A Case Study of Reservoir Souring Despite Injection of Low-sulphate Seawater

Keith Robinson* and Eivind Samuelsen**

Abstract: The use of sulphate rejection membrane (SRM) technology to generate low-sulphate seawater (LSSW) for water injection is becoming more commonplace, primarily to avoid severe barium sulphate scaling problems but it is also being increasingly applied to avoid reservoir souring.

This paper presents some operational data and results of an investigation into hydrogen sulphide appearance in Hess's South Arne production facilities. The field produces from a 115°C chalk reservoir, and is located in the Danish sector of the North Sea.

In addition to achieving the primary objective of barium sulphate scaling control, 10 years of historical data from South Arne show that the injection of LSSW also significantly reduced the severity of reservoir souring to levels acceptable for the metallurgy used in the field's wells and production facilities. This is important information for oilfields in general, and especially for deep-sea fields where high-strength steel risers must be used, but which are susceptible to sulphide stress corrosion cracking.

Despite using SRM technology since December 2000, South Arne production facilities saw increasing concentrations of H_2S in late 2008, up to 15 ppm in the bulk gas and 35 ppm in gas from individual wells. Analyses of the produced water's ionic composition and H_2S concentrations in oil, water and gas showed that approximately 50% of the remaining sulphate introduced into the reservoir in the injection water was converted to H_2S.

Stable isotope measurements of sulphide in H_2S were consistent with sulphate-reducing prokaryotes metabolizing a high proportion of the available sulphate. Molecular microbiological methods (MMM) showed high concentrations of sulphate-reducing archaea (a group of thermophilic microorganisms producing H_2S, but genetically very different to sulphate-reducing bacteria) present in the produced fluids.

Although some H_2S was produced, despite use of LSSW from the very beginning of water injection, one study conclusion was that the residual microbiological sulphate reduction may have minimized the field's barium sulphate scaling risk by lowering the sulphate concentrations in the waterflood water below those achievable by SRM alone.

Overall, the use of SRM to enable injection of LSSW was very successful in the control of potentially severe barium sulphate scaling and reservoir souring, although not entirely eliminating souring.

Keywords: Reservoir Souring, Low Sulphate Sea Water, Barium Sulphate Scaling, Molecular Microbiology, Sulphate Reducing Prokaryotes, Nano-filtration

INTRODUCTION

The South Arne Field is located in the North Western area of the Danish North Sea, and is operated by Hess Denmark. The oil reservoir is in the Tor and Ekofisk chalk formations, at approximately 115°C reservoir temperature.

The field development plan changed significantly as more reservoir data became available, beginning in 1997 with a depletion case, but with an option to install seawater injection for secondary oil recovery, and that option was decided upon in 1998. However the inorganic scale risks were unknown at that time due to very limited sampling of the formation water, and also because the high barium and strontium contents of the formation water were unexpected since they did not occur in any other Danish chalk reservoirs, even one as close as 5 km away. In 1999, new wells showed very high barium and strontium concentrations in the formation water samples and so the decision was made to install a sulphate-removal plant to treat the injection seawater.

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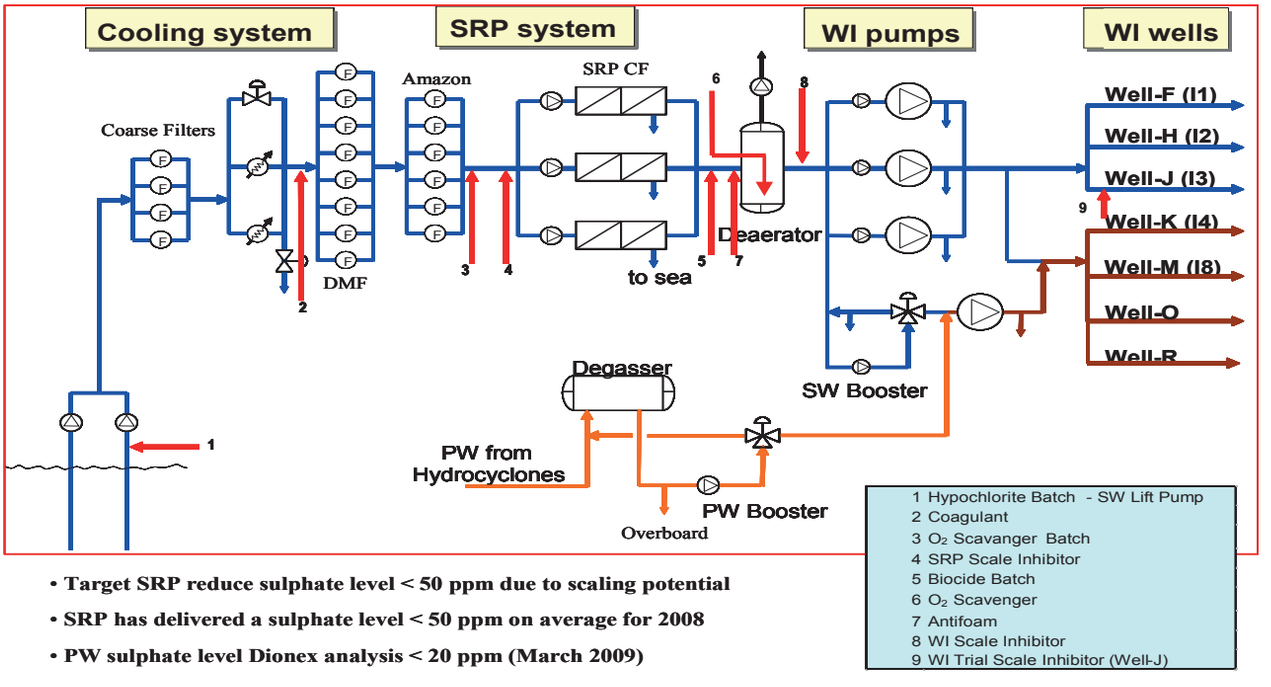
The sequential decisions and the limited platform space available had an impact on the seawater treatment process train in that the sulphate-removal unit (SRU) had to be installed upstream of the deaerator, rather than downstream which is more common, although there are advantages and disadvantages to both options, as described further below.

