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# Adoption of a Process to Prevent Souring Associated with Seawater Waterflooding in the Ursa-Princess Fields, Deepwater Gulf of Mexico

John Walsh, SPE, Shell E & P; John McElhiney, SPE, Pratt Technology Management; Stephen Maxwell, SPE, Commercial Microbiology; Edward Burger, SPE, EB Technologies; and Roy Davis, SPE, Sulfate Removal Systems

## Abstract

A comprehensive evaluation of the potential for preventing reservoir souring through the use of Sulphate Rejection Membranes (SRM) was made for the Ursa-Princess Waterflood (UPWF), deepwater Gulf of Mexico. The operator, Shell Exploration and Production Company (SEPCO) has long believed that injection of seawater is a precursor to souring; the question is not 'if' but 'when' souring would occur.[1] Metallurgy of the producer well tubing, casing, safety valves and topsides is not consistently sour safe and retrofitting would have rendered the waterflood project economics unviable. Therefore, prevention of souring by SRM was investigated, evaluated and adopted in order to avoid retrofitting the metallurgy. This is the first time that an SRM has been selected by a major operator for a seawater waterflood project based primarily on prevention of souring, while accepting SRM as proven for scale control.

## Introduction

### Field Description

The Ursa Tension Leg Platform (TLP) produces from the Ursa and Princess Fields in the Mississippi Canyon area of the Gulf of Mexico, roughly 150 miles southeast of New Orleans. These fields comprise eight offshore continental shelf (OCS) blocks.

The Ursa field was discovered in 1990. First oil through the Ursa platform was in 1999. The Princess Field was discovered in 2000. First oil from Princess, through a subsea tieback to the Ursa platform, was in December 2003. Total production from the Ursa platform peaked in the 2004 period at close to 150,000 BOPD. This phase of production was based on primary depletion driven by fluid expansion and natural compaction of the sedimentary rock with no appreciable aquifer support. Such compaction creates stability problems, including potential sand failures, and a range of drilling challenges. Following several years of primary production from these two fields, it was decided to install a seawater waterflood.

The decision to waterflood was based on a number of factors including improving sand stability, maintaining reservoir pressure, improving the long-term sustainability of the production drive, and improving the long term economic benefits associated with increased ultimate recovery.

The Ursa and Princess Fields have their main reservoirs in common and are in pressure communication. The Yellow reservoir is the largest and most productive. Waterflood is targeted exclusively for the Yellow reservoir which does not have natural aquifer support. It is an Upper Miocene turbidite reservoir of some 12,000 acres. Produced fluids are sweet and relatively light (average 27°API), with a bubble-point pressure of 5,900 psi at a reservoir temperature of 175 °F. Reservoir pressure had dropped significantly from an initial value of 11,800 psi. At the time that the decision was made to implement a waterflood the flowing bottom hole tubing pressure was already 5,500 psi.

The initial strategy of the waterflood is to provide sufficient waterflood injection volumes to outpace production volumes and hence boost reservoir pressure. Once this is accomplished, the subsequent strategy is to keep pace

with production and provide voidage replacement. Four waterflood injector wells will be installed, each with a relatively high injection rate of between 30,000 to 40,000 BWPD per well, delivering water at 7,500 psig at the wellhead.

In the initial several years of the waterflood it is expected that five barrels of water injected will result in one additional barrel of daily oil production. The significance of this ratio is primarily felt in platform operations where it gives the operators a firm grasp of the value of waterflood uptime and injection volumes. For example, if only 100,000 BWPD is injected, against a target of 140,000 BWPD, then a 5:1 ratio equates to 8,000 Bbl oil deferred daily oil production. To an operator, this is significant. They can make decisions regarding priorities, staffing, maintenance, surveillance and troubleshooting based on this value. The ratio was calculated by running two reservoir simulations, one with waterflood and one without. The difference in platform production on a short term basis, usually one year, is averaged to obtain the ratio of barrels of water injected to additional barrels of oil produced for that one year time period.

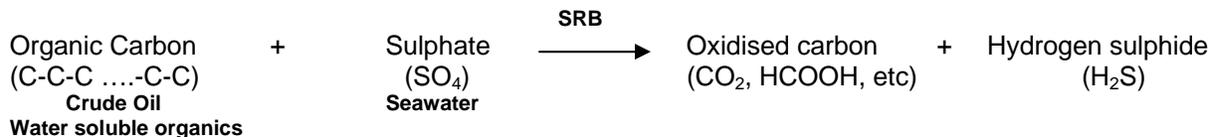### Potential Souring Impact from Waterflood

In the original development of the Ursa field, it was thought that reservoir souring would not occur.  The thinking was that waterflood may not be necessary and if it were required, then by that time new technology would be deployed to prevent souring. The materials selection for well casing and tubing therefore did not include the requirement for Sulfide Stress Corrosion Cracking (SSCC) resistance.  This resulted in the use of P110 and CY-P110 casing and 13Cr tubing in the Ursa producing wells. These materials have low tolerance to $H_2S$. At levels as low as 20 ppm $H_2S$, failure may occur relatively quickly. The consequence of a well failure for a TLP in deepwater would be severe, with a worst case scenario including multiple loss of life. Thus, even low levels of reservoir souring from a seawater waterflood would not be acceptable. If seawater waterflood was to be implemented, then a robust souring prevention strategy would be required.

### Biological Souring and Souring Prevention Technologies

With the application of seawater flooding for pressure support and sweep efficiency comes the potential to sour the reservoir due to the growth and activity of sulphate-reducing bacteria (SRB) and archaea within the formation.[2,3,4]  There are several proposed mechanisms whereby the activity of SRB can be stimulated to the extent that sufficient $H_2S$ is generated and transported to the producing wells to result in sour production. Included are where the SRB activity is:

- Restricted to near the injection well ("biofilm" model) [5,6]
- In a  preferential dynamic zone which changes and moves as the waterflood progresses ("viability shell" and "mixing zone" models)[7,8,9]
- Dominating along the path(s) of least resistance and in fractures ("fracture" model)[10, 11]
- Restricted to near the production well ("well souring" model)

