

On-site Quantification of Monoethanolamine in Crude Oils

Sai R Pinappu
COQA 2014 Fall Meeting
San Francisco, CA

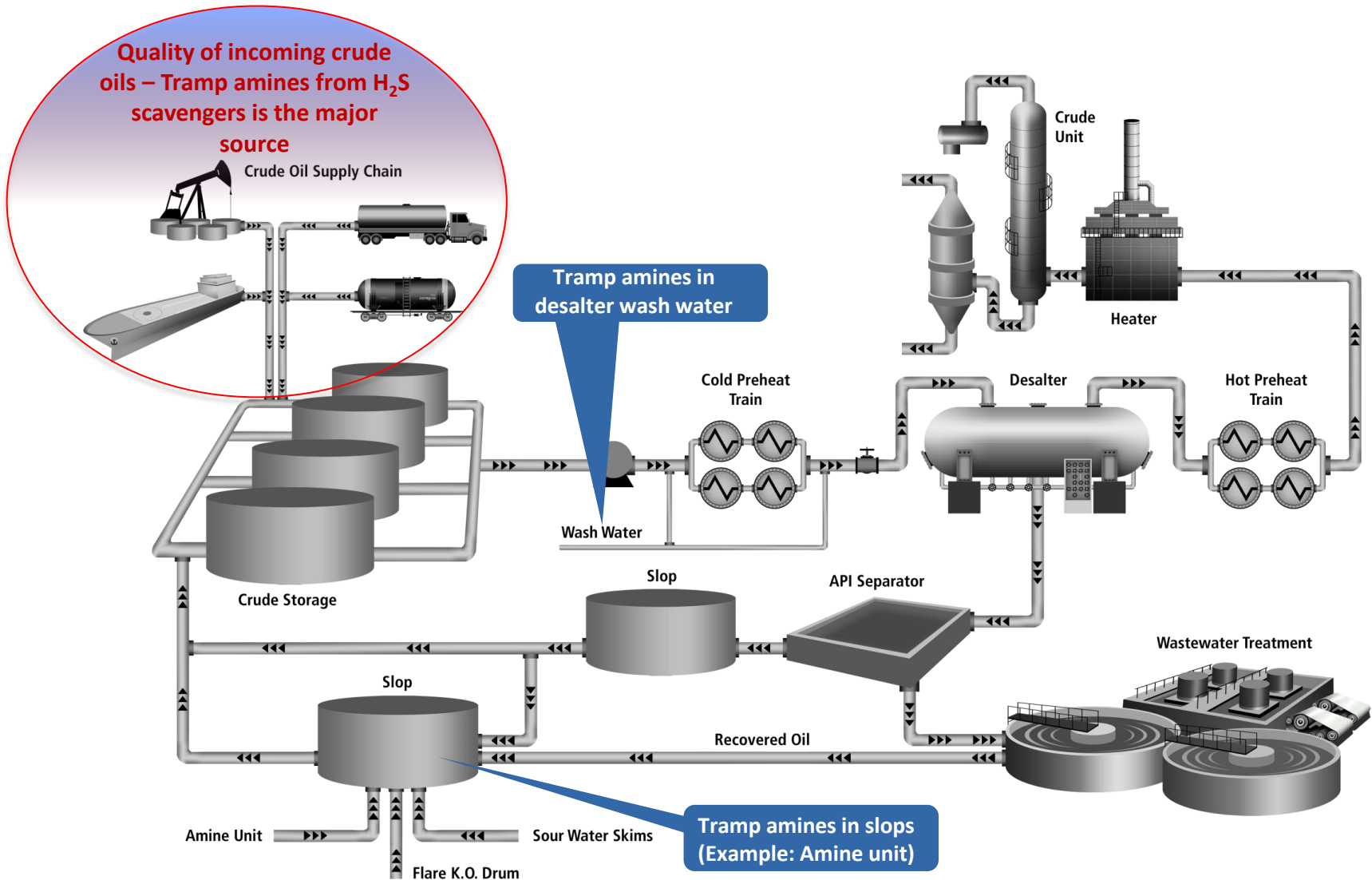


Outline

- Tramp amine sources
- Challenges processing tramp amine contaminated crudes
- Tramp monitoring technologies
- Today's tramp amine monitoring requirements
- Improved solution: TOPGUARD™ field amine measurement services (FAMS)
- Field application