Water injection began in 2000 using de-sulphated seawater, sometimes described as low-sulphate seawater (LSSW), from the onset, but as produced water became available this was sent to separate injection wells, to those injecting LSSW, although now (2010) all wells receive a mixture of treated produced water and deaerated LSSW. The sequence of events was that LSSW injection commenced in December 2000, initially into the northern area of the field, then in mid-2001 into the southern area. A produced water re-injection (PWRI) trial began in 2004 into a southern area well and, as this was successful, PWRI was extended into all southern area wells, and then into all wells in mixture with deaerated LSSW in 2009; see Fig. 1 (Robinson *et al* 2010).

Sulphate removal from seawater is used primarily to reduce the risk of barium and strontium sulphate scale precipitation, which could result from mixture of normal-sulphate seawater with the formation/produced water, and that is a notably high risk with South Arne formation water due to its barium ion concentration of approx. 900 mg/l, and a similar strontium concentration (approx. 800mg/l). The LSSW would also reduce any risks of calcium sulphate scales (gypsum and/or anhydrite) and of calcium carbonate too as the membrane process also removes some of the natural bicarbonate ion from the seawater.

Initial oil and gas production, which began in 1999, was sweet (<3 ppm H_2S in gas) but increased concentrations of H_2S have been observed recently, starting in late 2008, although routine monitoring was not comprehensive in the years between, until a high value was reported during one offloading operation from the platform's oil storage tank to the shuttle tanker. That high value was speculated to be either a result of microbial activity within the oil storage tank, or within the topsides process train, or from reservoir souring associated with seawater injection. All three possibilities could involve sulphate-reducing bacteria (SRB) and/or sulphate-reducing archaea (SRA), together identified as sulphate-reducing prokaryotes (SRP) (Larsen *et al* 2009). The implementation of sulphate-removal can be expected to greatly the reduce the potential for reservoir souring (Alkindi *et al* 2007, and Walsh *et al* 2008), but may not entirely prevent it, depending on the level of sulphate reduction achieved by the sulphate rejection membranes (SRM) in the sulphate removal unit (SRU).

In addition to reservoir souring, the possibilities of H_2S generation by SRP in the topsides vessels,



- **Target SRP reduce sulphate level < 50 ppm due to scaling potential**
- **SRP has delivered a sulphate level < 50 ppm on average for 2008**
- **PW sulphate level Dionex analysis < 20 ppm (March 2009)**

Fig. 1. Process flow diagram for the South Arne Water Injection System Showing the Points of Chemical Injection

pipe-work and process vessels had been suggested as contributory factors to the observed H_2S concentrations in produced fluids. Oil is stored in a concrete tank which forms the 'gravity base system' (GBS) of the platform, located on the seabed. In this, the stored crude oil is supported from below by (ballast) seawater, and is open to the sea such that 'new' seawater enters below the oil while oil is being offloaded to tanker (ship), typically every 20 days. The 'new' seawater is chlorinated, but not otherwise treated, as it enters the GBS system. That water is then displaced back to sea as the storage tank then gradually refills with oil from the production wells/ topside separation train. There were some concerns about H_2S development in the GBS, contributing to H_2S in the export oil

Twelve oil production wells are operated, each with gas-lift, using field (export) gas which contains low concentrations of H_2S, as the majority of the H_2S has been removed from the separated produced gas by liquid H_2S scavenger: see Fig. 2. The oil producing wells all have horizontal completion sections, some 2-3 km long from toe to heel, and all were acid-fractured for stimulation and with proppant injected.

In light of the above, Hess Denmark initiated a study with the primary objectives of determining the source(s) of the H_2S and its behaviour through the system. The study included an 8-day visit to South Arne in 2009 to sample a full round of production well tests and a tanker offload, and some key results are reported herein, with more details in reference papers (Lundgaard *et al* 2010; Robinson *et al* 2010).

SULPHATE REMOVAL PROCESS

The use of membrane filters, which are often described as nano-filters (NF) since they are intended to filter water down to nanometre specifications (10^{-9} m, or 0.001 micrometres), has been practiced in the offshore oil industry for over 20 years, since the first application on Marathon Brae platform in the North Sea in 1988, using membranes manufactured by Dow. That application was used, successfully, to prevent a severe barium sulphate scale problem developing in the oil production wells and topside facilities upon breakthrough of injected seawater along with formation/produced water. Since then over 50 offshore platforms and FPSOs are operating with SRUs (Walsh *et al* 2008), primarily to prevent that same scale problem, but also, and increasingly, to prevent or greatly limit the development of reservoir souring in sweet, deep-water oilfields, in which very high strength risers are required, as they

