

**SUBSEA DEOXYGENATION IN A WATER INJECTION PROCESS PLANT****BACKGROUND**

This invention relates to equipment, systems, and methods used to deoxygenate seawater. More specifically, the invention relates to a subsea catalytic deoxygenation unit in a subsea water injection process plant.

Current seawater injection process plants include topsides treatment steps, with equipment for each step placed on a platform (*see* FIG. 1). The treatment steps include seawater filtration and biofouling control by way of chemical additions. The filtration takes place at mesh sizes ranging from coarse strainers (to exclude fish and sand) to reverse osmosis membranes (to exclude monovalent ions). The chemical additions include in situ generated hypochlorite (electrochlorination). A deoxygenation or deaeration step is then added topsides so all gases are removed from the seawater.

Some seawater injection process plants are being located subsea (*see* FIG. 2). However, deoxygenation or deaeration, if used, must occur topsides.

The deaeration equipment used topsides relies on mass transfer processes. The most common of these processes is vacuum deaeration. This process cannot be implemented subsea due to the hydrostatic head above the equipment (*e.g.* 3000 m of water).

The deoxygenation equipment can be a catalyst bed-based seawater deoxygenation unit to remove dissolved oxygen from seawater by reacting it with hydrogen (*see e.g.* FIGS. 3–5 and US 2014/0054218 A1 hereby incorporated by reference). This reaction occurs on the open areas of the catalyst bed.

Removal of oxygen from seawater has value to a well operator because seawater with oxygen is highly corrosive. If a well operator wants to inject seawater that has not been deoxygenated, the operator needs to use pipework or tubulars made of an expensive corrosion resistant alloy or lined carbon steel. Even lined carbon steel is not perfect. Any tools put into the well to service it can damage a polymer lining or coating, leading to carbon steel corrosion.

Seawater without oxygen — for example, having an oxygen content no more than about 20 to 50 parts per billion — is relatively benign. Therefore, the pipework conveying the injection water to the reservoir can be made of low cost carbon steel.

#### SUMMARY

A preferred embodiment of a subsea water injection process plant includes a catalytic deoxygenation unit located subsea that makes use of a reducing agent sent from topsides in liquid form. The catalyst is preferably a palladium catalyst or its equivalent. The reducing agent is an oxygen scavenger such as but not limited to hydrazine, carbohydrazide, sodium erythorbate, methyl ethyl ketoxime (“MEKO”), hydroquinone, diethylhydroxylamine (“DEHA”), formic acid (methanoic acid). A chemical umbilical can be used to deliver the reducing agent to a mixer located upstream of the deoxygenation unit, where the agent is mixed with seawater containing oxygen. Hydrogen could be used as the reducing agent but is not preferable because of the practical difficulties of producing it subsea or delivering it subsea.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic of a prior art topsides water injection process plant.

FIG. 2 is a schematic of a subsea water injection process plant that does not deoxygenate the seawater.

FIG. 3 is a schematic of a prior art topsides catalytic bed-based deoxygenation unit that uses two-stage nanofiltration membrane system upstream of the unit.

FIG. 4 is a schematic of a prior art topsides catalytic bed-based deoxygenation unit that uses a single stage reverse osmosis membrane system upstream of the unit.

FIG. 5 is a schematic of a prior art topsides catalytic bed-based deoxygenation unit that uses a single stage microfiltration or ultrafiltration membrane system upstream of the unit.

FIG. 6 is a schematic of a preferred embodiment of a subsea deoxygenation process train or system made according to this invention. The catalytic deoxygenation unit is located subsea and makes use of a liquid reducing agent that is sent to the unit via a chemical umbilical from topsides.

**Elements and Element Numbering Used in the Drawings and the Detailed Description**

|    |                                             |
|----|---------------------------------------------|
| 10 | Subsea deoxygenation system                 |
| 15 | Raw (untreated, unfiltered) seawater stream |
| 20 | Coarse strainer                             |
| 30 | Biofouling control (chemical dosing) means  |
| 40 | Filtration system                           |
| 41 | Fine filtration means                       |
| 43 | Sulfate ion removal means                   |
| 45 | Salinity reduction means                    |
| 50 | Catalytic deoxygenation unit                |
| 51 | Static mixer                                |
| 55 | Chemical umbilical                          |
| 60 | Reducing agent                              |
| 65 | Deoxygenated seawater stream                |
| 70 | Injection pump                              |

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Unlike the mass transfer processes used to deaerate or deoxygenate seawater, catalytic deoxygenation can achieve the required low oxygen concentration without the need for additional oxygen scavenging chemicals. More importantly, catalytic deoxygenation can operate at subsea ambient pressures whereas mass transfer processes cannot. However, the hydrogen gas needed for a catalytic deoxygenation unit located topsides is not practical to make subsea or deliver to a unit located subsea.

Deoxygenation according to this invention takes place entirely subsea. The process used includes the steps of delivering from topsides to subsea a reducing agent in liquid form; mixing the reducing agent with a seawater stream containing oxygen; and deoxygenating the mixture subsea using a catalyst bed-based deoxygenation unit.

