

**PROCESS FOR CORROSION CONTROL IN WATER SYSTEMS
WITH MINIMIZED ENVIRONMENTAL IMPACT**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Serial No. 63/578,519 filed August 24, 2023 and entitled "PROCESS FOR CORROSION CONTROL IN WATER SYSTEMS WITH MINIMIZED ENVIRONMENTAL IMPACT," which is hereby incorporated herein by reference in its entirety for all purposes.

**STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT**

[0002] Not applicable.

FIELD

[0003] The present disclosure relates generally to compositions and methods for scaling and/or corrosion control in industrial systems. More particularly, this disclosure relates to methods and composition for mitigating scaling and/or corrosion in systems utilizing industrial water.

BACKGROUND

[0004] Scaling and corrosion problems can occur in processes and equipment that utilize industrial water. Herein, "industrial water" refers to water used in an industrial operation such as fabricating, processing, washing, diluting, cooling, heating, or transporting a product; incorporating water into a product; or for sanitation needs. In industrial cooling systems, water such as from rivers, lakes, and ponds, is employed as the cooling media for heat exchangers.

[0005] Such natural waters often contain large amounts of suspended materials such as silt, clay, and organic waste. The cooling water from heat exchangers is typically passed through a cooling tower, spray pond, or evaporative system prior to discharge or reuse. In these systems, the cooling effect is achieved by evaporating a portion of the water passing through the system. Because of the evaporation which takes place during cooling, suspended materials in the water become concentrated. Fouling materials from the feedwater or as a result of evaporative concentration can settle in locations of low flow rates and cause corrosion and inefficient heat transfer. One of the most common scale deposits in cooling water systems is calcium carbonate. Calcium carbonate scale

normally results from the breakdown of calcium bicarbonate, a naturally occurring soluble salt. Calcium carbonate has a relatively low solubility and its solubility decreases with increasing temperature and pH.

[0006] Although phosphonate-containing materials are economical and effective at controlling scale formation, such phosphonate-containing materials contribute substantially to the waterborne phosphorous discharge of a facility.

[0007] Many water supplies contain low levels of orthophosphate or polyphosphate, either from the water source itself or from corrosion inhibitors added by the water supplier. This low level of orthophosphate or polyphosphate is referred to as the baseline level. As many older water supply networks still include lead pipes, the addition of up to 1 ppm of orthophosphate or polyphosphate is common practice for minimizing lead corrosion and lead ion contamination of potable water. Cooling towers concentrate all the species in the makeup water by factors of typically 2-10. This leads to a concentration of phosphate in the cooling tower water which contributes to the carbon steel corrosion inhibition. However, the amount of inhibition provided by this baseline phosphate is typically insufficient to meet industry standards. From an environmental perspective, it is not generally feasible or economical to reduce these low levels of phosphate through removal treatment of cooling tower makeup.

[0008] High levels of phosphorous-containing compounds in water can stimulate excess growth of algae, which leads to low dissolved oxygen levels, potential for harmful algal toxins, blockage of sunlight needed by organisms and plants in the water and degraded habitat conditions for benthic macroinvertebrates and other aquatic life. As such, an ongoing need exists for novel corrosion and/or scale inhibitors that overcome some of the aforementioned challenges.

DESCRIPTION OF THE DRAWINGS

[0009] For a detailed description of various exemplary embodiments, reference will now be made to the accompanying drawings in which:

[0010] Figure 1 is a bar graph depicting the corrosion of a steel coupon in the presence of an inhibitor of the type disclosed herein at either at 40°C or 60°C,

[0011] Figure 2 is a bar graph depicting the corrosion of steel coupons in the presence of reduced phosphate.

[0012] Figure 3 is a bar graph depicting the corrosion of steel coupons in the presence of an inhibitor of the type disclosed herein and orthophosphate.

[0013] Figure 4 is a bar graph depicting the corrosion of steel coupons in the presence of an inhibitor under ultralow phosphate conditions.

SUMMARY

[0014] Disclosed herein is a method of treating an industrial water utilizing system, the method comprising introducing to the system a composition comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) at least one compound selected from the group consisting of corrosion inhibitors, one or more low molecular weight anionic polymers or combinations thereof.

[0015] Also disclosed herein is a composition comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) a corrosion inhibitor.

DETAILED DESCRIPTION

[0016] The following discussion is directed to various exemplary aspects. However, one of ordinary skill in the art will understand that the examples disclosed herein have broad application, and that the discussion of any aspect is meant only to be exemplary of that aspect, and not intended to suggest that the scope of the disclosure, including the claims, is limited to that aspect.

[0017] The figures are not necessarily to scale. Certain features and components herein may be shown exaggerated in scale or in somewhat schematic form and some details of conventional elements may not be shown in interest of clarity and conciseness.

[0018] As used herein, the terms “approximately,” “about,” “substantially,” and the like mean within 10% (i.e., plus or minus 10%) of the recited value. Thus, for example, a recited angle of “about 80 degrees” refers to an angle ranging from 72 degrees to 88 degrees.

[0019] Unless the context dictates the contrary, all ranges set forth herein should be interpreted as being inclusive of their endpoints, and open-ended ranges should be interpreted to include only commercially practical values. Similarly, all lists of values should be considered as inclusive of intermediate values unless the context indicates the contrary.

