ANTI-OXIDIZING PROCESS FOR NON-CRYOGENIC NITROGEN

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Appl. No.: 11/283,335
Filed: Nov. 18, 2005

Publication Classification
Int. Cl.
E21B 43/25 (2006.01)
E21B 43/34 (2006.01)
U.S. Cl. 166/267; 166/305.1

ABSTRACT
Downhole equipment oxidation and injection well plugging consequential of non-cryogenic nitrogen utilities is prevented or alleviated by injecting a residual oxygen scavenging compound such as ammonium bisulfite into the predominately nitrogen and residual oxygen flow stream emerging from a non-cryogenic nitrogen concentration process.
ANTI-OXIDIZING PROCESS FOR NON-CRYOGENIC NITROGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to chemical pretreatments of oxidizing gases used in subterranean well drilling and production processes.

2. Description of Related Art

The petroleum drilling and production industry has a growing reliance on non-cryogenic inert gases for numerous downhole procedures. Non-cryogenic gas is usually produced by one of two processes such as described by U.S. Pat. No. 5,388,650. Production by one procedure includes the continuous transfer of low pressure (approximately 100 to 350 psi) air through a bundled assembly of elongated tubes having semi-permeable membrane walls. The semi-permeable tubes generally comprise a plastic sleeve having a wall that is perforated by countless, micron sized apertures. This tube bundle is enclosed within a substantially evacuated vessel. As air flow traverses the tube bundle length, oxygen and water vapor pass through the tube wall apertures into the vessel enclosure volume while nitrogen and other inert gases continue along the interior length of the tubes.

On a global average, atmospheric air comprises approximately 78% nitrogen and about 21% oxygen. The approximate 1% remainder is a mixture of water vapor, carbon dioxide, argon and other inert gases. The above described semi-permeable membrane separation process effectively removes about 95% of the airborne oxygen from the original mixture. It is the remaining 5% that is the source of oilfield difficulty. This remaining atmospheric oxygen is reactively free. Since most of the downhole equipment in petroleum production of service wells is fabricated of carbon steel, the iron constituency of the material has a high reactive affinity for oxygen. The reaction product is ferrous oxide, i.e. rust. Hence, the remaining 5% oxygen in the nitrogen flow stream reacts with the steel equipment and pipe walls downhole to produce rust particles. These rust particles are returned to the surface with the nitrogen circulation flow.

It is the most critical machined surfaces that are most exposed to aggressive oxidation. These are dynamic or fluid sealing surfaces that require a high degree of finish for reliable operation. When these critical surfaces oxidize, downhole valves do not open or do not close as required on pressure command from the surface, for example.

There is another, less publicized but significant, consequence of iron oxidation generation from non-cryogenic gas utility in a subterranean well.

Most, if not all, non-cryogenic gas utilities in the oilfield are circulation flow utilities. If drilling, the gas circulation flushes the borehole of bit cuttings. If the utility is gas lifting crude production, the well effluent is piped into an appropriately closed tank or tanks for separation of the fluid phases. In any case, most of the rust particle products of an oxidation reaction are suspended in the aqueous phase of the well effluent. The aqueous phase constituent of a well effluent is usually mostly water but may also contain various dissolved acids and minerals.

Environmental concerns dictate that this aqueous phase is returned to the earth in the approximate region and strata from which it was extracted. Accordingly, environmental injection wells are drilled to receive the water portion of the liquid phase extracted from the production well. As previously explained, this aqueous portion carries the rust particle products of the non-cryogenic gas oxidation. Resultantly, these rust particles are injected into the environmental well. Over time and usage, these injected rust particles will close or fill the earth formation interstices surrounding the environmental well injection zone. Eventually, the injection zone will be sufficiently sealed by the rust particle accumulation as to effectively prevent continued water injection. At this point, the well must be abandoned in lieu of another environmental well or chemically treated to dissolve the accumulated ferrous oxide.

It is an object of the present invention to teach a method and apparatus that, on the one hand, reduces or eliminates the oxidation of downhole well equipment and fixtures due to residual oxygen in a non-cryogenic flow stream.

Also an object of the present invention is a quest to develop a technology that prevents or mitigates the deposit of ferrous oxide particle into a water injection well.

SUMMARY OF THE INVENTION

Damage due to residual oxygen in a non-cryogenic gas utility in a well drilling or production enterprise may be reduced or eliminated by blending the non-cryogenic gas flow stream comprising predominately nitrogen in the presence of residual oxygen with an oxygen scavenger selected from the family including ammonium bisulfite.

