BIOGRAPHY

Collin W. Cross
Betz GE Water and Process Technologies

Collin Cross received his Ph.D. in Physical Chemistry from the University of Oklahoma in 1994. During this time he pursued studies of the computational physics of Liquid Crystals. Following this he accepted a postdoctoral fellowship with the Keck Center for Computational Structural Biology in Houston. In 1996 Collin joined Betz/GE Water and Process Technologies as an Analytical Chemist. Since that time he has occupied various roles in R&D, and the Enabling Technologies groups. All of these roles have revolved around supporting process chemicals. Collin now occupies a position in the Technical Marketing organization. His areas of responsibility are for Corrosion Control, Antifouling and Fuel Additives.

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**ABSTRACT**

**High Temperature Corrosion Control and Monitoring for Processing Acidic Crudes**

Collin W. Cross  
Betz/GE Water and Process Technologies

As the importance of heavy crudes and bitumen laden feedstock continues to increase, challenges also continue to increase regarding the ability to process them in a reliable and economical way. Unfortunately, estimations of the possible problems involved with processing these crudes are often fraught with uncertainty. Rules of thumb, experiential based strategies and reactionary tactics have dominated the industry in its approach to managing the associated risks. Due to the complexities involved with these estimations, many refiners adopt a conservative stance regarding the rate at which they utilize discounted crudes, or depend upon capital-intensive upgrades to equipment.

In order to gain the most benefit from heavy feedstock, new strategies and tactics based on data-driven decisions, are needed. By better understanding the interactions between a particular feed and a particular crude unit, it is possible to more accurately estimate the feasibility of successfully processing more challenging feeds. Additionally, the refiner is able to deploy a host of proactive measures allowing him to do so more confidently and reliably.

Better understandings of the complexities of the feeds corrosion potential, as well as the likelihood for this potential to manifest itself in a given crude unit, have been developed recently. Techniques based on these experiences will be discussed which are allowing many refineries to run more aggressive feed slates at higher levels.
High Temperature Corrosion Control and Monitoring for Processing Acidic Crudes

Dr. Collin Cross

Naphthenic Acid Crude Impacts
• Process Management Tool
• Designed to Maximize Refiner:
  – Operational Flexibility
  – Safety
  – Environmental Protection
  – Reliability
  – Profitability
A Complex Process

Naphthenic Acid Corrosion

- Temperature
- Sheer Stress
- Metallurgy
- Acid Characterization & Concentration
- Thermodynamics
- Sulfur
Atmospheric Column Nap Acid Corrosion

Crude Tanks
Slop Tanks

START

To Sat. Gas Plant
Lt. Nap.
Hvy. Nap.
Kerosene
Diesel
Lt. Gas Oil
Hvy Gas Oil
Steam
To Vacuum Unit

To Sat. Gas Plant
Vacuum Unit Nap Acid Corrosion

Crude Atm. Frac. Bottoms

START

1

2

3

Oil/Water Sep.

Lube Unit

FCC Unit

Coker, FCCU, Asphalt Blending

4

Steam

Vacuum Resid

Lt. Gas Oil

Hvy Gas Oil

Vacuum Unit Nap Acid Corrosion
Solution For Processing Naphthenic Acid Crude

**Crude Inputs**
- NAN & TAN
- Fingerprint & Corrosion
- Characterization Sulfur etc.

**Asset Inputs**
- Flow, Pipe Size, Velocity, Temperature, Pipe Configuration and Spatial Relationship, Pipe Geometry, Impingement Factor, Metallurgy,

**Predator Assessment Output**
- Highlight critical impact areas
- Identification of specific priority points within critical impact area
- Monitoring requirements/schedule, location & sensor type
- Analysis requirements/schedule & location
- Chemical injection requirements /chemistry & application
- Baseline conditions & entitlement (expected gain)
- Develop program controls /Data Interpretation / training / documentation & improvements
Predict - Determine the impact before it occurs

Monitor - Measure the asset condition and the rate of change

Control - Implement corrective actions to maintain the asset integrity and optimize process efficiencies
Total Acid Number vs. Nap. Acid Number Number

- Crude
- 350/500
- 600/650
- 750/900

TAN (Total Acid Number) and NAN (Nap. Acid Number) comparison for different fractions.
Predict

