Appendix 6

Genguard and advanced cooling solution

Roy Holliday (GE)

Minutes of EFC WP15 Corrosion in the Refinery Industry 23 April 2009

Corrosion Inhibition in Cooling Water



GE Water & Process Technologies

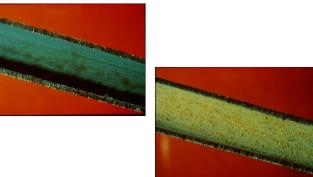
Roy Holliday April 2009



imagination at work

What do you need to inhibit corrosion?

Corrosion inhibitor(s) Is that all?



The right water chemistry for the corrosion inhibitor?

Better - The correct corrosion inhibitor for the water chemistry and metallurgies!

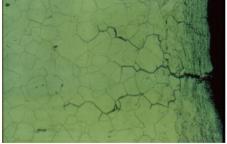
Maintain solubility and/or activity of the corrosion inhibitor(s)



Do you need anything else?

Stress corrosion cracking **Inhibitor**? Control concentration of causal chemical Metallurgy **Cleanliness!**

Under deposit or crevice corrosion Inhibitor **Cleanliness!** Pitting corrosion and tuberculation Inhibitor Cleanliness!





GE CONFIDENTIAL AND PROPRIETARY

magination at work

Summary

Corrosion inhibitor Suited to Metallurgy Water Chemistry **Treatment Programme** Suited to Metallurgy Water Chemistry System Design System Operation

Corrosion Inhibition Maintain inhibitor(s) soluble Scale Inhibition Deposit Control



Neutral pH

- Phosphate
- Zinc Phosphate





Alkaline pH

- Phosphate
- Zinc
- Zinc Phosphate
- Organic
- Molybdate

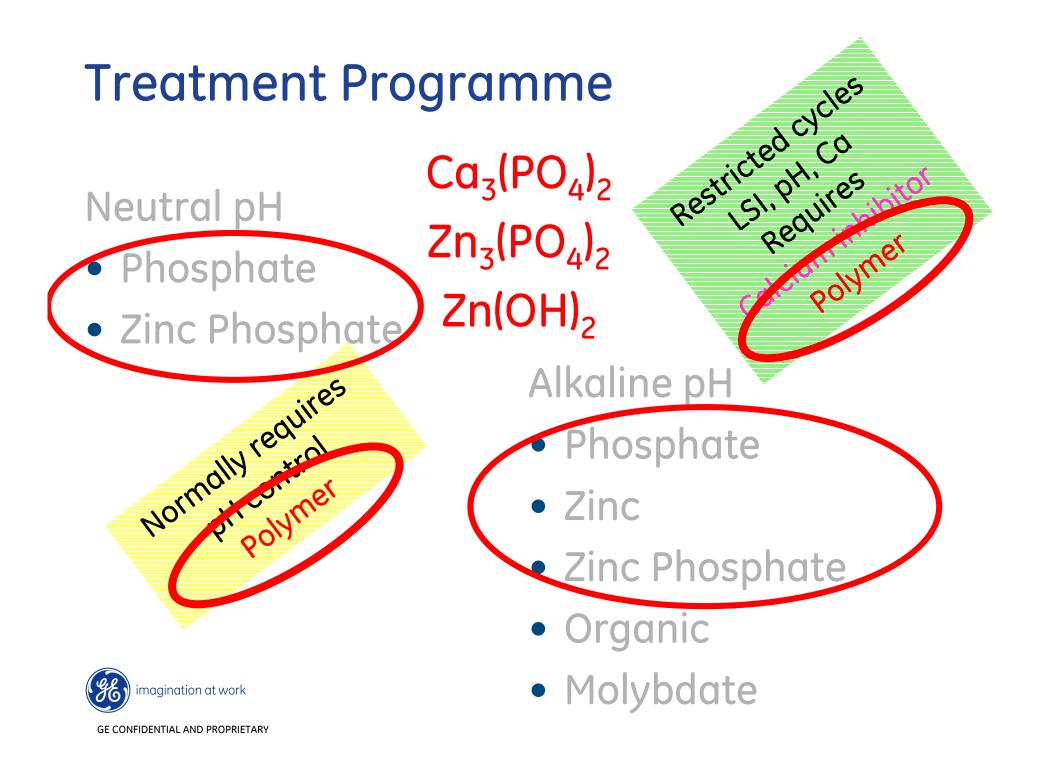
CaCO₃ inhibition

- Restricted CV Restricted CO LSI. PH. CO Requires - Traditionally Phosphonates
 - LSI limitation +2.5
- AEC
 - Contains no P
 - LSI up to +2.85

Alkaline ph

- Phosphate
- Zinc
- Zinc Phosphate
- Organic
- Molybdate





Polymer is a key component



-1 your the Growth Growth



Functionality

Keep corrosion inhibitors soluble/available

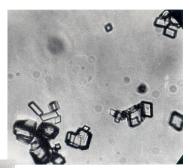
- Scale Inhibition

Deposit control

- Dispersion



What is the result of an effective Crystal Growth Inhibitor?



