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H_2S Inhibition By Nitrate Injection On The Gullfaks Field

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ABSTRACT

Injection water on all Gullfaks platforms have been treated with nitrate to reduce H_2S production caused by Sulfate Reducing Bacteria (SRB). Results from Gullfaks B (GFB) and Gullfaks C (GFC), which have had the most stable injection and production during the treatment period, show a decrease in H_2S production, when the treated injection water reaches the producers. In the water injection systems the change from biocide treatment to nitrate treatment resulted in more than 1000-fold reduction in SRB number and 10-20-fold reduction in sulphate respiration activity. Following nitrate injection, the SRB population was replaced with an equally large population of NRB in the biofilm and corrosion level in the water injection system dropped by more than 50%. This result corresponds well with the observations from a similar water injection treatment at Veslefrikk.

Keywords: H_2S, reservoir souring, corrosion, Gullfaks, nitrate, bacteria, SRB, NRB.

INTRODUCTION

The process of reservoir souring, caused by the growth of Sulfate Reducing Bacteria (SRB) in oil reservoirs, represents a major problem for the oil industry.

Introduction of nitrate as electron acceptor for anaerobic respiration is an alternative to biocide treatment. The idea has been that stimulation of nitrate reducing bacteria (NRB) could inhibit growth of SRB[1, 2, 3]. Nitrate has been used successfully to inhibit microbial sulfide production in oil-contaminated wastewater [4, 5]. Laboratory experiments with oil reservoir model columns have shown that injection of nitrate inhibits sulfide production [6,7]. Telang et al. [8] showed that nitrate injection in water injection wells led to enrichment of sulfide-oxidizing, nitrate-reducing bacteria in the reservoir. Jenneman et al. [9] showed reduced H_2S production from injection and production wells after treatment of injection water with 400 mg/L of NH_4NO_3.

Myhr et al. [7] showed in laboratory experiments that microbial H_2S-production is inhibited by nitrate, in concentrations that is applicable to offshore oil fields. As a result of this the injection water at the Veslefrikk field (North Sea) was treated with nitrate. Microbiological monitoring of the water injection system showed reduced growth and activity of SRB in the water injection system, and a concomitant reduction in microbial induced corrosion (MIC) in C-steel topside seawater injection systems [10].

On the basis of results obtained from the model experiments [7] and successful treatment of the water injection system at Veslefrikk [10], several oil fields on the Norwegian Continental Shelf have been treated with nitrate since 1999, among them all the Gullfaks platforms. In this paper results from nitrate treatment of the water injection system and the effect on H_2S production from the reservoir (reservoir souring) at Gullfaks B and C are presented.

MATERIALS AND METHODS

The Gullfaks platforms GFB and GFC

The Gullfaks field is located on block 34/10 in the northern part of the North Sea, west of Bergen city in Norway. The production start up was in 1986, 1988 and 1989 for the Gullfaks A, B, and C platforms respectively. The field uses gas and seawater injection (WAG) as pressure support. The water injection volumes have, from each platform, been varying between approximately 30.000 m^3 and 70.000 m^3. During the latest years, approximately 50.000 m^3 and 40.000 m^3 have been injected on GFB and C respectively. Injection pressure downstream of the water injection pumps are close to 200 bars. The seawater intake depth is 70 m on GFA/B and 120 m at GFC. Oxygen is removed by vacuum deaeration including bisulfite scavenger, to less than 20 ppb. Temperature downstream of the deaerator is approximately 25°C. On GF the water was originally filtered to less than 7 micron. The filter has since 1998 been bypassed on GFB. On GFC, the filtration is continuing, but from 2000, without the stringent filter specifications. Chlorine treatment of injection water on Gullfaks B and C was terminated in 1997.

Biocide and nitrate treatment

The biocide treatment of injection water on Gullfaks has been effectuated by using batch treatment of glutaraldehyde from field start up in 1986. Varying dosing regimes have been used, but for the latest 5 years until substitution by continuous nitrate injection late 1999, the injection rate implied 500 ppm (50% glutaraldehyde), 1 hr/week. The nitrate salt is added continuously at a dosing rate of 30-40 ppm of a 45% $Ca(NO_3)_2$ solution.

Sampling

Anaerobic water samples were taken after deaeration tower and at the wellhead. Sampling points for GFB and GFC are shown in figure 1. Biofilm and water samples were collected downstream of deaeration tower, and additional water samples at wellhead for selected wells. GFB has supply of treated injection water from GFA via 4 km pipeline in addition to separate GFB injection water treatment plant. Bioprobes and water samples were collected at the water reception from GFA, and additional water samples at wellhead manifold.

