

## **SELECTION OF AN ACTIVE SOURING MANAGEMENT SOLUTION FOR A GULF OF MEXICO WATERFLOOD**

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### **ABSTRACT**

This paper presents an overview of the factors involved in the selection of an active souring management solution for the Mars field, at which waterflood operations are due to commence in March 2004. It is well documented that the majority of similar seawater injection applications have experienced increased down-hole sulfate-reducing bacteria activity and the reservoir souring and H<sub>2</sub>S control difficulties associated with this. The Mars field was initially commissioned in 1996 with non-NACE MR0175 compliant materials used for well tubing and casing. Following detailed reservoir modeling, and HSE Risk Assessment, a plan was developed to change-out all production tubing to NACE materials, and a 100 % redundant H<sub>2</sub>S monitoring system was installed. However, replacement of production casing materials was cost prohibitive so a plan was developed to mitigate the predicted levels of souring by the use of an active souring control approach. Investigation into the various alternatives available, including sulfate removal membranes, biocide treatment and nitrate or nitrite injection, has determined that nitrate injection is likely to be the most effective souring prevention tool.

**Keywords :** Nitrate, Nitrite, Prevention, Souring, SRB, Waterflood.

### **INTRODUCTION**

The Mars field in the Gulf of Mexico has been producing since 1996 via a Tension-Leg Platform (TLP) host, located approximately 130 miles South East of New Orleans and moored in 3000ft of water. In order to prevent sand compaction and maintain high levels of production in the coming years it has become necessary to waterflood the reservoir. Due to the lack of a local aquifer and the distance of the TLP from shore, the only viable option has been to use a seawater flood injecting directly into the oil leg. The maximum output of the present injection system is 90,000 barrels of water per day (BWPD), although provision has been made for this to be increased to 130,000 BWPD later in the field life if this proves necessary.

It is well known that waterflood operations, undertaken with the aim of prolonging field life and increasing ultimate hydrocarbon recovery levels, often lead to souring of reservoirs as a consequence of the activity of sulfate-reducing bacteria (SRB) within the reservoir being stimulated by seawater injection<sup>(1)</sup>. Souring can increase production costs due to the requirement for the use of sour service materials, the need for chemical treatments to reduce H<sub>2</sub>S to acceptable levels, the generation and consequences of iron sulfide scaling, increased corrosion rates, health and safety considerations and, potentially, the shutting-in of affected wells.

A management of change (MOC) was issued in June 1995 documenting a change to P110 and CYP-110 sweet service casing for the production strings from NACE MR0175 compliant<sup>(2)</sup> C100 sour service materials on the grounds of a cost saving and on the basis that sulfate removal membranes would become a viable technology. It is this decision to specify non-H<sub>2</sub>S tolerant materials downhole that has subsequently shaped the requirement for the work considered in this document. This work has been performed in order to assess the uncertainties involved in the prediction of the future extent of reservoir souring and, ultimately, to develop an active souring management plan to allow continued production in a situation where the reservoir will have a propensity to sour following the commencement of waterflood operations.

A comprehensive study to determine the H<sub>2</sub>S exposure limits of the existing production metallurgy has resulted in the replacement of production tubing strings and their associated components. However, the original well casing is still in place due to the prohibitive cost of fully recompleting the wells.

## PREDICTION OF RESERVOIR SOURING

Much effort has been put into better understanding the likely souring behavior of the Mars reservoir following the commencement of waterflood operations. In the first instance the properties of the Mars field were considered in relation to a number of other Gulf of Mexico and North Sea seawater floods in order to determine if any suitable analogs existed from which to elucidate the likely level of souring that could be expected. However, none of these were a sufficiently close representation of the Mars reservoir to enable any direct conclusions to be drawn.

As a result, it became necessary to undertake predictive modeling to determine levels of H<sub>2</sub>S production expected during the life of the field. At the present time there are three fundamental forms of model used to predict reservoir souring, often described as the mixing zone, biofilm and thermal viability approaches. The first two models are recognized as being most appropriate for new waterflood developments and so these were applied to the Mars case.

The biofilm approach, as described by Tyrie<sup>(3)</sup> and used by operators such as Statoil and BP Amoco, makes the assumption that any bacterial growth is largely located in the region immediately adjacent to the wellbore. The main unresolved issues with this approach are the applicability of assuming that all bacterial activity occurs in the injector wellbore vicinity and that all the nutrients and compounds required for continued bacterial growth are available in the injected seawater. The model is supported by the observation that testing of injector backflow fluids finds levels of souring very much higher than those experienced at producers. Predictions using this form of model were developed for Mars by BP Amoco, who is partner in the development.