Small deformed crystals

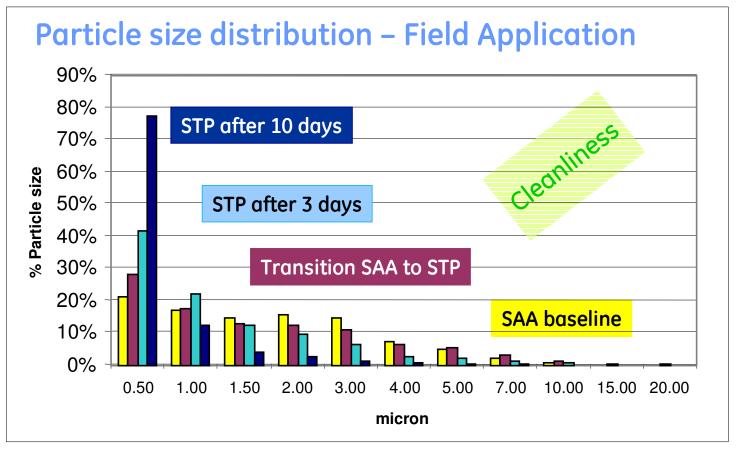
Easily dispersed Kept in suspension







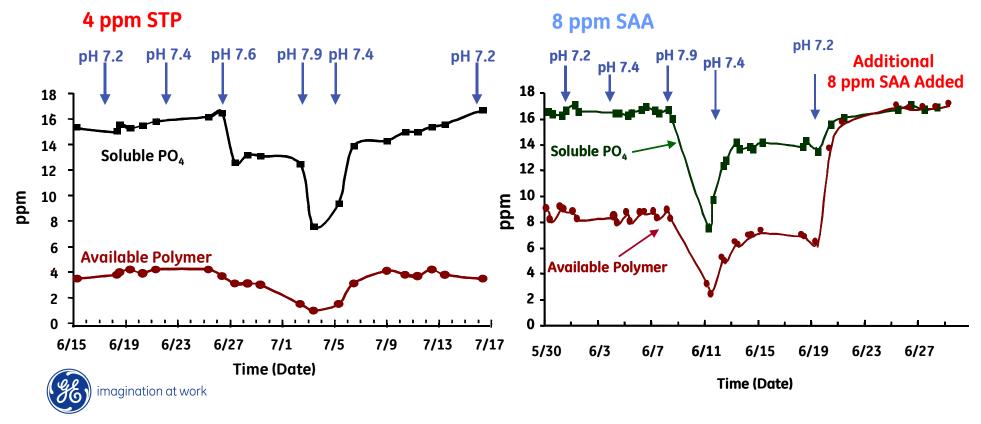
Crystal Growth Inhibitor



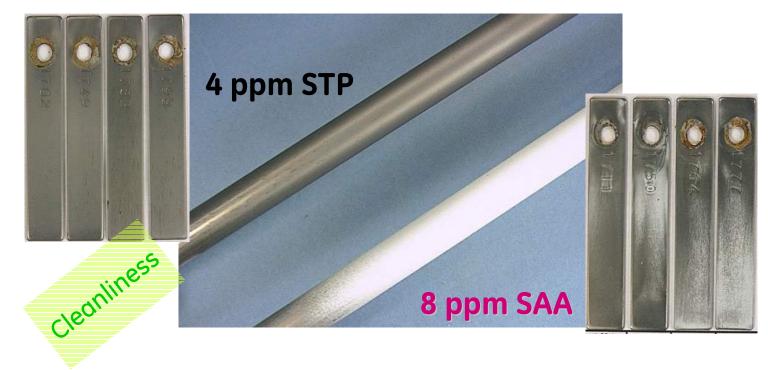
STP polymer generated much finer particles than the SAA polymer resulting in a lower potential for scale formation / precipitation



