35th International OLI User Conference

Use Of OLI Toolkit for Shell Applications

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Mission Statement

- Look for cost-effective and innovative ways to lower the maintenance costs of our customer’s corrosion abatement, scale control, salting/fouling and associated chemical injection programs
- Enhance the availability and reliability of our customer’s process equipment, while minimizing capital costs
- Provide “best in class” solutions, by suitably packaging custom IONICS models with sound Technical Services and Customer Support
Technical Service
Systematic Approach

Customer

Operability:
- Chemical/ Additive Monitoring
- De-bottle-Necking: Source Control Scale/Salt
- Scale Control
- Product Purity
- Efficiency: Injection Points Quality “Data” Chemical Choice
- Profitability: Lower Chemical Cost
- Execution: Current Opns. / Process & Chem. Changes
- Corrosion, Scale, Salt Mgmt. Improved Equipment Life
- Salting / Fouling
- Corrosion Management

IONICS
Potential Market

- Refineries and (Petro)chemical plants
- Lube Oil Facilities & Blending plants
- LNG Plants
- Environmental facilities
- Exploration and Production Topsides facilities
- Partnerships with Chemical Vendors
Technical Services Offered

• State-of-the Art Laboratory for Basic Data
  – Unique in-house Methods & Data
  – Data Delivery in Various Formats (e.g., Spreadsheets, Nomographs, Phase Diagrams, Computer Tools)
  – Field Corrosion Data Validation through Ionic Modeling

• Tools Selection / Maintenance / Gate keeping
  – Custom Delivery in Major Simulators
  – Short-Cut Methods
  – Plant Operating Procedures
  – Hands-On Training

• Support to Refineries / Chemical Plants / E&P Facilities
Methods to Inhibit Corrosion

• Reduce precursors to corrosives
  Good Desalting and Caustic Injection
  \[ \text{MgCl}_2 + 2\text{NaOH} \xrightarrow{\Delta} \text{Mg(OH)}_2 + 2\text{NaCl} \]
  \[ \text{CaCl}_2 + 2\text{NaOH} \xrightarrow{\Delta} \text{Ca(OH)}_2 + 2\text{NaCl} \]

• Dilute the Corrosives
  Water Washing

• Shield the Metal Surface with Filming Chemicals
  Solvent (Water, Oil), Dosage, Injection Scheme

• Neutralize the Corrosives
  Adjust pH with neutralizing amines / ammonia

• Upgrade the Metallurgy
  Alloy and Duplex Steels versus Carbon Steel
Ca Cl₂ + H₂O \xrightarrow{\Delta} CaO + 2HCl

MgCl₂ + H₂O \xrightarrow{\Delta} MgO + 2HCl

NaCl + H₂O \xrightarrow{napht,acid,\Delta} Na₂O + 2HCl

Rules of thumb:

(1). Ten pounds of “total salt” produce about one pound of Hydrogen Chloride.

(2). NaCl salt is most stable and does not decompose in preheat furnace.
Filming Amines Characteristics

- Form a barrier between the metal and the corrosive environment
- Adsorb onto the metal at the metal-liquid interface
- Generally are oil soluble and water dispersible
- Commonly used at a 2 –15 ppm level
- Injected into the overhead line: via an atomizing quill or with a slotted quill after dilution in a slipstream
- Should be cautiously mixed with: Aqueous Ammonia solutions or neutralizing amines especially water based ones

**Note:** Filming Amines contain the corrosion inhibitor, surfactants (demulsifier, defoamer, dispersant) and carrier solvent (water, alcohol, aromatic or aliphatic HC)
Neutralizing Amine Characteristics

- Increases pH of Aqueous Dew Point
- Elevates Aqueous Dew Point - Colligative Properties effect
- Causes plugging – Precipitation as dry hydrochloride salts, above aqueous dew point

