filtration (microfiltration, ultrafiltration, etc.), membrane distillation; ion exchange; and electrochemical methods to precipitate scale. Non-limiting examples of chemical treatment include chelation using at least one chelant such as ethylenediamine tetraacetic acid ("EDTA") or a salt thereof, or precipitation using one or more caustic and/or phosphate compound.

[0005] Various analytical methods can be employed to measure hardness in water entering, re-entering, or being used in an industrial process (hereinafter "industrial water"). Hardness concentrations can be measured by inductively coupled plasma ("ICP"), ion selective electrode ("ISE"), light absorbance, titration, atomic absorption ("AA"), or other methods known in the art. While all can produce accurate hardness concentration measurements, each has limitations.

SUMMARY

[0006] In a first aspect, the present disclosure is directed toward an automated method ~~for~~ of monitoring soluble magnesium concentration in ~~industrial~~ water where that ~~industrial~~ water contains soluble magnesium. The automated method comprises combining an aliquot of the water and a quantity of (1) a pH-buffered liquid and (2) a magnesium coordinating fluorescing reagent to produce a buffered water sample. The (2) magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the buffered water sample and produces a coordinated magnesium compound. The soluble magnesium concentration in the aliquot of water (and, hence, in the industrial water) can be quantified by using fluorescence measurement to measure the fluorescence produced by the coordinated magnesium compound in the buffered water sample. In this process, the (1) pH-buffered liquid comprises a water soluble, non-coordinating base capable of buffering the (1) pH-buffered liquid to a pH from 8 to 12; ~~and~~ the (2) magnesium coordinating fluorescing reagent is selected from the group consisting of a water soluble, aromatic, ortho hydroxyl substituted azo dye; a water soluble, fused-ring heterocycle; and combinations thereof; and wherein the water soluble, non-coordinating base is 1,2 diazabicyclo [2.2.2] octane.

[0007] In a second aspect, the present disclosure is directed toward an automated method ~~for~~ of monitoring and optionally controlling total hardness concentration in ~~industrial~~ water where that ~~industrial~~ water contains

soluble calcium and soluble magnesium. The automated method comprises combining an aliquot of water with (4) a magnesium-containing reagent. The (4) magnesium-containing reagent displaces the soluble calcium within the aliquot of water with soluble magnesium, thereby creating a modified water sample having an increased soluble magnesium content. The modified water sample is combined with a quantity of (1) pH-buffered liquid and (2) a magnesium coordinating fluorescing reagent to produce a buffered water sample containing soluble magnesium. The (2) magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the buffered water sample to produce a coordinated magnesium compound. The increased soluble magnesium content in the buffered water sample is quantified via fluorescence measurement of the coordinated magnesium compound, which allows for the determination of the total hardness concentration of the aliquot, and hence the industrial water. In this process, the (1) pH-buffered liquid comprises a water soluble, non-coordinating base capable of buffering the (1) pH-buffered liquid and the buffered water sample to a pH from 8 to 12; and the (2) magnesium coordinating fluorescing reagent is selected from the group consisting of a water soluble, aromatic, ortho hydroxyl substituted azo dye; a water soluble, fused-ring heterocycle; and combinations thereof.

[0008] In a third aspect, the present disclosure is directed toward an automated method ~~for~~ of monitoring and optionally controlling total hardness concentration of ~~industrial~~ water containing soluble calcium and soluble magnesium. The automated method comprises two sets of steps, Group A and Group B, and the sets of steps can be repeated as necessary.

[0009] As related to Group A, a first aliquot of water and quantities of (1a) a first pH-buffered liquid, (2a) a first magnesium coordinating fluorescing reagent, and (3a) a first inert fluorescing agent are combined to produce a buffered water sample. The (2a) first magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the first aliquot of water creating a coordinated magnesium compound within the buffered water sample. The concentration of any uncoordinated (2a) first magnesium coordinating fluorescing reagent in the buffered water sample is determined by light absorbance. The concentration of the (3a) first inert fluorescing agent in the buffered water sample is determined by fluorescence.