Effect of pH Excursion on Calcium Phosphate Control Neutral pH programme

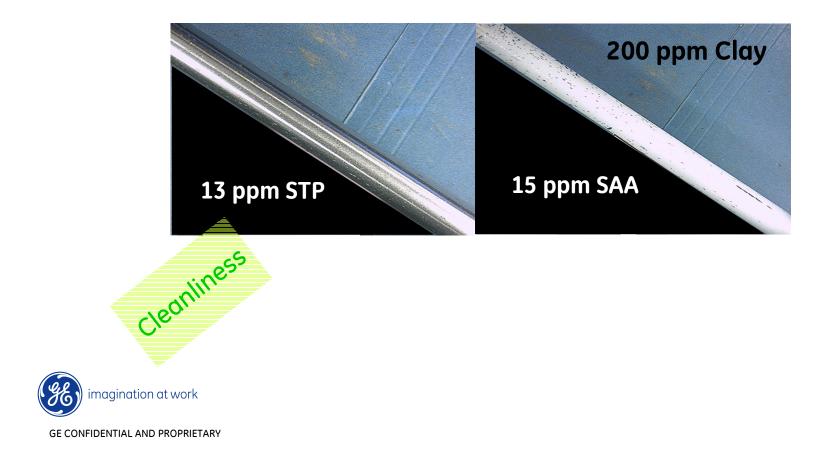


Effect of pH Excursion on Calcium Phosphate Control Neutral pH programme





Dispersion of Suspended Solids



Testing and Monitoring

Polymer Monitoring and Control

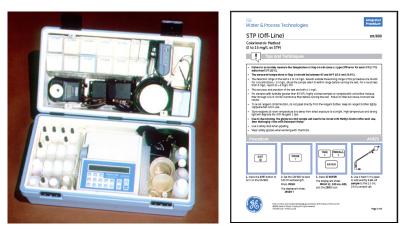
On Line

TrueSense

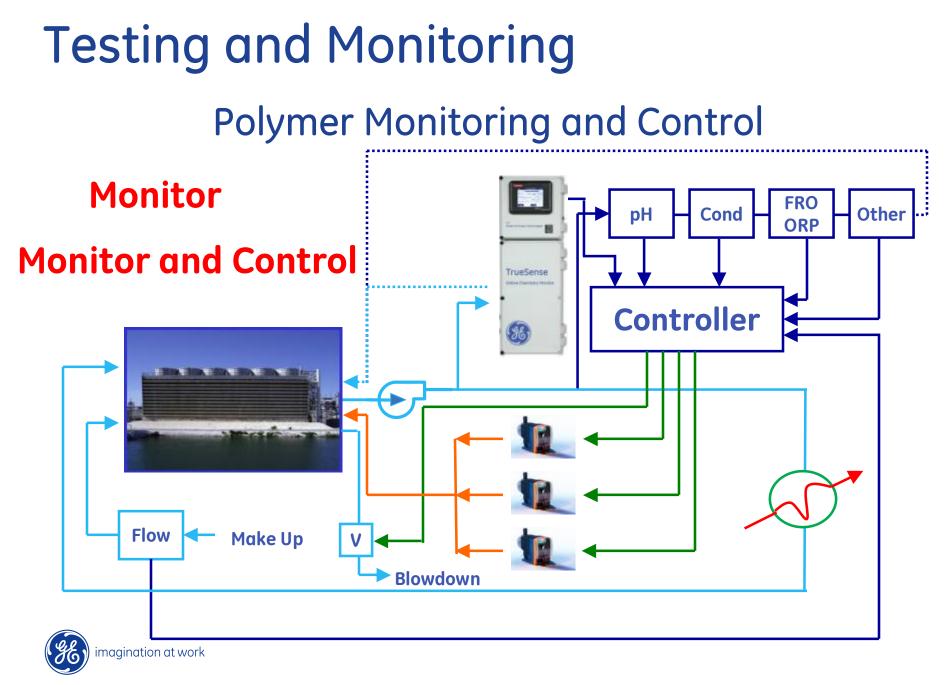
Online Chemistry Monitor

- Measures the polymer directly
 - No background fluorescence issues
 - No molybdate tracer to measure
 - No additional chemical manufacturing costs
- Simple calibration
- Responds to System Stresses