Microbiological monitoring

Microbial monitoring of the water injection system followed the same procedures as previously described for the Veslefrikk field [10]. The total number of bacteria was determined with epifluorescence microscopy after filtering samples on to a 0.2 μm nuclepore filter and staining with the DNA specific fluorescent dye DAPI [11]. SRB was determined by fluorescent antibody (FA) technique as described by Nilsen et al. [12]. A mixture of antibodies specific for SRB utilising lactate, acetate and long chained fatty acids was prepared and used for specific determination of these physiological SRB groups. The antibodies are polyclonal and specific for SRB previously isolated from water injection systems at the Statfjord and Gullfaks field (North Sea).

Viable counts of SRB were determined with the "most probable number" method (MPN) using a medium described by Postgate [13], targeting lactate oxidising SRB. The medium was dispensed in aliquots of 9 ml into nitrogen-flushed 10 ml serum bottles, and sealed with butyl rubber stoppers and aluminium crimp seals. Cultures were incubated at 30°C for 4 weeks and assayed for H_2S production and bacterial growth.

SRB activity was determined by radiorespiratory measurement using ^{35}S labelled sulfate as described by Paulsen et al. [14].

Nitrate reducing bacteria (NRB) were quantified by MPN method using a sulfate free mineral medium described by Myhr et al.[7]. The carbon sources were a mixture of (final concentration); acetate (20 mM), butyrate (5 mM), caproate (5 mM) and lactate (8.2 mM). Lactate was added to the mineral medium before autoclaving, the remaining substrates were sterile filtered and added after autoclaving. Two types of NRB media were used. One medium targeting facultatively anaerobic NRB was made anoxic by flushing the medium with nitrogen gas. The other medium, targeting obligatory anaerobic NRB, was in addition reduced with 2 mM Na_2S (final concentration) to remove traces of oxygen. The media were dispensed in aliquots of 9 ml into nitrogen-flushed 10 ml serum bottles, and sealed with butyl rubber stoppers and aluminium crimp seals. Cultures were incubated at 30°C for 4 weeks and assayed for bacterial growth.

The detection limit for SRB and NRB by the MPN method is 6 cells/cm^2 in biofilm samples and 0.3 cells/ml in water samples. The detection limit of SRB using the FA technique is 10^5 cells/cm^2 in biofilm samples and 255 cells/ml in water samples.

Enrichment cultures

For enrichment cultures of SRB a mineral medium described by Widdel and Pfennig [15] was used, to which different carbon sources were added. Palmitate (final concentration 1.5 mM) was used to enrich for SRB able to oxidise long chained fatty acid, benzoate (final concentration 0.25 mM) was used to enrich for SRB able to oxidise aromatics, and acetate (final concentration 20 mM) was used to enrich for acetate oxidising SRB. Growth of SRB was determined by sulphide production as described by Cord-Ruwish [16]. The method was modified by adding 0.5 ml culture sample in 2 ml copper reagent and visually determining positive sulfide production based on the intensity of colouring compared to a blank medium sample. For enrichment cultures of NRB nitrogen flushed and reduced media were made using the same mineral media as used for NRB-MPN series, with palmitate, benzoate and acetate as carbon sources (in the same concentrations as used for SRB). Growth of NRB was determined as increase in cell numbers. 45 ml medium was inoculated with 5 ml water sample or 1 ml biofilm sample and incubated at 30°C for up to three months and assayed for H_2S production and /or bacterial growth.

Corrosion monitoring

Corrosion monitoring in the water injection system was performed by weight loss coupons, on GFB at point of treated injection water reception from GFA, and downstream the deaerator on GFC. Flush mounted C-steel bio coupons are arranged close to the corrosion monitoring equipment. The metallurgy of the water injection system downstream the deaerator is C-steel.

Measurement of H_2S

H_2S was measured with a Dræger tube apparatus in the gas phase from test separator (as ppm H_2S in the hydrocarbon gas phase) or as ppm H_2S in the sales gas.

The H_2S data from Gullfaks are based on single well test separator measurements. The H_2S concentration is measured in the gas phase and multiplied with the amount of gas produced. This gives total kilos of H_2S produced. The kilos produced are then divided by the amount of produced water; which is mainly injected seawater, to give a concentration in the water.

Only wells, which, during the observation period, have not been recompleted and have had a water production higher than 500 m^3/day, have been included in the survey. This was done because oil and gas has a background level of H_2S and back calculating that amount into a small water volume, will give erroneous high concentration.

On this basis data from 14 wells on GFB and 11 wells on GFC have been included. Data from GFA was excluded because of few stable wells and an extensive WAG process.

RESULTS

Microbial activity in the water injection system prior to nitrate injection

At the beginning of the monitoring period starting at GFB in 1989 and GFC in 1992, SRB dominated the bacterial community in the biofilm (figure 2 and 4), as detected with FA. Lactate oxidizing SRB, detected as viable counts as recommended by API RP-38 [17], were only sporadically detected in this period. Staining with specific FA indicated that the population was dominated by acetate and fatty acid oxidizing SRB, not able to grow in the standard MPN medium.

