Paper No.

**MCI46** 



# Effects of Reservoir Souring from Water Flooding and in an Onshore Oil Field

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## ABSTRACT

Historical trends of bio-generated Hydrogen Sulfide ( $H_2S$ ) levels in an onshore oilfield have been determined based on field measurements to provide a basis for forecasting future  $H_2S$ production using a mechanistic reservoir souring model. The reservoir is currently under produced water reinjection along with make-up water taken from an underground water reservoir. Such  $H_2S$  production forecast is to plan mitigation measures for both short and long terms.

Sulfate is the limiting reactant in the  $H_2S$  bio-generation process within the field. The reservoir souring model has shown that there is almost complete conversion of sulfate to  $H_2S$  by the sulfate-reducing bacteria within the reservoir. The makeup water has high sulfate content and is the key source of sulfate for the bacteria. While the sulfate level produced water (which is re-injected) has been declining, the use of make-up water is increasing the concentration of sulfate injection into the field.

As the surface facilities have not been designed to handle  $H_2S$  production, various mitigation measures have been put in place. A strict biocide program is being followed in the field along with down-hole  $H_2S$  scavenger dosing. In order to minimize risks and mange within the available infrastructure, priority for treatment of wells was decided based on  $H_2S$  production and weld hardness.  $H_2S$  detection systems and  $H_2S$  analyzers have been installed across the field.

Since limiting sulfate in injection water is the only certain procedure for mitigating  $H_2S$  biogeneration and production in this field, sulfate removal in make-up water will dramatically decrease  $H_2S$  production from the field within two years. The same is planned to be implemented in the field shortly.

Key words: Hydrogen Sulfide, H<sub>2</sub>S, reservoir souring, sour crude, mitigation, scavenger, biocide, sulfate reducing bacteria, SRB

#### INTRODUCTION

Cairn Oil & Gas, a vertical of Vedanta Limited, in joint venture with ONGC, is the operator of Contract area RJ-ON-90/01 in the state of Rajasthan, North West India as indicated in the below map. Cairn discovered various oil and gas fields in RJ-ON-90/01 block, named them as Mangala, Aishwariya, Bhagyam, Saraswati, Shakti, Raageshwari and others. Out of which Mangala, Bhagyam and Aishwariya are the most substantial oil fields located in northern part of RJ block.

Production from various well pads of Mangala, Bhagyam and Aishwariya and other satellite fields are processed at Mangala Processing Terminal (MPT) in Barmer district, Rajasthan. MPT is currently operational with three oil processing trains. The oil train primarily consists of slug catcher, production heaters, production separator and settling tank for oil water separation and degassing. Stabilized oil is further treated in electrostatic dehydrators and exported.

Produced water separated from the oil trains is treated in produced water handling facility. Subsequently, treated produced water along with makeup aquifer water (from Thumbli) is heated, filtered, and pumped to respective fields for injection / circulation / artificial lift purposes.

Polymer flood process has the potential to significantly improve sweep efficiency in the fields with viscous oil, due to unfavorable water-flood oil-water mobility ratio resulting in a relatively inefficient water-flood. A successful field implementation would lead to extended production plateau and increased ultimate recovery. Mangala oil field is the largest discovered field with significant oil production potential (Total estimated water flood recovery of around 37 %). The field which contains moderately viscous but waxy oil with high pour point is currently under hot water flood to provide pressure support, sweep and prevent any in-situ wax drop-out. Post success of a polymer pilot trial, the full field polymer flood project has been implemented in the field with the concept of a Central polymer preparation plant distributing the concentrated polymer mother solution to the injection wells which are scattered across the field. The mother solution is diluted with the injection it is expected to yield additional recovery of 5-7% of the STOIIP over base water flood.

#### **PRODUCTION OF HYDROGEN SULFIDE**

Significant production of  $H_2S$  was observed in Mangala field in March 2013 ( $H_2S$  production of ~300 kg/day). The cause of souring in the Mangala reservoir was investigated with detailed field study and was determined to be the introduction of sulfate reducing micro-organisms during drilling and or subsequent water injection activities. The majority of the sulfate now present in the Mangala reservoir comes from the sulfate in the Thumbli aquifer injection water. The original produced water would have been very low in sulfate and all of the wells in the Mangala field have had injection water breakthrough by that time.

