Agenda

• Corrosivity – Amine Hydrochlorides
  – Impact of overhead corrosion

• Overhead Corrosion
  – Crude Unit Operation
  – Controlling Overhead Corrosion
  – Electrolyte Modeling

• Case Study - Use of OLI Stream Analyzer
  – Vacuum Tower
  – Coker Fractionator

• Summary
Salts and corrosion products flowed out of exchanger where corrosion was occurring.
Corrosivity - Amine Hydrochlorides

- Leaks in equipment develop leading to **Health and Safety** issues
- Unscheduled shutdown of equipment results in **Lost Production**
Salt Hydrolysis
\[ \text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HCl} \text{ (g)} \]
\[ \text{CaCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HCl} \text{ (g)} \]
\[ \text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HCl} \text{ (g)} \]

Salt Formation
\[ \text{NH}_3\text{(g)} + \text{HCl(g)} \leftrightarrow \text{NH}_4\text{Cl(s)} \]
\[ \text{R-NH}_2\text{(g)} + \text{HCl(g)} \leftrightarrow \text{R-NH}_2\text{HCl(s)} \]

Corrosion
\[ \text{NH}_4\text{Cl(s)} \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]
\[ \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq}) \leftrightarrow \text{NH}_3(\text{aq}) + \text{HCl(\text{aq})} \]
\[ \text{R-NH}_2\text{HCl(s)} \leftrightarrow \text{R-NH}_3(\text{aq}) + \text{Cl}^-(\text{aq}) \]
\[ \text{R-NH}_3(\text{aq}) + \text{Cl}^-(\text{aq}) \leftrightarrow \text{R-NH}_2(\text{aq}) + \text{HCl(\text{aq})} \]
\[ \text{Fe} + 2\text{HCl(\text{aq})} \rightarrow \text{FeCl}_2 + \text{H}_2 \]

** Similar crude contaminants in slop oil**
Liquid Amine Salts Corroding the Bottom Side of the 18-inch Carbon Steel Pipe Leaving the Top Pump-around Draw off of the Crude Tower

Naphtha Line Corrosion – High Corrosion Rate of in 6 O’clock position
Equilibrium Salt Formation

Equilibrium Constant, $K_p$, psia$^2$

Temperature, deg F

Salt will form

No salt will form
Controlling Overhead Corrosion

- Reduce contaminant levels
  - Improve desalting performance, desalter wash water quality, re-route slop streams
- Increase tower overhead temperature
- Water washing overheads
- Inject neutralizer
  - Change overhead chemistry

Benefits of different corrosion control options can be evaluated using a good overhead system model
Refining Overheads – Electrolyte Modeling

Input
- Flows
- Temperature
- Pressure
- Water Analysis
- Properties of hydrocarbons
- Neutralizer

Output
- Water dew point
- Salt Point (ammonia, amine)
- Aqueous pH
- Phase behavior

OLI Equilibrium Thermodynamic Model
How can overhead modeling help?

– Proper selection of amines for overhead system
  • Different amines form salts at different temperatures
  • Neutralizer amines exhibit differences in ability to control pH at water dew point
  • Model can help analyze effect of various neutralizer amines

– Troubleshoot events
  • Did changes in unit operation create a corrosive environment?
  • Identify significant shifts in unit operation
    – NH₄Cl/Amine-HCl salt point
    – Water dew point

Overhead modeling can improve overall unit performance and reliability
Case Study – Vacuum Tower

Concern: Is there ammonium chloride salt formation potential in the main overhead line of the vacuum tower?
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Inputs
Pressure: 5 mmHg
Off-gas: 6.5 mscfh
Distillate oil: 10 gpm
Steam: 11600 lb/hr
Contaminants:
  - HCl 3 ppm
  - NH₃ 6 ppm
  - H₂S 10 ppm
Results

- calculated salt formation temperature was 129 deg F (close to the temperature where the tower overhead operates)

**Modeling shows high risk for NH$_4$Cl salt formation**

in the main overhead line
Case Study – Coker Fractionator

Concern: Increased pressure drop observed across the overhead fin fan exchanger of the coker fractionator would lead to equipment shutdown

What is causing the plugging across the fin fan tubes?
Very low scaling tendency for ammonium bisulfide (NH₄HS) in the coker fractionator overhead

- NH₄HS salt formation unlikely in this temperature region
- Water dew point 192 deg F
Performed survey calculation (vary chloride composition)

NH₄Cl salt can form when HCl concentration gets near 213 ppm in the system
- salt formation temperature 199 deg F
- water dew point 192 deg F

Distillate wash caused spike in overhead chlorides

From overhead 285 F (141 C) → 185 F (85 C) → 100 F → To accumulator

Fin Fan
Summary

Corrosion never takes vacation
– Health and Safety issues and LPO

Ammonia/amine salts are major contributors to refining unit overhead corrosion

Modeling the crude unit overhead system can improve overall unit performance and reliability
– Troubleshooting tool
– Unit monitoring

OLI Stream Analyzer has enabled us to model potential for salt formation in refining overhead systems

Understanding when liquid amine salts form via ionic models is important to reliable unit operation
– Need better understanding of properties that best describe formation of amine salts
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