CLAIMS

1. An automated method ~~for~~ of monitoring soluble magnesium concentration in ~~industrial~~ water containing soluble magnesium, the method comprising:

combining an aliquot of water and a quantity of (1) a pH-buffered liquid and (2) a magnesium coordinating fluorescing reagent to produce a buffered water sample;

whereby the (2) magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the buffered water sample to produce a coordinated magnesium compound; and

quantifying the soluble magnesium concentration in the aliquot of water via fluorescence measurement of the coordinated magnesium compound in the buffered water sample;

wherein the (1) pH-buffered liquid comprises a water soluble, non-coordinating base capable of buffering the (1) pH-buffered liquid to a pH from 8 to 12;

~~and~~ wherein the (2) magnesium coordinating fluorescing reagent is selected from the group consisting of a water soluble, aromatic, ortho hydroxyl substituted azo dye; a water soluble, fused-ring heterocycle; and combinations thereof; and

wherein the water soluble, non-coordinating base is 1,2 diazabicyclo [2.2.2] octane.

2. The automated method of claim 1, wherein the (2) magnesium coordinating fluorescing reagent is present in the (1) pH-buffered liquid when combined with the aliquot of water.

3. The automated method of claim 2, wherein the (2) magnesium coordinating fluorescing reagent is a dry powder combined with the (1) pH-buffered liquid on site.

4. The automated method of claim 1, wherein the water has a total hardness concentration greater than zero and not more than 2000 ppb as calcium carbonate.

5. The automated method of claim 1, wherein the (1) pH-buffered liquid is buffered to a pH from 9 to 11.

6. The automated method of claim 1, wherein the (2) magnesium coordinating fluorescing reagent is a water soluble, aromatic, ortho hydroxyl substituted azo dye

selected from the group consisting of Plasmocorinth B, Eriochrome Black T, Calmagite, 8-hydroxyquinolone-5-sulfonic acid, and combinations thereof.

7. The automated method of claim 1, wherein the (2) magnesium coordinating fluorescing reagent is 8-hydroxyquinolone-5-sulfonic acid.

8. The automated method of claim 2, wherein the (2) magnesium coordinating fluorescing reagent is present in the (1) pH-buffered liquid at a concentration from 1 to 50 ppm.

~~9. The method of claim 1, wherein the water soluble non-coordinating base is 1,2 diazabicyclo [2.2.2] octane.~~

~~10~~9. The automated method of claim 1, wherein (3) an inert fluorescing agent is additionally combined with the aliquot of water at a known (3) inert fluorescing agent-to-(1) pH-buffered liquid ratio, and concentration of the (1) pH-buffered liquid in the aliquot of water is confirmed by fluorescence measurement of the (3) inert fluorescing agent.

~~11~~10. The automated method of claim 1, wherein the water is boiler feed water.

~~12~~11. An automated method ~~for~~ of monitoring and optionally controlling total hardness concentration in ~~industrial~~ water containing soluble calcium and soluble magnesium, the method comprising:

combining an aliquot of water with (4) a magnesium-containing reagent whereby the soluble calcium within the aliquot of water is displaced by soluble magnesium, thereby creating a modified water sample having an increased soluble magnesium content;

combining the modified water sample with a quantity of (1) a pH-buffered liquid and (2) a magnesium coordinating fluorescing reagent to produce a buffered water sample containing soluble magnesium;

whereby the (2) magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the buffered water sample to produce a coordinated magnesium compound;

quantifying the increased soluble magnesium content in the buffered water sample via fluorescence measurement of the coordinated magnesium compound thereby determining the total hardness concentration of the water;

wherein the (1) pH-buffered liquid comprises a water soluble, non-coordinating base capable of buffering the (1) pH-buffered liquid and the buffered water sample to a pH from 8 to 12;

and wherein the (2) magnesium coordinating fluorescing reagent is selected from the group consisting of a water soluble, aromatic, ortho hydroxyl substituted azo dye; a water soluble, fused-ring heterocycle; and combinations thereof.

~~13~~12. The automated method of claim ~~12~~11, wherein the (2) magnesium coordinating fluorescing reagent is present in the (1) pH-buffered liquid when the pH buffered liquid is combined with the aliquot of water.

~~14~~13. The automated method of claim ~~13~~12, wherein the (2) magnesium coordinating fluorescing reagent is a dry powder combined with the (1) pH-buffered liquid on site.

~~15~~14. The automated method of claim ~~12~~11, wherein the soluble magnesium concentration in the industrial water is known, but the soluble calcium concentration in the water is unknown, and the soluble calcium concentration is determined by subtracting the known magnesium concentration from~~comparing~~ the total hardness concentration ~~to the known magnesium concentration~~.

