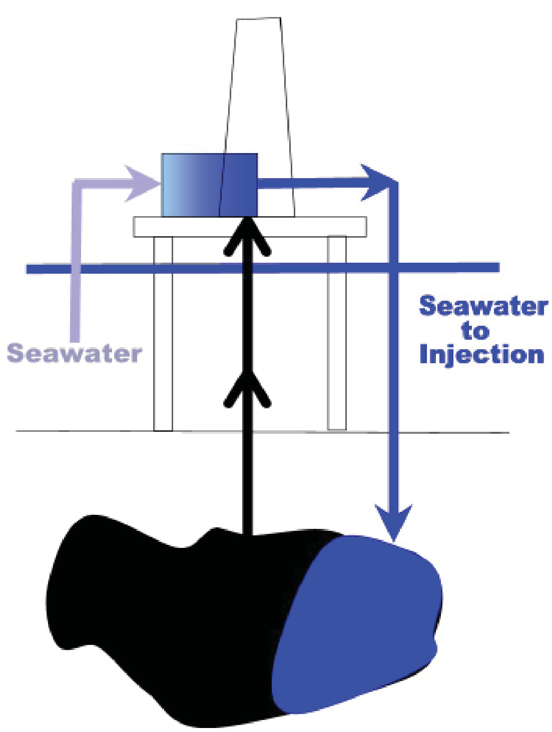
Application Note
Dissolved O_2 in Offshore Waterflood

Oil & Gas: Offshore

Introduction

Maturing oil fields both onshore and offshore account for the majority of oil production today. Enhanced Oil Recovery (EOR) techniques are important to increase efficiency and total recovery of these assets (reservoirs). EOR can account for 10 to 20% greater total recovery[1] amounting to billions of dollars of additional production. In order to meet upcoming demand and increased production targets operators plan additional implementations of waterfloods along with the need to improve reliability, uptime and efficiency of the existing systems.

Waterflood or water injection is integral to the overall EOR strategy for subsea developments. Waterflood is performed by injecting water downhole to the bottom of the reservoir to keep reservoir pressure as hydrocarbons are removed and to displace, or "sweep," the hydrocarbons towards the producing wells. The quality of the injection water is essential for protecting the permeability and quality of the reservoir along with protection of the capital equipment from corrosion and foulants. Oxygen removal and accurate reliable monitoring down to the ppb level is a critical parameter in assessing overall performance of the waterflood operations.



Water Quality

The precise chemical strategy, techniques and unit operations can differ from user to user however the most basic components and key strategies are listed here along with their purpose.

Particulates Removal
- Prevent plugging and fouling of the equipment
- Quality of the well-head permeability

Dissolved Oxygen (O_2) Removal
- Prevent microorganism growth
- Prevent corrosion of the unit operations and high pressure injection well pipe-works

Sulphates (SO_4^{2-}) Removal
- Prevents H_2S production (souring of the reservoir) which can occur via bacteria and sulphates under reduced oxygen condition

Chemical Dosing
- Anti-foaming and anti-corrosion
- Scavengers for trace removal of O_2, SO_4^{2-} and residual chlorine

Process Overview

A typical waterflood process (Figure 2) contains several unit operation stages along with chemical treatment additions to achieve the required water quality. In its most basic form it consist of filtration to remove solids, deaeration (DA) or oxygen stripping to reduce the oxygen, sulfate removal unit, along with chemical additions to purify against organism growth (barnacles, mussels, micro-organisms and bacteria) and compliment the above unit operations.

