Solid sulfur deposition: Why, how and where

- Sulfur solvents: - Physical and chemical
  - Regeneration or once through?

Method for field application
# THE COMPOSITION OF RAW SOUR NATURAL GAS

## Major Components

<table>
<thead>
<tr>
<th>Lean Gas</th>
<th>Rich Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>Heavier hydrocarbons</td>
</tr>
<tr>
<td>Hydrogen Sulfide (H₂S)</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td></td>
</tr>
</tbody>
</table>

## Minor Components

<table>
<thead>
<tr>
<th>Lean Gas</th>
<th>Rich Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane and Propane</td>
<td>Waxes (C₂₀-C₅₀)</td>
</tr>
<tr>
<td>Condensed Water</td>
<td></td>
</tr>
<tr>
<td>Produced Water</td>
<td>Organosulfur Compounds</td>
</tr>
<tr>
<td>Elemental Sulfur (S₈)</td>
<td></td>
</tr>
<tr>
<td>Diamondoids [in some cases]</td>
<td></td>
</tr>
<tr>
<td>Depositable Salts [rarely significant]</td>
<td></td>
</tr>
</tbody>
</table>
Sources of H₂S in Oil and Gas

Sulfur combined in living precursor material (natural amino acids)

- Methionine
- Cysteine

Microbial Reduction of Sulfates (eg., CaSO₄)

\[
\text{sulfate (SO}_4^{2-}) \xrightarrow{\text{Bacteria (< 100°C)}} \text{H}_2\text{S} \quad \text{Oil} \quad \text{Gas}
\]

Thermochemical Sulfate Reduction (TSR)

\[
\text{CH}_4 + \text{CaSO}_4 \rightarrow \text{H}_2\text{S} + \text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]
ISOTOPIC EVIDENCE FOR TSR MECHANISM

Determination and comparison of $\delta^{34}S$ values for $H_2S$ in gas versus $SO_4^{2-}$ in local anhydrite layers.

$$\delta^{34}S = 1000 \left( \frac{^{34}S/^{32}S}{{^{34}S/^{32}S}_{\text{Standard}}} \right)_{\text{Sample}},$$

where the standard reference is troilite (FeS) found in the Canyon Diablo meteorite.

Briefly there is isotopic fractionation with MSR but not TSR. Stable isotope analysis of gases and solids have confirmed the TRS mechanism for sulfur and $H_2S$ formation


Also, both Carbon and Oxygen isotope analyses have been used to confirm TSR
A CLOSER LOOK AT TSR – ELEMENTAL SULFUR FORMATION

\[ \frac{3}{4} \cdot x \text{ H}^+ + \frac{3}{4} \cdot x \text{ CaSO}_4(s) \rightleftharpoons \frac{3}{4} \cdot x \text{ Ca}^{2+} + \frac{3}{4} \cdot x \text{ HSO}_4^- \]

Sulfate/Hydrogen Sulfide Reaction

\[ \frac{3}{4} \cdot x \text{ HSO}_4^- + \frac{9}{4} \cdot x \text{ H}_2\text{S} + \frac{3}{4} \cdot x \text{ H}^+ \rightleftharpoons 3x \text{ S}^0 + 3x \text{ H}_2\text{O} \]

Oxidation of Hydrocarbon by Elemental Sulfur

\[ 3x \text{ S}^0 + C_{x+1}\text{H}_{2x+4} + 2x \text{ H}_2\text{O} \rightarrow 3x \text{ H}_2\text{S} + x \text{ CO}_2 + \text{CH}_4 \]

\[ \frac{3}{4} \cdot x \text{ CO}_2 + \frac{3}{4} \cdot x \text{ H}_2\text{O} \rightarrow \frac{3}{4} \cdot x \text{ HCO}_3^- + \frac{3}{4} \cdot x \text{ H}^+ \]

\[ \frac{3}{4} \cdot x \text{ Ca}^{2+} + \frac{3}{4} \cdot x \text{ HCO}_3^- \rightarrow \frac{3}{4} \cdot x \text{ CaCO}_3(s) + \frac{3}{4} \cdot x \text{ H}^+ \]