At GFB, SRB (as enumerated by MPN) were regularly detected with viable counts from April 1994 (figure 2). Over the next two years a rapid increase in SRB viable counts was observed, until the viable counts matched the FA counts and stabilized at $1 \cdot 10^6$ to $6 \cdot 10^6$ SRB/cm^3, making up 1 to 3% of the total bacterial population. The increase in viable counts was accompanied by an increase in sulfate reducing rate in the biofilm to an average of 4.6 μg H_2S/cm^2/day and increased corrosion (figure 3).

At GFC a similar trend was observed. Before nitrate injection viable counts of SRB reached a maximum of $1 \cdot 10^7$ SRB/cm^3, and made up 6% of the total bacterial population (figure 4). The increase in viable counts was accompanied by an increase in sulfate reducing rate to 11.9 μg H_2S/cm^2/day (average) in the biofilm and increased corrosion, but in contrast to what was observed on GFB, the SRB activity measurements dropped to a low level after reaching a maximum in January 96 (figure 5).

NRB were present in low numbers in the water injection systems at both platforms prior to the start of the nitrate treatment (10^3 NRB/cm^2 in May 1999 at GFB and 10^5 NRB/cm^2 in September 1999 at GFC, figure 2 and 4). Enrichment cultures showed that the NRB in water and biofilm samples from both platforms were able to utilize a broad range of carbon sources including acetate, palmitate, benzoate and lactate.

The total number of bacteria in the biofilm was close to 10^8 cells/cm^2 throughout the monitoring period (figure 2 and 4) at both GFB and GFC.

Microbial activity after nitrate injection

At GFB nitrate injection started in October 1999. The first reduction in SRB was detected 1 month after nitrate injection, as a decrease in viable counts in the biofilm. A further decrease in the viable SRB counts were observed during the next few months until stabilizing at approximately 10^3 SRB/cm^2. The FA counts showed large fluctuations over the next two years, and high values (more than 10^5 SRB/cm^2) were observed, before dropping dramatically below the detection level (figure 2).

Nitrate injection resulted in an enrichment of NRB in the biofilm (figure 2). A significant rise in NRB numbers were detected, and after approximately 10 months viable counts had increased about 1000 fold, and stabilized at 10^6 NRB/cm^2. The highest viable counts of NRB were observed with the medium targeting facultative anaerobic NRB, which ended up at 5% of the total bacterial population. The substrate diversity in the NRB population remained diverse after nitrate injection. Nitrate treatment did not result in changes in the total number of bacteria in the biofilm.

Also at GFC the first reduction in SRB was detected as a decrease in viable counts, which were reduced 1000 fold from more than 10^5 to approximately 10^2 SRB/cm^2. FA counts could no longer be detected

after 16 months nitrate injection. As observed at GFB the decrease in SRB numbers were accompanied by a reduction in sulfate respiration activity (figure 5). During nitrate treatment, sulfate respiration rate in the biofilm dropped and stabilized at 1.3 μg $H_2S/cm^2/day$.

As observed at GFB, nitrate injection resulted in 1000-fold increase in NRB numbers in the biofilm. NRB numbers reached an average of $2 \cdot 10^7$ NRB/cm^2 after approximately 10 months, making up 10% of the total bacterial population.

Bacteria in water samples

The changes in the bacterial community observed in biofilm samples were also evident in the water samples, but less pronounced. The number of viable counts of SRB in anaerobic water samples from both GFB and GFC before nitrate injection was generally low, less than 1 SRB/ml was detected. Enrichment cultures showed that SRB able to grow on lactate were present in samples of anaerobic injection water throughout the glutaraldehyde treatment period. After the start of nitrate treatment SRB able to grow on lactate, acetate, benzoate and palmitate were detected in enrichment cultures. Enrichment cultures also showed that NRB were able to utilize the same substrates as SRB, and that they were already present in water samples prior to nitrate injection. The total number of bacteria in water samples was constant and close to 10^5 cells/ml throughout the monitoring period.

Corrosion measurements

Corrosion measurements on C-steel coupons showed that, during the period with glutaraldehyde injection, weight loss increased from an initial low value to 1.06 mm/year at GFB and 0.76 mm/year at GFC. Nitrate treatment reduced corrosion rates to 0.4 mm/year (GFB) and 0.28 mm/year (GFC) (Figure 3 and 5). Increased pitting was not observed.

H_2S production

Average H_2S concentration in produced water (seawater cut is app. 80%) on GFB and GFC was until 2000 increasing, from an original value of app. 0.05 mg/l, to app. 2 and 4 mg/l respectively before breakthrough of nitrate treated seawater in the producers. Since May 2000 the H_2S concentration has dropped to app. 1 and 2 mg/l at GFB and GFC respectively.

