Defluorinator / KOH Treater Corrosion

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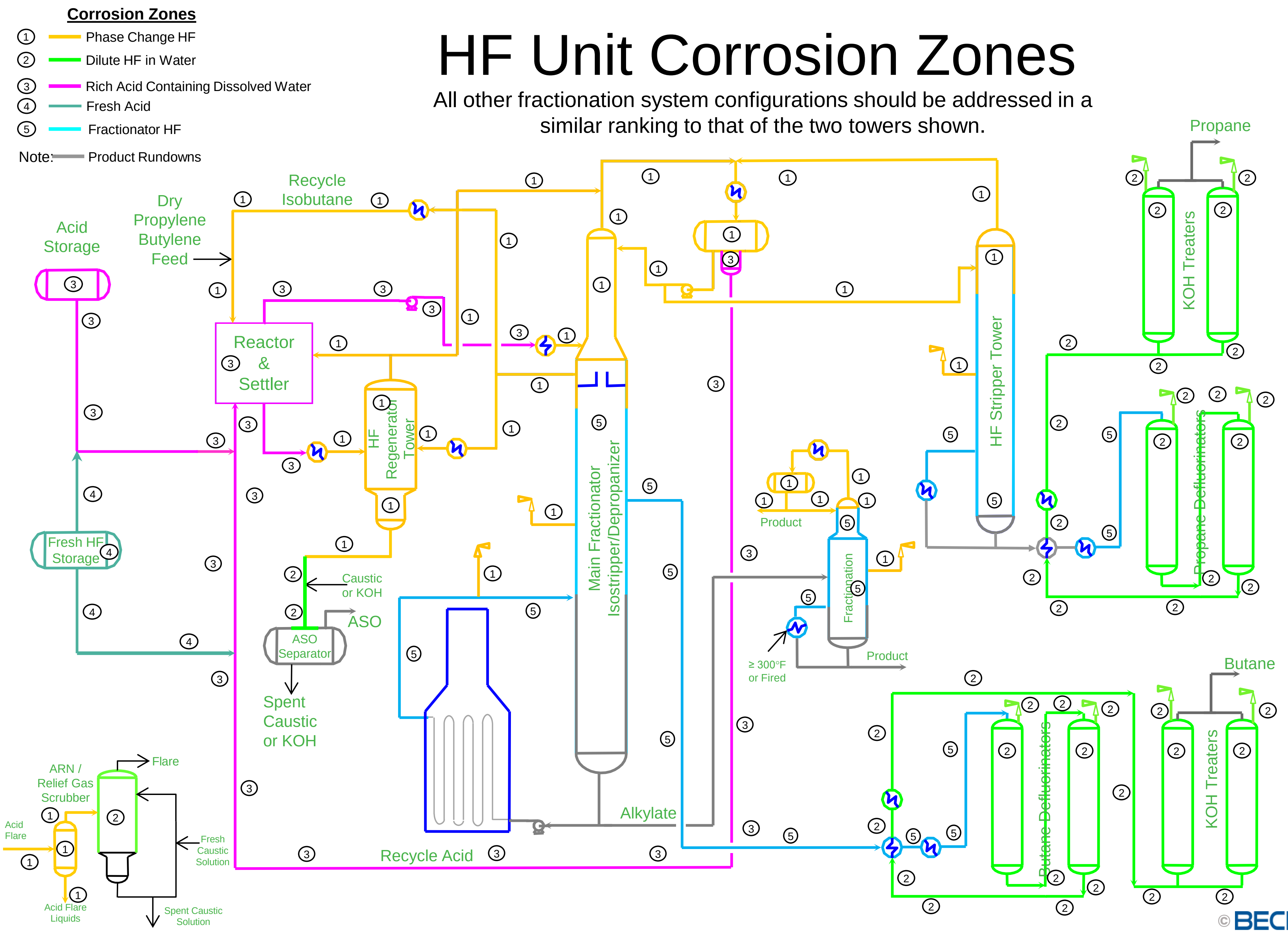
HF Unit Corrosion Zones

All other fractionation system configurations should be addressed in a similar ranking to that of the two towers shown.



