Reservoir Souring:
It is all about risk mitigation

Shell Research
PTI/WD

Cor Kuijvenhoven

Content

- What’s new in reservoir souring?
  - Unconventional gas plays
- Reservoir souring risk assessment
- How to model?
- Can we mitigate without risks?
- How to us the new monitoring tools?
- Take home message

Origin of H2S in produced fluids

- H_2S present from day 1 (take into account initial scavenging by Carbon Steel)
- H_2S generated as result of heat/rock interaction (steam injection; can be dramatic).
- Leaking from other reservoirs.
- Fluid dynamics

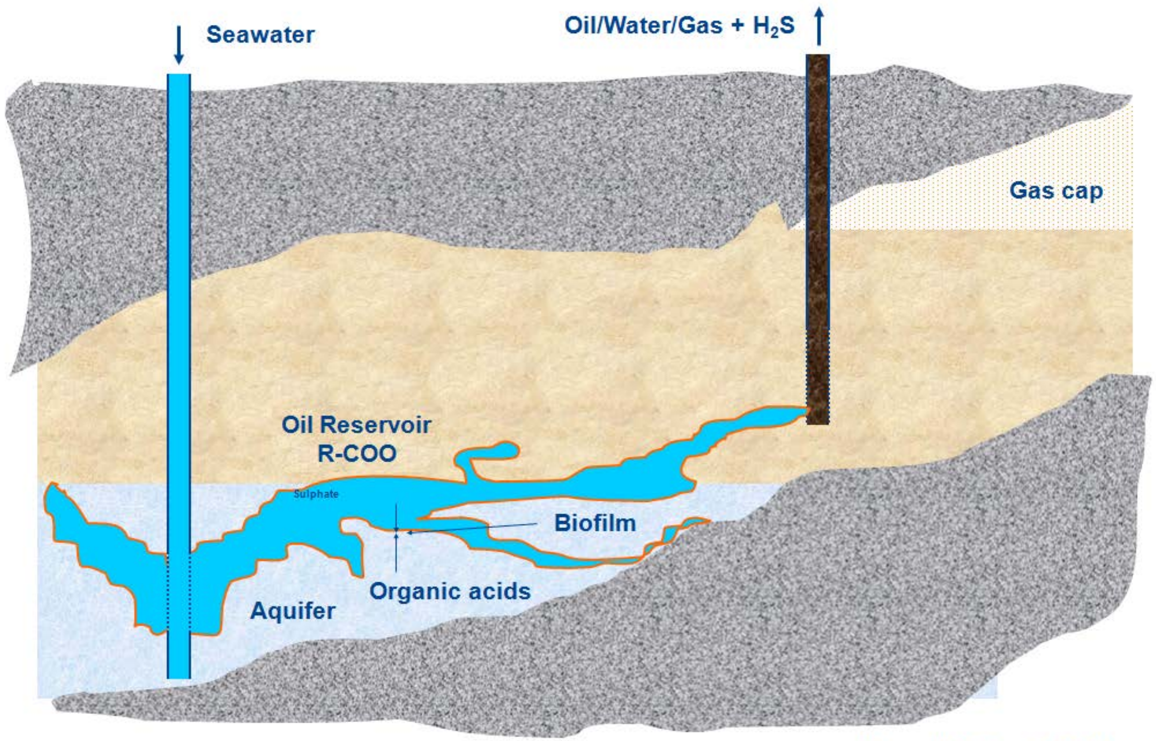
Not related to bacteria & no treatment of bacteria required

- Biogenic reservoir souring

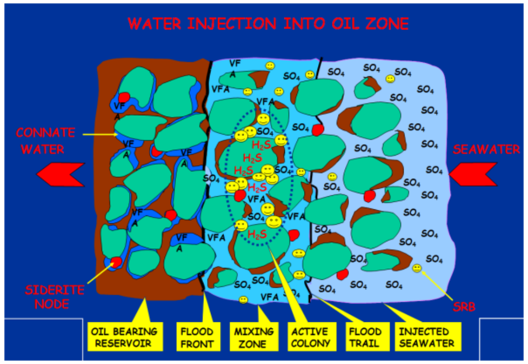
Concentration (ppm)	Time	Effect
0.2	Instant	Odour detectable
10	8 hours	Long term exposure limit
15	15 minutes	Short term exposure limit
20	1 hour	Eye irritation (reversible)
50	1 hour	Nose/throat irritation
100	3 minutes	Sense of smell lost
200	30 minutes	Pulmonary oedema (irreversible)
500+	Instant	Unconciousness - death

What is new in reservoir souring?