The results are presented in figures 6 and 7.

DISCUSSION

Microbial activity and corrosion in the water injection system

Prior to nitrate injection, at both Gullfaks B and Gullfaks C, the water injection system contained a stable and diverse SRB population, counting approximately 10^6 SRB/cm^2 (as shown by both FA and viable counting). The average sulfate reduction rate at GFB and GFC was 4.6 and 11.9 μg $H_2S/cm^2/day$ respectively, and enrichment cultures from water and biofilm showed the presence of SRB capable of

utilizing a wide range of carbon sources. NRB were also present, in both water and biofilm, but in low numbers (10^3 NRB/cm^2 at GFB and 10^4 NRB/cm^2 at GFC). Enrichment cultures showed that NRB utilized the same range of carbon sources as SRB.

The change from biocide treatment to nitrate treatment resulted in more than 1000-fold reduction in SRB number and 10-20-fold reduction in sulphate respiration activity. Over a year following nitrate injection, the SRB population was replaced with an equally large population of NRB and today NRB constitute approximately 10% of the total population in the biofilm. Corrosion rates at GFB and C were never very high, reaching a maximum of 1.0 and 0.7 mm/year at GFB and GFC respectively prior to nitrate treatment. Upon nitrate treatment the corrosion level dropped by more than 50%. This result corresponds well with the observations from a similar water injection treatment at Veslefrikk [10]. At Veslefrikk SRB numbers were reduced 20 000 fold and SRB activity 50 fold after 32 months of nitrate treatment and corresponding to the decrease in SRB, growth of nitrate reducing bacteria (NRB) was stimulated. Corrosion measurements on metal coupons showed a decrease in weight loss from 0.7 mm/year to 0.2 mm/year. The results from Gullfaks confirm that nitrate treatment could efficiently inhibit growth of SRB and control MIC.

Reservoir souring

In the early 1990s, the Gullfaks A platform experienced severe reservoir souring. Single wells had several thousand ppm H_2S in the produced gas, corresponding to app. 35 mg H_2S/l in the produced water. On the bases of these wells and lab work, a reservoir-souring model was developed [18]. Using the biofilm option in the model, a typical H_2S production profile as shown in figure 8, can be expected.

Although H_2S generation at the injector starts immediately after seawater is injected, the breakthrough of H_2S in the producers is delayed by several pore volumes (p.v.). This delay in H_2S breakthrough is caused by adsorption and equilibrium with rock and residual oil in the reservoir.

The reduction in H_2S production observed upon nitrate treatment of injection water corresponds well with the results obtained from laboratory experiments. Myhr et al. [7] showed that injection of 0.5 mM nitrate for 2.5-3.5 months led to complete inhibition of H_2S-production from an oil reservoir model column. As expected the observed effect of nitrate treatment is delayed in a field compared to a model system due to longer residence time for water.

Even more important is the fact that when stopping the H_2S generation, by using nitrate, part of the adsorbed H_2S will from equilibrium reasons, enter the water on its way to the producers, so it my take a long time to reach pre souring H_2S values.

It is also important to notice, that when measuring in the gas from test separator, only a part of the total H_2S in the well stream is accounted for. The size of the fraction depends on the pressure in the test separator and also the gas/oil/water ratios. When the pressure is lowered further through the separation train, more H_2S will be released into the gas phase. On the Gullfaks platforms, the H_2S concentration in the sales gas (before scavenging) is two to three times higher than the H_2S concentration estimated from test separator values.

CONCLUSIONS

- H_2S concentrations in produced water have decreased in most parts of the Gullfaks field after starting with nitrate injection.
- In the water injection system nitrate injection led to reduction in SRB numbers and activity and a concomitant enrichment of NRB.
- Corrosion measurements on metal coupons in the water injection system showed a decrease in weight loss of more than 50% after changing from biocide to nitrate treatment.

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REFERENCES

1. Jenneman, G.E. et al. 1986. Effect of nitrate on biogenic sulfide production. Appl. Environ. Microbiol. 51: 1205-1211.
2. MacInerney M.J. et al. 1992. Evolution of a microbial method to reduce hydrogen sulfide levels in a porous rock biofilm. J. Ind. Microbiol. 11:53-58.
3. Hitzman, D.O. and G.T. Sperl, 1994. A new microbial technique for enhanced oil recovery and sulfide prevention and reduction. Soc. Petrol. Eng. SPE 22752:171-179.
4. Subletti, K.L. et al. 1994. A field demonstration of sour-produced water remediation by microbial treatment. SPE Production and Facilities 9: 183-187.
5. Londry, K.L. and J.M. Suflita, 1999. Use of nitrate to control sulfide generation by sulfate-reducing bacteria associated with oily waste. J. Indust. Microbiol. Biotech. 22: 582-589.
6. Reinsel et al. 1996. Control of microbial souring by nitrate, nitrite or glutaraldehyde injection in a sandstone column. J. Ind. Microbiol. 17: 128-136.
7. Myhr, S., B-L.P. Lillebø, J. Beeder, E. Sunde, and T. Torsvik, 2002. Effect of nitrate injection on H_2S production and microbial community composition in an oil reservoir model system. Appl. Microbiol. Biotechnol. 58: 400-408.
8. Telang, A.J. et al. 1997. The effect of nitrate injection on the microbial community in an oil field as monitored by reverse genome probing. Appl. Environ. Microbiol. 63:1785.