Dilute HF Acid Corrosion

Dilute HF Corrosion

- Primary water stream with ≈ 1% HF created in defluorination
  - Organic fluorides are converted to HF and H2O over hot alumina
  - HF primarily captured on the alumina
  - Hot water vapor released (with residual HF) and to be captured by solid KOH treater.
  - IOW to monitor defluorinator to determine HF capture consumption to avoid excess HF release, lead/lag defluorinators.
- Very corrosive if dilute HF allowed to condense
  - Dew point function of amount of organic fluorides (water make) sent to defluorination.
    - Impacted by Reaction system operation creating fluorides. IOWs to minimize and monitor fluorides.
  - IOW for minimum cooled defluorination stream prior to KOH treater to operate above dew point.
    - Typically difficult to control / manage. Often upgrade to Alloy 400 required.
    - Deadlegs in system very susceptible.
  - Also impacted by a different form of residual element corrosion (See Type 8B corrosion).

  - **Note critical to avoid free HF to defluorinator bed as creates excessive exotherm and possible stress rupture. (IOWs in depropanizer/HF Stripper to avoid HF carry under and temperature monitoring/shutdown).**

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Dilute HF in Water Corrosion Zone

- Dilute HF in water corrosion zone occurs where a water phase can form, which will contain a low concentration of HF
  - Similar to old “Trace HF” zones
- Water phase can be corrosive
- the impact of Silica contamination of defluorination alumina media that can be absorbed by HF acid and produce a highly corrosive fluorosilicic acid $(H_3O)_2SiF_6$. Defluorinator media should be specified to contain < 0.1 wt. % Silica.
- Higher galvanic corrosion potential

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  - Can lead to hydrogen damage/blistering
  - 5-20 mpy rate or higher if HF breakthrough

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Dilute Deadleg Expsoures

- In the alumina treater / defluorination section of the unit, residual organic fluorides are converted to water with a small amount of HF by heating the stream to over 400°F and passing over an alumina bed.
- Defluorinator PSV inlets condensing vapor space can see accelerated corrosion

Carbon Steel Residual Elements

- Higher base corrosion rate=higher RE corrosion rate
- To minimize corrosion:
- C ≥ 0.18 wt % and Cu + Ni ≤ 0.15 wt % for base metals
- Cu + Ni + Cr ≤ 0.15 wt % for welds or areas of low carbon content< 0.18 wt %
- **In Dilute HF, galvanic effects dominate, where high RE components can be more noble than low RE**
- RE effects have been seen throughout unit
- PMI of importance to an RE program
- ASTM supplementary specs now exist, but purchasing challenges may exist
- Further discussed in new requirements

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Hydrogen Damage – HF (40)

- Damage types same as Wet H_2S exposures.
  - Hydrogen generated by exposure to HF and Fe during scale forming and corrosion processes.
    - Hydrogen Stress Cracking (HSC) – hard weld/HAZs/bolts/components – Compliance to NACE MR0103 limits and SP0472 welding controls (CE, preheat/PWHT).
    - Blistering/HIC/SOHIC managed by:
      - Plate quality – Enhanced quality requirements specified to minimize inclusions
      - Amount of corrosion (minimize per 37 discussion), hydrogen poison (Arsenic*)
      - Stresses – PWHT now specified for vessels in all acid services.
      - Inspections – Surface WFMT and subsurface UT (blistering/SOHIC at welds).
    - *Arsenic – As acts similarly as CN^- in Wet H+S service. Drives more corrosion hydrogen into steel.
      - As can be high in some supply of anhydrous HF. Specify IOW limit (< 10 wppm) in delivered.
      - Arsenides can come in with olefin feed from non hydrotreated feed FCC's
        - Monitor by measuring As in spent defluorinator alumina.