Examples of Neutralizing Amines:
- Morpholine, branched-Morpholine
- Ethylene Di-Amine (EDA)
- Mono-Ethanol-Amine (MEA)
- 3-Methoxy, Propyl-Amine (MOPA)
- sec-Butyl-Amine (SBA)
- Ammonia
Corrosion Chemistry

Explained by Multiple Chemical reactions – Not simple Equilibria

\[ \text{Fe}_\text{(s)} + 2\text{H}^+_{\text{(aq)}} \rightarrow \text{Fe}^{2+}_{\text{(aq)}} + \text{H}_2(g) \]

\[ \text{Fe}_\text{(s)} + 2\text{HCl}_{\text{(aq)}} \rightarrow \text{Fe}^{2+}_{\text{(aq)}} + \text{H}_2(g) + 2\text{Cl}^-_{\text{(aq)}} \]

\[ \text{Fe}_\text{(s)} + \text{H}_2\text{S}_{\text{(aq)}} \rightarrow \text{Fe}^{2+}_{\text{(aq)}} + \text{H}_2(g) + \text{S}^-_{\text{(aq)}} \]

\[ \text{Fe}^{2+}_{\text{(aq)}} + \text{S}^-_{\text{(aq)}} \rightarrow \text{FeS}_{\text{(s)}} \]

**FeS Film Destabilization by Cyanide Complexing**

\[ \text{Fe}^{2+}_{\text{(aq)}} + 6\text{CN}^-_{\text{(aq)}} \rightarrow \text{Fe} (\text{CN}^-)^{4-}_{6\text{(aq)}} \]

*(Prussian Blue precursor)*

**Cyanide Scavenging by APS**

\[ (\text{NH}_4)^+_{2\text{(aq)}} \text{S}^5_{\text{(aq)}} + \text{CN}^-_{\text{(aq)}} \rightarrow (\text{NH}_4)^+_{2\text{(aq)}} \text{S}^4_{\text{(aq)}} + \text{SCN}^-_{\text{(aq)}} \]
Inhibitor Chemical Issues

- Filmer and Neutralizer must be stable (i.e., not decompose) below 300 °F
- Choice of Filming Inhibitor and Neutralizer amine must be compatible with each other
- Carrier fluids (e.g., water, alcohol, aromatic or aliphatic Hydrocarbon) should not react with the choice of filming/neutralizer chemicals
- Presence of surfactants in the filming inhibitor can cause downstream problems in columns, pump-around, etc. due to emulsified water
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Process Operations Issues

- **Use** of water-soluble, or oil-soluble, Neutralizing Amine (NA)?
- Should injection be neat or with carrier? If so, should carrier be a heavy hydrocarbon, light hydrocarbon, or water? Should atomized steam be used to disperse neutralizing amine in small droplets to enhance NA vaporization? If use of carrier is alternative, at what point do we mix NA and the carrier?
- Should Neutralizing Amine be injected before Filming Amine? - or - Filming Amine injected before neutralizing amine? - or - Mixed Filming amine and neutralizing amine in common injection point?
- Should the injection be done using a spray nozzle or quill? If spray nozzle is selected, must use carrier to get volume flow up to disperse and have enough pressure drop over the spray nozzle. Concern is over possible spray nozzle fouling, but nozzle enhances volatilization.
- Check strainers, pumps, flow meters, check valves to ensure that NA is not injected in pulses..........HCl comes into the overhead continuously.
Typical setup involves the following equations:

- **Equilibrium Equations** – Need to know Free Energy and Temperature dependence, activity coefficients and fugacities
- **Charge Balance Equation**
- **Gas or Vapor Phase Material Balance Equation**
- **Species Material Balance Equations**

**Solution of system of equations is not trivial!!!**

Use of computational package like ESP (Environmental Simulation Program) from OLI Systems Inc., or PRO II (electrolytes), or Aspen-OLI, or HYSYS (EO), needed to solve system of non-linear equations.
Do Rigorous Electrolyte Simulation of Process Outputs