[0020] Disclosed herein are methods and compositions for maintaining the integrity of surfaces in systems such as cooling tower systems. In one or more aspects, the compositions are used to mitigate scaling, corrosion, or both. Scaling herein refers to a deposit formed on surfaces (e.g., the inside of piping and heat transfer surfaces) when the water is heated and impurities precipitate or settle out. These deposits can build up

and interfere with heat transfer or, in extreme cases, cause system failure. Corrosion refers to the breakdown of metal elements of a material and can happen for a variety of reasons. Hereinafter, a composition that mitigates scaling and corrosion of one or more surfaces is designated a scaling and corrosion inhibitor ("SCX").

[0021] In one or more aspects, a method of the present disclosure comprises introducing to a system utilizing industrial water an SCX comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) at least one compound selected from the group consisting of corrosion inhibitors, one or polymers or combinations thereof.

[0022] In one or more aspects, the SCX comprises an amount of phosphorous-containing compounds that is equal or less than about 10 weight percent (wt.%) based on the total weight of the SCX, or less than about 9 wt.%, or less than about 8 wt.%, or less than about 7 wt.%, or less than about 6 wt.%, or less than about 5 wt.%, or less than about 4 wt.% or less than about 3 wt.%, or less than about 2 wt.%, or less than about 1 wt.% or from about 0.01 wt.% to about 10 wt.%, or from about 0.1 wt.% to about 5 wt.% or from about 0.5 wt.% to about 2 wt.%. In some aspects, the SCX is substantially free of phosphorous-containing compounds. Nonlimiting examples of phosphorous-containing corrosion inhibitor include orthophosphate, phosphoric acid, zinc orthophosphate, polyphosphates, tetrapotassium pyrophosphate (TKPP), sodium hexametaphosphate (SHMP), glassy phosphates, bimetallic phosphates, $\text{Na}_2\text{PO}_3\text{F}$, Na_2HPO_4 , $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ and combinations thereof.

[0023] In one or more aspects, the SCX comprises a makeup water. Herein "makeup water" refers to water that is introduced to the system from a source. For example, cooling tower make-up water is needed to replace water lost in a cooling cycle after its evaporation and the blowdown required to control solids buildup. Surface water from rivers or lakes is generally used as a source for cooling tower make-up water. The chemical composition of makeup water in a cooling tower typically includes dissolved minerals like calcium, magnesium, sodium, iron, silica, chloride, sulfate, and bicarbonate, with calcium and magnesium being the primary contributors to hardness, often measured as calcium carbonate equivalent (CaCO_3) due to their potential to form scale deposits within the cooling system. It is contemplated that the makeup water may be obtained from any suitable source consistent with user and/or process goals. In some aspects, the makeup water comprises from about 0.1 ppm to 10 ppm of a phosphorous-containing compound (e.g., orthophosphate), or from about 0.1 ppm to about 9.5 ppm, or from about 0.1 ppm to about 9 ppm, or from about 0.1 ppm to about 8 ppm, or from

about 0.5 ppm to about 7 ppm or from about 0.5 ppm to about 6 ppm, or from about 1 ppm to about 5 ppm or from about 0.1 ppm to about 1.5 ppm.

[0024] In an aspect, a SCX comprises one or more sugar oxidation products (SOPs). In an aspect, the one or more sugar oxidation products comprise aldonic acid, uronic acid, aldonic acid, or combinations thereof and a counter cation.

[0025] Additionally, or alternatively, in an aspect, the one or more sugar oxidation products comprise a glucose oxidation product, a gluconic acid oxidation product, a gluconate, or combinations thereof. The glucose oxidation product, gluconic acid oxidation product, or combinations thereof may be buffered to a suitable pH.

[0026] Additionally or alternatively, the one or more sugar oxidation products comprise glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products or combinations thereof. Additionally or alternatively, in one or more aspects, the one or more sugar oxidation product comprises disaccharides, oxidized disaccharides, uronic acid, aldonic acid or combinations thereof.

[0027] Additionally or alternatively, the one or more sugar oxidation products comprise gluconic acid, glucaric acid, glucuronic acid, n-keto-acids, C2 to C6 diacids, or combinations thereof.

[0028] Additionally or alternatively, the one or more sugar oxidation products comprise galactonic acid, galactaric acid, an oxidation product comprising predominantly (e.g., greater than about 50 weight percent) galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C2 to C6 diacids, or combinations thereof. Additionally or alternatively, in one or more aspects, the one or more sugar oxidation products comprise glutamic acid. Additionally or alternatively, the one or more sugar oxidation products comprise glucodialdose, 2-ketoglucose, or combinations thereof.

[0029] In such aspects, the buffered glucose oxidation product, the buffered gluconic acid oxidation product, or combinations thereof are buffered to a suitable pH. For example, the glucose oxidation product, gluconic acid oxidation product, or combinations thereof may be buffered to a pH in the range of from about 1 to about 5. Buffering of the one or more sugar oxidation product may be carried using any suitable acid, base, or combinations thereof.

