H₂S Management

Ole Avaldsnes | Schlumberger Production Technologies

20th February, 2019
Agenda

- Introduction
  - Schlumberger Production Technologies North Dakota

- H₂S Origin
  - Thermogenic vs. biogenic

- H₂S Management Options
  - Fixed bed systems
  - Liquid scavengers and chemistries
Local Presence

Office & Lab Location

- Typical field analysis:
  - pH
  - Bicarbonate alkalinity
  - Dissolved CO₂ and H₂S
  - Gas analysis specifically for H₂S

- Inductively Coupled Plasma (ICP) for complete water analysis

- Other tests conducted in the Williston facility:

<table>
<thead>
<tr>
<th>Water</th>
<th>Oil</th>
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<tbody>
<tr>
<td></td>
<td>TDS</td>
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<td>Chlorides</td>
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<td>Conductivity</td>
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<td>Solids Identification</td>
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<td>Complete Water Analysis</td>
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<td></td>
<td>Inhibitor Residuals (corrosion)</td>
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</tbody>
</table>
H$_2$S

Origin

- Thermal decomposition of sulfides in kerogen and/or oil - Baltic Sea Shales
- Thermochemical reduction of sulfate (TRS) to H$_2$S - Sichuan Basin
- Microbial metabolic sulphidogenesis - Danish Basin/Central Graben

Injector well
- Elector donor (C source) and acceptor (SO$_4$$^{2-}$, S$_2$O$_3$$^{2-}$, etc.)
- Trace elements + N + P + vitamins supply
- H$_2$S production in the near wellbore zone

Reservoir minerals adsorb limited portion of H$_2$S

H$_2$S is transported with injection fluid to producer

H$_2$S is produced in zones closer to producer

Sulphate Reducing Bacteria (SRB)
Sulphate Reducing Archaea (SRA)
H₂S in Bakken
Origin – Thermogenic vs. Bacteria

The following was determined in a study¹:
1. The upper known temperature limit of microbial life is 122 °C (252 °F). Seven of the eight wells studied equal or exceed this limit

2. Isotopic analysis of sulfur isolated from H₂S evaluated to be thermogenic in origin

3. All eight wells yielded no measurable or negligible amounts of DNA

4. Total dissolved solids (TDS) were relatively high (8–9 fold the salinity of seawater), which can hinder microbial growth

5. Modeling studies indicate that production of H₂S from anhydrite is thermodynamically feasible at 110 – 140 °C (230 – 284 °F)

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H$_2$S Management Strategy

H$_2$S generated by Bacteria & Prevention Solutions

- **H$_2$S origin considerations for management strategy**
  - If H$_2$S is not by bacteria then biocide treatment can be debated…
  - Risk matrix based on temperature, salinity, and bacteria

**Microbial InstaCheck Bacteria Monitoring Service**

- Variability in oil and gas water makes bacteria testing difficult
  - Chemical, biological, solids
- Standard bacteria tests not designed for oil and gas applications
  - Time / speed of analysis, Sample preservation

<table>
<thead>
<tr>
<th>Technique</th>
<th>Processing Time</th>
<th>Cost</th>
<th>Margin of Error</th>
<th>Portability</th>
<th>Skill Required</th>
<th>Live/Dead Differentiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microbial InstaCheck</td>
<td>30 minutes</td>
<td>Low</td>
<td>±5%</td>
<td>Yes</td>
<td>Low</td>
<td>Yes</td>
</tr>
<tr>
<td>Serial Dilution</td>
<td>7-28 days</td>
<td>High</td>
<td>±100%</td>
<td>Yes/No</td>
<td>High</td>
<td>No</td>
</tr>
<tr>
<td>ATP</td>
<td>30 minutes</td>
<td>Low</td>
<td>±100%</td>
<td>Yes</td>
<td>Low</td>
<td>No</td>
</tr>
</tbody>
</table>
H₂S Management Strategy

Removal Solutions

- Chemical reactions that convert it to a form that is more easy to handle or more acceptable to discharge

- The decision on which removal solution to implement will normally be taken at the field design stage.
  - Expected H₂S amount produced?
  - Changes during field lifetime?
  - High CAPEX vs. high OPEX.

- Regenerative
  - Construction of special processing equipment

- Non-regenerative
  - Direct injection scavengers for treating oil/water/gas streams by continuous application
  - Can also be used in contactor towers / bubble towers.
Purification Solutions

Fixed Bed Reactors

- Gas passed through a bed containing an engineered adsorbent, and \( \text{H}_2\text{S} \) is selectively removed to < 0.1 ppmv
  - SULFATREAT - iron oxide
  - SELECT - mixed metal oxides
- Environmentally safe, both new and used
- It is safe to handle, non-pyrophoric
- Simple technology, and requires minimal operator attention
- Used at > 1000 locations worldwide
**H₂S Management Strategy**

Removal Solutions

- **Non-regenerative liquid scavengers**
  - Direct injection scavengers or contactor towers / bubble towers.
  - Consider phase distribution of H₂S vs. chemical.
  - Consider target concentration for each phase and the best chemical to scavenge that phase.