A non-cryogenic nitrogen utility pursuant to the present invention comprises a low pressure, high volume compressor for atmospheric air. Low pressure discharge from the high volume compressor is channeled into a bundled, semi-permeable membrane tank. Following transit through the main flow stream channel within the bundled tubes, the concentrated main stream, comprising predominately nitrogen and a small quantity of residual oxygen, is further compressed to the downhole utility pressure.

Prior to well injection, however, the high pressure mixture of nitrogen and oxygen is further mixed with an oxygen scavenger compound such as ammonium bisulfite binder. Upon circulated return to the surface, the well effluent is phase and gravimetrically separated. Some of the gaseous effluent may be recycled back into the concentrated nitrogen makeup stream. The liquid phase effluent comprising predominately water and the dissolved oxygen complex, for example, is preferably injected back into the earth in an environmental disposal well.

BRIEF DESCRIPTION OF THE DRAWING

With respect to FIG. 1, the single figure of the drawing, a flow schematic is represented to illustrate a non-cryogenic gas production and oilfield utility system that incorporates the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawing schematic, a low pressure, high volume compressor 10 draws in atmospheric air and
compresses it to the range of about 100 psi to 400 psi. A conduit or storage vessel 11 transfers the compressed air into a semi-permeable membrane bundle 14. The membrane bundle 14 is enclosed by an oxygen transfer vessel 15 for confinement of the oxygen that passes through the semi-permeable walls of the bundle.

[0017] The oxygen effluent 17 is drawn out of the membrane vessel by a pump not shown and either released to the atmosphere, bottled or piped to another utility such as an engine or fuel cell.

[0018] The predominately nitrogen mainstream 19 is piped into a high pressure compressor 26. The high pressure compressor charges the concentrated nitrogen mainstream to the pressure required of the downhole utility and delivers the concentrated and pressurized nitrogen mainstream into a conduit or accumulation vessel 28. Valves 30 or other flow regulation devices regulate flow of the high pressure stream of concentrated nitrogen through appropriate conduits 32 into a mixing valve 33.

[0019] The mixing valve 33 proportionally blends a suitable oxygen scavenging compound with the concentrated nitrogen mainstream 32. A presently preferred example of oxygen scavenging compound is a liquid form of ammonium bisulfite (NH₄HSO₃) having the essential property of either reacting with the residual oxygen in the nitrogen mainstream or complexing with the free oxygen present in the concentrated nitrogen mainstream to bind it from further reaction with the materials of downhole equipment. Of course, the reaction product of the additive and the residual oxygen must remain in fluid suspension throughout the remaining steps of the process. The additive quantity is determined as a function of the nitrogen mainstream flow rate and the separation efficiency of the semi-permeable membrane bundle. These two functions determine the flow rate quantity of residual oxygen in the mainstream whereby the reactive potential of the residual oxygen is blocked or preempted. Other possibly useful compounds may include ammonium hydrogen sulfite solution, ammonium acid sulfite solution, monoammonium sulfite solution and sulfurous acid monoammonium salt solution.

[0020] In the case of a production utility, the treated nitrogen stream 34 may be piped into the casing annulus of well 35 and returned with formation fluid up the inside flow bore of a production tube 36. If the treated nitrogen utility is drilling, the flow route is somewhat reversed. The high pressure delivery conduit would enter the drill string through a fluid swivel mechanism not shown and be expelled from the well 35 casing annulus.

[0021] In either case, the well discharge stream 38 carries the well effluent to appropriate separation tankage 40. Although such tankage is conveniently represented by the drawing as a single vessel 40, in fact, numerous complex vessels are involved in the effluent separation process.

[0022] The separation vessels 40 receive a mixed phase flow stream 38 and induce separation of the three fluid phases. Traditionally, the phases are separated gravimetrically. The lighter, gaseous portion of the return flow stream 38 may contain natural gas (hydrocarbon fuel gas), helium or any number or naturally occurring in situ formation gases in addition to the treated nitrogen originally charged into the well. Some of these natural gases may be useful to the downhole utility and therefore recycled with the treated nitrogen. Others may be corrosive or of greater value in other utilities and are therefore separated. Those of skill in the art will be familiar with those separation processes.

[0023] The recycled gases 42 may be directed into a recycle compressor 44. A flow regulation system 46 meters the recycled gas flow into the treated nitrogen make-up flow 24.

