of the makeup silica residual (mg/L SiO₂), as determined from an initial analysis of the source water. When source makeup water is naturally soft, with less than 10 mg/L hardness as CaCO₃, pretreatment removal of hardness ions may be bypassed in some systems. Thereafter, the conductivity (non-neutralized) in the aqueous system is controlled such that the same is maintained at some measurable level (i.e., at least 1 μmhos). Alkalinity is then controlled as quantified by pH at 9.0 or higher, with a pH of 9.6 being more highly desired in some applications along with control of soluble silica at residual concentrations approaching or exceeding 200 mg/L, but not less than 10 mg/L, with control at more highly desired residuals in some applications approaching or exceeding 300 mg/L as SiO₂. With respect to the latter, the SiO₂ may be adjusted by the addition of a silica/silicate agent, such as sodium silicate, or by simply removing a portion of the aqueous system water through such well known techniques or processes as evaporation and/or distillation.

DETAILED DESCRIPTION OF THE INVENTION

The detailed description set forth below is intended as a description of the presently preferred embodiment of the invention, and is not intended to represent the only form in which the present invention may be constructed or utilized. The description sets forth the functions and sequences of steps for constructing and operating the invention. It is to be understood, however, that the same or equivalent functions and sequences may be accomplished by different embodiments and that they are also intended to be encompassed within the scope of the invention.

According to the present invention, there is disclosed methods for inhibiting silica and silicate scale in aqueous systems and providing exceptional metal corrosion protec-

tion that comprise the removal of hardness from the makeup source water prior to being fed into the aqueous system and thereafter controlling the aqueous system within specified water chemistry control ranges. Specifically, hardness ions (calcium and magnesium) are removed from the makeup source water using pretreatment methods known in the art, which include methods such as ion exchange resins, selective ion removal with reverse osmosis, reverse osmosis, electrochemical removal, chemical precipitation, or evaporation/distillation. Multivalent metal ions such as those from iron, copper, zinc, barium, and aluminum are usually at low concentrations in treated municipal and well source waters used for make up to cooling systems. These low level concentrations will not typically require removal if the total concentration of these metals in addition to hardness ions (calcium and magnesium) following pretreatment are below the maximum ratio specified based on source water silica residual. However, some water sources such as well, reclaimed or untreated surface waters may have higher residuals of these metals as well as other objectionable materials. Such waters may require pretreatment with alternative methods for reduction of these multivalent metal ions in addition to the pretreatment methods specified by the method for removal of calcium and magnesium multivalent metal ions.

The pretreatment methods will preferably maintain the total hardness ratio in the makeup water at less than 20% of the makeup silica residual (mg/L SiO_2). In a more highly preferred embodiment, the pretreatment methods will maintain the total hardness ions present in the makeup water at less than 5% of the makeup silica residual. As will be appreciated by those skilled in the art, the silica residual can be readily determined by utilizing known techniques, and will preferably be determined prior to the application of the methods of the present invention. Along these lines, when source makeup water is naturally soft, with less than 10 mg/L hardness as CaCO_3 , pretreatment removal of hardness ions may be bypassed in some systems.

Conductivity (non-neutralized) is established in the aqueous system such that at least some measurable conductivity is present, which is defined as at least 1 μmhos and preferably at least 500 μmhos . Control of conductivity may be conducted through control or elimination of blowdown wastage from the system. In a more highly preferred embodiment, conductivity will be maintained between 10,000 and 150,000 μmhos . Conductivity levels attained in method treated systems will depend upon system capability to concentrate source water, level of dissolved solids (conductivity) in the pre-treated or natural source water, and potential addition of adjunct alkalinity or chemical to attain required control residuals. The higher level of ionic strength in the more highly preferred embodiment control range of 10,000 to 150,000 μmhos will increase the solubility of multivalent metal salts that are less soluble at lower ionic strengths of other methods. This residual control parameter also provides indirect control of silica and alkalinity (pH) residuals contributed by concentration of available silica and alkalinity in the pre-treated or natural source water or by addition of adjunct forms of these chemicals.

Aqueous system pH is maintained at 9.0 or greater as contributed by the cycled accumulation of alkalinity from the source water or through supplemental addition of an alkalinity adjunct, such as sodium hydroxide, to the system when required. The minimum pH will provide increased solubility of silica and control of silicate scale and support corrosion protection for metals. Along these lines, in certain

preferred embodiments of the present invention, the pH may be raised and maintained to a level of 9.6 or higher.