Whilst arguments continue as to which, if any, of the proposed mechanisms is dominant, a common parameter in all models is that there must be mixing, co-mingling or diffusion between the injected seawater and interstitial formation water or crude oil.  At the most simple level, seawater provides the sulphate and the reservoir supplies the organics to allow the anaerobic activity summarized below:

$$\text{Organic Carbon} + \text{Sulphate} \xrightarrow{\text{SRB}} \text{Oxidised carbon} + \text{Hydrogen sulphide}$$

| Organic Carbon (C-C-C ….-C-C) **Crude Oil** **Water soluble organics** | + | Sulphate ($SO_4$) **Seawater** | $\xrightarrow{\text{SRB}}$ | Oxidised carbon ($CO_2$, HCOOH, etc) | + | Hydrogen sulphide ($H_2S$) |

Injected seawater also brings with it marine SRB cells, growth factors (vitamins) and other nutrients essential to enhanced bacterial growth (e.g. phosphorous, trace metals, etc.) which may have been depleted over geological time within the formation water.  The source of the SRB and archaea (seawater or reservoir) is not confirmed and there are arguments that support both alternatives.  There is also discussion that the BTEX (Benzene, Toluene, Ethylbenzene and Xylene) components in the oil may be toxic for SRB growth until they are diluted by the washing effect of several pore volumes of injected seawater.

Many uncertainties remain, therefore, as to the mechanism(s) controlling the rate and stoichiometry of biological sulphide generation within seawater flooded oil reservoirs.  Nevertheless, backflowed injection water from sour reservoirs typically show soluble sulphide concentrations of between 25 – 100 mg/L sulphide.[12]  This required respiration of approximately 70 – 300 mg/L sulphate, which is in excess of any soluble sulphate found in the majority of formation waters.  There would appear, therefore, to be clear evidence that the predominant source of sulphide is from the respiration of the sulphate provided by the seawater.

### *Utilisation of Sulphate*

Many formation waters contain sulphate, albeit at a relatively low concentration (<1 to about 100 mg/L) compared to seawater (2,700 – 2,900 mg/L). Whilst seawater is accepted as the dominant source of sulphate for souring of the reservoir, the reason why indigenous sulphate is not biologically reduced is arguable. A variety of reasons can be put forward:

- No indigenous viable SRB active in the formation before drilling
- Interstitial water may be an inhospitable environment for bacterial activity due to toxic hydrocarbons
- Essential nutrient-limitation due to historic bacterial activity during/after diagenesis

Whatever the reason, the available sulphate concentration for SRB growth during seawater flooding should include that amount available from the formation water in addition to the injected seawater. The impact of this indigenous sulphate when mixed or diffused into the injected seawater needs to be considered on a case by case basis.

Sulphate can be assimilated into bacterial cells as a source of essential sulphur for growth. However, as the total dry weight of bacterial cell biomass in the reservoir may be of the order of only several kilograms, of which the sulphur content may be less than 1%, then it can be assumed that the requirement for assimilated sulphate is infinitely small compared to sulphate availability and, therefore, assimilated sulphate demand for growth can be ignored.

Dissimilatory sulphate reduction required for sulphate respiration is, therefore, the only reaction considered. The rate of SRB growth can be regulated by the concentration of nutrients, including sulphate, but only at low sulphate concentrations. The saturating nutrient concentration is defined as that allowing the SRB to grow at the maximum specific growth rate ($\mu_{max}$). Monod kinetics demonstrate that the specific growth rate ($\mu$) will be half of the maximum specific growth rate when the concentration of sulphate is equal to the half-saturating substrate concentration ($K_s$).

$$\mu = \mu_{max} \times \frac{[S]}{[S] + K_s}$$

where:
$\mu$ = specific growth rate
$[S]$ = substrate concentration
$K_s$ = half saturation constant for $[S]$
$\mu_{max}$ = specific growth rate

Published data for SRB report $K_s$ values as low 3.2 mg/L,[13] indicating that a sulphate concentration below 7 mg/L would be required before SRB growth rates are decreased. Given that the residence time of injection water in the reservoir is generally measured in months or years, the rate of SRB growth may not be the key parameter to long term sulphide control. By decreasing the concentration of sulphate available, however, the overall mass of sulphide that could potentially be produced is decreased significantly.

### *Biocide*

Historically it was thought that an attractive and direct strategy to mitigate reservoir souring would be to accomplish a total kill of the SRB in the seawater and prevent them from growing into active communities within the reservoir. Many oilfields already include batch addition of biocide (e.g. glutaraldehyde, THPS, etc.) into seawater injection systems as a means of controlling Microbiologically Influenced Corrosion (MIC) by SRB. North Sea experience has clearly demonstrated, however, that many reservoirs soured despite this practice and it was concluded that the dose (concentration and time) and frequency of the batch treatments was insufficient to control SRB growth. Extended (i.e., 6 months or longer) continuous injection biocide treatments have been performed on waterfloods following the appearance of souring. Results appeared to indicate that such treatments had a negligible effect on souring, with reports from the Ninian, Skold and Thistle fields all indicating that sour production continued or was only partially and temporarily inhibited.

Initially it was felt that the biocide treatments had not been successful either because the biocide did not reach the areas where the SRB were active or that insufficient biocide chemical was dosed to assure a kill of a significant proportion of the SRB population. However, it may be possible that the biocide treatments were having some inhibitory effect, but that this was masked by the sulfide partitioning characteristics of the formation rock minerals and residual oil. Models indicate that following extensive souring, even if biocide treatment inhibits further sulfide production in the reservoir, the reservoir will continue to produce sulphide due to reversed partitioning of sulfide, i.e., releasing it from immobilised oil and connate water and possibly some minerals.

Whatever the ultimate reason for continued sulfide production in the presence of biocide, it is clear that it would be far more desirable to prevent the reservoir from souring in the first place than attempting to remediate an already sour field

### Nitrate

A novel (to the oilfield) approach to souring control was attempted in the North Sea in the early 1990's whereby nitrate salts were injected to stimulate nitrate reduction.[14] The application of nitrate has been practiced in the sewage industry for many years as a means of hydrogen sulfide and odour control. In oilfield applications, the mechanism is not clearly identified, but it is understood that there are a range of competitive and inhibitory processes. Simple laboratory sand pack experiments clearly demonstrate the potential for this technology both as a probiotic treatment and for bioremediation. Extensive field trials have been performed and some North Sea operators now apply nitrate as the primary means of biological sulphide control.