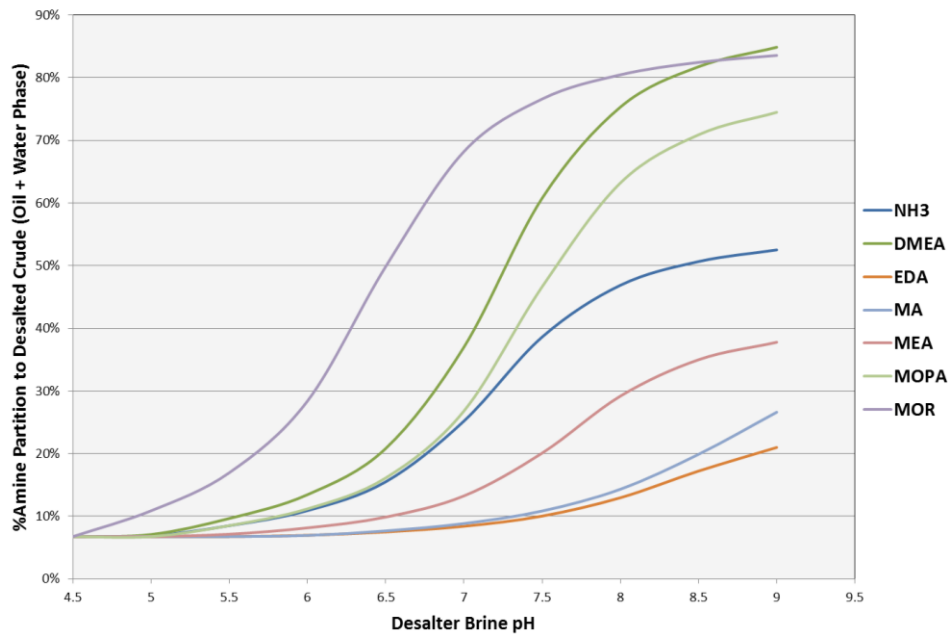
Tramp Amine Sources



Tramp Amines Increase Desalter pH

- Increased partitioning of amines to crude oil
- Stabilized emulsion layer
 - Increased BS&W in the desalted crude
 - Higher chloride concentration in the overhead water
 - $\text{RNH}_2 + \text{HCl} \rightleftharpoons \text{RNH}_3\text{Cl}$

Amine Partitoning Across Desalter



Current Industry Standard Tramp Amine Monitoring Methods

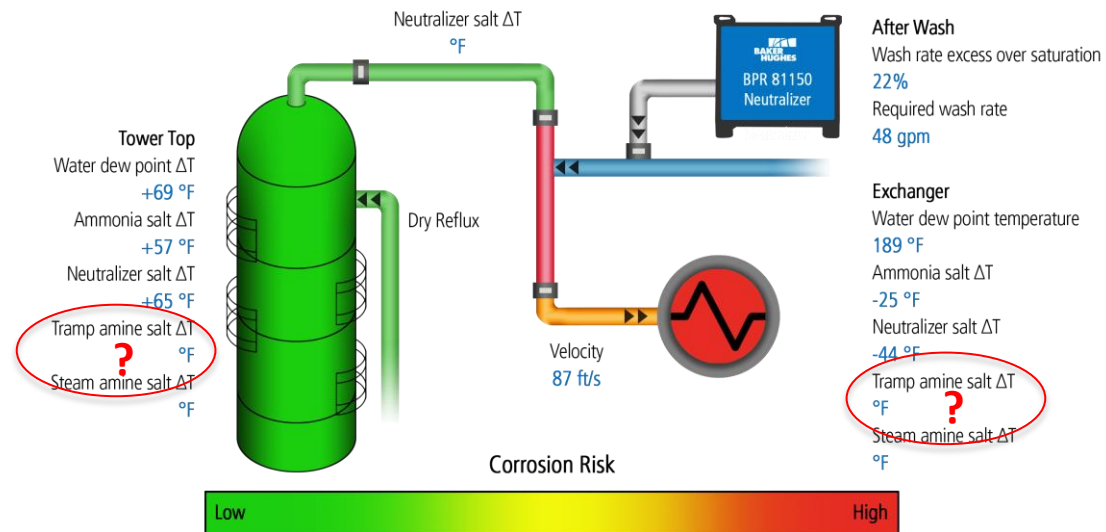
Analytical Technique	Detection Limit	Lab/Field	Interferences/ Limitations	Typical Analysis Time	Specialist Requirement
IC ASTM D6919-09, E1151	0.1 ppm	Lab	Other aliphatic amines, high conductivity ,not specific	1-2 days	Yes
GC/GC-MS ^{1,2}	0.4 ppm	Lab	Nitriles, aromatic amines, derivatization required	1-2 days	Yes
LC ³	0.2 ppm	Lab	Derivatization required	1-2 days	Yes

1. S.Meseguer Llouret., C.Molins Legua., P. Campins Falco., Journal of Chromatography A 978 (2002) 59-69
2. F. Sacher., S. Leng., H,J, Brauch., Journal of Chromatography A 764 (1997) 85-93
3. Y. Moliner Martinez., R. Herraez Hernandez., P. Campins Falco., Journal of Chromatography A 1164 (2007) 329-333

Current Baker Hughes Monitoring and Modelling Capabilities

- Ion Chromatography
 - Modified ASTM method
 - Often takes several days to receive results
- Total Nitrogen method
 - Relies on subtraction of N from neutralizer and NH_3 from the total N
 - If excess N remains, it is labeled “tramp”
 - Does not specify whether tramp N is from MEA
 - Cases where MA is the primary source

Corrosion Risk Monitor



Baker Hughes recognized the need for a new, fast, on-site method to quantify MEA to support enhanced corrosion risk prediction and mitigation.