[0030] In one or more aspects, the one or more sugar oxidation products comprise aldonic acid, uronic acid, aldonic acid, a gluconic acid oxidation product, a gluconate, glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, galactonic acid, galactaric acid, glutamic acid, a lactone of gluconic acid, a lactone of glucaric acid, a

lactone of galactaric acid, a lactone of galactonic acid, glucodialdose, 2-ketoglucose, disaccharides, oxidized disaccharides, n-keto-acids, C2 to C6 diacids, salts thereof, or combinations thereof.

[0031] In an aspect, the one or more sugar oxidation products comprise a glucose oxidation product, a gluconic acid oxidation product, a gluconate, glucaric acid, an oxidized glucuronolactone, a uronic acid oxidation product, or combinations thereof. Additionally or alternatively, the one or more sugar oxidation product comprises a buffered glucose oxidation product, a buffered gluconic acid oxidation product or combinations thereof. In some such aspects, the buffered glucose oxidation product, the buffered gluconic acid oxidation product, or combinations thereof are buffered to a pH within a range disclosed herein with any suitable acid or base such as sodium hydroxide. In an example of such aspects, the one or more sugar oxidation product comprises a mixture of gluconic acid and glucaric acid and further comprises a minor component species comprising n-keto-acids, C2-C6 diacids or combinations thereof.

[0032] In an aspect, the one or more sugar oxidation products comprise glucodiamine, glucodialdose, 2-ketoglucose, glucaric acid, lactones of glucaric acid, gluconic acid, lactones of gluconic acid, galactonic acid, lactones of galactonic acid, galactaric acid, lactones of galactaric acid, galactonic acid glucoheptonic acid, lactones of glucoheptonic acid, or combinations thereof.

[0033] In an aspect, the one or more sugar oxidation products suitable for use in the present disclosure comprise less than about 5 wt.% maltose, maltotriose, fructose, higher molecular weight polysaccharides, oxidation products thereof, or combinations thereof based on the total weight of the sugar-derived carboxylic acid.

[0034] In an aspect, the one or more sugar oxidation products comprise a metal chelation product commercially available from Solugen, Houston Texas as Biochelat[™] or Altiv[™].

[0035] In an aspect, the SCX comprises a mixture of gluconic acid and glucaric acid. In such aspects, the ratio of gluconic acid:glucaric acid may range from about 0.1:10 to about 10:0.1, alternatively about 0.15:10, or about 0.5:10, about 1:10, about 1:5, about 1:4, about 1:3, about 1:2, about 1:1, about 10:0.1, about 10:0.5, about 10:1, about 5:1, about 4:1, about 3:1, or about 2:1.

[0036] In one or more aspects, the SCX comprises one or more sugar oxidation products, which may be present in an amount of about 0.1 wt.%, or about 0.25 wt.%, or about 0.5 wt.%, or about 0.75 wt.%, or about 1 wt.%, or about 1.25 wt.%, or about 1.5

wt.%, or about 1.75 wt.%, or about 2 wt.%, or about 2.25 wt.%, or about 2.5 wt.%, or about 2.75 wt.%, or about 3 wt.%, or about 3.25 wt.%, or about 3.5 wt.%, or about 3.75 wt.%, or about 4 wt.%, or about 4.25 wt.%, or about 4.5 wt.%, or about 4.75 wt.%, or about 5 wt.%, or about 10 wt.%, or about 12.5 wt.%, or about 15 wt.%, or about 17.5 wt.%, or about 20 wt.%, or about 22.5 wt.%, or about 25 wt.%, or about 27.5 wt.%, or about 30 wt.%, or about 32.5 wt.%, or about 35 wt.%, or about 37.5 wt.%, or about 40 wt.%, or about 42.5 wt.%, or about 45 wt.%, or about 47.5 wt.%, or about 50 wt.%, or about 52.5 wt.%, or about 55 wt.%, or about 57.5 wt.%, or about 60 wt.%, or about 62.5 wt.%, or about 65 wt.%, or about 67.5 wt.%, or about 70 wt.%, or about 72.5 wt.%, or about 75 wt.%, or about 77.5 wt.%, or about 80 wt.%, or about 82.5 wt.%, or about 85 wt.%, or about 87.5 wt.%, or about 90 wt.%, or about 92.5 wt.%, or about 95 wt.%, or about 97.5 wt.%, or about 100 wt.%, or about 0.1 wt.% to about 100 wt.%, or about 1 wt.% to about 95 wt.%, or about 5 wt.% to about 90 wt.%, or about 10 wt.% to about 90 wt.%, or about 15 wt.% to about 85 wt.%, or about 20 wt.% to about 80 wt.%, or about 25 wt.% to about 75 wt.%, or about 40 wt.% to about 60 wt.%, or about 50 wt.%, or about 0.1 wt.% to about 10 wt.%, or about 1 wt.% to about 20 wt.%, or about 5 wt.% to about 50 wt.%, or about 1 wt.% to about 80 wt.%, or from about 5 wt.% to about 80 wt.%, or from about 1 wt.% to about 55 wt.% or alternatively from about 20 wt.% to about 75 wt.% based on the total weight of the SCX. In some aspects, the SCX comprises one or more sugar oxidation products, which may be present in an amount between any of the end points listed herein.

[0037] In one or more aspects, any oxidation product of one or more sugars, or combinations thereof as disclosed herein, may further comprise a counter-cation such as sodium, potassium or ammonium.