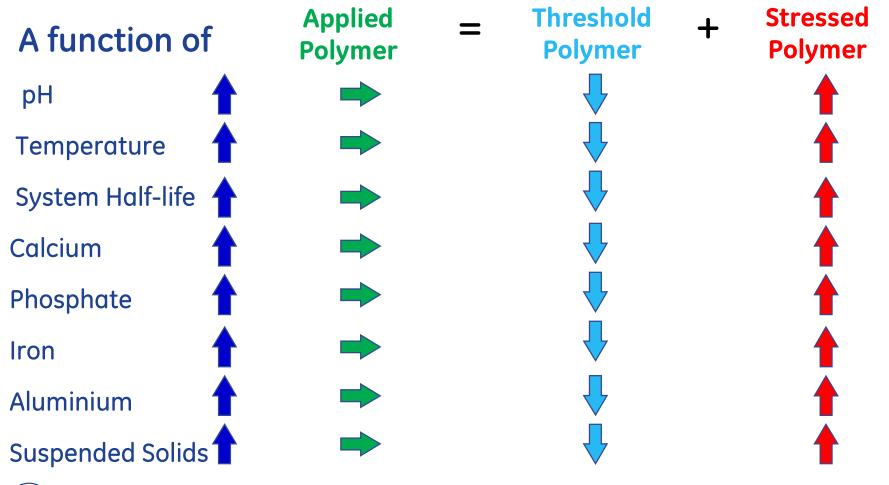
Off Line





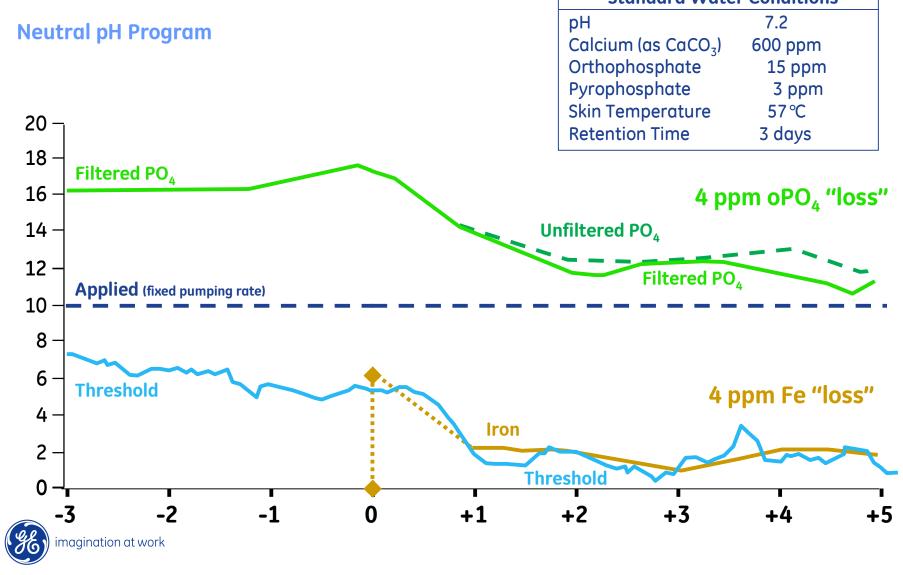


Threshold Polymer Concentration

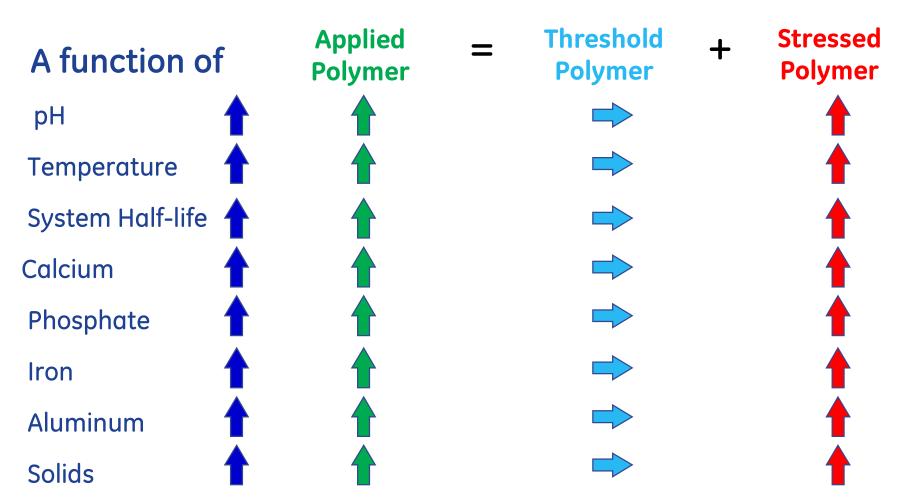




TrueSense Online Dynamic Laboratory Study Without Polymer Control

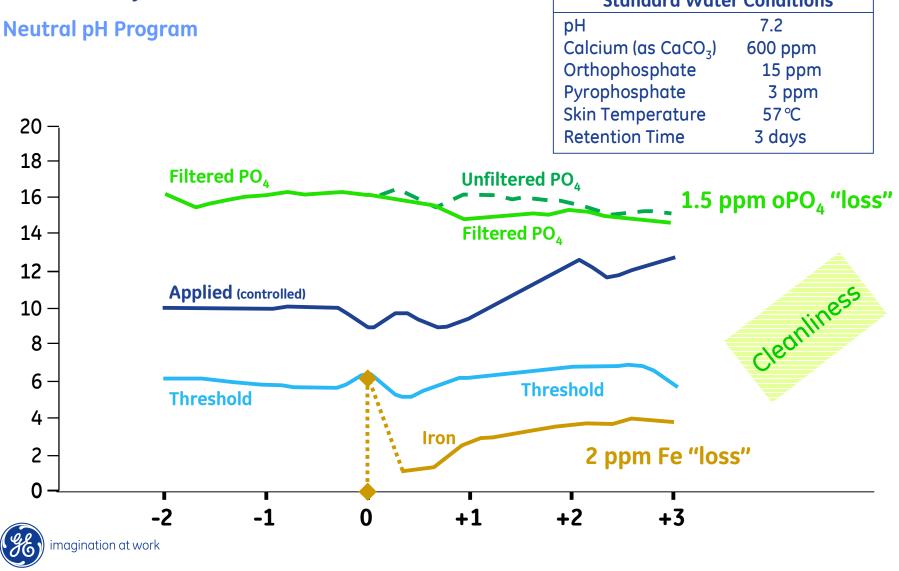


Threshold Polymer Concentration





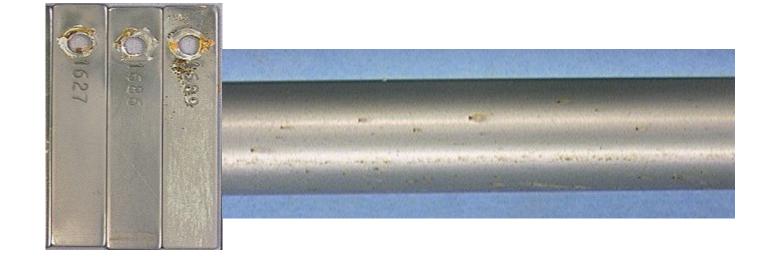
TrueSense Online Dynamic Laboratory Study With Polymer Control



And Corrosion Inhibition?

4 ppm SAA

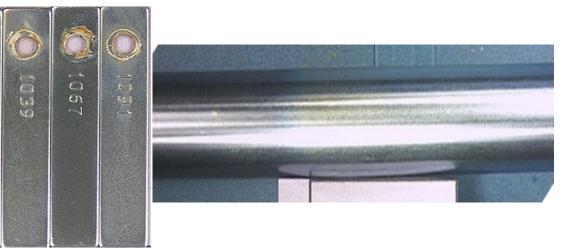
LCS - 0.6 mpy ADM - 0.2 mpy



2 ppm STP

LCS <0.5 mpy ADM <0.2 mpy





GE Advanced Cooling Solution



What is GenGard?

 Features GE's patented Stress Tolerant Polymer (STP)

• Superior Performance

- Under Neutral pH Conditions
- Under Alkaline pH Conditions
- Halogen Stable
- Analysable
 - Off-line
 - On-line

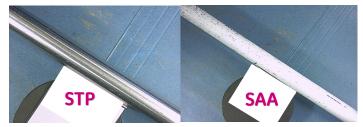
• No Heavy Metals



GenGard / STP Technology Benefits

Improved Productivity & Equipment Reliability

Superior Performance Phosphate Inhibition Zinc Inhibition pH upset recovery Crystal particle size Dispersion





GenGard / STP Technology Benefits

Reduce Chemical Usage



Active polymer concentration



GenGard / STP Technology Benefits

Threshold polymer concentration Controlled dosing Relative to requirements Responsive to variations and demands

