
(57) **Abstract:** According to another aspect of the present invention, there is provided a gas bubbler for use in water treatment in the oil industry, said gas bubbler adapted to be used inside a tank having walls, wherein said gas bubbler comprises: at least one inlet; a loop made of at least one tubing length designed to be inserted inside the tank; said loop being positioned horizontally and defining a plane and wherein said tubing containing a plurality of apertures disposed along the tubing underneath said plane, said apertures facing the walls at a 45° angle. The invention is also directed to the use of such device in the treatment of waters used in the oil industry.
TANK GAS BUBBLER

FIELD OF THE INVENTION

The present invention relates to a gas bubbler, more specifically for use in the treatment of waters used in the oil industry and methods of use thereof.

BACKGROUND OF THE INVENTION

In the oil industry, extraction of oil from oil wells will typically yield in the range of 30% of the actual content in the reservoir being exploited. The process of water flooding refers to the method of injecting water into a reservoir resulting in an increase in pressure and subsequent increase in oil extraction. The flood water is injected into a reservoir and allows to maintain or increase the pressure inside the reservoir and replaced the extracted oil. It also allows to displace oil within the reservoir and push it towards a well. The use of flood water allows for more production from a well and therefore increased savings by extending the production expectancy of a well.

US2012/0152546AI describes a process for water treatment specifically for SAGD operations. There is described a process which uses chemical oxidation (CO) or electromagnetic treatment (ET) to destroy or degrade organics in the produced water. It is stated that a primary purpose of the produced water treatment steps described above is to provide water of suitable quality to the steam generator.

US 7694736B2 generally describes a method and system for producing steam for extraction of heavy bitumen including the steps of mixing carbon or hydrocarbon fuel. It is stated that with its simple direct contact, above ground adiabatic nature, and its high pressure and temperature solid removal, the invention will minimize the amount of energy used to produce the mixture of steam and gas injected into the underground formation to recover heavy oil. It is stated that it adds the adiabatic direct contact steam and carbon dioxide generation unit to reduce the disadvantages of the prior art and to allow for expansion with use of a low quality water supply, reject water from existing facilities and the use of low quality fuel supplies. Also, there is no need for high quality separation of the oil from the produced water and water purification processes with this invention. It is stated that the mixture produced at the EOR production well 65 is separated into gas (mainly carbon dioxide and natural gas), oil and water. The produced water contains heavy oil remains, dissolve minerals, sand and clay. The separated low quality produced water 64 is used for steam generation 61 without any additional treatment.
There is a need for a device which effectively removes H$_2$S and other gases from large volumes of waste water such as polymer flood waters. The present invention is directed to the use of a gas bubbler to treat recovered (or used) polymer flood waters, used in the oil extraction industry. The polymer flood waters are being recycled in order to limit water usage and reduce discharge of used water containing numerous contaminating compounds.

SUMMARY OF THE INVENTION

Recovered polymer flood waters are found to contain several contaminants which affect its quality. The contaminants also impact the amount of polymer used when re-using the recovered waters. As H$_2$S when present with oxygen (H$_2$S and O$_2$) have a substantial impact on polymer degradation up to a 400 ppm or more polymer required to make the desired viscosity fluid. ¾ S is one key contaminant that is efficiently removed by the bubbler according to the present invention.

Moreover, removal of H$_2$S leads to improved safety and handling of the water system. The operations performed downstream from gas removal will be done so under safer conditions as currently H$_2$S can vent out of the plant equipment at various locations within the water system process piping and vessels.

In order to increase the efficiency of the water treatment process and to allow savings in polymer usage and therefore economic savings, the use of a gas bubbler has been found to yield treated water which can more easily and advantageously be reused in polymer flood water, steam assisted gravity drainage and/or alkaline surfactant polymer flood water.

According to an embodiment of the present invention, there is provided a gas bubbler designed to be used inside a tank having walls, said tank adapted to receive a liquid to be treated, wherein said gas bubbler comprises: at least one inlet; at least one tubing length designed to be inserted inside the tank; said at least one tubing length positioned horizontally and defining a plane and wherein said tubing containing a plurality of apertures disposed along the tubing underneath said plane, said apertures facing the walls but positioned at an angle less than perpendicular to the walls of said tank.

Preferably, the apertures are positioned at an angle ranging from 20° to 60° with respect to the walls. More preferably, the apertures are positioned at an angle of 45°.
Preferably, the gas bubbler comprises two inlets and two separate and distinct tubing lengths spaced apart from one another each defining a specific plane and where one tubing length is generally positioned above the other tubing length.

According to another aspect of the present invention, there is provided a gas bubbler designed to be used inside a tank having walls, said tank adapted to receive liquid to be treated, wherein said gas bubbler comprises: at least one inlet; at least one tubing length designed to be inserted inside the tank; said at least one tubing length defining a plane and wherein said tubing containing apertures disposed underneath said plane, said apertures being positioned at a downward angle of 45° in relation to the walls of said tank.

According to another aspect of the present invention, there is provided a method for removing ¾ S from water used in the oil industry, said method comprising the steps of:

- introducing water requiring degassing into a tank fitted with a gas bubbler,
- injecting natural gas into the gas bubbler at a ratio of 1:1 natural gas volume injected: offgas (containing H₂S) volume present in the used water; and
- removing the gas extracted at the surface of the water;

said gas bubbler comprising a tubing defining a horizontal plane, said tubing having apertures disposed therealong at a 45° angle underneath the plane defined by the tubing.