Where the nitrate was dosed to remediate already sour reservoirs, results have been varied with some operators reporting good or partial success and others reporting no significant effect. Successful treatments have been reported by Statoil[14] and Maersk Olie og Gas,[12] but in some cases the treatment could not be sustained due to logistical factors related to the need to provide a continuous supply of nitrate into the treated systems. The most recent information is still somewhat confused. There are several published reports of significant remediation of soured waterfloods. There have also been reports of nitrate delaying the onset of souring, but not inhibiting souring completely. There is general agreement that the issues related to determining an effective dose over a range of different field physicochemical conditions may be responsible for the apparent inability to optimise nitrate treatments at this relatively early phase of development. Currently applied concentrations vary from around 34 mg/L to over 200 mg/L whilst attempting to determine the optimum dose.

In those fields where the nitrate has been employed from the start of waterflood, no significant souring has yet been reported. However, it may be several years before a true understanding of the effectiveness of nitrate emerges. Nevertheless, some operators have adopted nitrate treatment as the souring control strategy for new waterfloods in the Gulf of Mexico and offshore West Africa.

### Radiation

At least one field has applied radiation (from UV) as a strategy for bacterial killing for reservoir souring control.[15] Whilst the UV units will sterilise the water passing through, the inability to drill sterile wells, control drill mud contamination or assure 100% availability of a lethal radiation dose, indicate that the strategy is flawed. Once SRB activity develops downstream of the UV unit, then there can be no further lethal effect from the radiation and growth and activity will continue uninhibited within the reservoir.

### Sulphate Removal

Sulphate removal technology (SRT) has been used in the petroleum industry for sulphate scale prevention since the early 1990's.[16] Sulphate removal for prevention of souring was first investigated in 1994.[17] It is reasonable to expect that decreasing the sulphate concentration in seawater will decrease the mass of sulphide generated by SRB activity. In the presence of excess organic carbon, SRB metabolize one mole of sulphate to produce one mole of hydrogen sulphide. Low sulphate seawater (LSSW) from a standard SRT plant contains 40 mg/L of sulphate and this can stoichiometrically be converted to produce 14.2 mg/L of hydrogen sulphide. The rate of sulphate reduction will probably still occur at or near maximal rates for the given environmental niche. Lower sulphate concentrations can be achieved with additional membranes, but it is the combination of limiting the mass of sulphide that can be produced with the sulphide scavenging capacity of the reservoir rock and residual oil that provides the key to assessing the application of SRT as a souring control.

There are now over 50 SRMs built and operating, or in the design and construction phases, with a total capacity of over 4 million barrels per day of LSSW. There were about a dozen of these plants with enough low sulphate water injection history (5 years or more) that could be reviewed when SRT was being considered (in 2003) for souring prevention for the UPWF. In a later section of this paper the historical performance of these plants is discussed, but none to date shows any evidence of hydrogen sulphide being produced after LSSW was injected.

## Investigation of SRM for the UPWF

In 2004, a project team was formed to gather laboratory data and industry field information to evaluate the suitability of the three souring control strategies for the UPWF, and to prove or disprove the operability and reliability of Sulfate Rejecting Membrane systems.

### Operability / Reliability Concerns

To understand reliability and operability of SRM systems, all of the major operators of sulfate units in the world were contacted. At that time, there were roughly 12 units in operation. A team of engineers visited one of the facilities in the North Sea (Heidrun TLP).

Among the significant findings it was learned that most of the problems experienced in the early days of SRM implementation have not occurred in the more recent designs. While implementing an SRM system is technically

challenging, the major equipment vendors have developed reliable systems that can be operated with a reasonable number of offshore staff. Some vendors provide on-site training and some degree of hands-on operations support. In general, the systems that tend to operate the best are those that involve strong process and equipment integration and those for which adequate weight and space are available to accommodate conventional pre-treatment filtration packages such as strainers, multimedia filters, followed by a guard bed cartridge filter system. If an inadequate filtration system is selected, then membrane fouling could result which is costly and requires significant operator intervention. Unfortunately, the selection of the pre-treatment filtration system is made difficult by the fact that conventional systems are usually heavy and large. The added weight and space of a conservative pre-filtration design is difficult to justify in deepwater where there is tremendous pressure to reduce weight and space.

Proper sea water filtration is critical to prevent fouling from particulates, colloidal material and to assist in the prevention of biofouling of the membranes. In general, seawater contains a large number of very small particles that can be carried long distances from shore and it contains colloidal material, single cell and multicell organisms that result from natural biogenic processes that occur in the sea surface waters. The precise type of filtration required for a given facility depends on proximity to shore runoff areas, sea currents, nutrient content of the seawater, and other characteristics that can vary significantly from one location to another.

For the UPWF, a pilot filtration study was conducted[18] on the Ursa platform over several months.  Also, data from the neighboring Mars platform was analyzed. The study showed, among other things, that the seawater in the deep Mississippi Canyon location of these platforms is relatively clean and not affected by Mississippi river runoff. Options to draw water from below the keel level were examined and rejected after discussions with Texas A&M University Oceanographers which indicated that such deeper water suction would not provide sufficient improvement in water quality year round to justify the additional cost.  Water is therefore lifted from the keel level (located 90 ft below mean sea level).  Back-washable strainers and cartridge filtration provide the complete filtration system.  While this is not an entirely conservative approach, it does provide a reasonable compromise between added weight, added space, and added complexity of additional filtration.

### HSE Concerns
The original Health Safety and Environmental (HSE) Case for the Ursa asset did not include the hazard of $H_2S$-containing fluids due to seawater waterflood.  At the very least, a new Safety Case was required.  In the last ten years or so the oil and gas industry has seen an improvement in technical risk analysis and in the tools available for identifying hazards and designing control, response and mitigation measures.  The waterflood team therefore rigorously applied an HSE Management System approach to the waterflood.  In the process of developing a new safety case, options for reducing the risk of souring due to waterflood were investigated.

One of the tools in the HEMP (Hazards and Effects Management Process) approach to risk reduction is the Bow Tie analysis.  To construct a Bow Tie, the hazards are identified, as well as the consequence and probability of the hazardous event.  Various controls are then proposed to prevent the hazard from being released.  In this case, the hazard was identified as loss of well control due to SSCC caused by reservoir souring.  The team then proposed a barrier strategy based on:

- Confirmed injection of desulfated seawater containing <45 mg/L Sulphate.

- Monitoring and response (for seawater breakthrough and $H_2S$)

- Recompletion of the Direct Vertical Access (DVA, dry tree) wells using Shell qualified materials.