Optimum and Controlled Dosing







Appendix 7

Max Amine acid gas removal program

Andre Vanhove (GE)

CORROSION CONTROL IN REFINERY AMINE TREATING UNITS

GE Water & Process Technologies

0

David Owen Andre Vanhove

Types of Amine Systems

Primary Amine Unit

Tail Gas Unit

Hydrogen Plant Amine Unit

Natural Gas Plant

Sulfiban Unit



Removes H₂S and CO₂

Removes H₂S Selectively

Removes CO₂

Removes H₂S and / or CO₂

Removes H₂S, HCN & CO₂

Key Operating Variables

Pressure

Temperature

- Amine Concentration (wt%)
- **Amine Circulation Rate**
- Hydrocarbon Feed Rate (gas or liquid)
- Hydrocarbon Composition
- **Steam Rate**



Absorption-Regeneration Acid Gas Absorption (High P, Low T)

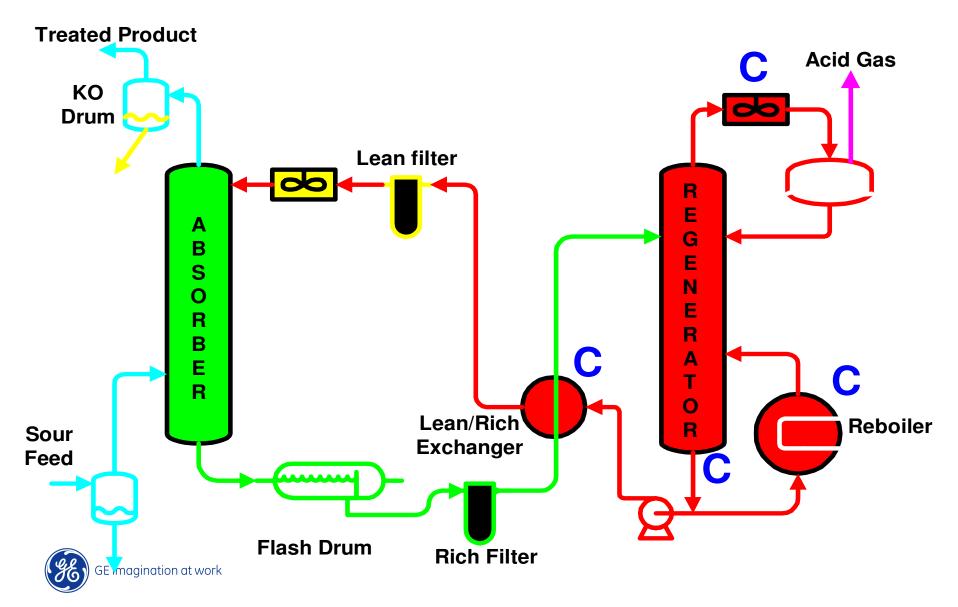
H_2S + Amine ---->> Amine-H⁺ + HS⁻

Amine Regeneration (Low P, High T)

H_2S + Amine <<---- Amine-H⁺ + HS⁻



Areas of Corrosion



Types of Amines

Common Amines

- MEA Monoethanolamine
- **DEA** Diethanolamine
- **DIPA** Diisopropanolamine
- **MDEA** Methyl Diethanolamine
- DGA Diglycol Amine

Formulated & Blends

Selection Criteria

- Bulk or Selective Acid Gas Removal
- Mercaptan Removal
- Required Heat Duty
- Required Concentration
- Hydrocarbon Solubility
- Ease of Reclaiming
- Cost



Corrosion Overview

Causes

Areas

Symptoms

Control Measures



Causes of Corrosion

- Rich Amine Flashing
- •Lean Loading
- •Circulation Rates and Velocities
- •Heat Stable Amine Salts
- Amine Degradation Products



Areas of Corrosion

Reboiler/ Regenerator bottom piping

> Temperature, Low amine pH, HSAS dissociation , Degradation products, Lean loading too high or low

L/R Exchanger Lean Side

> Temperature, HSAS dissociation, Lean loading, Circulation rate

L/R Exchanger Rich Side

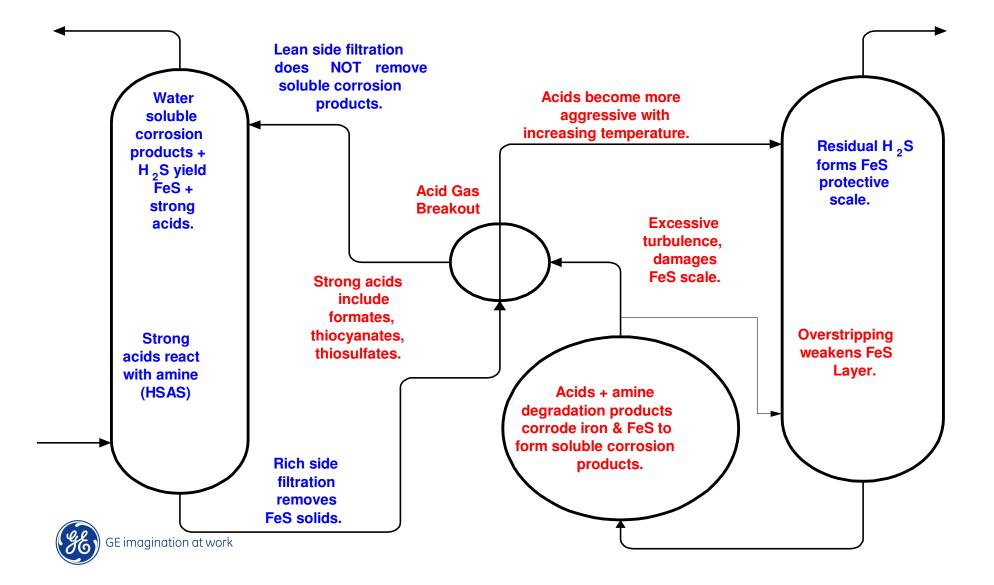
> Rich loading, Pressure reduction, Free acid gas, Circulation rate