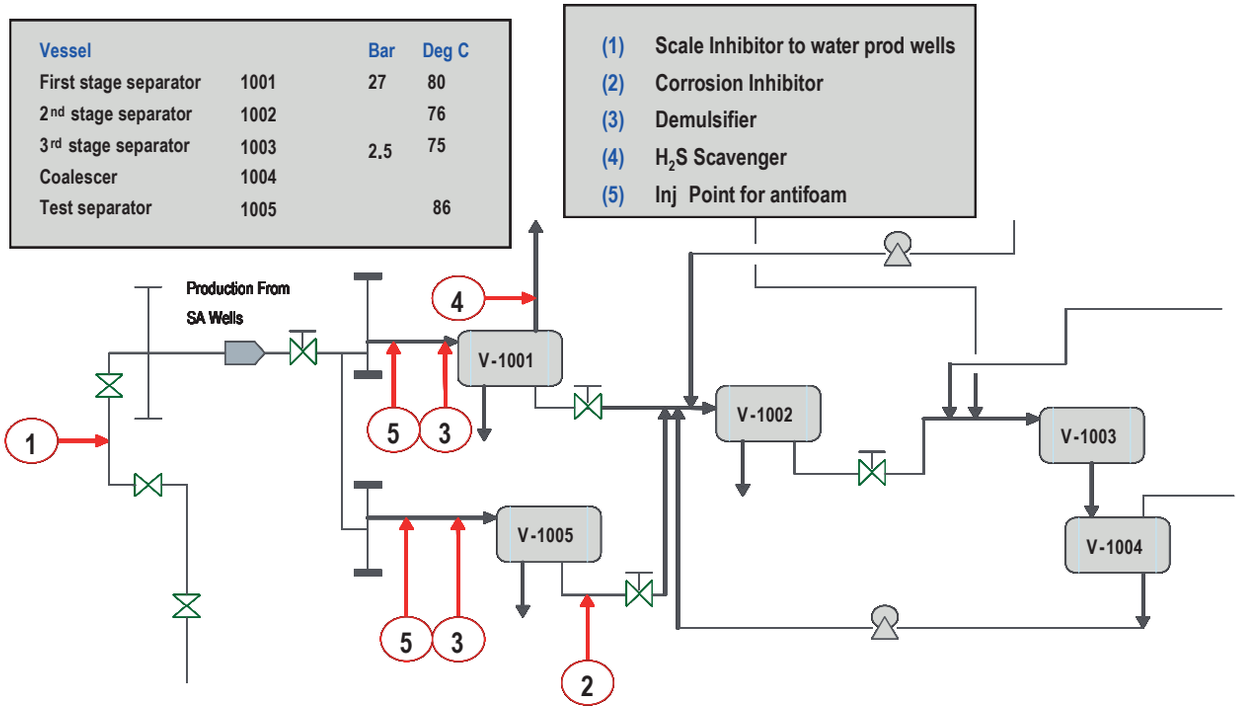


Fig. 2. Process flow diagram for the South Arne Production System Showing the Points of Chemical Injection

may be particularly susceptible to sulphide stress corrosion cracking (SSCC).

Although the South Arne field is not located in very deep seawater, concerns over SSCC and other forms of corrosion involving H_2S still apply, for wells, risers, topside process trains, oil storage GBS, and oil and gas export routes.

The nano-filters are highly selective for removal (rejection) of relatively large dissolved ions such as sulphate (SO_4^{2-}), which has 5 atoms and is divalent, whilst allowing through the smaller mono-element, monovalent ions sodium (Na^+) and chloride (Cl^-). Thus the filtered seawater is not desalinated but has a much lowered sulphate content, reduced from approx. 2800 mg/l typical of oceanic seawater to around 20 – 50 mg/l. The process is similar to the more widely known reverse osmosis, using spiral-wound membranes, but with a more permeable, larger pore size, and so the SRM can be operated at a lower feed pressure and higher flux rates than can RO membranes. That makes the process cost-effective and practicable for treatment of oilfield injection seawater in cases of very high barium sulphate ($BaSO_4$) and/or strontium sulphate ($SrSO_4$) scale potentials (Vu *et al* 2000).

In addition to removing almost all of the sulphate from seawater, the NF membranes also remove some of the other large or divalent ions which are naturally present in seawater, i.e. bicarbonate (HCO_3^-), calcium (Ca^{2+}) and magnesium (Mg^{2+}), and that may also be helpful in reducing the scaling potential of seawater injected into a hot oil reservoir, particularly of calcium carbonate, $CaCO_3$.

The field cases using SRUs to mitigate reservoir souring alone are relatively recent, but where their use can greatly reduce the potentials for both severe $Ba/SrSO_4$ scaling and reservoir souring too, then their inclusion in the seawater treatment process train is logical, as was the case for South Arne. However, it must be appreciated that there may still remain some potential for both the $BaSO_4$ scale, since it is extremely insoluble in water (only a few mg/l) and the 20 – 50 mg/l SO_4^{2-} residual typically achieved in the LSSW is sufficient to cause both some precipitation of it and perhaps also leave some SO_4^{2-} available for bacterial conversion to sulphide (HS^-/H_2S). As will be seen later in this paper, the two mechanisms may be competitive for the remaining sulphate ion in the LSSW in this case.

On South Arne, the LSSW sulphate ion concentration is rather higher than that reported on some other platforms, at ~ 50 mg/l, for a variety of reasons. In part, this stemmed from the need to install the SRU upstream of the deaerator which meant that, in effect, additional sulphate is added to the SRU-treated LSSW by way of injecting ammonium bisulphite oxygen scavenger into the deaerator to chemically remove any dissolved oxygen remaining after the vacuum stripping stage. The ammonium ion part of the oxygen scavenger also stays in the injection water going to the wells and reservoir. Had it been possible to install the SRU downstream of the deaerator then those ions (ammonium, excess bisulphite and sulphate formed from reaction of bisulphite ion with any dissolved oxygen remaining after vacuum stripping) would largely have been removed too. However, locating a deaerator upstream of the SRU does require the deaerator to be rated for approx. 33% greater water flow-rate to allow for the 25% reject (concentrate) stream of the SRU. That reject stream is necessary to keep the membrane units functioning correctly by carrying away, back to sea, the rejected sulphate ions plus the other large/divalent (scaling) ions and any suspended solids remaining in the water after the upstream filter stages.

Fig. 1 shows that on South Arne the upstream filters are coarse filters followed by DMF, which means Dual Media Filters (e.g. deep beds of anthracite granules above granules of fine garnet) and then a bank of (Amazon) disposable cartridge filters. Such a train of filtration is common where SRU are installed, because the membranes in the SRU are very prone to blockage if the feed water is not very clean, despite the cross-flow design (across the membrane's surface) being intended to carry away any remaining filterable suspended solids.

Fig. 1 also shows batch injection of sodium hypochlorite (for chlorination of the feed water as a primary control chemical for macro- and micro-organisms) which is somewhat unusual, as most water injection systems have continuous chlorination from on-board electrochlorinators. As the SRM are not tolerant at all to a strong oxidizing chemical such as chlorine/hypochlorite, the water must be de-chlorinated prior to contacting the membranes, and some ammonium bisulphite oxygen scavenger is injected for that purpose: it reacts more quickly with hypochlorite to remove it than it does with dissolved oxygen. As the hypochlorite is batch-injected, in this particular system, then so too must be the oxygen scavenger (but downstream, into the deaerator itself, there the main dose of oxygen scavenger is continuously injected).