To support corrosion inhibition, soluble silica residuals will preferably be maintained in the aqueous system at levels approaching or exceeding 200 mg/L, but not less than 10 mg/L, as contributed by the cycled accumulation of silica from the source water or through supplemental addition of adjunct forms of silica to the system when required. In certain applications, such levels may be maintained at levels of greater than 300 mg/L. A 200 mg/L minimum residual of soluble silica will support corrosion inhibition for metals, and more particularly, inhibit corrosion of carbon steel to less than 0.3 mpy and less than 0.1 mpy for copper, copper alloys and stainless steel alloys present in the aqueous system. The method will control carbon steel corrosion at less than 5 mpy (less than 0.3 mpy for copper) in treated systems controlled at silica residuals less than 200 mg/l (as SiO_2), with reduction of source water multivalent metal ions (hardness) to specified residuals and pH control at 9.0 or greater.

With respect to the mechanisms by which the methods of the present inventions effectively achieve their results, excess source water silica (beyond the soluble residuals attained with specified pH control) is probably adsorbed as non-adherent precipitates that form following reaction with small amounts of metals (Ca, Mg, Fe, Al, Zn) or solids introduced by source water or scrubbed from the air by the tower system. This is the probable result of the expanded solubility of the monomeric and multimeric species of silica with the methods of the present invention that impede polymerization of excess silica until it reacts with these incrementally introduced adsorption materials to form small quantities of non-adherent precipitants. The adsorption and precipitation of high ratios of silica on small amounts of solids such as magnesium hydroxide has been demonstrated by the Freundlich isotherms, and is common experience in water treatment chemical precipitation processes. The small quantity of precipitate is removed from the circulating water through settling in the tower basin or drift losses.

Control of the lower solubility hardness scale formations and resultant nucleation sites on cooling system surfaces are controlled with the methods disclosed herein, through pretreatment removal of the majority of the scale forming (hardness) metal ions and control of system water at the specified higher ionic strength control ranges. The higher level of ionic strength in the preferred control range increases the solubility of scale forming metal salts. Such approach is well suited to address a further complication in controlling silica and silicate fouling brought about from the phenomena that colloidal silica tends to be more soluble as temperature is raised, while the polyvalent metal salts of the silicate ion tend to be less soluble with increasing temperature. As a result, control or minimization of polyvalent metals in the aqueous solution will prohibit formation of the insoluble salts on heat transfer surfaces, and promote increased solubility of other forms of silica at the elevated temperatures of heat transfer surfaces. The present methods thereby eliminate potential reaction of insoluble silica forms with hardness scale or metal salt deposits on system surfaces and their nucleation sites that initiate silica or silicate scale formations. The method will control silica scale formation in treated systems with silica residuals exceeding those permitted by prior art (maximum solubility 125 to 180 mg/l monomeric silica), with reduction of source water multivalent metal ions (hardness) to specified residuals and pH control at 9.0 or higher.

The higher residuals of soluble silica and higher pH levels maintained via the present methods of the present inventions provide highly effective polarization (corrosion barrier formation) and exceptional corrosion protection for carbon steel, copper, copper alloy and stainless steel metals (less than 0.3 mpy for mild steel, and less than 0.1 mpy copper, copper alloy, and stainless steel). Moderately higher corrosion rates may be acceptable to end users when low silica source waters do not permit attainment of residuals approaching or exceeding 200 mg/l SiO₂ in the method treated water at the system's maximum attainable source water concentrations. Such moderately elevated corrosion levels are superior or equivalent to current art. Comparable corrosion rates for carbon steel in aqueous systems with existing methods of the present inventions are optimally in the range of 2 to 5 mpy. When pH is increased to levels higher than 9.0, and residuals of silica are increased, approaching 200 mg/l SiO₂, corrosion levels will be reduced to those levels disclosed in Applicants' co-pending patent application (Serial Number not yet assigned), the teachings of which are incorporated herein by reference. Maximum attainable source water concentrations may be limited by low evaporative load and/or uncontrollable system water losses (such as tower drift). If the end user does require lower corrosion rates, such results are attainable by supplemental addition of adjunct silica to the cooling water to provide residuals approaching or greater than 200 mg/L SiO₂.