The use of sulfate removal and reservoir scavenging as a barrier to souring is novel and it was therefore decided that at least one Shell qualified barrier be installed in the well to cater for the residual risk of souring.  In the Princess subsea wells this barrier is the existing casing and in the Ursa DVA wells it will be the new completion tubulars.  The plan is to measure the $H_2S$ content in each well stream using a combination of online and manual methods to confirm the SRM is preventing reservoir souring. If $H_2S$ is detected, then the HSE Case requires that the well be shut-in and a reassessment of the operating risks be conducted before further production. In the case where $H_2S$ is thought to be a continuing presence, the well zone may have to be abandoned.


**Investigation into Sulphate Removal as a Barrier for Prevention**

### Historical Application for Scale Prevention
When an SRM is used for seawater injection, conventional wisdom says that $H_2S$ will be reduced, but not entirely eliminated.  This is because the low sulphate seawater produced by a standard SRM still has approximately 40 mg/L of sulphate remaining in it.  Stoichiometric conversion of this sulphate will yield 14.2 mg/L sulphide, provided sulphate is the limiting substrate for SRB.

$$\text{Carbon (e.g. fatty acids)} \quad + \quad SO_4 \quad \xrightarrow{\text{SRB}} \quad CO_2 \quad + \quad H_2S$$
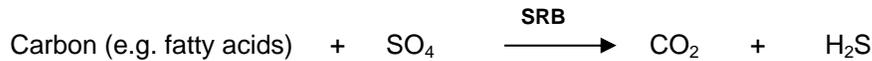
This argument is refuted by empirical field data (discussed below) that shows no $H_2S$ is produced when an SRM is employed from the first day of seawater injection.

### Review of Existing Installations for Souring – The Anecdotal Case

At the time (2003) Shell was investigating the advisability of installing an SRM for prevention of souring, there were only 12 SRMs in the world. All of these historical applications have been for the mitigation of sulphate scale and none of these projects has had any sulphide produced even though seawater has broken through in production wells in a number of these.

Table 1 summarizes the data from these installations. Two of the SRM installations (Brae and Tiffany) each provided waterfloods for two distinct and separate fields. One installation was not used for waterflood (ETAP) and one was never commissioned (Petronius). Consequently, there were a total of 12 seawater waterfloods associated with 10 of the 12 installations. In examination of the data from these installations for anti-souring, six fields were judged to have "clean" data. "Clean" is defined as having substantiated evidence of: a) the breakthrough of significant volumes of injected low sulphate water, and b) the complete absence of $H_2S$. These fields are: Central Brae, Ewing Banks 873, Tiffany, Tony (Tiffany water), Ceiba and Girassol. "Non-substantiated" field experience involves those fields that had pre-existing $H_2S$ and a) the breakthrough of significant volumes of injected low sulphate water, and b) no increase in $H_2S$ upon low sulphate water breakthrough. These include South Brae and South Arne. Also included in the "non-substantiated" category is Janice, where high levels of sulphate injection (calcium instead of barium scale control needs) taint any conclusive evidence.

In all cases, $H_2S$ levels neither occurred nor increased from concentration levels prior to low sulphate water breakthrough. The data shown were verified by operators in 2004 and, insofar as we know, no souring has occurred in the interim. These field data suggest that use of an SRM will result in no $H_2S$ for an Ursa installation.

### Reservoir Modeling

A flash-partitioning model[19] was used to estimate the concentration of $H_2S$ that would be produced from the field if waterflooded with sulphate-reduced (SRM) seawater containing 40 mg/L sulphate. It was assumed that the injected sulphate was totally bioconverted to $H_2S$ by sulphate-reducing bacteria in a region relatively close to the injection wells, yielding a maximum concentration of $H_2S$ in the flowing reservoir water of 14.2 mg/L. The waterflooded region of the reservoir and the near well bore region of the production well were considered in this analysis. Figure 1 schematically shows these locations. The reservoir fluid analysis from well A-6 production was used to characterize seven simulated hydrocarbon fractions and live crude properties for the flash-partitioning model.

The worst case scenario assumes that 14.2 mg/L $H_2S$ is contained in the water flowing to the producer well. This $H_2S$ partitions into the three produced phases (oil, water, and gas) as the pressure decreases up the well bore to the surface separation system. However, due to the partitioning of $H_2S$ into the residual oil in the waterflooded regions of the reservoir and potential scavenging of the $H_2S$ by siderite reactions and other potential processes such as adsorption, the expected $H_2S$ concentration in the water arriving at the producer well will be less than 14.2 mg/L. Figure 2 presents the expected concentration of $H_2S$ at equilibrium with the residual oil in the reservoir as a function of residual oil saturation ($S_{orw}$), temperature, and assumed pressure in the absence of scavenging. These results assume that the entire waterflood region is at that specific condition (of temperature, pressure, and $S_{orw}$), while in reality the water reaching the producer will be at an integrated dissolved $H_2S$ level.

The bottom hole pressure of the producer well was assumed to be at the fluid bubble point, or at about 5900 psia based on reservoir fluid analyses. However, the flash model determined a much lower bubble point of about 3000 psia. Output from the model at the determined bubble point and 83°C was corrected to 5900 psia using estimated $H_2S$ partition coefficients as indicated in Figure 3. Figure 4 shows the $H_2S$ concentration in the gas as a function of water cut as determined by the model and also as corrected to 5900 psia, while Figure 5 presents the corrected results in terms of $H_2S$ partial pressure (in psia). These results assumed that the $H_2S$ concentration in the water flowing to the wellbore was a worse-case 14.2 mg/L. However, based on the reservoir partitioning study (Figure 2), a more reasonable assumed $H_2S$ concentration would be about 8.5 mg/L. This results in a reduction of the calculated gas concentrations and partial pressures by 40% as shown by the lower curve in Figure 5.

The flash-partitioning calculations indicate that the $H_2S$ partial pressure in the gas at bottom hole conditions will exceed the NACE limit of 0.05 psia for water cuts in excess of about 25% if the effects of partitioning into residual

oil and scavenging of the $H_2S$ within the reservoir are neglected. The residual oil in the waterflooded portions of the reservoir will potentially hold about 40% of the biogenerated $H_2S$ and this effect alone will increase the allowable water cut to about 40% before the NACE limit is exceeded in the production tubulars.

### Scavenging Mechanisms

Since the model utilized for Ursa did not contain adsorption mechanics, a series of adsorption tests were performed on Ursa core at Oil Plus, Ltd to investigate this additional effect.[20] Static jar testing on disaggregated material and core flooding on friable, preserved cores were performed. A comparison of reservoir mineralogy from North Sea cores used in a U. K. Atomic Energy Authority (AEA) study and the Ursa cores may be found in Table 2. All were sandstone cores.