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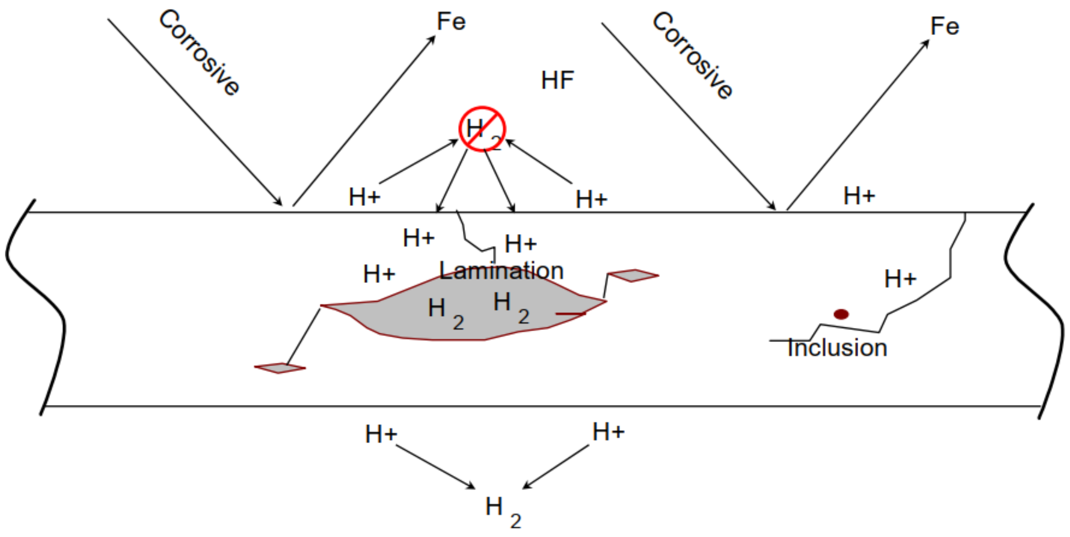
Carbon Steel

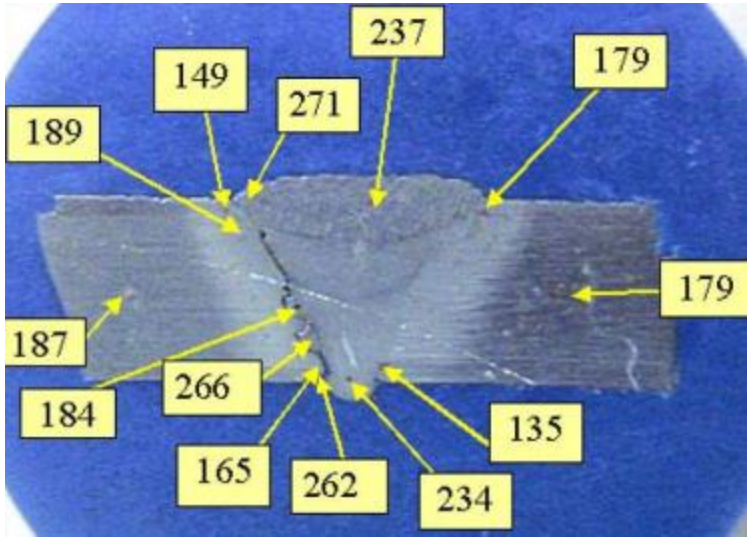
- Atomic hydrogen is generated from the HF acid corrosion reaction

- $2HF + Fe \rightarrow FeF2 + 2H$
- Similar to wet H2S, this can initiate HSC, HIC, SOHIC and blistering



Carbon Steel Environmental Cracking

- Base metal, weld deposits, and HAZ can all be susceptible
- Plate materials most susceptible
- Can be hardness driven