- **Consider application variables / system design**
  - Surface area of aerosol (atomizer)
  - Gas flow rate, which affects mixing
  - Retention time to achieve optimum reaction time
  - Pressure, which affects the H₂S partial pressure
  - Temperature
  - Etc.
Amines and Reaction Products

Liquid Scavenger

- Most common H₂S scavenger used in the industry.
- Typically applied in a wet gas stream or in a bubble tower.

Pros:
- Cheap
- Fast scavenging kinetics
- Main reaction products are water soluble

Cons:
- Alkaline → can increase carbonate scaling risk.
- Decompose at 120 – 150 °C (250 – 300 °F), can form corrosive products.
- Low scavenging capacity

Investigation of the Chemistry of Liquid H₂S Scavengers
J. B., Buhaug
Metal Carboxylates and Chelates

Liquid Scavenger

- Water- and oil-soluble high-valence metal chelates
- Drilling fluids and production applications.

- A typical product is zinc carboxylate made from a long-chain fatty acid.

- Pros:
  - Oil soluble
  - Fast scavenging kinetics
  - Reaction products has no environmental impact

- Cons:
  - Forms salt precipitations.

\[
\text{Zn(OOCR)}_2 + \text{H}_2\text{S} = \text{ZnS} + 2\text{HOOCR}
\]
Aldehydes
Liquid Scavenger

- **Pros:**
  - Typically greater capacity (H₂S uptake) than triazines.
  - Additional biocidal properties
  - Do not raise the pH which can cause carbonate scaling and exacerbate emulsion tendencies (multiphase application suitable).
  - Typically no nitrogen present that can damage refinery catalysts.

- **Cons:**
  - Typically slower reaction kinetics compared to triazines – residence time should be considered.
  - Reaction products with H₂S can be poorly water soluble
  - Can be hazardous
  - Can be corrosive
HR-2746
Patented Aldehyde Releaser

- Main advantages:
  - Easy to handle
  - Stoichiometric reaction ratio much lower than triazines, and also other chemistries in used in multiphase systems
  - Does not contribute to increased alkalinity (pH) and downstream scale issues
  - Compatible with a range of other chemistries, do not impact performance of SI and CI chemicals applied
  - Compatible with a wide range of materials, both metallic and non-metallic
  - Contributes to hydrate inhibition
  - TSCA approval last year – available in the U.S.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>l/kg H₂S</th>
<th>gal/lbs H₂S</th>
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</thead>
<tbody>
<tr>
<td>HR-2746</td>
<td>1.5</td>
<td>0.18</td>
</tr>
<tr>
<td>Triazine (~ 50 - 70%)</td>
<td>4.5 - 6</td>
<td>0.54 - 0.72</td>
</tr>
<tr>
<td>Glyoxal (~40%)</td>
<td>5.1</td>
<td>0.61</td>
</tr>
<tr>
<td>Acrolein (~90%)</td>
<td>2.2</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Stoichiometric reaction ratio

TSCA approval last year – available in the U.S.
HR-2746

Case Study

- Two wells chocked back due to high $\text{H}_2\text{S}$ that posed an integrity risk for the flexible risers from the subsea template.

- HR-2746 was qualified for subsea and field tested.
  - $> 90\%$ of $\text{H}_2\text{S}$ scavenged from Well A and B, restoring full production.
  - 130 ppm implemented for continuous injection.
  - No negative impact on the efficiency of the process (separation)
  - No increased particles or scale in the produced fluids
  - No detectable increase of sulfur in oil

- Chemistry also formulated in a combined $\text{H}_2\text{S}$ scavenger and corrosion inhibitor (KI-3138).

Multifunctional $\text{H}_2\text{S}$ Scavenger and Corrosion Inhibitor: Addressing Integrity Challenges and Production Output of the Mature Field. SPE-190911-MS
Summary

H₂S Management

1. Consider source of H₂S when selecting a management / treatment strategy

2. Consider amount of H₂S produced.
   a) Does it change over time?
   b) Direct injection vs. fixed bed systems

3. For liquid scavengers consider the phase distribution of the H₂S and consider the solubility of the scavenger chemical.

4. Consider the pros and cons with the various H₂S scavenger chemicals
   a) Cost vs. performance
   b) System compatibility
   c) Reaction products
   d) QHSE
Thank You Very Much for Your Attention

Questions?

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