Overhead Condenser

> Salt - Ammonium bisulphide - under deposit



Corrosion & Fouling Cycle



Symptoms of Corrosion

- •Amine leaks and Increased consumption
- Off spec products
- Diluted amine
- •High metals concentrations Fe, Mn, Ni, Cr
- Fouling
- Increased filter changes
- •Grey-black amine colour
- Foaming



Corrosion Control Measures

- **Operational Issues**
 - > Feed Preparation
 - > **Temperature**
 - > Steam Rate
 - > Pressure Changes
 - > Amine Concentration and Circulation Rate
 - > Oxygen Elimination



Corrosion Control Measures

- •Regular Analysis of the lean amine
- •Install Corrosion Probes /coupons
- Proper filtration
- •HSS Management Programme
- Metallurgy and Fabrication
- Upstream Operations
- Corrosion Inhibitors



CORROSION CONTROL IN REFINERY AMINE TREATING UNITS

GE Water & Process Technologies

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David Owen Andre Vanhove

Appendix 8

Update on active corrosion scenarios in refineries assessed by hydrogen flux monitoring Frank Dean (Ion Science)



Hydrogen flux: correlation with corrosion and hydrogen damage risk in refineries.

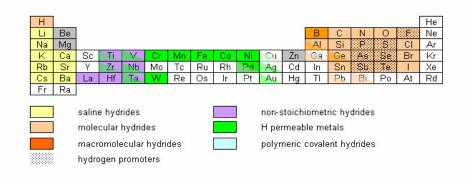
EFC WP 15 Spring Meeting, Borealis, Wien, 23 April, 2009.



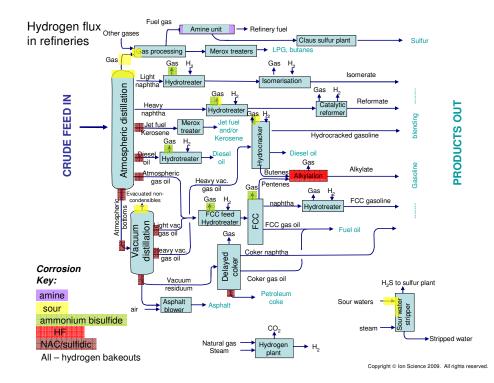
Advanced Gas Sensing Technologies

Hydrogen Hydrogen flux in refineries Linking flux with corrosion and crack risk Correlation graphs

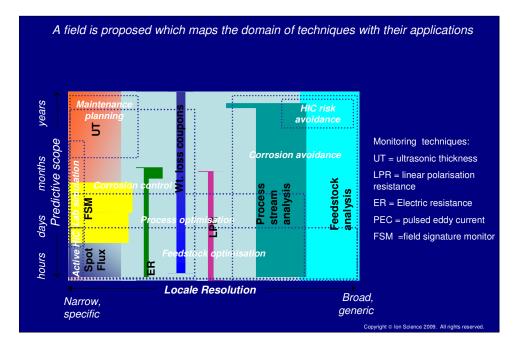
Hydrogen and the periodic table



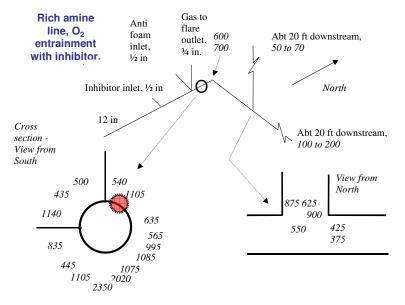
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Monitoring domains



Find, diagnose, control (1a)



See F.W.H.Dean, Corrosion 2002, NACE, Paper 2344.

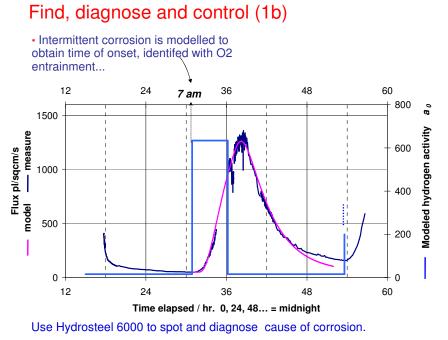
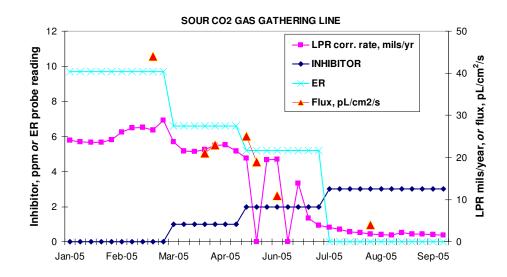


Illustration F.W.H.Dean, Corrosion 2002, NACE, Paper 2344.



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Methane reactor subject sour corrosion.