Carbon Steel Environmental Cracking

- Hydrogen Stress Cracking (HSC) – hard weld/HAZs/bolts/components – Compliance to NACE MR0103 limits and SP0472 welding controls (CE, preheat/PWHT)
  - Blistering/HIC/SOHIC managed by:
  - Plate quality – Enhanced quality requirements specified to minimize inclusions
  - Amount of corrosion
  - hydrogen poison (Arsenic*)

$$CE = \%C + \left[\frac{\%Mn}{6} + \frac{(\%Cu + \%Ni)}{15} + \frac{(\%Cr + \%Mo + \%V)}{5} \right]$$

- Stresses – PWHT now specified for vessels in all acid services.
- *Arsenic – As acts similarly as CN- in Wet H+S service. Drives more corrosion hydrogen into steel.
- As can be high in some supply of anhydrous HF. Specify IOW limit (< 10 wppm) in delivered.
- Arsenides can come in with olefin feed from non hydrotreated feed FCC’s
- Monitor by measuring As in spent defluorinator alumina.
- Inspections – Surface WFMT and subsurface UT (blistering/SOHIC at welds).

Carbon Steel Environmental Cracking

- A few reported cases of blistering in KOH treaters
  - None well documented root causes in NACE/AMPP, primarily anecdotal and both cases Becht is aware of blistering was historic and not considered active
  - Drives question of upset event driven vs. routine
- Carbonyl sulfide noted as potential contaminant, could cause acidic formation of H_2S if brine turns acidic
- Regardless if Wet H_2S cracking driven or HF blistering driven, acidic exposures in the KOH treater increase KIC/SOHIC/Blistering risk

IOW Monitoring

- Propane Stripper Bottoms or nC4 draw fluoride content
  - Sampling of the nC4 or propane to measure fluorides from the Propane Stripper or nC4 draw should be undertaken if a single defluorinator is used to treat the propane, with the intention that proactive life consumption of alumina can be estimated, and water dew point can be calculated for the defluorinator effluent.
  - For double defluorinators, fluoride sampling is still not needed for product fluoride controls, yet it is useful for troubleshooting in event of apparent rapid consumption of alumina and useful to establish water dew point for the defluorinator effluent.

IOW Monitoring

- Lead/between and lag/outlet Defluorinator fluoride monitoring
  - The output of defluorinators needs to be closely monitored to ensure that the propane meets maximum fluorides specification required by the unit and does not contain corrosive free HF due to the alumina being spent
  - In most units, there are typically two defluorinators in series with monitoring (sampling or bubbler) of the propane after the lead defluorinator, to flag the onset of free HF breakthrough where the propane is still protected by the lag defluorinator.
- Minimum Defluorinated Temperature Prior to KOH Treater
  - To avoid condensation of acidic dilute HF acid out of the defluorinator and prior to the caustic treater the cooling needs to be limited to avoid condensation. This is defined based on the amount of fluorides being converted in the nC4 draw or proane which determines the amount of water make and hence dew point. This can range from 40-50 °F to above 100 to 120°F. In some cases units add water upstream of the KOH treater due to such little water make due to low fluorides to avoid salt formation in the KOH treater

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Corrosion Zone 2 – Dilute HF in Water

- Dilute HF in water corrosion zone occurs where a water phase can form, which will contain a low concentration of HF. Any hydrocarbon present can be in the liquid phase, vapor phase, or both. In some cases, the water phase can be very corrosive.
- Locations of interest for dilute HF in water corrosion include:
  A) the defluorinators and downstream equipment all the way to the downstream caustic treaters,
  B) various unit dead-legs, and
  C) in the acid flare header.

