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(54) Title: METHOD OF OBTAINING OR MAINTAINING OPTICAL TRANSMITTANCE INTO DEAERATED LIQUID

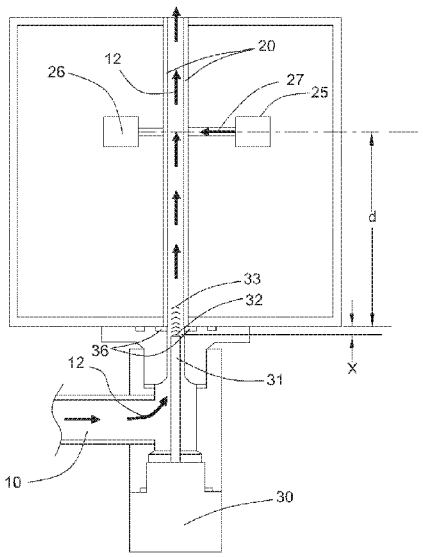

FIG. 2

(57) Abstract: Methods of obtaining or maintaining optical transference into deaerated liquid in contact with a light transference medium are disclosed. The methods comprise contacting a liquid chemical agent to a wetted surface of a light transference medium. The liquid chemical agent is selected from an acid, a chelant, a reducing agent, or combinations thereof, for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The methods may further comprise applying ultrasonic energy at a wavelength (λ) into deaerated liquid in contact with a light transference medium.

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METHOD OF OBTAINING OR MAINTAINING OPTICAL TRANSMITTANCE INTO DEAERATED LIQUID

[0001] This application is a PCT application claiming priority to U.S. Patent Application Serial Nos. 14/592,219 and 14/596,691, the disclosures of each of which are incorporated herein by reference in their entirety.

BACKGROUND

[0002] Measurement of parameters in liquids using optical sensors is commonplace. Reliable measurement of such parameters generally requires light to pass into the liquid, which generally requires light to first pass through a reasonably transparent medium, *e.g.*, a light transference medium. Reliability issues can arise in the event of obstruction of optical transference through the medium, which may be caused by particulate matter.

[0003] Generally, boiler liquids are deaerated liquids that have unique features. Some unique features of boiler liquids include having very low levels of dissolved oxygen (*e.g.*, less than about 10 ppb dissolved oxygen in conventional boiler feedwater) and having a pH of from about 9 to about 11. Particularly in boiler systems utilizing a form of treatment control based on light detection and/or measurement (*e.g.*, fluorometry), some amount of corrosion will occur over time and deposit in the form of particulate matter onto a light transference medium, thereby causing some amount of optical obstruction of the light transference medium. Regarding detection and measurement methods that utilize light transference, the unique conditions of deaerated liquids, particularly boiler liquid, present a challenge to the user when a light transference medium becomes optically obstructed. Ideally, optical obstruction can be altogether prevented, and if optical obstruction occurs, it can be removed without disrupting detection, measurement, and/or treatment control via the light transference.

SUMMARY

[0004] A method of obtaining, or of maintaining, optical transference into deaerated liquid in contact with a light transference medium is provided. The method comprises applying ultrasonic energy at a wavelength (λ) into deaerated liquid in contact with a light transference medium. The ultrasonic energy at wavelength (λ) originates at a distance (d) from an optical signal transmitted into the light transference medium such that optical

transference into the deaerated liquid via the light transference medium is obtained or maintained.

[0005] A clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system is provided. The clean-in-place method comprises contacting a stream of boiler water with a wetted surface of a light transference medium in optical communication with an optical sensor. Data related to a parameter of the boiler liquid measured by the optical sensor is input to a control scheme of a boiler system. The optical sensor is electronically isolated from the control scheme, which maintains control of the boiler system based on the input data related to the parameter of the boiler liquid. A liquid chemical agent contacts the wetted surface of the light transference medium for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The liquid chemical agent is selected from an acid, a chelant, a reducing agent, and combinations thereof. The liquid chemical agent is removed from the wetted surface of the light transference medium, and the optical sensor is electronically de-isolated from the control scheme.

[0006] Additionally, a clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system is provided. The clean-in-place method comprises flowing a stream of boiler liquid to contact a wetted surface of a light transference medium in optical communication with an optical sensor. Data related to a parameter of the boiler liquid measured by the optical sensor is input to a control scheme of a boiler system. The flow of the stream of boiler liquid to contact the wetted surface of the light transference medium is discontinued. The optical sensor is electronically isolated from the control scheme, which maintains control of the boiler system based on the input data related to the parameter of the boiler liquid. A liquid chemical agent contacts the wetted surface of the light transference medium for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The liquid chemical agent is selected from an acid, a chelant, a reducing agent, and combinations thereof. The liquid chemical agent is removed from the wetted surface of the light transference medium, the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium is resumed, and the optical sensor is electronically de-isolated from the control scheme.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0007] FIG. 1 illustrates an embodiment of a system capable of performing at least one inventive method described herein;

[0008] FIG. 2 illustrates a variation of the illustrative embodiment shown in FIG. 1;

[0009] FIG. 3 illustrates an embodiment of a system capable of performing at least one inventive method described herein;

[0010] FIG. 4 illustrates an embodiment of a system capable of performing at least one inventive method described herein;

[0011] FIG. 5A illustrates an embodiment of a system incorporating a sleeve as described herein;

[0012] FIG. 5B illustrates an embodiment of a system incorporating a lossy surface;

[0013] FIG. 6 is a plot of experimental data collected during the execution of Example 1;

[0014] FIG. 7 is a plot of experimental data collected during the execution of Example 2;

[0015] FIG. 8 is a plot of experimental data collected during the execution of Example 3;

[0016] FIG. 9 illustrates an embodiment of a system that may be used to carry out the methods disclosed herein;

[0017] FIG. 10 is a plot of results of Example 4 related to treatment using urea hydrochloride;

[0018] FIG. 11 is a plot of results of Example 5 related to treatment using oxalic acid; and

[0019] FIG. 12 is a plot of results of Example 6 related to treatment using sodium hydrosulfite.

DETAILED DESCRIPTION

[0020] While embodiments encompassing the general inventive concepts may take various forms, there is shown in the drawings and will hereinafter be described various illustrative and preferred embodiments with the understanding that the present disclosure is to be considered an exemplification and is not intended to be limited to the specific embodiments.

[0021] A method of maintaining optical transference into deaerated (*e.g.*, degassed) liquid in contact with a light transference medium. The method includes applying ultrasonic energy into the deaerated liquid so as to contact the light transference medium at a particular locus of points suitable for obtaining, or for maintaining, reliability in a system comprising an optical sensor. In certain embodiments, liquid is deaerated prior to being utilized in a heating application (*e.g.*, a boiler). Liquid is generally deaerated in an attempt to minimize corrosion of metals that come in contact with the steam and/or liquid. Illustrative deaerated liquids include, but are not limited to, deaerated boiler make-up feedwater and boiler liquid, which further includes boiler blowdown liquid and boiler condensate liquid. The phrase "deaeratedboiler make-up feedwater" is used to describe the boiler make-up feedwater that has undergone a deaeration process. The term is not used to describe the various boiler liquids, as it is understood by those skilled in the art that boiler liquids have already undergone a deaeration process prior to becoming boiler liquid.

[0022] As it pertains to this disclosure, unless otherwise indicated, "controller" refers to an electronic device having components such as a processor, memory device, digital storage medium, cathode ray tube, liquid crystal display, plasma display, touch screen, or other monitor, and/or other components. Controllers include, for example, an interactive interface that guides a user, provides prompts to the user, or provides information to the user regarding any portion of the method of the invention. Such information may include, for example, building of calibration models, data collection of one or more parameters, measurement location(s), management of resulting data sets, etc.

[0023] The controller is preferably operable for integration and/or communication with one or more application-specific integrated circuits, programs, computer-executable instructions or algorithms, one or more hard-wired devices, wireless devices, and/or one or more mechanical devices such as liquid handlers, hydraulic arms, servos, or other devices. Moreover, the controller is operable to integrate feedback, feed-forward, or predictive loop(s) resulting from, *inter alia*, the parameters measured by practicing the method(s) of the present disclosure. Some or all of the controller system functions may be at a central location, such as a network server, for communication over a local area network, wide area network, wireless network, extranet, the Internet, microwave link, infrared link, and the like, and any combinations of such links or other suitable links. In addition, other

components such as a signal conditioner or system monitor may be included to facilitate signal transmission and signal-processing algorithms.

[0024] By way of example, the controller is operable to implement the method of the invention in a semi-automated or fully-automated fashion. In another embodiment, the controller is operable to implement the method in a manual or semi-manual fashion.

[0025] Data transmission of any of the measured parameters or signals to a user, chemical pumps, alarms, or other system components is accomplished using any suitable device, such as a wired or wireless network, cable, digital subscriber line, internet, etc. Any suitable interface standard(s), such as an ethernet interface, wireless interface (*e.g.*, IEEE 802.lla/b/g/n, 802.16, Bluetooth, optical, infrared, other radiofrequency, any other suitable wireless data transmission method, and any combinations of the foregoing), universal serial bus, telephone network, the like, and combinations of such interfaces/connections may be used. As used herein, the term "network" encompasses all of these data transmission methods. Any of the components, devices, sensors, etc., herein described may be connected to one another and/or the controller using the above-described or other suitable interface or connection. In an embodiment, information (collectively referring to all of the inputs or outputs generated by the method of the invention) is received from the system and archived. In another embodiment, such information is processed according to a timetable or schedule. In a further embodiment, such information is processed in real-time. Such real-time reception may also include, for example, "streaming data" over a computer network.

[0026] As it pertains to this disclosure, unless otherwise indicated, "control scheme" refers to providing output based on input from a controller as defined herein.

[0027] A method of obtaining, or of maintaining, optical transference into deaerated liquid in contact with a light transference medium. The method comprises applying ultrasonic energy at a wavelength (λ) into deaerated liquid in contact with a light transference medium. In certain embodiments, the ultrasonic energy at wavelength (λ) originates at a distance (d) from an optical signal transmitted into the light transference medium so as to obtain or maintain optical transference into the deaerated liquid via the light transference medium. Preferably, the distance (d) is defined by Formula 1 below:

$$d = (a + 0.5*n) * \lambda \qquad \text{Formula 1}$$

wherein λ is the wavelength of the ultrasonic energy, a is a constant ranging from about -0.2 to about 0.2, and n is an integer ranging from 1 to 30. In certain embodiments, a is a constant ranging from about -0.15 to about 0.15, or from about -0.1 to about 0.1.

[0028] Ultrasonic energy follows the laws of acoustics. If the speed (v) of the ultrasonic energy is known, or approximately known, wavelength (λ) can be defined by frequency (f) according to Formula 2 below:

$$v = f * \lambda \qquad \text{Formula 2}$$

The speed (v) of the ultrasonic energy will be known or approximately known based on the medium of travel of the ultrasonic energy. For example, ultrasonic energy travels through deaerated water at a speed (v) of approximately 4800 ft/s at 68°F (approximately 1480 m/s at 20°C). Assuming a constant medium of travel, and therefore a constant speed (v), the frequency (f) and wavelength (λ) of the ultrasonic energy are proportionally related to one another.

[0029] The terms "optical" and "light" are used interchangeably herein. Utilization of the phrase "into deaerated liquid" is intended to cover light transmission in any direction between the deaerated liquid, the light transference medium, a light source, and/or a light detector. For example, the optical signal may originate from within the deaerated liquid and be transferred to a sensor via the light transference medium (*e.g.*, fluorometric emission), or from a light source through the light transference medium and into the deaerated liquid (*e.g.*, fluorometric excitation). Illustrative embodiments of optical sensors that perform optical measurements using optical signals include, but are not limited to, devices capable of detecting or sensing absorbance, colorimetric, refractometric, spectrophotometric, luminometric, and/or fluorometric signals, or images. In a preferred embodiment, the optical signal comprises a fluorometric excitation and/or emission.

[0030] The method is directed to obtaining or maintaining optical transference into deaerated liquid in contact with a light transference medium. The method can be utilized to remove obstructions that may be present on the light transference medium. Removal of obstruction from the light transference medium sufficient to allow for optical transference, thereby allowing for performance of an optical measurement of the deaerated liquid, is also achieved by the method of the present invention.

[0031] An advantage of the present invention is that the preferred method can be performed without interrupting the process responsible for supplying the deaerated liquid.

For example, a boiler and its related treatment processes can continue to operate during performance of the preferred method described herein.

[0032] Ultrasonic energy is applied into deaerated liquid in contact with a light transference medium. The ultrasonic energy is applied to effectuate removal of optical obstruction that may be present on the light transference medium, particularly at a location of the light transference medium where an optical signal passes through, or should pass through.

[0033] In preferred embodiments, the deaerated liquid in contact with the light transference medium is flowing across the light transference medium as defined herein. In other embodiments, the deaerated liquid in contact with the light transference medium is not flowing across the light transference medium, *i.e.*, is static.

[0034] In embodiments where the deaerated liquid flows across the light transference medium, the liquid may do so under conditions described as laminar, turbulent, and/or transitional flow, though the deaerated liquid may be static while in contact with the light transference medium. The deaerated liquid may have a Reynolds number of from about 0 to about 4000, including from about 400 to about 3000, and including about 800 to about 2300.

[0035] For embodiments where the deaerated liquid is flowing across the light transference medium, the ultrasonic energy may originate upstream or downstream from a location of a light transference medium where an optical signal passes through, or should pass through. In a preferred embodiment, the ultrasonic energy originates upstream from a location of a light transference medium where an optical signal passes through, or should pass through.

[0036] The ultrasonic energy may have a frequency of from about 20 kHz to about 200 kHz. The ultrasonic energy may have a frequency of from about 20 kHz, or from about 25 kHz, or from about 30 kHz, or from about 40 kHz, to about 200 kHz, or to about 150 kHz, or to about 100 kHz, or to about 80 kHz, or to about 70 kHz, or to about 60 kHz. In some embodiments, the ultrasonic energy has a frequency of from about 20 kHz to about 80 kHz. In further embodiments, the ultrasonic energy has a frequency of from about 30 kHz to about 60 kHz, which includes about 40 kHz. In even further embodiments, the ultrasonic energy has a frequency of from about 25 kHz to about 30 kHz, which includes about 28 kHz.