1. Aqueous Dew Point Temperature
2. Salt Formation / Scaling Tendency
3. pH Profile
4. Corrosion Rate Prediction for choice Metallurgies
5. Inhibitor Neutralizer/Filmer chemicals to use, w/ dosage and injection points design
**Objective:** Accuracy and rigor maintained, along with simplicity & quick results

- Nomographs – pH as a function of inhibitor dosage
- Spreadsheets – Salt Delta T sheet to determine incipient salt formation
- Phase Diagrams – Provides system behavior information based on P,T
- Computer Process Models – in ProVision (Electrolytes), Aspen-OLI, Hysys (EO), and/or ESP/OLI Programs
Deposition of NH4Cl Salt From Gas Phase

\[ \text{NH}_3(g) + \text{HCl}(g) = \text{NH}_4\text{Cl}(s) \]
Salt $\Delta T$ Precipitation Spreadsheet
Salting Tendency Criteria

**Salt formation temperature** determined by Ionic Modeling from:
- Pressure profile in overhead system
- Temperature profile in overhead system
- Composition profile in overhead system (including ionic species)
- Vapor Flow Rate

**Salting Tendency** obtained from “Salt $\Delta T$”, where “Salt $\Delta T$” is defined as:

$$Salt \Delta T = T_{\text{system}} - T_{\text{salt formation}}$$

**Interpretation** of Salt $\Delta T$ value

- If $Salt \Delta T > 0$ No salt formation
- If $Salt \Delta T = 0$ Incipient salt formation
- If $Salt \Delta T < 0$ Salt formation

Salt $\Delta T$ values in the $+10$ to $-10$ range are considered to be in the “maybe” region
Salting Tendency in Typical LDU Overhead System

(Computer Process Model Approach)

LDU Column Overhead Flow Diagram

<table>
<thead>
<tr>
<th>Column Overhead - F1</th>
<th>E197</th>
<th>E196</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vapor Flow Rate &amp; Composition</strong></td>
<td><strong>Vapor Composition</strong></td>
<td><strong>Aqueous Dew Point</strong>*</td>
</tr>
<tr>
<td>lb mol/hr</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>NH₃ 7.000 E-03</td>
<td>6.91</td>
<td>8.92</td>
</tr>
<tr>
<td>MEA 2.263 E-02</td>
<td>22.31</td>
<td>27.54</td>
</tr>
<tr>
<td>MOPA 3.800 E-03</td>
<td>3.74</td>
<td>4.34</td>
</tr>
<tr>
<td>HCl 1.026 E-02</td>
<td>10.14</td>
<td>13.12</td>
</tr>
</tbody>
</table>

*Given - Aqueous Dew Point occurs in exchanger E196 @ 223°F and pH 4.4
IONICS Technical Apps.
2. Cat Feed Hydrotreater Separator Train (3 Studies).
3. Lube Distillate Unit Overhead System (2 Studies).
4. Delayed Coker Main Fractionator Wet Gas Compressor Train, including Gas Plant (3 Studies).
5. Fluid Cat Cracker Unit Main Fractionator Wet Gas Compressor Train, including Gas Plant (3 Studies).
6. Hydro-Fluoric Acid Tower Overhead (1 Study).
7. Vacuum Tower Steam Eductor Separation Train (1 Study).
10. Mercury Clean-Up of Refinery Streams (1 Study).
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FCCU Main Fractionator O/H Corrosion Control

- Predict Corrosive Conditions in typical FCCU Main Fractionator Column Overhead, Based on Analyses of Field Data

- Measure, Screen, Evaluate Physical Properties and Phase Equilibria Data for Potential Corrosion Inhibition (Ammonium PolySulfide - APS - injection)

- Evaluate & Recommend Corrosion Management Program:
  - Current Water Wash Program
  - Alternate Water Sources for Water Wash
  - Inhibitor (APS) Dosage
  - Inhibitor (APS) Injection Points
  - Fate of APS in FCCU Main Fractionator Overhead
  - Most Cost Effective Inhibition Program
Chemicals Success Stories

