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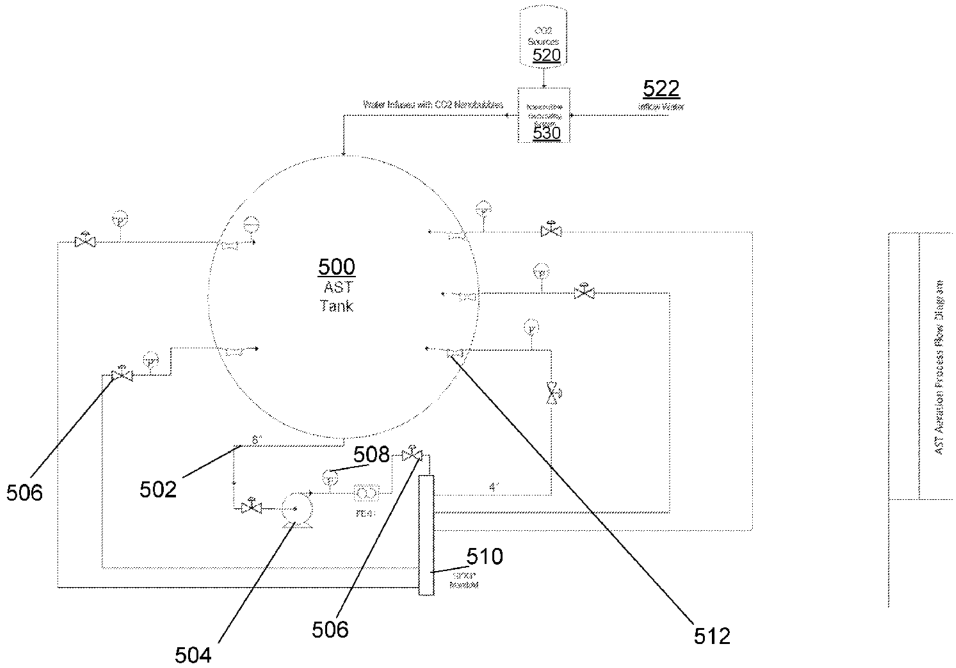

FIG. 22

(57) **Abstract:** A combined aeration system supplemented with a nanobubble delivery system to capture and store carbon, typically in the form of carbon dioxide (CO_2) (i.e., "carbon capture"). Produced water is generated as a byproduct of oil and gas extraction. Carbon dioxide is introduced to produced water in the form of nanobubbles. Aeration is used as a pre-treatment to oxidation and to preserve disinfection in produced water, and also reduces the higher temperature of produced water from the wellhead This reduction in temperature allows more carbon dioxide to be absorbed by the produced water, and the absorption process is accelerated by adding carbon dioxide to the airstream used in the aeration process.

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COMBINED AERATION AND NANOBUBBLE DELIVERY SYSTEM FOR WATER TREATMENT AND CARBON CAPTURE

This application claims benefit of and priority to U.S. Provisional Application No. 62/978,893, filed Feb. 20, 2020, which is incorporated herein in its entirety by specific reference for all purposes.

FIELD OF INVENTION

This invention relates to an apparatus and system for automatically and dynamically treated produced water from oil and gas production operations.

BACKGROUND OF THE INVENTION

A variety of oil and gas operations generate large volumes of water mixed with hydrocarbons and various contaminants, generally referred to in the industry as "produced water." Most produced water is contaminated with inorganic salts, metals, organic compounds, and other materials, such as emulsifiers or other agents that may be injected for various types of enhanced recovery operations. Typical hydrocarbons in produced water include semivolatile organic compounds ("SVOCs") and volatile organic compounds ("VOCs"). In most operations, produced water is treated by a variety of means to separate hydrocarbons from the fluid stream, and remove or treat contaminants before ultimate disposal. Examples of systems and methods for treating produced water are described in Sullivan, et al., US 2009/0101572, Ikebe, et al., US 2010/0264068, Folkvang, US 2014/0346118, Patton, US Pat. App. No. 16/246,646, filed March 22, 2019, and Patton, US Pat. App. No. 16/701,210, filed Dec. 3, 2019, all of which are incorporated herein in their entireties by specific reference for all purposes.

Patton, US Pat. App. No. 16/661,899, filed Oct. 23, 2019, which is incorporated herein in its entirety by specific reference for all purposes, describes an automated treatment system that injects an apparatus and system for dynamically treating injection fluids or fracturing fluids or produced fluids with micro-bubbles and/or nano-bubbles for various oil and gas operations, including, but not limited to, produced water or salt water disposal/injection wells, waterflooding or other forms of enhanced oil recovery (EOR) operations, and hydraulic fracturing operations.

SUMMARY OF THE INVENTION

In various exemplary embodiments, the present invention comprises an automated treatment system that injects ozone or an ozone-oxygen mixture upstream of the separators, with the dose rate changing dynamically as the produced water quality changes (as determined by continuous monitoring of the produced water quality by a plurality of sensors that detect water quality parameters in real time). In several embodiments, the system may operate as a "slipstream" injection system, that draws a portion of produced water from the produced water pipeline and injects ozone or an ozone-oxygen mixture back into the pipeline with disrupting or slowing normal operations. Disinfectants or other additives may also be injected. The ozone is consumed rapidly by bacteria, iron, sulfides and other reducers in the produced water stream, while the oxygen bubbles in the produced water provides an Induced Gas Flotation (IGF) effect in the downstream separators. The IGF effect clarifies the water by removing suspended matter in the produced water, such as oil or solids. The oxygen bubbles provide lift, floats lighter solids, and improves the oil/water separation process.

In the ozone generation process, oxygen is separated from ambient air, with the remaining "reject gas" typically vented to the atmosphere in prior art operations. In the present process, the reject gas instead is directed to the separation tanks, where it is used as a blanket gas in the tanks. The reject gas comprises mostly nitrogen and thus is inert, and is used as a gas phase maintained above the liquid (i.e., produced water) in the separation tanks or other vessels to protect the liquid from air contamination and to reduce the hazard of explosion or fire. Some or all of the reject gas (i.e., in conjunction with, or as an alternative to, the use of the reject gas as a blanket gas) may also be injected into the produced water or fluid stream using a nano-bubble diffuser prior to disposal in an injection well. The nano-bubble diffuser introduces the inert gas (mostly nitrogen) into the produced water in the form of micro- or nano-bubbles, which provide friction reduction in the fluid, and reduces the injection/disposal well pump pressure.

Various combined systems may introduce ozone/oxygen just prior to injection for "on-the-fly" disinfection and treatment, while also providing friction reduction benefits, in combination with a secondary system that introduces nitrogen or nitrogen-rich gas in the form of micro- and/or nano-bubbles (through nano-bubble diffusers) to increase or optimize friction reduction. The nitrogen nano-bubble delivery system also may be used independently as an "on-the-fly" stand-alone friction reduction system. A nitrogen concentrator also may be used to add nitrogen or increase the nitrogen concentration in a gas prior to forming the bubbles.

In further embodiments, during the ozone/oxygen injection step described above, some of the oxygen in larger bubbles will phase separate and create gas pockets within the pipeline. This gas typically off-gasses at the first release point. By use of a de-aerator (e.g., a riser under a vacuum), separated oxygen may be recovered and reinjected using a nano/micro-bubble type injection system. This will allow the oxygen to stay in suspension and provide additional treatment/oxidation from the reinjected oxygen. This oxygen gas stream may be reinjected upstream of the treatment by the main system to provide pre-treatment. Alternatively, such as when pre-treatment is not necessary, the injected oxygen gas can be added post-treatment as a pre-aeration step for produced water going into a storage system. Produced water going into a storage system is typically aerated to preserve the water. This posttreatment option will reduce and possibly eliminate the need for aeration during the storage phase.

In a further embodiment, the present invention comprises a combined aeration system supplemented with a nanobubble delivery system to capture and store carbon, typically in the form of carbon dioxide (CO_2) (i.e., “carbon capture”). As described in detail below, produced water is generated as a byproduct of oil and gas extraction. Carbon dioxide is highly soluble in water, but is reduced at higher temperatures (see addendum below for details). Produced water at the wellhead often is in excess of 100 degrees F. In the present invention, carbon dioxide is introduced to produced water in the form of nanobubbles.

Gases introduced into water form bubbles. Depending on the size of the bubbles and the solubility and stability of the gases, the bubbles may rise to the surface and produce “off gas,” or may go into solution or be dissolved in the water. This process is dependent on the pressure and temperature of the water. Very small bubbles, called “nanobubbles,” generally stay in suspension in the fluid, do not rise to the surface, and rely more on Brownian Motion for movement. Nanobubbles are also very stable and will remain in the water (or other fluid) for long periods of time (the stability of the particular gas being a factor). Nanobubbles also allow for much higher concentrations of gases to be introduced well beyond the saturation point, thereby allowing for super-saturated concentrations of the gas.

In water, carbon dioxide often will convert to carbonates, bicarbonates and, to a lesser degree, carbonic acid. This converted carbon dioxide does not enter the atmosphere as carbon dioxide gas. This process can be accelerated catalytically to form compounds such as calcium carbonate. In water storage systems, the formation of carbonates often increases the likelihood of "scaling" (although the use of scale inhibitors in oilfield water management can mitigate this). However, this concern is further mitigated as carbon dioxide in nanobubble form will itself help prevent scaling.

Aeration is a process of introducing oxygen into water to help control bacteria and improve the overall quality of the water. In the management of produced water, aeration is used as a pre-treatment to oxidation and to preserve disinfection. The higher temperature of produced water from the wellhead can be reduced through the process of aeration. This reduction in temperature allows more carbon dioxide to be absorbed by the produced water. This absorption process can be accelerated by adding carbon dioxide to the airstream used in the aeration process. Aeration in accordance with the present invention allows for additional carbon capture by decreasing the temperature of the produced water, and increasing the concentration of carbon dioxide introduced to the produced water.

DESCRIPTION OF THE DRAWINGS

Figure 1 shows a diagram of an exemplary embodiment of the present invention.

Figure 2 shows a diagram of another exemplary embodiment of the present invention.

Figure 3 shows a diagram of an embodiment with reject gas injection.

Figures 4-10 show exterior and interior views of single and dual unit embodiments of the present invention.

Figure 11 shows an example of a system status display screen.

Figure 12 shows a top view of a single unit embodiment of the present system.

Figures 13-15 show top views of a dual unit embodiment of the present system.

Figures 16-19 show examples of combined systems with friction reduction.

Figures 20-21 show examples of an oxygen de-aeration or de-gassing system in combination with one or more of the above systems.

Figures 22-24 show diagrams of exemplary embodiments of the present invention with carbon dioxide.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

Produced water originates at the wellhead, and then typically travels via pipeline **10** to tank batteries, where held for a gathering system for processing and treatment. In general, oil or other hydrocarbons are separated and collected, and the remaining wastewater is directed to an injection or disposal well **30**. One of the most common oil/water separation systems use one or more "gun barrel" separation tanks **20**, as seen in Figure 1.

As the produced water travels from the wellhead and through the gathering system, it is subjected to various treatments or processes. For example, the produced water receives injections of chemicals at or near the well head, either in batch or continuous treatments. As the produced water slows down in the gun barrel separators **20**, bacteria can accumulate and hydrogen sulfide can form. To counter this, biocidal agents typically are added upstream of the gun barrel separators. Chemical biocides generally are added at a predetermined, constant dose rate, but as produced water quality changes, this constant dose rate becomes ineffective.

In several embodiments, the present invention comprises an automated treatment system **2** that injects ozone or an ozone-oxygen mixture **40** upstream of the separators, with the dose rate changing dynamically as the produced water quality changes (as determined by continuous monitoring of the produced water quality). While ozone-oxygen may be added directly, in a preferred embodiment, as seen in Fig.1, the system may operate as a "slipstream" injection system **40**, that draws a portion of produced water from the produced water pipeline and injects ozone or an ozone-oxygen mixture into this drawn-off portion, which is then introduced back into the main produced water pipeline without disrupting or slowing normal operations. Disinfectants or other additives may also be injected into the drawn-off portion (or directly into the main produced water pipeline).

The ozone is consumed rapidly by bacteria, iron, sulfides and other reducers in the produced water stream, while the oxygen bubbles in the produced water provides an Induced Gas Flotation (IGF) effect in the downstream separators. The IGF effect clarifies the water by removing suspended matter in the produced water, such as oil or solids. The oxygen bubbles adhere to suspended matter, provide lift, floats lighter solids to the surface of the water, and improves the oil/water separation process.

In the ozone generation process, oxygen is separated from ambient air, with the remaining "reject gas" (i.e., the oxygen-depleted ambient air left after separation) typically vented to the atmosphere in prior art operations. In several embodiments of the present process, this reject gas instead is directed to the separation tank **20**, where it is used as a blanket gas **50** in the tanks, as seen in Fig. 2. This reject gas comprises mostly nitrogen and thus is inert, and is used as a gas phase maintained above the liquid (i.e., the produced water being treated) in the separation tanks or other vessels to protect the liquid from air contamination and to reduce the hazard of explosion or fire.

In yet a further embodiment, as seen in Fig. 3, some or all of the reject gas (i.e., in conjunction with, or as an alternative to, the use of the reject gas as a blanket gas **50**) may also be injected **60** into the produced water or fluid stream using a nano-bubble diffuser prior to disposal in the injection well **30**. The nano-bubble diffuser introduces the inert gas (mostly nitrogen) into the produced water in the form of micro- or nano-bubbles, which provide friction reduction in the fluid being injected into the injection/disposal well, and reduces the injection/disposal well pump pressure.

While the system may be a permanently installed component of a produced water treatment facility, in various alternative embodiments, as seen in Figures 4-10, the system is contained in one or more portable, movable containers or trailers **110** with ventilation **112**, such as a modified shipping container or wheeled trailer. One or more doors **120** allow user access to the interior, which contains the components of the system.

The container/trailer is moved to a desired location next to a section of the produced water pipeline, and fluid connection is made. The present system can thus be easily retro-fitted to existing produced water treatment facilities, removed when operations are terminated, or moved from location to location as needed. The system is fully automatic once installed, monitoring water quality and adjusting disinfectant and oxidation dosages automatically as water quality changes, and can be monitored and operated remotely, using a remote computer or mobile computing device (e.g., cell phone, tablet) (an example of a system monitoring display **122** is shown in Fig. 11).