[0038] In one or more aspects, the SCX comprises a corrosion inhibitor. Nonlimiting examples of corrosion inhibitors include heterocyclic organic compounds, molybdates, metal salts, water soluble organic polymers, and combinations thereof.

[0039] In an aspect the corrosion inhibitor is a heterocyclic organic compound. Nonlimiting examples of heterocyclic organic compounds include thiazoles, triazoles, imidazoles and combinations thereof. Thiazoles and triazoles are five-atom aromatic ring molecules that contain a nitrogen atom and at least one other atom selected from the group consisting of nitrogen, oxygen, and sulfur as part of the ring. The azole-based compounds can be divided into three major classes, namely, N-, N&O-, and N&S-containing azole sets.

[0040] In an aspect, the corrosion inhibitor comprises imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pentazole, oxazole, isoxazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole, thiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, mercaptobenzothiazole, mercaptobenzimidazole, butyl benzotriazole 1,3,4-thiadiazole, benzotriazole, tolytriazole, (2-pyrrole carbonyl) benzotriazole, (2-thienyl carbonyl)-benzotriazole, amino-1,2,4-triazole, diamino-1,2,4-triazole, mercapto-1H-1,2,4-triazole, methyl-2-phenyl-imidazole, amino-3-hydrazino-5-mercapto-1,2,4-triazole, phenyl-1-H-tetrazole, derivatives thereof, or combinations thereof.

[0041] In one or more aspects, the corrosion inhibitor is a molybdate or a heteropolymolybdate. Nonlimiting examples of molybdates for use as a corrosion inhibitor include ammonium orthomolybdate, lithium molybdate, sodium molybdate, magnesium molybdate, potassium molybdate, calcium molybdate, and combinations thereof.

[0042] The corrosion inhibitor may be present, singularly or in combination in amounts ranging from about 1 ppm to about 100 ppm, or from about 2 ppm to about 90 ppm, or from about 5 ppm to about 75 ppm, or from about 10 ppm to about 50 ppm, or about 1 ppm, about 5 ppm, about 7.5 ppm, about 10 ppm, about 12.5 ppm, about 15 ppm, about 17.5 ppm, about 20 ppm, about 22.5 ppm, about 25 ppm, about 27.5 ppm, about 30 ppm, about 32.5 ppm, about 35 ppm, about 37.5 ppm, about 40 ppm, about 42.5 ppm, about 45 ppm, about 47.5 ppm, or about 50 ppm.

[0043] In one or more aspects, the SCX comprises one or more anionic low molecular weight polymers or anionic copolymers such as polyacrylic acid, polymaleic acid, polylactic acid, polyaspartic acid or combinations thereof. In such aspects, the polymers is present in the SCX in an amount of greater than about 5 milligrams/liter (mg/L), about 7.5 mg/L, about 10 mg/L, about 12.5 mg/L, about 15 mg/L, about 17.5 mg/L, about 20 mg/L, about 22.5 mg/L, about 25 mg/L, about 27.5 mg/L, about 30 mg/L, about 32.5 mg/L, about 35 mg/L, about 37.5 mg/L, about 40 mg/L, about 42.5 mg/L, about 45 mg/L, about 47.5 mg/L, about 50 mg/L, about 52.5 mg/L, about 55 mg/L, about 57.5 mg/L, about 60 mg/L, about 62.5 mg/L, about 65 mg/L, about 67.5 mg/L, about 70 mg/L, about 72.5 mg/L, about 75 mg/L, about 77.5 mg/L, about 80 mg/L, about 82.5 mg/L, about 85 mg/L, about 87.5 mg/L, about 90 mg/L, about 92.5 mg/L, about 95 mg/L, about 97.5 mg/L, about 100 mg/L, about 102.5 mg/L, about 105 mg/L, about 107.5 mg/L, about 110 mg/L, about 112.5 mg/L, about 115 mg/L, about 117.5 mg/L, about 120 mg/L, about 122.5 mg/L, about 125 mg/L, about 127.5 mg/L, about 130 mg/L, about 132.5 mg/L,

about 135 mg/L, about 137.5 mg/L, about 140 mg/L, about 142.5 mg/L, about 145 mg/L, about 147.5 mg/L, about 150 mg/L, about 152.5 mg/L, about 155 mg/L, about 157.5 mg/L, about 160 mg/L, about 162.5 mg/L, about 165 mg/L, about 167.5 mg/L, about 170 mg/L, about 172.5 mg/L, about 175 mg/L, about 177.5 mg/L, about 180 mg/L, about 182.5 mg/L, about 185 mg/L, about 187.5 mg/L, about 190 mg/L, about 192.5 mg/L, about 195 mg/L, about 197.5 mg/L, about 200 mg/L, about 202.5 mg/L, about 205 mg/L, about 207.5 mg/L, about 210 mg/L, about 212.5 mg/L, about 215 mg/L, about 217.5 mg/L, about 220 mg/L, about 222.5 mg/L, about 225 mg/L, about 227.5 mg/L, about 230 mg/L, about 232.5 mg/L, about 235 mg/L, about 237.5 mg/L, about 240 mg/L, about 242.5 mg/L, about 245 mg/L, about 247.5 mg/L, about 250 mg/L, about 252.5 mg/L, about 255 mg/L, about 257.5 mg/L, about 260 mg/L, about 262.5 mg/L, about 265 mg/L, about 267.5 mg/L, about 270 mg/L, about 272.5 mg/L, about 275 mg/L, about 277.5 mg/L, about 280 mg/L, about 282.5 mg/L, about 285 mg/L, about 287.5 mg/L, about 290 mg/L, about 292.5 mg/L, about 295 mg/L, about 297.5 mg/L, or about 300 mg/L.