- A sweet reservoir (no H_2S production) turning sour (H_2S production) due to uncontrolled activity micro-organisms (SRBs & SRAs) $\Rightarrow$ reaction sulfate to sulfide.

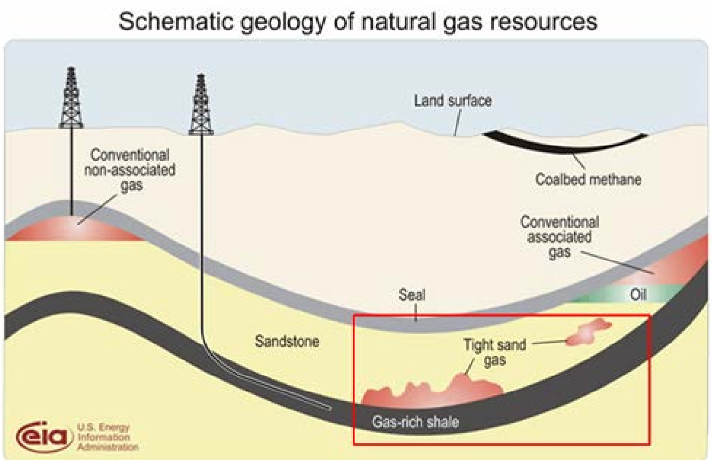


Maxwell & Spark, 2005



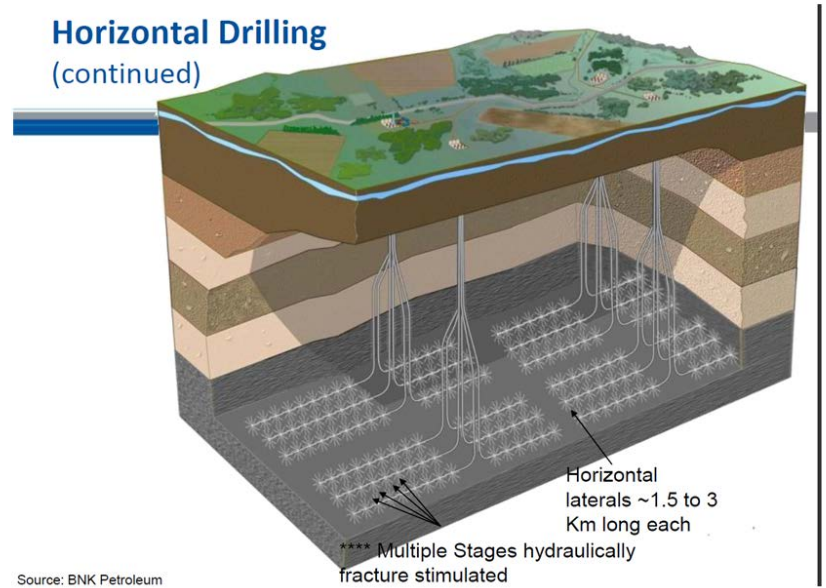
- Continuous injection
- Injection water temp

Reservoir souring risk in unconventional gas field



Source: Wikipedia

Unconventional gas reservoirs



Source: BNK Petroleum

- Bacteria development is one of the main concerns in unconventional gas field. Biocides are continuously used in frac fluids.
  - Bacteria in frac fluid → develop frac fluid viscosity
  - Bacteria in the reservoir → souring and plugging
  - Bacteria at surface → souring and water treatment