Though not fully understood, several corrosion inhibition mechanisms are believed to be contributing to the metals corrosion protection provided by the methods of the present invention, and the synergy of both anodic and cathodic inhibition functions may contribute to the corrosion inhibition process. Control at lower silica residuals probably reduces the effectiveness of corrosion inhibition due to reduction of available monomeric silica and converted multimeric forms of silica that provide anodic corrosion inhibition to metals with the method. Higher concentrations of silica and higher pH levels will provide increased multimeric silica residual concentrations for optimum anodic protection afforded by the method. Operating at lower soluble silica concentrations will also reduce the corrosion inhibition effectiveness of method treated systems if pretreatment upsets lead to elevated hardness levels in the source water exceeding those specified in the method, since high source water residuals of hardness salts can then more easily absorb and deplete the reduced multimeric silica residuals formed by the method at low silica residual conditions.

In this regard, an anodic corrosion inhibitor mechanism results from increased residuals of soluble silica provided by the present methods, particularly in the multimeric form. Silicates inhibit aqueous corrosion by hydrolyzing to form negatively charged colloidal particles. These particles migrate to anodic sites and precipitate on the metal surfaces where they react with metallic ion corrosion products. The result is the formation of a self-repairing gel whose growth is self-limited through inhibition of further corrosion at the metal surface. Unlike the monomeric silica form normally found in source water that fails to provide effective corrosion inhibition, the methods of the present invention provide such beneficial effect by relying upon the presence and on control of total soluble silica residuals, with conversion of natural monomeric silica to the multimeric forms of silica at much higher levels, through application of the combined control ranges as set forth above. In this respect, the removal of most source water calcium and magnesium ions is operative to prevent reaction and adsorption of the multimeric silica

forms on the metal oxide or metal salt precipitates from source water, which is believed to be an important contribution to the effectiveness of this corrosion inhibition mechanism afforded by the present invention. The resultant effective formation and control of the multimeric silica residuals with such methods of the present invention has not heretofore been available.

In addition to an anodic corrosion inhibition mechanism, a cathodic inhibition mechanism is also believed to be present. Such inhibition is caused by an increased hydroxyl ion concentration provided with the higher pH control range utilized in the practice of the present invention. In this regard, iron and steel are generally considered passive to corrosion in the pH range of 10 to 12. The elevated residual of hydroxyl ions supports equilibrium with hydroxyl ion produced during oxygen reduction at the cathode, and increases hydroxyl ion availability to react with iron to form ferrous hydroxide. As a consequence, ferrous hydroxide precipitates form at the metal surface due to very low solubility. The ferrous hydroxide will further oxidize to ferric oxide, but these iron reaction products remain insoluble at the higher pH levels attained by implementing the methods described herein to polarize or form a barrier that limits further corrosion. At the 9 to 10 pH range (as utilized in the practice of the present invention), effective hydroxyl ion passivation of metal surfaces may be aided by the pretreatment reduction of hardness ions (calcium and magnesium) in the source water that may compete with this reaction and interfere with metal surface barrier formation.

Galvanized steel and aluminum may be protected in general by the silicate corrosion inhibitor mechanism discussed herein, but protective films may be destabilized at water-air-metal interfaces. Steel, copper, copper alloy, stainless steel, fiberglass, and plastic are thus ideal aqueous system materials for application of the methods of the present inventions of the present invention.

The extensive improvement in corrosion protection provided by the methods of the present invention is not normally attainable with prior art methods when they utilize significantly higher residuals of aggressive ions (e.g., chloride and sulfate) and the accompanying greater ionic or electrolytic strength present in the aqueous system water. This may result from either use of acid for scale control and/or concentration of source water ions in the aqueous system. As is known, corrosion rates generally increase proportionately with increasing ionic strength. Accordingly, through the ability to protect system metals exposed to this increased electrolytic corrosion potential, opportunity for water conservation and environmental benefits that result with elimination of system discharge used with previous methods to reduce corrosion or scaling problems in aqueous systems can be readily realized through the practice of the methods disclosed herein. Indeed, significant water conservation can still be obtained with the method, even operating with silica residuals less than 200 mg/L, through elimination of blowdown wastage and subsequent concentration of source water dissolved solids (conductivity) to higher levels, without silicate scale formation or excessive corrosion.