MICROBIAL CONVERSION OF SULPHATE TO SULPHIDE

For decades it has been well known that sulphate-reducing prokaryotes (SRP) can, under favorable conditions, convert sulphate ion to hydrogen sulphide, and those conditions do exist in many oil reservoirs, as well as pipelines, storage tanks, tankers, etc.(Ollivier and Magot, 2005; Barton and Hamilton, 2007). However, culture-based methods of traditional microbiology (i.e. most probable number, MPN) applied to the microbiological processes involved in oilfield reservoir souring pose a threat of yielding inadequate and contradictory results (Larsen *et al* 2005). For that reason molecular microbiological methods (MMM) were applied in this study and showed high concentrations of sulphate-reducing archaea (SRA) in produced fluids while the traditional MPN techniques gave zero readings (Lundgaard *et al* 2010). It is generally accepted that any cultivation step, in bacterial analysis procedures, will, almost certainly, alter the population characteristics and thus the results upon which any evaluation will be based. Therefore, enumeration of microbes via the MPN method alone and decisions made based upon those results should be taken with great care (Skovhus *et al* 2007).

The general key chemical reactions responsible for souring and their stoichiometries are summarised below, where acetate, propionate and butyrate are volatile fatty acid (VFA) anions dissolved in the water phase, and which are the main carbon sources utilised by SRP (SRA and SRB) in reservoir souring.

$CH_3COO^- + SO_4^{2-} \rightarrow S^{2-} + H_2O + CO_2 + HCO_3^-$
Acetate
i.e. 1 acetate, 59 mg → 1 sulphide, 32 mg

$4CH_3CH_2COO^- + 7SO_4^{2-} \rightarrow 7S^{2-} + 12H_2O + 12CO_2$
Propionate
i.e. 1 propionate, 73 mg → 1.75 sulphide, 56 mg

$2CH_3(CH_2)_2COO^- + 5SO_4^{2-} \rightarrow 5S^{2-} + 8H_2O + 8CO_2$
Butyrate
i.e. 1 butyrate, 85 mg → 2.5 sulphide, 80 mg

Somewhat confusingly, VFAs are also known as non-volatile weak acids (NVWA), and in chemical terminology are all carboxylic acids or carboxylate ions from the -COO^- ending. The anions, such as acetate, will not be volatile at all, and so describing these nutrient carbon compounds as VFAs can be very misleading to those not versed in the subject as they are neither acids nor are they volatile, unless at much more acidic pH values than in oilfield waters. So, acetate, etc., anions should really be referred to as a NVWAAs, but most practitioners of oilfield microbiology and production chemistry realize what is meant when VFAs are mentioned.

HOW MUCH SULPHIDE COULD BE PRODUCED?

There were indications that the South Arne reservoir fluids contained a trace of H_2S from the very beginning of production in 1999, but at <3 ppm in the produced gas it was considered to be 'sweet'. It is possible that the traces of H_2S were erroneous measurements, or were as a result of minor contamination of the produced well(s) at the drilling stage (with some sulphate and SRP introduced in drilling fluids, say), or could have been falsely low readings as a consequence of somewhat higher natural reservoir H_2S reacting with the newly installed steel well tubulars. However, H_2S scavenger has been in continuous use since 2000 and its use may have masked any increases in H_2S concentrations because the gas export flow-rate has also decreased over that period, as described in the South Arne Results section below.

Since 2008, however, there has been a clear increase in H_2S concentrations, despite the installed SRU operating fully since the beginning of water injection. There was, therefore, a need to identify the source(s) of the H_2S and quantify the potential for further increases in produced fluids, and also in the export oil from the 'raw' seawater-displaced oil storage tank, especially as an export shuttle tanker had reported high H_2S concentrations in headspace gas.

Looking at how much H_2S could theoretically develop in the produced fluids, simple stoichiometry of sulphate to sulphide (a 3:1 molecular weight ratio, i.e. 96 → 32) shows the following maxima, in the water as that is where the microbes grow:

SO_4^{2-}	→	**S^{2-}**
MW 96	→	MW 32
e.g. 2840 mg/l	→	947 mg/l
or 25 mg/l	→	8.3 mg/l
or 50 mg/l	→	16.6 mg/l

These concentrations can be achieved in water provided that:

- There are no nutrient limits (assimilable carbon

e.g. acetate / propionate, N, P, trace elements);
- There is no temperature restriction (e.g. reservoir is too hot for SRP);
- There is no pressure restriction (e.g. reservoir pressure is not too high);
- There are no sulphide 'sinks' or scavenger minerals in the reservoir rocks (e.g. siderite, $FeCO_3$, or adsorbent clays);
- The generated sulphide has not reached a self-toxic limit to SRB and SRA;
- No souring control chemicals have been added (e.g. biocides, nitrate);
- Relevant strains of SRB and SRA are in place, and;
- 100% conversion of sulphate to sulphide.

It is also necessary to consider the varying mixtures of the seawater, whether full-sulphate or LSSW, with the reservoir formation water. This is because the seawater will be nutrient-limited (especially carbon) and so the reactions basically rely on obtaining nutrients from the formation water, via mixing/dilution, in order to obtain any assimilable carbon ,e.g. acetate, propionate, etc.

Nevertheless, if we use the 16.6 mg/l S^{2-} value from above (maximum generated from 50 mg/l SO_4^{2-}), how will that translate into an H_2S in gas concentration, as that is often the key parameter that operators often have limits on – rightly or wrongly, as from a corrosion perspective it is actually in the water phase that H_2S is corrosive, including SSCC.

As noted above, the microbial H_2S is generated in the water phase (injection water alone or mixture of injection and formation waters), but in passage through an oil zone in the reservoir there will be some exchange, or partitioning, of H_2S into the oil, and/or partitioning will occur in the oil production well(s), flowlines, and surface/topside separation vessels. The amount of partitioning will depend upon pH, pressure, temperature, salinity (or Total Dissolved Salts, TDS) and oil & gas compositions, and the relative proportions of the three phases, i.e. gas: oil ratio (GOR) and water: oil ratio (WOR). The pH effect is very significant, and occurs because H_2S ionises, reversibly, in the water, i.e.:

$$H_2S \Leftrightarrow H^+ + HS^- \Leftrightarrow 2H^+ + S^{2-}$$

At lower pH values, <7, the reactions are 'driven' (as in Le Chatelier's Principle) to the left-hand side of this equation, because of the increased concentration of H^+ ions at lower pH, and that increases the partitioning of H_2S into the oil and gas phases, since ions can only exist in a water phase but molecular H_2S can dissolve in oil and transfer into gas.