Net Reaction

\[ \frac{3}{4} \cdot x \text{CaSO}_4(s) + C_{x+1}\text{H}_{2x+4} \rightarrow \frac{3}{4} \cdot x \text{H}_2\text{S} + \frac{1}{4} \cdot x \text{CO}_2 + \frac{1}{4} \cdot x \text{H}_2\text{O} + \frac{3}{4} \cdot x \text{CaCO}_3(s) + \text{CH}_4 \]
FACTORS THAT INFLUENCE FORMATION RATE OF ELEMENTAL SULFUR

\[ [S_8] = \frac{k_1 k_2 [H^+] [CaSO_4]^x [H_2S]^y}{k_3 [C_{2+}]^z} \]

TEMPERATURE – Sulfate reduction is to slow at low temperatures.

ANHYDRITE DISTRIBUTION/MORPHOLOGY/EXPOSURE

WATER – Sulfur formation can occur to a greater extent when liquid water is associated with hydrocarbon in the pore space.

\( H_2S \) – initially formed from earlier microbial reduction or thermal maturation of organo-sulfur species in hydrocarbon.

HYDROCARBON – Ultimate reductant – otherwise we end up with native sulfur deposit in limestone.

TIME – Onset of thermal maturation processes; rate is finite.

\( pH \)

RESERVOIR MINEROLOGY
T = 140°C

\[ P \approx 40 \text{ mPa} \]

- In this case, liquid \( S_8 \) is present in the reservoir
- \( S_{8(\text{vap})} \) is dissolved in the gas at reservoir conditions
PRECIPITATION OF LIQUID SULFUR IN THE RESERVOIR

Wellhead Saturation Solubility

\[ T = 36^\circ C \quad p = 10 \text{ MPa} \]
\[ [S_8]_{satn} = 0.0003 \text{ g Sm}^{-3} \]

Reservoir Saturation Solubility

\[ T = 120^\circ C \quad p = 38 \text{ MPa} \]
\[ [S_8]_{satn} = 1.83 \text{ g Sm}^{-3} \]
Wellhead Saturation Solubility
$T = 36^\circ C \quad p = 10 \text{ MPa}$
$[S_8]_{satn} = 0.0003 \text{ g Sm}^{-3}$

Reservoir Saturation Solubility
$T = 105^\circ C \quad p = 38 \text{ MPa}$
$[S_8]_{satn} = 1.25 \text{ g Sm}^{-3}$
PRECIPITATION OF SOLID SULFUR IN THE RESERVOIR

SOLID SULFUR: AN IMMOBILE PHASE THAT REDUCES PERMEABILITY
THE CHALLENGE OF SULFUR DEPOSITION IN SOUR GAS PRODUCTION

- Decreasing T and P results in \(S_8\) deposition throughout the gas gathering system
- Solid sulfur reduces gas flow and leads to line corrosion

\[
\begin{align*}
Fe + S_8 & \rightarrow FeS \\
& \text{1. Contact} \\
& \text{2. } H_2O(l)
\end{align*}
\]
SQUEEZE THROUGH PERFORATIONS
- for obstructed perforations and near wellbore damage

BATCH SOAK OF PRODUCTION TUBING WITH SUITABLE SOLVENT
- for well string blockage

ALTERNATING ACID/SOLVENT SOAKS
- for deposits of FeS/S₈

PERIODIC SOLVENT INJECTION INTO FLOWLINES
- for well streams reaching the saturation point en-route to the gas plant

CONTINUOUS SOLVENT INJECTION (REGENERATION ?)
- for sour gas wells with very high carried sulfur loadings
TYPICAL SULFUR SOLVENT UPTAKES AT $T \approx 20^\circ C$
HOW DO ORGANIC DISULFIDES WORK?

\[ \text{RSSR} + S_8 \xrightleftharpoons{\text{catalyst}} RSS_xSR \]

\[ R = \text{alkyl or aryl} \]

(DMDS) (DADS)

Chemical and physical solution of sulfur.
RELATIVE SULFUR UPTAKE PERFORMANCE OF DIALKYLDISULFIDES AS A FUNCTION OF ALKYL SUBSTITUENT