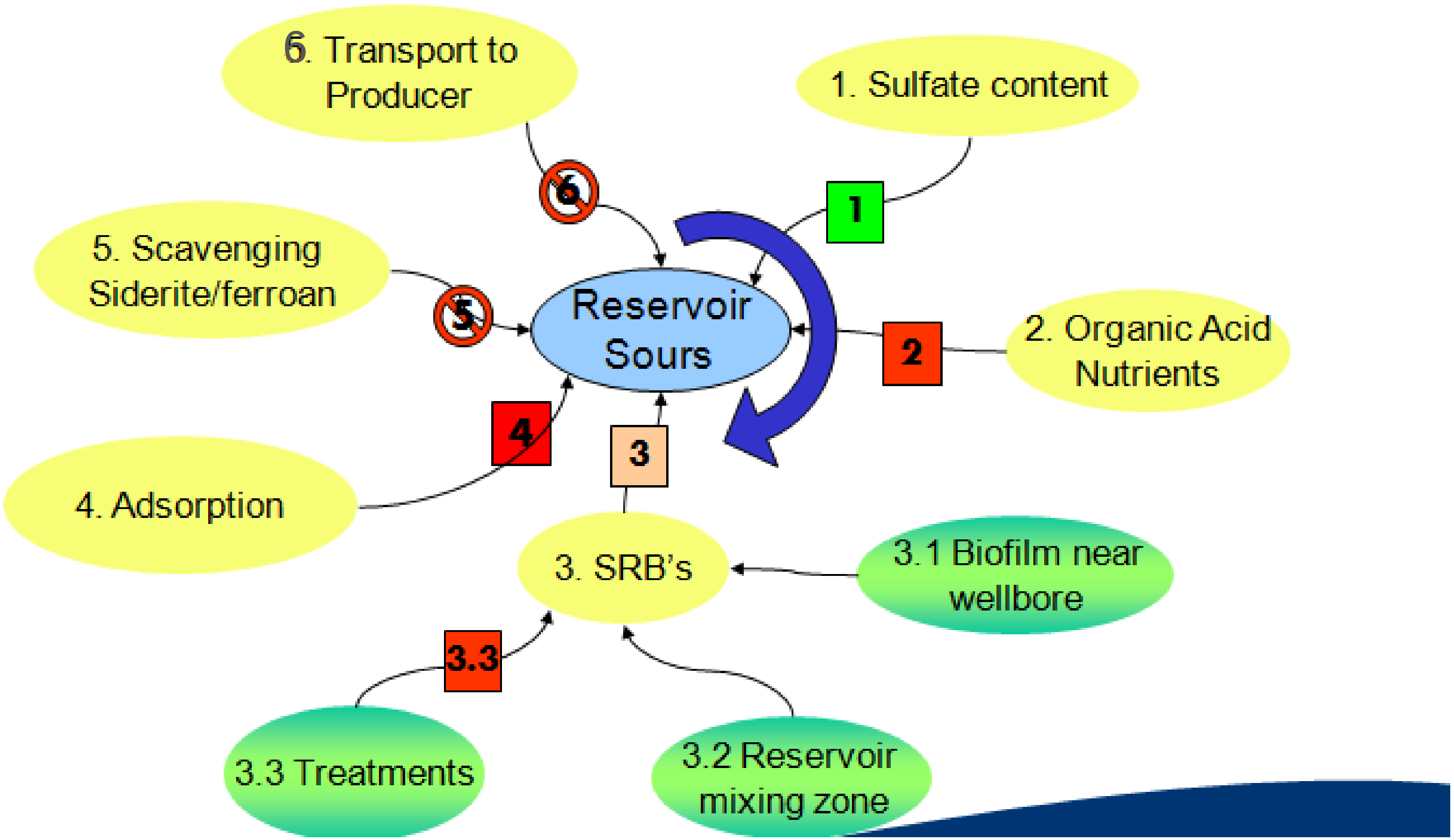
Souring in water floods - status

- Souring after seawater injection in ~70% of North Sea fields
  - Seawater injection starting decades ago.
- Souring more severe when seawater injection is followed by PWRI ?
  - Acetate, propionate etc present in formation water levels above 50 mg/l up to above 1000 mg/l
- Difficult to predict souring due to PWRI and to take remedial action
  - Short term tests will not reveal long term effects.
- Long term experiences PWRI still to be gained (schmoo)
  - Long term effects to be demonstrated, incl. effectiveness of nitrate injection
- Are we fully aware of the risks?
  - Deepwater is having low H_2S tolerance
  - EOR applications

Full risk assessment Reservoir souring

Typically:

$$\text{Acetate} + SO_4^{-2} + 3H^+ \longrightarrow 2CO_2 + H_2S + 2H_2O$$



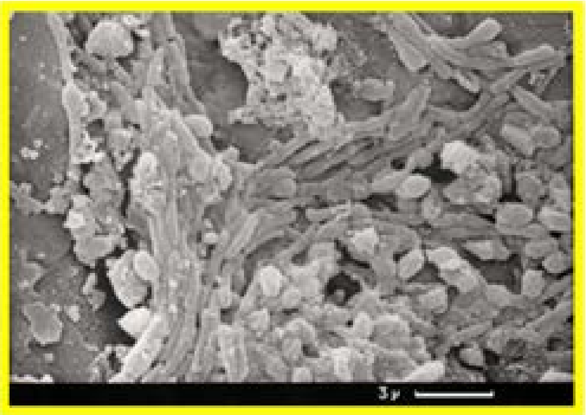
SRB and SRA Physiology

- All SRB are obligate anaerobes
  - SRB grow only in oxygen-free environment
  - SRB can withstand long periods of O_2 exposure but eventually will die
  - Biofilm provide a locally anaerobic environment
- SRB utilize sulfate as electron donor
  - Dissimilatory (not assimilated into cell material)
- Sulfide is toxic to SRB
  - Iron ties-up/detoxifies sulfide
  - High redox potential shuts down SRB