The SRP generate the sulphide from sulphate absorbed into their cells, via specific pores in the cell membrane. Enzymes within the cells convert sulphate ions to sulphide ions, and the cells then 'pump out' the sulphide ions, again via pores in the cell membrane. Some fractionation of sulphur atoms occurs, from the absorbed sulphate ion, due to slightly more frequent binding by the enzymes to the lighter isotope ^{32}S, compared to the slightly heavier ^{34}S, such that the generated sulphide is slightly enriched in the lighter isotope ^{32}S. Conversely the generated sulphide is slightly depleted in ^{34}S, and this is often expressed in $\delta^{34}S$ ($^{o}/_{oo}$ vs CDT), i.e. parts per thousand relative to that found in the standard material of the Canon Diablo Troilite (a meteorite), and so bacterially produced H_2S is typically negative on this scale, often ranging from 0 to -40 $^{o}/_{oo}$ $\delta^{34}S$, which compares to the sulphur in sulphate of oceanic water at +20 $^{o}/_{oo}$ $\delta^{34}S$. This 'signature' can be a useful, but not necessarily conclusive, indicator that the detected H_2S was generated by SRP rather than being of geological origin. The considerable variation in the microbially generated $\delta^{34}S$ is dependent, in part, on the starting water's sulphate ion concentration (Sharp, 2007) as an excess of sulphate ion leads to a slow reaction rate and a larger fractionation, i.e. more negative $\delta^{34}S$, whereas when sulphate is limited then the sulphur isotope fractionation will be smaller. Other factors such as temperature, nutrients, types of microbes, etc., doubtless have an influence too. The low sulphate content in LSSW may result in a $\delta^{34}S$ signature in SRP-generated H_2S which is different to that from oceanic seawater, but any value below zero is well below the +20 $^{o}/_{oo}$ $\delta^{34}S$ value of seawater and so a strong indicator of any H_2S being of microbial origin. However it should also be recognised that if all the sulphate in the original water was converted to sulphide then the total sulphide must have the same $\delta^{34}S$ as the starting water, or +20 $^{o}/_{oo}$ $\delta^{34}S$ for oceanic (including North Sea) water.

The pH of the water outside of the SRP cells then governs how much stays as S^{2-}, or ionises to HS^- or forms molecular H_2S, or, indeed, precipitates as FeS, say, or converts $FeCO_3$ to FeS or FeS_2. The water pH will depend almost entirely on the natural pH values of the water in that local environment, be that deaerated LSSW, formation water, or those two waters in various mixture ratios within the oil reservoir pores or fracture network, or in the

produced water or the ballast seawater in the GBS, say. Furthermore, some H_2S, and only the molecular H_2S but not ionic S^{2-} or HS^- , may partition into any hydrocarbon phases present, i.e. oil and/or gas, either locally near the SRP or more distantly wherever the sulphidic water and oil/gas come together, e.g. in the producing wells and oil/gas/water separation process train.

The concentrations of H_2S in gas, which is often the high-focus parameter in any oilfield, depend very strongly on the relative volumes of gas, oil and water, plus physico-chemical parameters such as partitioning coefficients, pressures and temperatures, To illustrate the effects of gas: oil ratio (GOR) alone on H_2S in gas concentrations consider the following example, which has used water, oil and gas compositions not detailed here:

The following conditions were used in a proprietary H_2S partitioning model:

TDS = 35,000 mg/l
Separator Pressure, P = 30 psig/44.7 psia (2 barg/3 bara)
Separator Temperature, T = 60°C
Separator Water pH = 7
Liquid Rate (oil and water) = 10,000 bpd (417 m^3/h)
Water Cut = 80%

Calculated H_2S concentrations from 16.6 mg/l S^{2-} in water were:

Variable GOR, scf/stb	H_2S Mass Rate, kg/d	H_2S in Water at P,T, mg/l	H_2S in Oil at P,T, mg/l	H_2S in Gas at P, T, ppm (v/v)
10	22.4	14.4	10.9	781
500	22.4	6.0	4.6	326
2000	22.4	2.2	1.6	117

Note: liquid concentrations in mg/l; gas concentrations in ppm (v/v).

As can be seen, the total mass rate of H_2S (generated) is the same for each GOR used in the example and the differences seen in calculated H_2S concentrations in each of the three phases is due to establishing equilibrium conditions, with appropriate transfers of H_2S from the oil and water phases into the gas phase. Thus a higher GOR dilutes the molecular H_2S (gas) but also gives a greater transfer from the oil and water phases to reach the equilibrium condition. Whether, or not, equilibrium is reached, during passage from the reservoir, up the wells, through valves and separators, will depend on the amount of turbulence experienced and on the phase contact times. It will also depend on many other factors, e.g. oil- or water-continuous flow, phase viscosities, laminar or turbulent flow, etc.

In the case of South Arne, the use of gas lift in the producing wells will give increased turbulence and so probably lead to equilibrium being established between the three phases before the fluids reach the individual wellheads. It is, of course, necessary to allow for the lift gas mass flow and its H_2S content in any mass balance calculations, although with only 2 ppm (v/v) H_2S in the lift gas (which has been prior-treated with a 'scavenger' chemical to remove H_2S) its contribution to well-flow H_2S is very small.

The above example is a simple equilibrium calculation and prediction of real well and field H_2S development profiles ideally involves the use of sophisticated 3D souring simulators coupled to the output of the specific oil reservoir simulator, or at least combinations of multiple well-pair 2D simulations. Combining reservoir and souring simulators allows for the very considerable complexities of real oil reservoirs in terms of multiple layers, say, or fractures, well positions, well orientations, well production histories, etc.

From the above example, it may be appreciated that even low concentrations of sulphate in injection water may lead to sufficient sulphide generation by SRP to give potentially unacceptable concentrations of H_2S in gas (above 5 ppm can give SSCC conditions to susceptible steels at high pressures, according to the NACE/ISO standard MR0175/ISO15156, dependent on the *in-situ* water pH).

In addition, the potential for microbiologically-influenced corrosion (MIC) should not be ignored as biofilm/colonies of SRP can extract sulphate from low concentrations in almost any water and generate under-deposit corrosion and the pitting which is a well-known characteristic of SRB

SOUTH ARNE RESULTS AND DISCUSSIONS

The field audit involved sampling all 12 oil production wells via test separators, and then throughout the oil processing train. A variety of on-site analytical techniques was used in order to obtain valid data, as sample preservation and much later analysis in onshore laboratories often renders results questionable.