Figure 12 shows a top view of a schematic diagram of an exemplary insulated container **110** 30 feet long and 7.5 feet wide with double doors **110** at one or both ends. The air/water handling system (e.g., air compressor, chiller, CDA) and water processing systems (O2 concentrator, O2 tank, ozone tank, injection system) are both contained in the same unit, and may be separated by an insulated panel **130** which also may have a door. The system in this configuration has a processing capacity of 15,000 BPD (barrels per day). The interior comprises power supply connections, programmable logic controller (PLC), air compressor, compressed/clean dry air package, oxygen concentrator, oxygen gas tank, chilling unit, ozone generator, air conditioning unit, transformer, quality testing unit, and fluid connections and pumps (as also seen in Figures 8-10). On one side of the unit is the injection and water quality "slipstream" piping **160** with pump(s) **162**, which may be contained in or suspended above a spill containment tank, pool, or pit. Some of the slipstream piping may or may not enter the interior of the unit, although as shown, the slipsteam piping is outside and adjacent thereto.

Figures 13-15 shows a top view of dual container units **110a, 110b** (Fig. 13 shows a view of both units, Figure 14 shows a close-up view of the "remote" air/water handling system unit not directly connected to the slipstream piping, and Figure 15 shows a close-up view of the water processing unit with the slipstream piping), each 20 feet long, with a processing capacity of 30,000 BPD. Several system components are doubled (e.g., two chillers, two air compressors, two ozone tanks, two O2 concentrators, and so on) for greater capacity, and the air/water handling system and water processing system are separately installed in respective container units as shown. Piping and conduits **114** extend between the units (e.g., A/C power conduits/cables, PLC communication conduits/cables, cooling water pipes, compressed air pipes).

While the figures show a side-by-side dual configuration, other configurations with two or more container units are possible, and are within the scope of this invention. The container units may be of various sizes, and the components therein may vary in placement and size from the figures.

In several embodiments, combined systems may be used to introduce ozone/oxygen (as described above) prior to or just prior to injection for "on-the-fly" disinfection and treatment, while also providing friction reduction benefits, in combination with a secondary nitrogen nano-bubble system that introduces nitrogen or nitrogen-rich gas in the form of micro- and/or nano-bubbles (through nano-bubble diffusers) to increase or optimize friction reduction. The nitrogen nano-bubble delivery system may be contained in a container(s) or trailer(s) in the same manner as described above for oxygen/ozone systems. The nitrogen nano-bubble delivery system **200** also may be used independently (i.e., without the ozone/oxygen system) as an "on-the-fly" stand-alone friction reduction system. A nitrogen concentrator also may be used to add nitrogen or increase the nitrogen concentration in a gas prior to forming the bubbles.

Figure 16 shows two examples of optional placement for a nitrogen nano-bubble delivery system **200a, b** at an oil/gas produced water (e.g., salt water) disposal facility. As seen, the system may be located just prior to **200a** injection in the disposal well, or further upstream, such as prior to **200b** treatment in a desander tank and gun barrel tanks (as described above). Figures 17 and 19 show similar options for fracking water treatment (e.g., typically prior to **200c** or after **200d** storage in the frac water tanks).

Figure 18 shows a schematic of a nitrogen nano-bubble delivery manifold **220**. A portion of produced water is drawn off, passed through strainers **222**, and injected with nitrogen nano-bubbles **224**, then mixed **226** back with the produced water. The treated water **230** then flows downstream for further treatment (if any) and injection. Flow meters are used to monitor fluid flow and control the introduction rates of nitrogen nano-bubbles.

In further additional embodiments, as seen in Figure 19-21, during the ozone/oxygen injection step described above, the ozone reacts almost immediately, but some of the oxygen in larger bubbles will phase separate and create gas pockets within the pipeline. This gas typically off-gasses at the first release point. By use of a de-aerator or de-gasser **300** (e.g., a riser under a vacuum), as seen in Figures 19-21, separated oxygen may be recovered and re-injected using a nano/micro-bubble type injection system. This will allow the oxygen to stay in suspension and provide additional treatment/oxidation from the reinjected oxygen. This oxygen gas stream may be reinjected as a pre-aeration step upstream **310** (either into water source storage or otherwise prior to the oxygen/ozone injection point) of the treatment by the main system to provide pre-treatment. Alternatively, such as in addition to pre-treatment or when pre-treatment is not necessary, the injected oxygen gas can be added into the water post-treatment **320** as a pre-aeration step or post-aeration step for produced water going into a storage system. Produced water going into a storage system is typically aerated to preserve the water. This posttreatment option will reduce and possibly eliminate the need for aeration during the storage phase. Figure 20 shows a salt-water or saline-water disposal operation, with both upstream **310** and downstream **320** injection of oxygen gas.

In various exemplary embodiments, the present invention comprises a combined aeration system supplemented with a nanobubble delivery system to capture and store carbon, typically in the form of carbon dioxide (CO_2) (i.e., "carbon capture"). As described in detail below, produced water is generated as a byproduct of oil and gas extraction. Carbon dioxide is highly soluble in water, but is reduced at higher temperatures (see addendum below for details). Produced water at the wellhead often is in excess of 100 degrees F. In the present invention, carbon dioxide is introduced to produced water in the form of nanobubbles.

Gases introduced into water form bubbles. Depending on the size of the bubbles and the solubility and stability of the gases, the bubbles may rise to the surface and produce "off gas," or may go into solution or be dissolved in the water. This process is dependent on the pressure and temperature of the water. Very small bubbles, called "nanobubbles," generally stay in suspension in the fluid, do not rise to the surface, and rely more on Brownian Motion for movement. Nanobubbles are also very stable and will remain in the water (or other fluid) for long periods of time (the stability of the particular gas being a factor). Nanobubbles also allow for much higher concentrations of gases to be introduced well beyond the saturation point, thereby allowing for super-saturated concentrations of the gas.

In water, carbon dioxide often will convert to carbonates, bicarbonates and, to a lesser degree, carbonic acid. This converted carbon dioxide does not enter the atmosphere as carbon dioxide gas. This process can be accelerated catalytically to form compounds such as calcium carbonate. In water storage systems, the formation of carbonates often increases the likelihood of "scaling" (although the use of scale inhibitors in oilfield water management can mitigate this). However, this concern is further mitigated as carbon dioxide in nanobubble form will itself help prevent scaling.

Aeration is a process of introducing oxygen into water to help control bacteria and improve the overall quality of the water. In the management of produced water, aeration is used as a pre-treatment to oxidation and to preserve disinfection. The higher temperature of produced water from the wellhead can be reduced through the process of aeration. This reduction in temperature allows more carbon dioxide to be absorbed by the produced water. This absorption process can be accelerated by adding carbon dioxide to the airstream used in the aeration process. Aeration in accordance with the present invention allows for additional carbon capture by decreasing the temperature of the produced water, and increasing the concentration of carbon dioxide introduced to the produced water.

Exemplary applications of the present invention are described below.

1. Produced Water Recycling/Re-use.

In produced water reuse/recycle applications, as seen in Figs. 22-24, the produced water is stored in large pits and tanks (e.g., aboveground storage tank, or AST **500**, or a treatment pit **600**. Aeration is employed in these storage devices to preserve the water and provide ongoing bacterial control; in the embodiment show, produced water is removed from the AST **500** by pipe **502** and pump **504** (flow is controlled by various valves **506** and monitored by various meters **508**). The produced water is then directed to a manifold **510** and reinjected back into the tank **500** through a plurality of pipes (with control valves and meters) with Venturi mixers **512** to agitate and promote mixing of the produced fluid in the tank.

The introduction of carbon dioxide in nanobubble form allow these storage devices to become carbon capture systems. Carbon dioxide from a source **520** is mixed with inflowing produced water **522** in a nanobubble generator **530**. The water becomes super-saturated with carbon dioxide through the creation and utilization of nanobubbles. The nanobubbles also will reduce the friction of the produced water while in storage (e.g., in the storage tank).

When the produced water is reused/recycled, as seen in Figure 23, this reduced friction will reduce pump pressures and increase the efficiency of the pumps, thereby reducing emissions. In the well completion process, using water infused with carbon dioxide nanobubbles **540** also benefits from the lower friction water by reducing the need for chemical friction reducers to be added to the completion fluid. The well completion process also becomes an additional carbon capture system when the completion fluid remains underground.

2. Waterfloods/EOR.

In waterflood applications, water and produced water are used in conventional oil well development by being injected through a plurality of injection well into underground hydrocarbon reservoir/formations to add pressure, thereby enhancing the recovery of oil from the formation (resulting in increased production from production wells in that formation). Adding carbon dioxide in the form of nanobubbles to the injection water improves the hydraulic characteristics of the injection water (e.g., through reduced friction). This also results in a better storage process for the carbon dioxide, as carbon dioxide in the present invention remains in nanobubble form. This is an advantage over the simple introduction of carbon dioxide gas to underground formations as a carbon capture technology, as the gas in that form will often migrate upwards to the surface and re-enter the atmosphere, thereby reducing its effectiveness for carbon capture. In addition, as mentioned above, the present invention avoids the conversion (and thus removal or elimination) of carbon dioxide.

3. Emissions Flaring.

Patton, US Pat. App. No. 16/653,864, filed Oct 15, 2019, which is incorporated herein in its entirety by specific reference for all purposes, describes a system and apparatus for flaring hydrocarbon gas from oilfield operations using produced water (referred to as the “hydroflare process”). Emissions from flaring are scrubbed. Ozone may be added. In the flaring combustion process, carbon dioxide is formed, which can be captured through a variety of processes (e.g., amine systems). Carbon dioxide from the hydroflare process can be used for the applications and processes described above. A unique benefit from this use is combining the reduction of emissions from the treatment of oilfield gas with the increased carbon capture through new uses for the captured carbon dioxide in nanobubble form. Introducing carbon dioxide in the form of nanobubbles provides a unique way of storing carbon dioxide in a stable form by injecting it underground, particularly where produced water is already being used as an injection fluid.

Thus, it should be understood that the embodiments and examples described herein have been chosen and described in order to best illustrate the principles of the invention and its practical applications to thereby enable one of ordinary skill in the art to best utilize the invention in various embodiments and with various modifications as are suited for particular uses contemplated. Even though specific embodiments of this invention have been described, they are not to be taken as exhaustive. There are several variations that will be apparent to those skilled in the art.

CLAIMS

What is claimed is:

1. A method for storage of carbon, comprising:

infusing a fluid stream with carbon dioxide in the form of nanobubbles; and

storing the infused fluid stream in one or more of the following: a storage tank, a fluid treatment pit, or an underground formation or formations.

2. The method of claim 1, wherein the infused fluid stream is stored in an underground formation or formations by a well completion process.

3. The method of claim 1, wherein the carbon dioxide is obtained from flaring of hydrocarbon gas in oilfield operations.

4. The method of claim 1, wherein the fluid stream is produced water from oilfield operations.

5. A fluid treatment system for treating a fluid stream and storing carbon, comprising:

a fluid injection or disposal well;

one or more fluid treatment tanks, wherein the one or more fluid treatment tanks comprise at least one separator;

one or more downstream pipes connecting the one or more fluid treatment tanks with the fluid injection or disposal well;

upstream pipes in fluid connection with the one or more fluid treatment tanks;

an ozone injection system configured to inject ozone gas or an ozone-oxygen mixture gas into the fluid stream prior to the fluid reaching the fluid injection or disposal well;

an oxygen de-gasser or de-aerator, configured to remove gaseous oxygen from the fluid stream;

a carbon dioxide nanobubble generator, configured to introduce carbon dioxide into the fluid stream.

6. The system of claim 5, wherein the ozone injection system injects the ozone gas or ozone-oxygen mixture gas upstream of the one or more fluid treatment tanks.

7. The system of claim 5, wherein the ozone injection system is a slipstream injection system configured to draw off a portion of the fluid stream for ozone gas or ozone-oxygen mixture gas injection.

8. The system of claim 5, wherein the ozone injection system injects a dose rate of ozone gas or ozone-oxygen mixture gas that varies over time.

9. The system of claim 8, wherein the dose rate varies dynamically as the quality of the fluid stream changes based upon continuous monitoring of the fluid stream quality.

10. The system of claim 5, wherein the ozone gas or an ozone-oxygen mixture gas is injected as nano-bubbles or micro-bubbles.

11. The system of claim 5, wherein the ozone injection system produces oxygen-depleted reject gas in the process of producing oxygen and/or ozone.

12. The system of claim 5, wherein the reject gas is directed to the at least one separator as blanket gas.

13. The system of claim 5, wherein the ozone injection system is contained in whole or in part in a moveable container.

14. The system of claim 5, wherein the ozone injection system is contained in whole or in part in two or more moveable containers or trailers.

15. The system of claim 5, wherein the fluid stream is produced water from oil or gas wells.

16. The system of claim 5, wherein the fluid stream is fracturing fluid for a hydrocarbon fracturing operation.

17. The system of claim 5, further comprising a nitrogen nano-bubble delivery system, configured to inject nitrogen or nitrogen-rich gas into the fluid stream.

18. The system of claim 5, wherein nitrogen or nitrogen-rich gas is injected downstream of the one or more fluid treatment tanks.

19. The system of claim 17, wherein said nitrogen nano-bubble delivery system comprises a manifold with one or more strainers and a mixer.

20. The system of claim 5, further comprising an oxygen gas injector configured to reinject said gaseous oxygen in nano-bubble or micro-bubble form into the fluid stream at different points from the point of removal.