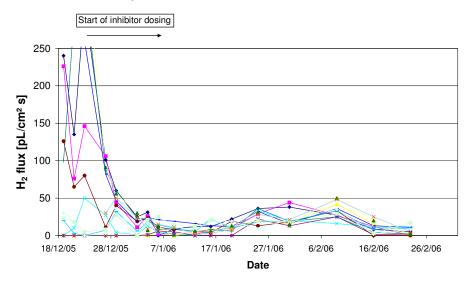
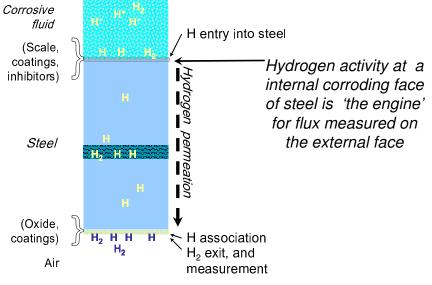


Illustration B.Otzitz, A.Gourzoulidou, Frank Dean, Klaus Bernemann, Petroleum Technology Quarterly, 2 (2009), 102.

Linking flux to corrosion and H damage risk (1)



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Linking flux to corrosion and H damage risk (2)

Normalisation for temperatutre and thickness

Flux
$$J = P. \boldsymbol{a}_{o} / w$$

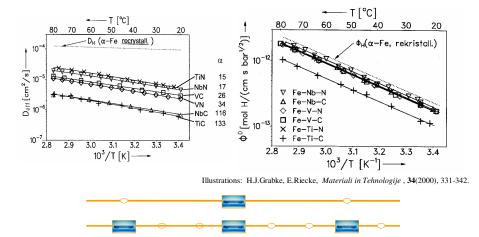
where P (Ncm³/cm/s/bar^{1/2}) = permeability, a_0 (bar^{1/2}), the hydrogen activity at entry face and **w** (cm) the thickness.

So, compensating for permeation of hydrogen through a steel of known temperature and thickness we obtain a measure of corrosivity and prospective damage risk.

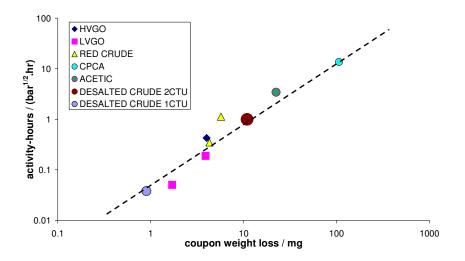
$$P = P_0 \exp(-E_a/RT)$$

Linking flux to corrosion and H damage risk (3)

Is permeability P, determined from T, invariant between steels? Yes. P = D.S. As hydrogen diffusion coefficient D increases due to hydrogen trapping, so solubility S increases inversely. D values, for typical low alloy steels vary by some 10 fold, whereas permeabilities P vary some +-20%...



Experimental correlation of activity with corrosion rate (high T)

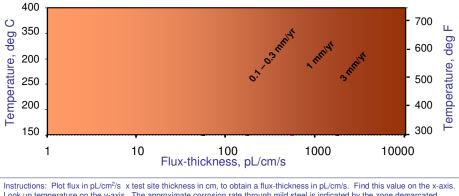


F.W.H.Dean, S.J.Powell, NACE Paper 06426, Corrosion 2006, NACE.





A few 10's of pL/cm²/s indicates significant corrosion. A few thousand pL/cm²/s have been registered in very acid streams. Naphthenic acid is in fact a large family of acids found in crude oil. Corrosion generally occurs at pipe bends and reducer sections. The correlation below is based on limited lab experiments. The chart is also applicable to other acidic corrosion at temperatures above about 150 °C, 300 °F. Please contact Ion Science for further technical information.



Look up temperature on the y-axis. The approximate corrosion rate through mild steel is indicated by the zone demarcated between lines.

eg, flux = 200 pL/cm²/s, thickness = 1 cm, => flux-thickness = 200 pL/cm/s. At T = 300 °C, corrosion rate is approx 0.5 mm/yr.

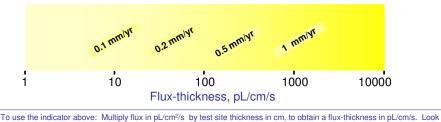
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SOUR CORROSION



Typically, a clear flux of more than 5 pL/cm²/s is used as a corrosion indicator before and after mitigation. 100 pL/cm²/s usually indicates moderate corrosion. Corrosion occurs in distillation units, overhead, eg in condensers, fin-fan units, coolers and sour flare lines. It can be very severe (>500 pL/cm²/s) and is often associated with hydrogen damage. It is usually episodic, occurring usually after equipment installation, inspection, or sometimes during process changes (eg air ingress, water washes, pH changes). The chart below may also be used to assess corrosion under deposits, eg in amine units.

Please contact Ion Science for further details.



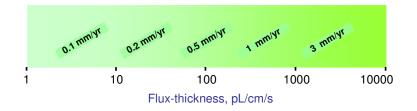
To use the indicator above: Multiply not in pLCnPs by lest site interflexion controls in Cin, to obtain a not-tinckness in pLCnPs. Look along bottom of chart for corrosion rate. Note corrosion flux correlation varies in a complex way with other corrosion variables, not least temperature. This makes the correlation very approximate. *eg*, flux = 20 pL/cm²/s, thickness = $\frac{1}{2}$ in = 1.25 cm => flux-thickness = 25 pL/cm/s. Corrosion rate is very approximately 0.2 mm/yr.

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LOI .

AMMONIUM BISULFIDE – HCN CORROSION

Typically a clear flux of >10 pL/cm²/s can be used as a corrosion indicator. 100 pL/cm²/s is significant. 1000 pL/cm²/s is severe. Corrosion occurs in the overhead streams from hydrodesulfurization columns, hydrotreaters and catalytyic crackers, in presence of hydrogen cyanide from high nitrogen high sulfur containing feedstock. Can be very severe and associated with hydrogen damage. Occasional.