For example, pH measurements were conducted on-line and still under pressure, to avoid loss of the acidic gases CO_2 and H_2S, since their loss would lead to a rise in the measured pH, as shown by Fig. 3, in which the pressure was deliberately reduced during tests on produced fluids flowing through

test separators from two wells, Well-B and Well-E, and from the production train first and second stage separators.

Similarly, special techniques were used for H_2S measurements in the oil and water phases, using what is known as the 'double-bomb' method to depressurise the samples, taken at system pressure in Teflon-lined sample cylinders, and strip out the H_2S using oxygen-free nitrogen. The total stripped H_2S was then measured using a series of the standard (ASTM, 2005) length-of-stain detector tubes (Gastec type): the results for the wells are shown on Fig. 4, with the distribution between phases illustrated more clearly on Fig. 5.

For the process train, the H_2S concentrations are shown in Table 1, with calculated mass rate, in kg/d, given in Table 2, and that data was used to calculate the mass balance as shown on Fig. 6. With regards to the high H_2S value reported in an offload to tanker, that was correlated with re-starting production from Well-L (see Fig. 4) after a 2-year shut-in and successful water shut-off work-over, and during that time the near well-bore area had been cooled due to dump-flooding from Well-F, so creating a local reservoir environment perhaps suited to growth of SRA and/or SRB.

In addition to the pH and H_2S measurements,

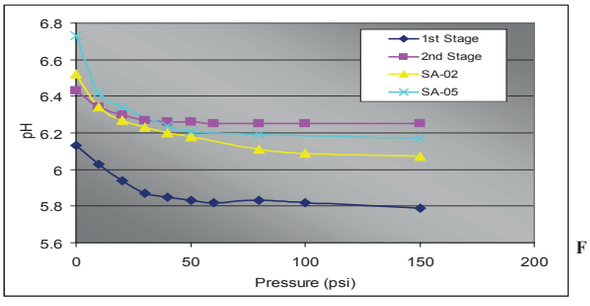


Fig. 3. pH vs. Pressure – Separators and Selected Wells

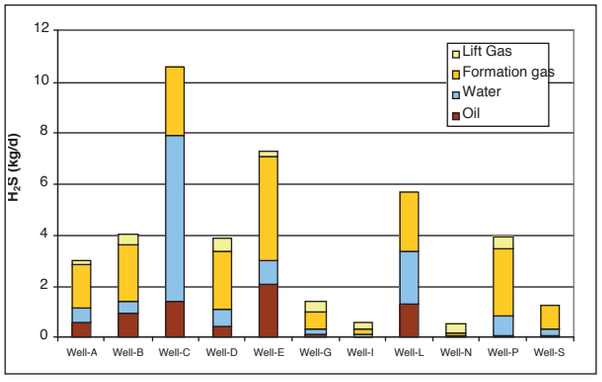


Fig. 4. H_2S Mass Flow Rates from Production Well Tests

Table 1 H_2S Concentrations in Process System

	1st Stage	2nd Stage	3rd Stage	Coalescer	Degasser
Pressure (barg)	26.4	11	2.6	2.6	0.1
Temp (°C)	76	71	70	70	53
H_2S (gas, ppm)	14	53	75	-	190
H_2S in water (mg/l)	2.12	1.3	-	0.32	0.82
H_2S in oil (mg/l)	2.94	1.61	1.11	1.09	-

Table 2 H_2S Mass Rates in Process System

H_2S leaving 1st Stage Separator		H_2S leaving process system	
Gas	36.6 kg/d	1st stage gas	36.6 kg/d
Water	13.0 kg/d	2nd stage gas	2.1 kg/d
Oil	9.7 kg/d	3rd stage gas	3.3 kg/d
-		Rundown crude	3.5 kg/d
-		Degasser (water)	5.3 kg/d
Total:	59.3 kg/d	Total:	50.8 kg/d

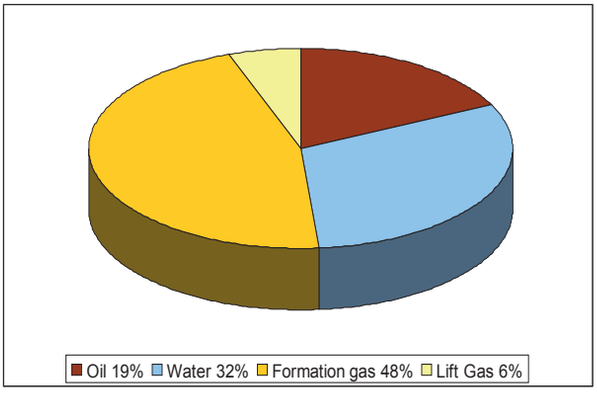


Fig. 5. H_2S Distribution between Phases from Well Tests

many other parameters were measured on site or on samples suitably preserved for onshore analysis. The following parameters were measured, although not all data is given here since only some is relevant to this paper on reservoir souring involving LSSW:

- CO_2 in gas.
- Total Suspended Solids.
- Bacteria and Archaea.
- Cations in water: barium; calcium; iron; lithium; magnesium; potassium; sodium; strontium.
- Anions in water (excluding NVWAA): bicarbonate; borate; bromide; chloride; silicate;