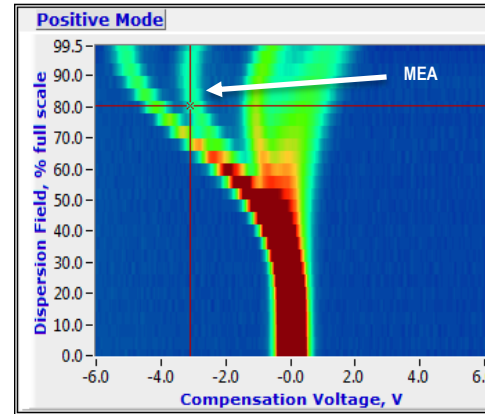
Today's Tramp Amine Monitoring Requirements

- Fast onsite quantification
- Lower detection limits
- Onsite prediction of corrosion risk potential
- Timely mitigation strategies
- Flexibility to use for multiple analytes
- Portable
- Ease of use

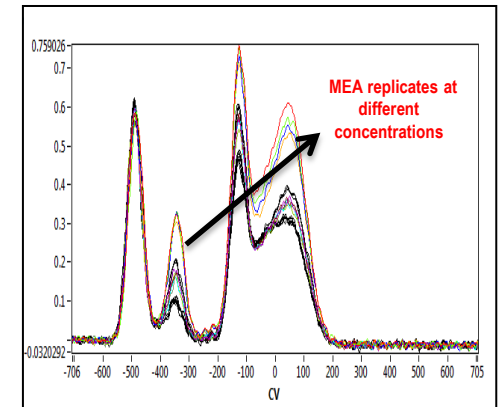


TOPGUARD Field Amine Measurement Services

- Field asymmetric ion mobility spectrometry was identified as potential technology platform
- Developed customized methodology to determine MEA in crude oils
 - Proprietary sample preparation protocols were developed
 - Minimized interferences and increased sensitivity
 - Instrument operating parameters were optimized
 - Proprietary data processing and modeling capabilities are applied



TOPGUARD FAMS SCAN

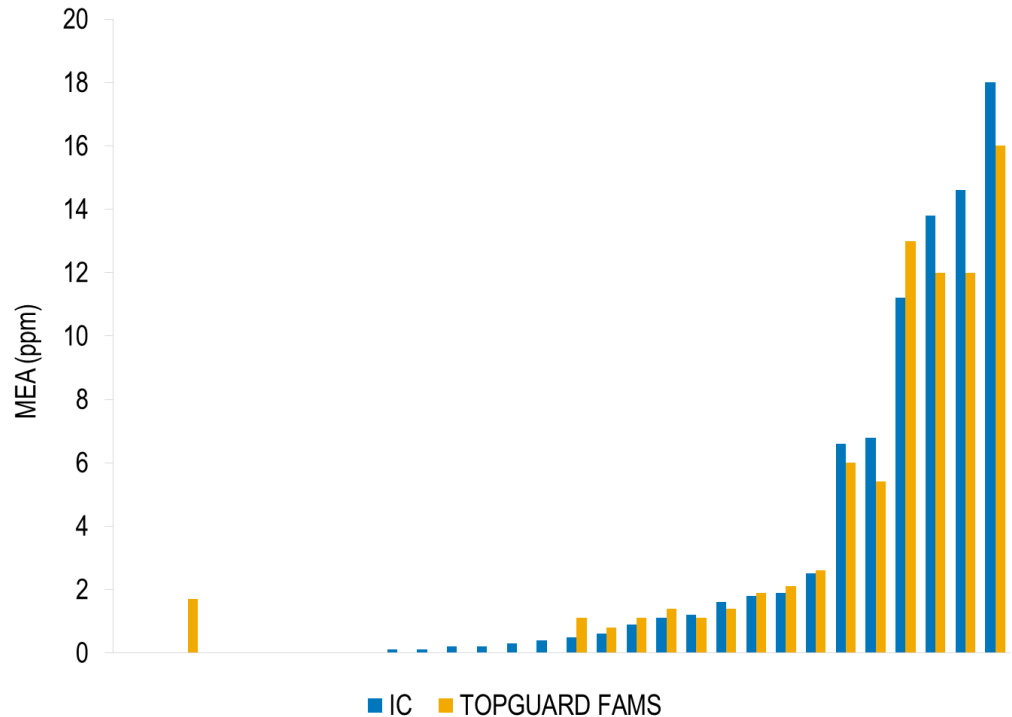


MEAs Detection & Reproducibility at Various Concentrations

MEA peak location identified and quantified down to 1 ppm
with excellent reproducibility ($RSD \leq 10\%$)

TOPGUARD FAMS Correlates with IC

- Good agreement with IC data on crude samples, $\pm 20\%$ of the IC result
- Calculated overhead MEA using TOPGUARD FAMS in agreement with IC
- Detection of MEA down to 1 ppm in crude oils