9. Jenneman, G.E. et al. 1999. Sulfide removal in reservoir brine by indigenous bacteria. SPE Prod. & Facilities 14 (3): 219-225.
10. Thorstenson, T., G. Bødtker, B-L.P. Lillebø, T. Torsvik, E. Sunde and J. Beeder, 2002. Biocide replacement by nitrate in seawater injection systems. In: Corrosion NACExpo 2002 57th Annual Conference and Exposition. Denver, Colorado, USA.
11. Porter, K.G. and Y.S. Feig, 1980. The use of DAPI for identifying and counting aquatic microflora. Limnol. Oceanogr. 25: 943-948.
12. Nilsen, R.K., J. Beeder, T. Torsvik and T. Thorstenson, 1996. Distribution of thermophilic marine sulfate reducers in North Sea oil field waters and oil reservoirs. Appl. Environ. Microbiol. 62: 1793-1798.
13. Postgate, J.R. 1984. The sulfate-reducing bacteria, 2nd ed., Cambridge University Press, London, 1984.
14. Paulsen, J.E. 1986. Radiorespirometric measurement of sulfate reduction in *Desulfovibrio*. Thesis in General Microbiology. University of Bergen. Norway. (in Norwegian
15. Widdel, F. and N. Pfennig, 1984. Dissimilatory sulfate- and sulphur-reducing bacteria. In: Kieg, N.R., J.G. Holt, (eds.) Bergey's manual of systematic bacteriology, vol. 1. Williams & Wilkins. Baltimore, London, pp. 663-679.
16. Cord-Ruwish, R. 1985. A quick method for determination of dissolved and precipitated sulfides in cultures of sulfate-reducing bacteria. J. Micobiol. Meth. 4: 33-36.
17. API RP-38, 1975. Recommended practice for biological analysis of subsurface injection waters. American Petroleum Institute.
18. Sunde, E., T. Thorstenson, T. Torsvik, J.E. Vaag and M.S. Espedal, 1993. Field-Related Mathematical Model to Predict and Reduce Reservoir Souring. Paper SPE 25197, presented at the SPE International Symposium on Oilfield Chemistry in New Orleans, LA, USA. March 2-5.

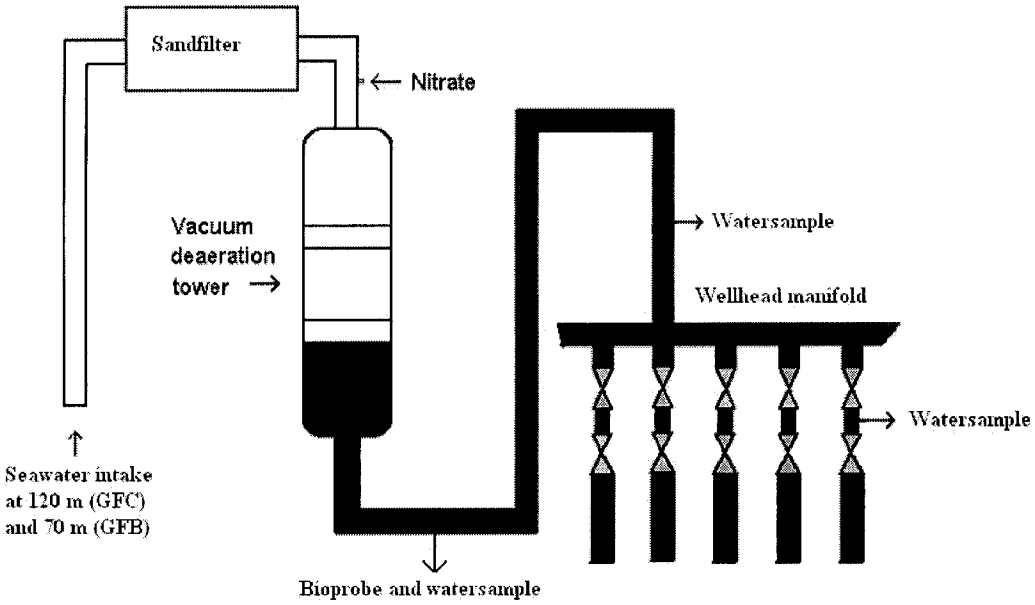

Figure 1. The water injection system at Gullfaks C. Water is abstracted at 70 meter at GFB and at 120 meter at GFC. Both nitrate and biocide (before Oct. 1999) were added before deaeration tower. The anaerobic part of the water injection system is marked in black. Biofilm and water samples were collected downstream of deaeration tower, and additional water samples at wellhead for selected individual wells.