- Cumene Column Failure
- Metals purification
- Kraton Purification
- Epi-Chloro-Hydrin Column
- Oligomerization Pyrolysis Unit Tops
- Nitrite/Sulfite Salt Precipitation - simple & mixed salts
- Olefin Preparation Unit Overhead (2 Studies)
- Fuel Gas System Salting / Corrosion
- Phosphates Precipitation
- Support to NH4HS Corrosion Control Document
Upstream (E&P) Success Stories

E&P

- Barite Scaling in Wells
- CO₂ Leaks in Produced Water
- Acid Carryover from Stimulation Fluids
- Salting Precipitation (Inorganic Salts: NaCl, KCl, Na₂CO₃/NaHCO₃)
- Acid Gases Equilibria at High Pressures
- Chemical Control of H₂S in Well Servicing & Production Operations
- Thermodynamics & Phase Behavior of H₂S / Salt / Water Systems at High Pressure and High Temperature
- Data Reconciliation of Laboratory Data for Produced Waters
Other Success Stories

Other

Joint Industry Partnership Support – NH₄HS Corrosion Experiments Support to InterCorr Labs

Water Softening / Zeolites

Supporting OLI Products on the CITRIX Metaframe (multi-user network environment)
• Shell is sponsoring a Sour Water Joint Industry Program (JIP) to measure and predict corrosion rates for different metallurgies.
• Main focus of the program is to determine corrosion rates via laboratory experiments designed to mimic process conditions.
• Laboratory experiments incorporate high temperature, high pressure and dangerous chemicals (e.g. H₂S).
• Need a predictive tool (model) to help design experiments and choose ranges of operating conditions (a priori) for the experiments that would yield most informative results while maintaining safety.
• OLI ESP was used to predict pH of NH₄HS at varying conditions (e.g. excess H₂S or NH₃ conditions, high temperature/pressure etc.).
• OLI ESP also used to help probe physical limits of experimental setup (e.g. maximum attainable [NH₄HS], temperature / pressure effects, etc.)
NH₄HS Experimental Setup
Using Aspen OLI
NH₄HS Experimental Setup Using Aspen-OLI

- JIP project utilizes Aspen Plus with OLI ESP engine.
- Original model was developed as Microsoft Excel spreadsheet and evolved to Aspen Plus.
- Incorporated Aspen optimization tools to specify [NH₄HS], vapor volume, liquid volume and H₂S (or) NH₄HS partial pressure.
- Sensitivity analysis allowed multiple cases to be consecutively run.
- Autoclave was modeled using Aspen-OLI ESP 3-phase flash to calculate pH at varying [NH₄HS].
- Helgeson EOS provided wider pressure operating range the Aspen Elec-NRTL model.
- Results compared very well to experimental results.
- Cost savings resulted from using model output as a tool to choose which lab experiments to run and avoiding experiments that offered little or no additional information.
Deploying OLI Products on Citrix MetaFrame
A Case Study: StreamAnalyzer, ScaleChem

- **What is Citrix MetaFrame?** Citrix is the company, MetaFrame is the application (for us, running on Windows 2000 Server and Terminal Services)

- MetaFrame provides remote multi-user, Thin-Client access to applications running on central computers.

- Applications run locally on central computers and only the application interface is presented to remotely connected computers/terminals. It has the “look-and-feel” of a local Windows application.

- **Why use it?**
  - Software deployment to end users can be centrally managed.
  - Application updates can be quickly implemented with less impact to end users.
  - Users can access multiple applications from remote locations.
  - Provides more efficient use of licensed applications.
Most applications are not written for a multi-user environment. Applications usually require some “tweaking” to work.

StreamAnalyzer did require some minimal changes to work in a multi-user environment
- our needs required a unique working directory structure for each user
- users needed their own copy of configuration file(s)

These needs require changes to the registry
- can be accomplished “on-the-fly” (via scripting) as users log in

User-specific files / settings can be saved when logging off and reloaded during future logins.