TOPGUARD FAMS Features & Benefits

Features

- On-site measurement
- Portable
- Fast: 1 hour per sample
- MEA sensitivity down to 1 ppm in crude oil
- Ease of use

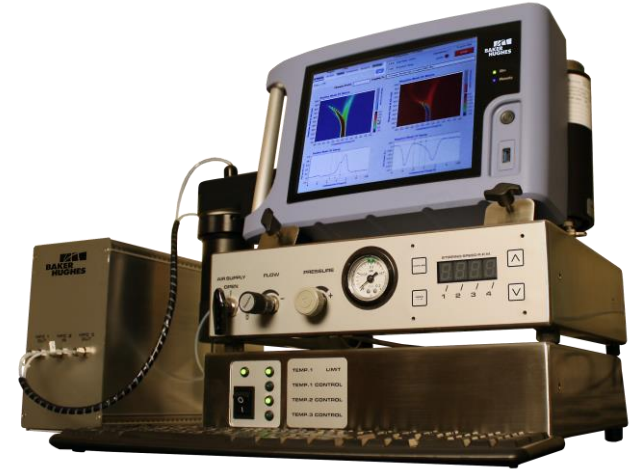
Benefits

- Real-time screening of feedstock for amine content
- Improved prediction of corrosion risk potential
- Flexibility to use for multitude analytes

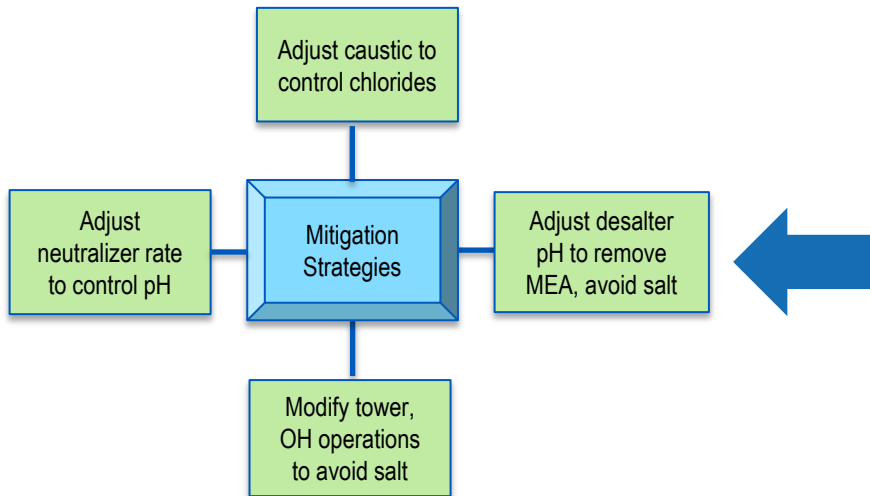
TOPGUARD FAMS – Analysis Process



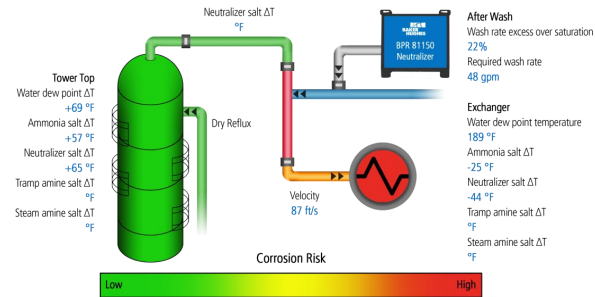
Step 1 - Sample Collection & Preparation