[0044] In some aspects, the SCX further comprises a solvent. In general, any solvent compatible with the SCX and/or activity to be undertaken may be utilized. In an aspect, the solvent comprises water, an alcohol, or a polyol and may comprise the remainder of the SCX once all other components are accounted for.

[0045] In an aspect, an SCX may function to effectively inhibit corrosion and scale in a water-utilization system (e.g., cooling tower) using only phosphorous species originating in the makeup water.

[0046] A SCX may be introduced into an aqueous system in amounts effective to facilitate some user and/or process targeted activity. For example, to effectively inhibit corrosion, the formulation may have to be present above a certain concentration. The minimum inhibitor level required to prevent scale deposition and/or corrosion is commonly referred to as "minimum inhibitory concentration" (MIC) or "minimum effective concentration" (MEC). In one or more aspects, a system having a SCX introduced may be monitored to ensure the amount of the formulation retains some MIC or MEC for that system.

[0047] There has been a significant effort to develop effective non-phosphorous alternatives for the control of corrosion and scaling in water utilizing systems such as those described herein (e.g., cooling towers).

[0048] The processes and compositions disclosed herein (e.g., SCX) addresses these problems by utilizing inhibitive components in the source/makeup water to a system

(e.g., cooling tower). In one or more aspects, the SCX comprises (i) gluconic acid, glucaric acid or mixtures thereof and (ii) makeup water. In one or more aspects, the SCX comprises (i) gluconic acid, glucaric acid or mixtures thereof; (ii) makeup water; (iii) a heterocyclic organic compound; and (iv) a solvent. In one or more aspects, the SCX comprises (i) gluconic acid, glucaric acid or mixtures thereof; (ii) makeup water; (iii) a molybdate-containing compound; and (iv) a solvent.

[0049] The competitive advantage of the processes and compositions disclosed herein provide a treatment approach which makes maximal usage of the baseline level phosphate provided by makeup water without further addition of phosphorous species. The treatment method itself will be "phosphorous neutral" in that no additional phosphorous is added by the SCX.

ADDITIONAL DISCLOSURE

[0050] A first aspect which is a method of treating an industrial water utilizing system, the method comprising introducing to the system a composition comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) at least one compound selected from the group consisting of corrosion inhibitors, one or more low molecular weight anionic polymers or combinations thereof.

[0051] A second aspect which is a method of the first aspect wherein the makeup water comprises from about 0.1 ppm to 10 ppm of a phosphorous-containing compound/

[0052] A third aspect which is the method of any of the first through second aspects wherein the one or more sugar oxidation products comprise aldonic acid, uronic acid, aldaric acid, a gluconic acid oxidation product, a gluconate, glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, galactonic acid, galactaric acid, glutamic acid, a lactone of gluconic acid, a lactone of glucaric acid, a lactone of galactaric acid, a lactone of galactonic acid, glucodialdose, 2-ketoglucose, disaccharides, oxidized disaccharides, n-keto-acids, C2 to C6 diacids, salts thereof or combinations thereof.

[0053] A fourth aspect which is the method of any of the first through third aspects wherein the one or more sugar oxidation products comprise a mixture of gluconic acid and glucaric acid.

[0054] A fifth aspect which is the method of the fourth aspect wherein the ratio of gluconic acid:glucaric acid ranges from about 0.1:10 to about 10:0.1.

[0055] A sixth aspect which is the method of any of the first through fifth aspects wherein the one or more sugar oxidation products is present in an amount of from about 5 wt.% to about 90 wt.% based on the total weight of the composition.

[0056] A seventh aspect which is the composition of any of the first through sixth aspects wherein the corrosion inhibitors comprise heterocyclic organic compounds, organic polymers, polyvalent metal ions, molybdates or combinations thereof.

[0057] An eighth aspect which is the method of any of the first through seventh aspects wherein the corrosion inhibitors comprise imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pentazole, oxazole, isoxazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole, thiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, mercaptobenzothiazole, mercaptobenzimidazole, butyl benzotriazole, 1,3,4-thiadiazole, benzotriazole, tolyltriazole, (2-pyrrole carbonyl) benzotriazole, (2-thienyl carbonyl)-benzotriazole, amino-1,2,4-triazole, diamino-1,2,4-triazole, mercapto-1H-1,2,4-triazole, methyl-2-phenyl-imidazole, amino-3-hydrazino-5-mercapto-1,2,4-triazole, phenyl-1-H-tetrazole, derivatives thereof or combinations thereof.

[0058] A ninth aspect which is the method of any of the first through eighth aspects wherein the corrosion inhibitor comprises ammonium orthomolybdate, lithium molybdate, sodium molybdate, magnesium molybdate, potassium molybdate, calcium molybdate or combinations thereof.