According to another aspect of the present invention, there is provided a method for removing ¾ S from water used in oil extraction, said method comprising the steps of:

- introducing water requiring degassing into a tank fitted with a gas bubbler;
- injecting natural gas into the gas bubbler; and
- removing the gas extracted at the surface of the water;

said gas bubbler comprising a tubing defining a horizontal plane, said tubing having apertures disposed therealong at a 45° angle underneath the plane defined by the tubing, and wherein the concentration of H₂S in the water is decreased. Preferably, the concentration of ¾ S in the water is decreased to a level such that results in a 100 ppm to 400 ppm polymer usage reduction.

According to another aspect of the present invention, there is provided a gas bubbler for use in water treatment in the oil industry, said gas bubbler adapted to be used inside a tank having walls, wherein said gas bubbler comprises:

- at least one inlet;
- a loop made of at least one tubing length designed to be inserted inside the tank;
said loop being positioned horizontally and defining a plane and wherein said tubing containing a plurality of apertures disposed along the tubing underneath said plane, said apertures facing the walls at a 45° angle. Preferably, the gas bubbler is positioned at a lower portion of the tank and around the inside perimeter of the tank.

Preferably also, the tubing is positioned at a distance ranging from a third of the length of the radius of the tank to half of the length of the radius of the tank.

Preferably, the gas bubbler comprises an upper loop and a lower loop, wherein the upper loop is positioned generally directly above the lower loop.

The tank gas bubbler according to a preferred embodiment of the present invention is made of linear tubing, positioned in an horizontal plane, comprising holes positioned to be at a 45° downward angle towards the walls of a tank in which it is inserted. It has been determined by the inventor that the above specification would allow for increased removal of H₂S present and other gases from the waters to be treated. The gasses are removed as they have been shown to have deleterious effects on polymers used in polymer flood waters.

According to a preferred embodiment of the present invention, the gas bubbler used in the treatment of polymer flood waters allows to effectively remove H₂S from the sour saline (grosmont) and produced waters which, in turn, improves the polymer loading for subsequent polymer flood treatment. This leads to substantial savings in polymer usage to meet viscosity target.

The tank gas bubbler can be used for any water fluid requiring removal of gasses, such as H₂S, from a system. This, in turn, greatly improves the downstream safety of fluid handling having reduced H₂S levels. Another advantage of the tank gas bubbler according to the present invention is that the installation is simple and cost efficient and can be adapted to accommodate wide ranges of water:gas rates. The piping sizes can vary when used in this design to meet the rigorous process conditions and be adapted for any tank size. It is worth noting that the process controls based on water flow to gas flow rates ratio control program.

The use of a tank gas bubbler according to the present invention can lead to reductions in polymer usage ranging from 100 to 400 ppm over standard reuse of polymer flood waters when conducting polymer flood water operations.
The spacing between apertures on the tubing and the size of the apertures is dependent on the tank size (i.e. total volume) as well as the type of liquid being treated (i.e. the content of gas to be extracted) and the flow rate of the gas being used in the operation.

In one embodiment according to the present invention, the apertures were located 12 inches apart on ¼ inch stainless steel tubing and had a diameter of 1/8 inch.

**BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 is a schematic representation of a process using the gas bubbler according to a preferred embodiment of the present invention where the produced water is treated to be reused as polymer flood water.

Figure 2 is a schematic representation of a process using the gas bubbler according to a preferred embodiment of the present invention where the produced water is treated to be reused in steam assisted gravity drainage operations.

Figure 3 is a schematic representation of a process using the gas bubbler according to a preferred embodiment of the present invention where the produced water is treated to be reused in alkaline surfactant polymer flood water.

Figure 4 is a perspective view of the double loop gas bubbler according to a preferred embodiment of the present invention inserted into a cylindrical tank.

Figure 5 is a front view of a tubing length of the gas bubbler according to a preferred embodiment of the present invention.

Figure 6 is a view of the cross-section of a tubing length of the gas bubbler according to a preferred embodiment of the present invention.
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The invention will be better understood by referring to figures which illustrate preferred embodiments thereof. In Figure 4, the tank square double loop gas bubbler according to an embodiment of the present invention and used in the treatment of polymer flood water was made of linear tubing. The two loops overlapping each other and positioned in a horizontal plane, comprising holes positioned to be at a 45° downward angle towards the walls of a tank in which it is inserted. It was determined by the inventor that the above specification would allow for substantial and efficient removal, from the waters to be treated, of ¾ S present and other gases which have deleterious effects on polymers used in polymer flood waters.

According to one embodiment of the present invention, a double loop gas bubbler as shown in Figure 4 is provided for insertion into a tank of 2000 bbl capacity. The gas bubbler is positioned inside a tank so that the lower loop is located at 12 to 18 inches from the bottom of the tank. The gas bubbler is preferably installed so that the first tube (lower tube) is at a distance of approximately 1 - 1.5 feet off of the bottom floor of the tank. The second tube (upper tube) is installed approximately 10 inches to 1.0 feet vertically above the lower. Of course, the distance can be modified as one of the factors that need to be considered in the determination of this distance include gas flow rate. A person skilled in the art could consider adapting the system to include additional tubes depending on the tank size or gas volumes.