Thumbli Aquifer Water is a very clean, low salinity brine, consisting predominantly of sodium chloride (~2700 ppm chloride), with a pH of 6.85. The sulfate content is relatively high, at around 500 mg/l, while the barium content is very low. At 45 °C, the temperature of the aquifer is ideal for bacteria to grow.

In order to identify the origin of Hydrogen Sulphide or cause of souring, often Sulfur isotopes techniques used. For Mangala reservoir fluids, the  $\delta^{34}$ S results for the sulfur in the gas phase are very similar to the  $\delta^{34}$ S results for the sulfate in the water phase with less  $\delta^{32}$ S. As the Thumbli aquifer water is the only source of sulfate for the microbes to utilize, microbial activity has generated the H<sub>2</sub>S utilizing the sulfate in the Thumbli aquifer. The typical chemical reaction are shown below:

$$1 \operatorname{CH}_{3} \operatorname{COO} + 1 \operatorname{SO}_{4} \to 2 \operatorname{HCO}_{3} + 1 \operatorname{HS}$$
(1)

Since the production of  $H_2S$  from the reservoir was not envisaged as part of original field design, the surface facilities were not design for handling sour fluids. In light of this, a study was carried out to assess the impact of  $H_2S$  production on the surface facilities in light of NACE MR0175/ISO 15156 which is a Materials Standard that may be used to assess the suitability of oilfield equipment material to provide resistance to Sulphide Stress Cracking (SSC).<sup>2</sup> The study was completed in September 2013.

Most of the equipment of MPT were found to fall in the NACE MR0175/ISO 15156 Region 0 where no special precautions are normally required with respect to steels under these conditions in 2013. The exceptions to this were four Mangala wells where the  $H_2S$  partial pressures suggest that these steels (from the flow arms) are likely to fall in the Region 1 Category where SSC is possible. It was concluded that the risk of SSC is likely to increase as the field matures and water cut increases.

Another study was carried out to assess the sour service risk for  $H_2S$  ranging from 50 to 500 ppmv at six discrete concentrations viz., 50, 100, 200, 300, 400 and 500 ppmv. It was determined that there is a risk of sour service for well pads piping, well pad cluster flow lines and production pipeline system. Nearly all well pads piping and flow lines falls under sour service risk at  $H_2S \ge 300$  ppmv. All pipelines fall under sour service at  $H_2S \ge 400$  ppmv. The surface facilities of the MPT do not fall under sour service. Hence, there is no sour service risk was envisaged.

It was recommended that during sour service, the weld joints of the well pads piping, pipelines and weld joints which are not stress relieved shall be inspected by nondestructive testing at an interval of six months minimum or the next available opportunity.

#### **MITIGATION MEASURES**

Based on study results mentioned above, the following mitigation and preventive measures were taken to safeguard the Mangala facilities against the impact of  $H_2S$  production.

- Downhole dosing of H<sub>2</sub>S scavenger In order to arrest the risk of SSC in the well flow arms, down-hole dosing of 1,3,5 Triazene as H<sub>2</sub>S scavenger was commenced across Mangala production wells. A rigorous H2S monitoring program was launched with each of the 100 Mangala wells being checked for H<sub>2</sub>S levels at least once every month. The H<sub>2</sub>S production data was meticulously recorded and H<sub>2</sub>S partial pressure was monitored to determine the high priority wells for scavenger dosing. Since the dosing infrastructure was not readily available for all wells, the flow arms with higher hardness were prioritized.
- H<sub>2</sub>S scavenger dosing at MPT The oil stabilization tanks at MPT are operated at a low pressure of 2 kPag. The H<sub>2</sub>S levels in the gas liberated at these tanks very high (~1000 ppm). 1,3,5 Triazene is also dosed in these tanks to protect the downstream gas compressors from high H<sub>2</sub>S levels.
- 3. Biocide Treatment Alternating biocides are dosed in the injection water tanks at MPT in order to control the levels of SRB in the system. The dosing is carried out every fourth day. A similar biocide program is also followed at Thumbli in order to arrest SRB growth the sulfate rich Thumbli water coming to MPT.
- 4. H<sub>2</sub>S detectors In order to prevent any H<sub>2</sub>S related safety incidents, H<sub>2</sub>S detectors and alarm systems have been installed across MPT and Mangala well pads. All field personnel also carry hand held H<sub>2</sub>S detectors for personnel safety