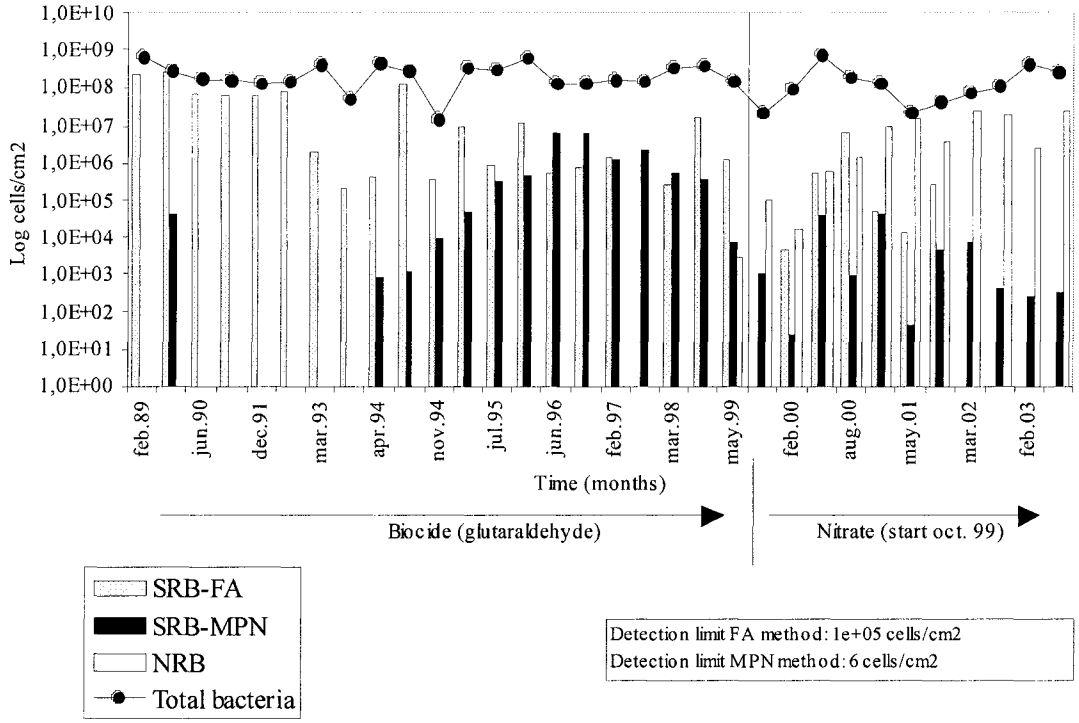

Figure 2. Number of bacteria in biofilm collected from biocupons mounted downstream of deaeration tower at GFB. Column marked NRB show cell number in MPN series targeting both facultatively and obligatory anaerobic NRB.

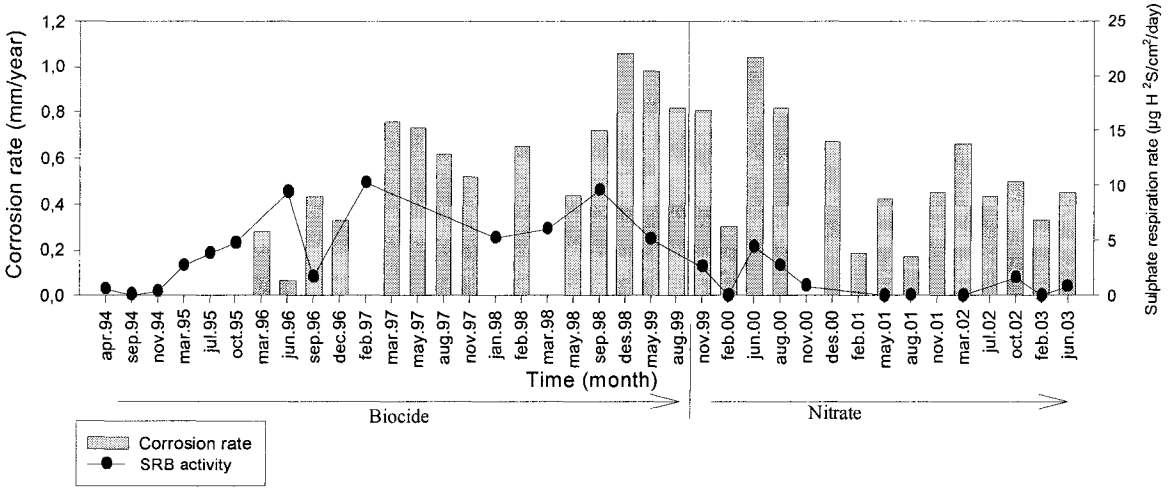

Figure 3. SRB activity and corrosion rate at GFB.