TAN Vs. NAN

TAN VS NAN

Kerosene
0.75 mg/g Vs. 0.35 mg/g

Diesel
1.74 mg/g Vs 0.96 mg/g

AGO
1.95 mg/g Vs 1.09 mg/g

Crude Charge
1.34 mg/g Vs. 0.93 mg/g

To Vacuum Unit

Vacuum Resid
0.89 mg/g Vs 0.12 mg/g

Hvy Gas Oil
1.74 mg/g Vs 1.54 mg/g

Lt. Gas Oil

TAN

- Organic & inorganic acids
- Esters
- Phenolic compounds
- Lactones
- Resins
- Salts of weak acids (soaps)
- Basic salts of polyacidic bases
- Salts of heavy metals
- Additives--i.e., inhibitors & detergents

TAN Vs.

NAN

Predict

5th NCUT Upgrading and Refining Conference 2009
Predict

Crude Oil Assessment

Crude A

Crude B

Crude C
Sulfide Inhibiting Effect

Corrosion of CS and SS at TAN = 5.0
Predict Predator Assessment

• Tools to develop strategies for processing opportunity crude
  – Opportunity Crude Oils
  – Monitoring Program
  – Chemical injection Points
  – Operating parameters

• Establishes
  – Base line conditions
  – Opportunity Improvement
  – KPI
  – Criteria for success
  – Plans for continuous improvement
Impingement Factor & Velocity

Pumps

Downstream of Welds and orifice plates

Pipe Bends
Especially with Thermocouple Points

Thermo Couple

Control Valves
Refinery piping configuration obtained during Predator Assessment

Pipeline configuration simplified in terms of components and geometry

Corrosion models developed for individual components

- Corrosion potential
- RCM placement
- Chemical injection locations
#### Predator Assessment

<table>
<thead>
<tr>
<th>Asset</th>
<th>From</th>
<th>To</th>
<th>Temp</th>
<th>Metallurgy</th>
<th>TAN mg/KOH</th>
<th>Velocity ft/sec</th>
<th>Prior 1-10</th>
<th>Calc Risk</th>
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</thead>
<tbody>
<tr>
<td>Piping</td>
<td>G-46 Discharge Expander</td>
<td>E-7 Heat Exchanger</td>
<td>680 F</td>
<td>9 Cr</td>
<td>0.3</td>
<td>6.0</td>
<td>7.4</td>
<td>Treat</td>
</tr>
</tbody>
</table>

**Risk Area & Justification**

Priority: Piping -- JUSTIFICATION: Temperature, Flow Impingement

<table>
<thead>
<tr>
<th>Circuit/Segment</th>
<th>Asset Class</th>
<th>From</th>
<th>To</th>
<th>Pipe Size</th>
<th>Pipe Spec</th>
<th>Schedul e</th>
<th>Physical Stat</th>
<th>Inlet Deg F</th>
<th>Outlet Deg F</th>
<th>Metallurgy</th>
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<tr>
<td>AGO</td>
<td>Piping</td>
<td>G-46 Discharge</td>
<td>E-7 Heat Exchanger</td>
<td>4.0</td>
<td>HAZ-NC</td>
<td>40</td>
<td>Liquid</td>
<td>680</td>
<td>680</td>
<td>9 Cr</td>
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<table>
<thead>
<tr>
<th>Flow BPD</th>
<th>Bulk Velocity ft/sec (75)</th>
<th>Predicted TAN (Based on Feed) mg/l</th>
<th>Predicted d N/N</th>
<th>Priority Areas</th>
<th>Calculated Priority</th>
<th>Priority Justification</th>
<th>Monitor ing</th>
<th>Location of Monitoring</th>
<th>Chemic</th>
<th>Injection Point</th>
<th>Inspection History</th>
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<tbody>
<tr>
<td>5,800 BPD</td>
<td>5.0 ft/sec</td>
<td>0.29</td>
<td>0.25</td>
<td>Piping</td>
<td>7.39</td>
<td>Temperature, Flow</td>
<td>RCM &amp; UT</td>
<td>Pump discharge prior to expansion</td>
<td>Upstream</td>
<td>Upstream</td>
<td>&lt; 5.0 mpy</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulfur</th>
<th>S/N Ratio</th>
<th>S/NAN Ratio</th>
<th>Imp Factor</th>
<th>Iron</th>
<th>Nickel</th>
<th>Fe/Ni</th>
<th>Geomet ry</th>
<th>Predicted Corrosion Rate</th>
<th>Segment Identification</th>
<th>Drawing Number</th>
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<td>0.77</td>
<td>2.7</td>
<td>3.1</td>
<td>12.5</td>
<td>0.9</td>
<td>0.2</td>
<td>5.3</td>
<td>30.0</td>
<td>5.6 mpy</td>
<td>1110</td>
<td>10A</td>
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</table>

