Use of nitrate in souring control of an oil field with low bottom hole temperature

Sasha Grigoryan, Adewale Lambo, Shiping Lin, Sabrina Cornish, Tom Jack, Rhonda Clark and Gerrit Voordouw

Petroleum Microbiology Research Group, Department of Biological Sciences, University of Calgary, Calgary, Alberta, Canada

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Topics to be covered:

1. Souring control by nitrate injection in low temperature fields
2. What is the electron donor for nitrate reduction in the Enermark field?
3. Can injected nitrate oxidize iron sulfide formed downhole?
4. Microbial community in low temperature oil field under nitrate injection
• The production of sulfide in oil reservoirs (reservoir souring) can be remediated by injection of nitrate.

• Nitrate injection activates 2 new metabolic groups:

Oil organics: Volatile fatty acids (VFA, a mixture of acetate, propionate and butyrate) used in tests
High-temperature oil fields:
sulfide production limited to injection well bore region because of:

- Cooling of injector well bore region by water injection
- High temperature (60-80 °C) elsewhere in reservoir
- Nutrient-richness by mixing of injection and reservoir waters

Sulfide production effectively remediated by nitrate because only a limited region of the field needs to be treated.

Gullfaks field
Sunde & Torsvik, 2005
Can fields at: lower depth (1000 m) and, therefore, lower downhole temperature be successfully treated with nitrate?
2 Field Sites in the WCSB

[Map showing locations of MHGC in 1996 and Coleville in 2007]
• In a water plant produced water and makeup water are mixed to give injection water
• The field is operated by produced water reinjection (PWRI)
2. Sourcing control by nitrate injection in onshore fields of low temperature

**New project MHGC field:**
- 850 m depth, 30 °C downhole temperature
- Heavy oil (16 degrees API gravity)
- 2000: start of water injection
- Injection water (IW) 3500 m³/day
- Oil production 1000 m³/day
- Produced water re-injection (PWRI)
- Makeup water 4 mM (400 ppm) sulfate
- IW (PW : make-up water = 3 : 1) is 1 mM sulfate
- PW 0 mM sulfate and on average 0.1 mM sulfide

**Evidence for Sourcing:**
- 2006: sulfide (gas phase) increasing
- Delay caused by sulfide scavenging of reservoir rock

**Souring could have been prevented by:**
- using make-up water with 0 sulfate
Gas phase sulfide concentrations determined by field personnel

Site 6;13-15

H2S (ppmv)

Date

11-29-06 1-18-07 3-9-07 4-28-07 6-17-07 8-6-07 9-25-07 11-14-07 1-3-08 2-22-08
MHGC long-term field-wide nitrate injection:

- Injected nitrate concentration 2.4 mM field-wide
  
  \[= 150 \, \text{ppm nitrate} = 1.2 \, \text{mM Ca(NO}_3\text{)}_2 = 200 \, \text{ppm calcium nitrate}\]

  Still going on today

- Weekly nitrate squeezes at 14-IW from January 2008 – April 2009

We monitor:

- 3 Makeup waters (MWs)
- 3 Water plants (WPs)
- 2 Injection wells (IWs)
- 15 production wells (PWs)

every 2-3 weeks
Sampling at Waterplant 1-WP

Waterplant

Nitrate tanks

Sampling Point
Make-up water 22-MW → Water plant 1-WP → Water plant 17-WP → Injection wells e.g. 14-IW → Injection wells e.g. 8-IW → Production wells 6-PW, 7-PW etc. → Nitrate

Production wells 2-PW, 3-PW etc. → Nitrate

Nitrate
$y = 0.9293x$
$R^2 = 0.9397$

Difference is caused by biocide dosing
Overall conclusions:

• Nitrate delivered effectively by the injection system to the field
• Losses during transport (due to wall growth of NRB) are 7-15%.
Producing wells – 15 monitored
Most are horizontal wells and receive water from more than one injection well

Sampling Point
Average sulfide concentration for 12 PWs

The first 5 weeks look great but why the recovery?
• Injection water contains 1 mM sulfate
• This is reduced to 1 mM sulfide by SRB present as a biofilm close to the injection wellbore
• Nitrate injection gives initially strong inhibition of sulfate reduction in this region
• However, because the field is low temperature bacteria can grow anywhere
• SRB re-grow as a biofilm deeper in the reservoir
• Sulfide concentrations recover to initial levels.

• Hence NRB and SRB grow in different adjacent zones.
• We refer to this as microbial stratification
• Can the stratification be broken by changing the continuous nitrate injection into a pulsing nitrate injection regime?
• Bioreactor studies suggest that this is so (see poster by Cameron Callbeck)
Nitrate Squeezes at 14-IW

- Weekly; 1000 L slug of 45% calcium nitrate injected directly into injection well 14-IW feeding producer 13-PW
Sulfide production ceased on breakthrough of nitrate/nitrite
Can a pulsing nitrate injection strategy also work field-wide?

High nitrate doses were injected for 1 week at the two main water plants.
This gave nitrate/nitrite breakthrough at 7-PW
Fig. 4

(A) 2-PW

(B) 2-PW

(C) 2-PW

(D) 3-PW

(E) 3-PW

(F) 3-PW

(G) 12-PW

(H) 12-PW

(I) 12-PW

Time (weeks)

C$_{\text{sulfide}}$ (mM)

Water (m$^3$/day)

Sulfide (mol/day)
Average concentration and total sulfide production for all PWs show:

• stabilization during pulsing nitrate injection

• pattern dominated by 2-PW
Conclusions:

• Nitrate (2 mM) dosed effectively through the field

• Field-wide sulfide decreased 70% in the first 5 weeks followed by recovery; a model explaining the recovery was presented

• Local increased nitrate dose from weeks 33-101 eliminated production of sulfide at one production well

• Application of field-wide higher doses from weeks 64-96 stabilized sulfide production

• We should concentrate on PWs that contribute most to total sulfide production
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Microbial community composition at 13-PW before and after nitrate breakthrough

**Methodology:**
- Isolate DNA directly from produced waters
- PCR amplify using bacterial or archaeal universal 16S primers
- Separate amplicons by DGGE
- Identify by sequencing

- Bacterial component showed increased NRB
- Archaeal (methanogen) component showed decreased diversity
13-PW: Bacteria

Before

- other 53%
- firm 22%
- d 33%
- e 7%

After

- other 14%
- firm 22%
- a 11%
- b 3%
- e 33%
- d 17%
13-PW: Archaea

Before

- Methanocalculus: 73%
- Methanolobus: 10%
- Methanoseta: 7%

After

- Methanocalculus: 80%
- Methanolobus: 20%
Thanks to “the team” (on first sampling trip to MHGC field)
Tom Jack
Adjunct Professor

Adewale Lambo
PDF

Sasha Grigoryan
PDF

Shiping Lin
Technician

Johanna Voordouw
Technician

Sabrina Cornish
Graduate Student

Rhonda Clark
Project Manager

MHGC oil field study:

Kirk Miner
Baker Petrolite

Ryan Ertmoed
Baker Petrolite

Pat Stadnicki
Enerplus

Bill Clay
Enerplus
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