Step 2 - TOPGUARD FAMS Analysis



Step 4 – Determine Appropriate Mitigation Strategy



Step 3 - TOPGUARD CRM Calculations



Mitigation Options

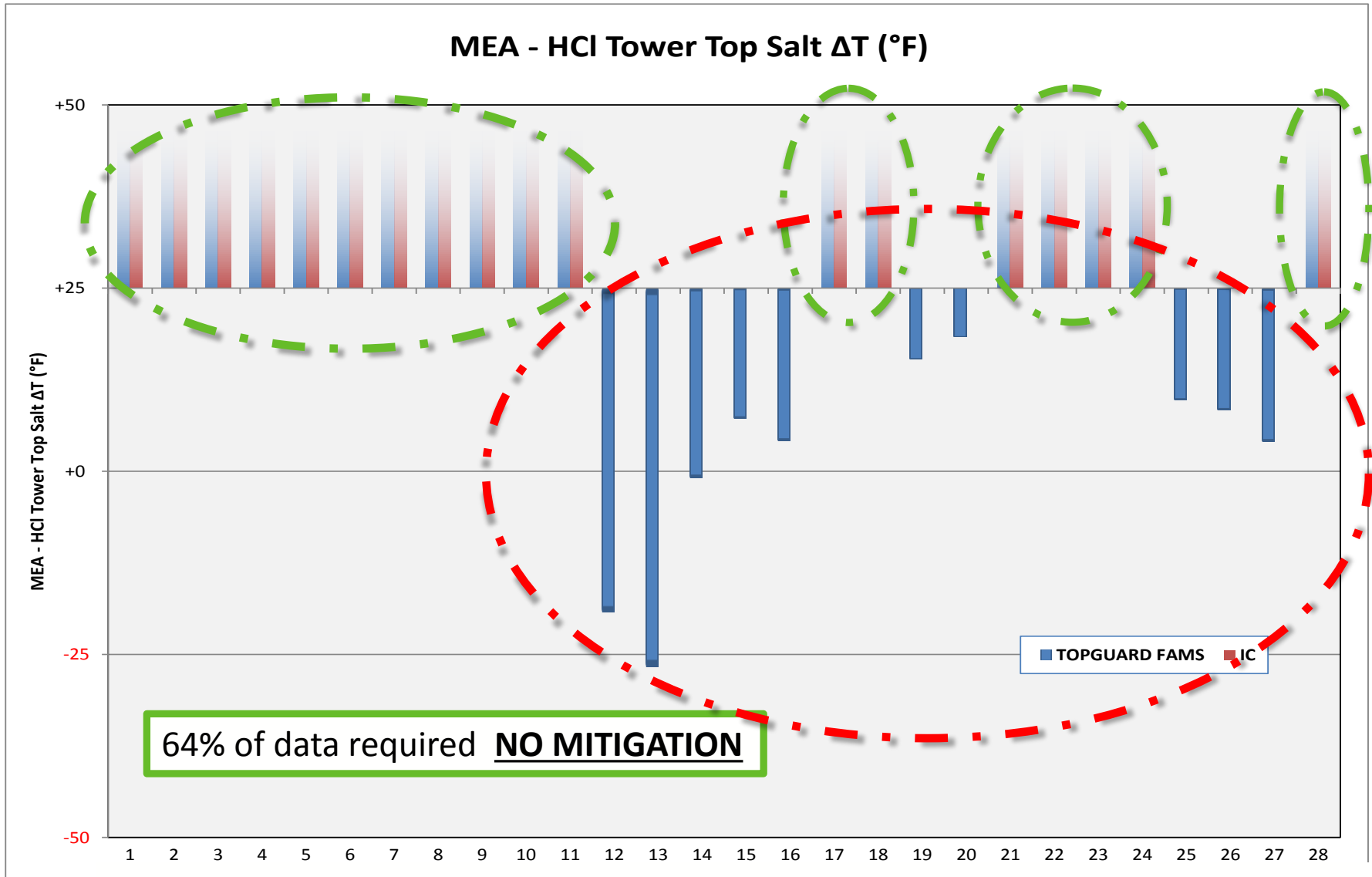
- **Apply caustic**
 - Reduces overhead chlorides, thus reducing MEA –HCl salt formation temperature
- **Use EXCALIBUR™ contaminant removal program**
 - Reduces MEA to the overhead, thus reducing MEA – HCl salt formation temperature
- **Make operational changes (e.g. increase tower operating temperature)**
 - Increases “Salt ΔT ,” thus reducing the risk of salt deposition
 - Often a costly and undesirable option
- **Adjust crude blend ratio**
 - Reduces contaminants to the overhead, thus reducing the risk for salt deposition
 - Often a costly and undesirable option