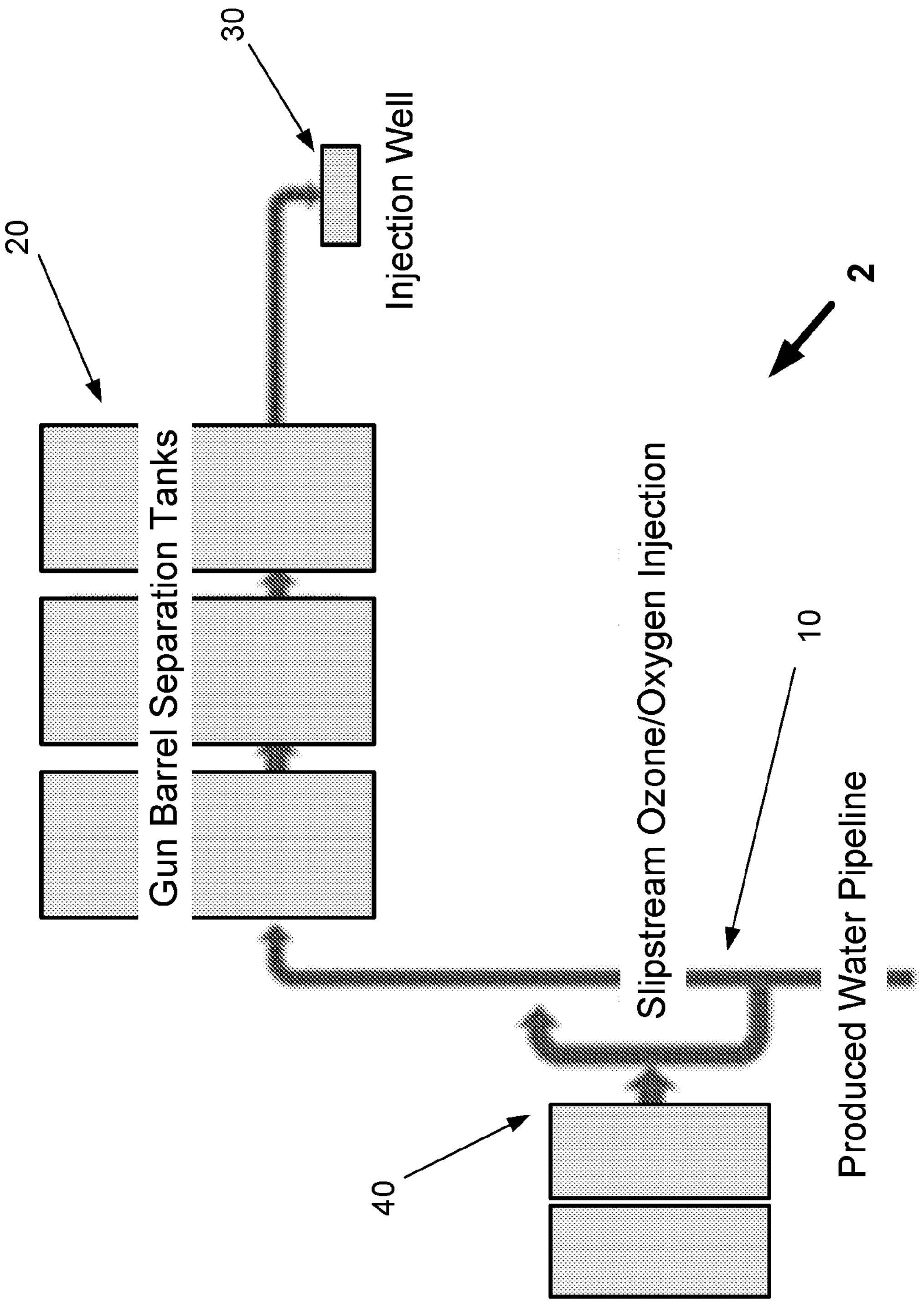

30
Injection Well
20
Gun Barrel Separation Tanks
2
Slipstream Ozone/Oxygen Injection
10
Produced Water Pipeline
40

FIG. 1

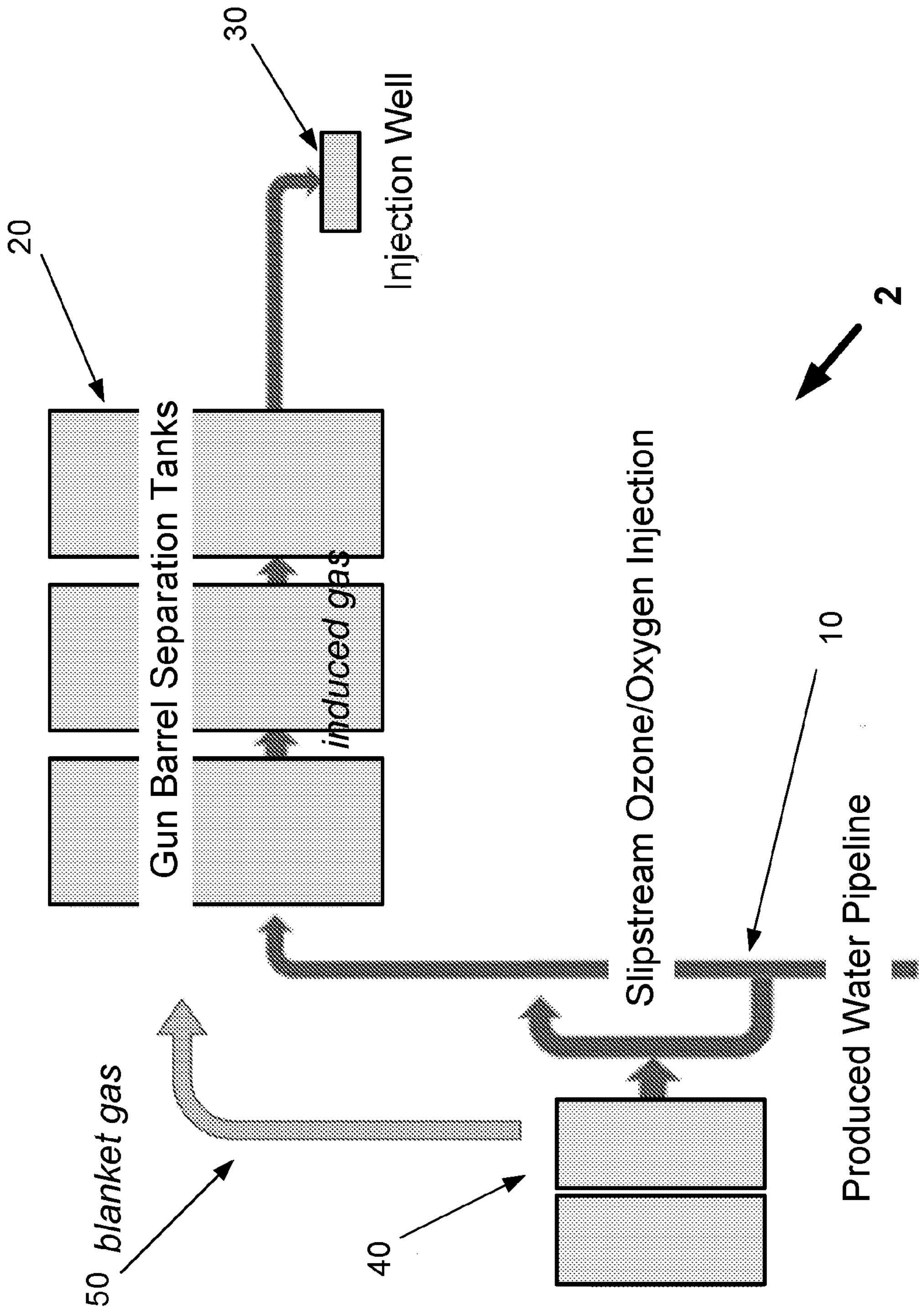

30
Injection Well
20
Gun Barrel Separation Tanks
induced gas
2
Slipstream Ozone/Oxygen Injection
10
Produced Water Pipeline
blanket gas
50
40

FIG. 2

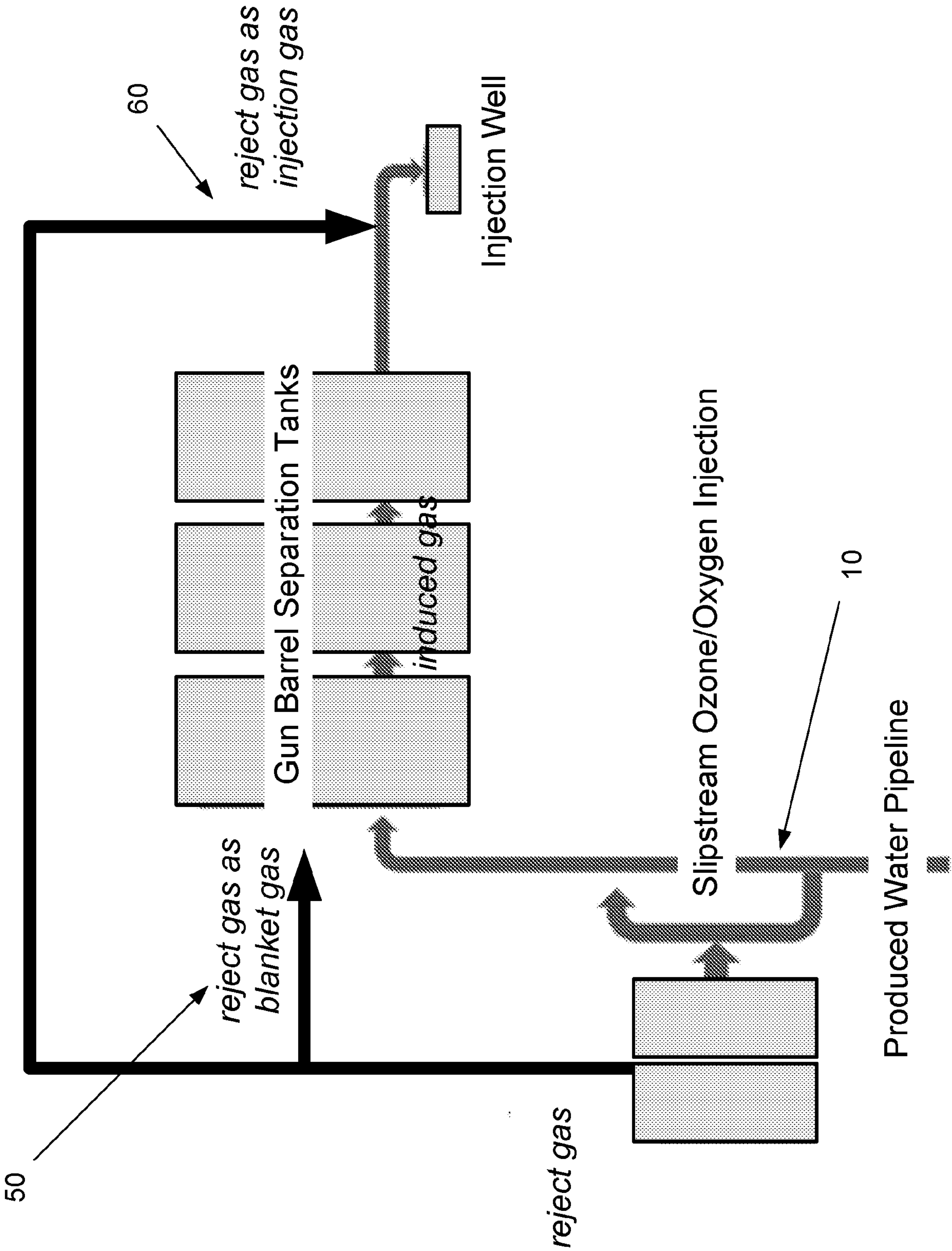

60
reject gas as injection gas
Injection Well
Gun Barrel Separation Tanks
induced gas
Slipstream Ozone/Oxygen Injection
10
Produced Water Pipeline
reject gas as blanket gas
50
reject gas

FIG. 3

110

FIG. 4

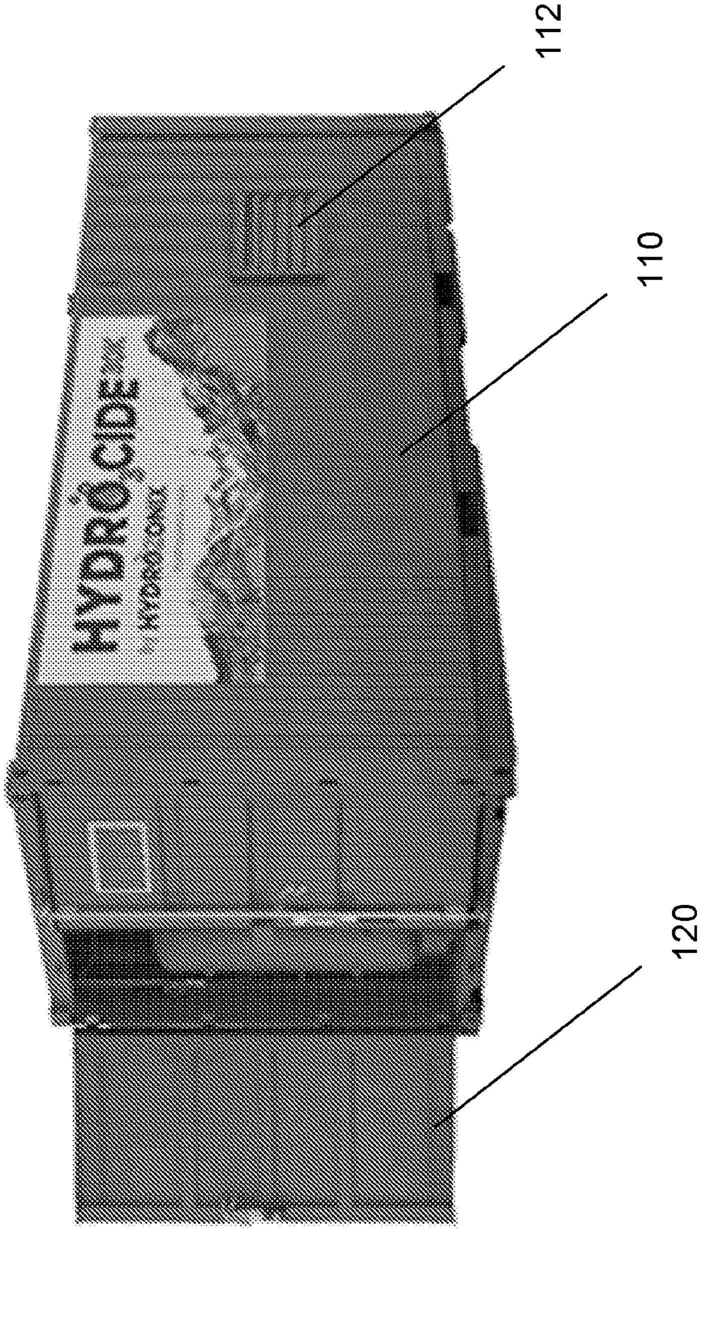
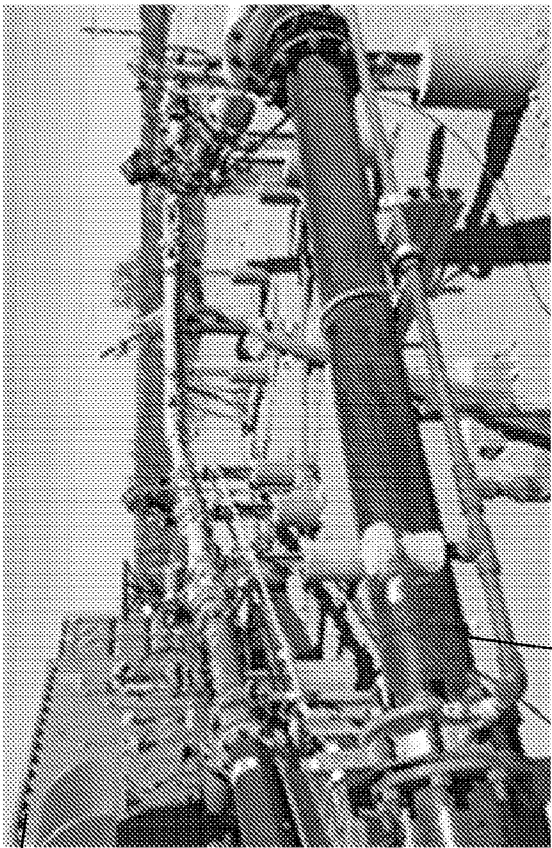