[0037] In certain embodiments, the ultrasonic energy is applied at a rate of from about 1 $W/cm^2/sec$ to about 400 $W/cm^2/sec$. The ultrasonic energy may be applied at a rate of from about 1 $W/cm^2/sec$, or from about 10 $W/cm^2/sec$, or from about 50 $W/cm^2/sec$, or from about 100 $W/cm^2/sec$, to about 400 $W/cm^2/sec$, or to about 300 $W/cm^2/sec$, or to about 200 $W/cm^2/sec$.

[0038] The wavelength of the ultrasonic energy is dependent upon the frequency and the velocity of the ultrasonic energy, which is essentially constant. The frequency, and therefore the wavelength, is chosen so as to provide enough energy to prevent or remove particulate matter that may become deposited onto a light transference medium in contact with deaerated liquid. Ideally, the frequency of the ultrasonic energy will be sufficient to remove such particulate matter, or prevent the particulate matter from depositing onto the light transference medium, while not damaging the light transference medium. However, a user may attempt to minimize or prevent damage to the light transference medium by utilizing one or more of several modifications discussed herein.

[0039] As described herein, the ultrasonic energy originates at a distance (d) from an optical signal transmitted into the light transference medium, which is preferably set to optimize the energy applied into the deaerated liquid at a point relative to the light transference medium, to effectively obtain or maintain light transference. Preferably, the distance (d) is defined by Formula 1 herein. For example, in embodiments that apply ultrasonic energy using an ultrasonic probe, the tip of the ultrasonic probe is located at a distance (d) such that particulate matter deposited onto the light transference medium becomes dislodged, thereby maintaining optical transference into the deaerated liquid in contact with the light transference medium. In certain embodiments, the distance (d) within certain ranges defined herein, thereby causing the ultrasonic energy to "originate" from the distance (d).

[0040] In certain embodiments, the ultrasonic energy originates at a distance of from about 30% to about 70%, or from about 35% to about 65%, or from about 40% to about 60%, of the wavelength of the ultrasonic energy. In other embodiments, the ultrasonic energy originates at a distance from an optical signal transmitted into the light transference medium of from about 80% to about 120%, or from about 85% to about 115%, or from about 90% to about 110%, of the wavelength of the ultrasonic energy. In certain embodiments, the ultrasonic energy originates at a distance of from about 130% to about 170%, or from about 135% to about 165%, or from about 140% to about 160%, of the

wavelength of the ultrasonic energy. In other embodiments, the ultrasonic energy originates at a distance from an optical signal transmitted into the light transference medium of from about 180% to about 220%, or from about 185% to about 215%, or from about 190% to about 210%, of the wavelength of the ultrasonic energy. In certain embodiments, the ultrasonic energy originates at a distance of from about 230% to about 270%, or from about 235% to about 265%, or from about 240% to about 260%, of the wavelength of the ultrasonic energy. In other embodiments, the ultrasonic energy originates at a distance from an optical signal transmitted into the light transference medium of from about 280% to about 320%, or from about 285% to about 315%, or from about 290% to about 310%, of the wavelength of the ultrasonic energy. In certain embodiments, the ultrasonic energy originates at a distance of from about 330% to about 370%, or from about 335% to about 365%, or from about 340% to about 360%, of the wavelength of the ultrasonic energy. In other embodiments, the ultrasonic energy originates at a distance from an optical signal transmitted into the light transference medium of from about 380% to about 420%, or from about 385% to about 415%, or from about 390% to about 410%, of the wavelength of the ultrasonic energy. In certain embodiments, the ultrasonic energy originates at a distance of from about 430% to about 470%, or from about 435% to about 465%, or from about 440% to about 460%, of the wavelength of the ultrasonic energy. In other embodiments, the ultrasonic energy originates at a distance from an optical signal transmitted into the light transference medium of from about 480% to about 520%, or from about 485% to about 515%, or from about 490% to about 510%, of the wavelength of the ultrasonic energy.

[0041] In certain embodiments, a parameter of the deaerated liquid in contact with the light transference medium is measured by transmitting the optical signal into the deaerated liquid via the light transference medium, and detecting a response. In certain embodiments, the parameter comprises fluorescence, light absorbance, temperature, chemiluminescence, optical scattering (*e.g.*, Rayleigh, Mie, and Raman scatter), imaging, transmittance, particle size, particle count, or turbidity, or any combination thereof.

[0042] In certain embodiments, the method is a clean-in-place method. A clean-in-place method does not require disassembly of the system in order to conduct the method. In other words, the light transference medium is not removed from the system, and the system is not disconnected for the purpose of accessing the light transference medium.

[0043] In certain embodiments, treatment of the deaerated liquid is controlled by utilizing the measured parameter in a control scheme. Treatment of the deaerated liquid may include, but is not limited to, at least one of physical treatment and chemical treatment. Non-limiting examples of physical treatment include adjustment of any of the following parameters of the deaerated liquid: temperature, pressure, physical phase, flow rate (*e.g.*, circulation, blowdown, and/or make-up), flow path, and mixing. Non-limiting examples of chemical treatment include adjustment of any of the following parameters, all related to a treatment chemical: chemical species selection, chemical species concentration, chemical species dosage rate, chemical species dosage location, and deaeration completeness.

[0044] In certain embodiments, the measured parameter is inputted into a control scheme. The control scheme is generally an automated method that inputs a plurality of several measured parameters and operates several process devices, *e.g.*, pumps, valves, etc. For example, a certain measured parameter may indicate that treatment chemical concentration has fallen outside a lower tolerance limit. For the present example, the measured parameter may trigger the control scheme to operate a feed pump, which in turn adds treatment chemical to the process.

[0045] In certain embodiments, the optical transference through the light transference medium is at least partially obstructed by particulate matter or scaling. In some embodiments, the particulate matter may comprise a metal oxide. In certain embodiments, the light transference medium is obstructed by deposition of a chemical species comprising iron, copper, manganese, titanium, chromium, nickel, calcium, magnesium, oxide, phosphate, carbonate, or silicate, or any combination thereof. In certain embodiments, the light transference medium is obstructed by scale comprising calcium, magnesium, phosphate, carbonate, or silicate, or any combination thereof.

[0046] In other embodiments, the particulate deposition may comprise particulate matter found in raw water, *e.g.*, mud, sand, silt, etc.

[0047] In certain embodiments, the deaerated liquid may be conditioned prior to contacting the light transference medium. For example, particularly when the deaerated liquid is boiler blowdown liquid or boiler condensate liquid, the deaerated liquid may be "enthalpy-rich." At elevated temperature and pressure (*e.g.*, 300–1500°F and corresponding pressures for saturated steam/liquid), the deaerated liquid may be conditioned such that a portion of the enthalpy (measured in the form of temperature and

pressure) are removed prior to the deaerated liquid contacting the light transference medium. In certain embodiments, the deaerated liquid in contact with the light transference medium has a temperature of from about 20°F to about 200°F, including from about 40°F to about 150°F, and including from about 60°F to about 130°F. In certain embodiments, the deaerated liquid in contact with the light transference medium has a pressure of from about 5 psig to about 100 psig, including from about 10 psig to about 70 psig, and including from about 15 psig to about 50 psig.

[0048] The timing of the application of the ultrasonic energy to the deaerated liquid may take any one or more of several forms. In one embodiment, the ultrasonic energy is continuously streamed into the deaerated liquid, which preferably includes while the system utilizing the deaerated liquid is operational. In another embodiment, the ultrasonic energy is applied intermittently, *e.g.*, for a timed duration at timed intervals. In yet another embodiment, the ultrasonic energy is applied on an as-needed basis, which can be determined, *e.g.*, by comparing historical data related to the relevant sensor and light transference medium. For example, if obstruction of the light transference medium grows to an unacceptable value, *e.g.*, a setpoint of from about 1 to about 5% obstruction, ultrasonic energy is then applied to the wetted surface of the light transference medium as described herein.

[0049] Examples of light transference media include a flow cell, an optical window, a reflective surface, a refractive surface, a dispersive element, a filtering element, and an optical fiber sensor head. In embodiments where the light transference medium is transparent or nearly transparent, the light transference medium is generally constructed of a material that is transparent or nearly transparent and having a hardness of at least about 7 on the Mohs scale. The term "transparent or nearly transparent" refers to the ability of light to pass through a substance sufficient to use light for detection and/or measurement purposes as discussed herein, which includes transparency as defined by ASTM D1746. In certain embodiments, the light transference medium is constructed of quartz, sapphire, diamond, or boron nitride.

[0050] In certain embodiments, the light transference medium is constructed of any suitable transparent or nearly transparent composition, and is coated with a transparent or nearly transparent substance having a hardness of at least about 7 on the Mohs scale. For example, the light transference medium may be constructed of a substance having a Mohs scale hardness of at least about 7 (*e.g.*, quartz), and then coated with a substance having an

even higher Mohs scale rating. In certain embodiments, the coating substance has a Mohs scale rating of from about 8 to 10, or from about 9 to 10, or 10. Illustrative embodiments of substances suitable for coating a light transference medium include, but are not limited to, diamond, titanium diboride, boron nitride, and sapphire.

[0051] In certain embodiments, the light transference medium takes the form of a reflective surface. In embodiments utilizing a reflective surface, an optical window may be utilized in concert with the reflective surface to provide observation from outside the deaerated liquid.

[0052] FIG. 1 illustrates a system capable of performing the inventive method. A deaerated liquid 10, which flows in a direction 12, contacts a light transference medium 20. Light transference medium 20 is a flow cell, and deaerated liquid 10 flows through the flow cell via direction 12. A light source 25 and a detector 26 are located so as to transmit an optical signal 27 through light transference medium 20 and deaerated liquid 10, and detect the resulting behavior caused by the transmitted optical signal 27, which may include fluorescence, light absorbance, temperature, chemiluminescence, optical scattering (*e.g.*, Rayleigh, Mie, and Raman scatter), imaging, transmittance, particle size, particle count, turbidity, and combinations thereof. An ultrasonic transducer 30 is operably attached to an ultrasonic probe 31 having a tip 32 that emits ultrasonic energy 33 at a wavelength (λ), with tip 32 being located at a distance (d) from the optical signal 27, with distance (d) being defined by Formula 1 presented herein. Optionally, the ultrasonic probe 31 may be positioned such that tip 32 emits ultrasonic energy 33 at an angle α of from 0 to about 45 degrees, or to about 35 degrees, or to about 25 degrees, or to about 15 degrees, or to about 5 degrees, as illustrated. In certain embodiments, the ultrasonic probe 31 is positioned such that tip 32 projects ultrasonic energy 33 substantially in the direction of flow 12 of deaerated liquid 10 across light transference medium 20. FIGs. 1, 2, 4, 5A, and 5B illustrate embodiments including a mount that seals ultrasonic transducer 30 to light transference medium 20 utilizing a seal 36, which in certain embodiments is a washer. In certain embodiments, seal 36 is constructed of an elastomer. Exemplary embodiments of elastomers include, but are not limited to, nitrile-butadiene rubber ("nitrile"), hydrogenated nitrile-butadiene rubber, ethylene propylene diene monomer ("EPDM"), silicone, fluoroelastomer, and polychloroprene.

[0053] FIG. 2 illustrates an embodiment, wherein the tip 32 of the ultrasonic probe 31 is positioned so as to create an offset X from light transference medium 20. Utilization of

offset X can be of particular importance to allow sufficient ultrasonic energy at wavelength (λ) into the light transference medium when a relatively soft material (*e.g.*, seal 36) is present in the direction of the ultrasonic energy. The ultrasonic energy will be less likely to be dampened by the relatively soft material due to the low energy level at the location of the relatively soft material. In embodiments that incorporate a relatively soft material between an ultrasonic probe 31 and a light transference medium 20, the distance (d) should be measured from a point beyond the relatively soft material to light transference medium 20, as illustrated in FIG. 2. In certain embodiments utilizing offset X, offset X is defined by Formula 3 below:

$$X = (b + 0.25*(2n - 1)) * \lambda \qquad \text{Formula 3}$$

wherein λ is the wavelength of the ultrasonic energy, b is a constant ranging from about -0.2 to about 0.2, and n is an integer ranging from 1 to 30. In certain embodiments, b is a constant ranging from about -0.15 to about 0.15, or from about -0.1 to about 0.1.

[0054] FIG. 3 illustrates yet another embodiment of a system capable of performing the inventive method. A deaerated liquid 10, which flows in a direction 12, contacts a light transference medium 20, which can be, for example, mounted via a tee pipe fitting 100. Light transference medium 20 takes the form of an optical window of a combination light source/detector 25/26, and deaerated liquid 10 flows across the optical window. Combination light source/detector 25/26 is located so as to transmit an optical signal 27 through light transference medium 20 (the optical window) and into the deaerated liquid 10, and detect the resulting behavior caused by optical signal 27, which may include fluorescence, light absorbance, temperature, chemiluminescence, optical scattering (*e.g.*, Rayleigh, Mie, and Raman scatter), imaging, transmittance, particle size, particle count, turbidity, and combinations thereof. While FIG. 3 shows an embodiment utilizing a combination light source/detector 25/26, a person skilled in the art will readily recognize that the light source and the detector may be separate units operably connected to a control unit (not shown). An ultrasonic transducer 30 is operably attached to an ultrasonic probe 31 having a tip 32 that emits ultrasonic energy 33, with tip 32 being located at a distance (d) from the optical signal 27, with distance (d) defined by Formula 1 presented herein.