The distance inside a tank between the loops of the gas bubbler and the interior walls of the tank depends on the tank size but is preferably located at a distance equal to the radius of the tank divided by 2 or radius of the tank divided by 3.

In one embodiment of the present invention, the tubing of the gas bubbler is made of ¾ inch stainless steel with apertures at every 12 inch and positioned at 45° facing downward towards the walls of the tank.

The instrumentation that was used in the experiments included the following: pressure transmitters (one for the tank and one for the gas line downstream of the flow valve); a pressure control valve (model: 4 inch Globe Valve 150# rating; 0 to 20,544 mV/day rate); inlet gas ESDV valve (model: 2 inch valve 150# rating; 0 to 10000 mV/day); flow control valve (model: D body - Globe 1 inch body - ¾ inch; 150# rating; 0 to 10000 mV/day); and flow meters (rotameter or turbine) (model: Rosemount 0 to 10 cubic feet/day).

The tubing material used was Dual-Certified P8 316/316L Austenitic Stainless Steel. The inspection performed included a 100% visual inspection on all welds, 100% RT of the entire circumference on all
butt welds. 100% LPI of all welds that were not radiographic tested. Ferrite measurements were performed on 5% of all butt welds. There is at least one ferrite test per welder/WPS/brand consumable/wall thickness. All fabricated piping was hydrotested for a minimum of one hour.

The gas bubbler tube used 316L SS material for corrosion protection from sour fluids. The diameter of pipe depends on the gas flow rate to meet the pressure drop calculations. Trials were conducted using ½ inch diameter size up to 1.5 inch size. However, a person skilled in the art would know that he could use larger tubing depending on the equipment used and the requirements for gas flow rate and distribution.

The tested parameters to indicate improvement in the water in terms of H₂S content was determined by testing the inlet H₂S ppm in the inlet water versus the outlet H₂S in the effluent water.

The spacing between apertures on the tubing and the size of the apertures is dependent on the tank size (i.e. total volume) as well as the type of liquid being treated (i.e. the content of gas to be extracted) and the flow rate of the gas being used in the operation.

The distance between holes (apertures) and the diameter of holes on the tubing and flow rate of the gas injected is determined based on the diameter of the tubing and of the holes. Both 1/16 inch holes and 1/8th inch hole sizes were trial tested. The advantage of the 1/8th inch holes size was that they were easier to drill.

The distance between holes (apertures) depends on the required surface area for the required gas injection volume — based on pressure drop calculations

\[
\text{Total \# of holes} = (\text{required surface area} / \text{hole size area})^* 3.0
\]

\[
\text{Distance between holes on each tube line} = \\
\text{length of each tube line} / (\text{total \# of holes} / 2 \ (# \ of \ tubes})
\]

The amount of overlap between the upper and the lower tubes (in the case of a double loop gas bubbler) covered a distance of about ½ to ¾'s of the way back to the inlet area where the tubes split. Trials were performed using the shorter ½ length and the longer ¾ length overlap. However, the overlap may be more or less given other parameters including, but not limited to, gas flow rate, tank size.
Some of the advantages of using a double loop bubbler include the ability to reduce the H$_2$S that normally stays entrained in the water in systems. Also, it is believed that since the gas injected bubbles outward towards wall of the tank, because of the use of holes at a 45 degree angle, there is created a substantial agitation and swirling of the fluid present in the tank.

Preferably, the gas bubbler is inserted and secured within the tank through the use of support angle irons, footings, and wire with clamps to support to hold suspended in the tank fluid space - attached to nozzles across tank to hold in place if available in the tank.

Preferably, the flow rate of the gas is matched to a 1:1 gas volume rate to the sour flashing gas volume rate off the water rate.

The present invention can be better understood by referring to the figures. Figure 4 is a perspective view of the invention (the double loop gas bubbler) which is inserted in a cylindrical tank (note the dashed outline, as well as the entry point of the tube into the tank).

In the preferred embodiment illustrated in Figure 4, the gas bubbler (505) is positioned inside a tank (500) having a cover (502) and an outlet (501) for the gas extracted. The valve system (540) allows the gas to reach the gas bubbler (505) tubes (510) through a common inlet line (550) that splits into the two lines of the double loop: the upper loop (520) and the lower loop (530). The inlet flow control valve (not shown) can be equipped with a pressure override - gas flow meter ratio control back to the inlet water flow rate and water gas GWR (gas water ratio). When in operation, gas such as natural gas will be injected into the tank (500) via the inlet (550) and will circulate through the tubing (510) into the upper (520) and lower loop (530). Once the gas in the liquid reaches the top of the tank it is removed from the tank through a gas outlet (501).

Figure 5 is a simple cross-sectional view of the tubing (510) used in the gas bubbler (405) which shows the aperture (511) within the tube at an angle of 45° facing downwards. The tubing (510) is positioned inside the tank horizontally defining a plane (600) underneath which the apertures (511) are positioned for increased gas removal.