SRB biofilms; what required to produce H2S

- 1 cell → $1*10^6$ cells in 20 days; $1*10^8$ in 27 days
- Active biofilm → $1*10^8$ cells/cm^2
- H_2S production → $1*10^{-13}$ moles H_2S/cell/day

Consider a slab (e.g. near-wellbore slab):
2 m^3 (70 ft^3) of reservoir sand stone →
11,500 m^2 surface area in slab
$1x10^{16}$ cells in slab
$1x10^3$ Moles of H2S produced / day →
40 kg of H2S produced / day

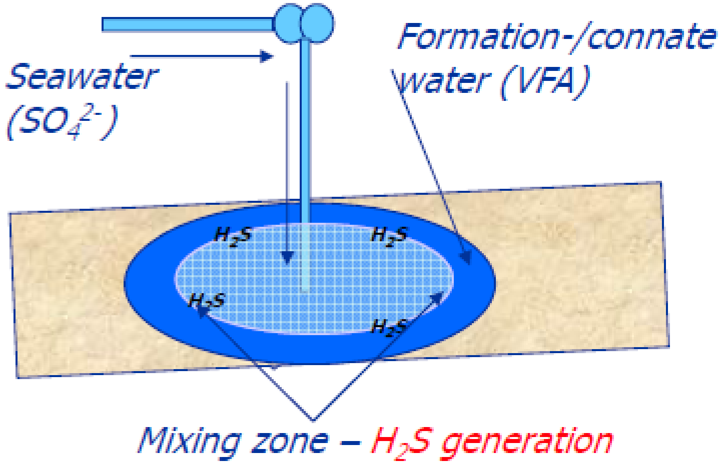


Biogenic reservoir souring modeling

- Generation in waterphase – requirements?
  - Anaerobic environment, no oxygen
  - Sulphate, below 10 mg/l no activity
  - Metabolizable Carbon Energy source (Volatile Fatty Acid like acetate & hydrocarbons)
  - Nitrogen, Phosphorous, trace elements
- Partitioning between oil/water and gasphase – once formed it will travel through reservoir ending in producers
- Mitigation methods – what to do to combat?