[0024] Generally, the liquid hydrocarbon products C₄H₈ are lighter than water. Hence, the hydrocarbon liquids may be decanted through an intermediate flow stream 48.

[0025] Volumetrically, water may be the most abundant fluid product of a declining well. Although the heaviest liquid is here characterized as “water”, rarely does the liquid consist of the pure binary compound. No only are numerous dissolved minerals present but also present are numerous dissolved and immiscible acids. Hence, this aqueous well effluent characterized as “water” is, in reality, a toxic liquid cocktail.

[0026] Being the most dense of the phases and therefore the heaviest, the water separates gravimetrically at the bottom of a static separation vessel 40 as graphically represented by the drawing. The water drainage is carried away by conduits 50 into high pressure injection pumps 52. The high pressure discharge 54 from the pumps 52 is connected into the injection tube 58 flow bore of an environmental well 60. The injection tube 58 discharges the water into a suitable earth formation 56.

[0027] Presumptively, the only compound present in the well injected “water” that was not present in the original production are the complex products of ammonium bisulfite and oxygen. These, however, remain in liquid solution with other minerals originally present and therefore migrate away from the injection zone of the well 60.

1. A conditioning process for a subterranean well utility gas containing free oxygen, said process comprising the step of mixing an oxygen scavenging compound with said utility gas prior to well injection.

2. A well utility gas conditioning process as described by claim 1 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite.

3. A well utility gas conditioning process as described by claim 1 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite solution, ammonium hydrogen sulfite solution, ammonium acid sulfite solution, monoammonium sulfite solution and sulfurous acid monoammonium salt solution.

4. A process for extracting fluid from a subterranean well comprising the steps of:

   a. generating a flow stream of non-cryogenic nitrogen containing residual quantities of oxygen.

   b. mixing an oxygen scavenger compound with said flow stream;

   c. injecting the mixed flow stream comprising non-cryogenic nitrogen and oxygen scavenger into a subterranean well;

   d. recovering fluids extracted from said well; and

   e. separating said extracted well fluids by phase and gravity.
5. A process for extracting fluid from a subterranean well as described by claim 4 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite.

6. A process for extracting fluid from a subterranean well as described by claim 4 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite solution, ammonium hydrogen sulfite solution, ammonium acid sulfite solution, monoammonium sulfite solution and sulfurous acid monoammonium salt solution.

7. A process for extracting fluid from a subterranean well as described by claim 4 wherein portions of separated fluid containing water are returned to a subterranean formation.

8. A process for conditioning a non-cryogenic nitrogen drilling fluid containing residual oxygen, said process comprising the step of mixing an oxygen scavenging compound with said drilling fluid.

9. A process as described by claim 8 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite.

10. A process as described by claim 8 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite solution, ammonium hydrogen sulfite solution, ammonium acid sulfite solution, monoammonium sulfite solution and sulfurous acid monoammonium salt solution.

11. An apparatus for supplying utility gas to a subterranean well, said apparatus comprising:
   a. a first compressor of atmospheric air having a first discharge flow stream;
   b. a semi-permeable membrane bundle receiving said first discharge flow stream for substantial separation of oxygen from said atmospheric air, said membrane having a second discharge flow stream substantially comprising nitrogen mixed with a substantially reduced quantity of oxygen;
   c. a second compressor receiving said second discharge flow stream and discharging a third flow stream;
   d. a proportional mixing valve receiving said third flow stream and a forth flow stream comprising an oxygen scavenging compound for generating a fifth discharge flow stream, said mixing valve combining said oxygen scavenging compound with said third flow stream at a rate sufficient to substantially preempt the reactive potential of residual oxygen in said third flow stream; and,
   e. utilizing said fifth discharge flow stream in a subterranean well development.

12. An apparatus as described by claim 11 wherein said subterranean well development is a well drilling operation.

13. An apparatus as described by claim 11 wherein said subterranean well development is a well fluid extraction operation.

14. An apparatus as described by claim 11 wherein said oxygen scavenging compound is ammonium bisulfite.

15. An apparatus as described by claim 11 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite.

16. An apparatus as described by claim 11 wherein said oxygen scavenging compound is selected from the group comprising ammonium bisulfite solution, ammonium hydrogen sulfite solution, ammonium acid sulfite solution, monoammonium sulfite solution and sulfurous acid monoammonium salt solution.

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