The mixing zone approach taken by Shell assumes that bacterial activity is primarily limited to the region of the reservoir where the formation water and the flood front are in direct contact<sup>(4)</sup>, although the most recent version also incorporates a near wellbore souring component. Due to the presence of seawater and formation water this region contains all the necessary compounds and nutrient sources required for bacteria growth. This approach is supported by laboratory work that finds that some degree of formation water and seawater mixing is necessary for SRB to proliferate. However, there are a number of assumptions involved in this approach, the most fundamental being that bacteria are always present at the flood front, either by being resident in the formation or by moving at the rate of the injected seawater.

The outputs from the models were also influenced by other factors beyond the water chemistry and the fundamental assumptions underlying their respective approaches to reservoir souring prediction. Primary amongst these is the presence of significant siderite contents in many of the Mars reservoirs. Iron-bearing minerals of this type have been found to act as a partial barrier to the production of H<sub>2</sub>S by sequestering sulfide and so increasing the time before production souring occurs. Siderite is an iron-carbonate compound that reacts with H<sub>2</sub>S to generate bound FeS and which has been identified as a major factor in increasing the time to souring for many North Sea waterfloods. Examples include fields such as Brent and North Cormorant, where a delay in H<sub>2</sub>S generation of up to two years following seawater breakthrough at the producers has been observed.

A further factor that may beneficially influence the progression of souring at the Mars field is the high total dissolved solids (TDS) content of the connate water. This has been measured from existing production as being around 220,000 mg/l, with a corresponding chloride concentration of 130,000 mg/l. Such conditions are often found to represent a difficult environment for bacterial growth<sup>(5)</sup>, a fact that has been confirmed during laboratory testing of SRB activity in Mars produced water and seawater mixtures.

It is not considered that the temperature of the Mars reservoirs will be sufficient to inhibit SRB activity. The typical reservoir temperature is approximately 170°F, whilst the expected bottom-hole temperature at the injectors is expected to fall to within the region of 105°F. As such, it can be expected that the initial reservoir temperature will be suitable for the growth of thermophilic bacteria and that mesophilic populations will become viable in the regions around the injectors. To account for this cooling of the reservoir following seawater injection associated laboratory testing was conducted at a range of temperatures, from ambient up to 140°F.

There are two additional factors that none of the existing models are able to adequately deal with, largely as a result of a fundamental lack of understanding regarding certain aspects of the souring process. Firstly, SRB do not necessarily require VFA as a source of carbon to proliferate successfully, although this is an inherent assumption in all models and predictive tools. Certain species have shown the ability to grow by utilizing components in crude oils such as benzene, toluene, ethylbenzene and xylene (BTEX) and n-alkanes<sup>(6)</sup>. Furthermore, bacteria may not be the only type of organism to affect the souring of reservoirs. It is now known that archaea are also present in reservoirs, although their ability to sour production has not been clarified<sup>(7)</sup>. What is known is that Archaea are able to tolerate conditions far beyond the range of SRB, particularly in relation to temperature and salinity, and that they are able to persevere in reservoirs for very long periods of time.

Review of a detailed modeling and souring prediction exercise, along with intensive consideration of the uses and limitations of the various predictive approaches, resulted in the conclusion that souring at many of the Mars producers would occur to a level beyond the 10ppm(v) identified as the safe material tolerance of the production strings before the end of the economic production life at these sites. This instituted the need for a souring control program, as discussed in the following sections.

## **SOURING MITIGATION AND PREVENTION TECHNOLOGIES**

In the last few years a number of potential souring mitigation and prevention tools have been studied for application to the issue of reservoir souring, including sulfate removal, biocide injection and nitrate/nitrite injection. The benefits, disadvantages and risks associated with each of these approaches are considered in more detail below. Certain other techniques that have found limited application in laboratory or field trial conditions, such as the injection of fully oxygenated seawater or the injection of alternating seawater and high salinity brines<sup>(5)</sup>, were not compatible with Mars operations and so were not considered further.