[0055] FIG. 4 illustrates a further embodiment of a system capable of performing the inventive method is illustrated. A deaerated liquid 10, which may flow in a direction 12,

contacts a light transference medium 20. Light transference medium 20 includes a transparent portion 20a and an optional reflective portion 20b, and deaerated liquid 10 contacts each of transparent portion 20a and reflective portion 20b. A combination light source/detector 25/26 is located so as to transmit an optical signal 27 through transparent portion 20a and into deaerated liquid 10, and detect the resulting behavior caused by optical signal 27, which may include fluorescence, light absorbance, temperature, chemiluminescence, optical scattering (*e.g.*, Rayleigh, Mie, and Raman scatter), imaging, transmittance, particle size, particle count, turbidity, and combinations thereof. Optical signal 27 may be transmitted from combination light source/detector 25/26 via optical fibers capable of receiving and transmitting fluorescent emission to the combination light source/detector 25/26. Alternately, the system may be configured to utilize a light source 25 and detector 26 in addition to or in place of the combination light source/detector 25/26, wherein light source 25 and detector 26 are not aligned opposite one another. While a combination light source/detector 25/26 is illustrated in this particular embodiment, a person of skill in the art will readily recognize that the light source and the detector may be separate units connected to a control unit (not shown). An ultrasonic transducer 30 is operably attached to an ultrasonic probe 31 having a tip 32 that emits ultrasonic energy 33, with tip 32 located at a distance (d) from optical signal 27, with distance (d) being defined by Formula 1 presented herein.

[0056] In certain embodiments, an enhancer is utilized to assist in performing the methods described herein. When utilized, the enhancer allows ultrasonic energy to be applied in a manner that provides beneficial removal of obstruction while protecting the light transference medium from damage that may be caused by the application of ultrasonic energy. Particularly when applied at sharp angles (*e.g.*, perpendicular) toward the light transference medium, ultrasonic energy can damage the light transference medium. The utilization of one or more enhancers can limit or prevent the occurrence of such damage. When utilized, the enhancer may comprise at least one of a sleeve and a lossy surface. It is important to note that these particular enhancers may be used individually or in combination, or in some embodiments of the methods, not used at all. Whether to use an enhancer depends on a number of factors, including, but not limited to, the durability of the light transference medium, and the angle and frequency of the ultrasonic energy.

[0057] In embodiments utilizing a sleeve as an enhancer, the sleeve is generally positioned so as to protect a portion of the light transference medium located near the source of ultrasonic energy. Generally, the sleeve is constructed and positioned so as to prevent dampening of the ultrasonic energy in the vicinity of the transmission of the optical signal into the light transference medium. More particularly, the sleeve should protect the light transference medium from damage that may be caused by ultrasonic energy traveling perpendicular or nearly perpendicular from the ultrasonic energy source toward the light transference medium. When utilized, the sleeve should be constructed of a material suitable for providing protection to the light transference medium. For example, the sleeve may be constructed of stainless steel.

[0058] In other embodiments, the sleeve is constructed of a substance that is not completely rigid, but is not so soft as to absorb an undesired amount of the ultrasonic energy. For example, in embodiments that utilize a sleeve, the sleeve may be constructed of a substance compatible with contacting liquid(s). Furthermore, the sleeve may be constructed of a substance having a Shore "A" hardness of from about 60 to about 90. In certain embodiments, the sleeve is constructed of an elastomer as defined herein. FIG. 5A demonstrates an illustrative embodiment of a system that incorporates sleeve 70a into its design. Example 3 provides further information related to an embodiment of a sleeve utilized to prevent over-dampening.

[0059] In embodiments utilizing a lossy surface as an enhancer, the lossy surface is generally positioned so as to protect a portion of the light transference medium located near the source of ultrasonic energy. Generally, the lossy surface is positioned so as to dampen a portion of the ultrasonic energy traveling toward the light transference medium, and particularly the ultrasonic energy traveling perpendicular or nearly perpendicular from the ultrasonic energy source toward the light transference medium. In certain embodiments, the lossy surface is a surface that is generally rough, such as, *e.g.*, a grooved, threaded, or jagged surface. Generally, a lossy surface is rough such that at least a portion of the ultrasonic energy is scattered away when coming in contact with the lossy surface. FIG. 5B demonstrates an illustrative embodiment of a system that incorporates lossy surface 70b into its design.

[0060] A clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system is provided. The clean-in-place method comprises contacting a stream of boiler water with a wetted surface of a

light transference medium in optical communication with an optical sensor. Data related to a parameter of the boiler liquid measured by the optical sensor is input to a control scheme of a boiler system. The optical sensor is electronically isolated from the control scheme, which maintains control of the boiler system based on the input data related to the parameter of the boiler liquid. A liquid chemical agent contacts the wetted surface of the light transference medium for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The liquid chemical agent is selected from an acid, a chelant, a reducing agent, and combinations thereof. The liquid chemical agent is removed from the wetted surface of the light transference medium, and the optical sensor is electronically de-isolated from the control scheme.

[0061] A clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system is also provided. The clean-in-place method comprises flowing a stream of boiler liquid to contact a wetted surface of a light transference medium in optical communication with an optical sensor. Data related to a parameter of the boiler liquid measured by the optical sensor is input to a control scheme of a boiler system. The flow of the stream of boiler liquid to contact the wetted surface of the light transference medium is discontinued. The optical sensor is electronically isolated from the control scheme, which maintains control of the boiler system based on the input data related to the parameter of the boiler liquid. A liquid chemical agent contacts the wetted surface of the light transference medium for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The liquid chemical agent is selected from an acid, a chelant, a reducing agent, and combinations thereof. The liquid chemical agent is removed from the wetted surface of the light transference medium, the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium is resumed, and the optical sensor is electronically de-isolated from the control scheme.

[0062] The terms "optical" and "light" are used interchangeably herein. Utilization of the phrase "into boiler liquid" is intended to cover light transmission in any direction between the boiler liquid, the light transference medium, a light source, and/or a light detector. For example, the optical signal may originate from within the boiler liquid and be transferred to a sensor via the light transference medium (*e.g.*, fluorometric emission), or from a light source through the light transference medium and into the boiler liquid (*e.g.*, fluorometric excitation). Illustrative embodiments of optical sensors that perform

optical measurements using optical signals include, but are not limited to, devices capable of detecting or sensing absorbance, colorimetric, refractometric, spectrophotometric, luminometric, and/or fluorometric signals, or images. In a preferred embodiment, the optical signal comprises a fluorometric excitation and/or emission.

[0063] The method is directed to obtaining or maintaining optical transference into boiler liquid in contact with a light transference medium. The method can be utilized to remove obstructions that may be present on the light transference medium. Removal of obstruction from the light transference medium sufficient to allow for optical transference, thereby allowing for performance of an optical measurement of the boiler liquid, is also achieved by the methods of the present invention.

[0064] The term "clean-in-place" is utilized herein to describe a method that is performed without disassembly of the system. For example, the light transference medium is not removed from the system, and the system is not disconnected to gain physical access to the light transference medium (*e.g.*, to be manually wiped), to carry out a clean-in-place method. Related to the methods described herein, the light transference medium remains operably connected to a boiler system, though the stream of boiler liquid may be diverted so as to not contact the wetted surface of the light transference medium during performance of the disclosed methods.

[0065] When performing the methods described herein, the optical transference through the light transference medium may be at least partially obstructed by particulate matter. The particulate matter may comprise particulate matter typically found in raw water, *e.g.*, mud, sand, silt, etc. The particulate matter may comprise a metal oxide. The oxide may be of a metal selected iron, copper, manganese, titanium, chromium, or nickel, or any combination thereof. Metal oxide deposition is of particular concern for boiler liquid, particularly boiler blowdown liquid. In certain embodiments, the particulate matter comprises at least one of silica, a calcium oxide, a calcium salt, a magnesium oxide, and a magnesium salt.

[0066] The timing of the contacting of the liquid chemical agent to the wetted surface of the light transference medium may take any one or more of several forms. In certain embodiments, the liquid chemical agent is added continuously to the boiler liquid, which preferably includes during operation of the system utilizing the liquid chemical agent. In other embodiments, the liquid chemical agent is added intermittently to the boiler liquid, *e.g.*, for a timed duration at timed intervals. In further embodiments, the liquid chemical

agent is added on an as-needed basis, which can be determined, *e.g.*, by comparing historical data related to the relevant sensor and light transference medium. For embodiments where the flow of the stream the boiler liquid is discontinued, the liquid chemical agent may be contacted intermittently or on an as-needed basis.

[0067] In embodiments of the present invention, the light transference medium is in optical communication with an optical sensor, which allows the optical sensor to be utilized to monitor a substance using optical detection methods. For example, a flow cell is generally used to allow for fluorometric detection of a component of a liquid flowing through a conduit. The flow cell allows for light to pass between a fluorometer and the flowing liquid via the wall of the flow cell, thereby allowing the fluorometer to carry out its monitoring without physically contacting the flowing liquid. For the given situation, the fluorometer is said to be in optical communication with the flow cell.

[0068] Examples of light transference media include, but are not limited to, a flow cell, an optical window, a reflective surface, a refractive surface, a dispersive element, a filtering element, and an optical fiber sensor head. The light transference medium may be constructed of a material that is transparent or nearly transparent. The light transference medium may have a hardness of at least about 7 on the Mohs scale. The term "transparent or nearly transparent" refers to the ability of light to pass through a substance sufficient to use light for detection and/or measurement purposes as discussed herein, which includes transparency as defined by ASTM D1746. The hardness of the light transference medium becomes increasingly important when ultrasonic energy is utilized to supplement the general clean-in-place methods disclosed herein. In certain embodiments, the light transference medium is constructed of quartz, sapphire, or diamond.

[0069] In certain embodiments, the light transference medium is constructed of any suitable transparent or nearly transparent composition, and is coated with a transparent or nearly transparent substance having a hardness of at least about 7 on the Mohs scale. For example, the light transference medium may be constructed of a substance having a Mohs scale hardness of at least about 7 (*e.g.*, quartz), and then coated with a substance having an even higher Mohs scale rating. In certain embodiments, the coating substance has a Mohs scale rating of from about 8 to 10, or from about 9 to 10, or 10. Illustrative embodiments of substances suitable for coating a light transference medium include, but are not limited to, diamond, titanium diboride, boron nitride, and sapphire.

[0070] In certain embodiments, the light transference medium takes the form of a reflective surface. In embodiments utilizing a reflective surface, an optical window may be utilized in concert with the reflective surface to provide observation from outside the boiler liquid.

[0071] In certain embodiments, treatment of the boiler liquid is controlled by utilizing the measured parameter in a control scheme. Treatment of the boiler liquid may include, but is not limited to, at least one of physical treatment and chemical treatment. Non-limiting examples of physical treatment include adjustment of any of the following parameters of the boiler liquid: temperature, pressure, physical phase, flow rate (*e.g.*, circulation, blowdown, and/or make-up), flow path, and mixing. Non-limiting examples of chemical treatment include adjustment of any of the following parameters, all related to a treatment chemical: chemical species selection, chemical species concentration, chemical species dosage rate, chemical species dosage location, and deaeration completeness.

[0072] In the methods disclosed herein, the measured parameter is inputted into a control scheme. The control scheme is generally an automated method that inputs a plurality of several measured parameters and operates several process devices, *e.g.*, pumps, valves, etc. For example, a certain measured parameter may indicate that treatment chemical concentration has fallen outside a lower tolerance limit. For the present example, the measured parameter may trigger the control scheme to operate a feed pump, which in turn adds treatment chemical to the process.

[0073] In certain embodiments, the optical sensor is electronically isolated from the control scheme. A sensor is said to be electronically isolated if it generates data that is intentionally ignored or otherwise intentionally not acted upon by a controller, or provides no data because of an action of the controller (*e.g.*, automatically shut down) or the user (*e.g.*, unplugged). A sensor that is electronically isolated in the exemplary manner may allow for the sensor to be cleaned, *e.g.*, via liquid chemical treatment, without providing false or misleading data acquired during said liquid chemical treatment. An electronically isolated sensor would not need to be physically isolated from the stream of boiler liquid, but isolated only from the control scheme. The term "meaningful data" as used herein refers to data that describes a parameter of a substance and may be input into and reliably acted upon by a control scheme.

[0074] In certain embodiments, flow of the stream of boiler liquid in contact with the wetted surface of the light transference medium is discontinued in order to carry out the contacting the liquid chemical agent step. A light transference medium can be said to undergo "system isolation" when the flow of the stream of boiler liquid is discontinued to carry out a clean-in-place method such as, *e.g.*, those disclosed herein. System isolation allows for the liquid chemical agent to contact the wetted surface of the light transference medium for an extended period of time, as opposed to dosing the liquid chemical treatment into the flowing stream of boiler liquid.

[0075] After the liquid chemical agent has contacted the wetted surface for a period of time and at a concentration sufficient to clean the wetted surface, the liquid chemical agent is removed from the wetted surface and flow of the stream of boiler liquid is resumed. In certain embodiments, the liquid chemical agent is removed by resuming the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium.

[0076] In embodiments that carry out system isolation, the liquid chemical agent may be brought into contact with the wetted surface and remain static for a period of time. In a further embodiment, after the liquid chemical agent has been removed from the wetted surface, a further liquid chemical agent, whether it be the same species of liquid chemical agent or a different species of liquid chemical agent, may be brought into contact with the wetted surface and remain static for a period of time, prior to resuming the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium. In other embodiments that carry out system isolation, the liquid chemical agent may contact the wetted surface by being passed across the wetted surface for a period of time, *e.g.*, in a liquid chemical treatment loop, or the liquid chemical agent may be pass across the wetted surface only once.

[0077] In embodiments of the inventive methods, cleaning via liquid chemical agent contact requires that the liquid chemical agent contacts the wetted surface for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium. The period of time and the concentration generally depend on each other, with a shorter period of contact time generally necessary to achieve cleaning using higher liquid chemical agent concentrations, and a longer period of contact time for lower liquid chemical agent concentration, assuming that all other factors remain constant (temperature, species of liquid chemical agent, materials of construction, etc.). A period of time sufficient to clean the wetted surface may be nearly instantaneous, *e.g.*, 1 second

or less, for a given liquid chemical agent dosed to a slightly-obstructed light transference medium at a reasonably high concentration and otherwise under preferential conditions. Cleaning a heavily-obstructed light transference medium may require a significantly longer contact time, *e.g.*, 20 minutes or greater, depending on *inter alia* liquid chemical agent selection and concentration. In a preferred embodiment, the period of time is from about 30 seconds to about 20 minutes, including from about 1 minute to about 10 minutes.