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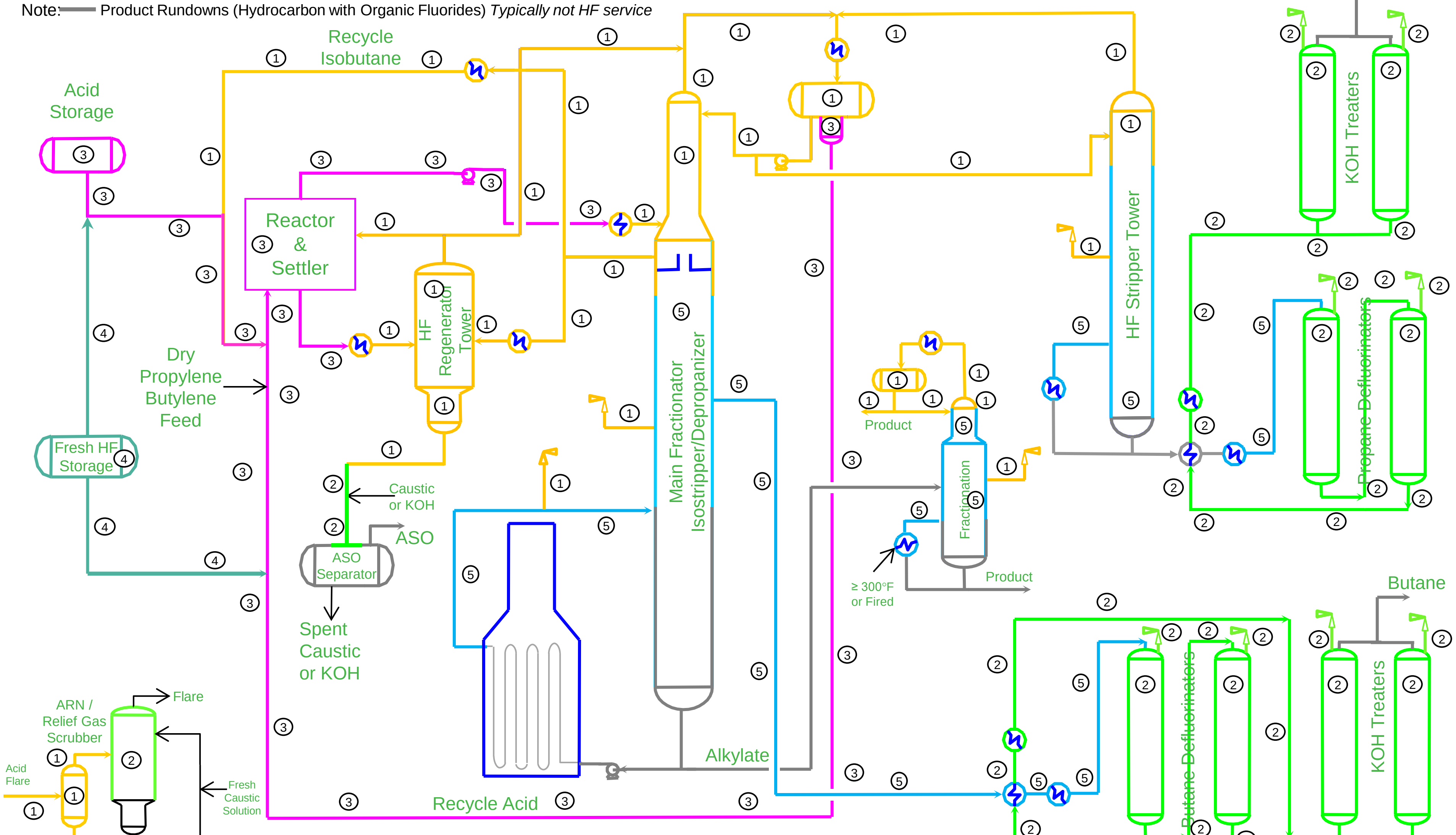
HF Unit Corrosion Zones

All other fractionation system configuration should be addressed in a similar ranking to that of the two towers shown.

Corrosion Zones

1. Phase Change HF
2. Dilute HF in Water*
3. Rich Acid Containing Dissolved Water
4. Fresh Acid
5. Fractionator HF

Note: Product Rundowns (Hydrocarbon with Organic Fluorides) *Typically not HF service*



*In areas where you have condensing acid and water is the continuous phase, galvanic corrosion can be an issue especially downstream of the Defluorinators. Deadlegs such as lines into relief devices in any of these systems are considered Acid with Phase Change in most cases.