Initial assessments of the Mars waterflood injection facility requirements and the impact of souring and scaling, both conducted in 1999, included the requirement for a sulfate removal system to be fitted on board the Mars TLP to treat the injected seawater. At this time it was projected that the performance of such systems would improve significantly in the interim period before waterflood installation was necessary and that the weight and footprint of the equipment would also reduce dramatically over the same period.

The use of sulfate removal membranes was pioneered by Marathon on the Brae platform in the North Sea in the late 1980's as a technique for the mitigation of reservoir scaling. The systems have subsequently been proposed as a possible means of souring mitigation<sup>(8)</sup>, but no field applications in this role have been documented to date. Current sulfate removal systems are able to reduce the sulfate content of injected seawater from approximately 2700ppm to 40-50ppm. This is not the level of relative performance gain that was envisaged in 1995 when sweet service materials were specified for the Mars field and contemporary modeling has indicated that introduced sulfate concentrations at this level would still be sufficient to generate souring in excess of the 10ppm(v) H<sub>2</sub>S operating limit placed on the production metallurgy.

A further, largely unproven, approach for the control of reservoir souring is the application of biocides to target downhole microbial populations. Biocides have traditionally been used for topsides corrosion prevention, rather than as a means to mitigate or prevent reservoir souring, but experience from the North Sea suggests that those fields with

rigorous, high frequency biocide programs have not appreciably soured. However, it is also the case that poor biocide control has not necessarily resulted in the souring of equivalent reservoirs <sup>(7)</sup>.

An example of a successful biocide application in this role has been reported from the Maersk Skjold field, where a controlling influence of THPS additions on producer H<sub>2</sub>S levels in short transit time injector/producer pairs was identified <sup>(9)</sup>. Unfortunately, it remains unclear what the efficacy of this approach would be if applied to extended water transit applications such as those encountered in the Mars reservoir, where breakthrough times of the order of three years will be typical. An anthraquinone-based biostat has also been developed that has the ability to target SRB specifically, rather than having the more general biocidal effect typical of compounds such as THPS and glutaraldehyde, and this approach also shows promise.

Biocide application to the Mars field was carefully considered, but was rejected on the grounds that a zero bacterial kill could not be guaranteed, even close to the injector wellbore. Furthermore, the surface-active nature of biocides is such that it could not be expected that a significant penetration into the reservoir would occur should bacterial populations flourish in any area immediately beyond the injection perforations. Results of laboratory-based testing concerning the repeated application of biocide is presented in Figure 1 for a 12 inch (30 cm) sand pack arrangement flushed at a rate of approximately one pore volume every four hours. Whilst repeated biocide application causes a decrease in SRB activity, this is at a level considered to be insignificant when related to the abundance of SRB under actual reservoir conditions. An interesting consequence of THPS application to the sand pack was that each dose of biocide was followed by a spike of H<sub>2</sub>S generation above that seen before and after. The cause of these peaks has not been positively identified, but it has been postulated that they may result from the break up of existing biofilms.

Whilst the respective suitability of biocide and sulfate removal were being evaluated, a number of developments in nitrate injection technology caused this process to be considered for application to the Mars field. Nitrate injection is an approach to the mitigation and prevention of reservoir souring that is seeing increased interest and application in conjunction with waterflood projects, but that is still widely considered as an emerging technology.

At the most basic level, nitrate injection is effective because it causes nitrate-reducing bacteria (NRB) populations to supplant SRB in the reservoir and so decrease the amount of H<sub>2</sub>S that can be produced. The mechanism by which this occurs is not simply that the two types of bacteria compete for the same nutrient, vitamin and energy sources. The reactions inherent in NRB activity can alter the redox potential of the reservoir and generate by-products such as nitrite, both of which will act to inhibit SRB activity and favor the further proliferation of NRB. A more detailed description of NRB activity can be found in a recent Energy Institute publication <sup>(10)</sup>.

Laboratory studies can not fully characterize the nature of the reactions involved in introducing nitrate to any given reservoir to the point that they can be predicted with certainty from bench testing. For this reason, much of the evaluation of the technique involved in assessing its suitability for application with the Mars waterflood has relied upon data from field trials and practical experience. A significant number of operators have reported the results of previous nitrate and nitrite injection trials as being effective in reducing H<sub>2</sub>S production from sour reservoirs <sup>(9)(11)(12)</sup>. In addition, a number of well-publicized field-wide nitrate applications are also ongoing in the North Sea. Of these applications, that of the greatest relevance to the Mars situation is being undertaken by Maersk at their Halfdan field <sup>(13)</sup>. Maersk has become the first operator to inject nitrate from day one of waterflood operations with the aim of preventing reservoir souring from occurring. Waterflood operations were commenced in January 2001 and first seawater breakthrough was detected in late 2002, with three wells in the North Western section of the field now seeing produced seawater. To date the results from the field indicate that nitrate is being successful in inhibiting SRB activity.