FIG. 5

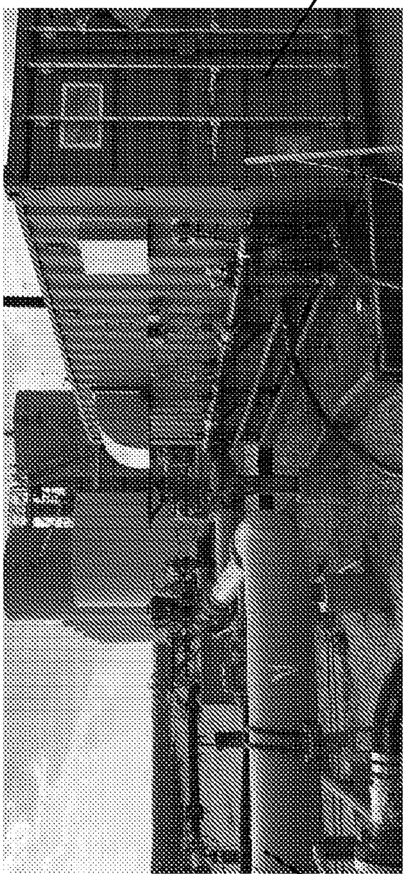


10

110

FIG. 6

110



10

FIG. 7

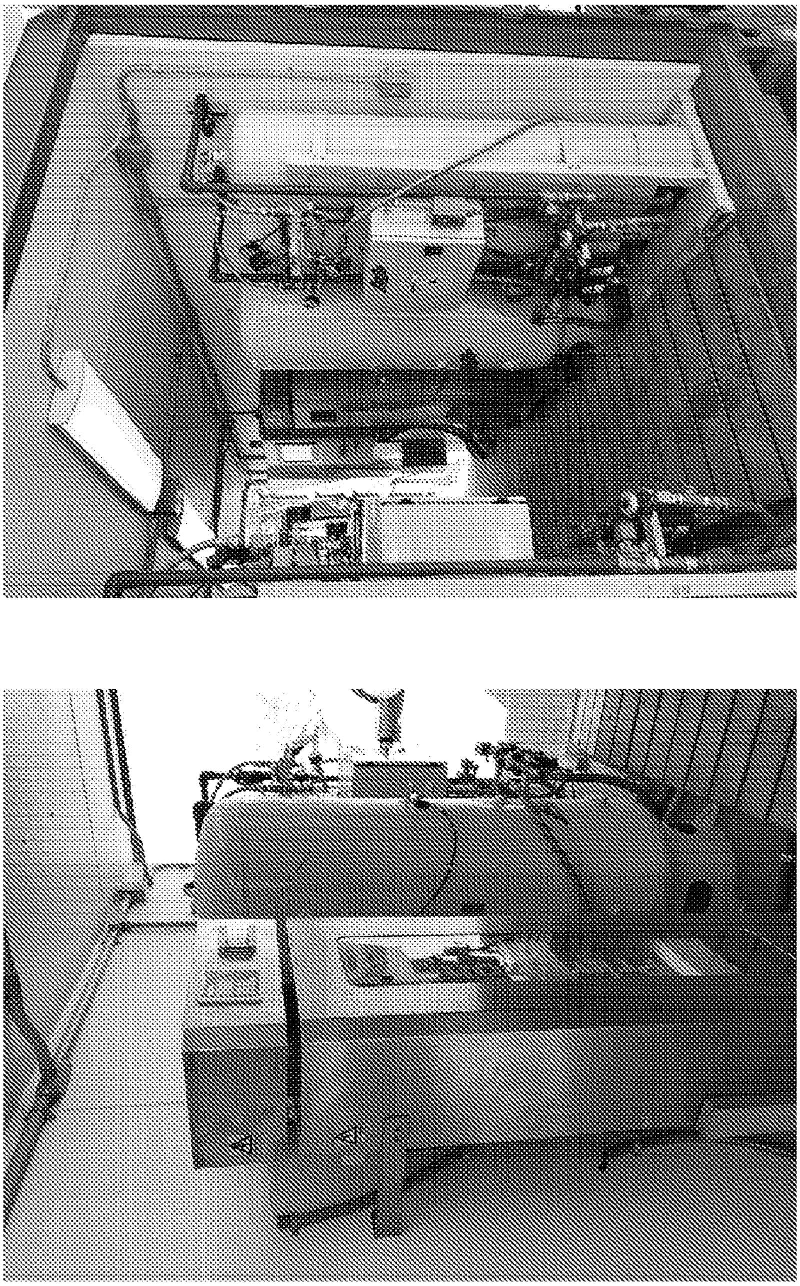


FIG. 8

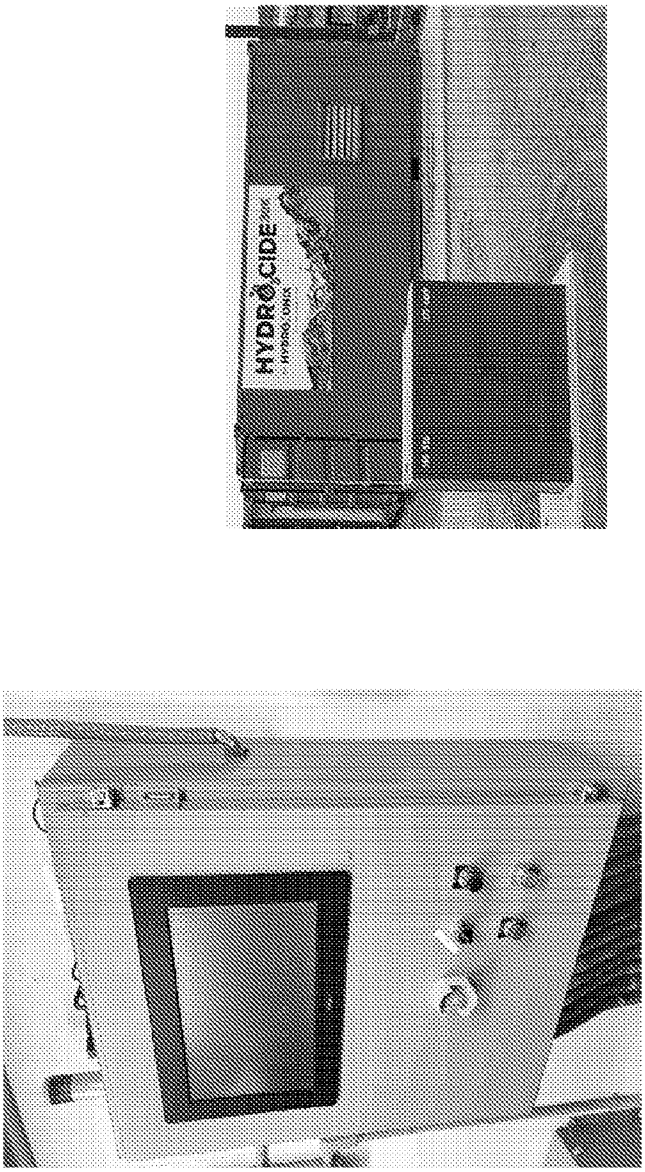


FIG. 9

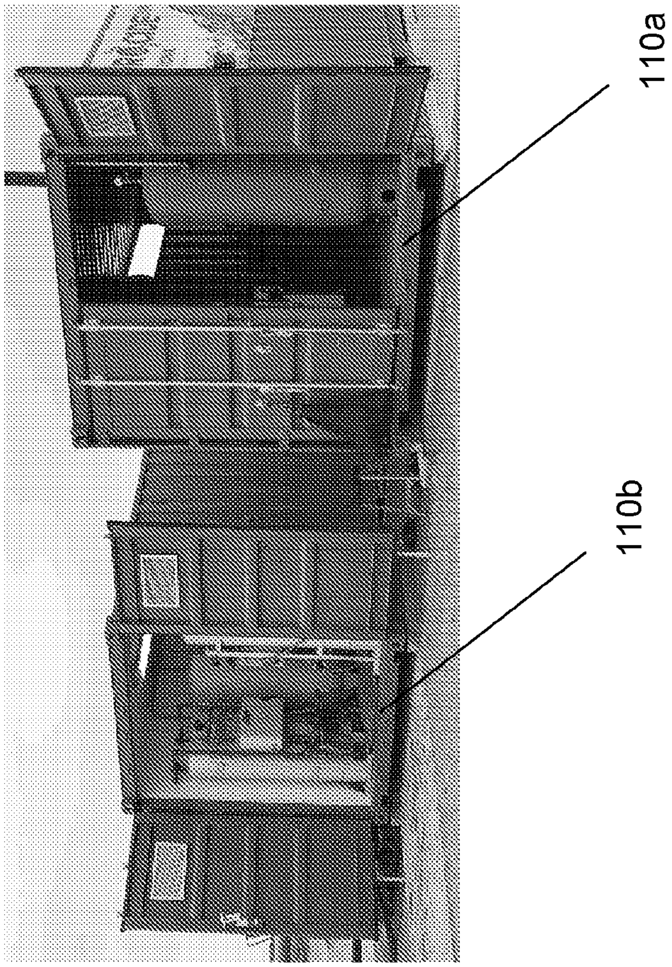


FIG. 10

122

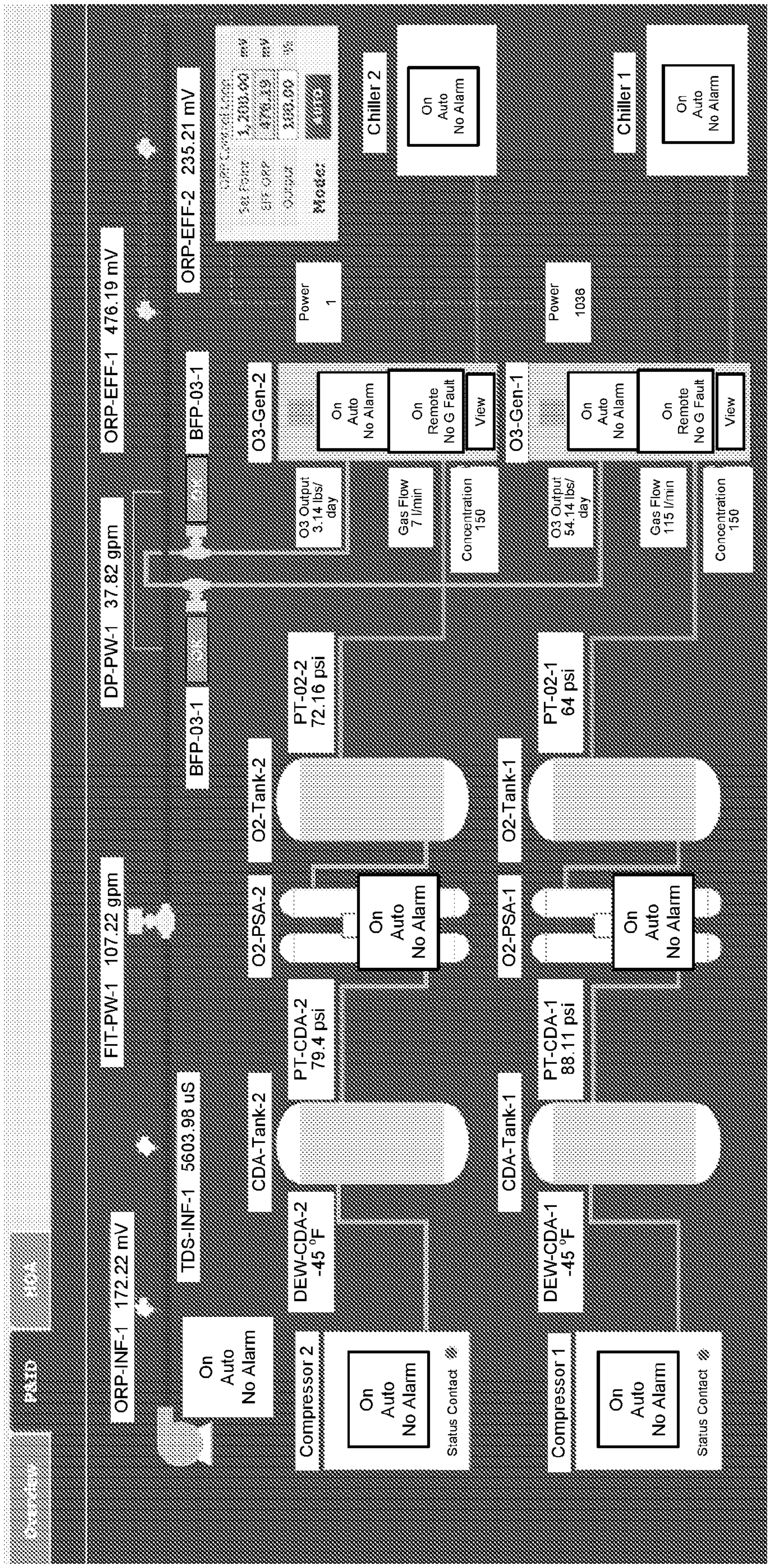

P&ID
HOA
ORP-INF-1 172.22 mV
On
Auto
No Alarm
TDS-INF-1 5603.98 uS
FIT-PW-1 107.22 gpm
DP-PW-1 37.82 gpm
ORP-EFF-1 476.19 mV
ORP-EFF-2 235.21 mV
BFP-03-1
BFP-03-1
Compressor 2
On
Auto
No Alarm
Status Contact
DEW-CDA-2
-45 °F
CDA-Tank-2
PT-CDA-2
79.4 psi
O2-PSA-2
On
Auto
No Alarm
O2-Tank-2
PT-02-2
72.16 psi
O3 Output
3.14 lbs/
day
Gas Flow
7 l/min
Concentration
150
O3-Gen-2
On
Auto
No Alarm
On
Remote
No G Fault
View
Power
1
Mode:
Chiller 2
On
Auto
No Alarm
Compressor 1
On
Auto
No Alarm
Status Contact
DEW-CDA-1
-45 °F
CDA-Tank-1
PT-CDA-1
88.11 psi
O2-PSA-1
On
Auto
No Alarm
O2-Tank-1
PT-02-1
64 psi
O3 Output
54.14 lbs/
day
Gas Flow
115 l/min
Concentration
150
O3-Gen-1
On
Auto
No Alarm
On
Remote
No G Fault
View
Power
1036
Chiller 1
On
Auto
No Alarm