Adsorption onto surfaces of reservoir petrofabric (clays, minerals, etc) is an effective process for removal of $H_2S$ generated *in situ* by SRBs. Reservoir pressure is above the bubble point and $H_2S$ in solution partitions between the oil and water phases and is subsequently adsorbed. In 1993 a reservoir modeling study for Gullfaks Field was performed using Statoil's biofilm model.[6] The adsorption values used to history match several wells, including the $H_2S$ concentrations in the gas streams, are given. Core flooding work on reservoir rock from three North Sea oilfields was later performed at the AEA labs at Winfrith and was reported in 1997.[21] Later this data was utilized in reservoir modeling to show the efficiencies of adsorption in delaying SRB-generated $H_2S$ breakthrough in production wells.[22]

Small core plugs (2.60 cm diameter x 3.85 cm length for Ursa; 3.75 cm diameter x 3.00 – 4.5 cm length for the North Sea) were used in both sets of core floods. Porosities were 0.20 – 0.22 with permeabilities approximately one Darcy. The Ursa core plugs were flooded at low rates with 100% brine containing a fixed, soluble concentration of $H_2S$ ('brine'); the North Sea core plugs were flooded both with brine only and with brine at residual oil saturation. The brines used in both the Ursa and North Sea core floods were similar at approximately 100,000 TDS and both had pH in the 5.0 – 5.36 range where $H_2S$ disassociates into its ionic components $HS^-$ and $H^+$. Although adsorption can be reversible, no $H_2S$ was ever desorbed in the several pore volumes of floodwater after $H_2S$ breakthrough, i.e., no discernible increase in concentration was ever noted above the concentration of $H_2S$ in the injected brine.

The results of these core floods are shown in Table 3. Several observations are noteworthy. First, note that in the North Sea core floods the $H_2S$ retention values at residual oil are higher than retention values in 100% brine floods. The method of measurement of retention involved taking the difference in concentration between an inert tracer and the $H_2S$ concentration in the effluent, so any additional loss could have been $H_2S$ in solution in the residual oil saturation. Second, note that the Ursa adsorption values are 2-3 times those of the North Sea values although in two of the North Sea cases the maximum in $H_2S$ had not been reached. This is largely unexplainable since flooding conditions and rock petrofabric do not appear to be greatly different. The Ursa core floods were run at a higher temperature where adsorption kinetics would be accelerated.[21] The two primary effects in these floods were temperature and pH. Secondary effects were mineralogy, flow rate and $H_2S$ concentration in the floodwaters.

The main factor to mention here is that Tyrie and Ljosland[6] used 0.15 mg/kg as the adsorption capacity in their modeling study and McElhiney and Davis[22] used 1.0 mg/kg in their conceptual modeling study. Gullfaks, the reservoir modeled by Tyrie and Ljosland, is a naturally fractured reservoir and it was postulated in their work that adsorption affected only areas of reservoir rock near the natural fractures which were oriented directly between injectors and producers. McElhiney and Davis' model was that for a competent sandstone system. The actual experimental values, measured by both AEA and Oil Plus for the North Sea and Ursa core floods, were over two orders of magnitude greater, suggesting that the adsorption capacity for $H_2S$ by reservoir rocks is enormous.

### The 'Clean Water' Theory

Early models of SRB activity concentrated on thermophilic activity deep in hot reservoirs. Mesophilic SRB are active only up to about 40°C, while thermophilic SRB can tolerate temperatures up to 100°C. Since many reservoirs are warmer than 40°C, the tendency was to assign responsibility to thermophiles since they were the only strain capable of operating at higher temperatures. This interpretation was discredited when it was further realized that injection of cool seawater into a reservoir reduced temperatures in the neighborhood of the injection wells to within bounds for mesophilic SRB to be active. Thus, the thermal viability shell (TVS) theory was established.[7] Essentially all the nutrients and substrates necessary for SRB to reduce sulphate to sulphide were around the injection wells. With cooler temperatures, constant replenishment of dormant SRB spores from the incoming seawater, abundant sulphate and low molecular weight fatty acids in the formation water; the mesophilic

biofilm model then came into prominence.  The mesophiles attach themselves to the reservoir rock near injection wells and carry on their cycle of life.  As more water was injected, the TVS grows in radius to include larger and larger cooled areas away from the injectors.  Thermophiles reside downstream and just what part they may play is less well known.  Near wellbore backflow samples at injectors have verified the biofilm theory.[11]

When processed through a membrane, seawater requires pre-filtration through media filters or the equivalent, de-aeration, and further filtration through a 5-10 micron guard filter before entering the membranes.  The membranes are nanofiltration membranes, i.e., they remove all particles down to $10^{-9}$ meters.  Dormant SRB spores found in seawater are no smaller than 1 micron,[23] i.e., they are 1000 times larger than the molecular sized 'holes' in the membranes.  Consequently there is no way any dormant SRB spores can physically enter the reservoir with the injected seawater.  In addition, neither algae nor bacterial material carried by the processed seawater can pass through the membranes.  The sulphate content is low and is most likely limiting in content (rather than fatty acids) for sulphide production.

What else could contribute to diminishing SRB activity?  Phosphate and nitrates must be available in trace amounts for SRB metabolism to take place.  Phosphate ions have similar characteristics as sulphate ions.  It is possible that they can be removed by membranes in similar fashion as sulphate ions.  Phosphate is available in seawater at approximately 130 - 150 ppb (by weight) concentration levels[24]. The literature suggests that a phosphate limiting metabolism threshold exists for SRB[25].  Phosphate is known to occur in certain reservoir rocks but how widespread this may be is unknown. Even if phosphate is removed from seawater by membrane processing, we do not know if it is normally available in reservoir rocks or whether it can be replenished from within the reservoir.  Phosphate is neither routinely measured in formation water[26] nor is it measured in permeate and reject water from membranes and is below most normal analytical measurement limits. Although some progress has already been made, further technical development of a phosphate rejection membrane is required before reliability can be established.