The problems with the application of either sulfate removal or biocide application for use as a souring prevention tool are such that nitrate/nitrite injection was identified as the most likely means of actively gaining control over souring of the Mars reservoirs. In consequence, the decision was made in early 2002 to undertake a detailed study to determine the applicability of the technique to the Mars situation and to identify the nature and magnitude of the risks associated with using nitrate/nitrite in this way.

The decision was made shortly into this process to concentrate on the application of nitrate rather than nitrite, with the justification for this being twofold. Firstly, nitrate has the greatest track record of successful application and, secondly, nitrate is converted to nitrite in the reservoir. In this way a dual benefit is gained in that NRB are stimulated by nitrate injection, so removing nutrient and vitamin sources that could otherwise be utilized by SRB, and nitrite is

generated that acts as an inhibitor to SRB growth. Furthermore, recent evidence suggests that certain species of SRB may be able to develop a tolerance to nitrite during long-term application<sup>(14)</sup>.

## NITRATE INJECTION CONSIDERATIONS

Study and evaluation of the nitrate injection approach to controlling reservoir souring has highlighted a number of benefits associated with successful application, along with several risks and concerns related to data gaps in the present understanding and experience of the technique. The factors identified as being particularly pertinent to the Mars asset are listed below.

### Benefits

The 10ppm(v) H<sub>2</sub>S limit placed on the Mars production system means that even a slight amount of souring will result in prohibitively high work-over costs and deferred production. The economic benefits of maintaining sweet production therefore become highly attractive as a result. There are also a number of operating and process benefits to be gained by operating a sweet rather than a sour system, although these are all secondary drivers when compared to the metallurgy issue.

Corrosion issues resulting from the deposition of iron sulfide on production tubing, pipework and vessels can be created under souring conditions as the cathodic nature of the scale can cause an increased propensity for metal dissolution in areas of damaged or discontinuous scale. Additional process issues that arise during the production of sour fluids also include inadvertent overboard discharge of oil-coated iron sulfide particulates, compatibility issues with certain corrosion inhibitors, foam control difficulties in separator vessels, gas export constraints and deferred production.

A less quantifiable benefit is in terms of the advantages to health, safety and environment (HSE) imparted by not having to operate a production system under sour conditions. Whilst the cost in man hours saved by removing the need for additional monitoring, safety training, safety management and dual working can be assessed relatively easily, the cost in terms of preventing potential injury or loss of life as a result of exposure to H<sub>2</sub>S is incalculable in anything but the most basic financial sense.

Nitrate has an advantage not shared by many chemicals used in the offshore production environment in that it is not regulated by overboard discharge requirements. The solute solutions typically used for nitrate injection are considered non-hazardous, although it is recommended that eye protection is used and that rubber gloves are worn where repeated or prolonged skin contact is possible. The solution itself is not combustible, but prolonged exposure to fire may boil off the water and leave an oxidizing solid residue of nitrous oxides. Nitrate compounds will dissolve in water, are biodegradable and do not bioaccumulate. There is, however, a risk of serious complications if the solution is ingested and bacterial reduction of nitrate to nitrite occurs in the gastro-intestinal system.

Nitrate has no known compatibility issues with other oilfield chemicals, such as oxygen scavengers, drag reducing agents, scale control formulations and biocides. This has subsequently been verified by compatibility testing with the production and water injection treatments applied to the Mars system.

### Risks and Concerns

There are a number of risks or data gaps associated with the use of nitrate injection, but the factors tend to be field specific and very difficult to quantify with any accuracy prior to the commencement of injection or the breakthrough of treated water at the producers.

Firstly, and arguably most importantly, the success of nitrate application in a reservoir largely rests upon a population of uncharacterized microbes. Furthermore, present monitoring techniques may not be able to identify the important species, even where samples have been successfully gathered. Identification of the downhole bacterial population is also complicated by the fact that it is a dynamic system. Populations will continue to shift and change during advancement of the waterflood as pH gradients and seawater/formation water ratios change over time.