Figure 6 is a perspective view of a tubing (510) segment as used in an embodiment of the gas bubbler (505) according to the present invention. The apertures (511) are located beneath the horizontal plane (600).
The process according to the present invention is intended for use in treating various used waters reclaimed from operations in the oil industry, more specifically, polymer flood waters, SAGD waters and alkaline surfactant brine waters, for their subsequent reuse.

The use of a tank gas bubbler can lead to reductions in polymer usage for subsequent polymer flooding activities ranging from 100 to 400 ppm when conducting polymer flood water operations.

**Polymer Flood Water Treatment**

The polymer flood water treatment unit incorporating a gas bubbler according to an embodiment of the present invention, may also comprise an inlet mixing/solids tank with a gas bubbler; an electrocoagulation unit; a solids removal/handling system; one or more multimedia filtration units; and one or more chemical injection systems.

The polymer flood water treatment unit incorporating a gas bubbler according to another embodiment of the present invention, may comprise an inlet mixing/solids tank (without a gas bubbler); an electrocoagulation unit; a solids removal/handling system; one or more multimedia filtration units; and one or more chemical injection systems.

An advantage of using a gas bubbler according to a preferred embodiment of the present invention is the removal of \( \frac{3}{4} \) S from the polymer produced and makeup water streams. \( \text{H}_2\text{S} \) and \( 0_2 \) have a substantial impact on polymer degradation. Moreover, there is improved safety and handling of the water system, i.e. safer for operations when there is no \( \text{H}_2\text{S} \) venting from the plant equipment. Processing used waters leads to selective ion removal from water streams to reach the desired water specification. There is also bacteria removal from water, since bacteria consume polymer that is added to the flood water — require no bacteria for potential future CDG gels if gels were to be used in future instead of polymers. It is worthy of mention that die process described herein allows for the removal of oil and grease residual from water as well as reducing the total dissolved solids (TDS) of the water each time it is processed. The intent is to have lower TDS in the water stream for SAGD future water requirements. As benign water is created there are subsequent savings on materials for construction of pipelines and polymer hydration and injection facilities. The process leads to the creation of a stable polymer when using a treated water stream; solids removal from water streams - incoming solids from makeup waters i.e. gross solids handled at one location versus the multiple solids deposition locations; and ability to blend the polymer produced water and makeup water streams prior to treatment system — optimized with mixing.
As most often add, in a transition process, the necessary assessment of between 22775 processes required annually, the amount of water involved in the assessment of 2200 ppm polymer loading prior to the implementation of the processes described herein averaged 88550 t...
The pilot allowed to determine a water specification for polymer flooding activities and helped in finding a more economical water treatment process that provided lower polymer loading. Elemental analytical results from the electrocoagulation testing were analyzed to determine the impact of each element on the polymer loading.

The following desired or preferred water specification for polymer flooding was determined as a result of the pilot conducted:

<table>
<thead>
<tr>
<th>Element</th>
<th>Water Spec</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.5 – 10.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;20 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>100 – 220 ppm</td>
</tr>
<tr>
<td>Total Hardness as CaCO₃</td>
<td>400 – 800 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>15000 - 25000 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>&lt;5 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt; 50 ppb</td>
</tr>
<tr>
<td>Sulphide</td>
<td>&lt; 60 ppm</td>
</tr>
<tr>
<td>Sodium</td>
<td>6000 - 9000 ppm</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>1500 – 2500 ppm</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt;100 NTU</td>
</tr>
<tr>
<td>TSS</td>
<td>&lt;250 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt; 1 ppm</td>
</tr>
</tbody>
</table>

For the Brintnell waters tested, it was determined that the following parameters impacted the polymer loading the most:

- pH ≤ 9.0 or pH > 10.5, had an impact of about 200 - 300 ppm polymer loading increase
- H₂S and O₂ reaction, - H₂S > 50 ppm and O₂ > 50 ppm, had an impact of about 400 - 800 ppm polymer loading increase
- solids - TSS (total suspended solids) > 250 ppm, had an impact of up to 500 ppm in polymer loading increase
- calcium ion > 20 ppm, had an impact of up to 400 - 500 ppm in polymer loading increase
- Total hardness level of 0 ppm (no calcium or magnesium present) - increased the polymer loading by 200- 300 ppm.
From the trial results, it was determined that a tank gas bubbler followed by electrocoagulation (EC) water treatment process; then followed by multimedia filtration (MMF) provided optimal efficiency with respect to polymer loading in comparison to all other configurations. The combination of tank gas bubbler/EC/MMF decreased polymer loading up to 1050 ppm range on all waters tested, when all fluids were adjusted to a pH range of 9.0 - 9.5.

Three other process steps resulted in improved polymer loading. The savings noted for each individual process enhancement and cannot be necessarily combined for cumulative savings. These three other processes involved a gas bubbler, a nitrogen blanket, and fresh water for mother solution hydration. The utilization of a gas bubbler in the water inlet tank to degas out the gases HjS and CO₂ from the water resulted in polymer loading savings of up to 400 ppm. The use of a nitrogen gas blanket on the polymer mixing and aging tank in polymer injection skid resulted in polymer loading savings of up to 300 ppm. The use of fresh water to hydrate the polymer mother solution resulted in an additional polymer loading savings of up to 300 ppm.