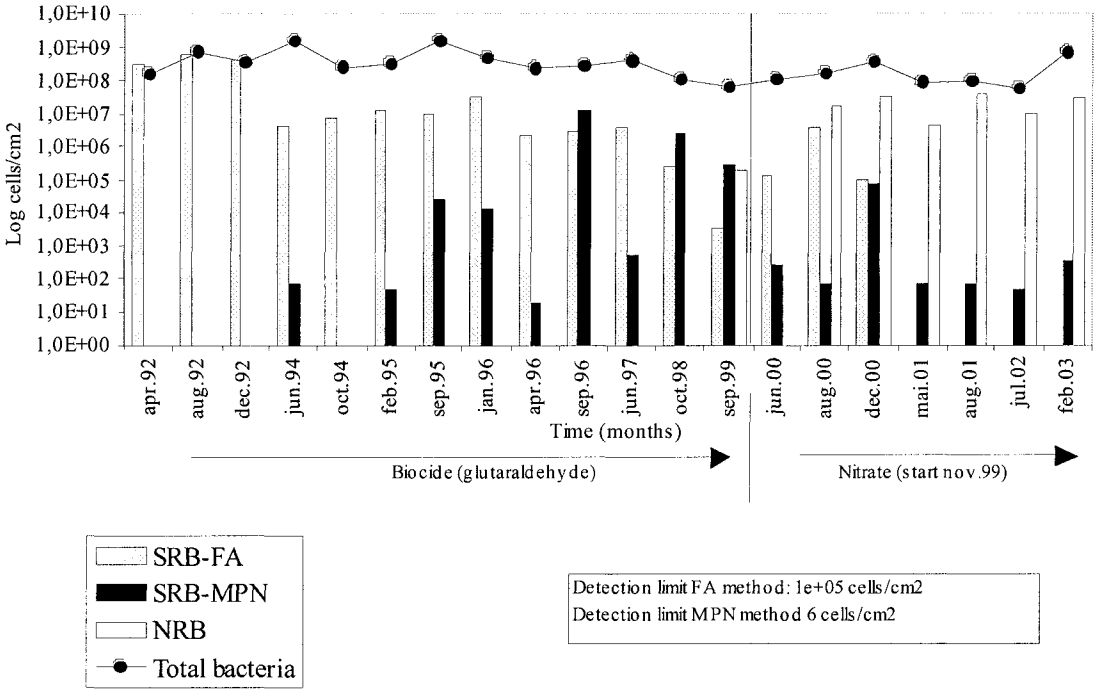

Figure 4. Number of bacteria in biofilm collected from biocupons mounted downstream of deaeration tower at GFC. Column marked NRB show cell number in MPN series targeting both facultatively and obligatory anaerobic NRB.