[0078] The liquid chemical agent should be selected and dosed so as to provide cleaning of the wetted surface without corroding or otherwise damaging the surfaces contacted by the liquid chemical agent. With few exceptions, a higher concentration of liquid chemical agent will generally provide better cleaning activity when contacting the wetted surface. One notable exception is sulfuric acid, which may perform better when fully-protonated. In embodiments that utilize sulfuric acid, the sulfuric acid may have a concentration of from about 5 weight percent to about 98 weight percent in aqueous solution. In a preferred embodiment that utilizes sulfuric acid, the sulfuric acid has a concentration of from about 5 weight percent to about 15 weight percent, including about 10 weight percent, in aqueous solution. In embodiments that utilize citric acid, the citric acid may have a concentration of from about 5 weight percent to about 30 weight percent in aqueous solution. In a preferred embodiment that utilizes citric acid, the citric acid has a concentration of from about 5 weight percent to about 15 weight percent, including about 10 weight percent, in aqueous solution.

[0079] In embodiments that do not carry out system isolation of the light transference medium subject to the clean-in-place methods disclosed herein, the liquid chemical agent may contact the wetted surface of the light transference medium at a flow rate of about 1 mL/min to about 40 mL/min at a concentration of about 0.1 weight percent to about 80 weight percent, depending on, *inter alia*, the liquid chemical agent utilized. In a preferred embodiment, the liquid chemical agent contacts the wetted surface of the light transference medium at a flow rate of about 1 mL/min to about 40 mL/min at a concentration of about 1 weight percent to about 20 weight percent chelant in aqueous solution. In another preferred embodiment, the liquid chemical agent contacts the wetted surface of the light transference medium at a flow rate of about 1 mL/min to about 40 mL/min at a concentration of about 0.1 weight percent to about 10 weight percent reducing agent in aqueous solution. In yet another preferred embodiment, the liquid chemical agent contacts the wetted surface of the light transference medium at a flow rate of about 1 mL/min to

about 40 mL/min at a concentration of about 30 weight percent to about 60 weight percent acid in aqueous solution. Each preferred embodiment is further described herein in the context of components of the liquid chemical agent.

[0080] In certain embodiments that undergo electronic isolation or system isolation of a light transference medium and/or optical sensor, control of the boiler system may be maintained based on data input into the control scheme prior to the electronic or system isolation. Control of the boiler system may be maintained based on data gathered from a period of time previous to the electronic or system isolation. The period of time previous to the electronic or system isolation may be, *e.g.*, the last recorded value(s) prior to the electronic or system isolation, or *e.g.*, one minute, or five minutes, or one hour, or five hours, etc. The gathered data may be manipulated as is known in the art to implement the maintenance of boiler system control. Averaging data over a period of time is an example of manipulating data.

[0081] As mentioned in the previous paragraph, the boiler system may be maintained based on the last recorded value prior to the electronic or system isolation. By way of example, the optical sensor may input a data point related to a parameter of the boiler liquid, and the optical sensor and its corresponding light transference medium may be electronically or systemically isolated immediately following the input of the data point. In this preferred embodiment of the invention, the control scheme continues to maintain control of the boiler system as if the optical sensor continues to input the same data that was input immediately prior to the electronic or system isolation. Instead of utilizing the immediate predecessor data point to maintain control, further exemplary embodiments may utilize, for example, several prior data points, a mean of several data points, a median of several data points, a mode of several data points, or a statistical trend of several data points.

[0082] In embodiments of the inventive methods, the liquid chemical agent comprises a component selected from an acid, a chelant, a reducing agent, and combinations thereof. Single component liquid chemical agents can be used to successfully clean a light transference medium according to the inventive methods disclosed herein. However, in a particularly preferred embodiment, the liquid chemical agent comprises an acid of one chemical species and a chelant of a second chemical species. In another particularly preferred embodiment, the liquid chemical agent comprises a reducing agent of one chemical species and a chelant of a second chemical species. The phrase "of one chemical

species…of a second chemical species" is used to describe the utilization of distinct chemicals for each named genus. For example, a liquid chemical agent comprising a reducing agent of one chemical species and a chelant of a second chemical species may be a liquid chemical agent comprising sodium hyposulfite (a reducing agent of one chemical species) and oxalic acid (a chelant of a second chemical species). An exemplary embodiment of a liquid chemical agent comprising an acid of one chemical species and a chelant of a second chemical species is a liquid chemical species comprising urea hydrochloride (an acid of one chemical species) and oxalic acid (a chelant of a second chemical species).

[0083] In certain embodiments, the component of the liquid chemical agent is an acid selected from urea hydrochloride, hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, acetic acid, citric acid, carbonic acid, bicarbonic acid, sulfamic acid, or any combination thereof. In a preferred embodiment, the acid in the liquid chemical agent is urea hydrochloride.

[0084] When selected, the acid may be present in the liquid chemical agent at a concentration of from about 5 weight percent to about 98 weight percent in aqueous solution, including from about 20 weight percent to about 80 weight percent acid in aqueous solution, and further including at least about 20 weight percent, or at least about 30 weight percent, or about 40 weight percent to about 50 weight percent, to about 60 weight percent, to about 70 weight percent, to about 80 weight percent acid in aqueous solution. In a preferred embodiment, the acid is present in the liquid chemical agent at a concentration of about 30 weight percent to about 60 weight percent.

[0085] In certain embodiments, the component of the liquid chemical agent is a chelant selected from: citric acid, oxalic acid, ethylenediaminetetraacetic acid, diethylene triamine pentaacetic acid, an organic phosphonate, salts thereof, or any combination thereof. In a preferred embodiment, the chelant in the liquid chemical agent is oxalic acid.

[0086] When selected, the chelant may be present in the liquid chemical agent at a concentration of from about 0.1 weight percent to about 20 weight percent chelant in aqueous solution, including at least about 0.1 weight percent, or at least about 0.5 weight percent or at least about 1 weight percent, to about 3 weight percent, or about 5 weight percent, or about 10 weight percent, or about 20 weight percent chelant in aqueous solution. In a preferred embodiment, the chelant is present in the liquid chemical agent at

a concentration of from about 1 weight percent to about 3 weight percent chelant in aqueous solution.

[0087] In certain embodiments, the component of the liquid chemical agent is a reducing agent selected from an acid sulfite, an acid bisulfite, an acid hydrosulfite, an acid phosphite, phosphoric acid, oxalic acid, formic acid, ascorbic acid, or erythorbic acid, salts thereof, or any combination thereof. In a preferred embodiment, the reducing agent in the liquid chemical agent is sodium hydrosulfite.

[0088] When selected, the reducing agent may be present in the liquid chemical agent at a concentration of from about 0.1 weight percent to about 10 weight percent reducing agent in aqueous solution, including from about 0.1 weight percent, or about 0.3 weight percent, or about 0.5 weight percent, to about 3 weight percent, or to about 7 weight percent, or to about 10 weight percent reducing agent in aqueous solution. In a preferred embodiment, the reducing agent is present in the liquid chemical agent at a concentration of from about 0.5 weight percent to about 3 weight percent reducing agent in aqueous solution.

[0089] Of note, a particular chemical species may overlap into any two, and in some instances, all three, of the three chemical genuses of the present invention. For example, citric acid and oxalic acid can be considered both an acid and a chelant. Furthermore, several acids, including oxalic acid and phosphoric acid, can be considered to be reducing agents in addition to acids and/or chelants.

[0090] Though different reference numerals may be utilized in FIG. 9 compared to other figures presented herewith, like-named elements are to be construed as being the same or similar to like-named elements present in other figures (e.g., FIGs. 1–5B). For example, light transference medium 20 of FIG. 1 should be construed as being the same or similar to light transference medium 1020 of FIG. 9, and so forth. Referring to FIG. 9, operation of a boiler treatment system generally involves boiler liquid 1010 flows through solenoid valve 1012a and continues through light transference medium (*e.g.*, flow cell) 1020, contacting wetted surface 1021, and usually out to auxillary operations via valve 1012b or to treatment or a drain via valve 1012c. A parameter of boiler liquid 1010 is measured using optical sensor 1022 (*e.g.*, fluorometer), which is in operable communication with light transference medium 1020, and data related to the parameter is input into a control scheme (*e.g.*, relayed to controller 1100). Optical sensor 1022 is electronically isolated from the control scheme, which maintains control of the boiler

system based upon the previously input data. A liquid chemical agent, *e.g.*, present in container 1050, is brought into contact with wetted surface 1021 via pump 1054, flowing through valve 1052 and check valve 1056 and on to wetted surface 1021. Optionally, boiler liquid 1010 can be diverted to bypass line 1070 by closing valve 1012a and opening valve 1012d. As is readily recognized by one skilled in the art, valves 1012a and 1012d can be replaced by a single three-way valve (not shown), which could be operably configured to divert boiler liquid 1010 from wetted surface 1021 of light transference medium 1020 and to bypass line 1070. Optionally, valves 1012a, 1012b, 1012c, and 1012d can be operably actuated to provide system isolation of light transference medium 1020. The liquid chemical agent may continuously or intermittently contact wetted surface 1021, or may be periodically contacted and removed from wetted surface via system isolation as described herein.

[0091] To supplement the more general clean-in-place methods disclosed herein, ultrasonic energy may be applied as described herein into the liquid chemical agent during at least a portion of the contacting of the liquid chemical agent to the wetted surface of the light transference medium. When utilized, the ultrasonic energy further effectuates cleaning of the wetted surface of the light transference medium. When utilized, the ultrasonic energy may be applied prior to, simultaneously, and/or subsequent to contacting the liquid chemical agent to the wetted surface of the light transference medium. The ultrasonic energy may be applied via an ultrasonic probe and ultrasonic transducer in a manner disclosed in U.S. Patent Application Publication No. 2013/0186188, filed January 19, 2012, to Bradley et al., or in a manner disclosed in U.S. Patent Application Serial No. 14/592,219, filed January 8, 2015, to Hicks et al., each disclosure of which is incorporated herein by reference in its entirety. The embodiment illustrated in FIG. 9 includes optional ultrasonic probe 1201 operably attached to optional ultrasonic transducer 1202, which may be configured as described herein, and more particularly as in FIGs. 1–5B presented herewith.

[0092] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

[0093] FIG. 6 is a plot of obstruction of light transference media in the form of particulate deposition onto flow cells. Two light transference media (flow cells for this

Example) were used to perform the experiment: ultrasonic energy was applied to the test flow cell, and no cleaning method was implemented for the control flow cell. In the example, the flow cells were initially clean and of the same type. The flow cells were exposed to the same blowdown stream of a 1500 psi recovery boiler of a paper mill. The flow cells were quartz glass tubes, each having an outer diameter of 0.312" (7.9 mm), an inner diameter of 0.236" (6 mm), and a length of 4.69" (11.9 cm). The ultrasonic energy was applied via a probe positioned at a distance (d) of 58 mm according to FIG. 1 and Formula 1 (*i.e.*, n = 3), with the tip of the ultrasonic probe positioned flush with the end of the light transference medium. The blowdown of the recovery boiler flowed through the flow cells after being conditioned from saturated, *e.g.*, 1515 psig at 597°F, to less than 40 psig and less than 120°F. The conditioned blowdown is expected to flow through the flow cells under laminar flow, as the flow rate is approximately 500 mL/min and having a Reynolds Number of approximately 1800.

[0094] Ultrasonic energy was applied to the test flow cell at 40 kHz, which was intermittently applied at 2.2% duty. In other words, the ultrasonic energy was applied to the test flow cell for 1 minute per 45 minutes (*i.e.*, 1 minute / 45 minutes = 0.022).

[0095] The experiment was carried out over 20 days for the control flow cell, which continued to accumulate particulate deposition up to about 75% obstruction. The experiment was carried out over 14 days for the test flow cell, which accumulated virtually no obstruction over the 14-day trial. Obstruction of the light transference medium was virtually eliminated by the application of ultrasonic energy at a frequency of 40 kHz.

EXAMPLE 2

[0096] FIG. 7 is a plot of particulate deposition being removed from a light transference medium, in this instance a flow cell, over time by the application of ultrasonic energy to the flow cell. In the example, the flow cell was exposed to a blowdown stream of a powerhouse boiler. The flow cell was the same as the test flow cell of Example 1 herein, except that the distance (d) was 56 mm, and the tip of the ultrasonic probe was 10 mm beyond the end of the flow cell (offset (X) = 10 mm) as shown in FIG. 2. Offset (X) fits Formula 3, with n = 1. The flow cell was approximately 100% obstructed at the beginning of the experiment. Blowdown of the powerhouse boiler flowed through the flow cell at 300 mL/min after being conditioned as in Example 1 herein.

[0097] Ultrasonic energy was applied to the flow cell at 28 kHz, which was intermittently applied at 50% duty (*i.e.*, one minute "on" for every minute "off"), as opposed to the 2.2% duty to the test flow cell of Example 1. The experiment was carried out over approximately 250 minutes. By approximately the 170th minute, substantially all of the particulate deposition had been removed, and the flow cell was substantially unobstructed.

EXAMPLE 3

[0098] FIG. 8 is a plot of the effect of the utilization of an enhancer in combination with an EPDM washer used to seal the ultrasonic energy source to a light transference medium, for this Example flow cells as described in Examples 1 and 2 herein. Each EPDM washer used to seal the flow cells had a Shore "A" hardness of about 55 to about 75. For this Example, the enhancer was a sleeve covering the EPDM washer and part of the light transference medium of the test flow cell. The control flow cell incorporated the EPDM washer seal but did not incorporate an enhancer. In the example, each of the two flow cells were initially 100% obstructed by particulate deposition and were exposed to the same conditioned blowdown stream as in Examples 1 and 2, except that the pre-conditioned blowdown stream was initially saturated at 700 psig and 503°F. The conditioned blowdown stream (less than 40 psig and less than 120°F) flowed through the flow cells at approximately 300 mL/min. Ultrasonic energy was applied to both the control flow cell and the test flow cell. The distance (d) for the test flow cell was 62 mm, and the tip of the ultrasonic probe was 6 mm beyond each flow cell (offset (X) = 6 mm, but only for the control flow cell). Because the EPDM washer was covered by an enhancer for the test flow cell, the distance (d) followed FIG. 1 and Formula 1, with n = 2. For the control flow cell, the distance (d) was 56 mm and offset (X) was 6 mm, as shown in FIG. 2, which falls within the parameters of Formula 3. However, incorporation of the enhancer of the test flow cell was clearly beneficial in minimizing the dampening effect of the EPDM washer.