Zone 2 Materials of Construction

- The typical material of construction for the Defluorinators, KOH Treaters, exchangers and associated piping is carbon steel. In some cases, the piping and exchangers downstream from the Defluorinators have been upgraded to Monel where the corrosion historically has been high. Generally, upgrades in these areas are related to fluoride break through from the treaters.

Zone 2 Damage Mechanisms

- HF acid corrosion
- Erosion corrosion (velocity assisted HF acid corrosion)
- Corrosion under deposit (HF acid corrosion under fluoride scale)
- Localized weld metal corrosion (selective HF acid corrosion at high residual element welds)
- HF SCC (HiC / SoHiC) primarily propane KOH Treater
- Galvanic corrosion at welds (only location where low RE can corrode preferentially to high RE)

Zone 2 Typical Locations for Damage

- The propane and butane Defluorinators and KOH treaters are typically of similar design.
- Depending on the amount of residual HF / organic fluorides or iron fluoride scale and the temperature, some amount of dilute HF acid can be generated downstream of the Defluorinators. As previously noted, this typically results from breakthrough of the HF in the alumina bed.
- Butane treaters often have more corrosion issues from fluorides that the propane treaters.

Zone 2 Inspection

- Corrosion is more likely in the piping downstream from the treaters than in the treaters themselves. Low points, drains, and the extrados of elbows (vertical down to horizontal) and intrados of elbows (horizontal to vertical down) can be specific location of higher corrosion rates from HF acid generated in the treaters. Include UT for general metal loss on piping and scanning or RT for local inspection at drains / elbows.
- Treaters should be internally inspected at change out of the beds, specifically nook for corrosion at the vessel bottom head and outlet nozzle. Include UT for general metal loss and UT Shear Wave, TOFD or UTPA for any concerns for cracking damage. Blistering and HF HiC/SoHIC are also possible on all of the fixed equipment in the treater section in this area, however, the KOH Treater has a higher potential for blistering / cracking (5 cases were reported to NACE).
- Similar to the Towers, the piping to the RV’s (vapor deadleg) should be inspected foriron fluoride scale and corrosion.