[0059] A tenth aspect which is the method of any of the first through ninth aspects wherein the corrosion inhibitor is present in an amount of from about 1 ppm to about 100 ppm.

[0060] An eleventh aspect which is the method of any of the first through tenth aspects wherein the polymer comprises one or more anionic low molecular weight polymers, one or more anionic copolymers or combinations thereof.

[0061] A twelfth aspect which is the method of the eleventh aspect wherein the polymer comprises polyacrylic acid, polymaleic acid, polylactic acid, polyaspartic acid or combinations thereof.

[0062] A thirteenth aspect which is the method of any of the first through twelfth aspects wherein the polymer is present in an amount of from about 5 mg/L to about 300 mg/L.

[0063] A fourteenth aspect which is the method of any of the first through thirteenth aspects wherein the composition comprises less than about 10 wt.% of a phosphorous-containing compound based on the total weight of the composition.

[0064] A fifteenth aspect which is a composition comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) a corrosion inhibitor.

[0065] A sixteenth aspect which is the composition of the fifteenth aspect wherein the one or more sugar oxidation products comprise a mixture of gluconic acid and glucaric acid.

[0066] A seventeenth aspect which is the composition of any of the fifteenth through sixteenth aspects wherein the ratio of gluconic acid:glucaric acid ranges from about 0.1:10 to about 10:0.1.

[0067] An eighteenth aspect which is the composition of any of the fifteenth through seventeenth aspects wherein the one or more sugar oxidation products is present in an amount of from about 5 wt.% to about 90 wt.% based on the total weight of the composition.

[0068] A nineteenth aspect which is the composition of any of the fifteenth through eighteenth aspects wherein the corrosion inhibitors comprises heterocyclic organic compounds, molybdates and combinations thereof.

[0069] A twentieth aspect which is the composition of any of the fifteenth through nineteenth aspects wherein the corrosion inhibitors comprise imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pentazole, oxazole, isoxazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole, thiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, mercaptobenzothiazole, mercaptobenzimidazole, butyl benzotriazole 1,3,4-thiadiazole, benzotriazole, tolyltriazole, (2-pyrrole carbonyl) benzotriazole, (2-thienyl carbonyl)-benzotriazole, amino-1,2,4-triazole, diamino-1,2,4-triazole, mercapto-1H-1,2,4-triazole, methyl-2-phenyl-imidazole, amino-3-hydrazino-5mercapto-1,2,4-triazole, phenyl-1-H-tetrazole, derivatives thereof or combinations thereof.

EXAMPLES

[0070] The presently disclosed subject matter having been generally described, the following examples are given as particular aspects of the subject matter and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

EXAMPLE 1

[0071] The ability of an SCX to function as a corrosion inhibitor was investigated by conducting a series of benchtop corrosion tests. A 1-liter sample of water having the mineral and additive composition was prepared from deionized water and laboratory-grade mineral salts. The sample composition is presented in Table 1. The water was

heated to either 40 °C or 60 °C using a thermostatically controlled hotplate and aerated. A linear polarization probe with carbon steel tip specimens was inserted into the solution, and the corrosion of the specimens over time was measured using a Cosasco linear polarization instrument. The corrosion rate was monitored over time and reached a steady state value after 48 hours. A number of additive actives at various dosages (expresses as mg/liter active were added to the test water, Table 2. The final steady state corrosion rates are expressed in mils/year of metal loss, Table 3.

TABLE 1

SPECIES	CONCENTRATION (ppm CaCO ₃)
Ca ²⁺	500
Mg ²⁺	250
M alkalinity	50-400
Cl ⁻	500
SO ₄ ²⁻	250

TABLE 2

Additive	Description
o-PO ₄	Orthophosphate, from sodium phosphate salts
p-PO ₄	Pyrophosphate from tetrapotassium pyrophosphate
HEDP	Hydroxyethylidine diphosphonic acid
K798	Calcium phosphate inhibitor, LUBRIZOL K798
TT	Tolyltriazole, copper corrosion inhibitor
HCA	Gluconate, glucarate mixture
p-Asp	Polyaspartic acid, GLOBAL GREEN TECHNOLOGIES
PAA	Polyacrylic acid, DOW ACUMER 1000

PMA	Polymaleic acid, BELCLEN 200
Zn	Zn ⁺² from zinc chloride
Sn	Sn ⁺² from stannous chloride