Cumulatively when creating the overall required polymer water specification mixture for injection, the testing found that one could also use treated produced water blended with some fresh water (with tank gas bubbler/EC/MMF treated water being used for the blend water and fresh water being used for polymer mother solution hydration) which resulted in an additional 175 ppm in polymer savings - total polymer usage decreased from 1050 ppm down to 875 ppm polymer loading.

A separate system containing only filtration and chemicals was also tested for comparison to the tank gas bubbler/electrocoagulation/multimedia unit. Filtration and chemicals provided polymer reduction but this reduction was lower at around 400 ppm. Although this alternate system was very effective as the filtration and chemical treatment utilizing ceramic Macrolite® media with chlorine and sulphite added were able to break up and remove the oil and grease, polymer, and solids from the waters effectively and reduced turbidity of the waters.

Additionally, for direct comparison to the electrocoagulation unit, the use of Dow RSC resin was tested to see if could remove NORMS with the resin product in a filter vessel. The Dow resin tested allowed for the reduction of radium levels in the waters by 36 to 59% removal of inlet to outlet stream.
The process incorporating a gas bubbler according to a preferred embodiment of the present invention is described with reference to specific processes illustrated in Figures 1 - 3 and described in Examples 1 to 3 below.

Example 1 - Polymer Flood Water Treatment Process

In a process to treat polymer flood waters used in oilfields for eventual reuse, there is provided the following steps which incorporate the use of a gas bubbler according to a preferred embodiment of the present invention:

1) Polymer flood water flows (5) into a cone bottomed storage tank (10) (or other mechanical separation equipment which may be equipped with an oil skimmer at the top of the tank or overflow or oil removal standpipe) where the solids (16) are removed from fluid as needed; and the oil (17) is skimmed off of the storage tank (10) as needed.

2) When the resulting fluid (15) shows signs of being sour (¾S is present), it flows into a tank which is equipped with a double loop square gas bubbler inside (20) and gas (23) (like natural gas) is bubbled into the storage tank fluid reservoir as the fluid flows in/out of the tank (20). This permits the stripping out of ¾ S and other gases (27) present in the fluid. Natural gas volume is added at a 1 to 1 ratio to the fluid offgas volume.

3) If the resulting fluid (25) requires additional oil removal prior to water treatment then a single or two stage polymer packing vessel (30) for oil adsorption/coalescence (37) are used (like Mycelx®).

4) If the resulting fluid's (35) oil and grease level is sufficient, then the fluid (35) is pumped and undergoes a pH adjustment (40Xif necessary) where the pH is raised in the fluid by adding a chemical (like caustic - sodium hydroxide (43)).

5) The fluid (45) is then sent through an electrocoagulation unit (50) – a closed cell design (like Waveionics®) this prevents gases from being released into the atmosphere during the step. The electrocoagulation step consists of metal plates with electrodes that are electrified as the fluid passes through the cell. During the step of electrocoagulation, the metal plates are consumed and the metal precipitates with the water solids (57).

6) Subsequently, there is another step of chemical addition (60) where additional chemicals (63) like caustic and coagulant, are added to the fluid (55) to assist with solids removal (67) by further raising the pH and promoting precipitation or agglomerating the particles.
7) If necessary, the fluid (65) undergoes another step of bulk solids removal stage (70X with a cone bottomed tank and/or solids clarifier) is performed with oil recapture (77) if applicable.
8) The resulting fluid (75) is sent to a cone bottomed tank (80) for surge volume and additional solids removal (86) and oil capture (87), if applicable.
9) The resulting fluid (85) is then pumped through multimedia filtration (90) (like ceramic media such as Macrolite®) in single or double filtration stages removing solids, oil and polymer (97).
10) If fine micron particle size is required then the fluid (95) is sent through bag filtration units (100) in single or double follows the multimedia filtration with filtration bags (such as 3M DuoFLO® followed by absolute 3M pillow bags)
11) The resulting fluid (105) is then sent into storage tanks (110) for further use.
12) From the storage tank the treated fluid may be pumped and sent to a main blend line and may also be sent to the polymer mixing system.
13) A polymer mixing system is typically used to create a thick mother solution and utilizes a softened fresh, raw fresh, or treated produced water supply for the hydration of the polymer prior to being blended into the main blend fluid stream,
14) The combined polymer water and blend water is then mixed to the desired viscosity and is injected into the wellbore, 

It is preferable to use solids capture and separation system (such as, but not limited to, cone bottom tanks) so that solids can be removed from the water during the process.

The treated water to be used from storage tanks to send backwash water to the filtration units and water treatment as required must preferably meet the desired backwashing and water properties for treatment.

Preferably, gas blanketing is desired on the process tanks and vessels to ensure that there is no oxygen ingress into the fluid.

A tank vapour recovery system is preferred to capture the offgases from the process.