FIG. 11

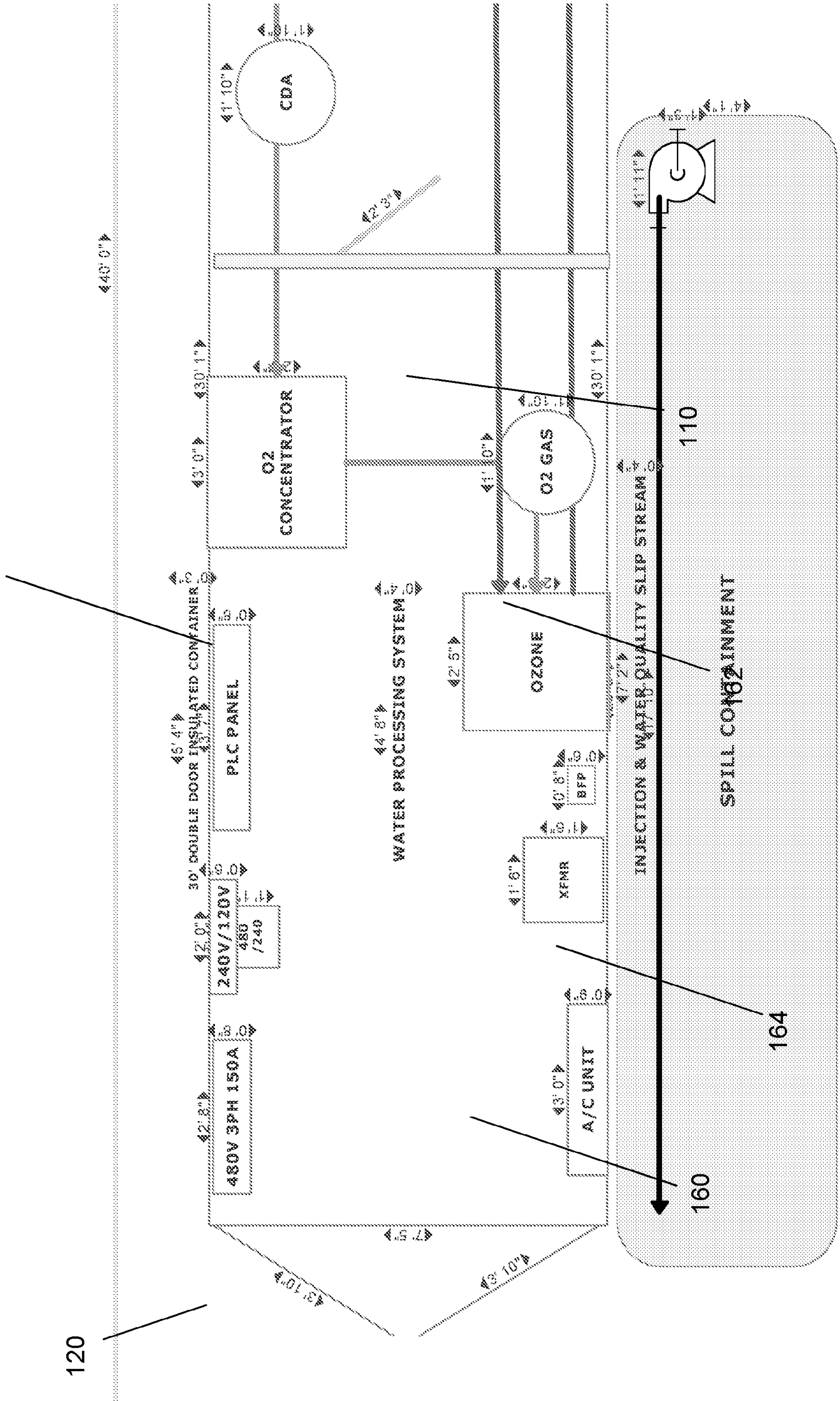

CDA
O2 CONCENTRATOR
O2 GAS
OZONE
30' DOUBLE DOOR INSULATED CONTAINER
PLC PANEL
WATER PROCESSING SYSTEM
INJECTION & WATER QUALITY SLIP STREAM
SPILL CONTAINMENT
BFP
XFMR
240V/120V
480 /240
480V 3PH 150A
A/C UNIT
110
120
130
160
162
164

FIG. 12

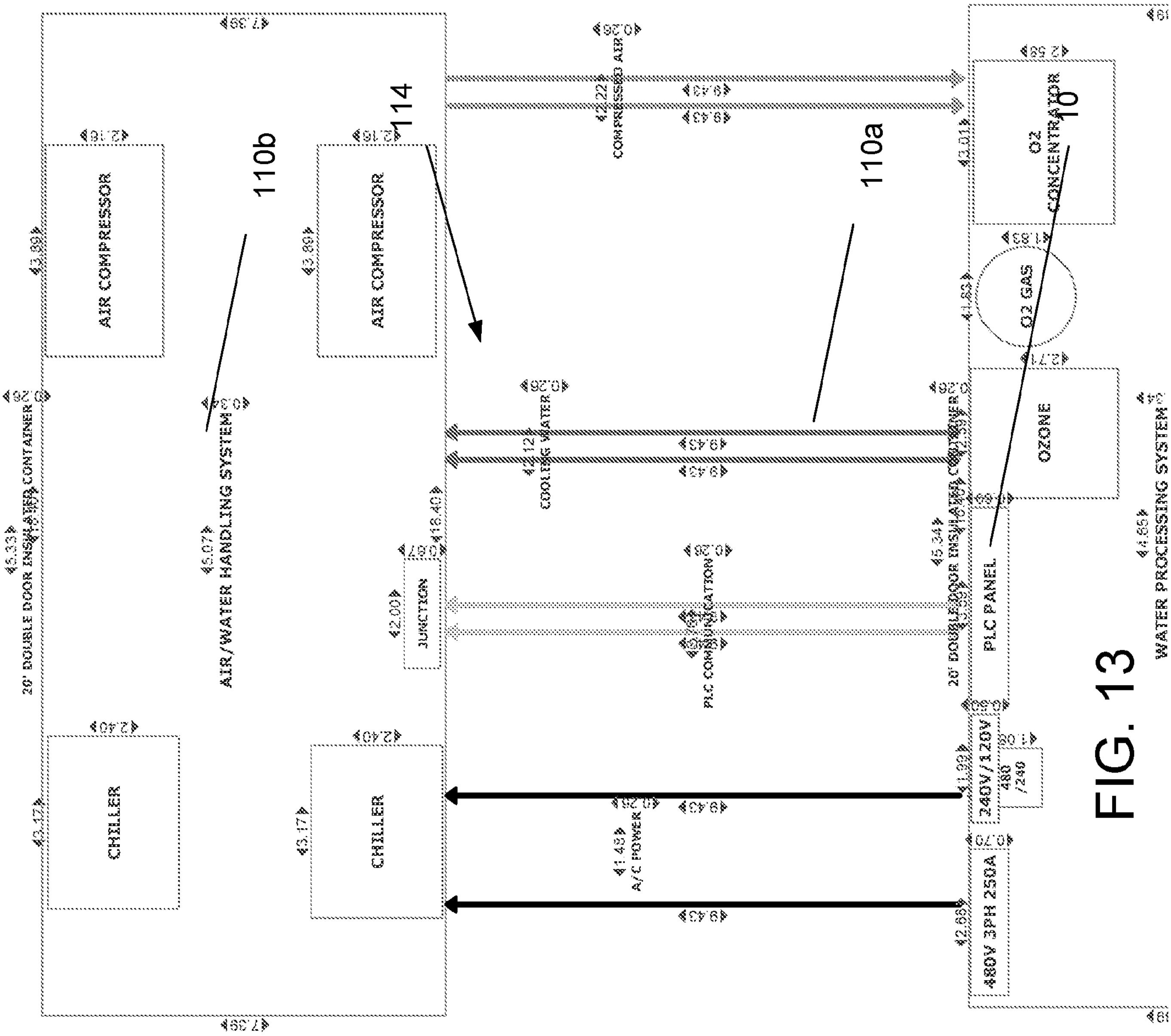

20' DOUBLE DOOR INSULATED CONTAINER
AIR/WATER HANDLING SYSTEM
110b
AIR COMPRESSOR
AIR COMPRESSOR
114
CHILLER
CHILLER
JUNCTION
COMPRESSED AIR
COOLING WATER
PLC COMMUNICATION
A/C POWER
110a
10
O2 CONCENTRATOR
O2 GAS
OZONE
PLC PANEL
240V/120V
480 /240
480V 3PH 250A
20' DOUBLE DOOR INSULATED CONTAINER
WATER PROCESSING SYSTEM

FIG. 13

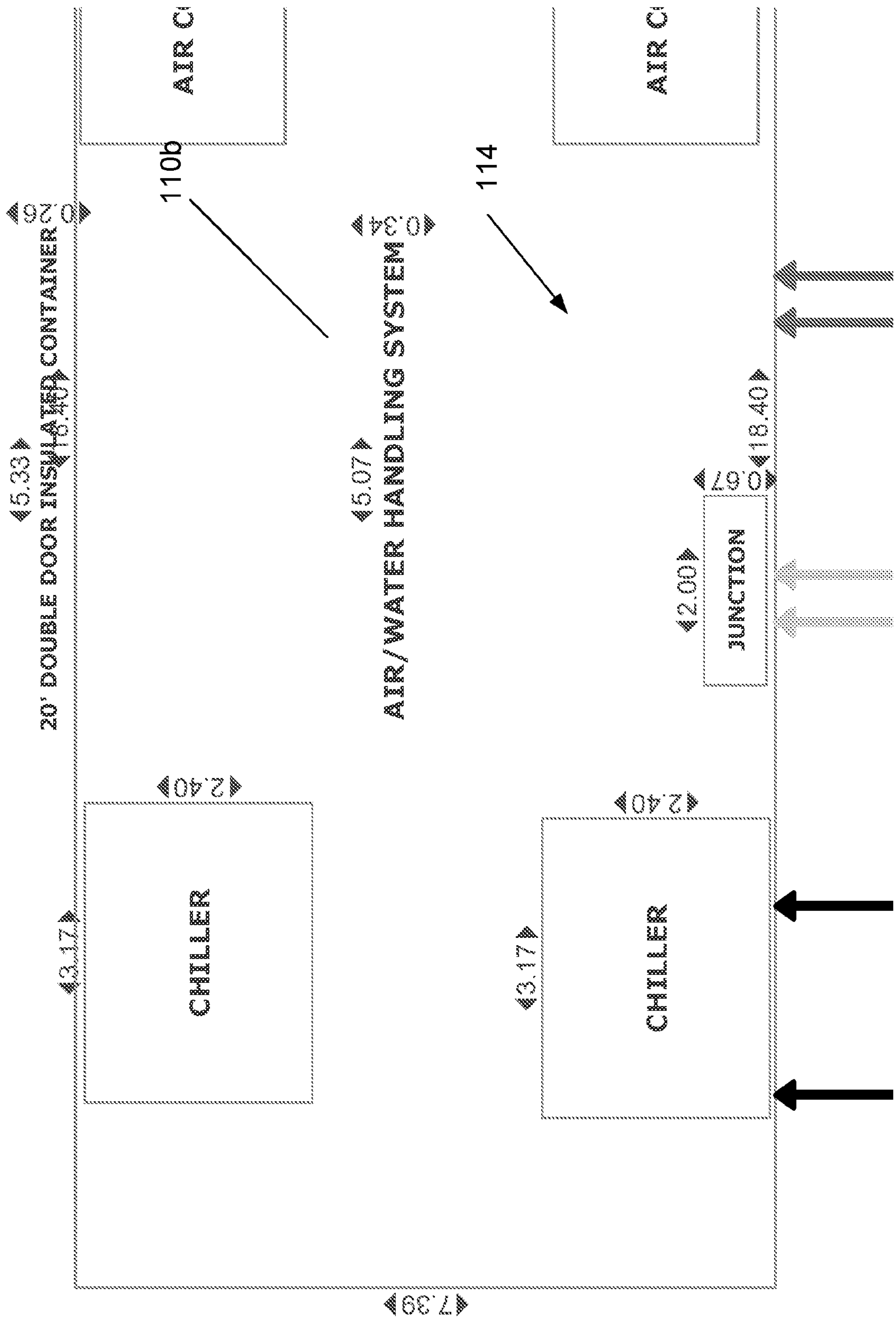

20' DOUBLE DOOR INSULATED CONTAINER
AIR/WATER HANDLING SYSTEM
110b
114
CHILLER
CHILLER
JUNCTION
0.26
5.33
18.40
0.34
5.07
0.67
2.00
2.40
2.40
3.17
3.17
7.39