TABLE 3

No.	Malk	pH	Temp	o-PO4	P-PO4	HEDP	K798	TT	HCA	p-Asp	PAA	PM A	Zn	Sn	MS Corrosion Rate MPY
1	50	7.5	40	12	6	2	10	3	0	0	0	0	0	0	2.5
2	50	7.5	40	6	3	1	5	1.5	20	0	0	0	0	0	2.5
3	50	7.5	60	12	6	2	10	3	0	0	0	0	0	0	9
4	50	7.5	60	12	6	2	10	3	0	0	0	0	0	0	4
6	50	7.5	40	6	0	0	10	0	10	0	0	0	0	0	2.07
8	50	7.5	40	6	0	0	10	10	10	0	0	0	0	0	1.65
9	50	7.5	40	6	0	0	10	0	10	10	0	0	0	0	2.4
10	50	7.5	40	6	0	0	10	0	10	10	0	0	3	0	0.62
11	50	7.5	40	6	0	0	10	0	10	10	0	0	0	3	0.61
12	200	8.5	40	6	0	0	10	0	0	0	10	0	0	0	10.91
13	200	8.5	40	6	0	0	10	0	10	0	10	0	0	0	2.6
15	200	8.5	40	6	0	0	10	10	10	0	10	0	0	0	15.5
16	50	7.5	60	6	0	0	10	0	0	0	0	0	0	0	52
17	50	7.5	40	3	0	0	10	10	10	0	0	0	0	0	5.7
18	50	7.5	40	6	0	0	10		10	25	0	0	0	0	2.3
19	200	8.5	40	3	0	0	10	0	0	0	0	0	0	0	28
20	200	8.5	40	3	0	0	10	0	10	10	0	0	0	0	2.73
21	200	8.5	40	3	0	0	10	3	30	10	0	0	0	0	3.02
22	200	8.5	40	3	0	0	5	3	30	10	0	0	0	0	2.88
23	300	8.7	40	3	0	0	5	3	30	10	10	10	0	0	1.82
24	400	8.8	40	0	0	0	0	3	10	10	10	10	0	0	1.48
25	400	8.8	40	0	0	0	0	3	10	10	10	10	0	3	4.33
26	400	8.8	40	0	0	0	7.5	3	10	10	10	10	3	0	2.91
28	200	8.5	40	3	0	0	10	3	0	0	10	10	0	3	6.45
29	200	8.5	40	3	0	0	10	3	0	0	10	10	3	0	2.97
30	300	8.7	40	0	0	0	0	3	10	10	10	10	0	0	3.88

31	400	8. 8	40	0	0	0	0	3	10	10	10	10	0	0	1.96
32	300	8. 7	40	3	0	0	5	3	30	0	10	10	0	0	2.01
33	400	8. 8	40	0	0	0	0	3	10	0	10	10	0	0	2.36

EXAMPLE 2

[0072] The effectiveness of a SCX in inhibiting scale and/or corrosion in a water cooling tower configuration was investigated. In a typical configuration the inhibitor will deliver 12 ppm of orthophosphate, 4 ppm of HEDP, 4 ppm of pyrophosphate at a pH of 7 to 8. Sample 1 contained HCA and 6 ppm PO_4^{3-} at 60 °C, sample 2 contained 12 ppm PO_4^{3-} at 60 °C, sample 3 contained 20 ppm HCA and 6 ppm PO_4^{3-} and sample 4 contained 12 ppm PO_4^{3-} . Figure 1 is a bar graph of the amount of steel corrosion in mils per year (MPY) for the indicated samples. Inclusion of an HCA additive reduced the amount of phosphate that delivers effective corrosion inhibition. The chart also shows that the reduced phosphate product delivers better performance at higher (60 °C vs 40 °C) water temperature. The phosphorous provided by the makeup water is usually insufficient to produce the high levels of phosphate found in a standard phosphate-based inhibitor program consequently an SCX is able to provide scaling and/or corrosion inhibition without the addition of a phosphorus-containing compound.

EXAMPLE 3

[0073] Phosphate-based corrosion inhibitors for cooling towers typically contain cathodic corrosion inhibitors in addition to the anodic orthophosphate ingredient. The chelating agent hydroxyethylidene diphosphonic acid (HEDP) and pyrophosphate are frequently used in this role. These components contain phosphorous and contribute to the total phosphorous discharge loading. The ability of a SCX to effectively inhibit corrosion in the absence of additional phosphorous-containing compounds was investigated. Sample 5 contained 20 ppm HCA and Sample 6 contained 12 ppm PO_4^{3-} . The results are present in Figure 2 which illustrates the utility of an SCX (specifically labelled HCA in the Figure) in eliminating the need for these inhibitors.

EXAMPLE 4

Effectiveness of SCX in reducing corrosion with 3 ppm of orthophosphate.

[0074] This effectiveness of an SCX in reducing mild steel corrosion in an environment of cycled makeup phosphate was investigated, Orthophosphate content of 0.5 ppm is commonly seen, particularly in treated municipal water. When that makeup water is cycled by a factor of 6 as is common in cooling towers, it results in an orthophosphate content in the cycled water of 3 ppm. Sample 7 had an SCX containing 3 ppm HCA, and 200 ppm polyaspartic acid and Sample 8 contained 3 ppm phosphate. The results are

presented in Figure 3 which illustrates the efficacy of the actives of a SCX in improving corrosion control without the addition of any additional orthophosphate.

EXAMPLE 5

[0075] This effectiveness of an SCX in reducing mild steel corrosion in an environment of lacking phosphate was investigated. Samples 9-12 lacked phosphate. Sample 9 contained HCA, Sample 10 contained HCA, Sample 11 contained HCA and Zn and Sample 12 contained HCA and Sn. Even in situations with very low makeup water orthophosphate, effective corrosion control can be achieved by increasing the alkalinity of the tower to 300-400 mg/l of total carbonate alkalinity in conjunction with an SCX and non-phosphorous calcium carbonate inhibitors. The results are presented in Figure 4.