Still further, the methods of the present inventions of the present invention can advantageously provide gradual removal of hardness scale deposits from metal surfaces. This benefit is accomplished through both pretreatment removal of the majority of the scale forming (hardness) metal ions and control of system water at the specified higher ionic strength control ranges. Solubility of hardness salts is increased by the higher ionic strength (conductivity) provided by the present methods of the present invention, which

has been determined with high solids water such as seawater, and may contribute to the increased solubility of deposits present within the aqueous environment so treated. Studies conducted with hardness scale coated metal coupons in treated systems demonstrated a significant deposit removal rate for CaCO₃ scale films in ten days. Control of source water hardness at lower specified residuals will probably be required to achieve optimum rate of hardness scale removal.

Furthermore, the present methods advantageously prohibits microorganism propagation due to the higher pH and dissolved solids levels that are attained. Biological fouling potentials are thus significantly reduced. In this regard, the methods of the present inventions disclosed herein create a chemical environment that inhibits many microbiological species that propagate at the pH and dissolved solids chemistry ranges used with previous treatment approaches. The reduction in aqueous system discharge as further provided as a by product of the present invention also permits use of residual biocides at more effective and economical dosages that impede development of problem concentrations of any microbiological species that are resilient in the aqueous environment generated through the practice of the methods of the present inventions disclosed herein.

A still further advantage of the methods of the present invention include the ability of the same to provide a lower freeze temperature in the aqueous system, comparable to ocean water, and avert potential mechanical damage from freezing and/or operational restrictions for systems located in freeze temperature climates.

Additional modifications and improvements of the present invention may also be apparent to those of ordinary skill in the art. Thus, the particular combination of parts and steps described and illustrated herein is intended to represent only certain embodiments of the present invention, and is not intended to serve as limitations of alternative devices and methods of the present inventions within the spirit and scope of the invention. For example, since the methods of the present invention provides both effective silicate scale control and corrosion inhibition when using high silica or high dissolved solids source waters, extensive variation in source water quality can be tolerated. These source waters might otherwise be unacceptable and uneconomical for use in such aqueous systems. In addition, such modifications may include, for example, using other conventional water treatment chemicals along with the methods of the present invention, and could include other scale inhibitors, such as for example phosphonates, to control scales other than silica, corrosion inhibitors, biocides, dispersants, defoamers and the like. As will be appreciated, however, control at lower conductivity levels may reduce the effectiveness of the method in removing existing hardness deposits, lowering of system water freeze temperature, and prohibition of microorganism propagation. Accordingly, the present invention should be construed as broadly as possible.

As an illustration, below there are provided non-restrictive examples of an aqueous water system that has been treated with methods conforming to the present invention.

Examples of Silicate Scale Inhibitor Method

The following analytical tests were performed on a cooling tower system treated with the methods of the present invention to demonstrate the efficacy of the present invention for controlling the solubility of silica and silicate species, and preventing scale deposition of these species. Two samples of each of the following: 1) varying source water; 2) the resultant treated system water; and 3) tower

sump insoluble accumulations, for a total of six samples were analyzed from different operating time frames.

Although the exact mechanism of action of the process is not completely understood, the methods of the present invention minimize the turbidity of the treated water, which is considered a demonstration of an effective silica and silicate scale inhibitor. Methods that produce treated water of less than eight nephelometric turbidity units (NTU) are considered improvements over the current available technology. Turbidity measurements (Table 1) performed on samples taken from the cooling systems, before and after filtration through a 0.45-micron filter, illustrate effective silicate inhibition in the treated water. The turbidity levels are well below typical cooling tower systems, in particular at such high concentrations (80 COC), and indicate the methods of the present invention provide controlled non-adherent precipitation of excess silica and other insoluble materials entering the system. Clean heat exchanger surfaces have confirmed that the method silica precipitation is non-adherent. The precipitated silica forms are contained in the cooling tower sump. However, the volume of precipitant and scrubbed accumulations in the tower sump were not appreciably greater than previous treatment methods due to reduction of insoluble multivalent metal salt precipitates by pretreatment removal.