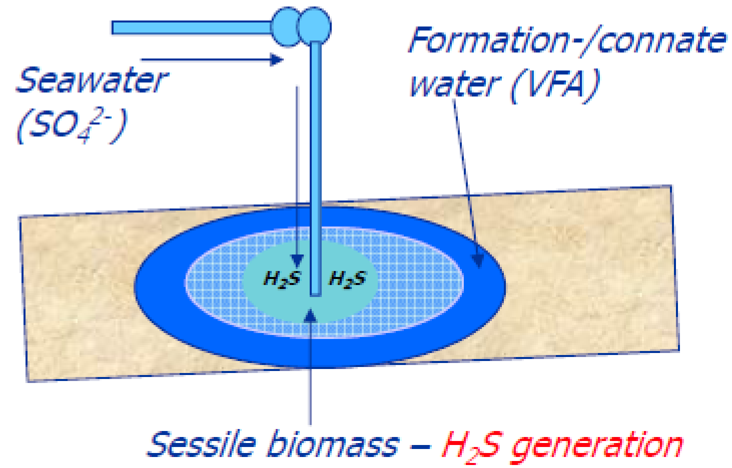
Biogenic reservoir souring models

Mixing Zone



- High SO_4/VFA availability
- Mobility sessile SRB
- High temp/TDS

Biofilm



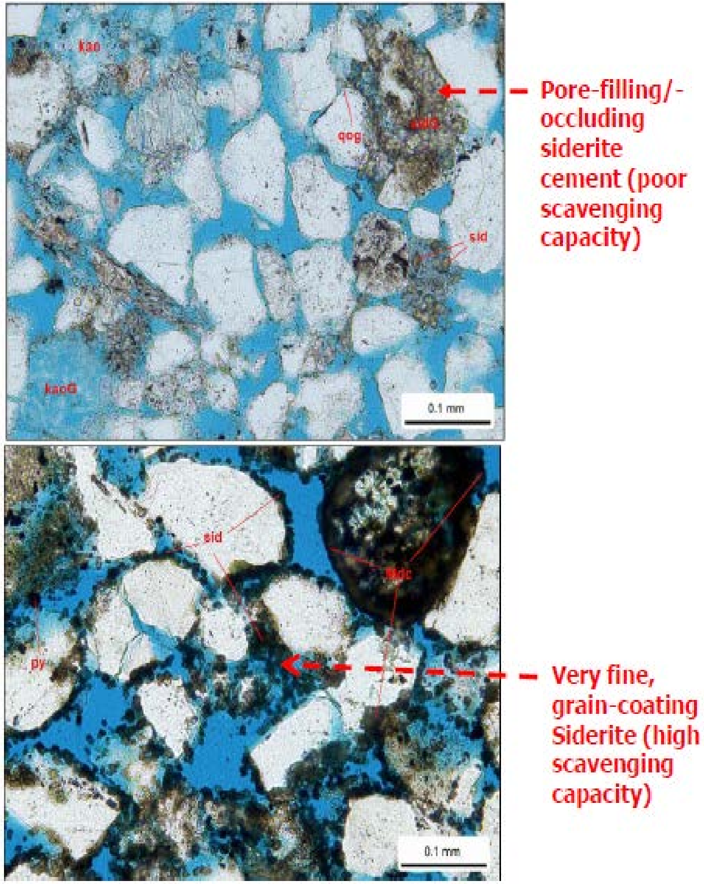
- Low temp/TDS/stationary sessile SRB
- Nutrient availability (C, P, N)

Viewpoint reservoir engineer

Viewpoint Petroleum Microbiologist

Factors controlling H_2S production

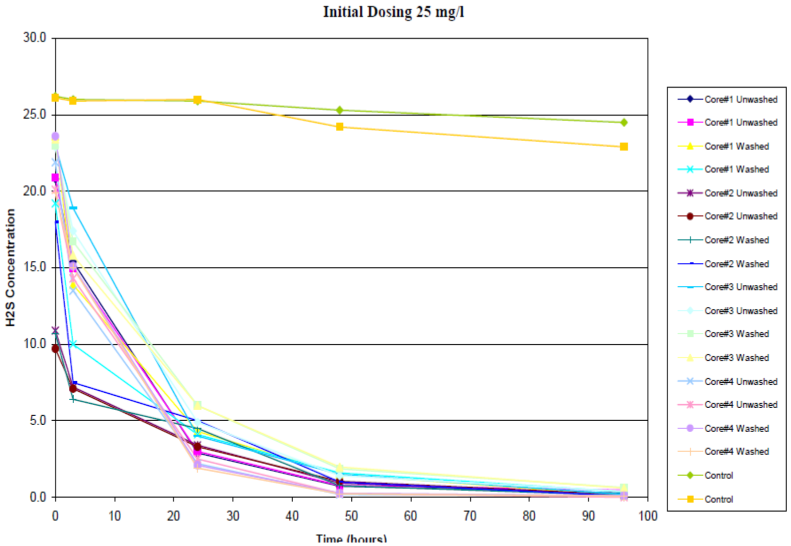
- Injection location:
  - Aquifer (pressure maintenance) – Low Risl
  - Oil leg (sweep) – High risk
- Extent biogenic souring/H_2S generation
- H_2S Partitioning over oil-, water-and gas phase – impacts H_2S transfer to producers (e.g. gas cap = H_2S sink)
- Presence of scavenging minerals:
  - Siderite ($FeCO_3$) + H_2S ➔ FeS
  - [Fe-containing] clay
  - Ad-/desorption ?