Example 2 - Steam Assisted Gravity Drainage (SAGD) or Cyclic Stimulation Steam (CSS) Thermal Water from Polymer Flood Water Treatment
If the TDS of the polymer flood returns water has reduced to the desired levels after treating the fluids with the process discussed in Example 1 then additional equipment can be added downstream of the process to make the water acceptable for thermal steam flood usage. The desired or preferred water specification for thermal steam flood usage is set out below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Water Spec</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.5 – 10.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;0.1 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>&lt;0.1 ppm</td>
</tr>
<tr>
<td>Total Hardness as CaCO₃</td>
<td>&lt;0.5 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>&lt;12000 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>0 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt;10 ppb</td>
</tr>
<tr>
<td>Sulphide</td>
<td>n/a</td>
</tr>
<tr>
<td>Sodium</td>
<td>&lt;9000 ppm</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>&lt;700 ppm</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt;2 NTU</td>
</tr>
<tr>
<td>TSS</td>
<td>&lt;1 ppm</td>
</tr>
<tr>
<td>iron</td>
<td>&lt;0.5 ppm</td>
</tr>
</tbody>
</table>

In a process to treat polymer flood waters used in oilfields for eventual reuse in Steam Assisted Gravity Drainage (SAGD) or Cyclic Steam Stimulation (CSS) thermal water, there is provided the following steps which incorporate the use of a gas bubbler according to a preferred embodiment of the present invention which will be better understood by referring to Figure 3:

1) Process fluid (5) recovered from polymer flood activities flows into a cone bottomed storage tank (10) (or other mechanical separation equipment equipped with an oil skimmer at the top of the tank) where the solids (16) are removed from fluid as needed; and oil (17) is skimmed off from the storage tank as needed.

2) When the resulting fluid (15) shows signs of being sour (¼S is present), the tank is equipped with a double loop square gas bubbler inside (20) and gas (23)(like natural ps) is bubbled into the storage tank fluid reservoir as the fluid flows in/out of the tank. This permits the stripping out the H₂S and other gases (27) present in the fluid. Natural gas volume is added at a 1 to 1 ratio to the fluid offgas volume.
3) Then, follows a step of oil removal (30) prior to water treatment - fluid (25) flows through a
single or two stage polymer packing vessel(s) for oil adsorption/coalescence (37) if such step is
necessary required (like Mycelx®) - there is recovery of an oil stream.
4) If the resulting fluid's (35) oil and grease level is sufficient, then the fluid (35) is then pumped and
the pH is raised in the fluid by adding a chemical (like caustic - sodium hydroxide (43)) if pH
adjustment (40) is needed.
5) The fluid (45) is then sent through an electrocoagulation unit (50) - a closed cell design (like
Waveionics®) this prevents gases from being released into the atmosphere during the step. The
electrocoagulation step consists of metal plates with electrodes that are electrified as the fluid
passes through the cell. The metal plates are consumed and the metal precipitates with the water
solids (57).
6) Then, what follows is another step of chemical addition (60) where additional chemicals (63) like
cauistic and coagulant, are added to the fluid (55) to assist with solids removal (67) by further
raising the pH and promoting precipitation or agglomerating the particles
7) Then, a chemical addition step is performed (370) where a chemical (like phosphate or lime)(373)
is added to the fluid (65) to remove additional hardness (calcium and magnesium) (377) not
removed by the electrocoagulation step above.
8) The fluid (375) then undergoes a bulk solids removal stage (380Xthrough the use of a tank, like a
cone bottomed tank and/or solids clarifier) where solids (386) are removed and oil (387) is
recaptured, if applicable.
9) If necessary, the fluid (385) undergoes another bulk solids removal stage (390)(through the use of
a tank, like a cone bottomed tank and/or solids clarifier) where solids (396) are removed and oil
(397) is recaptured.
10) The resulting fluid (395) is then pumped through multimedia filtration step (400)(like ceramic
media MacroHe®) in single or double filtration stages
11) If fine micron particle size desired is not attained, then the fluid (405) is sent through bag
filtration units (410) in single or double with filtration bags (like the nominal 3M DuoFLO®
followed by absolute 3 M pillow bags).
12) After filtration, the resulting fluid (415) will undergo a double pass reverse osmosis (420) which
is performed with membranes in series. The waste stream, concentrated RO reject, from the RO
system then needs to go to an evaporator to remove the contaminants, like alkalinity and silica,
and reduce the overall waste volume. The resulting fluid (425) then flows into storage tanks
(430) for future usage such as to make steam.
Alkaline Surfactant Polymer (ASP) or Alkaline Surfactant Brine Polymer (ASBP) Flood Water Treatment

The following desired or preferred water specification for alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) flood water was determined from laboratory small scale fluid testing and was further implemented onsite:

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<th>Parameter</th>
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<tbody>
<tr>
<td>pH</td>
<td>7.5 – 13.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>Total Hardness as CaCO3</td>
<td>30 - 70 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>8000 – 25000 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>0 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt; 50 ppb</td>
</tr>
<tr>
<td>Sodium</td>
<td>&lt; 8500 ppm</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>&lt; 5000 ppm</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt; 10 NTU</td>
</tr>
<tr>
<td>TSS</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt; 1 ppm</td>
</tr>
</tbody>
</table>

The site produced water is being treated with oil removal system and water treatment system as listed below in Example 3.

The goal was to confirm the water specification for alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) flooding activities determined in laboratory and help in finding a more economical water treatment process. It is estimated that the use of a process of treating ASP or ASBP polymer flood produced water prior to its reuse for the same purpose can yield reductions ranging from 200 to 400 ppm in the polymer usage.