TABLE 1

Tower Water Turbidity Analyses	
Sample No. 1: (Turbidity, NTU)	Neat, 4 NTU; Filtered, 2 NTU
Sample No. 2: (Turbidity, NTU)	Neat, 3 NTU

The cooling tower and makeup water analytical tests performed in Table 2 and Table 3 illustrate the effectiveness of the methods of the present invention in maintaining higher levels of soluble silica in the cooling tower system when parameters are controlled within the specified pH and low makeup hardness ranges. Soluble silica residuals are present at 306 and 382 mg/L in these tower samples at the respective 9.6 and 10.0 pH levels. The lower cycles of concentration (COC) for silica in these tower samples, as compared to the higher cycled residuals for soluble chemistries (chloride, alkalinity, conductivity), indicate that excess silica is precipitating as non-adherent material, and accumulating in the tower basin. This is confirmed by the increased ratio of silica forms found in tower basin deposit analyses. System metal and heat exchange surfaces were free of silica or other scale deposits.

TABLE 2

Cooling Tower Sample No. 1/Makeup/Residual Ratios (COC)			
SAMPLE/TESTS	Tower	Makeup (soft)	COC
Conductivity, μ mhos (Un-neutralized)	33,950	412	82.4
pH	10.01	8.23	NA
Turbidity, NTUs			
Neat	3	0.08	NA
Filtered (0.45 μ)	—	—	—
Copper, mg/L Cu	ND	ND	NA
Zinc, mg/L	ND	ND	NA
Silica, mg/L SiO ₂	382	9.5	40.2
Calcium, mg/L CaCO ₃	16.0	0.20	NA

TABLE 2-continued

Cooling Tower Sample No. 1/Makeup/Residual Ratios (COC)			
SAMPLE/TESTS	Tower	Makeup (soft)	COC
Magnesium, mg/L	3.33	0.05	NA
CaCO ₃			
Iron, mg/L Fe	ND	ND	NA
Aluminum, mg/L Al	ND	ND	NA
Phosphate, mg/L PO ₄	ND	ND	NA
Chloride, mg/L	6040	80	75.5
Tot. Alkalinity, mg/L	13200	156	84.6

ND = Not Detectable;
 NA = Not Applicable;
 COC = Cycles of Concentration

TABLE 3

Cooling Tower Sample No. 2/Makeup/Residual Ratios (COC)			
SAMPLE/TESTS	Tower	Makeup (soft)	COC
Conductivity, μ mhos (Un-neutralized)	66,700	829	80
pH	9.61	7.5	NA
Turbidity, NTUs			
Neat	4	0.08	NA
Filtered (0.45 μ)	2	—	—
Zinc, mg/L	ND	ND	NA
Silica, mg/L SiO ₂	306.4	11	28
Calcium, mg/L CaCO ₃	21.5	0.20	NA
Magnesium, mg/L CaCO ₃	0.65	0.05	NA
Iron, mg/L Fe	ND	ND	NA
Aluminum, mg/L Al	ND	ND	NA
Phosphate, mg/L PO ₄	ND	ND	NA

ND = Not Detectable;
 NA = Not Applicable;
 COC = Cycles of Concentration

Microscopic and chemical analysis of deposit samples from accumulated residue in the tower basin of a system treated by present methodology are shown in Exhibit 1 and Exhibit 2. Both analyses illustrate the significant ratio of silica materials in the deposit. The major proportion of this silica is the probable result of silica adsorption or reaction with insoluble precipitates of multivalent metals as they concentrated in the tower water. Visual inspections of heat transfer equipment in the system treated by this method have confirmed that it has remained free of silica and other scale deposits. System heat transfer efficiencies were also maintained at minimum fouling factor levels.

Exhibit 1
 MICROSCOPICAL ANALYSIS -
 POLARIZED LIGHT MICROSCOPY
 DEPOSIT DESIGNATION: Cooling Tower Basin Deposit

% ESTIMATED	CONSTITUENTS
>30	Amorphous silica, including assorted diatoms, probably including amorphous magnesium silicate; calcium carbonate (calcite)
1-2	Assorted clay material including feldspar; hydrated iron oxide; carbonaceous material

-continued

Exhibit 1
 MICROSCOPICAL ANALYSIS -
 POLARIZED LIGHT MICROSCOPY
 DEPOSIT DESIGNATION: Cooling Tower Basin Deposit

% ESTIMATED	CONSTITUENTS
<1	Silicon dioxide (quartz); assorted plant fibers; unidentified material including possibly aluminum oxide (corundum)

Exhibit 2
 CHEMICAL ANALYSIS - DRIED SAMPLE
 DEPOSIT DESIGNATION: Cooling Tower Basin Deposit

% ESTIMATED	CONSTITUENTS
12.1	CaO
8.5	MgO
5.2	Fe ₃ O ₄
3.7	Fe ₂ O ₃
<0.5	Al ₂ O ₃
13.2	Carbonate, CO ₂
51.1	SiO ₂
5.7	Loss on Ignition

Most probable combinations: Silica ~54%, Calcium Carbonate ~32%, Oxides of Iron ~9%, Mg and Al Oxides ~5%.