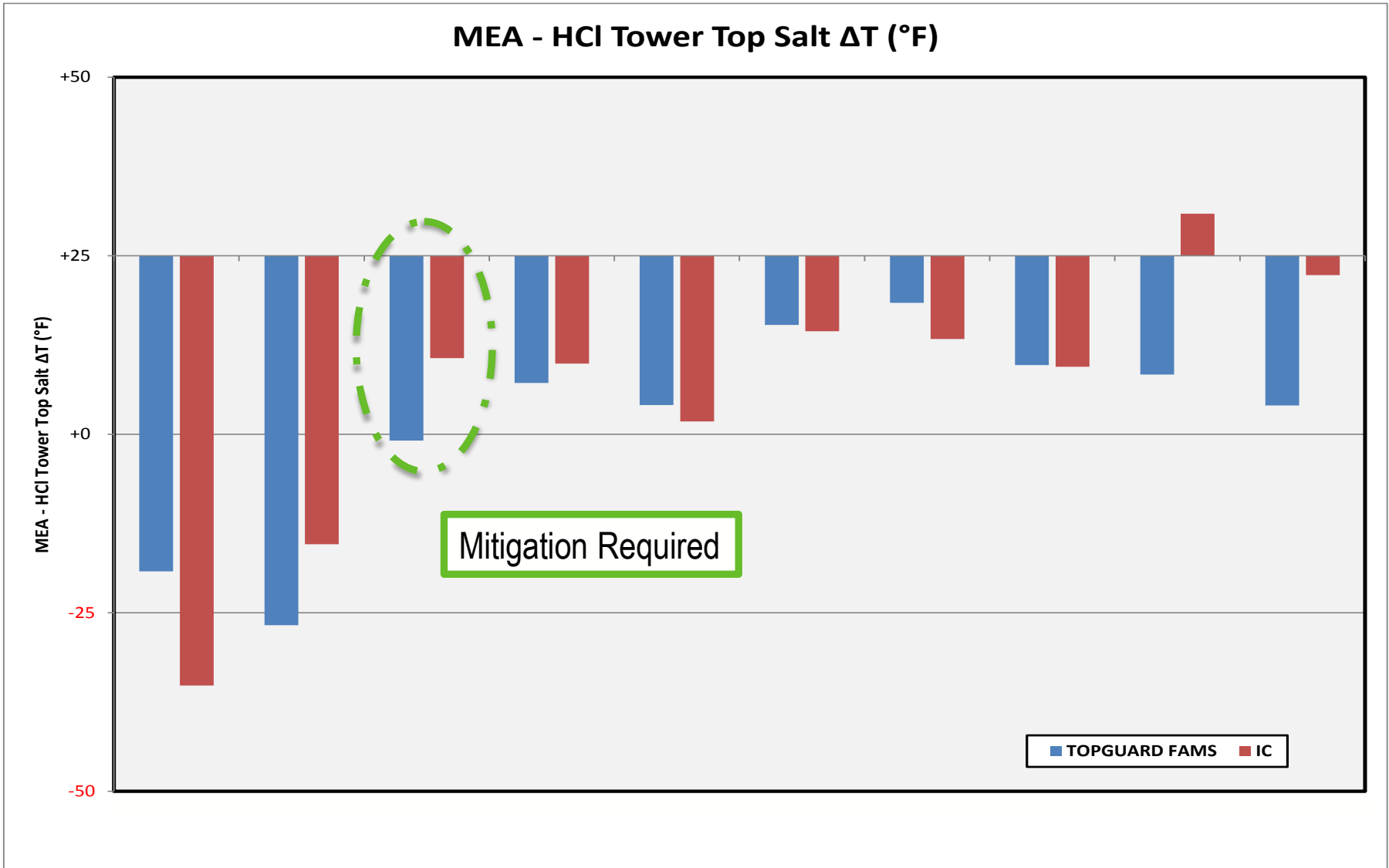
Process Refining Application

Gulf Coast Refinery

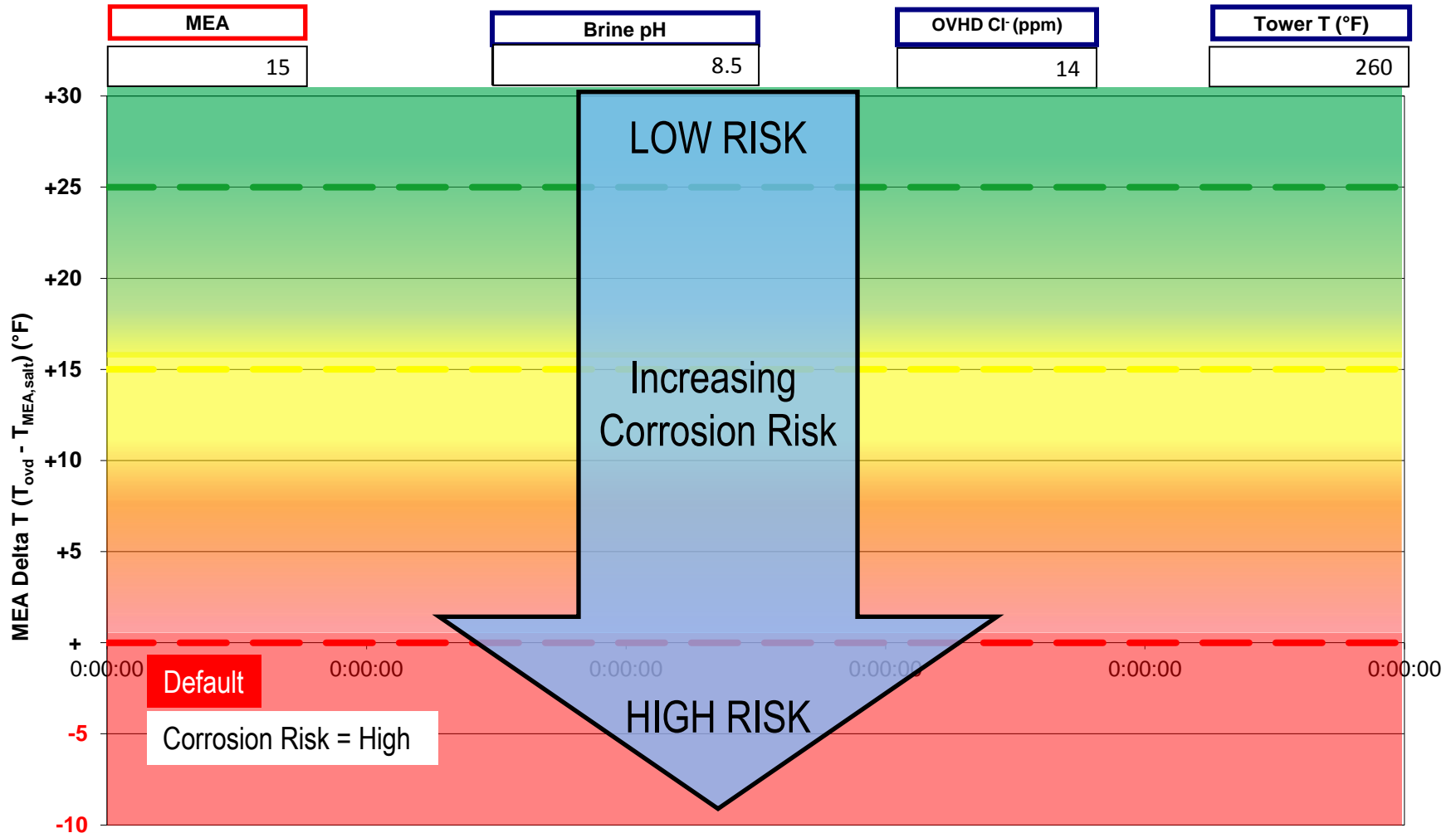
Corrosion Risk Free - No Mitigation Required