Alkaline Surfactant Polymer (ASE) or Alkaline Surfactant Brine Polymer (ASBP) Flood Water Spec

The alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) water specification for polymers for hydration was determined through field pilot scale testing at a rate of 450 m³/day.
According to an embodiment of the present invention, the alkaline surfactant polymer (ASP) or the alkaline surfactant brine polymer (ASBP) flood water treatment unit comprises: a tank gas bubbler, a Mycelx® oil water separator; a Mycelx® backwash vessel; at least one multimedia filtration unit (more preferably, in double train of dual multimedia filter vessels in series); a double train primary/polisher strong acid cation ion exchange vessels with brine and caustic reagent step, and one or more of chemical injection systems.

Some advantages of using a process incorporating a gas bubbler according to a preferred embodiment of the present invention for the preparation of an alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) flood water include: the removal of H₂S and other gases like CO₂ by the tank gas bubbler (optional), the removal and recovery of oil from the ASP or ASBP polymer produced water stream and the creation of a sales oil stream with the Mycelx® green polymer packing technology vessels (OWS and BW) - revenue from sales oil stream; the removal of the solid particles from the water stream with filtration; the removal of the hardness from the water with strong acid cation resin exchangers down to 5 - 10 ppm leakage (designed for some hardness leakage); the removal of the polymer, silicates, and oil and grease from the strong acid cation resin and multimedia filters with the addition of a caustic regeneration cycle step - to remove key foulants of other ASP polymer flood systems resins and medias; the savings on polymer loading, facilities and downhole scaling of lines and injection wells which translates into less downtime and less wellbore workover costs; and the reduced cost of softening - i.e. SAC/SAC regeneration with caustic step added to the brine step is cheaper than currently used WAC (weak acid cation) regeneration chemicals of acid and caustic; and the creation of a liquid waste to be disposed of from strong acid cation ion exchange softeners versus other technologies that may create a solids waste and liquid waste to deal with.

It is estimated that the use of a process of treatment of polymer flood water incorporating a gas bubbler according a preferred embodiment of the present invention can yield reduction in 200 to 400 ppm of polymer usage which is substantial given the cost of polymer and the amounts of water treated. These savings can amount to several million dollars yearly on a large scale project.

By having an optional chemical addition step at the end of the water treatment process one can adjust the conductivity of the fluid with brine to reduce amount of alkaline required for best surfactant activity.
The way to pretreat ASP or ASBP polymer flood water according to an embodiment of the present invention, allows one to utilize produced water for polymer mixing and reinjection versus disposal and using makeup waters.

Example 3 - Alkaline Surfactant Polymer (ASP) or Alkaline Surfactant Brine Polymer (ASBP) Flood Water Treatment

The polymer flood water treatment unit to yield water for eventual reuse in ASP or ASBP Polymer Flood Water, incorporates a gas bubbler according to an embodiment of the present invention, may also comprise a Mycelx® oil water separator; a Mycelx® backwash vessel; at least one multimedia filtration unit; a double train primary/polisher strong acid cation ion exchange vessels with brine and caustic regeneration step, and one or more chemical injection systems.

In a process to treat alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) flood water used in oilfields for eventual reuse, there is provided the following steps, which incorporate the use of a gas bubbler according to an embodiment of the present invention, the process will be better understood by referring to Figure 2:

1) Process fluid (5) recovered from polymer flood activities flows into a cone bottomed storage tank (10) (or other mechanical separation equipment equipped with an oil skimmer at the top of the tank) where the solids (16) are removed from fluid as needed; and oil (17) is skimmed off from the storage tank as needed.

2) When the resulting fluid (15) shows signs of being sour (H₂S is present), the tank is equipped with a double loop square gas bubbler inside (20) and gas (23Xlike natural gas) is bubbled into the storage tank fluid reservoir as the fluid flows in/out of the tank. This permits the stripping out the H₂S and other gases (27) present in the fluid. Natural gas volume is added at a 1 to 1 ratio to the fluid offgas volume.

3) Then, follows a step of oil removal (30) prior to water treatment - the fluid (25) flows through a single or two stage polymer packing vessel(s) for oil adsorption/coalescence (37) if such step is necessary (like Mycelx®) - there is recovery of an oil stream.

4) The fluid (35) is then pumped through multimedia filtration (90)(like ceramic media Macrolite®) in single or double filtration stages:
   a. Oxidant Chemical (91)(like bleach) is added upfront of filters to reduce fluid viscosity (destroy the remaining polymer) and to kill bacteria;
   b. Coagulating Chemical (92Xlike polyaluminum chloride PAC) is added upfront of filters to coagulate particles - which aids in the filtration; and
c. Reducing Chemical (93) (like sulphite) is added in downstream of first filter (upfront of second filter) to remove the oxidant chemical residuals (i.e. consume the bleach, if present);

d. There is a filter backwash step to include an additional step of addition of alkaline chemical (94) (like caustic) for polymer, silica, and oil removal from the filtration media;

5) Then, the fluid (115) passes through a shearing stage (120) of a inline static mixer followed by an inline jet nozzle and into a storage tank;

6) Then, the fluid (125) is pumped through anion exchangers (130), two strong acid cation resin vessels in series called SAC/SAC,

a. Due to the higher fluid total dissolved solids, the SAC/SAC is designed to leak from 5 ppm to 10 ppm hardness (calcium and magnesium) in effluent - to not achieve normal 0 ppm hardness leakage.

b. Optionally, it has an additional alkaline chemical injection step (like caustic) as part of the regeneration cycle - the alkaline chemicals are being utilized to remove polymer, silica, and oil from the strong acid cation resin beads.