FIG. 14

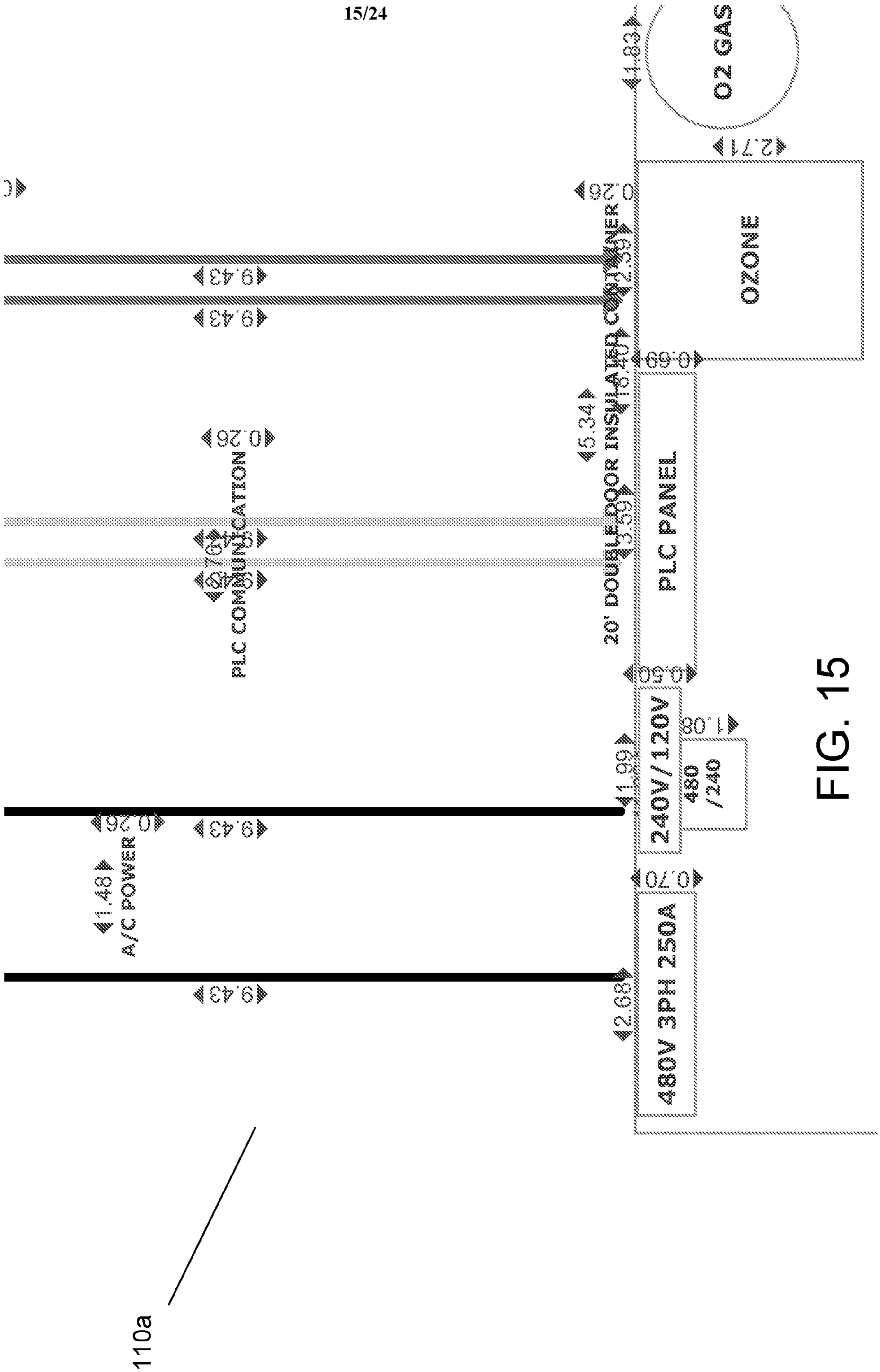

O2 GAS
OZONE
20' DOUBLE DOOR INSULATED CONTAINER
PLC PANEL
PLC COMMUNICATION
240V / 120V
480 /240
A/C POWER
480V 3PH 250A
110a

FIG. 15

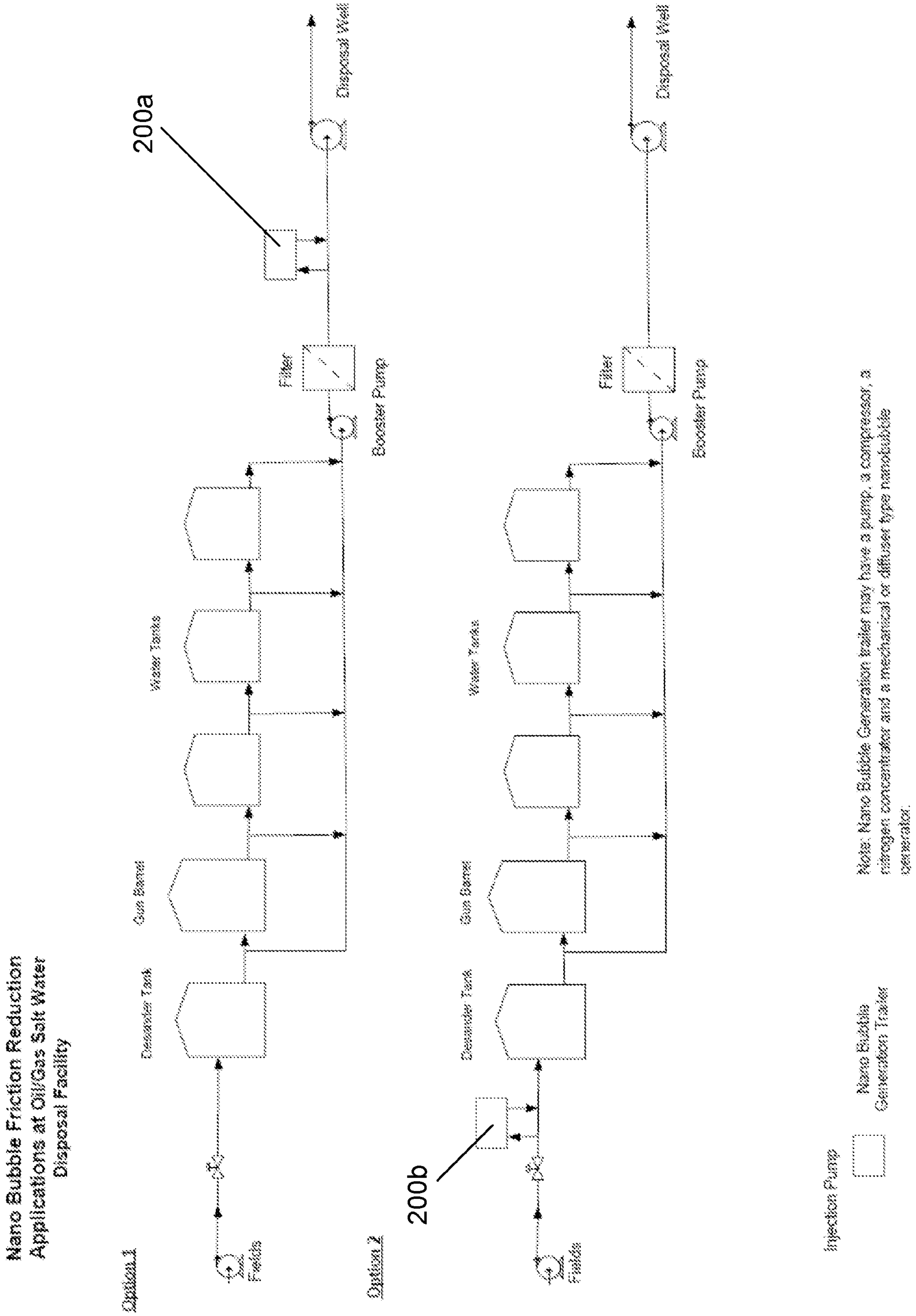

Nano Bubble Friction Reduction Applications at Oil/Gas Salt Water Disposal Facility
Option 1
Fields
Desander Tank
Gun Barrel
Water Tanks
Booster Pump
Filter
200a
Disposal Well
Option 2
200b
Fields
Desander Tank
Gun Barrel
Water Tanks
Booster Pump
Filter
Disposal Well
Injection Pump
Nano Bubble Generation Trailer
Note: Nano Bubble Generation trailer may have a pump, a compressor, a nitrogen concentrator and a mechanical or diffuser type nanobubble generator.

FIG. 16

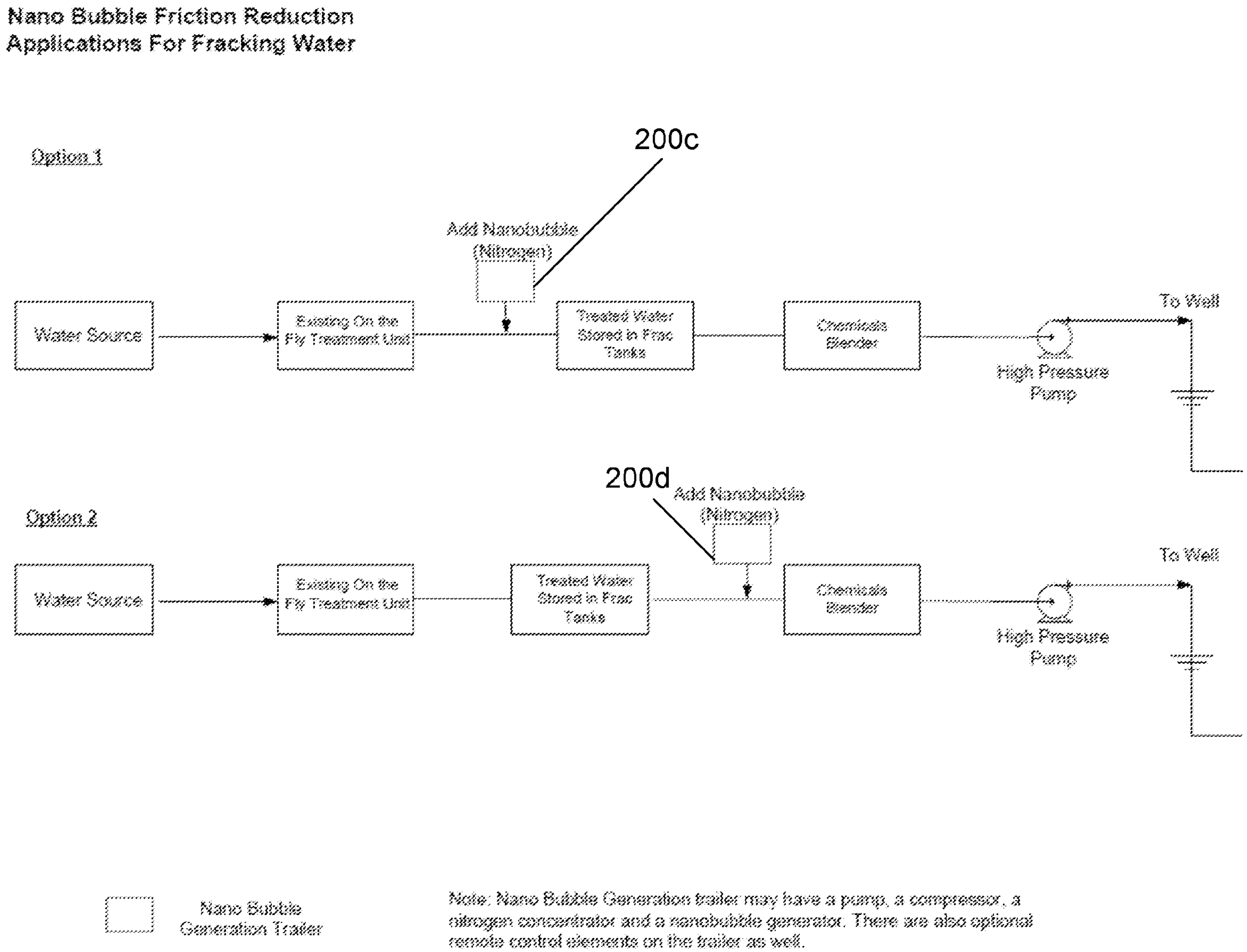

Nano Bubble Friction Reduction
Applications For Fracking Water
Option 1
200c
Add Nanobubble
(Nitrogen)
Water Source
Existing On the Fly Treatment Unit
Treated Water Stored in Frac Tanks
Chemicals Blender
High Pressure Pump
To Well
Option 2
200d
Add Nanobubble
(Nitrogen)
Water Source
Existing On the Fly Treatment Unit
Treated Water Stored in Frac Tanks
Chemicals Blender
High Pressure Pump
To Well
Nano Bubble Generation Trailer
Note: Nano Bubble Generation trailer may have a pump, a compressor, a nitrogen concentrator and a nanobubble generator. There are also optional remote control elements on the trailer as well.