## HYDROGEN SULFIDE PRODUCTION FORECAST

Since  $H_2S$  concentration in gas phase found in increasing trend, it was necessary to understand the future  $H_2S$  production levels for planning permanent mitigation levels. In 2015,  $H_2S$ forecasting developed for Mangala was able to match calculated historical  $H_2S$  production rates observed in the Mangala reservoir.<sup>3</sup> Calibration factors pertaining to the organic constituents being utilized by sulfate-reducing bacteria and siderite within the reservoir were used to forecast  $H_2S$  production rates based on future water injection and fluids production profiles.

Results indicated that the H<sub>2</sub>S production rate from the Mangala reservoir, about 2000 kg/day at the beginning of 2015, will probably peak by the end of 2015 (at about 2400 kg/day) and will decline significantly in the near future as sulfate injected into the reservoir is being depleted. However, H<sub>2</sub>S production will still be maintained at a moderate level (on the order of 1500 kg/day) until the mid-2020s before declining. The use of chemical H<sub>2</sub>S scavengers reduced the H<sub>2</sub>S rate to the MPT by about one third. The scavenger efficiency was estimated at about 0.1 kg of H<sub>2</sub>S removed per liter of scavenger.

The forecasting study also indicated that sulfate is the limiting nutrient (i.e., reactant) for the SRB within the Mangala reservoir. The reservoir contains low levels of indigenous sulfate in the formation water and each has low initial water or connate water saturation. Reservoir souring is occurring only due to sulfate being injected into the reservoir and essentially most of that sulfate is being converted to  $H_2S$  by the bacteria, leaving an excess of organic nutrients

It was recommended that with additional data, the model should be recalibrated every 12 to 18 months to update H<sub>2</sub>S forecasts based on new fluids production forecasts



Figure 1: Mangala H<sub>2</sub>S production forecast showing comparison with historical calculated rates (modeling done in 2015)

Another reservoir souring study was carried out in 2016 and 2017 to update the results stated above and to understand the changes. Results indicate that the level of  $H_2S$  production from the Mangala Field has probably peaked at almost 4 metric tons per day and will continually decline for the next four years. Increased water injection and production at that time will shift the  $H_2S$  production profile upward again which is based on the production and injection profiles forecast.

Sulfate is the limiting reactant in the  $H_2S$  bio-generation process within Mangala. The reservoir souring model has shown that there is almost complete conversion of sulfate to  $H_2S$  by the sulfate-reducing bacteria within the reservoir. The use of Thumbli makeup water is the key source of sulfate for the bacteria. While the sulfate level in the composite produced water (which is reinjected) has been declining, the use of Thumbli water as a polymer Mother Solution is now increasing the concentration of sulfate injection into the Mangala Field.

Water is a major factor in reservoir souring and  $H_2S$  production. Increased water injection provides more sulfate to the reservoir which is almost totally reduced to  $H_2S$ . Increased water production transports more  $H_2S$  to the surface. Changes in forecasted long term injection/production profiles will result in changes to the H2S forecast. Especially important is that increased water production compared to the forecasted rate will lead to an increased  $H_2S$  production rate.  $H_2S$  concentrations at the surface are a function of water cut, GOR and water pH and cannot be generalized based on  $H_2S$  production rate. The reservoir souring model was not able to exactly match the recent  $H_2S$  production rates for the Mangala Field. It is believed that most of the extra  $H_2S$  being produced is due to additional oil produced with the polymer flood, with that oil containing previously biogenerated  $H_2S$  that would have remained in the reservoir without EOR. While it could not be definitively concluded, model results have strongly indicated that the polymer most likely has not provided significant organic nutrients for SRB activity.