From testing of produced fluids it is apparent that there are pre-existing NRB and nitrate-reducing sulfate-oxidizing bacteria (NRSOB) populations in the Mars formation. However, as a result of the arguments above it is unclear whether these would be the species to predominate in the reservoir following any application of nitrate.

Selecting an appropriate nitrate dosage rate from the limited use of nitrate in initially sweet reservoirs does not provide a sufficient database from which to gather conclusive data. Laboratory testing has indicated that there is a distinct minimum effective dosage below which the transition from an SRB oriented population to one dominated by NRB will not occur <sup>(7)</sup>. In a reservoir the dosage at the location of bacterial activity is the important factor, rather than the injected nitrate concentration. The injected nitrate will be subjected to dilution effects and bacterial uptake, so it would be expected that the available nitrate will decrease as the flood front expands through the formation.

Laboratory testing has indicated that the suspension of nitrate injection can cause rapid souring of sand pack arrangements developed to represent the reservoir environment. It is not clear whether such a sudden change in NRB/SRB population dominance would be seen in practice, or how this would be manifest in terms of subsequent H<sub>2</sub>S production. This souring is extremely rapid and can occur to an ultimate level of H<sub>2</sub>S generation in excess of those measured in nominally identical systems that have not been treated with nitrate.

A typical set of short-term results from sand pack testing are presented in Figure 2. Note the low sulfide concentrations, which are a result of the high salinity (approximately 200,000 mg/l TDS) of the produced water acting to inhibit SRB activity. It is not clear whether the rapid increase seen in the rate of sulfide production following nitrate injection cessation is an artifact of the testing, or whether such behavior could be expected in a reservoir following the suspension of nitrate treatment. Certainly it is the case that the results from temporary nitrate injection trials in soured fields have not yet identified such a mechanism in practice.

At present, there are two mechanisms that have been postulated to explain such behavior. The first is that certain species of SRB may be able to utilize nitrate in addition to sulfate. In this situation the cessation of nitrate injection leads the SRB that were previously exhibiting nitrate-reducing behavior to revert to sulfate-reduction. The second theory is that the accelerated bacterial growth associated with NRB proliferation under the influence of nitrate injection results in the creation of a nutrient-rich environment that SRB rapidly utilize following the reduction in NRB and NRSOB activity resulting from nitrate depletion. It is possible that further laboratory tests could be commissioned to study this phenomenon, but the value of the data would remain largely academic until such time as an operator encounters this issue in the field or until such a time as experience determines that this is not a concern.

The introduction of nitrate to the reservoir is for the purpose of facilitating bacterial activity. The promotion of bacterial growth in the topsides and injectors as a result of nitrate injection is also possible due to the greater nutrient availability in the water. Such growth typically needs to be controlled by biocide treatments if the condition of the system is to be maintained. Testing for the Mars waterflood has shown that THPS batch treatments will not be sufficient to impact NRB proliferation in the reservoir, but that they will allow bacteriological control to be maintained in the topsides and injection system. To prevent the proliferation of NRB in the Mars deoxygenation vessels it has been recommended that the nitrate should not be injected into the water stream prior to this unit.

The increased microbial growth associated with the use of nitrate injection is recognized as having the potential to plug susceptible formations <sup>(10)</sup>, although no loss in injectivity has been noted in any of the trials reported to date. It seems reasonable to assume that if plugging occurs it will be most likely under matrix injection conditions. Consequently it would be expected that the use of fracture injection, as planned for the Mars reservoirs, will help prevent injectivity loss. However, this does remain a risk because there are no accepted methods available to treat a microbially plugged reservoir and no form of laboratory testing that can be used to quantify the propensity for this to occur in the formation.

A final concern associated with the use of nitrate injection is the potential for nitrate decomposition products to accelerate corrosion in the production system. The reduction of nitrate by NRB forms nitrite. Nitrite is often applied as a corrosion inhibitor for carbon steel in dosages in excess of 100ppm, but there is also concern that levels slightly below this can act to promote corrosion in the now imperfectly protected metal substrate <sup>(15)</sup>. The exact extent of this range for carbon steel is highly dependant upon environmental conditions and to date no testing has been conducted with corrosion-resistant alloys (CRA's) such as the 13% chrome used for the Mars producers. Furthermore, nitrite may also be reduced to species with an even greater potential to induce corrosion, such as NO, N<sub>2</sub>O, or N<sub>2</sub>O<sub>2</sub> <sup>(15)</sup>.