7) In the event that fine micron particle size is desired, then the fluid (135) flows through bag filtration units (100) in single or double will follow the anion exchangers (130) with filtration bags (like the nominal 3M DuoFLO® followed by absolute 3M pillow bags)

8) The resulting fluid (145) is then sent into a storage tank (140).

9) From the storage tank (140), the fluid (145) is pumped and chemicals 143 (like caustic, surfactant, brine, and polymer) are added to create the required alkaline surfactant polymer (ASP) or alkaline surfactant brine polymer (ASBP) mixture (155) to be injected downhole. In alkaline surfactant brine polymer (ASBP) the brine is added to increase the conductivity and reduce the alkaline volume required for the overall alkaline surfactant brine polymer mixture.

10) A polymer mixing system (150) is used to create a thick mother solution and utilizes a softened fresh (175), raw fresh, or treated produced water supply (5) for the hydration of the polymer (165) prior to being blended into the main chemical fluid stream (155).
CLAIMS

1. A gas bubbler designed to be used inside a tank having walls, said tank adapted to receive a liquid to be treated, wherein said gas bubbler comprises:
   - at least one inlet;
   - at least one tubing length designed to be inserted inside the tank;

said at least one tubing length positioned horizontally and defining a plane and wherein said tubing containing a plurality of apertures disposed along the tubing underneath said plane, said apertures facing the walls but positioned at an angle less than perpendicular to the walls of said tank,

2. The gas bubbler according to claim 1, wherein the apertures are positioned at an angle ranging from 20° to 60° with respect to the walls.

3. The gas bubbler according to claim 2, wherein the apertures are positioned at an angle of 45°.

4. The gas bubbler according to any one of claims 1 to 3, wherein there are two inlets and two separate and distinct tubing lengths spaced apart from one another each defining a specific plane and where one tubing length is generally positioned above the other tubing length.

5. A gas bubbler designed to be used inside a tank having walls, said tank adapted to receive liquid to be treated, wherein said gas bubbler comprises:
   - at least one inlet;
   - at least one tubing length designed to be inserted inside the tank;

said at least one tubing length defining a plane and wherein said tubing containing apertures disposed undemeath said plane, said apertures being positioned at a downward angle of 45° in relation to the walls of said tank.

6. A method for removing H₂S from water used in the oil industry, said method comprising the steps of:
   - introducing water requiring degassing into a tank fitted with a gas bubbler;
   - injecting natural gas into the gas bubbler at a ratio of 1:1 natural gas volume injected/offgas (containing H₂S) volume present in the used water, and
   - removing the gas extracted at die surface of the water;
said gas bubbler comprising a tubing defining a horizontal plane, said tubing having apertures disposed therealong at a 45° angle underneath the plane defined by the tubing.

7. A method for removing 3/4 S from water used in oil extraction, said method comprising the steps of:
   - introducing water requiring degassing into a tank fitted with a gas bubbler;
   - injecting natural gas into the gas bubbler, and
   - removing the gas extracted at the surface of the water;
said gas bubbler comprising a tubing defining a horizontal plane, said tubing having apertures disposed therealong at a 45° angle underneath the plane defined by the tubing, and wherein the concentration of H₂S in the water is decreased.

8. The method according to claims 7 where the concentration of H₂S in the water is decreased to a level that results in 100 to 400 ppm polymer reduction.

9. A gas bubbler for use in water treatment in the oil industry, said gas bubbler adapted to be used inside a tank having walls, wherein said gas bubbler comprises:
   - at least one inlet;
   - a loop made of at least one tubing length designed to be inserted inside the tank;
said loop being positioned horizontally and defining a plane and wherein said tubing containing a plurality of apertures disposed along the tubing underneath said plane, said apertures facing the walls at a 45° angle.

10. A gas bubbler according to claim 9, wherein it is positioned at a lower portion of the tank and around the inside perimeter of the tank.

11. A gas bubbler according to claim 10, wherein the tubing is positioned at a distance from the wall ranging from a third of the length of the radius of the tank to half of the length of the radius of the tank.

12. A gas bubbler according to any one of claims 9 to 11 comprising an upper loop and a lower loop, wherein the upper loop is positioned generally directly above the lower loop.
FIG. 1
FIG. 3
A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C02F I/20** (2006.01) , **B01F 13/02** (2006.01) , **E21B 43/40** (2006.01)

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: C02F (2006.01), B01F (2006.01), E21B (2006.01) 

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Canadian Patent Database, Questel Orbit (FamPat)

Keywords: hydrogen sulfide, gas, sparg*, bubb*, strip*, natural gas, methane, water, aqueous

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>US 201 /0272365 A1 (G. DEFOSS, L. L. MCCORRISTON), 1ONovember 2011(10-1 1-2011)</td>
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Date of mailing of the international search report


Authorized officer

Amy Westgate (819) 994-0442
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