<table>
<thead>
<tr>
<th>RSSR</th>
<th>R =</th>
<th>24 hr. S$_8$-uptake (wt.%) @ 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure alkyldisulfide (experimental measurements)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl</td>
<td>CH$_3$</td>
<td>100</td>
</tr>
<tr>
<td>Diethyl</td>
<td>CH$_2$CH$_3$</td>
<td>70</td>
</tr>
<tr>
<td>Di-n-propyl</td>
<td>CH$_2$CH$_2$CH$_3$</td>
<td>18</td>
</tr>
<tr>
<td>Di-n-butyl</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>18</td>
</tr>
</tbody>
</table>

$^a$ ASRL Quarterly Bulletin V.XVIII, No.2-4, July 1981-March1982
Uptake measurements may depend on catalyst type and contact methodology.
Quoted values intended to be used for relative performance only.
SULFUR UPTAKE PROPERTIES OF ARYLDISULFIDES

TEMPERATURE DEPENDENCY FOR COMMERCIAL DIARYLDISULFIDES

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight % Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>43</td>
</tr>
<tr>
<td>80</td>
<td>100&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>90</td>
<td>150&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>100</td>
<td>&gt;400&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Measurements very susceptible to temperature change

COMPOSITIONAL DEPENDENCY

(uptake in mole%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>10 min</th>
<th>30 min</th>
<th>24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SSCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>108</td>
<td>137</td>
<td>214</td>
</tr>
<tr>
<td>&lt;span&gt;CH&lt;sub&gt;3&lt;/sub&gt;&lt;/span&gt;SSCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>113</td>
<td>139</td>
<td>122</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SSCCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>106</td>
<td>114</td>
<td>111</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;SSCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>85</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SSCCH&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;C</td>
<td>80</td>
<td>88</td>
<td>83</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data varied ± 5 mole %

POTENTIAL DIFFICULTIES OF LONG-TERM ORGANIC DISULFIDE USE

a) Stability of organic di-/polysulfides at elevated temperature

\[ \text{CH}_3\text{S}_x\text{CH}_3 \xrightarrow{100^\circ\text{C}} \text{CH}_3\text{SH} + \text{CS}_2 \]  
\[(x = 2, 3, 4, ...)\]  
[Clark & Oriakhi, Energy & Fuels, 1992]

b) Stability in sour gas atmospheres

\[ \text{RSSR} + \text{H}_2\text{S} \rightleftharpoons 2\text{RSH} + 1/8 \text{S}_8 \]  
organic disulfides  
mercaptans

- Equilibrium process, mercaptans favoured by high H\(_2\)S partial pressure.
- What happens to the 1/8 S\(_8\)? Elemental sulfur can be corrosive.
CORROSION BY ORGANIC DISULFIDES

- Prompted by reports of corrosion in wellstrings where DADS had been used as sulfur solvent.

**Variables:**
- Aryldisulfides (DADS)
- Alkyldisulfides (DMDS)
- Sulfur: 0 to 20 weight %
- Time: 7 days
- Steel: 1018 Carbon Steel & Other Steels

**CORROSION RATES IN THE PRESENCE OF DIARYLDISULFIDES**

<table>
<thead>
<tr>
<th>Sour Gas Pressure (psi)</th>
<th>Temperature (°C)</th>
<th>DADS</th>
<th>H₂O/NaCl</th>
<th>Added Sulfur</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4800 (30% H₂S)</td>
<td>140</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>14 - 18 - 1</td>
</tr>
<tr>
<td>4800 (30% H₂S)</td>
<td>140</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>421 - 3 - 4</td>
</tr>
<tr>
<td>4800 (30% H₂S)</td>
<td>140</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>361 - 5 - 3</td>
</tr>
<tr>
<td>4800 (0% H₂S)</td>
<td>140</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>6 - 1 - 0.2</td>
</tr>
</tbody>
</table>

**Conclusions**
- Relatively little corrosion when DADS not present; sour gas/brine corrodes gradually.
- Sour gas/brine/DADS is very corrosive.
- H₂S must be present to cause DADS to corrode.

\[
ArSSAr + H₂S \rightleftharpoons 2ArSH + \frac{1}{8} S₈
\]
PROPOSED MECHANISM FOR CORROSION BY DISULFIDE/H₂S SYSTEM