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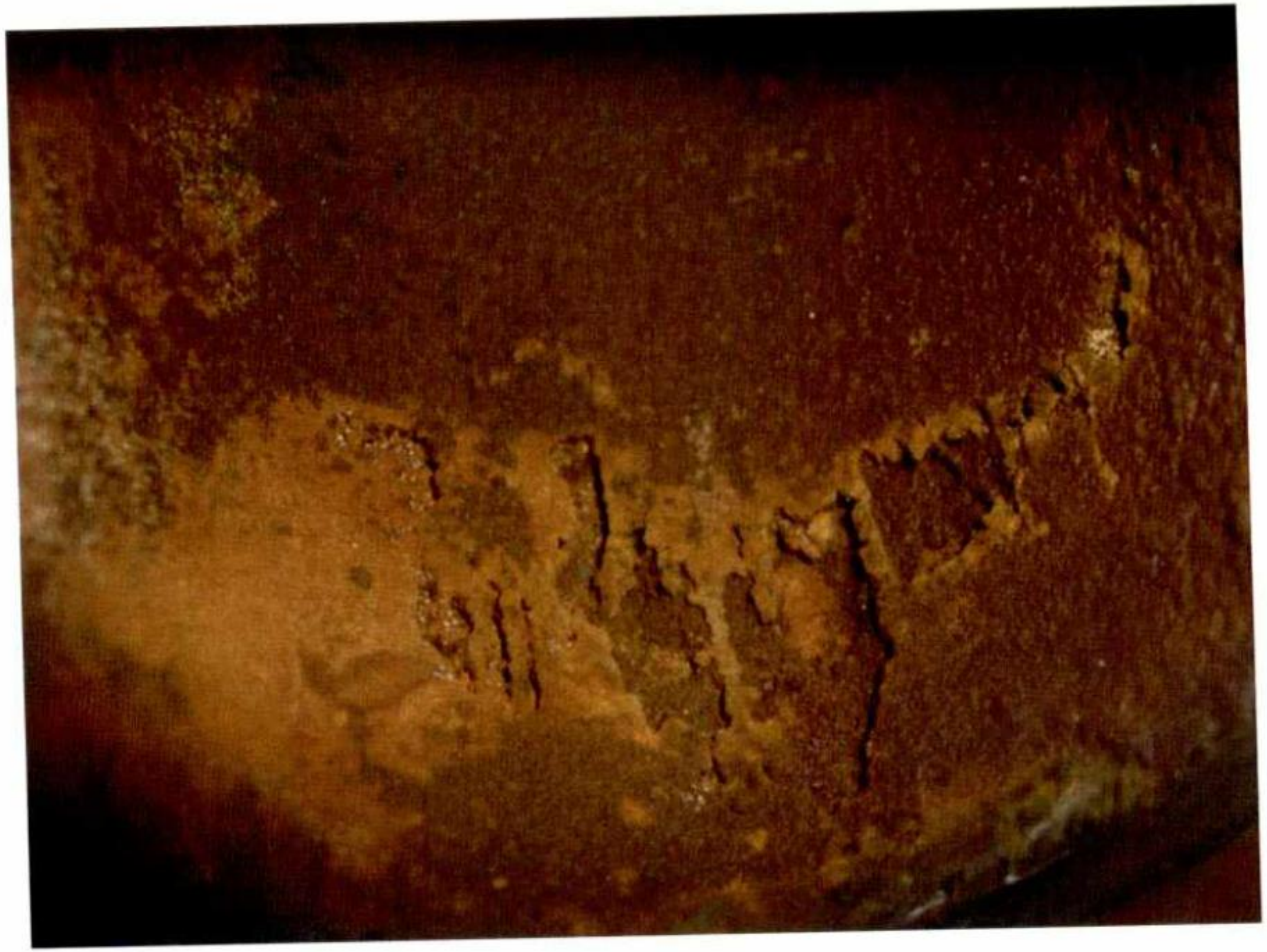
Zone 2 Additional Inspection Notes

- A special emphasis inspection program *shall* be developed and implemented at least once to inspect all individual carbon steel piping components and welds to identify areas of accelerated corrosion. The program shall be prioritized by corrosion zone with phase change HF and dilute HF in water corrosion zones given priority.
- RBI *shall not* be used to increase any inspection intervals for piping, piping components, and/or pressure vessels in the phase change HF and dilute HF in water corrosion zones above those required in this document.
- A maximum of 5 years *shall* be used for pressure vessels in phase change HF and dilute HF in water corrosion zones on-stream inspections.
- For pressure vessels in the phase change HF and dilute HF in water corrosion zones, an internal VT *shall* be conducted at every turnaround.
- RV testing *shall not* be extended beyond 10 years in phase change HF and dilute HF in water corrosion zones.
- For dead-legs in the rich HF, phase change HF, and dilute HF in water corrosion zones, the iron fluoride scale formed from corrosion can hydrate and grow in volume, potentially as much as 10-fold.

Case Studies

Propane Cooler Outlet Site A

- 2011 replaced end of life piping DS of propane condenser. 3” Sch80 Nom 0.300”. Hydro completed with water which wasn’t completely removed. New pipe holed through in 6 days – 18-20k mpy corrosion
- 2017 – propane cooler outlet – Thickness inspection October 2016 – nozzle 0.400” – holed through with significant widespread corrosion in January 2017 – 1200 mpy corrosion



Propane Cooler Outlet

- 4” Propane Cooler outlet nozzle
- Was replaced 2010, significant corrosion finding in 2016
- Suspected dew point at outlet of nozzle
- Intrados top side of elbow unexpected location of most accelerated corrosion
- Fabrication defect initiation?