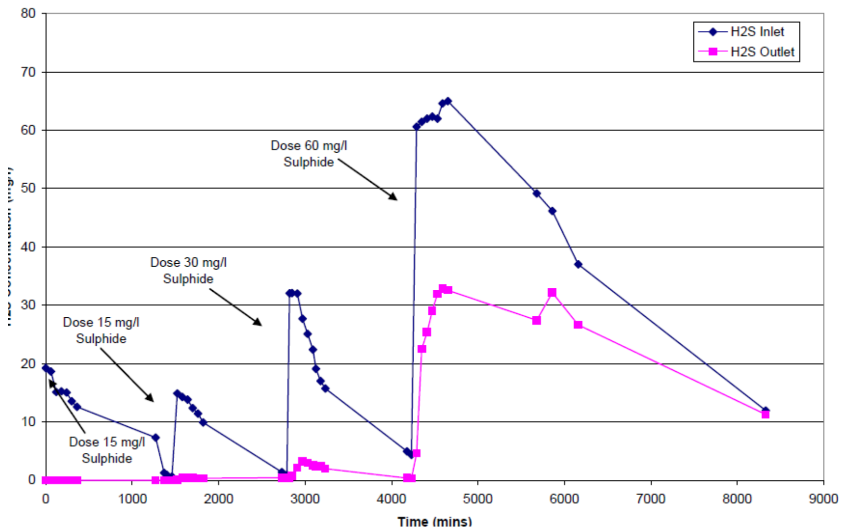
But what the risk to rely on scavenging capacity

- Scavenging capacity measurement not conclusive

Static



Dynamic (coreflow)



5000 mg/kg/day

320 mg/kg/day

In modeling, these levels are not making sense (none of the reservoirs will ever sour)

Reservoir Souring Mitigation (1) biocide and SRU

1. Biocide [THPS] treatment injection water
   - Batch-/continuous treatment
   - Iron chelating agent (reacts with FeS)
   - Ad-/desorption on rock?
   - Reacts with oxygen scavenger (ABS)

   Mainly applied to control activity at surface NOT in the reservoir

2. Sulphate removal from seawater (method to mitigate severe sulphate scaling)

   Sulphate Removal Unit (SRU) – Ursa Field: Nano-filtration of seawater to <40 mg/l SO_4 slow & significantly reduced H_2S generation

Reservoir Souring Mitigation (2) Nitrate

- Nitrate (NO_3) mitigation typical dosage 50 – 100 mg/l; addition required stociometrically
- Mechanism:
  - Increase redox potential due to NO_3 addition
  - Inhibitory nitrite production [NO_3 ➔ NO_2; literature 2.5-230 mg/l]
  - Carbon consumption by prolific Nitrate-Utilising Bacteria [NUB] ->

  Most likely mechanism but what about PWRI at high VFA

1. **Denitrifying Bacteria (DNB; $NO_3^-/NO_2^- \rightarrow N_2/NH_4^+$)**
2. **Nitrate Reducing Bacteria (NRB; $NO_3^- \rightarrow NO_2^-$)**
3. **Nitrate Reducing Sulphide Oxidizing Bacteria (NRSOB; $NO_3^- \rightarrow N_2/NH_4^+$ in presence of S^{2-})**

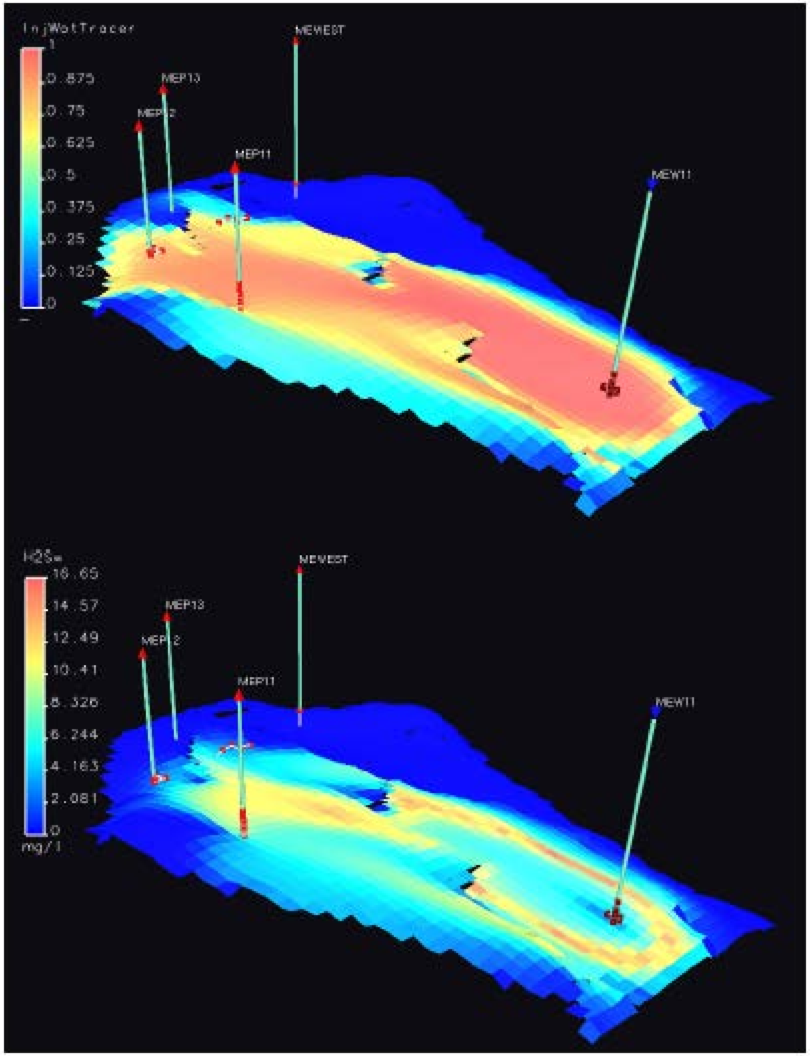
Reservoir Souring Mitigation (3) Nitrate