Where fields have produced nitrite following nitrate injection there have been no reported increases in producer corrosion. It is possible that this is because no problem exists, or it could be that as the majority of fields were already sour the comparison to the effects of souring-induced iron sulfide-generated corrosion and cracking could render any increase undetectable. For the Mars field it is considered that any corrosion of the production system as a result of nitrate injection is preferable to the embrittlement and fracture of components following exposure to H<sub>2</sub>S concentrations above their safe limit. In addition, once typical produced water chemistries are established following any nitrite breakthrough at the producers it will be possible to conduct flow loop testing to quantify the severity and likely extent of any corrosion generated by this phenomenon.

The presence of nitrite and sulfide together can generate additional problems, for instance during the treatment of sour fields with nitrate. Nitrite can oxidize sulfide, potentially generating elemental sulfur. This is a highly aggressive species that can cause rapid corrosion and subsequent perforation of steel components. Furthermore, where pre-existing sulfide films are present in production systems then nitrite may induce localized corrosion at defects in the film. However, these issues are not expected to be a problem at Mars because the field will be starting from an initially sweet condition.

### CHEMICAL SELECTION REQUIREMENTS

An evaluation of the composition and injection requirements for any nitrate application of the Mars TLP was undertaken as part of this study, where an overview of the conclusions drawn is presented below.

Nitrate has been used to successfully treat souring when ammonium, calcium and sodium have formed the cationic component of the injected compound <sup>(9)(10)(12)</sup>. This suggests that success of the treatment is relatively insensitive to the nature of the cation species, although limited experimental data has indicated that sodium and potassium nitrates may be marginally more effective in generating nitrite formation than calcium salts <sup>(10)</sup>.

The compound most widely used for the treatment of sour reservoirs is calcium nitrate. Sodium nitrate may be used in cases where calcium has a propensity for scaling in the reservoir, but it is often more expensive to procure and has a lower nitrate yield in the solutions typically marketed. For the Mars application it has been determined that the most cost-effective means of nitrate delivery is by using a 45% calcium nitrate solution, where laboratory testing has indicated that there is not a significant performance advantage to be gained by using a sodium solution and where modeling has determined that the introduction of additional calcium to the reservoir will not appreciably increase scaling in the formation.

Nitrate injection rates for sour fields are typically determined from a combination of laboratory data and field experience. This approach is not ideal in this instance because laboratory conditions do not necessarily reflect the conditions faced in the reservoir, whilst experience of injecting nitrate into sweet reservoirs is very sparse. The risk associated with under-dosing nitrate is that the level in the flood front will be depleted to a point at which SRB become viable and H<sub>2</sub>S is generated. Conversely, over-dosing is wasteful in terms of chemical costs and may also exacerbate issues such as producer corrosion or injector plugging.

A conservative approach to determining the nitrate injection dosage has been taken because even small levels of souring may result in the need to abandon or recomplete wells. An initial level of 100ppm(v) (1.61mM) nitrate has been selected and it is envisaged that this rate will be maintained through the three years until first seawater breakthrough occurs. This dosage represents concentrations known to be effective in reducing H<sub>2</sub>S production from moderately sour fields and is significantly higher than the 40 to 60ppm(v) used in comparable waterfloods <sup>(13)</sup>, although it is envisaged that chemical usage will be reduced in the future following seawater breakthrough, the verification of successful SRB inhibition and the measurement of nitrate and nitrite residuals at the producers.

The possibility of a nitrate pretreatment, perhaps taking the form of a squeeze treatment or period of high nitrate dosage, was also considered. However, as the selected dose rate is acknowledged to be a conservative value this was deemed to be unnecessary. In addition, subsequent fracturing through the treated zone when waterflood is initiated may negate the benefit of such an application.

## SOURING MANAGEMENT PLAN

Procedures have been developed to ensure that wells lacking NACE compliance do not fail in service.

- The primary criterion is to limit the produced H<sub>2</sub>S content in the individual wells to 10ppm(v), as measured in solution at the bubble point of the produced fluid. It is this requirement that has generated the need to implement an active souring management and mitigation program, because modeling and experience suggest that souring will progress beyond this value if left unchecked.
- The second approach is the use of observation wells that will detect the onset of reservoir souring prior to the arrival of H<sub>2</sub>S at the major producing sites.
- The third system in place is to shut-in those wells identified by computer modeling as being the most likely to generate H<sub>2</sub>S. An example of this is the A1 well, which is planned to be shut-in at a water cut of 20%. If the wells remain sweet then this may release additional recoverable reserves from locations of this type.
- If the reservoir sours to greater than 10ppm(v) H<sub>2</sub>S over more than one or two wells then the option remains to recompleat the wells and replace the gravel packs following any failure, although this is obviously an expensive alternative.