### Selection of SRM for the UPWF

Several factors were considered in selecting SRM as an anti-souring strategy for the UPWF.  First and foremost was the field data which suggests that where SRM is used, the field does not experience reservoir souring from seawater waterflood.  While this data is highly encouraging, some concerns were raised as to whether or not the data are entirely accurate in the sense that it is sometimes difficult for one operator to know the true quality of information without an intimate involvement with a field.  The other concern about the field data was that there is no direct laboratory simulation data that definitively confirms or explains the reasons why SRM water injection should result in no souring.  Indeed, some of the laboratory data suggest that stoichiometric amounts of $H_2S$ should be produced.  On the other hand, the core studies and reservoir scavenging studies suggest that large amounts of $H_2S$ can be adsorbed.  In the end, amongst all of the souring mitigation strategies considered, SRM appeared to be the most field tested.

Having accepted SRM as the anti-souring strategy of choice, the next step was to specify the operating parameters to ensure the lowest reasonably practical souring mitigation results.  This involved developing an operating target for sulfate in the injection water and a strategy for responding to high sulfate water in the case when a membrane might leak high sulfate water directly into the product water stream.  An initial engineering study demonstrated that 20 mg/L sulfate could reasonably be achieved, particularly in the early phase of waterflood when the membranes are new, clean and unfouled, and the waterflood volumes are less than peak due to a staged drilling campaign and only one stage of membranes would be required.  However for long-term operation it was decided to set the target at 40 mg/L.  This was less than the historical averages for the older fields that had not soured and still was within the practical limit of what could be achieved by an SRM of moderate size on a TLP.  Also, if sulfate levels exceed 60 mg/L for more than 48 hours, then the entire waterflood injection would be shutdown and the problems would be fixed before startup.

While simple stoichiometric calculations would suggest that some souring could potentially occur from SRM product water, the field data suggest that souring does not occur. The absence of souring is attributed to scavenging by minerals and by the oil/water left in place, and by the fact that an SRM system, when properly operated (no leaking membranes)  virtually eliminates SRB biomass (which would otherwise have an inoculating effect) and aerobic biomass and organic matter (which would otherwise be a food source for SRB).

### Conclusions
1) Membrane treatment of seawater produces low levels of sulphate in the treated water and therefore reduction to sulphide is greatly diminished,

2) scavenging processes in the reservoir (sulphide partitioning into the residual oil, adsorption onto the reservoir petrofabric, reaction with siderite, or lost to competing scaling mechanisms) potentially remove the small amounts of biogenerated sulphides,
3) phosphate may be reduced in treated seawater, thereby rendering SRBs unable to function,
4) membranes provide a physical barrier to inactive spores transported by the treated seawater, thereby preventing re-inoculation at the injection well, and
5) no field employing SRM has ever gone sour in spite of the fact that several are many years into production of injected low sulphate seawater at significant water-cuts. (See Table 1)

**Acknowledgements**

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**Table 1 - Summary of Field Data on H$_2$S from Fields Flooded with SRM Water***

| Company and Field | Date of SRM Startup | Seawater Breakthru/Date | Years Since SWBT | H$_2$S Measured |
|---|---|---|---|---|
| Marathon S. Brae | 1988 | Yes/1992-present | >10 | Background Level |
| Marathon Central Brae | Injection Began 1993 | Yes/1999 | 5 | 0 |
| Canadian Nat'l Oilfield - Tiffany | 1994 | Yes/1997 | 7 | 0 |
| CNO Tony | 1994 | Yes/1997 | 7 | 0 |
| Kerr-McGee Janice | 1999 | Yes/2001 | 3 | 0 |
| Amerada Hess South Arne | 2000 | Yes/2001 | 3 | Background Level |
| Amerada Hess Ceiba | 2001 | Yes/2003 | 1 | 0 |
| TFE Girassol | Feb 2002 | May 2003 | 1 | 0 |
| Exxon Mobil Kizomba A | 2003 | No | NA | NA |
| Statoil Heidrun | 2003 | No | NA | NA |
| Marathon Ewing Bank 873 | 1995 | 1999 | 5 | 0 |
| BP-Shell ETAP | 1998 | Dilute Prod Wtr | NA | NA |
| Petrbras FPSO Brazil | 2002 | No | NA | NA |
| Texaco Petronius | Installed/Not Operated | NA | NA | NA |

\* Survey taken 2004

**Table 2  -  Mineralogy of Reservoir Rocks from Ursa and Two North Sea Reservoirs, Wt %**

| Rock | Quartz | Kaolinite | K-feldspar | Plagiocase | | Siderite | Calcite |
|---|---|---|---|---|---|---|---|
| Ursa | 85.8 | 0.6 | 3.5 | 2.5 | trace | 1.0 | trace |
| N. Sea 1 | 92-93.5 | 1-2.5 | 1-2 | ---- | ----- | ---- | 0-2 |
| N. Sea 2 | 51-73 | 6-22 | 7-13 | 9-22 | trace | trace | trace |

**Table 3  -  Summary of H₂S Retention in Corefloods**

| Rock | pH | T,deg C | Porosity, fr | Perm, md | H₂S conc, ppm | H₂S ads, mg/kg |
|------|-----|---------|--------------|----------|---------------|----------------|
| URA 128 | 5.36 | 82 | 0.22 | est > 1000 | 25 | 797 |
| URA 127 | 5.36 | 82 | 0.22 | est > 1000 | 25 | 1058 |
| N. Sea 1 | 5.00 | 40 | 0.24 | 1218 | 550 | 146 |
| N. Sea 2 | 5.00 | 40 | 0.30 | 598 | 426 | >215* |
| N. Sea 1 | 5.00 | 70 | 0.20 | 1361/95** | 290 | 303 |
| N. Sea 2 | 5.00 | 40 | 0.29 | 464/80** | 410 | >348* |