Understanding is still developing, remaining risks?

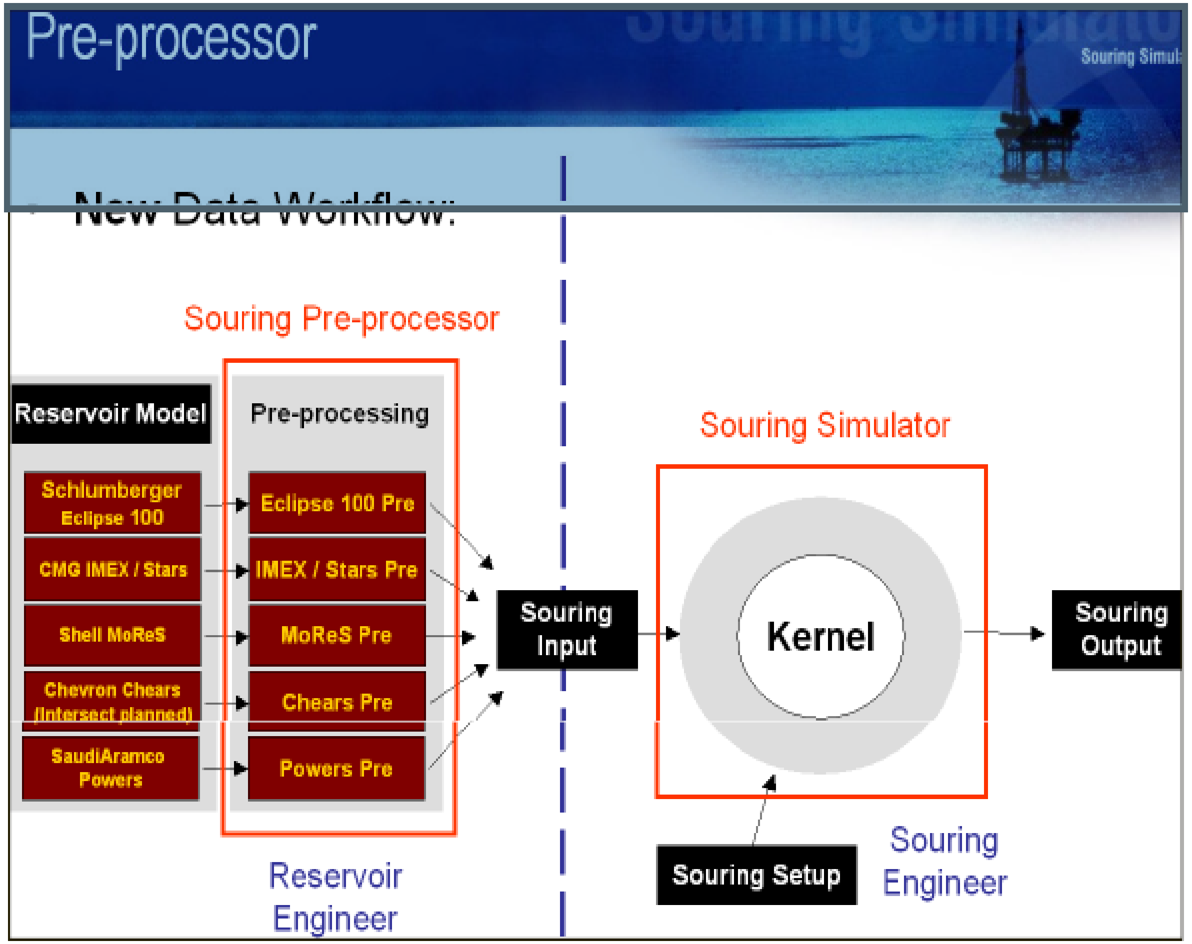
- SRBs switch from NO_3 metabolism back to sulfate upon NO_3 depletion
- NUB activity as function of temperature
  - 30 oC: DNB with $NO_3 \rightarrow N_2/NH_4$
  - 45oC: NRB with $NO_3 \rightarrow NO_2$ followed by DNB with $NO_2 \rightarrow N_2/NH_4$)
- As a result, difficult to establish C/NO_3 consumption ratios which determine mitigation efficiency
- NO_3 treatment difficult to model!!!!!