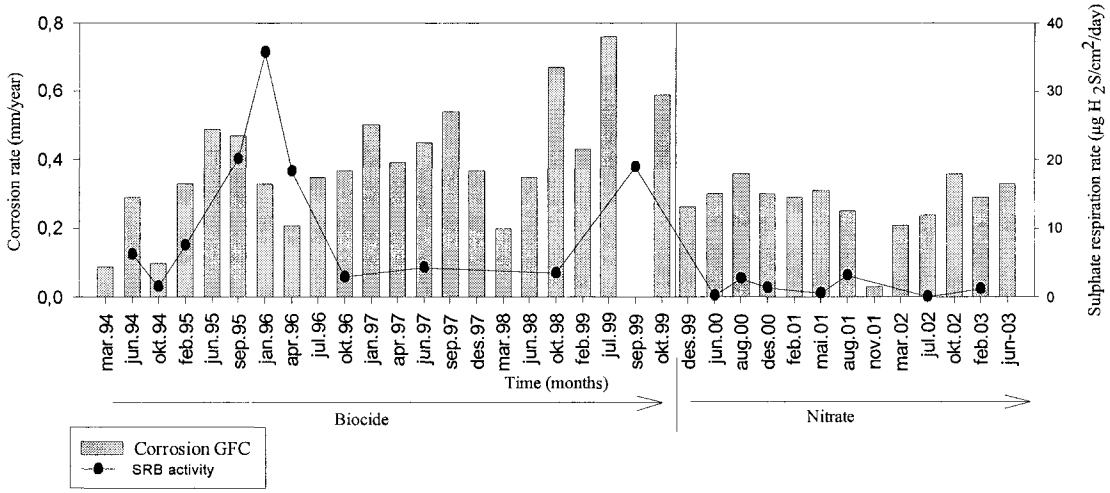

Figure 5. SRB activity and corrosion rate at GFC

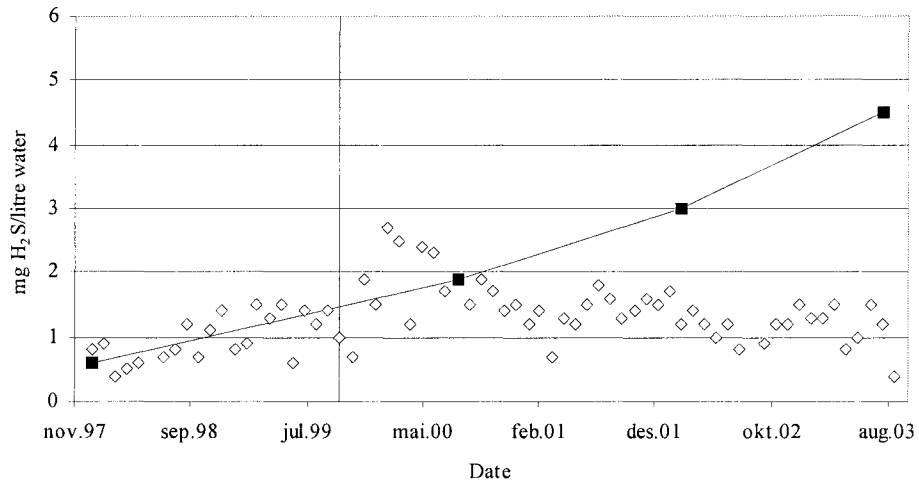

Figure 6 shows the mean H_2S concentration for 14 producers and theoretical H_2S development on GFB. ■ Theoretical H_2S development. ◊ Measured H_2S (mg) in produced water.

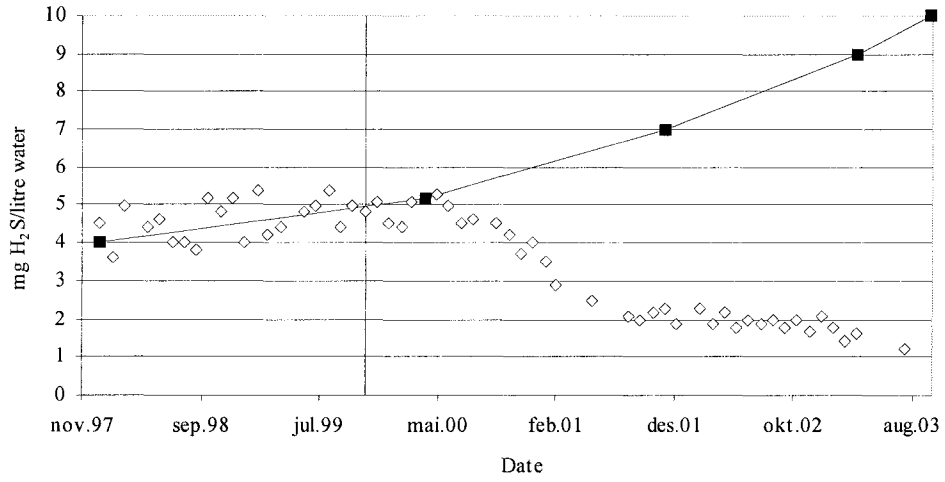

Figure 7 shows the mean H_2S concentration for 11 producers and theoretical H_2S development on GFC. ■ Theoretical H_2S development. ◊ Measured H_2S (mg) in produced water.

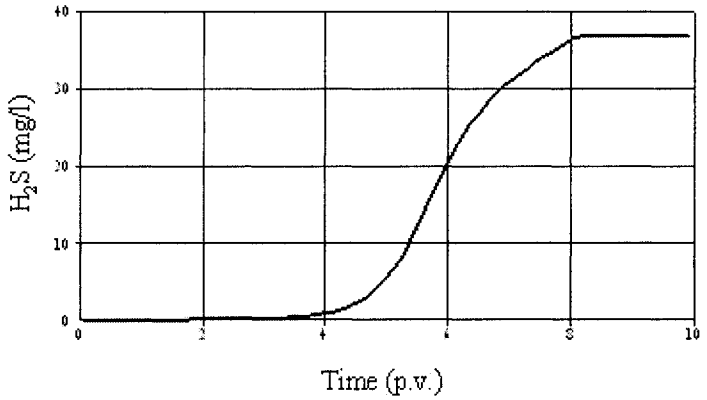

Figure 8: The amount of H_2S vs. dimensionless time (p.v.) for a production well with adsorption.