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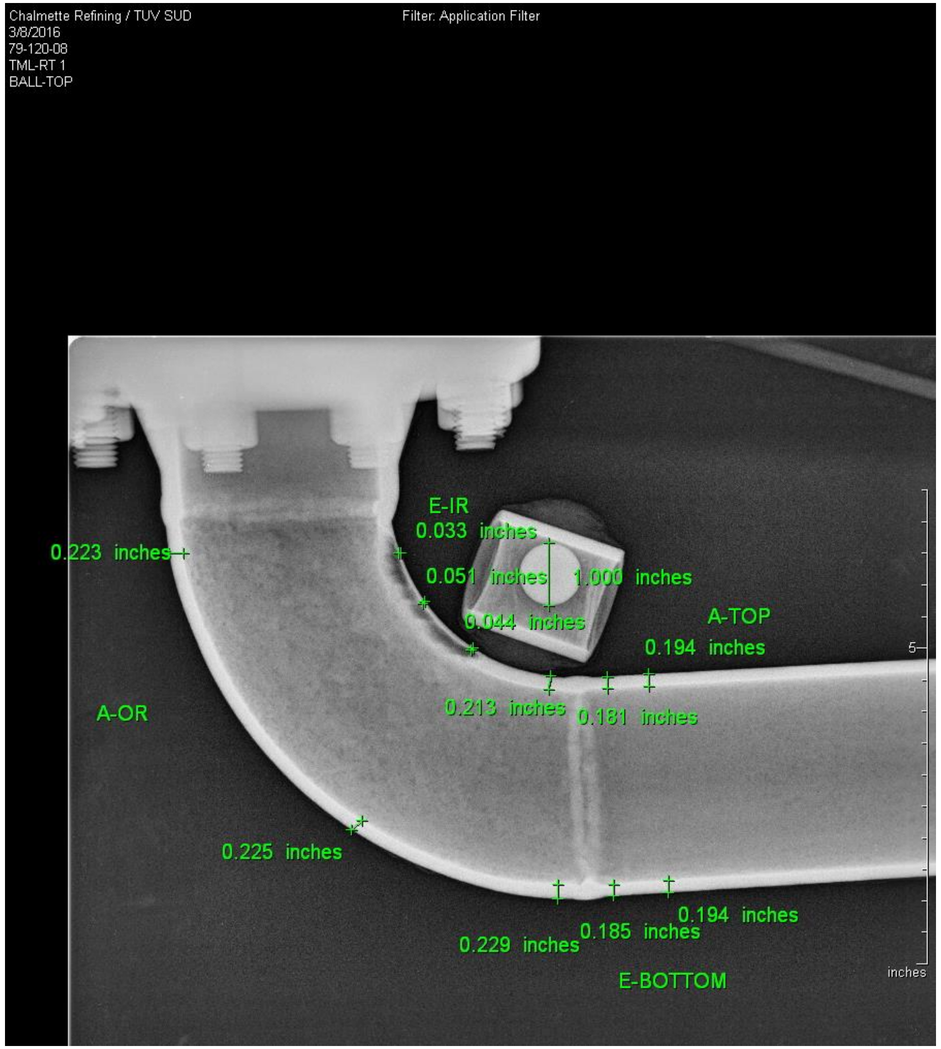
Chalmette Refining / TUV SUD
3/8/2016
79-120-08
TML-RT 1
BALL-TOP
Filter: Application Filter
E-IR
0.033 inches
0.223 inches
0.051 inches
1.000 inches
0.044 inches
A-TOP
0.194 inches
A-OR
0.213 inches
0.181 inches
0.225 inches
0.194 inches
0.185 inches
0.229 inches
E-BOTTOM
inches


Filter: Application Filter

Additional Sharings Site A

- Replaced a good portion of our piping D/S of the defluorinators up to the KOH treaters with Monel including Monel sleeves/distributor in the treater inlet nozzles.
- The KOH treaters themselves are HIC resistant PWHT CS (up flow design). We have just recently been inside the treaters and have seen minor ID surface blistering below the KOH briquette support grating. Treaters were replaced in ~2015 after discovery of step wise cracking.

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