Application Note
SAGD Water Treatment - pH and O_2

Oil & Gas: Enhanced Recovery

SAGD (Steam Assisted Gravity Drainage) is an Enhanced Oil Recovery (EOR) process common in oil sands deposits such as those found in central Canada. SAGD is extremely water intensive thus proper treatment is essential to eliminate corrosion and scale build-up. Analytical measurements such as pH and dissolved oxygen have traditionally been done in the lab if they were performed at all. The cost of ignoring or guessing about water quality has lead to costly piping failures and downtime. Now, new water treatment schemes are entering the market. In this paper we will examine the two most common water treatment strategies as well as look at solutions for continuous analytical measurements.

Introduction

All SAGD processes start with parallel wells drilled horizontally above each other. High pressure steam is injected into the upper well. The steam temperature reduces the viscosity of the trapped hydrocarbons. A mixture of oil and condensed water flow into lower well *(hence the name "gravity assisted").* The emulsion is pumped to the surface for additional separation. The liquid mixture consists of roughly 75% water and 25% heavy oil. The oil is transported off-site for refining while the water is returned to the process for reuse. The recycled water is referred to as "produced water". Because of the large volume of steam required to run a SAGD process it makes good economic and environmental sense to recycle as much water as possible. Ground water is the typical source for additional makeup water.

All water must go through additional purification before it can be turned back into steam. Produced water contains dissolved silica as well as residual hydrocarbons. The makeup water will also contain dissolved salts such as calcium. At high temperatures and pressures these salts form hard scale build-up on the inside of the boiler tubes. The scale reduces thermal efficiency thus increases the fuel expenditure to generate steam. Over time the scale will cause plugging and eventual failure. The total hardness of the water must be reduced.

The other danger present in the water is dissolved oxygen. Elevated dissolved oxygen is well known to cause pitting and corrosion in the boiler piping. If a deaerator is not used then an oxygen scavenger such as sodium sulfite must be injected to reduce oxygen to ppb levels.

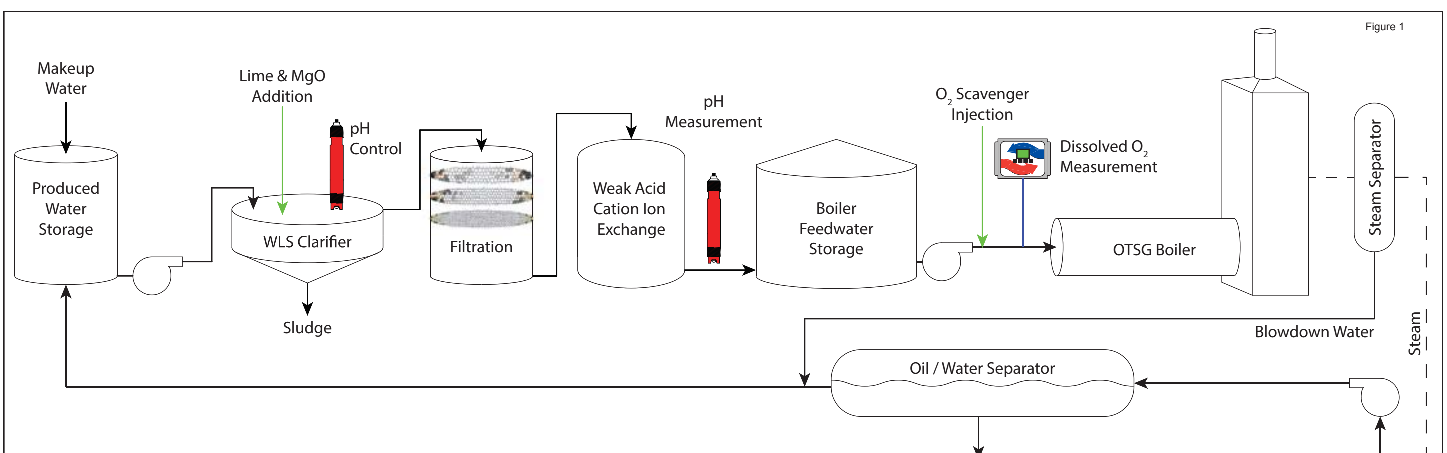
The thresholds for dissolved salts and dissolved oxygen will be dictated by the type of boiler used to generate steam (see fig. 2). Once Through Steam Generators (OTSG) are prevalent in this industry. These boilers produce low pressure, low quality (80% vapor, 20% liquid) steam. As the SAGD industry evolves there is a movement towards traditional drum style boilers for higher pressure, higher quality (100% vapor) steam.