[0076] Regarding claim transitional terms or phrases, the transitional term "comprising", which is synonymous with "including," "containing," "having," or "characterized by," is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. The transitional phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. The transitional phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. A "consisting essentially of" claim occupies a middle ground between closed claims that are written in a "consisting of" format and fully open claims that are drafted in a "comprising" format. Absent an indication to the contrary, when describing a compound or composition "consisting essentially of" is not to be construed as "comprising," but is intended to describe the recited component that includes materials which do not significantly alter the composition or method to which the term is applied. While compositions and methods are described in terms of "comprising" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components or steps.

[0077] While aspects of the presently disclosed subject matter have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the subject matter. The aspects described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the subject matter disclosed herein are possible and are within the scope of the disclosed subject matter. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g.,

from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0078] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an aspect of the present disclosure. Thus, the claims are a further description and are an addition to the aspects of the present invention. The discussion of a reference herein is not an admission that it is prior art to the presently disclosed subject matter, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A method of treating an industrial water utilizing system, the method comprising:

introducing to the system a composition comprising (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) at least one compound selected from the group consisting of corrosion inhibitors, one or more low molecular weight anionic polymers or combinations thereof.
2. The method of claim 1, wherein the makeup water comprises from about 0.1 ppm to 10 ppm of a phosphorous-containing compound.
3. The method of claim 1, wherein the one or more sugar oxidation products comprise aldonic acid, uronic acid, aldaric acid, a gluconic acid oxidation product, a gluconate, glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, galactonic acid, galactaric acid, glutamic acid, a lactone of gluconic acid, a lactone of glucaric acid, a lactone of galactaric acid, a lactone of galactonic acid, glucodialdose, 2-ketoglucose, disaccharides, oxidized disaccharides, n-keto-acids, C2 to C6 diacids, salts thereof or combinations thereof.
4. The method of claim 1, wherein the one or more sugar oxidation products comprise a mixture of gluconic acid and glucaric acid.
5. The method of claim 4, wherein the ratio of gluconic acid:glucaric acid ranges from about 0.1:10 to about 10:0.1.
6. The method of claim 1, wherein the one or more sugar oxidation products is present in an amount of from about 5 wt.% to about 90 wt.% based on the total weight of the composition.

7. The method of claim 1, wherein the corrosion inhibitors comprise heterocyclic organic compounds, organic polymers, polyvalent metal ions, molybdates or combinations thereof.
8. The method of claim 1, wherein the corrosion inhibitors comprise imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pentazole, oxazole, isoxazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole, thiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, mercaptobenzothiazole, mercaptobenzimidazole, butyl benzotriazole, 1,3,4-thiadiazole, benzotriazole, tolytriazole, (2-pyrrole carbonyl) benzotriazole, (2-thienyl carbonyl)-benzotriazole, amino-1,2,4-triazole, diamino-1,2,4-triazole, mercapto-1H-1,2,4-triazole, methyl-2-phenyl-imidazole, amino-3-hydrazino-5-mercapto-1,2,4-triazole, phenyl-1-H-tetrazole, derivatives thereof or combinations thereof.
9. The method of claim 1, wherein the corrosion inhibitor comprises ammonium orthomolybdate, lithium molybdate, sodium molybdate, magnesium molybdate, potassium molybdate, calcium molybdate or combinations thereof.
10. The method of claim 1, wherein the corrosion inhibitor is present in an amount of from about 1 ppm to about 100 ppm.
11. The method of claim 1, wherein the polymer comprises one or more anionic low molecular weight polymers, one or more anionic copolymers or combinations thereof.
12. The method of claim 11, wherein the polymer comprises polyacrylic acid, polymaleic acid, polylactic acid, polyaspartic acid or combinations thereof.
13. The method of claim 1, wherein the polymer is present in an amount of from about 5 mg/L to about 300 mg/L.
14. The method of claim 1, wherein the composition comprises less than about 10 wt.% of a phosphorous-containing compound based on the total weight of the composition.

15. A composition, comprising: (i) a makeup water; (ii) one or more sugar oxidation products; and (iii) a corrosion inhibitor.

16. The composition of claim 15, wherein the one or more sugar oxidation products comprise a mixture of gluconic acid and glucaric acid.

17. The composition of claim 15, wherein the ratio of gluconic acid:glucaric acid ranges from about 0.1:10 to about 10:0.1.

18. The composition of claim 15, wherein the one or more sugar oxidation products is present in an amount of from about 5 wt.% to about 90 wt.% based on the total weight of the composition.

19. The composition of claim 15, wherein the corrosion inhibitor comprises heterocyclic organic compounds, molybdates and combinations thereof.

20. The composition of claim 15, wherein the corrosion inhibitors comprise imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pentazole, oxazole, isoxazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole, thiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, mercaptobenzothiazole, mercaptobenzimidazole, butyl benzotriazole 1,3,4-thiadiazole, benzotriazole, tolyltriazole, (2-pyrrole carbonyl) benzotriazole, (2-thienyl carbonyl)-benzotriazole, amino-1,2,4-triazole, diamino-1,2,4triazole, mercapto-1H-1,2,4-triazole, methyl-2-phenyl-imidazole, amino-3-hydrazino-5mercapto-1,2,4-triazole, phenyl-1-H-tetrazole, derivatives thereof or combinations thereof.