Figure 2: H<sub>2</sub>S production forecast for Mangala, Bhagyam and Aishwariya fields (modeling done in 2016



Figure 3: Mangala Field Flow arm H<sub>2</sub>S concentration forecast

On the order of 1000 kg/day of  $H_2S$  is currently being chemically scavenged in Mangala surface flowlines in order to maintain gas-phase  $H_2S$  concentrations at safe levels for metallurgical considerations. Currently almost 2/3rds of Mangala flow lines are operating at  $H_2S$  partial pressures at or greater than the NACE limit of 0.05 psia.

#### NITRATE BIOCIDE TRIAL

Reservoir Souring is extremely difficult to mitigate in an ongoing waterflood unless measures are undertaken at Day Zero of the flood. Current technology for reservoir souring mitigation has not advanced rapidly, with nitrate treatments being a standard treatment into the reservoir and sulfate-removal utilized mainly when the economics of scale deposition come into play.

Nitrate is not a fool-proof technology and is not always effective, mainly because it is stoichiometrically-driven and depends on the level and type of organic nutrients and the availability of the correct nitrate-reducing bacteria within the reservoir.<sup>4</sup> Potentially, nitrate could have been successful in the Mangala Field if implemented full-field at the beginning of the waterflood, but that is hindsight and also doubtful considering what is now known about the Mangala reservoir souring process.

Following field monitoring and laboratory studies performed in 2013-14, a nitrate trial was run in the Mangala Field in 2014-15. A separate study carried out in2014, the results were mixed, with one well showing a drop in H<sub>2</sub>S production and one with an increase. The nitrate dosage for the test had been run based on laboratory results assuming only acetate as the DOC utilized by the SRB. Results from reservoir souring modeling studies have, however, shown that most of the H2S biogeneration in the reservoir is due to an almost limitless supply of higher order oil-soluble nutrients. The stoichiometry of nitrate usage therefore suggests that much higher nitrate dosages would be required to affect H<sub>2</sub>S production from the field. Subsequent laboratory studies have shown that the calcium nitrate solution is not compatible with the EOR polymer being used in the field, causing viscosity reductions, and therefore negating any potential full-field use and/or field trials with nitrate in the Mangala Field. A trial with nitrate solution remaining from the Mangala trial is currently ongoing in the Bhagyam Field prior to the initiation of polymer injection.

# WAY FORWARD

There are three ingredients required for reservoir souring: SRB, organic nutrients, and sulfate. It is impossible to eliminate the SRB from the reservoir even with massive amounts of biocide. Likewise, the supply of potential organic nutrients in an oil (i.e., hydrocarbon) reservoir is endless. Sulfate-removal is the only feasible method to now mitigate reservoir souring in the Mangala Field.

# Sulfate Removal from Thumbli Water

The modeling study indicated that reduction of sulfate from Thumbli water will drastically reduce the  $H_2S$  production rates from Mangala reservoir. Two levels of sulfate removal were studied: to 40 mg/L using nanofiltration and to 10 mg/L using a combination of nanofiltration and reverse osmosis. Sulfate removal will result in substantial decline in  $H_2S$  production from the three fields, with slight differences in the two sulfate removal cases. Very little sulfate will be produced from the field within one year; the only sulfate available for the SRB activity will be that not removed from the Thumbli makeup water and from newly contacted formation water within the reservoir.

It should be stressed that consistent operation of the sulfate removal facility is important. Since every kg of injected sulfate can result in the biogeneration of 0.35 kg  $H_2S$ .

Sulfate removal will result in an overall decline in  $H_2S$  transported to the MPT and also in the probable decline in required  $H_2S$  scavenging in the Mangala Field.



Figure 4: Forecast H<sub>2</sub>S production profiles for the Mangala Field with and without de-sulfated Thumbli makeup water.