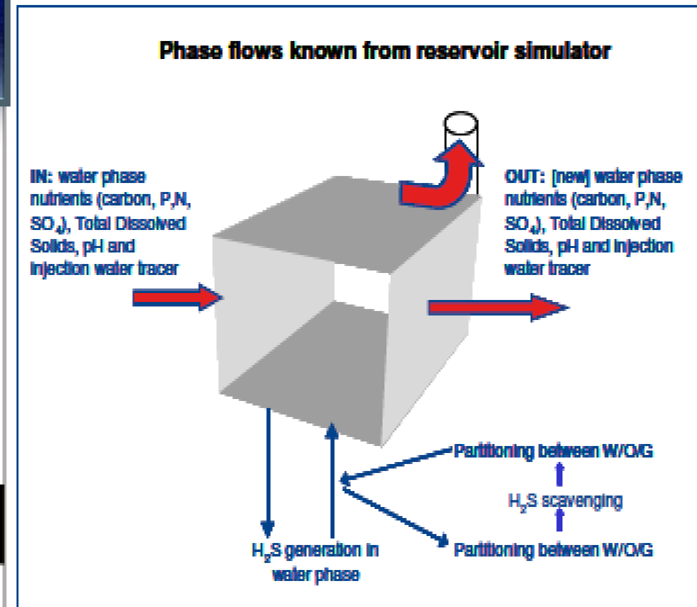
Reservoir Souring modeling tool

- SourSim®RL 3D reservoir model
- Joint Industry Project on development of reservoir souring prediction software
- Improvement on souring/H_2S prediction using a reservoir souring model.
- Main application assess the risk of the various options available. Requirement to have good reservoir model available (history matched).



Pre-processing reservoir simulation & model

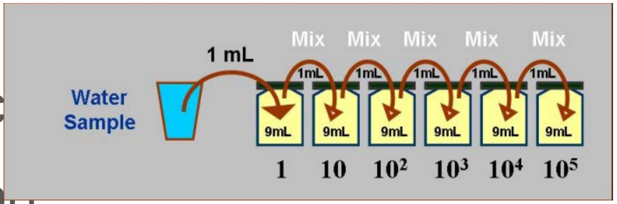




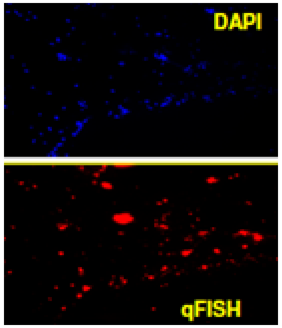
- Model is as good as the reservoir model

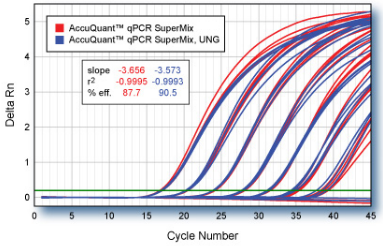
Microbial monitoring techniques

- Enumeration by Serial Dilution/MPN
  – typically cultures 1 - 5% of all planktonic bacteria present Easy, but time consuming



- Molecular Microbiology Methods (MMM)
  - qFISH: staining RNA; counts specific groups of living microbes
  - DAPI: staining DNA; counts living/inactive /dead cells
  - qPCR: simultaneously amplify/quantify targeted DNA; counts living/inactive/dead/decaying cells





- MMM has many advantages and are giving information about actual bacteria present BUT how to apply? What is risk to use MPN? Clear role for the experts (you!!)

Take home message

- Assess reservoir souring at the start of every water flood process
- If mitigation is required
  - Treatment at the beginning
  - Is fall back option required?
  - Be conservative
  - What is reaction if no H_2S is seen
    - No souring (risk overestimated)
    - Mitigation successful
- Souring is long term problem
  - What is done (or not done) now, has an effect later in field life
- Apply the right bacteria monitoring tools