A number of procedures have also been put in place to ensure that best practice is followed during field development and production operations in respect to H<sub>2</sub>S control and souring mitigation.

Field development operations have proven to be a source of souring in many fields following contamination of the reservoir by drilling and completion fluids and SRB. Examples include the Shell Cognac field in the Gulf of Mexico, where slight souring was observed at the producers prior to the commencement of waterflood activities, and the Maersk Halfdan field in the Danish sector of the North Sea <sup>(13)</sup>. In order to prevent or minimize the effect of such contamination at the Mars field a comprehensive selection and biociding program was applied to all fluids introduced to the reservoir.

Many of the items identified as being best practice for the production systems are already followed as part of normal operations on the Mars TLP. There is an ongoing requirement to keep the system clean from accumulated sludge and deposits, as these provide opportunities for the establishment of bacterial colonies, and there is already an established topsides bio-monitoring and biocide treatment program. Biocides and H<sub>2</sub>S scavengers are also included as additives to well stimulation fluids and provision for downhole injection of H<sub>2</sub>S scavenger has been made should this be required.

Whilst the above are examples of best practice, experience of a number of situations where production operations can result in increased H<sub>2</sub>S generation have also been identified. Where H<sub>2</sub>S production remains at reasonably consistent levels once a field has soured, such as where water cut and partitioning behavior remain constant, it is still possible to generate very significant spikes in H<sub>2</sub>S levels. An example of this was recorded at the Cognac field, where producer scaling problems necessitated the use of acid squeeze treatments. Produced H<sub>2</sub>S levels of below 20ppm(v) in the flash gas were typical, but these consistently spiked to values in excess of 50ppm(v) immediately following the undertaking of acid treatments. Other production operations known to have potential to elevate produced H<sub>2</sub>S levels are the conversion of injectors to producers <sup>(1)</sup> and the depressurization of reservoirs and associated gas-cap production. Neither of these two activities are planned for the Mars field and so acid stimulation remains as the only high-risk activity likely to be undertaken.

Oxygen control of the injected water is also considered to be important in terms of minimizing bacterial activity, as well as in limiting corrosion of the injection system. Common sense would seem to suggest that the oxygen control of injected seawater practiced by the majority of waterfloods, including Mars, is a factor in promoting SRB activity due to their strictly anaerobic nature. However, it is believed that poor oxygen control in a nominally deaerated system can in fact result in the promotion of SRB growth. The presence of even small levels of oxygen can lead to the growth of facultative aerobic species, where the biomass these generate can be used as both a habitat and a nutrient source by SRB. Furthermore, it has been proposed that poor oxygen control can, over time, result in the conversion of oil components such as naphthenates and aromatic compounds to oxidized forms with greater water solubility <sup>(7)</sup>. It is possible that these may then provide a further source of nutrients for microbial growth.

It is apparent that, if left unchecked, souring of the Mars formation will occur beyond the 10ppm(v) limit adopted as the maximum safe level of souring tolerable by the existing production metallurgy. Of the alternatives considered, only nitrate injection provides the necessary ability to prevent, rather than mitigate, H<sub>2</sub>S production resulting from SRB activity in the formation. Due to the relative novelty of the technique, particularly related to long-term application to sweet reservoirs, it is clear that this is not a risk-free solution. The possibility of reservoir plugging, producer corrosion and loss of SRB control following a significant shutdown in waterflood operations remain as very real concerns at this time. However, the consequences for the Mars asset should the reservoir sour to what are relatively slight levels are such that the use of nitrate injection is a justified option because a successful outcome has the ability to substantially increase the future profitability of the field.

## CONCLUSIONS

Alternative souring control methods do not have the ability of nitrate injection to prevent reservoir souring from occurring. Approaches such as biocide injection or sulfate removal are only likely to reduce H<sub>2</sub>S production by a proportion determined by the reservoir properties and the response of SRB to the treatment.