Water Treatment Hardness Removal - WLS

Traditional water treatment in SAGD applications uses Warm Lime Softening (WLS). This is a chemical precipitation process. Hydrated lime ($Ca(OH)_2$), is added to the produced water. Lime reacts with the bicarbonates in the water based on the following equations:

$$Ca(HCO_3)_2 + Ca(OH)_2 \blacktriangleright 2CaCO_3^- + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \blacktriangleright Mg(OH)_2^- + 2CaCO_3^- + 2H_2O$$

In additional to lime, magnesium oxide (MgO) is also



Warm Lime Softening (WLS) Process

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Application Note
SAGD Water Treatment - pH and O_2

added. It reacts with water to form magnesium hydroxide ($Mg(OH)_2$). The resulting carbonates drop out of solution and form a sludge at the clarifier. This sludge must be disposed of. Silica is removed by a complex absorption reaction with the $Mg(OH)_2$.

For this process to work properly both temperature and pH control are very important. 9.5 to 10pH at 120 - 140°F (49 - 60°C) are optimum. The high temperature reduces solubility while the elevated pH provides excess OH^- ions to aid in $Mg(OH)_2$ creation. In some facilities caustic (NaOH) will be added to the clarifier for additional pH control. Additional treatment after the WLS process includes filtration and weak acid ion exchange. An added benefit of the elevated pH is that oxygen scavengers such as sodium sulfite (Na_2SO_3) react more quickly at <8.5pH. For this reason the pH of the finished boiler feedwater should be tracked to aid in control of the scavenger addition. Final parameters of the OTSG boiler feedwater are listed in Figure 2.

pH Measurement Challenges - WLS Process

In WLS process high particulates in the clarifier can lead to coating and plugging problems with the pH sensor. Residual hydrocarbons will also be present. These unrefined hydrocarbons often have traces of hydrogen sulfide (H_2S) and heavy metals. H_2S is well known to poison the Ag/AgCl element in the pH sensor. The elevated temperature of the WLS process also tends to shorten sensor life. All three issues combine to make this a difficult pH measurement.

Water Treatment Hardness Removal - Evaporation

Traditional WLS processes works well enough to reduce total hardness of the produced water; however, the trend towards drum boilers has created the need for higher purity distilled water. GE and Veolia Water are the most well known proponents of evaporation technology for

Approximate Boiler Feedwater Values	WLS Process (OTSG)	Evaporator Process (Drum Boiler)
Silica (SiO_2)	< 50 ppm	< 1 ppm
pH	8.5 - 10 pH	8.8 - 9.6 pH
Total Hardness ($CaCO_3$)	< 0.5 ppm	< 0.05 ppm
Dissolved Oxygen*	< 10 ppb	< 10 ppb

* Downstream from O2 Scavenger addition

Figure 2

SAGD water treatment. In the evaporation process produced water is mixed with caustic (NaOH) to increase readings to 11 to 13pH. The resulting reaction removes hardness by the following reactions:

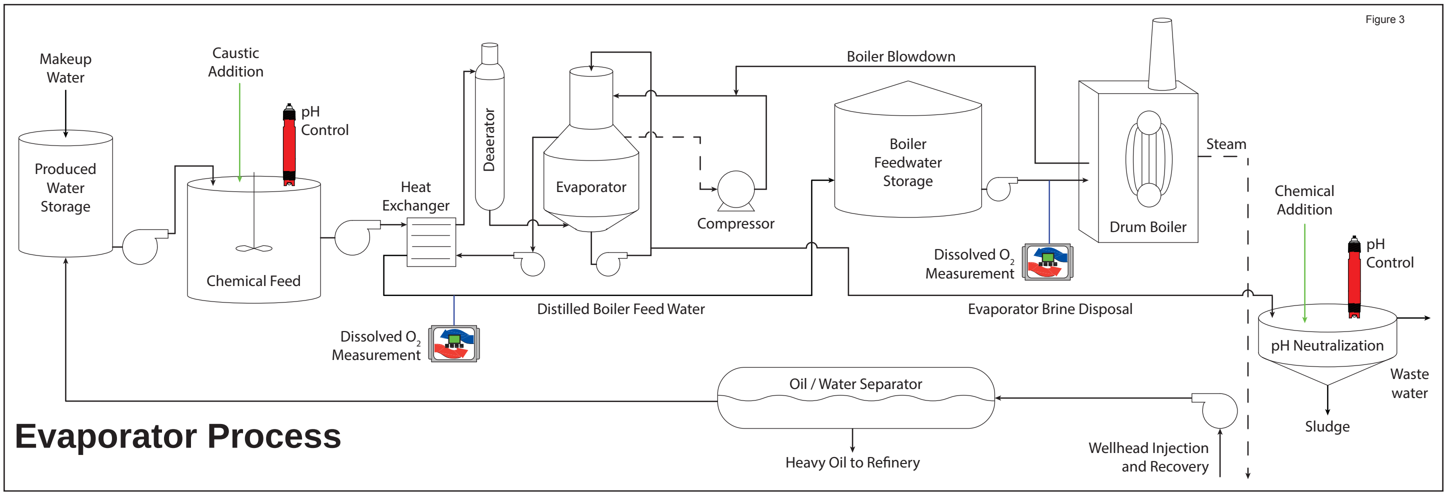
$SiO_2 + 2NaOH$ ► $Na_2SiO_3 + H_2O$
$Mg^{2+} + 2NaOH$ ► $Mg(OH)_2 + 2Na^+$
$Ca^{2+} + 2NaOH$ ► $Ca(OH)_2 + 2Na^+$

The chemically treated water is pumped through heat exchanger to bring it close to boiling point. From there the heated water passes through a deaerator to reduce dissolved gases such as oxygen and carbon dioxide. The water is then sent to the evaporator where it is continuously recirculated to convert to water vapor. This clean vapor is compressed and distilled to use as boiler feedwater. In the bottom of the evaporator an alkaline brine forms from residual salts. This brine is typically blown down (removed) and pumped to deep underground wells for disposal. In the evaporator and blowdown pipeworks the brine is kept at >11pH to maintain solubility of the silica. To meet environmental compliance, the brine requires pH neutralization prior to disposal. A clarifier is used to precipitate out the salts. If Zero Liquid Discharge (ZLD) is required than the brine will go to a crystallizer to remove solids.

pH Measurement Challenges - Evaporation Process

In the evaporation process (fig. 3) the pH sensor is used to control caustic addition. This sensor has to withstand 11 to

Figure 3



13pH. Such high pH can dissolve the glass measurement electrode and shorten the sensor's life. This sensor may also have issues with residual hydrocarbons entrained in the produced water. In this application temperature is less of an issue since the measurement is upstream of the pre-heater.

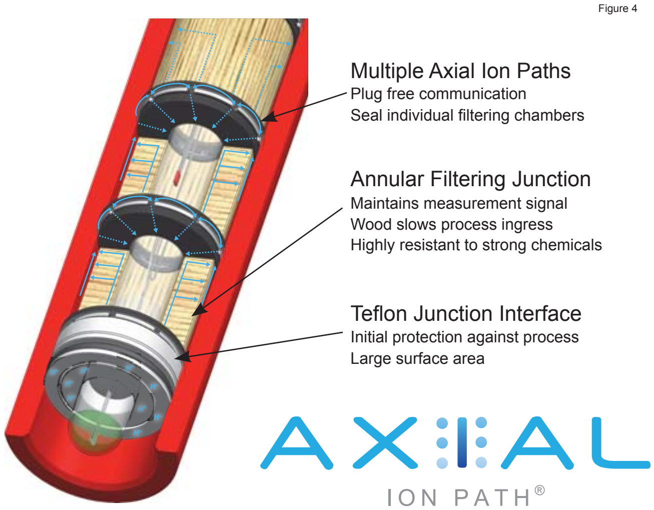
The second pH application in the evaporator process is the final treatment of the brine for environmental compliance. The pH is remains high to keep the dissolved salts in solution. At the clarifier these salts will precipitate out as the pH is lowered to neutral levels. The resulting sludge must be disposed of. Once again coating and plugging of the sensor due to high solids can become an issue.