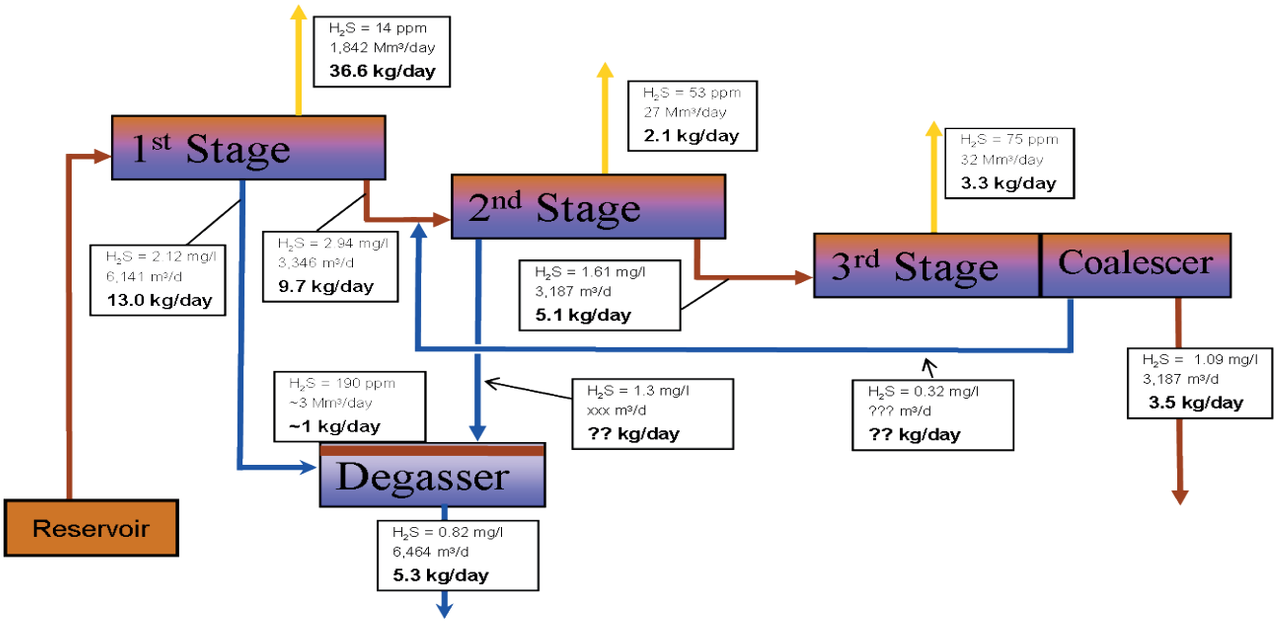


Fig. 6. H_2S Mass Balance for South Arne Process

sodium; sulphate.

- NVWAA: acetate, butyrate, formate; iso-valerate; propionate.
- Sulphur isotopes.

Of particular relevance to the study were the barium (Ba), strontium (Sr) and sulphate concentrations, plus the archaea and bacteria (SRP), and, of course, the H_2S and pH values.

The sulphur isotope results were somewhat inconclusive, in that they were below the +20 $^{o}/_{oo}$ $\delta^{34}S$ standard value for oceanic seawater, at 7.6 to 10.2 $^{o}/_{oo}$ $\delta^{34}S$ in three samples, but were not below zero, which is often the case for microbially-generated H_2S. However, as noted above, the apparently high conversion percentage of the sulphate remaining in LSSW (especially when 'diluted' by much lower-sulphate formation water) would tend to move the values towards the more positive end of the spectrum. The isotope results are, therefore, consistent with SRP metabolising a significant proportion of the available sulphate.

A variety of MMM techniques were used during this study: DAPI staining, FISH (Fluorescent *In-Situ* Hybridisation), qPCR (quantitative Polymerase Chain Reaction), and the traditional MPN technique (Serial Dilution to Extinction). The latter failed to give any positive results for the (hot) well and process train water samples, although did give useful results for the cooler samples from the GBS. Although the qPCR technique does not currently allow distinction to be made between active, inactive and dead microorganisms (see Fig. 7), the technique was particularly valuable for this study as it clearly showed that there were a great many of the extremophilic SRA present in the upstream, hotter parts of the production train, with no SRB in the test and first stage separators, but then almost equal numbers of SRA and SRB in the further downstream degasser and coalescer (in the produced water treatment train); see Fig. 8.

Interestingly, no SRA were found, using qPCR, in the LSSW deaerator outlet water, nor in the ballast water from the GBS.

Using the FISH technique to identify active bacteria, the results did indicate active SRB and not only SRA in the test separator sample, but no

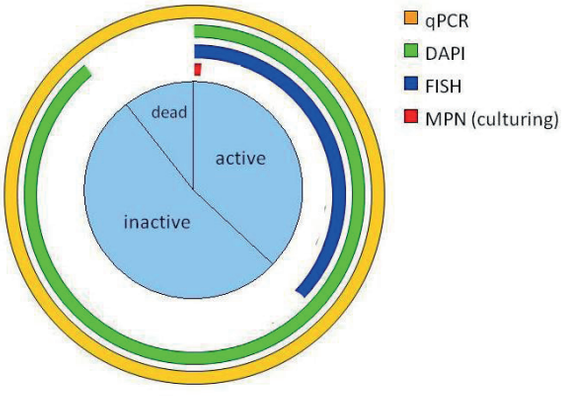


Fig. 7. An illustration of the different pools of microbes (active, inactive, and dead) that are included when employing different microbiological techniques (Lundgaard et al, 2010)

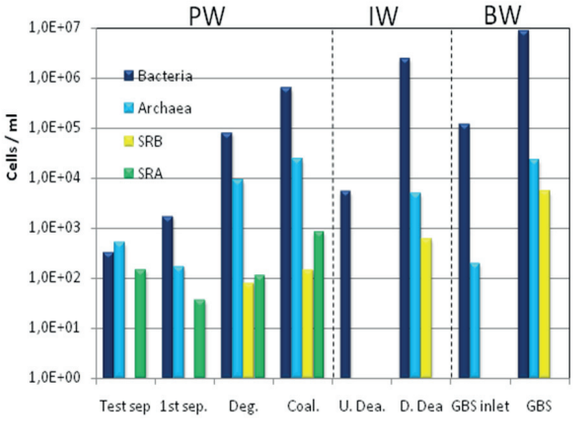


Fig. 8. qPCR data from eight sampling points in the South Arne water systems: Produced water (PW), injection water (IW) and ballast water (BW) (Lundgaard et al, 2010)

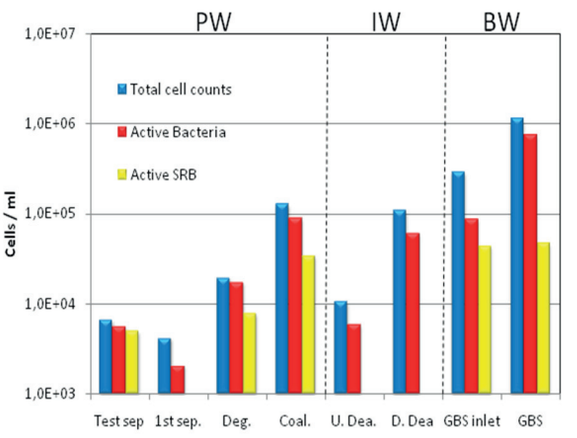


Fig. 9. Microscopy data (FISH/DAPI) from eight sampling points throughout South Arne water systems: Produced water (PW), injection water (IW) and ballast water (BW) (Lundgaard et al, 2010)

SRB in the continuously flowing, hot (75-85°C) first stage separator. SRB were found throughout the cooler (45-50°C) produced water train (degasser and coalescer) and the GBS ballast water, but not into or out of the LSSW deaerator, thus indicating that the SRM process achieves a useful degree of microbial control, which is not surprising of course for nano-filtration; see Fig. 9. Nevertheless, high counts of active non-SRB were still detected in the LSSW.