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Typical Waterflood Process

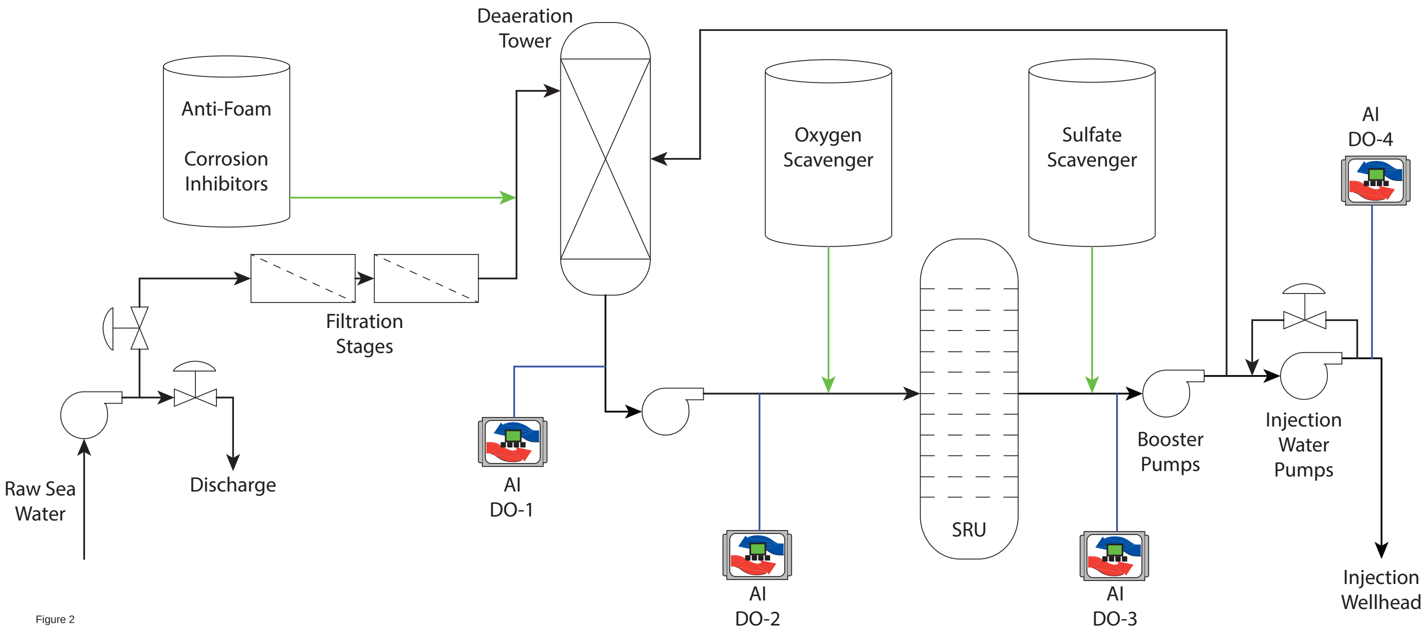


Figure 2

Measurement Points & Ranges (Figure 2)

- DO-1: Monitoring deareation tower to ensure performance of primary O_2 removal system [0.05 - 1.0 ppm DO]
- DO-2: Monitoring/control of oxygen scavenger chemical addition [0 – 10 ppb DO]
- DO-3: Monitoring for ingress of O_2 at SRU outlet [0 – 10 ppb DO]
- DO-4: Monitoring O_2 in final produced waterflood for water injection [0 – 10 ppb DO]

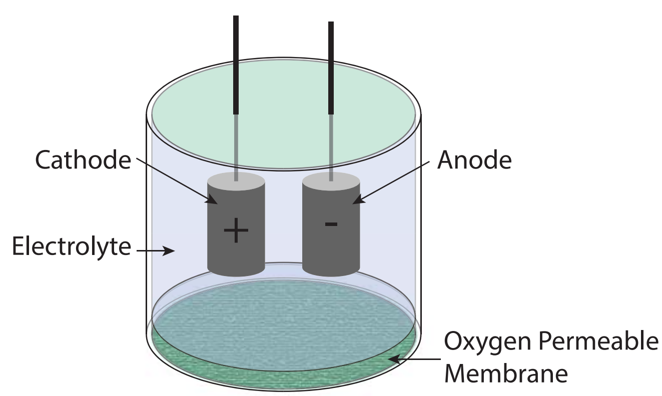
Issues with Traditional Dissolved Oxygen Sensors

Typically, electrochemical dissolved oxygen cells have been utilized throughout the industry and have proven very problematic for the waterflood applications. Poor reliability, accuracy and high-maintenance of the electrochem cells left technicians and operators with little faith in the measurement over time. All electrochem cells (Fig. 3) have anodes, cathodes, electrolyte solution and a sensitive membrane in contact with the process. The seawater salinity and process chemicals attack the cell's electrolyte and electrodes causing offsets and requiring frequent calibrations. The fouling present in the process coats the cell membrane also causing errors and high maintenance.

Cost Impact

- Cost to replace the electrochem cells is minimal compared to the high service costs in the offshore industry to perform the frequent calibration and maintenance to keep accuracy and reliability.
- Over-dosing of DO scavengers "just to be sure," causing high chemical cost ($100's k/yr)
- Over-dosing upsets the targeted

Electrochemical Dissolved O_2 Sensor



- Sensitive to flow and pressure changes
- Membrane sensitive to fouling, coating and attack
- Electrolyte poisoning
- Slow response to ppb after exposure to ppm levels