FIG. 17

Nanobubble Manifold

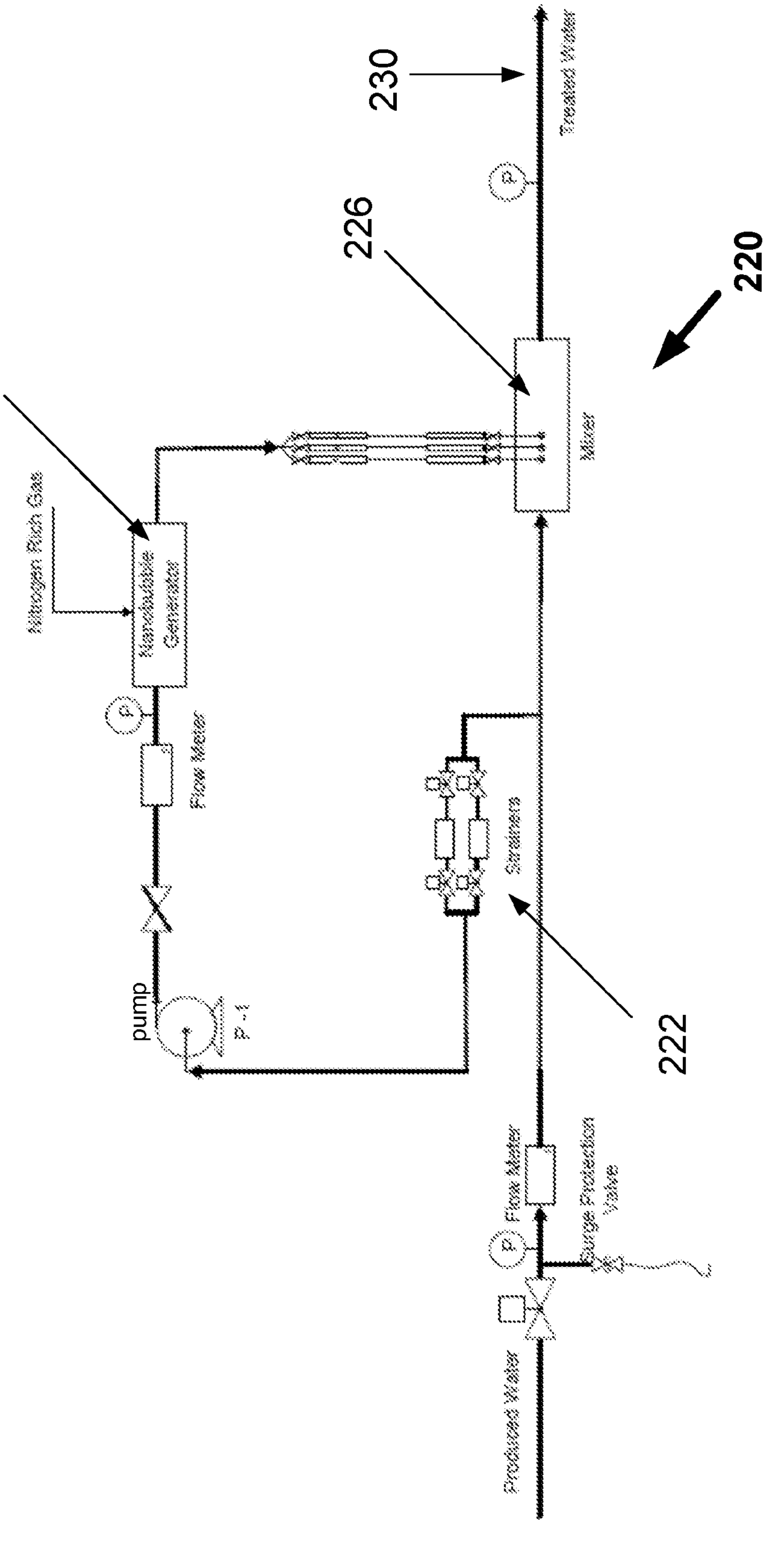


FIG. 18

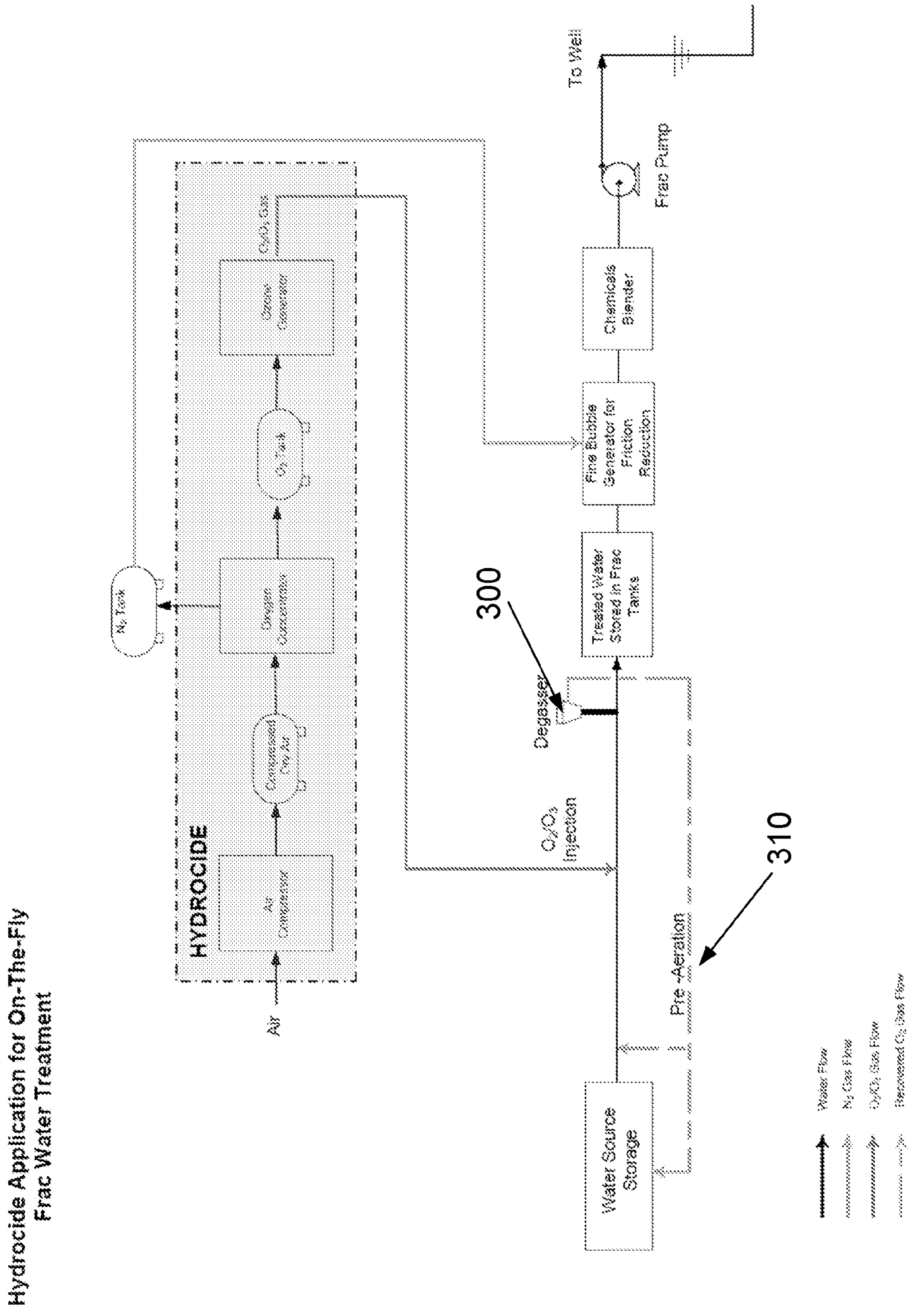

Hydrocide Application for On-The-Fly Frac Water Treatment
HYDROCIDE
Air
N_2 Tank
O_2 Tank
O_2/O_3 Gas
Water Source Storage
Pre -Aeration
310
O_2/O_3 Injection
Degasser
300
Treated Water Stored in Frac Tanks
Fine Bubble Generator for Friction Reduction
Chemicals Blender
Frac Pump
To Well
Water Flow
N_2 Gas Flow
O_2/O_3 Gas Flow
Recirculated O_3 Gas Flow

FIG. 19

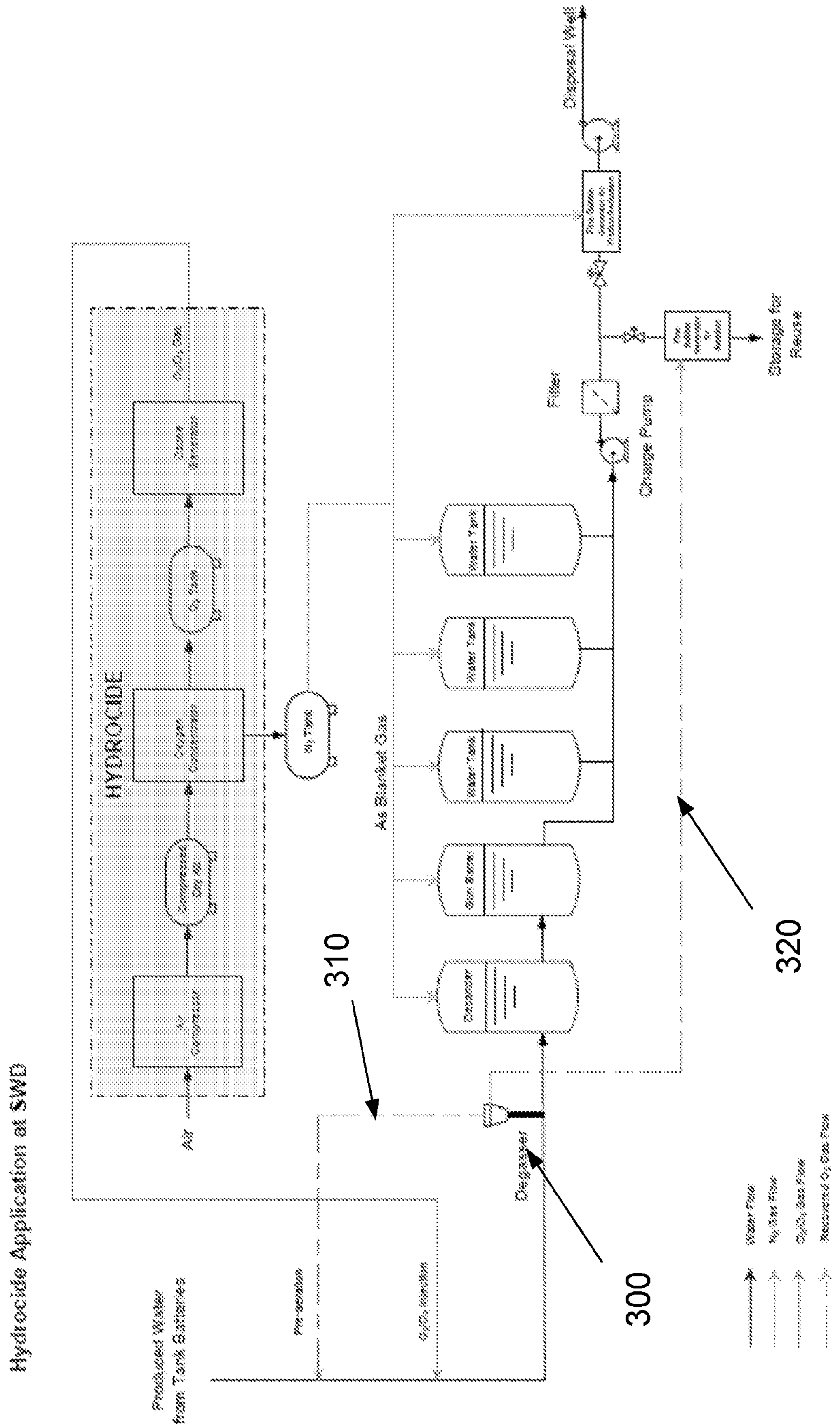

Hydrocide Application at SWD
HYDROCIDE
As Blanket Gas
Produced Water from Tank Batteries
Degasser
Charge Pump
Filter
Storage for Reuse
Disposal Well
300
310
320

FIG. 20

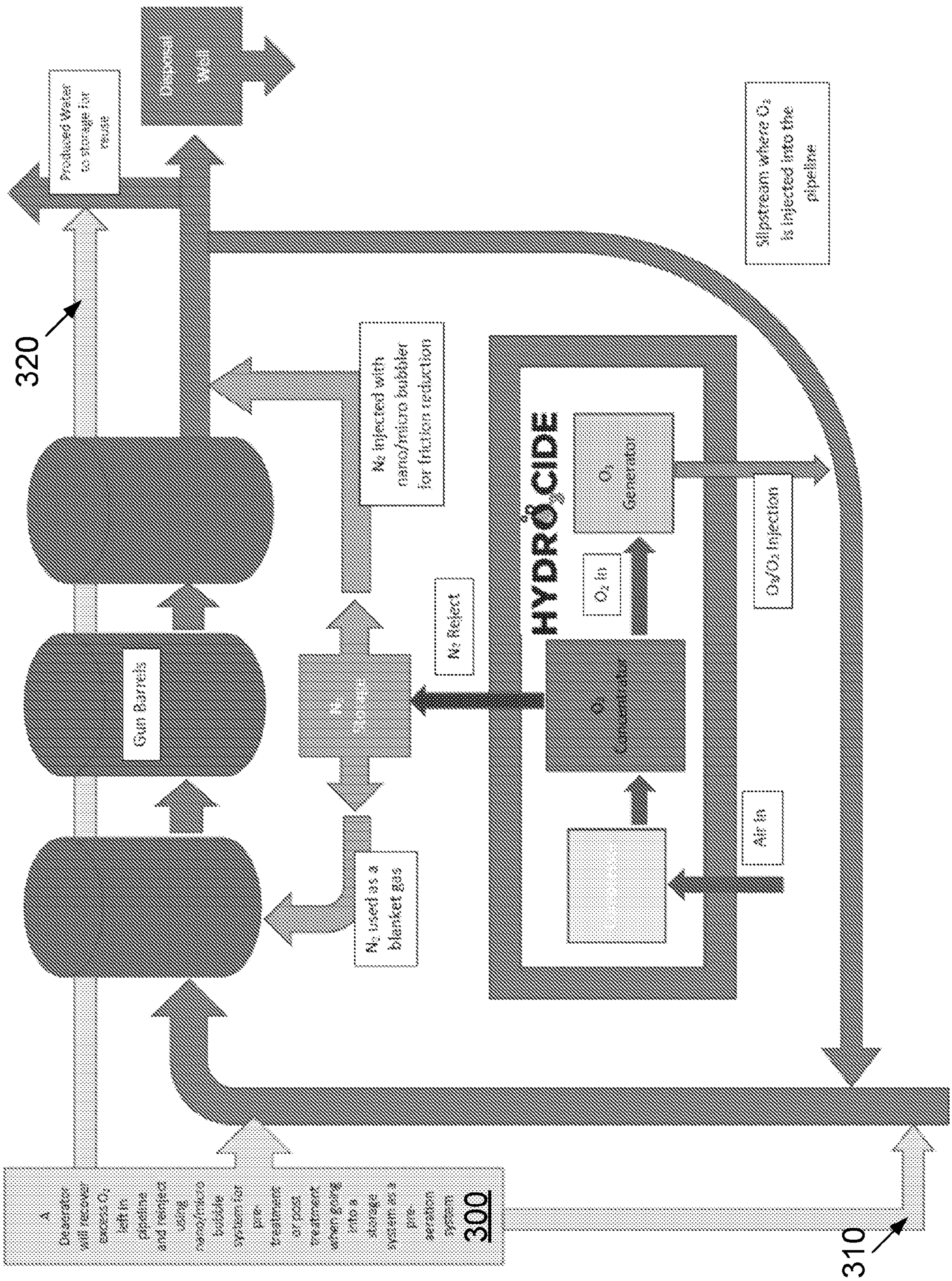

Produced Water to storage for reuse
Disposal Well
320
Slipstream where O3 is injected into the pipeline
N2 injected with nano/micro bubbler for friction reduction
HYDRO3CIDE
O3 Generator
O2 In
O3/O2 Injection
N2 Reject
Gun Barrels
O2 Concentrator
Air In
N2 used as a blanket gas
A Deaerator will recover excess O3 left in pipeline and reinject using nano/micro bubble system for pre-treatment or post treatment when going into a storage system as a pre-aeration system
300
310