**LIQUID PHASE**

**METAL SURFACE**

Oxidation State

| S²⁻ | → | S⁰ | → | 2e | → | S²⁻ |
| Fe⁰ |   | Fe²⁺ + 2e |   |     |   | Fe²⁺ |
Aromatic gas oils are preferred because of stability and uptake:

- Catalytic cracker
- Coker gas oil

These gas oils have some chemical reactivity:

[simplified example]

\[
2 R \text{CH} = \text{CH}_2 + 2 H_2S \rightarrow 2 R \text{CH}_2 \text{CH}_2 \text{SH} \\
\downarrow
\]

\[
R \text{CH}_2 \text{CH}_2 S-S-S- \text{CH}_2 \text{CH}_2 R + H_2S
\]

Formation of polysulfides increases uptake of sulfur by chemical mechanism.
Conclusion: Addition of styrene or other olefins can enhance sulfur uptake capacity.
Cracked gas oil → "Thermal treatment" → CGO (enhanced olefin content)

Refinery product

R CH₂ CH₃ → R CH = CH₂

S₈, H₂S, catalyst

Sulfurated S₈ solvent

S uptake to 10 wt% at 40°C (under trial in lab)

Field use

- Standard refinery product used to make hybrid physical – chemical solvent
METHODS FOR APPLICATION OF ENHANCE SULFUR SOLVENT

- Refinery
- Producing Oil Field
  - Sulfur-loaded solvent collection
  - Gas production system
  - Sour gas
  - Well injection of solvent
  - Sour gas production
  - Field distribution
  - “Chemical enhancement”
  - Refinery product
    - $S_8$ solvent
    - $H_2S$
    - Oil field pipeline

- Refinery product
  - Sour gas production system
  - Gas production system
  - Producing Oil Field
Aecom Technology Corporation
Air Liquide Global E&C Solutions / Lurgi
Ametek Process & Analytical Instruments/Controls Southeast
AXENS
Baker Hughes
BASF Catalysts LLC
Bechtel Corporation
Black & Veatch Corporation
Brimstone STS Ltd.
Canadian Energy Services/PureChem Services - Canwell
ConocoPhillips Company
Enviro-Industries Ltd.
CB&I
Chevron Energy Technology Company
Denbury Resources Inc.
Devco
Duiker CE
E.I. du Pont Canada Company / MECS Inc.
EnCana Corporation
Enersul Inc.
Euro Support BV
ExxonMobil Upstream Research Company
Flint Hills Resources
Fluor Corporation / GAA
HEC Technologies
Husky Energy Inc.
IPAC Chemicals Limited
Jacobs Canada Inc. / Jacobs Nederland B.V.

KT – Kinetics Technology S.p.A.
Linde Gas and Engineering (BOC)
M I SWACO
Nalco Champion
OMV Exploration and Production GmbH
Optimized Gas Treating, Inc.
Ortloff Engineers, Ltd.
Oxbow Sulphur Canada ULC. (former ICEC)
Petro China Southwest Oil and Gas Field Company/RINGT
Phillips 66 Company
Porocel Industries, LLC
Prosernat
Riverland Industries Ltd.
Sandvik Process Systems, Inc. / Brimrock Group Inc.
Saudi Arabian Oil Company (Saudi Aramco)ASC
SemCAMS ULC
Shell Canada Energy
SiiRTEC Nigi S.p.A.
Sinopec / Pugaung Branch Company
Sulfur Recovery Engineering (SRE)
Sulphur Experts Inc. (Western Research)
Suncor Energy Inc.
TECHNIP
The Petroleum Institute / Abu Dhabi National Oil Company (ADNOC)
Total S.A.
UniverSUL Consulting
Weatherford International LLC/ICTC
WorleyParsons
**PROPOSED REMEDIATION METHOD: ETHYLENE INJECTION**

![Diagram](image)

\[
2C_2H_4 + 2H_2S \rightleftharpoons 2C_2H_5SH
\]

\[
2C_2H_5SH + n/8S_8 \rightleftharpoons C_2H_5SS_{n-2}SC_2H_5 + H_2S
\]

\[
2C_2H_4 + n/8S_8 + H_2S \rightleftharpoons \text{Rock?} \quad C_2H_5SS_{n-2}SC_2H_5
\]

*Ongoing Research at ASRL*

*Processing plant*

*T < 120°C, sour gas*