[0099] The sleeve was constructed of 316-stainless steel "thin wall" tubing, having an outer diameter slightly less than the 0.236" inner diameter of the test flow cell. The ultrasonic energy was applied to each flow cell at 20 kHz, which was intermittently applied at 50% duty. As shown in FIG. 8, the control sample showed little removal of obstruction at 20 kHz at 50% duty for the 2000-minute test. However, utilization of a

sleeve covering the EPDM washer and a portion of the test flow cell allowed for nearly complete removal of the obstruction after about 1000 minutes of 20 kHz ultrasonic energy at 50% duty.

EXAMPLE 4

[0100] Three cleaning chemicals have been tested to be able to remove iron oxide particles from boiler water stream.

[0101] Urea hydrochloride, available as DC-14 from Nalco Company, 1601 West Diehl Road, Naperville, IL 60563, was tested as a liquid cleaning agent to clean a wetted surface of a flow cell used to monitor a boiler blowdown stream of a power house boiler. A control flow cell was continuously exposed to the same boiler blowdown stream and was not cleaned. The duration of the test was approximately 28 days. The urea hydrochloride had a concentration of 30–60% by weight in aqueous solution, having a pH of 1.5. Aqueous urea hydrochloride at this concentration generally vaporizes at normal operational conditions. The urea hydrochloride was dosed once per day at full concentration, *i.e.*, not further diluted, and allowed to contact the wetted surface of the test flow cell for 3 minutes under system isolation.

[0102] FIG. 10 illustrates the results of testing. The spikes in cell obstruction represent the periods of time during which the urea hydrochloride was dosed to the wetted surface of the flow cell. Notice the measured increase in cell obstruction of the control flow cell versus the significantly lower cell obstruction of the test flow cell during non-treatment time periods. For example, at Day 15, the control flow cell is nearly 40% obstructed while the test flow cell is less than 10% obstructed, which is believed to be unobstructed. While not wishing to be bound by theory, any amount of measured obstruction that is less than 10% is believed to be caused by light absorbance of water or LED decay of the optical sensor.

EXAMPLE 5

[0103] Oxalic acid was tested as a liquid cleaning agent to clean a wetted surface of a flow cell used to monitor a boiler blowdown stream of a power house boiler. A control flow cell was continuously exposed to the same boiler blowdown stream and was not cleaned. The duration of the test was approximately 25 days. The oxalic acid had a concentration of 12,000 ppm by weight in aqueous solution, having a pH of 2, which was

stable at 50°C. A higher pH would be expected at a lower concentration. The oxalic acid was dosed at full concentration, i.e., not further diluted, and allowed to contact the wetted surface of the test flow cell for 10 minutes under system isolation. FIG. 11 illustrates the results of testing, with the spikes in cell obstruction represent the periods of time during which the oxalic acid was dosed to the wetted surface of the flow cell. Notice the measured increase in cell obstruction of the control flow cell versus the significantly lower cell obstruction of the test flow cell during non-treatment time periods. For example, at Day 11, the control flow cell is approximately 10% obstructed while the test flow cell is almost completely unobstructed. Furthermore, when oxalic acid is not dosed to the test flow cell (e.g., Days 16–20), obstruction of the test flow cell generally tracks the obstruction of the control flow cell. However, obstruction of the test flow cell decreases dramatically after oxalic acid contacts the test flow cell's wetted surface.

EXAMPLE 6

[0104] Sodium hydrosulfite was tested as a liquid cleaning agent to clean a wetted surface of a flow cell used to monitor a boiler blowdown stream of a power house boiler. A control flow cell was continuously exposed to the same boiler blowdown stream and was not cleaned. The duration of the test was approximately 38 days. The sodium hydrosulfite had a concentration of 0.8–2.4 weight percent in aqueous solution, which decomposes to sulfur dioxide at above 50°C. The sodium hydrosulfite was dosed at full concentration, *i.e.*, not further diluted, and allowed to contact the wetted surface of the test flow cell for 10 minutes under system isolation.

[0105] FIG. 12 illustrates the results of testing. The spikes in cell obstruction represent the periods of time during which the sodium hydrosulfite was dosed to the wetted surface of the test flow cell under system isolation. Notice the measured increase in cell obstruction of the control flow cell versus the significantly lower cell obstruction of the test flow cell, particularly beginning at approximately Day 28.

EXAMPLE 7

[0106] Experiments were performed to test certain combinations of components of the liquid cleaning agents of Examples 1–3. The following aqueous agents were obtained or prepared: sodium hydrosulfite at 0.8–2.4% by weight; oxalic acid at 1.2% by weight (as dihydrate); and urea hydrochloride as 30–60% by weight. The following combinations were created from the aqueous agents, each blended at 1:1 volume ratios:

Combination No.	Agents
1	Sodium hydrosulfite + oxalic acid
2	Urea hydrochloride + oxalic acid
3	Urea hydrochloride + sodium hydrosulfite

[0107] Flow cells of various obstructions (60–100%) were placed in each of the combined liquid cleaning agents for 10 minutes at a time, removed, and observed to determine each combination's performance. Combinations 2 and 3 removed some of the obstructing deposition, and Combination 1 removed substantially all of the obstructing deposition.

[0108] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0109] The use of the terms "a" and "an" and "the" and "at least one" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term "at least one" followed by a list of one or more items (for example, "at least one of A and B") is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (*i.e.*, meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as," "illustrative") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0110] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

What is claimed is:

1. A clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system, the method comprising:

contacting a stream of boiler liquid with a wetted surface of a light transference medium in optical communication with an optical sensor;

inputting data related to a parameter of the boiler liquid measured by the optical sensor to a control scheme of a boiler system;

electronically isolating the optical sensor from the control scheme while maintaining control of the boiler system based on the input data related to the parameter of the boiler liquid;

contacting a liquid chemical agent to the wetted surface of the light transference medium, the liquid chemical agent comprising a component selected an acid, a chelant, a reducing agent, or combinations thereof, for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium; and

electronically de-isolating the optical sensor from the control scheme.

2. A clean-in-place method of maintaining optical transference through a light transference medium operably connected to a boiler system, the method comprising:

flowing a stream of boiler liquid to contact a wetted surface of a light transference medium in optical communication with an optical sensor;

inputting data related to a parameter of the boiler liquid measured by the optical sensor to a control scheme of a boiler system;

discontinuing the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium;

electronically isolating the optical sensor from the control scheme while maintaining control of the boiler system based on the input data related to the parameter of boiler liquid;

contacting a liquid chemical agent to the wetted surface of the light transference medium, the liquid chemical agent comprising a component selected from an acid, a chelant, a reducing agent, or combinations thereof, for a period of time and at a concentration sufficient to clean the wetted surface of the light transference medium;

removing the liquid chemical agent from the wetted surface of the light transference medium;

resuming the flow of the stream of boiler liquid to contact the wetted surface of the light transference medium; and

electronically de-isolating the optical sensor from the control scheme.

3. The clean-in-place method of claim 2, wherein the liquid chemical agent is removed by the resuming step.

4. The clean-in-place method of any one of claims 1 to 3, wherein the component is an acid selected from urea hydrochloride, hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, acetic acid, citric acid, carbonic acid, bicarbonic acid, sulfamic acid, or combinations thereof.

5. The clean-in-place method of claim 4, wherein the acid is present in the liquid chemical agent at a concentration of from about 5 weight percent to about 98 weight percent acid in aqueous solution.

6. The clean-in-place method of any one of claims 1 to 3, wherein the component is a chelant selected from citric acid, oxalic acid, ethylenediaminetetraacetic acid, diethylene triamine pentaacetic acid, an organic phosphonate, salts thereof, or combinations thereof.

7. The clean-in-place method of claim 6, wherein the chelant is present in the liquid chemical agent at a concentration of from about 1 weight percent to about 20 weight percent chelant in aqueous solution.

8. The clean-in-place method of any one of claims 1 to 3, wherein the component is a reducing agent selected from an acid sulfite, an acid bisulfite, an acid hydrosulfite, an acid phosphite, phosphoric acid, oxalic acid, formic acid, ascorbic acid, erythorbic acid, salts thereof, or combinations thereof.

9. The clean-in-place method of claim 8, wherein the reducing agent is present in the liquid chemical agent at a concentration of from about 0.1 weight percent to about 10 weight percent reducing agent in aqueous solution.

10. The clean-in-place method of any one of claims 1 to 9, wherein the liquid chemical agent comprises an acid of one chemical species and a chelant of a second chemical species.

11. The clean-in-place method of any one of claims 1 to 9, wherein the liquid chemical agent comprises a reducing agent of one chemical species and a chelant of a second chemical species.

12. The clean-in-place method of any one of claims 1 to 11, further comprising applying ultrasonic energy into the liquid chemical agent during at least a portion of the contacting of the liquid chemical agent to the wetted surface of the light transference medium.

13. The clean-in-place method of any one of claims 1 to 12, wherein the liquid chemical agent contacts the wetted surface of the light transference medium at a flow rate of about 1 L/min to about 40 L/min at a concentration of about 0.1 weight percent to about 80 weight percent.

14. The clean-in-place method of any one of claims 1 to 13, wherein the period of time is from about 1 minute to about 10 minutes.

15. The clean-in-place method of any one of claims 1 to 14, wherein the clean-in-place method further comprises applying ultrasonic energy to the wetted surface of the light transference medium.

16. The clean-in-place method of claim 15, wherein the ultrasonic energy is applied to the wetted surface prior to contacting the liquid chemical agent to the wetted surface of the light transference medium.

17. The clean-in-place method of claim 15, wherein the ultrasonic energy is applied to the wetted surface simultaneously with contacting the liquid chemical agent to the wetted surface of the light transference medium.

18. The clean-in-place method of claim 15, wherein the ultrasonic energy is applied to the wetted surface subsequent to contacting the liquid chemical agent to the wetted surface of the light transference medium.

