Corrosion Due to Elemental Sulfur in Sour Gas Production and Claus Sulfur Recovery Systems

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Wet Sulfur Contact Corrosion of Carbon Steel
The Safety Moment: Iron Sulfide and Fire

\[
\text{Fe} + S_8 + H_2O \rightarrow \text{FeS} \\
\text{FeS} + O_2 (\text{Air}) \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{Energy} \ (\Delta H = -1,226 \text{ kJ})
\]

The \( \text{Fe}_2\text{O}_3 \) becomes red hot igniting any flammable material (sulfur)

Result: Fires inside the Claus plant (catalyst beds), sulfur pits, tanks, sulfur forming plants and more
Electrochemical Mechanism of Sulfur Corrosion

Anodic: \[ xFe \rightarrow xFe^{2+} + 2xe^- \]

Cathodic: \[ S_x + 2xe^- \xrightarrow{[FeS]} xS^{2-} \] “autocatalytic”

Overall Corrosion Reaction: \[ xFe + S_x \xrightarrow{[FeS]} \text{iron sulfide (‘mackinawite’)} \]

FeS is pyrophoric when dry and finely divided

S-deficient FeS\(_{(1-x)}\) “non-stoichiometric”
Mechanistic Overview of Steel / Sulphur Corrosion

Non-stoichiometric e- conducting FeS layer
Effect of Moisture and Steel / Sulfur Contact

- Contact and moisture are essential for corrosion -
Effect of Temperature on The Rate of Wet Sulfur Contact Corrosion

- > 20°C most of the time
- PANAMA CANAL
- TRANS-ATLANTIC
- TRANS-PACIFIC
Partial Oxidation of FeS and Formation of Sulfuric Acid

FeS + O₂ (Air) → Partial oxidation → Fe₂(SO₄)₃

Fe₂(SO₄)₃ + H₂O → 2 Fe³⁺ [6 H₂O] + 3 SO₄²⁻ [6 H₂O]

Solvolysis

Fe³⁺ (H₂O)₆ → Fe²⁺ (H₂O)₅ OH + [H⁺]

- Iron sulfate forms acidic solutions (pH ≈ 1-2) which corrode steel
Two Examples of Sulfur Deposition in Sour Gas Production Facilities

S₈ Deposition within a Sour Gas Flow Line

S₈ Deposition in a Gas Plant Inlet Separator

+ Photograph courtesy of John Morgan, John M. Campbell & Company

* Photograph courtesy of Mark Townsend, Burlington Resources
Sulfur Deposition Arising from Oxidation of ppm Level H₂S

2. Courtesy of PG&E, Technological and Ecological Services (TES), San Ramon, California

Elemental sulfur confirmed by SEM/EDX analysis
In Situ Formation of Sulfur in Sour Gas Equipment

- The protective FeS coating becomes a catalytic layer

- The reaction is fast at high P; the amount of sulfur (H₂O) formed depends on amount of O₂ ingress
Sulfur is formed at FeS layer in the contactor and then transported around the amine loop.

Degradation occurs in the regenerator; ionic species enhance corrosion.

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“Combustion” of Steel with Sulfur in the Claus Furnace

- Acid gas
- Air
- Ceramic brick
- Process gas
- Brick failure
- $S_8$

Chemical reactions:

\[
\begin{align*}
\text{Fe} + S_2 &\rightarrow \text{FeS}_2 \\
H_2S &\leftrightarrow H_2 + \frac{1}{2}S_2 \\
\text{Fe} + H_2S &\rightarrow H_2 + \text{FeS} \quad \frac{1}{2}S_2 \rightarrow \text{FeS}_2
\end{align*}
\]

- $O_2$ is very rapidly consumed by $H_2S$ in the flame
- Steel is oxidized by sulfur forming a mixture of FeS and FeS$_2$
The alumina ferrule is chemically inert to all species.

Steel (Fe) is relatively inert to sulfur and other species < 400°C.
The Importance of Purging Sulfur From a Claus Unit During Shutdowns

- Ceramic brick and catalyst retains sulfur after unit shut down
- Conditions must be maintained to prevent condensation of sulfur in places other than the condensers
Corrosion in Off-Gas Line Below Water Dew Point

- Inadequate heating at line support allows water condensation
- Rapid Fe/S corrosion: \( \text{Fe} + \frac{1}{8} \text{S}_8 \xrightarrow{\text{H}_2\text{O}(l)} \text{FeS} \)
- Aqua Claus reaction: \( 2 \text{H}_2\text{S} + \text{SO}_2 \xrightarrow{\text{H}_2\text{O}(l)} [\text{H}_2\text{S}_x\text{O}_y] \xleftrightarrow{\text{H}_2\text{O}(l)} \frac{3}{8} \text{S}_8 + 2 \text{H}_2\text{O} \)
- Highly acidic aqueous solution is formed
Field Pictures of Corroded Claus Tail Gas Line

Pictures provided to ASRL by:

CSI
CONTROLS SOUTHEAST, INC.

AMETEK
THERMAL PROCESS MANAGEMENT
Mechanisms for Deterioration of Concrete in Sulfur Pits

- Migration of $\text{H}_2\text{S}$, $\text{SO}_2$, $\text{O}_2$, $\text{H}_2\text{O}$ and $\text{S} \,(\text{vap})$ into internal pore structure of the concrete followed by chemical reactions.