Figure 3

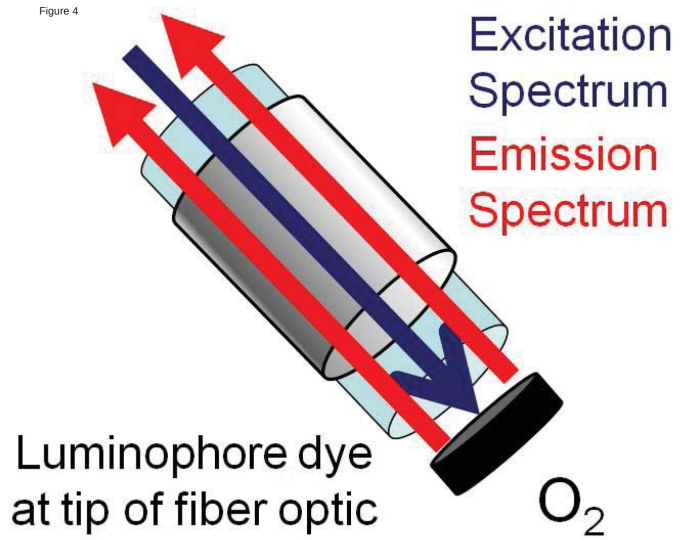
Using Precision Optical Oxygen Analyzer in Waterflood

Barben Analytical's precision oxygen analyzer, OXY 4401, uses a proven optical luminescence technique (Fig. 4) enabling high accuracy at ppb levels along with high dependability and low maintenance. The analyzer is hazardous area rated and compliant for offshore installation requirements. The sensor is unaffected by flow or pressure in liquid streams and can be placed in a simple sample stream (Fig 5). Coatings on the sensor tip may affect the measurement speed by slowing oxygen diffusion however do not affect accuracy. The optical technology does not contain electrolyte and does not react with the process and therefore the stability is excellent. Under normal "tough," operation users have set calibration periods for 30 or more days depending on expected accuracy.

Sensor and Features and Performance

- No membranes to foul or electrolyte to poison
- Limit of detection = 1 ppb DO, Accuracy = +/- 1 ppb or 3% of concentration
- Excellent long term stability, < 2 ppb drift in 30 days at 1 min sampling interval
- Fast response: gas phase T90 < 6sec, Liquid Phase T90 < 30sec
- Simple, replaceable sensor cap (lifetime expectancy is 6 months to 2 years, depending on active Cl2)
- Industrial format rated for pressures up to 1,500 psig @ 50°C
- Measurement accuracy is independent of flow velocity and line pressure allowing simple installation
  - Directly into sample line (only pressure reduction required for sample > 1,500 psig)
  - Simple sample and manual calibration station ensures quick, simple, repeatable calibration (Figure 6)

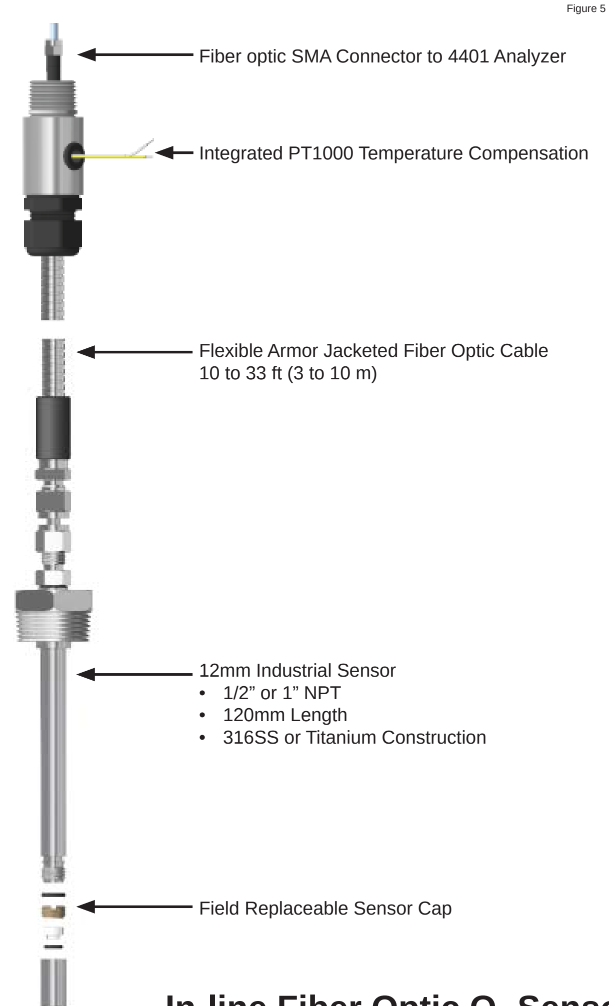
Figure 4



Analyzer

- NEMA 4X analyzer, 24 VDC or 120/240 VAC power options
- Sampling rate programmable from 5 seconds to 1 hour
- Local HMI, programmable 4-20 mA output and RS 232 digital interface
- Hazardous Area Approvals
  - US NEC and Canada CSA Class I, Div 2, Groups A, B, C and D
  - ATEX Ex II 3 G Ex nA IIC 135°C (T4)