\* > means adsorption had not reached maximum
\*\*  flood done at residual oil saturation, 100% brine/brine perm at residual oil saturation
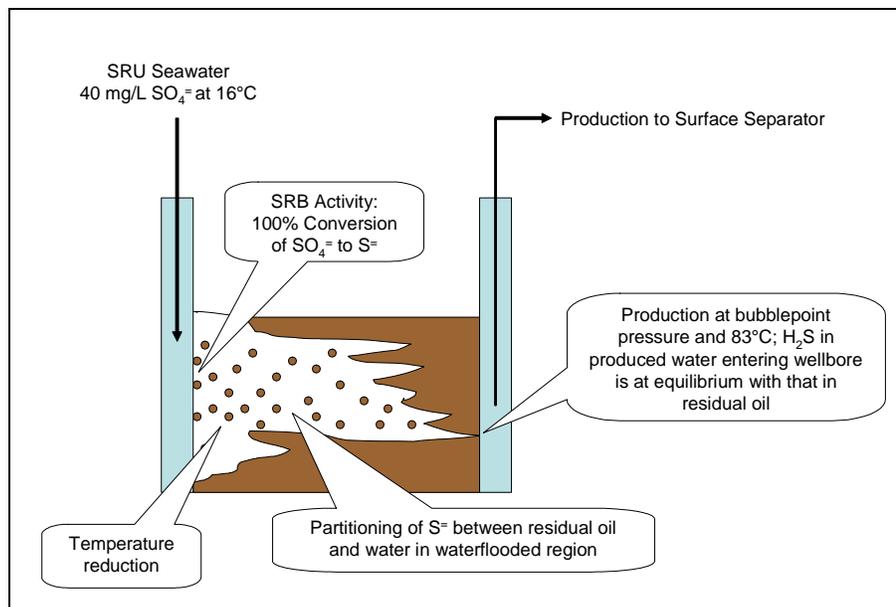


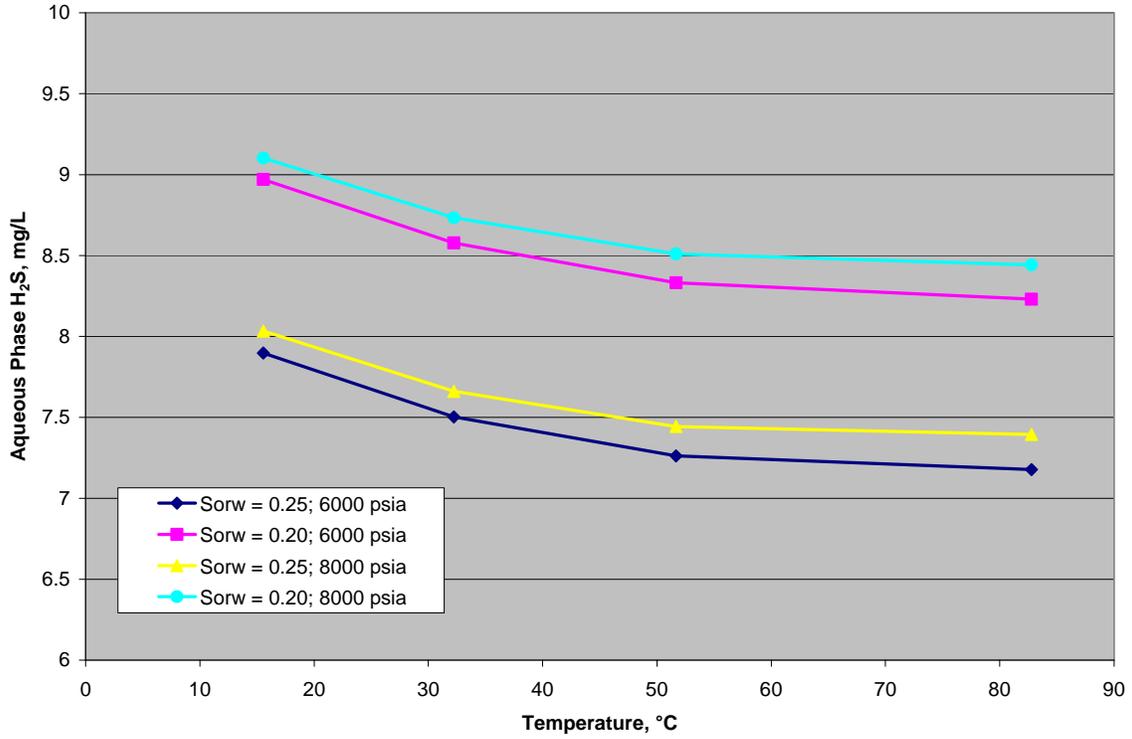**Figure 1.  Schematic of reservoir process to estimate H₂S distributions in flowing fluids.**

**Figure 2.  Aqueous phase H₂S concentration in equilibrium with residual oil in waterflooded regions of the reservoir.**
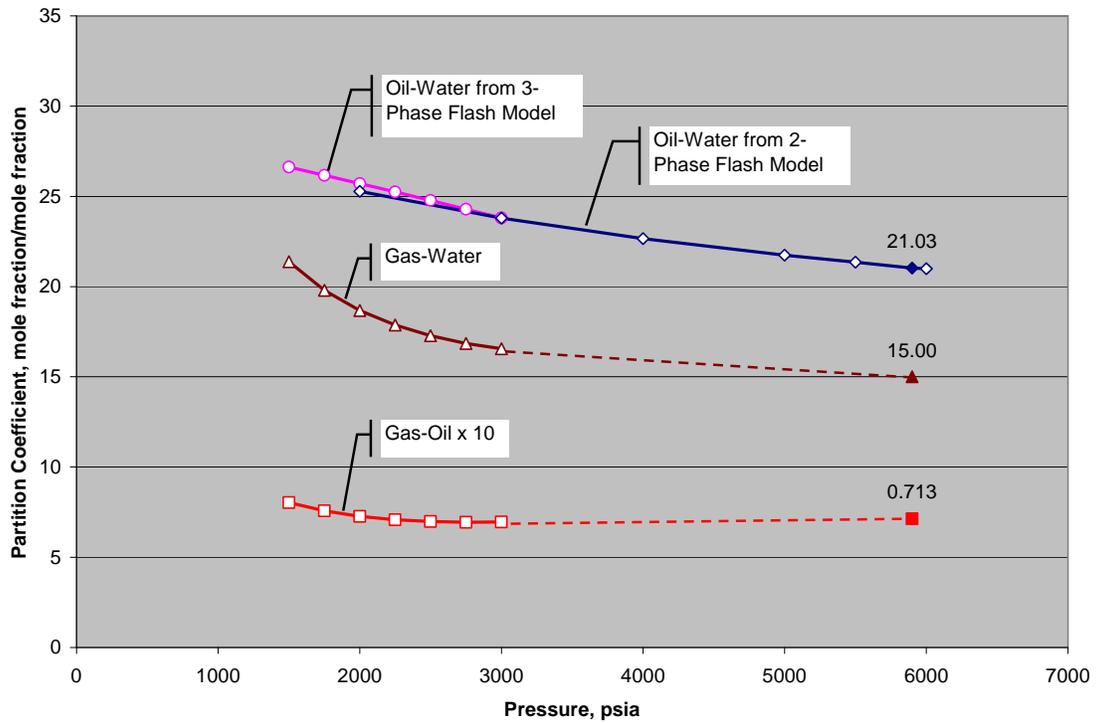