Nitrate injection to the Mars waterflood is only one aspect of the measures that have been put in place to control reservoir souring. Additional operational strategies, such as the biociding and compositional control of drilling and completion fluids, the addition of H<sub>2</sub>S scavenger to acid stimulation packages, the maintenance of clean topsides facilities and the microbial control of both the injection and production systems are all designed to minimize the propensity for SRB activity.

Nitrate injection is not a risk-free strategy, but the system will be closely examined and investigated throughout the field life to ensure that the optimum approach is being followed in terms of souring management and its influence on field production and profitability.

It is clear that there is still some way to go in understanding the fundamental aspects of the nitrate injection process. However, the technique has moved forward to the point where it is on the cusp of becoming an accepted technology, rather than a number of isolated research projects and small-scale trials. Should large, high profile projects such as Halfdan and the Mars waterflood prove to be successful then it is likely that the use of nitrate injection will grow to the point where it will be considered for the majority of future seawater injection projects.

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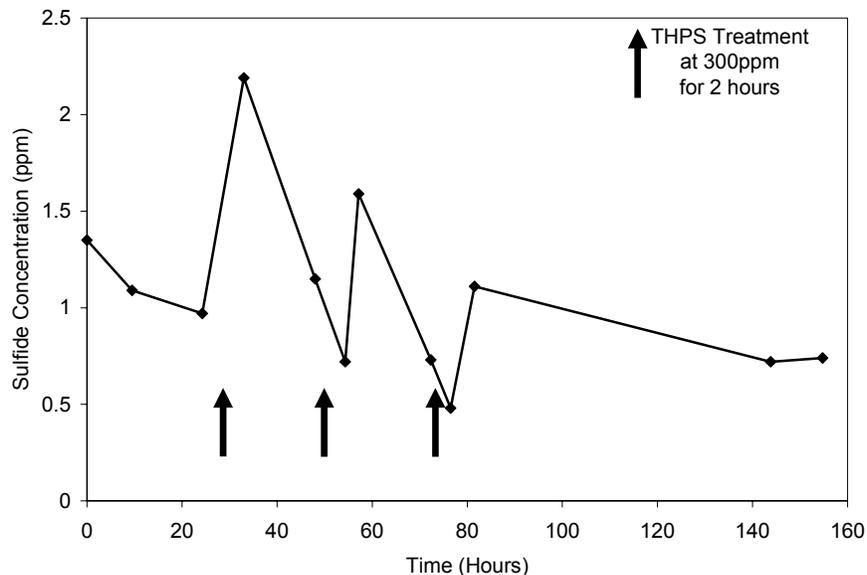


FIGURE 1 – Influence of Repeated Biocide Treatments upon SRB in a Laboratory Sand Pack at 70°F

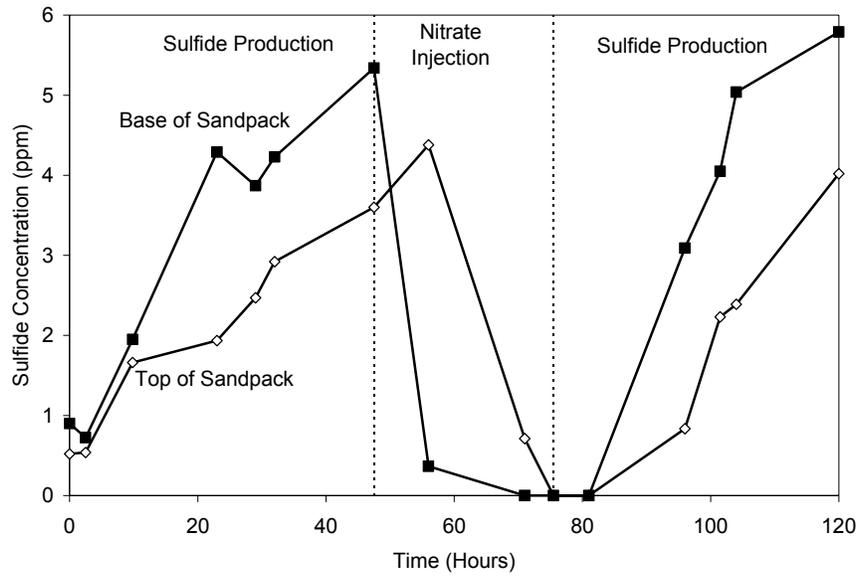


FIGURE 2 – Sand Pack Testing of 10% Mars Produced Water and 90% Seawater at 86°F