$\text{H}_2\text{S} + \text{S}_8 \overset{T \, ^\circ\text{C} = 90\rightarrow130}{\rightleftharpoons} \text{H}_2\text{S}_x$

$\text{AIR}$

$\text{S}_8$

$\text{Liq S}_8$

$\text{Liquid S}_8 \, 130^\circ\text{C}$
Formation of Sulfur Inside the Concrete

Detailed Chemistry

\[
H_2S + O_2 \xrightarrow{\text{Concrete pore structure}} SO_2 + H_2O
\]

\[
\frac{1}{8} S_8(\text{vap}) + \frac{1}{2} O_2 \rightarrow SO_2
\]

\[
2H_2S + SO_2 \xleftrightarrow{\text{Claus chemistry intermediates}} \frac{3}{8} S_8 + H_2O
\]

\[
\text{“CaO”} \rightarrow \text{CaSO}_4, \text{CaS}_2\text{O}_3
\]

Lower density, higher volume unconsolidated products.
Secondary Corrosion Processes at Concrete Pit Reinforcing Steel

**Secondary Corrosion**

- $\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2$
- $\text{CaO} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$

**Enhanced Sulfur Formation at Steel**

- $2\text{H}_2\text{S} + \text{SO}_2 \xrightarrow{\text{Fe}_2\text{O}_3} \frac{3}{8}\text{S}_8 + 2\text{H}_2\text{O}$
- $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Fe}_2\text{O}_3} \frac{1}{8}\text{S}_8 + \text{H}_2\text{O}$
Primary Corrosion in Sulfur Tanks – Air Drafted Systems

- Poor roof insulation (or poor heating) may result in inner roof temperature of < 100°C

**Consequences**

- S₈ solid deposition and water / H₂SₓOᵧ condensation (from SO₂ / H₂O)
- Fe / S₈ corrosion
  \[ \text{Fe} + \frac{1}{8} \text{S₈} \xrightarrow{\text{H₂O or H₂SₓOᵧ}} \text{FeS} \]
- Acid corrosion
  \[ 2 \text{Fe} + \text{H₂SₓOᵧ} \rightarrow 2 \text{Fe SₓOᵧ} + \text{H}_2 \]
Secondary Corrosion on Sulfur Tank Roofs – Air Drafted Tanks

- Without roof heating, T may fall to < 100°C, allowing H₂O or H₂SₓOᵧ condensation.
- Partial oxidation of FeS may reform S₈ at surface.
- Corrosion at “cool” roof surface may result from condensed acids (H₂SₓOᵧ), sulfur deposited or formed by chemical reaction.
Rupture of Steam Coils in Sulfur Tanks

Steam Coil Corrosion

Fe + H$_2$S $\rightarrow$ FeS + H$_2$

S$_8$ (H$_2$S) $\rightarrow$ FeS

FeS $\rightarrow$ Mechanical erosion
"Clean surface"

Steaming reaction:

Fe + H$_2$S $\rightarrow$ FeS + H$_2$

Mechanical erosion of FeS layer leads to thinning of carbon steel coils and eventual rupture.

Diagram:
- Air enters the system.
- Steam coil with temperature $\sim 140^\circ$C.
- Condensate/steam exits.
- S$_8$ (H$_2$S) inlet.
- Air/SO$_2$ (H$_2$S) outlet.
Shipping Sulfur By Rail

**Steel Box**
- Polymer coating to prevent iron-sulfur corrosion
- Keep sulfur dry by adding a cover or roof

**Aluminum Box [Don’t do it!]**
- Aluminum will melt if $S_8$ catches fire
- $\text{Al}/S_8$ react explosively at $T$ of burning sulfur to form $\text{Al}_2\text{S}_3$
- $\text{Al}_2\text{S}_3$ reacts with water producing $\text{H}_2\text{S}$
  \[
  \text{Al}_2\text{S}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{S}
  \]
Corrosion and Acidity Generation in a Ship Hold
- a Potentially Deadly Combination -

Corrosion: FeS / Sulfur layer may become H₂S saturated > 1000 ppmv.

FeS + H₂SO₄ → FeSO₄ + H₂S

denser than air — remains in the bottom of the hold.
Sulfur Loading to Limewashed Hold

31/8/2002
Development of Zinc-modified Limewash

**Chemistry:**

$$\text{Ca(OH)}_2 + \text{ZnSO}_4 \rightarrow \text{Zn(OH)}_2 + \text{CaSO}_4$$

net reaction

$pH = 12.4$

**Advantage:**

$$\text{Zn(OH)}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}$$

acidity build-up in cargo

'soluble'

• SUCCESSFULLY FIELD TESTED IN SHIP TRIAL

**Mitigation of Corrosion by Zn$^{2+}$:**

$$\text{Fe} + \frac{1}{8}\text{S}_8 \rightarrow \text{FeS}$$

$$\text{Zn (OH)}_2 + \text{FeS} \rightarrow \text{ZnS} + \text{Fe (OH)}_2$$

• ZnS is a perfect insulator stopping e-transfer at iron surface
Effect of Soluble Zn$^{2+}$ on Wet Sulfur Corrosion

solution phase addition of Zn$^{2+}$

Inhibition works by in-situ formation of insoluble ZnS barrier at steel / S contact area

$$\text{Zn}^{2+} + \text{S}^{2-} \rightarrow \text{ZnS} \quad \text{(stoichiometric)}$$

- pH 2
- [SO$_4^{2-}$] = 0.01 M
- soluble Zn$^{2+}$ inhibits S corrosion at concentrations even as low as $1 \times 10^{-2}$ M
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