Referring now to FIG. 6, a preferred embodiment of a subsea deoxygenation system 10 receives a raw (untreated, unfiltered) seawater stream 15 and passes the stream 15 through a coarse strainer 20, biofouling control means 30 such as in situ oxidant generation by electrolysis or non-oxidizing chemical injection, a filtration system 40, and a catalytic deoxygenation unit 50. The arrangement of this equipment can change based upon application-specific requirements. For example, the biofouling control means 30 can be placed ahead of the strainer 20 or the filtration system 40 (or a portion of it) can be located downstream of the catalytic deoxygenation unit 50.

The unit 50 can be arranged as a compact subsea unit housed in a flooded housing (not shown). A deoxygenated seawater stream 65 exits the unit 50 and enters an injection pump 70.

The catalyst used in unit 50 is preferably a palladium catalyst or its equivalent. One or more AUV- or ROV-retrievable canisters containing the catalyst could be used.

The reducing agent 60 is an oxygen scavenger in liquid form such as but not limited to hydrazine, carbohydrazide, sodium erythorbate, methyl ethyl ketoxime ("MEKO"), hydroquinone, diethylhydroxylamine ("DEHA"), and formic acid (methanoic acid). Hydrogen could theoretically be used as a reducing agent subsea, as it is used topsides, however due to the difficulties of either

making it subsea or transporting it from the surface to the seabed, the above liquid reducing agents are preferred. The reducing agent 60 is sent to the unit 50 via a chemical umbilical 55 from topsides.

A static mixer 51 blends the reducing agent 60 with an outlet or permeate stream 47 of the filtration system 40. The filtration system 40 can include fine filtration means 41 such as a micro- or ultrafiltration system, sulfate ion removal means 43 such as a nanofiltration membrane system, and reduced salinity means 45 such as a reverse osmosis membrane system. The catalytic deoxygenation unit 50 could be placed upstream of the filtration system 40 or within the filtration system 40 (*e.g.* between the sulfate ion removal means 43 and the reduced salinity means 45).

While preferred embodiments of a subsea deoxygenation system have been described in detail, a person of ordinary skill in the art understands that certain changes can be made in the arrangement of and types of components used in the process without departing from the scope of the attached claims.

## WHAT IS CLAIMED

1. A subsea water injection process plant (10) comprising:
  - a coarse strainer (20) located subsea upstream of a catalytic deoxygenation unit;
  - biofouling control means (30);
  - a filtration system (40) located subsea and arranged to receive a seawater stream (15);
  - a mixer (51) located subsea ahead of the catalytic deoxygenation unit and arranged to receive the seawater stream (15) and a reducing agent (60);
  - a catalytic deoxygenation unit (50) located subsea and arranged to receive the seawater stream (15) containing oxygen and the reducing agent (60); and
  - an injection pump (70) arranged to receive a deoxygenated seawater stream (65);wherein the catalytic deoxygenation unit (50) is arranged as a compact subsea unit housed in a flooded housing, and wherein the reducing agent (60) is in liquid form and is sent to the catalytic deoxygenation unit (50) via a chemical umbilical (55) from a topsides source.
2. A water injection process plant according to claim 1, wherein the reducing agent is selected from the group consisting of hydrazine, carbohydrazide, sodium erythorbate, methyl ethyl ketoxime, hydroquinone, diethylhydroxylamine, and formic acid.
3. A water injection process plant according to claim 1 or claim 2, wherein the filtration system includes one or more selectively permeable membranes (41, 43, 45).
4. A water injection process plant according to claim 3, wherein the one or more selectively permeable membranes includes a membrane selected from the group consisting of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

5. A water injection process plant according to claim 3 or claim 4, wherein at least one of the selectively permeable membranes is located downstream of the catalytic deoxygenation unit.
6. A method to deoxygenate a seawater stream subsea using the subsea water injection process plant of any preceding claim, the method comprising the steps of:
  - delivering from topsides to subsea a reducing agent (60) in liquid form;
  - mixing the reducing agent with a seawater stream (15) containing oxygen in mixer (51); and
  - deoxygenating the mixture subsea using the catalytic deoxygenation unit (50);wherein the reducing agent (60) is sent to the catalytic deoxygenation unit (50) via a chemical umbilical (55) from a topsides source.
7. A method according to claim 6, wherein the reducing agent is selected from the group consisting of hydrazine, carbohydrazide, sodium erythorbate, methyl ethyl ketoxime, hydroquinone, diethylhydroxylamine, and formic acid.
8. A method according to claim 6 or claim 7 further comprising the step of filtering the seawater stream using one or more selectively permeable membranes (41, 43, 45).
9. A method according to claim 8, wherein the one or more selectively permeable membranes includes a membrane selected from the group consisting of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.
10. A method according to claim 8 or claim 9, wherein at least one of the selectively permeable membranes is located downstream of the catalytic deoxygenation unit.