NACE INTERNATIONAL

CORROSION CONTROL IN THE REFINING INDUSTRY

Chapter 5
Hydrofluoric Acids Alkylation Units

Hydrofluoric Acid Alkylation

- Produce high octane fuel blending component
- React isobutane with olefins (butene, butylene, propene, propylene) to form isoparaffin (alkylate)
- Hydrofluoric acid is catalyst
- No moisture or sulfides in feeds

Reaction Section

- Isobutane + Olefins + HF acid
- Exothermic reaction; cooling required
- Acid emulsion flows to settler vessel
  - HF acid is recirculated to reactor
  - Hydrocarbons to fractionation
- UOP pumps acid back to reactor
- CP pumps hydrocarbons to fractionation

Fractionation Section

- First tower removes butane, isobutane, propane, and dissolved HF acid
- Isobutane recycled back to reactor
- Hydrocarbon light ends are condensed
- Free HF acid is condensed and recycled
- Alkylate product is tower bottoms

Fractionation Section

- Other towers (depropanizer / debutanizer) for further hydrocarbon fractionation
- Overheads may contain free HF acid
- HF stripper tower
- HF acid recycled to reaction section

Treating Section

- Products treated to reduce fluoride content
  - Propane
  - Butane
  - Alkylate
- Defluorinators with alumina
- Caustic treaters with potassium hydroxide

Acid Regeneration Section

- Dilution of HF acid can cause corrosion
- Acid soluble oils (ASO) and water removed
- Continuous or batch operation
- Acid regenerator or rerun tower
- Recover free HF for reuse
- Constant boiling mixture of HF + water, and ASO neutralized for disposal

Process Parameters

- Acid concentration > 80 wt % for CS
- Water content in acid = 2-2.5 wt % max.
- Temperature = 150°F (65°C) max. for CS

Materials of Construction

- Carbon steel
- Alloy 400
- 70/30 CuNi
- Alloy C-22 or C-276
- PTFE
- Graphite

Columns

- Vessel
  - Carbon steel
  - Alloy 400 clad
  - Solid alloy 400
- Internals
  - Carbon steel
  - Alloy 400

Heat Exchangers

- Shells
  - Carbon steel
  - Alloy 400 clad
  - Solid alloy 400
- Tubes
  - Carbon steel
  - Alloy 400
  - 70/30 CuNi

Piping Systems

- Lines
  - Carbon steel
  - Alloy 400
- Bolting
  - B7 or B7M
  - Alloy 400 or Alloy C-22/C-276

Piping Systems

- Pumps
  - Carbon steel
  - Alloy 400 (solid & trim)
- Valves
  - Carbon steel
  - Alloy 400 (valves & trim)

Carbon Steel Specification

- Residual elements content (Cu + Ni + Cr) restricted to < 0.15-0.20 wt %
- Joint Industry Program (JIP) results
  - Cu + Ni < 0.15 wt % if C > 0.18 wt %
  - Cu + Ni + Cr < 0.15 wt % if C < 0.18 wt %
- Available as ASTM supplementary requirement

Degradation Locations

- Depropanizer feed and overhead systems
- Isostripper feed and overhead systems
- Acid regeneration/rerun tower and overhead piping
- Acid relief systems
- Propane/butane treating rundown systems
- Pump/valve castings

Hydrofluoric Acid Corrosion

- Carbon steel is normal material
- Protective iron fluoride scale
- Low corrosion in main acid areas
- Corrosion in areas with trace amounts of acid where condensing or vaporizing occurs
- Contributing factors
  - Elevated temperature
  - Water content in acid
  - Low acid concentration
  - Velocity

Hydrofluoric Acid Corrosion

- Increased corrosion rate for higher residual element material in condensing/vaporizing acid streams
- Galvanic corrosion in alumina treating section - dilute (wppm) acidic water
  - Adjacent high and low residual element material
  - Increased corrosion rate for lower residual element material

Hydrogen Induced Damage

- Atomic hydrogen → molecular hydrogen
- Blistering and cracking
- Hydrogen induced cracking (HIC)
- Stress oriented hydrogen induced cracking (SOHIC)
- Hydrogen embrittlement (HE)
- HF mildly charging
  - Arsenic/arsine can poison (accelerate)

Mitigation

- Proper materials of construction
- Proper fabrication procedures
- Carbon steel specification
  - High quality
  - Restricted chemistry (CE)
- Post Weld Heat Treatment (PWHT)
  - Welds
  - Stress relief
- Hydrogen bake-out prior to repair

Corrosion Control

- Process variables
  - Acid concentration
  - Water content
  - Temperature
- Acid break-through in product treating sections

Corrosion Monitoring

- Hydrogen activity devices
  - External patch or probes
  - Intrusive probes—not normally used
- Corrosion probes not normally used due to safety issues with HF and LPG
- Cooling water pH probes to detect acid leaks into system

Inspection

- Corrosion
  - Ultrasonic Testing
  - Automated scans
  - Radiography
- Hydrogen induced damage
  - Wet Fluorescent Magnetic Particle Testing
  - Ultrasonic Testing
  - Acoustic Emission

Degradation Mechanisms of Particular Concern in HF Alkylation Units

- Hydrofluoric Acid Corrosion
  - CS requires protective iron fluoride scale
  - Trace amounts of acid or acidic water
  - Process parameters
  - May require alloys for resistance
- Hydrogen Induced Damage
  - Result of corrosion
  - Blistering and cracking

Summary

- HF Alkylation process
- Process parameters
- Degradation mechanisms and locations
- Materials of construction
- Mitigation
- Corrosion control
- Corrosion monitoring
- Inspection

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