Interestingly, the traditional MPN techniques did give low, but positive, SRB results downstream of the deaerator. The MPN technique was used both just before and just after a biocide treatment to the deaerator, and showed that this was effective in reducing planktonic SRB in water counts from 95 to 4.5 per ml (those are statistical most-probable numbers): the effectiveness of the biocide treatment to any sessile biofilms within the deaerator could not be assessed during this brief audit.

Overall, the results suggest that microorganisms able to produce H_2S are thriving in the reservoir and the topside oil production system despite high temperature and relatively low sulphate availability. Furthermore, signs of microbial growth were observed in all examined water systems. Data also suggested that a shift in population takes place through the production system, very likely due to a shift in temperature.

The ionic water chemistry data of particular significance to the study are the potential microbial nutrient anions, specifically the NVWAA (= VFA anions), and the potential scaling barium and sulphate ions. In addition, the chloride ion concentrations of the individual well waters, compared to a virgin formation water composition provided by Hess, were used to calculate a percentage content of the LSSW in each one. The assumption was that the LSSW had a constant content of 50 mg/l sulphate ion. The results were then used to calculate predicted sulphate ion contents should no sulphate have been 'lost' in passage through the reservoir. The solid line on Fig. 10 represents the amount of sulphate that would be expected if there were no loss of sulphate during the injection water's transit through the reservoir. The amount by which the measured value falls below this line represents the amount of sulphate lost in the reservoir.

The proportions of sulphate converted to H_2S are quite high, ranging from 32% to 76%. This suggests that SRB are acting on the sulphate before other major removal mechanisms (e.g. scaling with formation water barium) come into play. It also, significantly, suggests that without souring higher sulphate levels could be seen at the producers, which would bring an increased $BaSO_4$ scaling risk.

CONCLUSIONS

South Arne field has been injecting deaerated, low-sulphate seawater (LSSW) for 10 years, and mixtures of LSSW with produced water in part of the field since 2004 and into all wells since 2009. Although the formation water contains significant concentrations of available carbon in a form suitable for use by sulphate-reducing bacteria (SRB), e.g. acetate anion, the amount of H_2S that could be generated is stoichiometrically

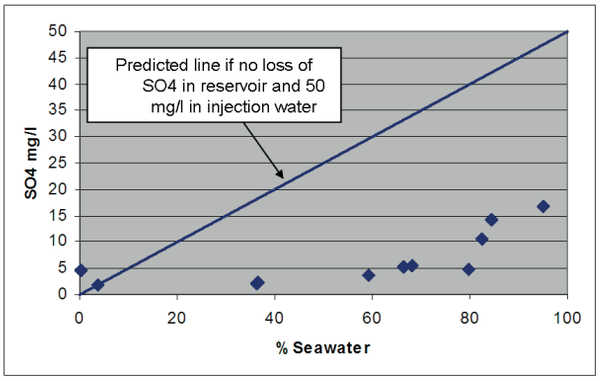


Fig. 10. Sulphate in Produced Water vs. Seawater Cut (Different Wells)

limited by the amount of sulphate ion injected, which is typically < 50 mg/l in the LSSW and < 10 mg/l in the produced water. Other operators which have described the use of sulphate-removal membrane (SRM) filters, primarily for the control of severe barium sulphate scaling potentials, have not reported on the development of reservoir souring, and so it was somewhat unexpected when Hess Denmark, the operator of South Arne, saw increasing concentrations of H_2S in produced fluids.

This study has shown, by modern molecular microbiological techniques (MMM), supported by sulphur isotope analyses, that the H_2S seen is a result of microbial reduction of sulphate to sulphide in the oil reservoir, although not by sulphate-reducing bacteria (SRB) but by sulphate-reducing archaea (SRA). The SRA are extremophiles and are tolerant to, and indeed prefer in this case, high temperatures. The SRA were found in fluids from production wells and in first stage process separators at 75-85°C, and SRB were only found in cooler (45-50°C), downstream parts of the process train.

The traditional SRB detection method of most probable number (MPN) by serial dilution to extinction in culture media did not detect these SRA, although the method still proved useful in lower temperature parts of the production and water injection process trains, including demonstrating that biocide injection is still needed to control bacteria, and so potential corrosion, in the produced fluids and even in the LSSW.

Despite the appearance of reservoir souring the use of LSSW has greatly limited how much H_2S can be generated, as well as meeting its primary objective of limiting the potential for barium sulphate scaling. The H_2S concentrations are low enough that the *in situ* 13% Cr steel well tubulars and completions remain acceptable.

Somewhat ironically, it is considered that the sulphate reduction to H_2S which is occurring is actually reducing any residual $BaSO_4$ scaling potential which would otherwise occur even with 50 mg/l sulphate ion in the injection water.

The produced H_2S is removed from the export gas using conventional liquid H_2S scavenger chemicals, at an acceptable cost because the H_2S mass rate (approx. 50 kg/d) is quite small, and much less than if normal-sulphate seawater had been injected.

Overall the injection of LSSW has been a big success for Hess Denmark and the South Arne Field partners and operations staff in greatly limiting both a severe barium sulphate scaling potential and a quite substantial reservoir souring potential, which otherwise would have given much higher operating costs, in chemicals and well work-overs, and increased hazards from high H_2S concentrations.

ACKNOWLEDGEMENTS

The authors wish to thank Hess, DONG Energy, Noreco and Danoil for permission to publish this paper, and the Danish Technological Institute (especially Torben Lund Skovhus and Thomas Lundgaard) plus William (Bill) Ginty, formerly at Hess but now at DONG Energy, for their substantial contributions to the studies leading to this paper.

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