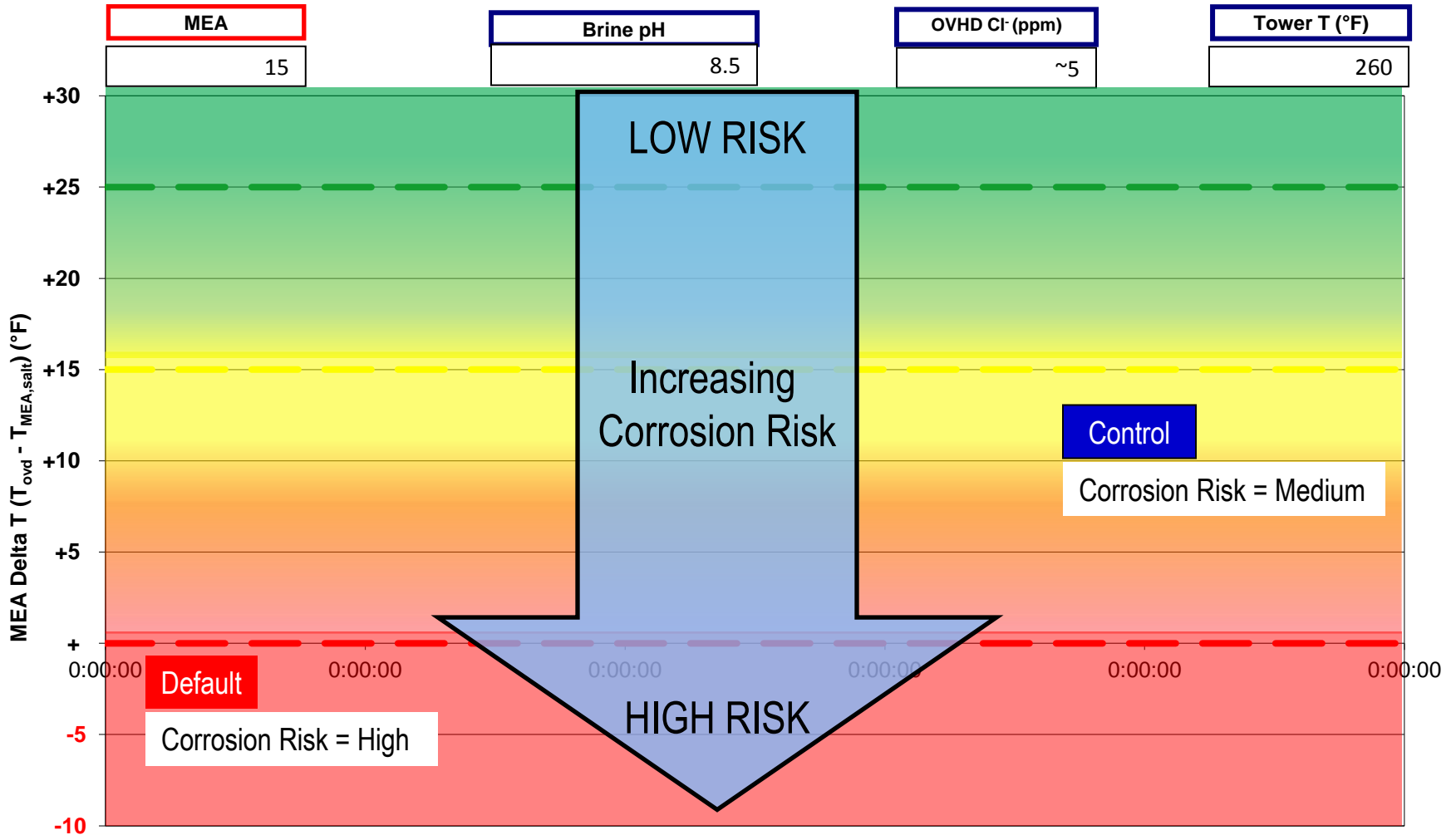
What to Do when Mitigation is Needed



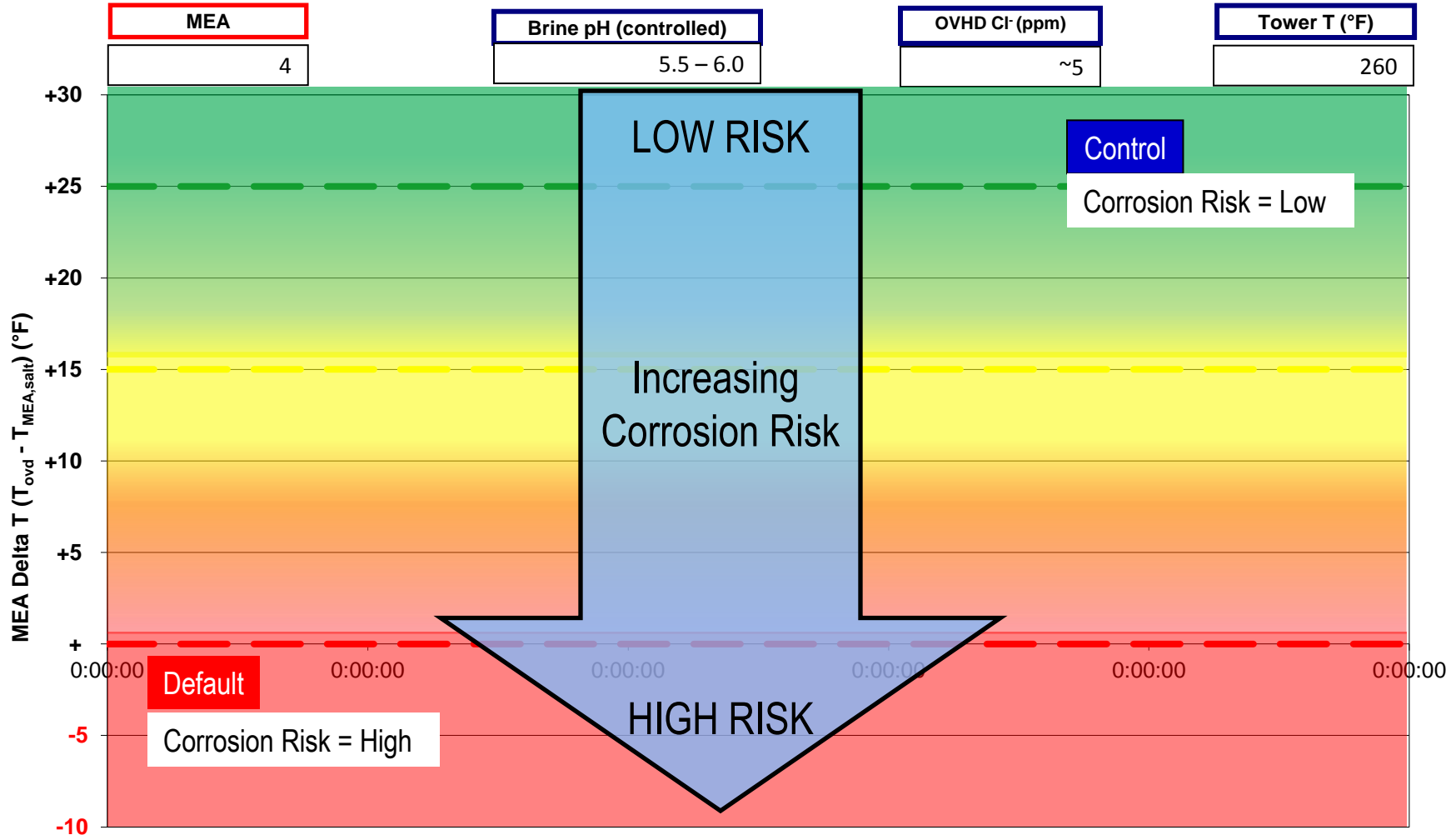
Mitigation: MEA ~15ppm, $\Delta T \sim (0 - 5)^\circ\text{F}$



Mitigation: Apply Caustic



Mitigation: Apply Caustic + EXCALIBUR program



Tramp MEA, MEA-HCI Risk Management

TOPGUARD field amine measurement services provides refiners:

- Quick identification of amine-contaminated crude oils
- Quantification of tramp amines and translation to corrosion risk potential
- Timely implementation of mitigation programs to minimize corrosion
 - Adjustments to crude tower operations
 - Optimization of EXCALIBUR contaminant removal program
 - Proactive planning and blending optimization
- Achievement of targeted operating efficiency and profitability goals

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