FIG. 21

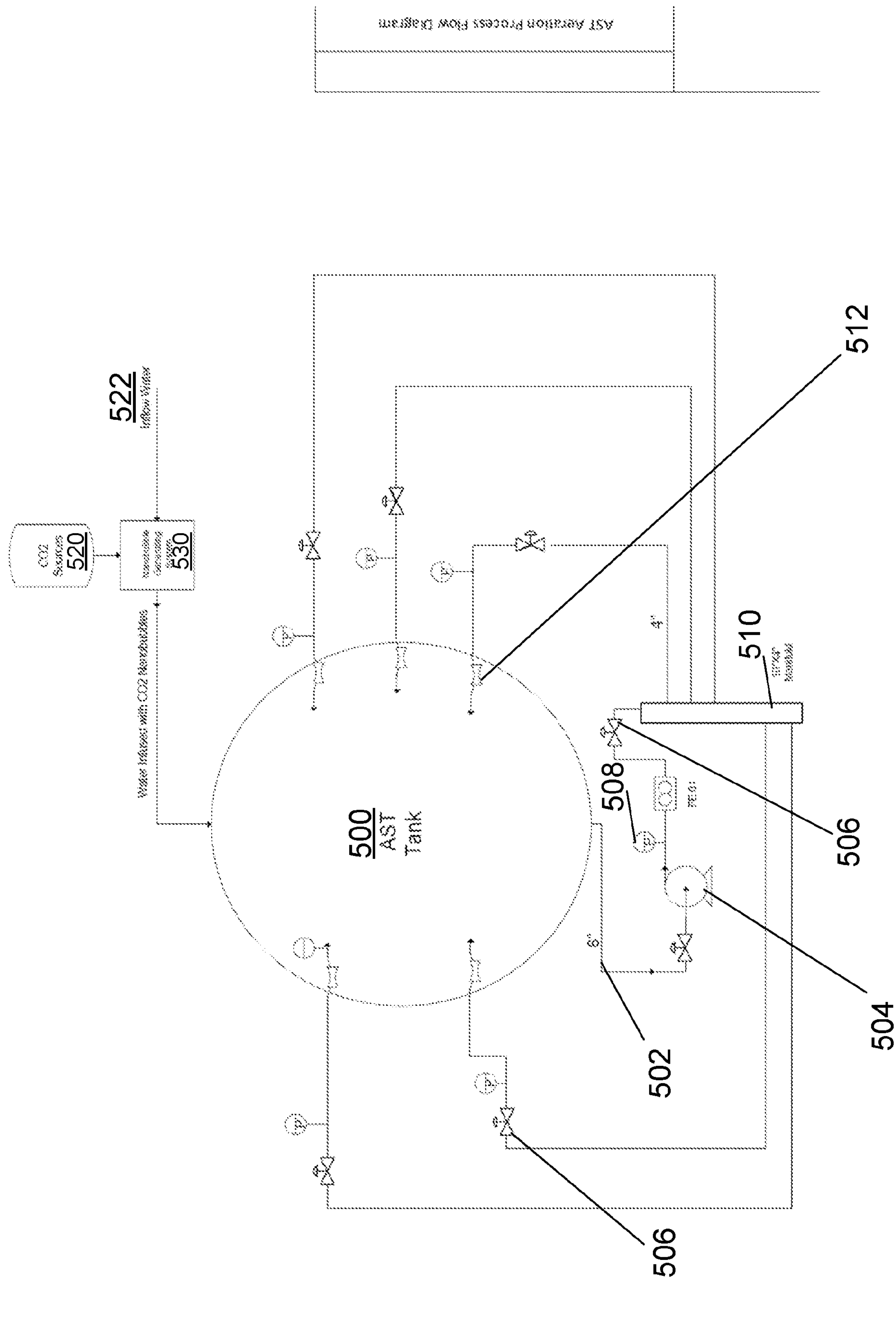

AST Aeration Process Flow Diagram
CO2 Sources
520
530
522
500
AST
Tank
6"
4"
502
504
506
508
510
512
506

FIG. 22

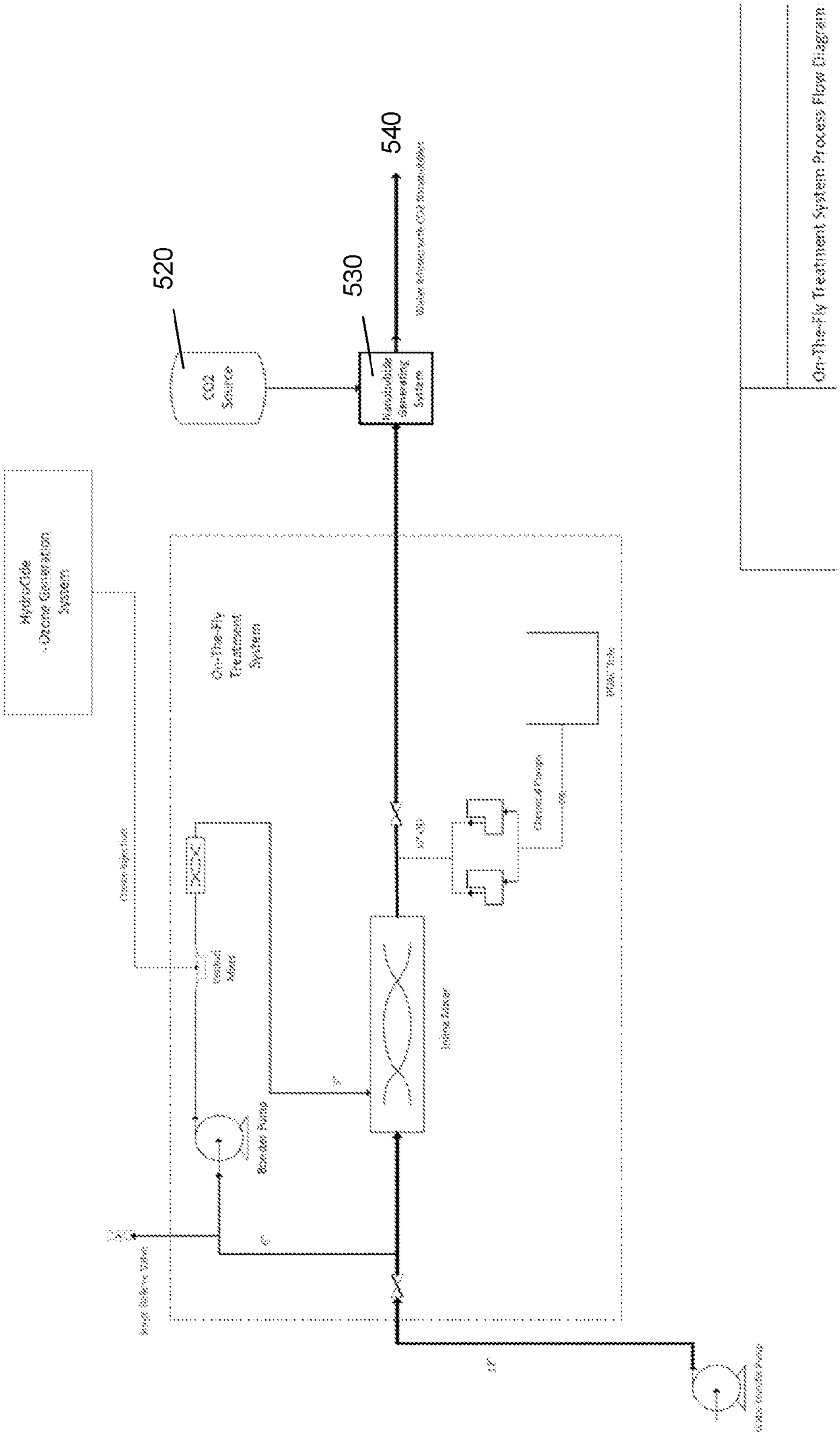

520
530
540
CO2 Source
Nanobubble Generating System
HydroCide Ozone Generation System
On-The-Fly Treatment System
On-The-Fly Treatment System Process Flow Diagram

FIG. 23

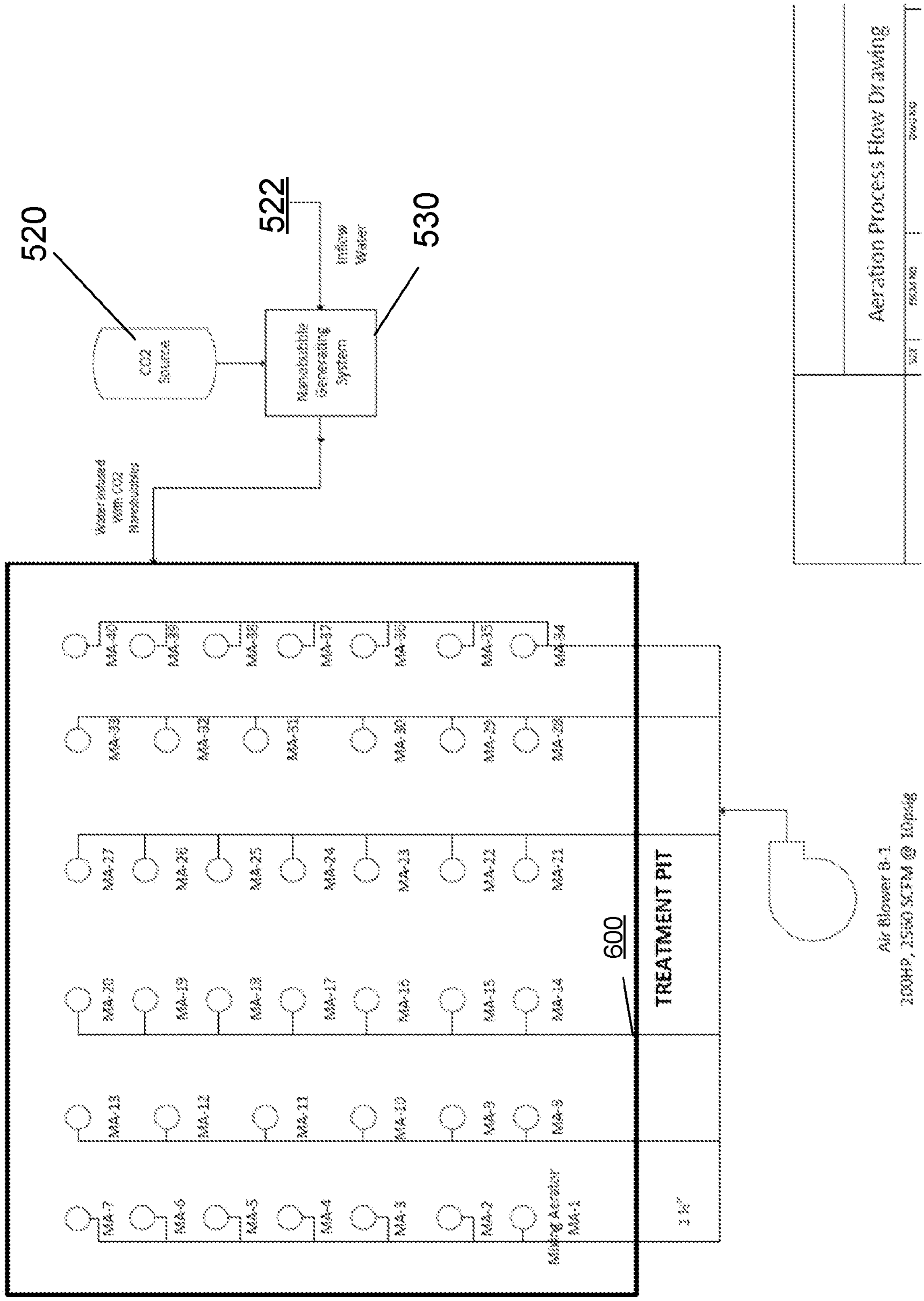

520
522
530
CO2 Source
Nanobubble Generating System
Inflow Water
Water infused With CO2 Nanobubbles
600
TREATMENT PIT
Mixing Aerator MA-1
Air Blower B-1
Aeration Process Flow Drawing

FIG. 24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/19088

A. CLASSIFICATION OF SUBJECT MATTER
IPC - C02F 1/78; C02F 9/00 (2021.01)

CPC - C02F 1/78; C02F 1/727; C02F 9/00; C02F 2103/10; B01D 2257/504; Y02C 20/40; Y02P 10/122

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)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0202304 A1 (Koide et al.) 13 August 2009 (13.08.2009); entire document, but especially: para [0002], para [0009], para [0012], para [0124]	1-4
Y	US 2019/0218122 A1 (Hydrozonix, LLC) 18 July 2019 (18.07.2019); entire document especially para[0005], [0016], [0020] and [0021]	5-20
Y	WO 2019/112492 A1 (KING ABDULAZIZ CITY FOR SCIENCE AND TECHNOLOGY) 13 June 2019 (13.06.2019); entire document especially page 1 line 10-12, page 4 line 8-10	5-20
A, P	WO 2020/234464 A1 (Orkuveita Reykjavkur et al.) 26 November 2020 (26.11.2020); entire document	1-20
A, P	US 2020/0290935 A1 (Columbia Machine, Inc.) 17 September 2020 (17.09.2020); entire document	1-20
A	JP 2018-43176 A (Obayashi Corporation) 22 March 2018 (22.03.2018); entire document	1-20
A	US 2011/0017456 A1 (Koide et al.) 27 January 2011 (27.01.2011); entire document	1-20
A	WO 2020/006636 A1 (CRH Group Canada Inc.) 09 January 2020 (09.01.2020); entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ 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
"D" document cited by the applicant in the international application
"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
29 June 2021 (29.06.2021)	JUL 27 2021

Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee Young Telephone No. PCT Helpdesk: 571-272-4300

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-4 directed to a method for storage of carbon.

Group II: Claims 5-20 directed to a fluid treatment system for treating a fluid stream and storing carbon.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

SPECIAL TECHNICAL FEATURES

The invention of Group I includes the special technical feature of a method comprising infusing a fluid stream with carbon dioxide nanobubbles and storing the infused fluid stream in a storage tank, a fluid treatment pit, or an underground formation or formations, not required by the claims of Groups II.

The invention of Group II includes the special technical feature of a fluid treatment system comprising one or more fluid treatment tanks, downstream pipes, upstream pipes, an ozone injection system, and an oxygen de-gasser or de-aerator, not required by the claims of Groups I.

COMMON TECHNICAL FEATURES

Groups I-II share the common technical feature of infusing a fluid stream with carbon dioxide nanobubbles and a well or underground formation. However, this shared technical feature does not represent a contribution over prior art as being obvious over US 2009/0202304 A1 to Koide et al., which discloses of a method comprising infusing a water stream with carbon dioxide microbubbles and injecting the mixture into a well (para [0009]: "The method includes a step for pumping up groundwater... to produce injection water. Carbon dioxide... is changed into fine bubbles, and the carbon dioxide bubbles are mixed with the injection water so as to produce a gas -liquid mixture. The gas-liquid mixture is injected through an injection well into the deep aquifer"; para [0124]: "A device for generating so -called microbubbles having a diameter of 50 micro m or less can be used"). Koide does not disclose that the carbon dioxide bubbles are nanobubbles. However, it would have been obvious to one of ordinary skill in the art through routine experimentation to generate carbon dioxide nanobubbles in order to optimize dissolution of the carbon dioxide in the water stream (para [0012]: "The carbon dioxide bubbles are dissolved in the injection water, and the gas-liquid mixture, which is a mixture of the fine bubbles of the carbon dioxide and the injection water, is injected into the deep aquifer").

As the common technical features were known in the art at the time of the invention, these cannot be considered special technical features that would otherwise unify the groups.

Therefore, Groups I-II lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/19088

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
---See Supplemental Sheet---

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.