pH Measurement Solutions

Barben Analytical Performance Series pH sensors offer an ideal design for produced water pH measurement. Most issues with pH measurement in these applications are due to reference failure. High particulates tend to plug the porous reference junction. Sulfides and heavy metals from the oil can attack the Ag/AgCl element in the reference. These same oils can plug up the reference junction increasing impedance and creating a noisy measurement.

The Barben Axial Ion Path® reference technology works extremely well to solve these issues. The filtering design of the reference keeps outside chemicals and particulates away from the internal Ag/AgCl element while still maintaining a strong signal path. Barben sensors are rated for use up to 266°F (130°C) thus are can easily withstand the elevated temperatures required in produced water applications.

Figure 4

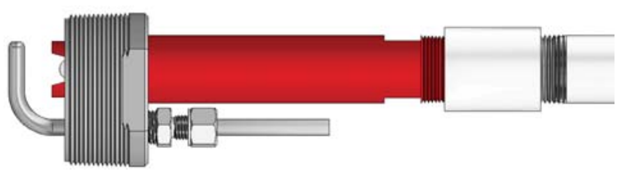


Barben sensors should be specified with "CR" high temperature, coating resistant glass electrodes. The coat resistant layer on the glass provides additional protection against strong caustic used in the evaporator process. Kynar (PVDF) should be specified as the sensor body material due to it's chemical compatibility and integrity at elevated temperatures.

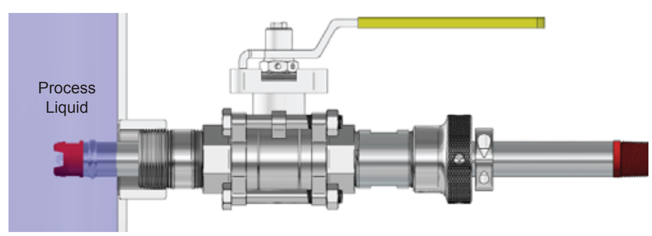
In vessels with recirculation lines, mounting the pH sensor in the piping instead of the vessel will help lessen coating issues. The flow velocity of fluid helps keep the sensor tip free of build-up. The Barben 547 retractable hot tap sensor is ideal for recirculation mounting. The sensor can be pulled for cleaning or calibration without shutting down the process. If the pH measurement is to be taken directly in the clarifier than The Barben 546 threaded submersible pH sensor used with a jet spray cleaner accessory can aid in keeping coating from forming on the sensor tip. Either air or water can be used to blast away build-up.

546 Submersible pH Sensor with Jet Cleaner

Figure 5



547 Retractable "Hot Tap" pH Sensor with Isolation Ball Valve



Dissolved Oxygen in SAGD

Dissolved oxygen should be one of the final measurements of the feedwater to the boiler. This measurement serves two purposes. When an oxygen scavenger is used, the measurement will determine the effectiveness of the chemical in removing oxygen. When the scavenger is properly dosed and has enough reaction time readings should be <10ppb. A dissolved oxygen reading is also very helpful in determining leaks in upstream valves, heat exchangers and pumps. These leaks will allow the ingress of oxygen which can be detected by the increasing reading.