**Figure 3.  H₂S partition coefficients at 83°C.**  Values for pressures below about 3000 psia were determined by the 3-phase flash model, while the gas-oil coefficients up to 6000 psia were determined by the 2-phase model.  Shown are the assumed values used for the 5900 psia bubble point study.
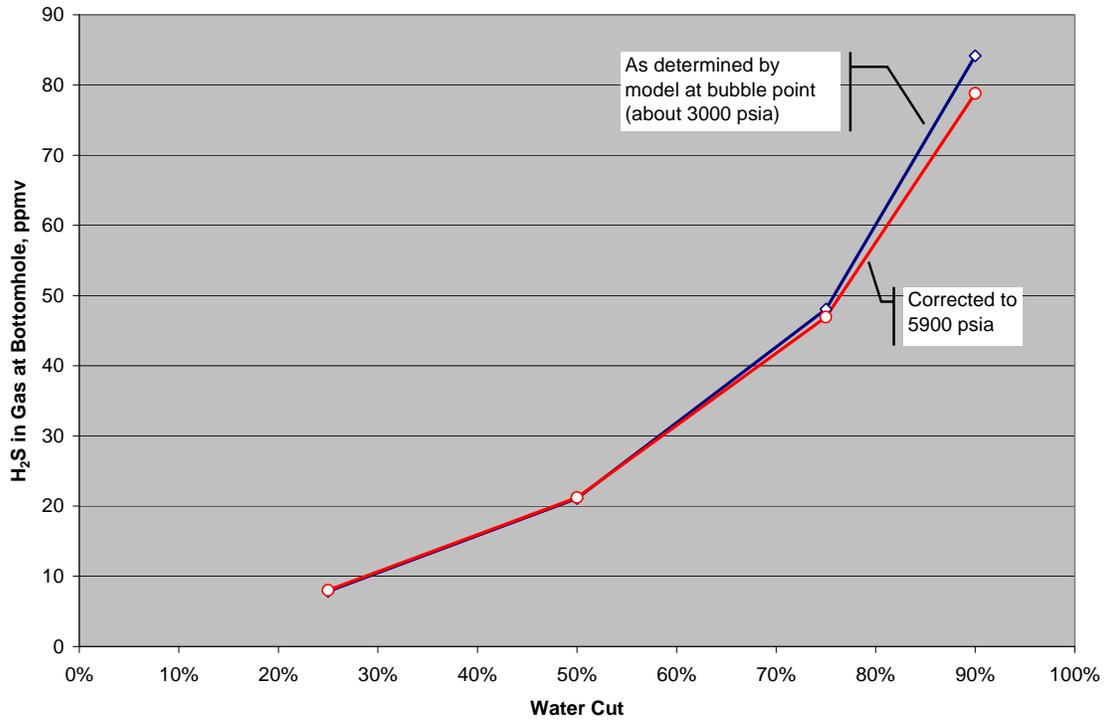
As determined by
model at bubble point
(about 3000 psia)

Corrected to
5900 psia

**Figure 4.  H$_2$S concentration in gas at bottomhole (83°C) bubble point conditions.**  Model-calculated values were corrected to 5900 psia as per assumed partition coefficients shown in Figure 3.
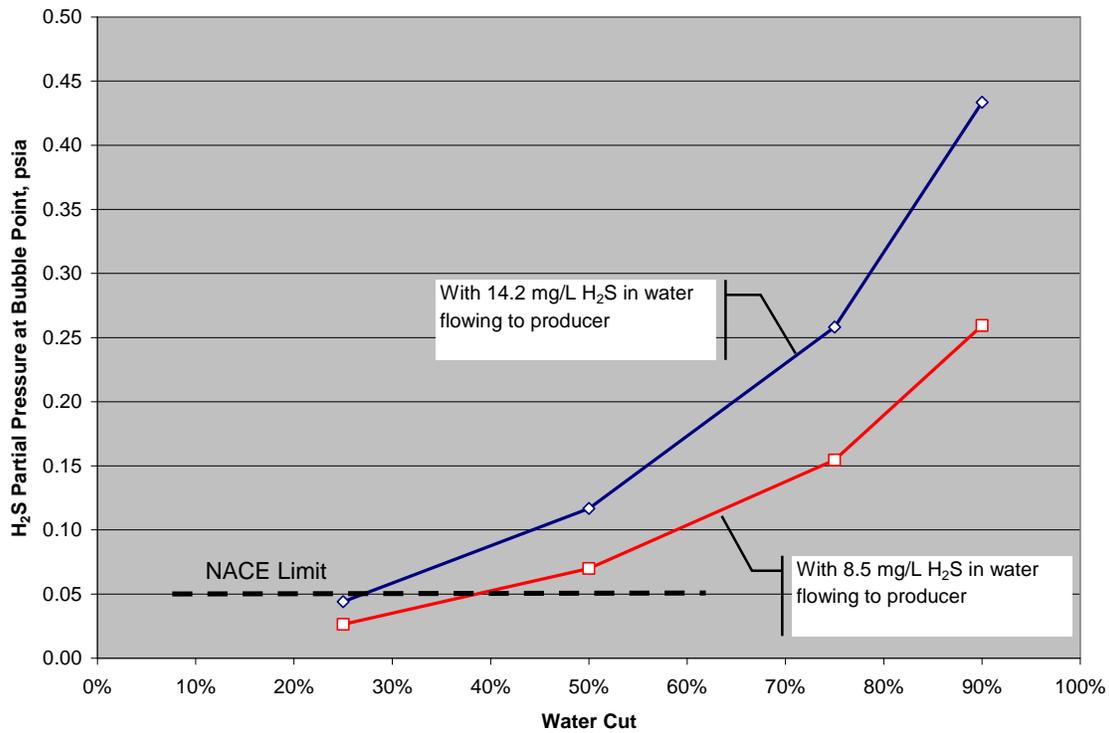


With 14.2 mg/L H$_2$S in water
flowing to producer

NACE Limit

With 8.5 mg/L H$_2$S in water
flowing to producer

**Figure 5.  H$_2$S partial pressure at bottomhole gas at bubble point.**  Shown are cases for maximum H$_2$S in flowing water and for an assumed level by accounting for H$_2$S solubility in the residual oil in res