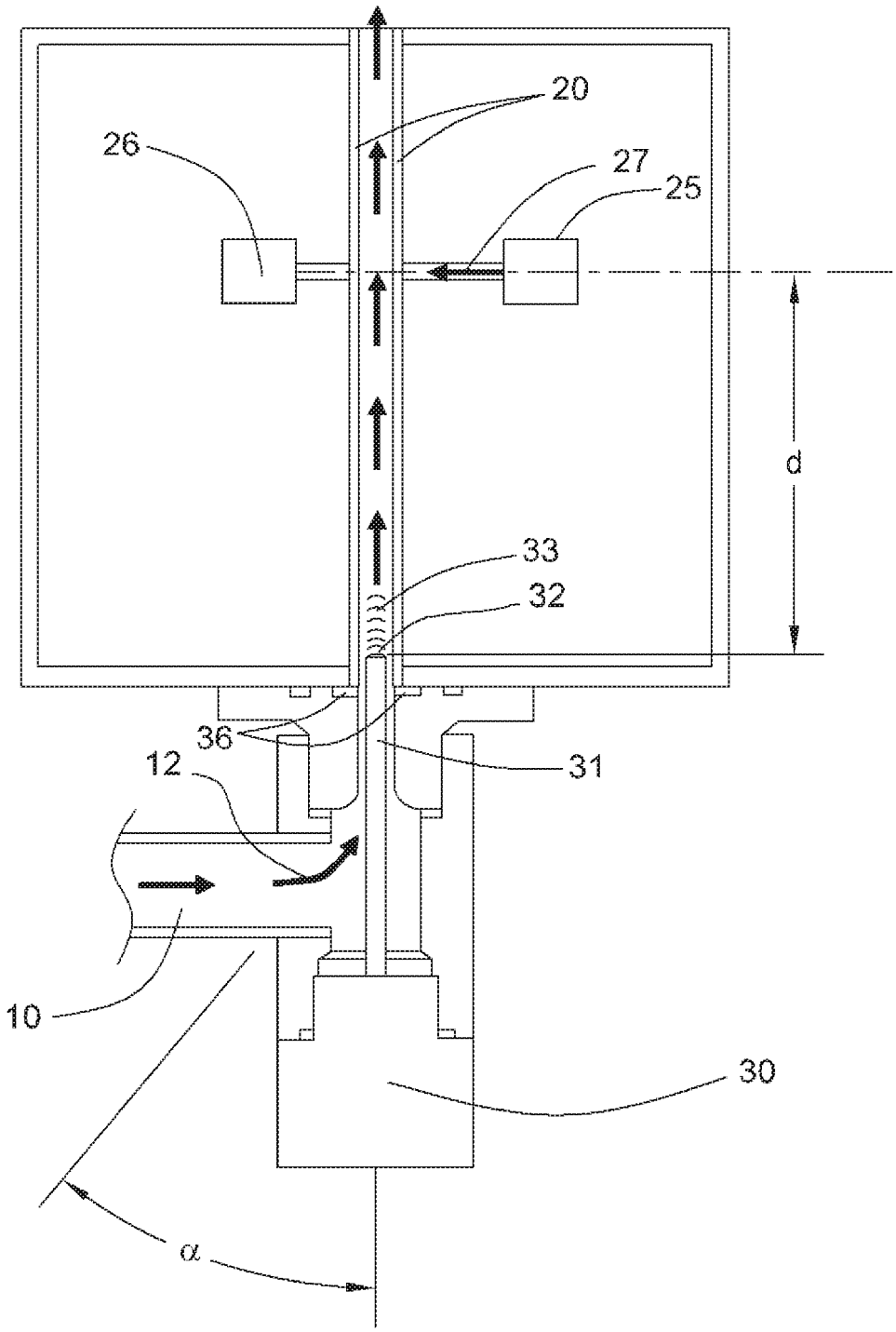

FIG. 1

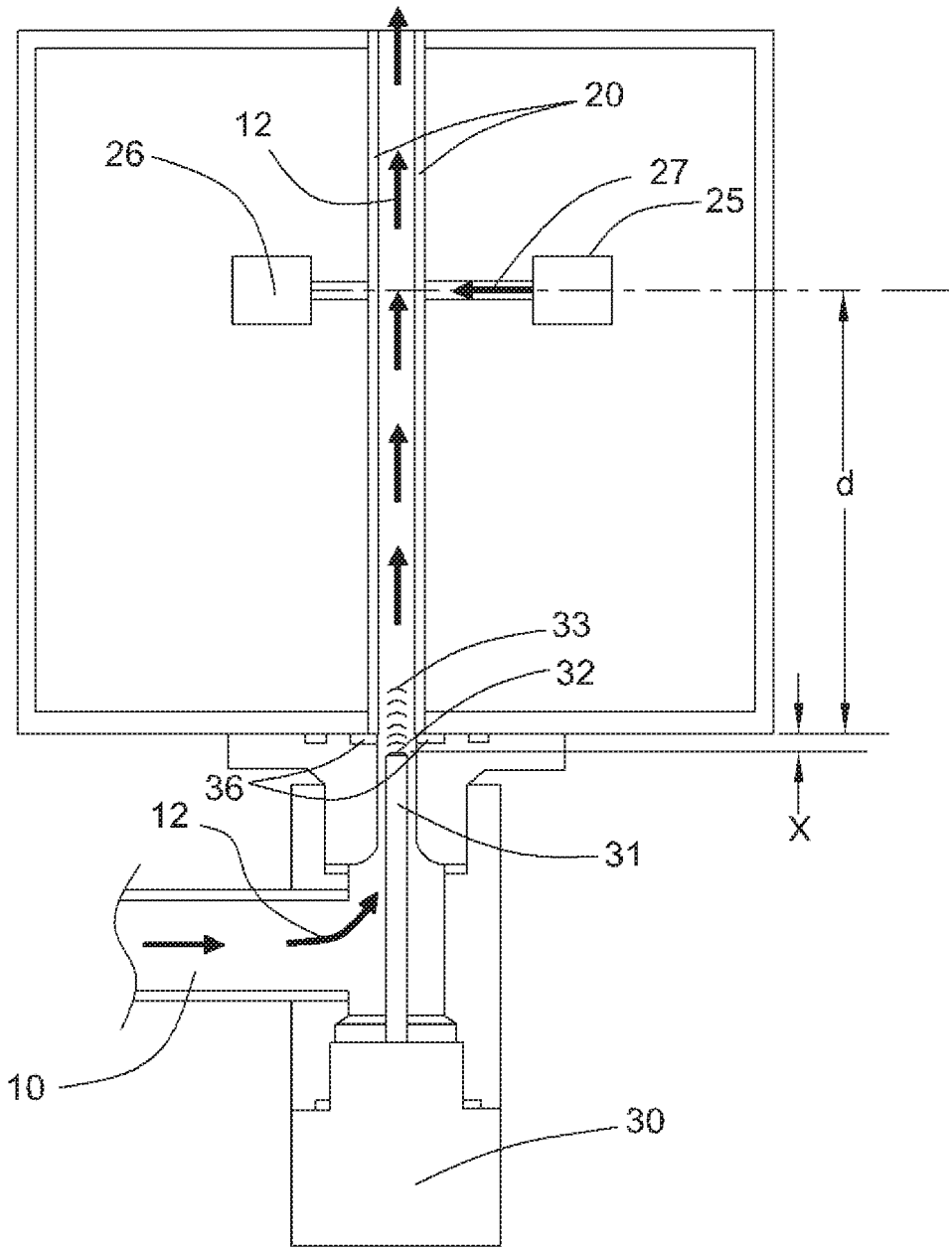

FIG. 2

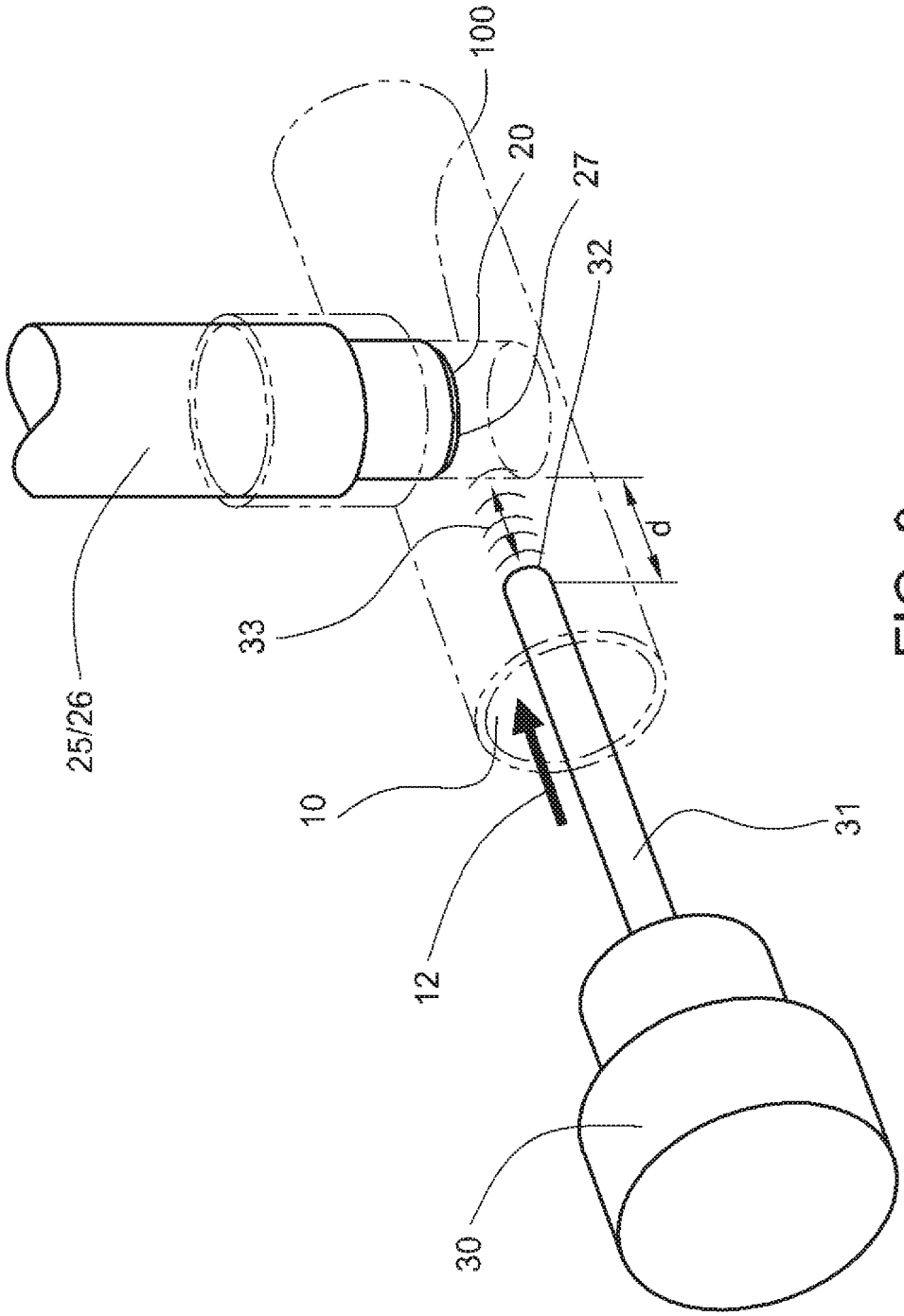

FIG. 3

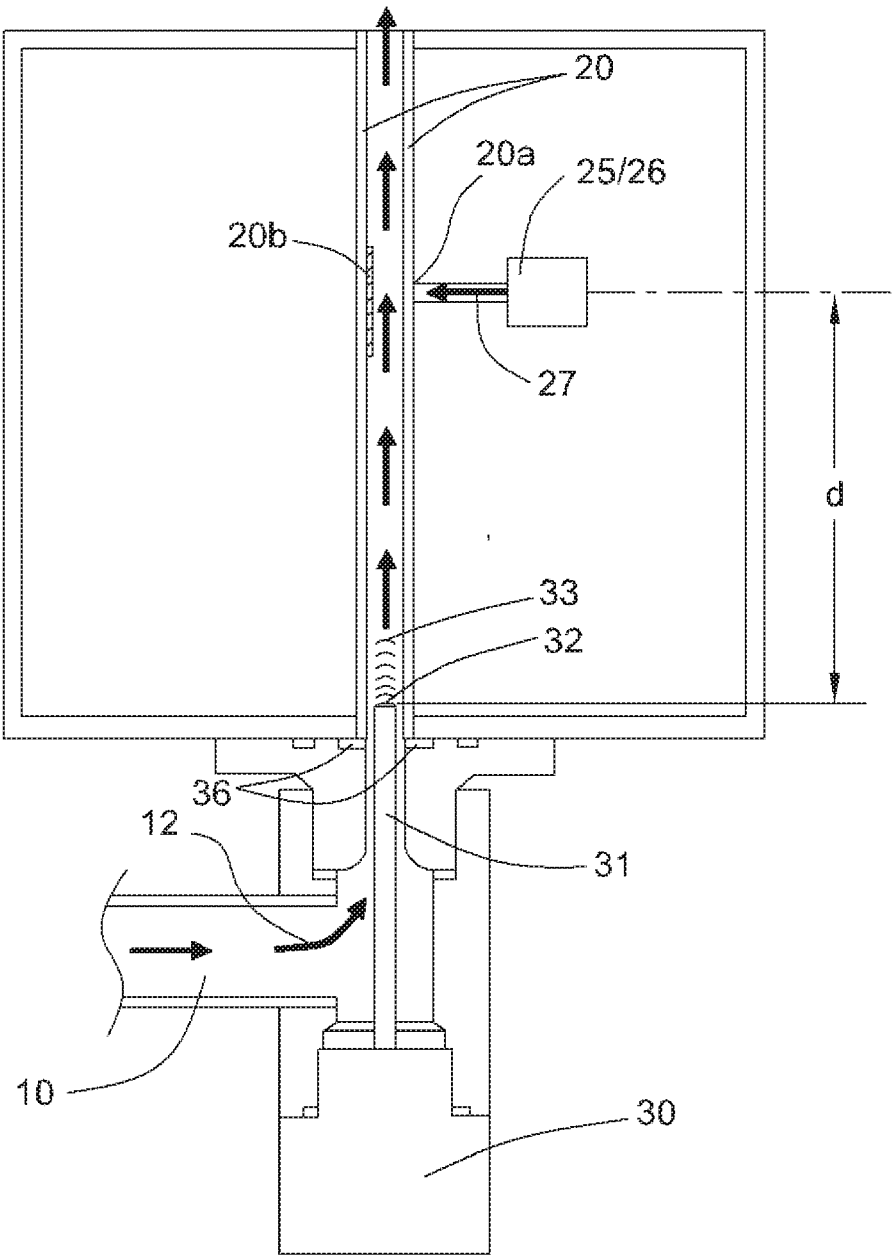

FIG. 4

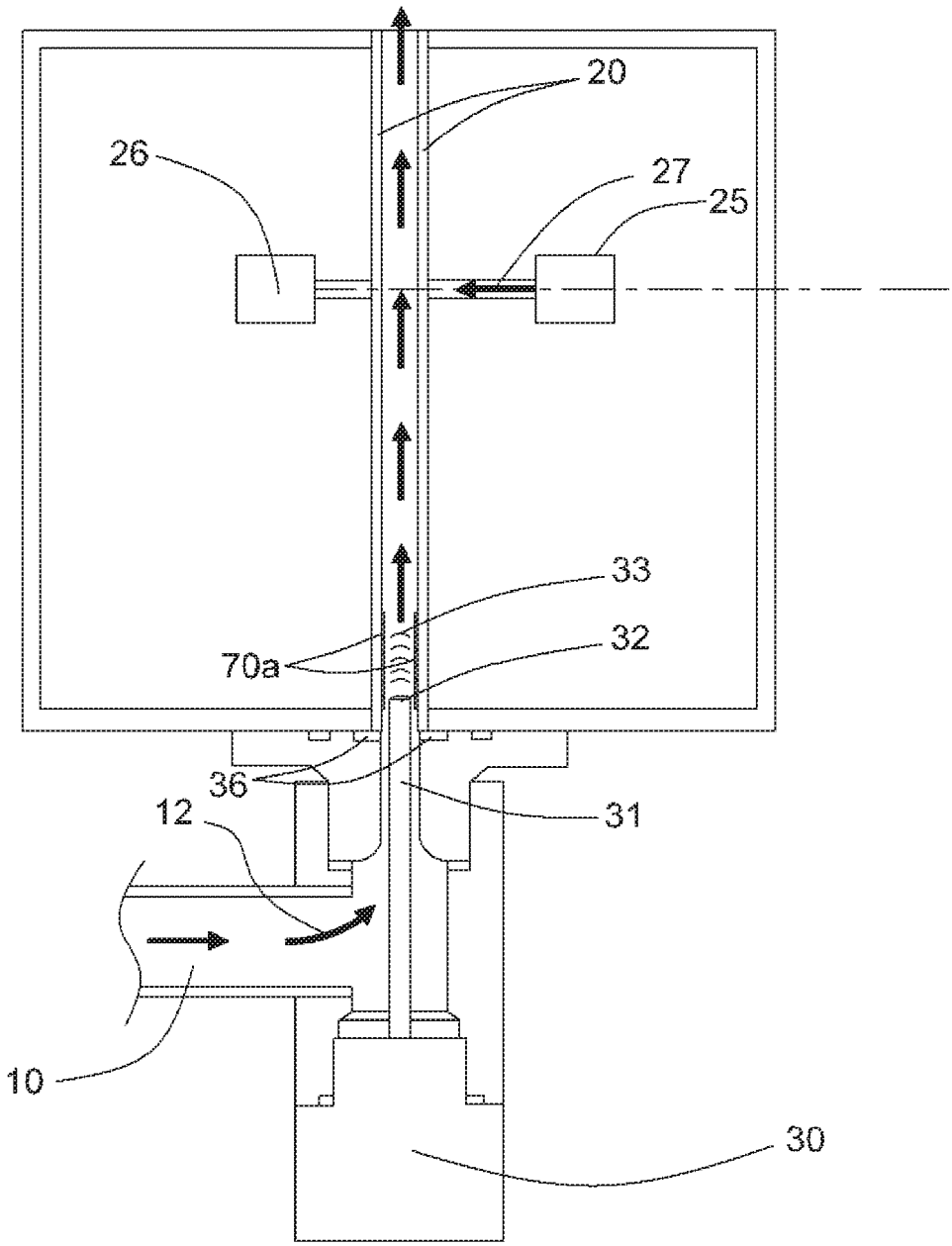

FIG. 5A

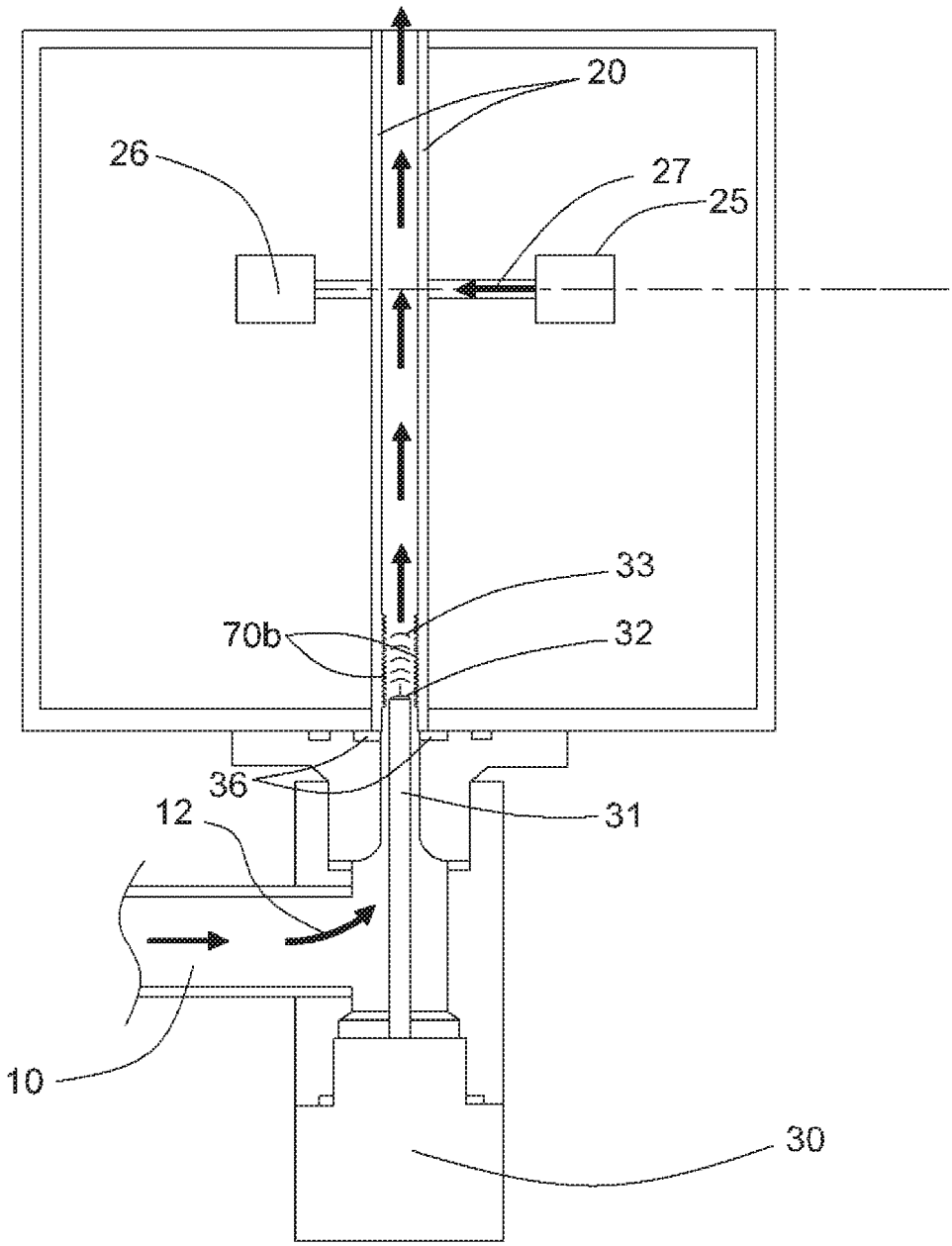

FIG. 5B

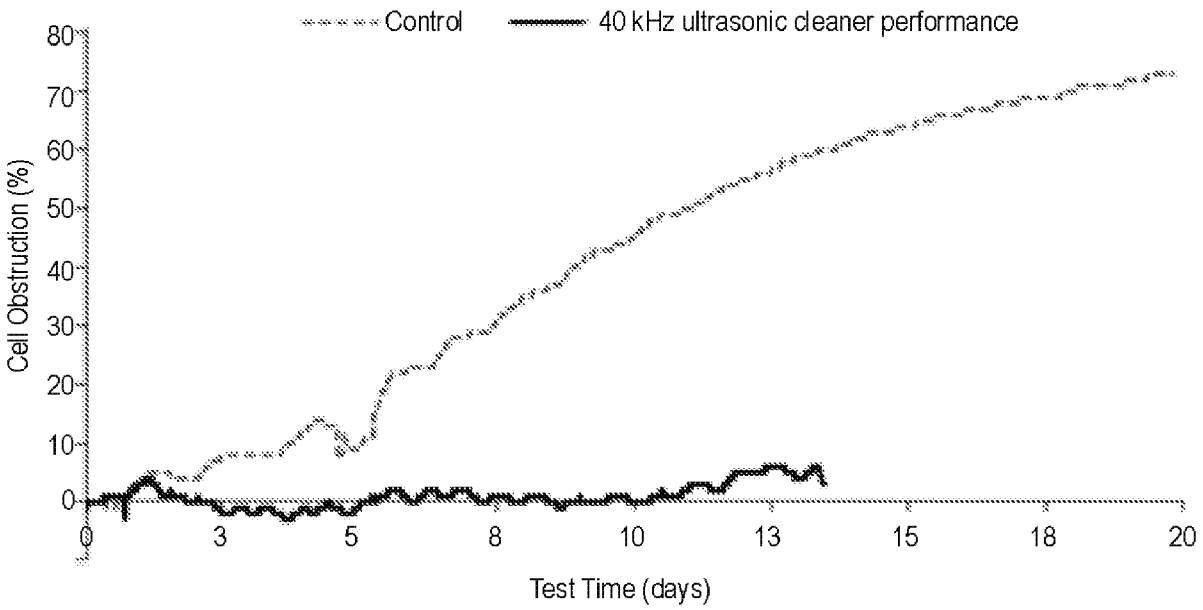
Control
40 kHz ultrasonic cleaner performance
Cell Obstruction (%)
80
70
60
50
40
30
20
10
0
0
3
5
8
10
13
15
18
20
Test Time (days)

FIG. 6

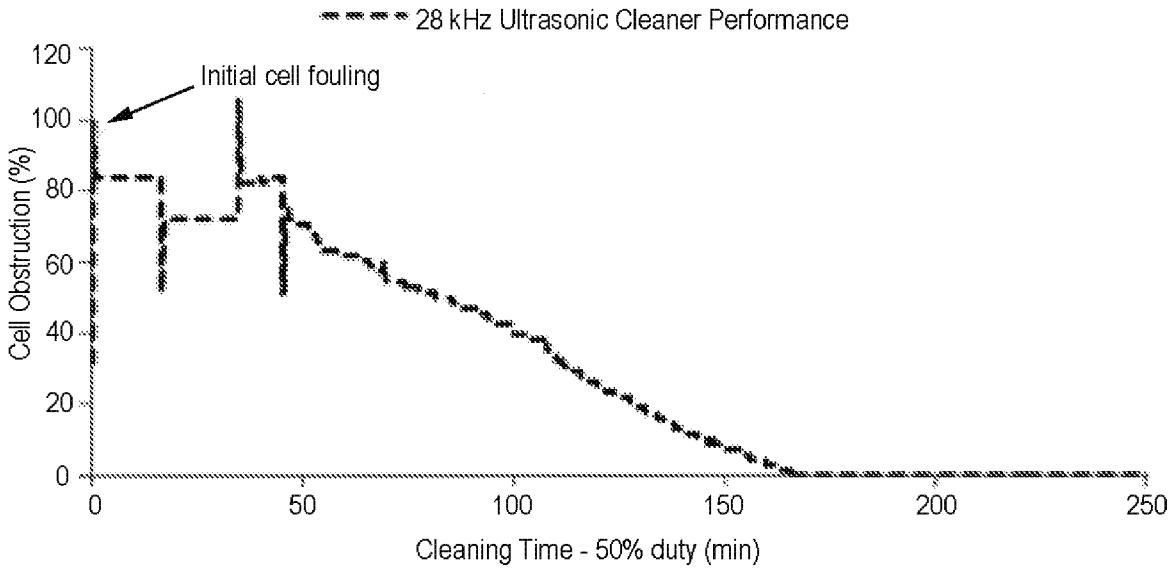