Figure 5: Proposed facility for Thumbli water Sulfate removal

#### CONCLUSIONS

We have already seen the start of sulfate removal in the field just due to the consumption of injected sulfate within the reservoir. Recycling the produced water containing lower and lower levels of reservoir–produced sulfate is contributing to a reduction in the H<sub>2</sub>S biogeneration. Produced water reinjection (PWRI) is not normally a recommended process when considering the potential of reservoir souring. PWRI adds SRB, organic nutrients and sulfate back into the reservoir. . However, for Mangala, PWRI might actually be beneficial since the level of reinjected organics is quite low and sulfate levels have decreased substantially since waterflood initiation.

Sulfate is the limiting reactant in the H2S biogenerating process within at least the Mangala and Bhagyam Fields. The reservoir souring model has shown that there is almost complete conversion of sulfate to H2S by the sulfate-reducing bacteria within the reservoirs. The use of Thumbli makeup water is the key source of sulfate for the bacteria. While the sulfate level in the composite produced water (which is reinjected) has been declining, the use of Thumbli water as a polymer Mother Solution is now increasing the concentration of sulfate injection into the Mangala Field. Limiting sulfate injection is the only appropriate method for mitigating H2S biogeneration and production in this field. Forecasting studies have shown that sulfate removal to 40 mg/L or lower in the Thumbli water will dramatically decrease H2S production from the Mangala Field within one to two years.

Treating the symptoms to reduce the level of  $H_2S$  is a control measure. That can only be done by treating the produced fluids on the surface to remove  $H_2S$  or by taking some action within the reservoir to retain the  $H_2S$  from being observed at the surface. Chemical scavengers have been used in the Mangala Field to reduce  $H_2S$  partial pressures in flow lines that are at risk due to high H2S concentrations.

H<sub>2</sub>S biogeneration is potentially occurring in the water injection lines from the MPT to the injection wells. Biocides will continue to be injected in these lines to control microbiological activity, H<sub>2</sub>S, corrosion and suspended solids (TSS) that could plug injectors. Injecting biocides in these lines will not have an impact on the overall reservoir souring process or H2S production level occurring in the field, but will help prevent under deposit corrosion.

Rigorous  $H_2S$  monitoring program along with  $H_2S$  scavenger dosing will be continued to manage  $H_2S$  levels in the field till sulfate removal plant is installed for Thumbli make up water

## ACKNOWLEDGEMENTS

We thank our colleagues in Cairn, especially to all the team members associated with Mangala for giving their support and expert advice that greatly assisted in preparation of the paper. We are immensely grateful to their comments on an early version of the manuscript. We also like to show our gratitude to the senior management team of Cairn for sharing their pearls of wisdom with us during the course of preparation of this paper and giving us this opportunity to present this paper.

#### REFERENCES

- Ligthelm D.J., de Boer R.B. and Brint J.F. 1991. "Reservoir Souring: Analytical Model for H<sub>2</sub>S Generation and Transportation in an Oil Reservoir Owing to Bacterial Activity." SPE Paper 23141 presented at SPE Offshore Europe Conference, Aberdeen, 3-6 September 1991.
- NACE MR0175/ISO 15156-1, Petroleum and natural gas industries-materials for use in H<sub>2</sub>S containing environments in oil and gas production. Part 1 NACE MR0175/ISO15156-1:2001; Part 2 MR0175/ISO15156-2:2003; Part 3 MR0175/ISO15156-3:2003.
- Burger, E.D., and G.E. Jenneman (2009): "Forecasting the Effects of Reservoir Souring from Waterflooding a Formation Containing Siderite," SPE Paper 121432 presented at 2009 SPE International Symposium on Oilfield Chemistry, The Woodlands, TX, 20-22 April 2009.
- Mitchell, A.F., I. Skjevrak, and J. Waage (2017): "A Re-Evaluation of Reservoir Souring Patterns and Effect of Mitigation in a Mature North Sea Field," SPE Paper 184587-MS presented at the SPE International Conference of Oilfield Chemistry, Montgomery, TX, 3-5 April 2017.