**Monitoring:** RCM & UT
Monitor

Fully Integrated Suite Covers Sensor Gaps

RCM

Hi Temp UT

Odometer

Integrated Measurement

Guided Acoustics

Fe / Ni Ratios

Rate Measurement

Probes / Coupons

PCOM

Global (less sensitivity)

Local (more sensitivity)

PCOM Plus

Hydrogen Diffusion

Speedometer

5th NCUT Upgrading and Refining Conference 2009
**Predator™ Resistance Corrosion Monitor**

- High temperature capability > 950 F
- Able to install without shutdown
- Calculates wall thickness by measuring the electrical resistance and comparing to the initial baseline
- Fully automated operation

- Measures 2% change in wall thickness with 6-Sigma accuracy
- Patented technology designed to eliminate electronic noise
- Optimum Coverage 1 Square Meter
RCM Terms

- Pin Matrix
- Reference Plate
- Pin Array
- Channel
- R_c
- Pin

RCM Response or output → Voltage measured between adjacent pins
Monitor

Sample Thickness Report

Plotting Threshold

Sample RCM Report

Remaining Wall

Wall < 320 mils
Start Date: 2/3/2005
Stop Date: 6/14/2005

Time Interval

Monitor
Monitor

RCM Corrosion Rate Report

- Each channel corresponds to unique real estate on pipe surface.
- Exception Reporting → Only channels above a threshold are plotted.

Sample RCM Report
Corrosion Rate > 5 MPY
Start Date: 2/3/2005
Stop Date: 6/14/2005
Monitor

Baseline Performance

AGO Corrosion-RCM & CFD

<table>
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<tr>
<th>Year</th>
<th>Wall Loss (mil)</th>
<th>Corrosion Rate (mpy)</th>
<th>Remaining Service Life</th>
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<tr>
<td>18</td>
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<tr>
<td>17</td>
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<td>1.9</td>
<td>3.2</td>
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<td>1.6</td>
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<td>1.7</td>
<td>2.9</td>
<td>2.0</td>
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<tr>
<td>14</td>
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<tr>
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</table>

~ One year data from the RCM indicates a maximum wall loss of 11 mil, a maximum corrosion rate of 11 mpy and 29+ years remaining service life.
Monitor

Baseline Performance

Corrosion Tower Shell

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<tr>
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</table>

21.4 mpy represents nominal 2.4% wall loss and indicates 17+ years remaining.
Control

- Blending
- Phosphate Ester “Best in Class”
- Non Phosphorous - Phosphorous efficacy without the fouling or catalyst poisoning
- New patent pending molecules
Effect of Inhibitor Type on Corrosion Rate

Control Phosphate Ester Comparisons

Conditions:
VEN LVGO, 600 F, 1018CS
100 ppm active
Control

ER Probe
Data Predator
61N

HVGO Corrosion

Patented Predator
61N
Started

Date

3-Jan 17-Jan 3-Feb 17-Feb 2-Mar 11-Mar 25-Mar 30-Apr 20-May 12-Jun 6-Jul

HVGO
Control

Fe / Ni Data
Predator 61N

Date

Fe/Ni Ratio
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45

Patented Predator 61 N Started

Desalted Crude
Vacuum Resid
Control  Case History  Predator 6tN1401

Atmos Tower

Atmos Bottoms

1.50
1.53

2.23
2.40

Diesel

Vacuum Tower

AGO

LVGO PA

2.20
2.65

1.96
2.47

HVGO

VTB

0.24
1.00

NAN
TAN
AGO Stream Corrosion - Previous Competitive Phosphorous Program

Case History 6N1401

Control

3 Week Rolling Average

Corrosion

0 5 10 15 20 25

1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Delivers

- Safety
- Environmental Protection
- Reliability
- Operational Flexibility
- Profitability