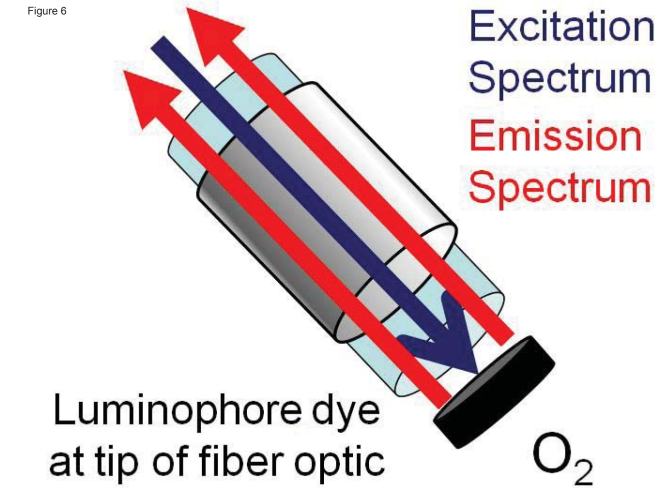
Since SAGD involves hydrocarbon recovery the dissolved oxygen analyzer may require agency approval for Division II or Zone 2 areas.

Application Note
SAGD Water Treatment - pH and O_2

Dissolved Oxygen Measurement Solutions

Recent advances in optical dissolved oxygen measurement allows virtually maintenance free measurement down to ppb levels. Optical technology relies on the quenching effect of oxygen on luminescent dye.

Figure 6



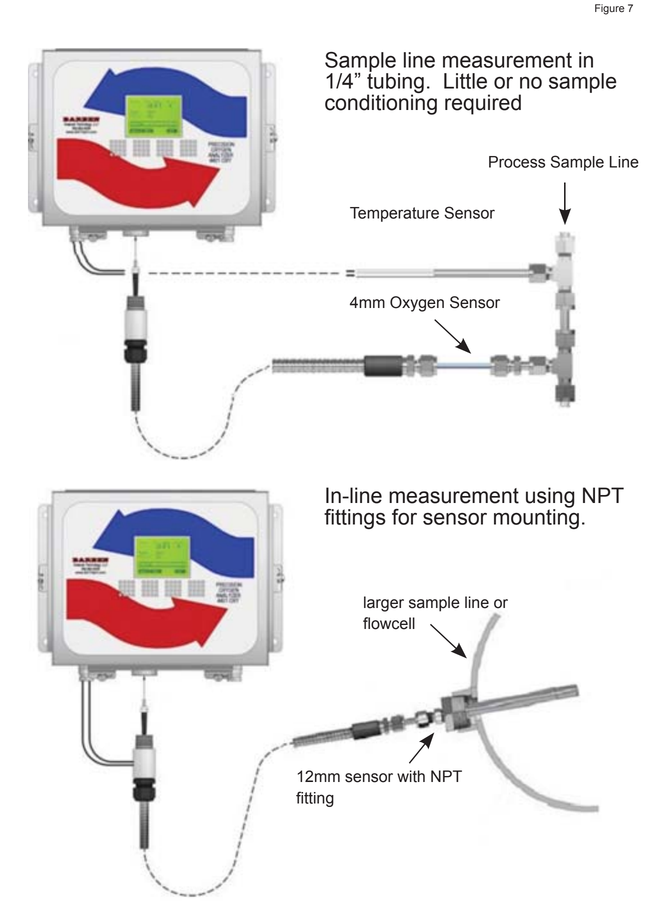
Pulsed light from the analyzer excites the luminophore oxygen sensor. Once excited, the luminophore emits light which is measured back at the analyzer. The duration and wavelength of the light will vary depending on the oxygen concentration in the liquid.

The Barben luminophore sensor is specifically designed for use in industrial applications such as SAGD water treatment. The sensor is unaffected by poisons such as H_2S or other chemicals that often damage traditional electrochemical sensors. The sensor uses no membrane thus cannot be fouled by particulates or oils. Calibration intervals are much longer than electrochemical cells with 3-6 months as typical.

The BOS1 sensor can be purchased for either flowcell mounting (1/2” or 1” NPT fittings) or wand style installation into 1/4” sample tubing.

The 4401 Optical Oxygen Analyzer is specified with the BOS1 sensor. Standard agency certification for Class I, Div. 2 Groups A,B,C,D and ATEX Ex II 3G, Ex nA IIC allow the analyzer to be mounted in applications where certification is required. Example installations can be seen in Figure 7.

Figure 7



Barben 4401 Optical Dissolved Oxygen with BOS1 Sensor options

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