Figure 5



In-line Fiber Optic O_2 Sensor

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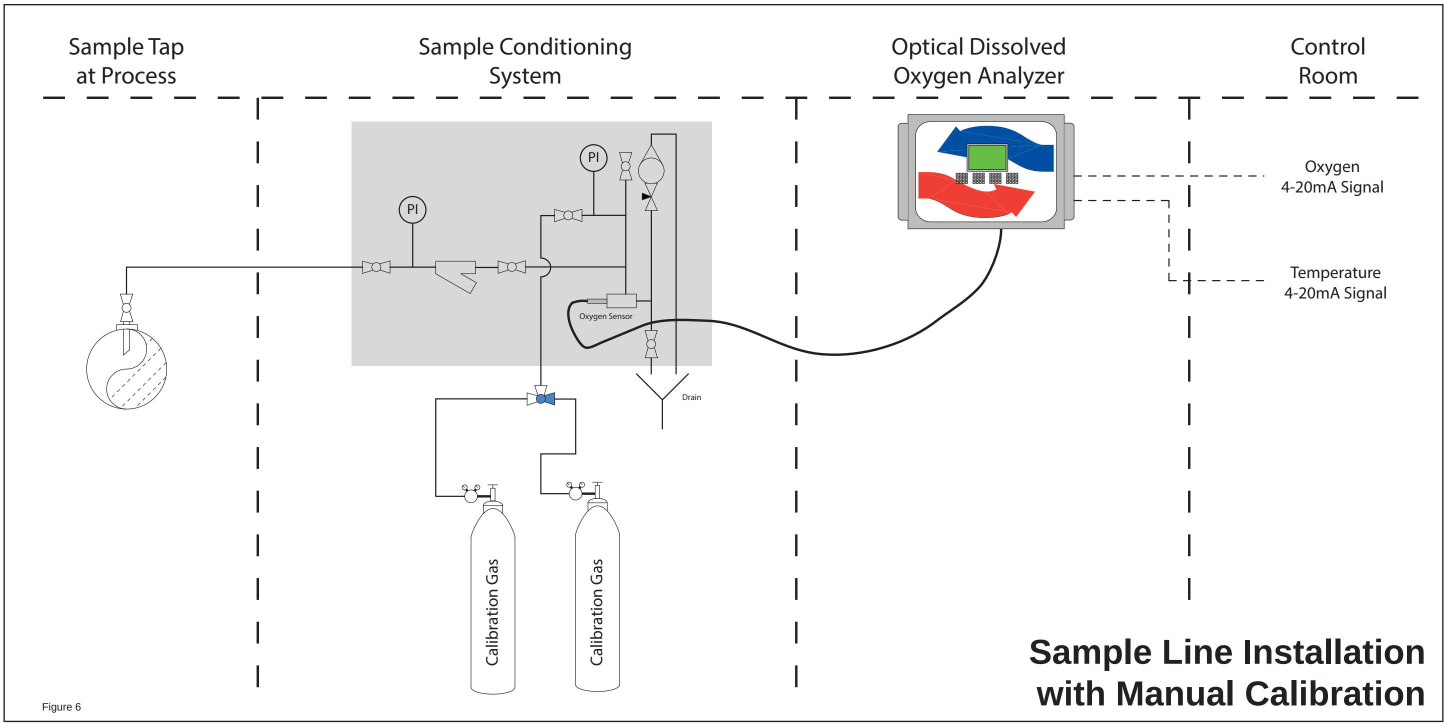

Figure 6

Additional Offshore Applications –Gas Phase O_2 Analysis in ppm to % level

The same analyzer and techniques can be used to measure O_2 in gas phase analysis in hydrocarbons, natural gas, methanol and nitrogen streams.

- Waterflood systems with countercurrent gas stripping in place of DA tower the 4401 OXY is ideal for these applications:
  - Nitrogen header for ppm to % level O_2 in gas phase
  - ppm O_2 in nitrogen with methanol (catalyst regeneration)
  - ppm O_2 in natural gas
- Nitrogen tank blanketing - % O_2
- Vapor recovery units – ppm to % O_2

References: [1] US Department of Energy, Washington DC (2011), "Enhanced Oil Recovery/ CO2 Injection." http://www.prnewswire.com/news-releases/eor-enhanced-oil-recovery-worldwide-131130908.html

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