28 kHz Ultrasonic Cleaner Performance
Initial cell fouling
Cell Obstruction (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
Cleaning Time - 50% duty (min)

FIG. 7

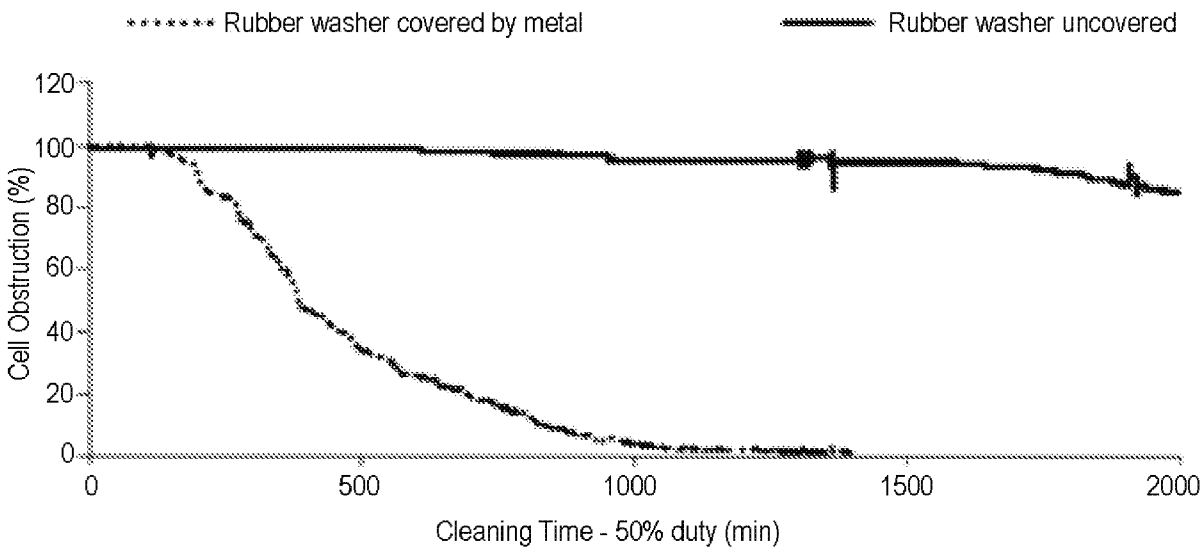
Rubber washer covered by metal
Rubber washer uncovered
120
100
80
60
40
20
0
Cell Obstruction (%)
0
500
1000
1500
2000
Cleaning Time - 50% duty (min)

FIG. 8

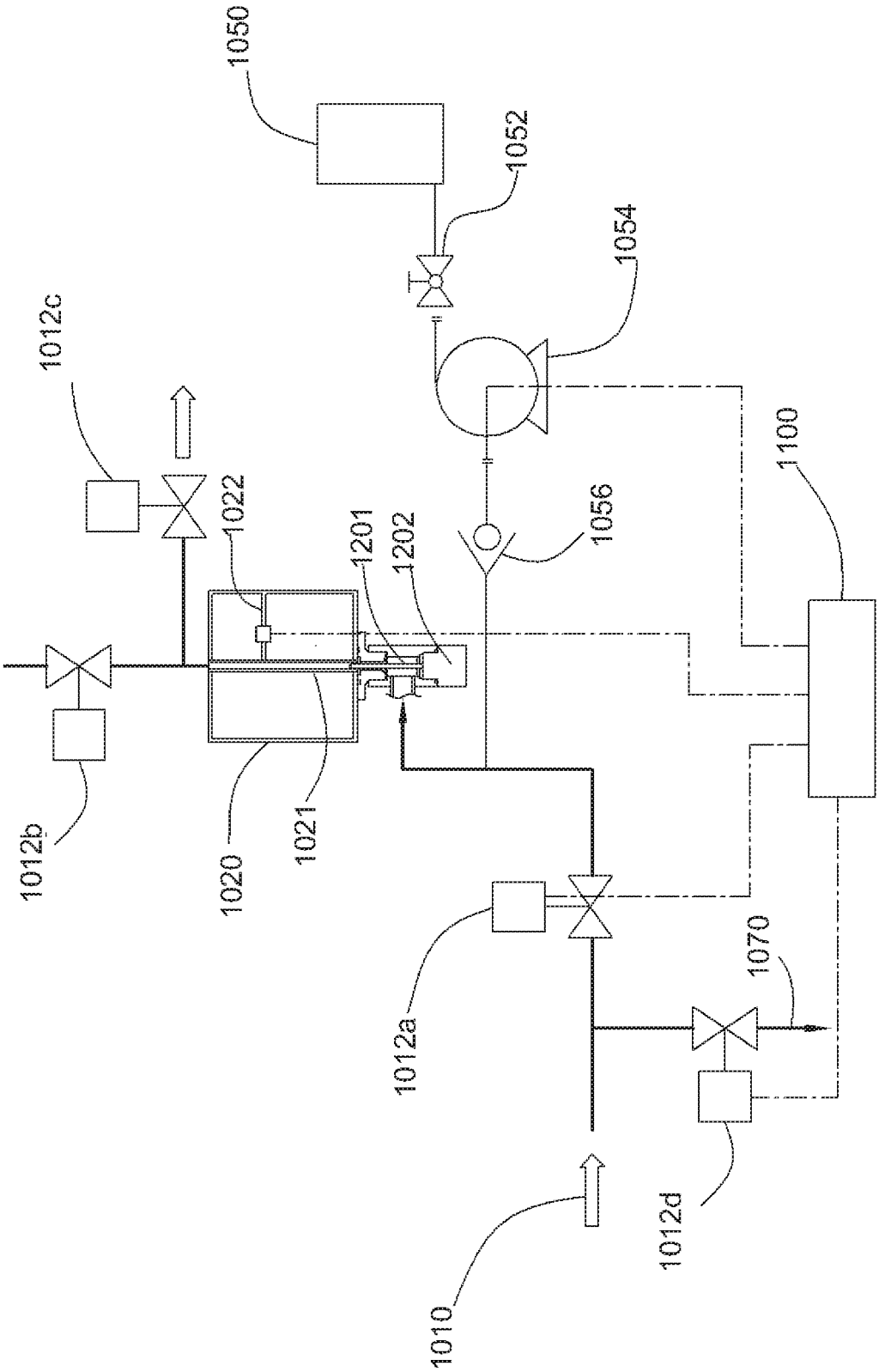
1050
1052
1054
1012c
1100
1022
1056
1201
1202
1012b
1020
1021
1012a
1070
1012d
1010