Examples of Corrosion Inhibition Methods of the Present Invention

The data in Table 4 illustrate the effectiveness of the methods of the present invention in inhibiting corrosion for carbon steel and copper metals evaluated by weight loss coupons in the system. No pitting was observed on coupon surfaces. Equipment inspections and exchanger tube surface testing have confirmed excellent corrosion protection. Comparable corrosion rates for carbon steel in this water quality with existing methods of the present inventions are optimally in the range of 2 to 5 mpy.

TABLE 4

CORROSION TEST DATA		
Specimen Type	Carbon Steel	Copper
Test location	Tower Loop	Tower loop
Exposure period	62 Days	62 Days
Corrosion Rate (mpy)	0.3	<0.1

Examples of Scale Deposit Removal

The data in Table 5 illustrate hardness (CaCO₃) scale removal from metal surfaces in a tower system treated with the methods of the present invention through coupon weight loss reduction. Standard metal coupons that were scaled with CaCO₃ film were weighed before and after ten days of exposure and the visible removal of most of the scale thickness. The demonstrated CaCO₃ weight loss rate will provide gradual removal of hardness scale deposits that have occurred in a system prior to method treatment.

TABLE 5

SCALE DEPOSIT REMOVAL TEST DATA		
Specimen Type	Carbon Steel	Copper
Test location	Tower Loop	Tower loop
Exposure period	10 Days	10 Days
Scale Removal (mpy)	8.3	8.1

What is claimed is:

1. A method for inhibiting corrosion of a metallic substance in an aqueous cooling water system containing soluble SiO₂ of greater than 10 mg/L wherein said aqueous system derives water from make-up source water, comprising the steps:

- a) removing hardness ions from said source water;
- b) controlling the ionic strength of the aqueous system water such that said aqueous system water possesses a measurable conductivity of at least 1 μmhos;
- c) elevating and maintaining the pH of said aqueous system water such that said aqueous system water possesses a pH of approximately 9.0 or greater; and
- d) cyclically contacting said aqueous system water with said metallic substance, wherein said pH and ionic strength increases the amount of soluble silica in the multimeric form present in said aqueous system water and inhibits corrosion of said metallic substance.

2. The method of claim 1 wherein in step a), said hardness ions comprise ions of calcium and magnesium.

3. The method of claim 1 wherein said aqueous system water contains soluble SiO₂ residual that is between 10 mg/L to 200 mg/L.

4. The method of claim 2 wherein in step a), said hardness ions are removed in amounts equal to or less than approximately 20% of the SiO₂ present within said source water.

5. The method of claim 2 wherein in step a), said hardness ions are removed in amounts equal to or less than approximately 5% of the SiO₂ present within said source water.

6. The method of claim 1 wherein in step c), said pH is maintained at 9.6 or higher.

7. The method of claim 1 wherein in step a), said hardness ions are removed via a method selected from the group consisting of ion exchange, selective ion removal with reverse osmosis, reverse osmosis, electro chemical removal, chemical precipitation, evaporation and distillation.

8. The method of claim 1 wherein in step c), said pH is elevated by adding an alkaline agent.

9. The method of claim 8 wherein said alkali agent comprises sodium hydroxide.

10. The method of claim 1 wherein in step c), said pH is elevated by evaporating a portion of said aqueous system water.

11. The method of claim 1 wherein in step c), said pH is elevated by distilling a portion of said aqueous system water.

12. The method of claim 1 wherein said metallic substance is selected from the group consisting of carbon steel, copper, copper alloy and stainless steel alloy.

13. The method of claim 1 wherein prior to step a), said methods of the present invention comprises the step:

- a) analyzing said source water to determine the concentration of SiO₂ present therein.

14. The method of claim 1 wherein in step b), said ionic strength of said aqueous system water is controlled such that said aqueous system water possesses a conductivity of at least 500 μmhos.

15. The method of claim 1 wherein said aqueous system water contains soluble SiO₂ of at least 200 mg/L.

* * * * *