~~16~~15. The automated method of claim ~~12~~11, wherein the water has a total hardness concentration greater than zero and not more than 2000 ppb as calcium carbonate.

~~17~~16. The automated method of claim ~~12~~11, wherein the (1) pH-buffered liquid is buffered to a pH from 9 to 11.

~~18~~17. The automated method of claim ~~12~~11, wherein the (2) magnesium coordinating fluorescing reagent is a water soluble, aromatic, ortho hydroxyl substituted azo dye selected from the group consisting of Plasmocorinth B, Eriochrome Black T, Calmagite, 8-hydroxyquinolone-5-sulfonic acid, and combinations thereof.

~~19~~18. The automated method of claim ~~12~~11, wherein the (2) magnesium coordinating fluorescing reagent is 8-hydroxyquinolone-5-sulfonic acid.

~~20~~19. The automated method of claim ~~12~~11, wherein the (2) magnesium coordinating fluorescing reagent is utilized in an amount sufficient to have a concentration from 1 to 50 ppm in the buffered water sample.

~~21~~20. The automated method of claim ~~12~~11, wherein the (1) pH-buffered liquid comprises water and a water soluble non-coordinating base.

~~22~~21. The automated method of claim ~~21~~20, wherein the water soluble non-coordinating base is 1,2 diazabicyclo [2.2.2] octane.

~~23~~22. The automated method of claim ~~12~~11, wherein the (4) magnesium-containing reagent comprises a magnesium-containing multidentate chelant.

~~24~~23. The automated method of claim ~~23~~22, wherein the magnesium-containing multidentate chelant comprises disodium magnesium 1,2-diaminecyclohexyl-N,N,N',N' tetraacetate.

~~25~~24. The automated method of claim ~~13~~12, wherein the displacement of soluble calcium by soluble magnesium occurs simultaneously with the combination of the aliquot of water and the magnesium-containing reagent, and the (4) magnesium-containing reagent is present in the (1) pH-buffered liquid prior to the pH-buffered liquid being combined with the aliquot of water.

~~26~~25. The automated method of claim ~~12~~11, wherein the water is boiler feed water.

~~27~~26. An automated method ~~for~~ of monitoring and optionally controlling total hardness concentration of ~~industrial~~ water containing soluble calcium and soluble magnesium, the method comprising:

A.

combining a first aliquot of water and quantities of (1a) a first pH-buffered liquid, (2a) a first magnesium coordinating fluorescing reagent, and (3a) a first inert fluorescing agent to produce a buffered water sample;

whereby the (2a) first magnesium coordinating fluorescing reagent coordinates with the soluble magnesium present in the first aliquot of water to create a coordinated magnesium compound within the buffered water sample;

measuring the soluble magnesium concentration in the modified water sample via fluorescence measurement of the coordinated magnesium compound, the measurement of which corresponds to measuring the total hardness concentration in the second aliquot of water and the total hardness concentration in the water;

optionally correcting the soluble magnesium concentration measured via fluorescence of the coordinated magnesium compound to account for one or more of the following: variation in mixing ratio, variation in background effects, and variation in temperature, thereby allowing for the calculation of an adjusted total hardness concentration in the water; and

optionally subtracting the soluble magnesium concentration of the first aliquot of water from the total hardness concentration of the second aliquot of water to arrive at the soluble calcium concentration in the water;

optionally taking action to control at least one process variable as a result of the measurements; and

optionally repeating A and B;

wherein the (1a) first and (1b) second pH buffered liquids are the same or different compositions having buffered pH from 8 to 12, the (2a) first and (2b) second magnesium coordinating fluorescing reagent are the same or different compositions, and the (3a) first and (3b) second inert fluorescing agent are the same or different compositions.

2827. The automated method of claim 2726, wherein the (4b) magnesium-containing reagent is present in the (1b) pH-buffered liquid at a concentration such that, when added to the second aliquot of water, the (4b) magnesium-containing reagent has a molar concentration from 10 to 10,000 times greater than the soluble calcium concentration.

2928. The automated method of claim 2726, wherein the quantities of the (2a) magnesium coordinating fluorescing reagent, and the (3a) inert fluorescing agent are present in the (1a) pH-buffered liquid prior to the combining.

3029. The automated method of claim 2726, wherein the quantities of the (2b) magnesium coordinating fluorescing reagent, the (3b) inert fluorescing agent, and