FIG. 9

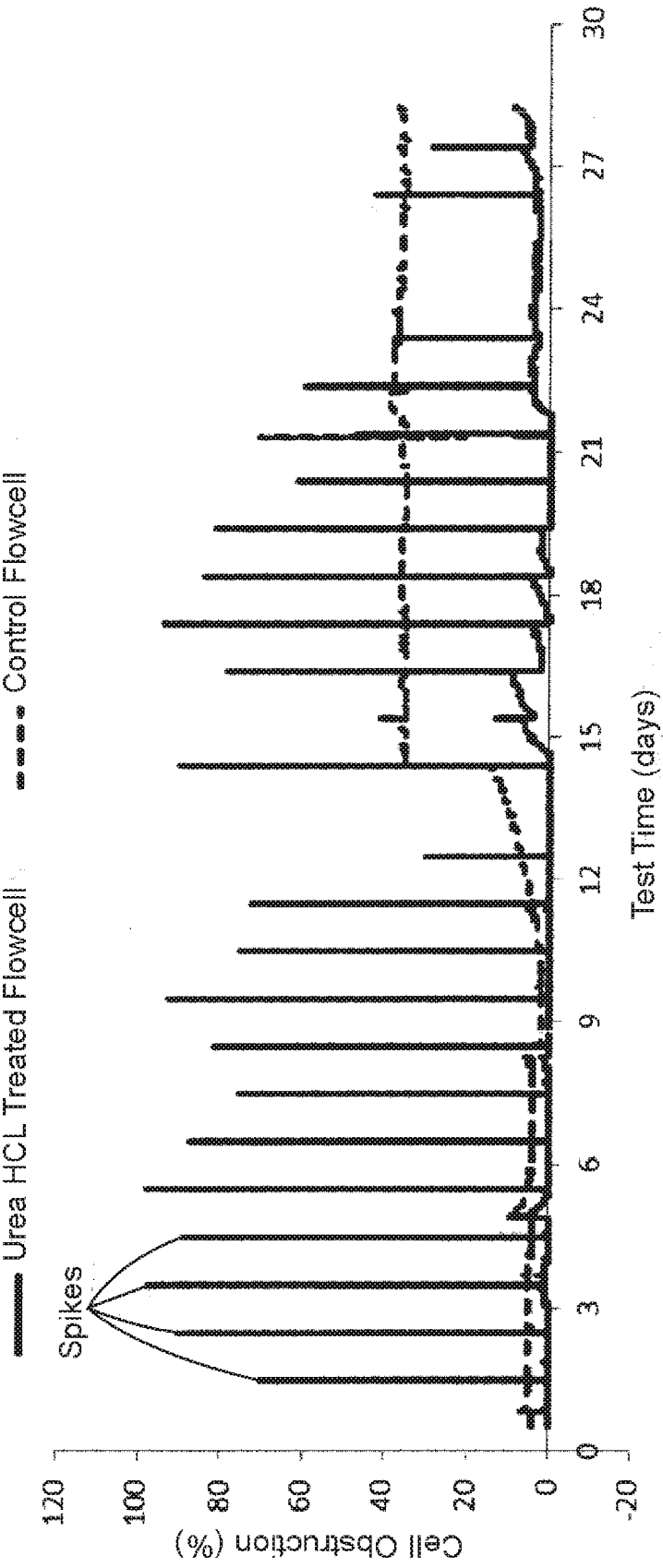
Urea HCL Treated Flowcell
Control Flowcell
Spikes
Cell Obstruction (%)
120
100
80
60
40
20
0
-20
0
3
6
9
12
15
18
21
24
27
30
Test Time (days)

FIG. 10

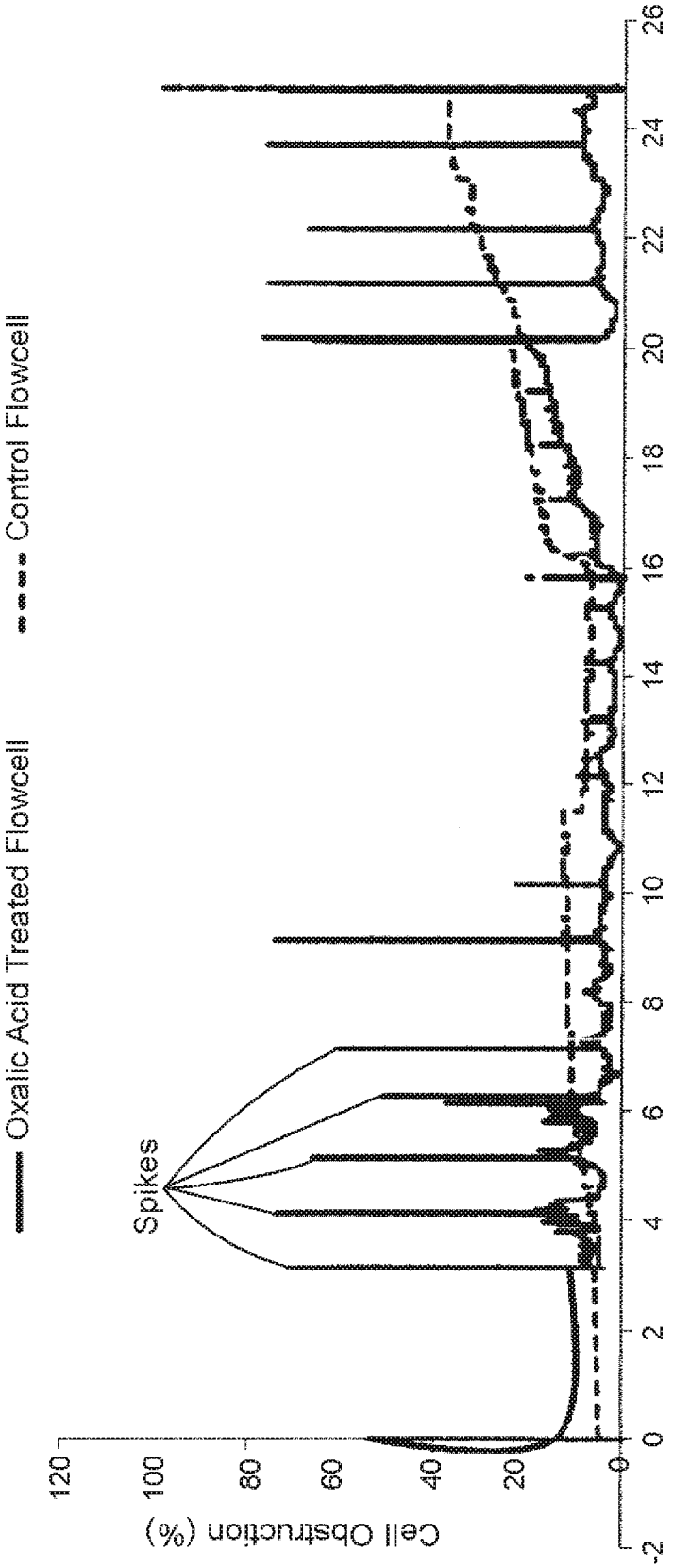
Oxalic Acid Treated Flowcell
Control Flowcell
Spikes
Cell Obstruction (%)
120
100
80
60
40
20
0
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Test Time (days)

FIG. 11

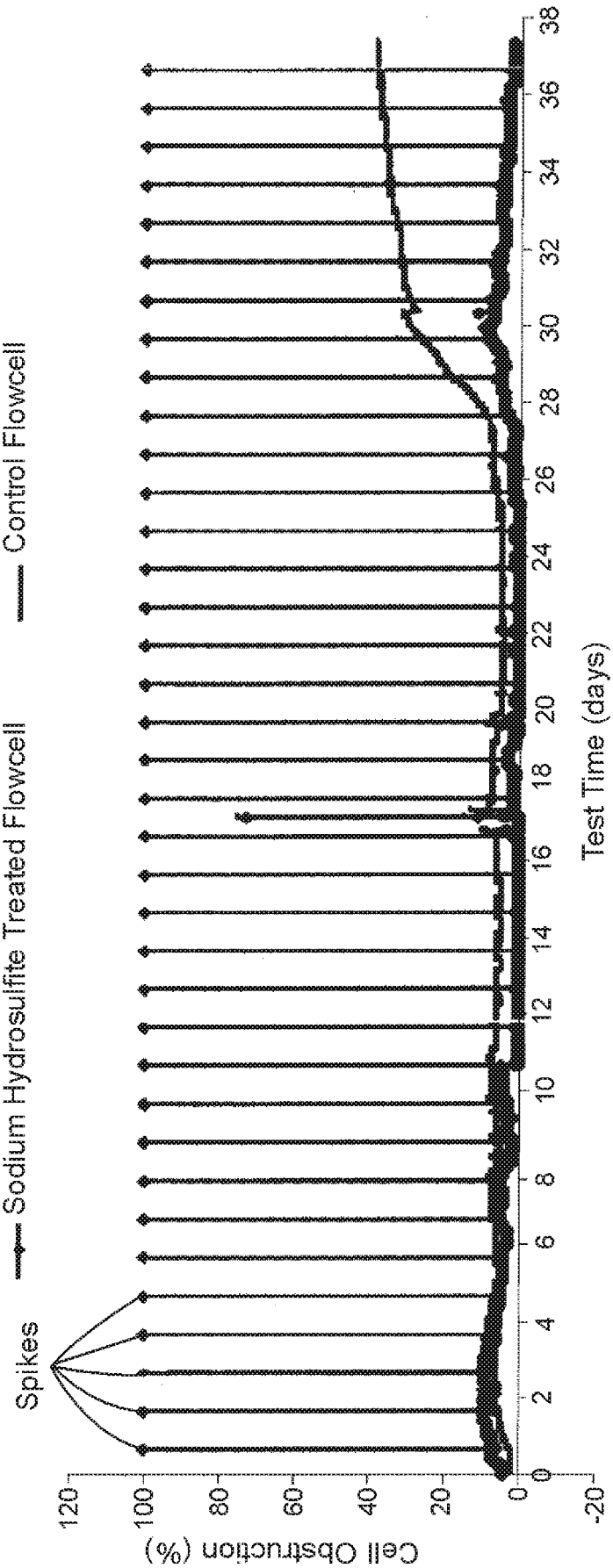
Spikes
Sodium Hydrosulfite Treated Flowcell
Control Flowcell
Cell Obstruction (%)
120
100
80
60
40
20
0
-20
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
Test Time (days)

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/012648

A. CLASSIFICATION OF SUBJECT MATTER
IPC (2016.01) G02B 27/00, G01N 21/15, B65G 45/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2016.01) G02B 27/00, G01N 21/15, B65G 45/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Databases consulted: FamPat database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013293881 A1 TOKHTUEV EUGENE; OWEN CHRISTOPHER J; SKIRDA ANATOLY; CHRISTENSEN WILLIAM M; ECOLAB USA INC 07 Nov 2013 (2013/11/07) The whole document	1-3
Y	The whole document	4-18
Y	US 2006060787 A1 MIOX CORPORATION 23 Mar 2006 (2006/03/23) The whole document	1-18
Y	US 2013186188 A1 BRADLEY MICHAEL E; MURCIA MICHAEL J; SCHWARZ DANIEL E; CHATTORAJ MITA; NALCO COMPANY 25 Jul 2013 (2013/07/25) The whole document	1-18
A	US 2007269366 A1 E.I. DU PONT DE NEMOURS AND COMPANY 22 Nov 2007 (2007/11/22) The whole document	1-18

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 May 2016	09 May 2016
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616	Authorized officer BITTON Oren Telephone No. 972-2-5657812

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/012648

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 6452672 B1 WYATT TECHNOLOGY CORPORATION 17 Sep 2002 (2002/09/17) The whole document	1-18
A	WO 2014060023 A1 STATOIL PETROLEUM AS 24 Apr 2014 (2014/04/24) The whole document	1-18

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2016/012648

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		AU 2013256467 B2	03 Mar 2016
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		EP 2844979 A4	27 Jan 2016
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2016/012648

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2016/012648

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		CA 2887947 A1	24 Apr 2014
		GB 201506984 D0	10 Jun 2015
		GB 2521327 A	17 Jun 2015
		NO 20150580 A	11 May 2015
		US 2015285733 A1	08 Oct 2015