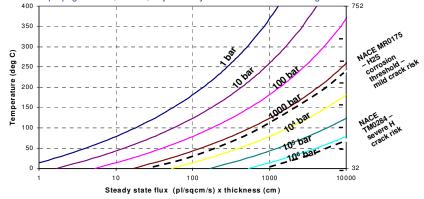
Instructions: Multiply flux in pL/cm²/s by test site thickness in cm, to obtain a flux-thickness in pL/cm/s. Look along bottom of chart for corrosion rate. eg, flux = 20 pL/cm²/s, thickness = ½ in = 1.25 cm => flux-thickness = 25 pL/cm/s. Corrosion rate is *very approximately* 0.2 mm/yr.

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HYDROGEN CRACKING

As a consequence of sour or HF corrosion, severe hydrogen activity may be generated in the underlying service steel. This activity dictates the hydrogen flux which permeates the steel and is measured on the external face and is a direct measure of crack severity. Generally, hydrogen cracks are initiatied in poor quality, non-sour service steels at activities as low as 10000 bar, whereas sour service steels can withstand at least 1,000,000 bar. After cracks have appeared, much lower activities are needed to propagate them, indeed, any flux may contribute to further crack growth.



Instructions: Plot flux in pL/cm²/s x test site thickness in cm, to obtain a flux-thickness in pL/cm/s. Find this value on the x-axis. Look up temperature on the y-axis. The hydrogen activity is indicated by the zone demarcated between lines. *eg*, flux 800 pL/cm²/s, thickness 1.5 cm, => Flux-thickness = 1200 pL/cm/s. At 30 °C, activity = 10⁶ bar, severe risk of cracking. For indication only. Copyright © Ion Science 2009. All rights reserved.

Hydrosteel 7000 T: transportable monitor



- Class 1 Division 2 approval
- User defined data freq.
- Up to 9 months use per battery charge
- · easy to install
- · easy to use
- easy to service
- light weight
- · intrinsically safe
- IP 66 rated



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• Hydrogen flux indicates active sour, HF and high temperature corrosion and HIC risk from petrochemical processing equipment which is now linked to corrosion wall loss and hydrogen crack risk severity.

• The technology is well established in the assessing the effectiveness of process and chemical corrosion control measures.

• Field worthy flux measurement technology is now available in the form of a spot measurement tool, battery powered monitor and fixed monitor.

• The technology is also being used in hydrogen bakeout monitoring.

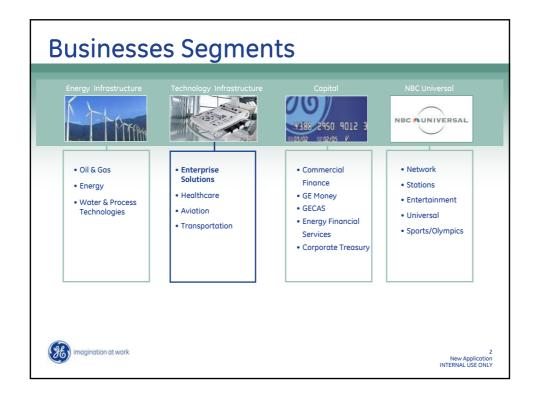
www.ionscience.com

Thank you for your attention.

Appendix 9

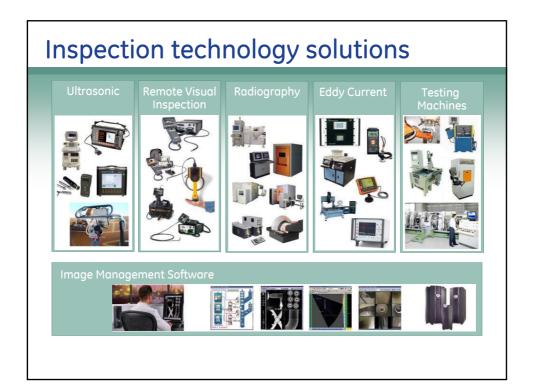
Online Corrosion Monitoring & Digital Radiography Jim Costain (GE S&I)













Downstream: Refinery/Chemical

Application:

General Corrosion Rates in High Temperature piping systems

Current methods:

Manual NDT wall thickness measurements for piping systems

Intrusive Coupons

New Solution:

•Permanently Installed High Temperature UT Sensors monitoring pipe wall thickness at critical plant locations

•High Accuracy Trending (2.5 micron) for daily report on corrosion rates

•Ability to create custom rule packs (process variables vs wall thickness), custom alarming, drive changes in chemical inhibitor dosage.

imagination at work



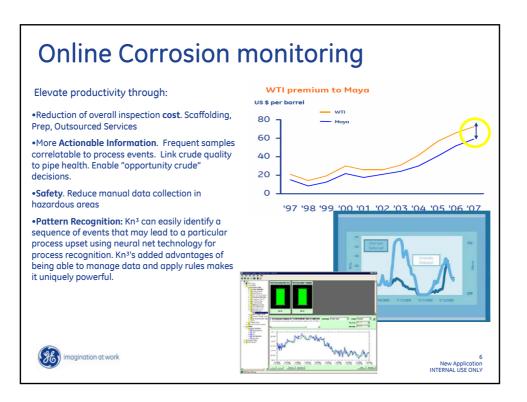
Product: Rightrax HT

•Optimization of cost/benefit relationship between crude slate, chemical injection cost, and plant reliability

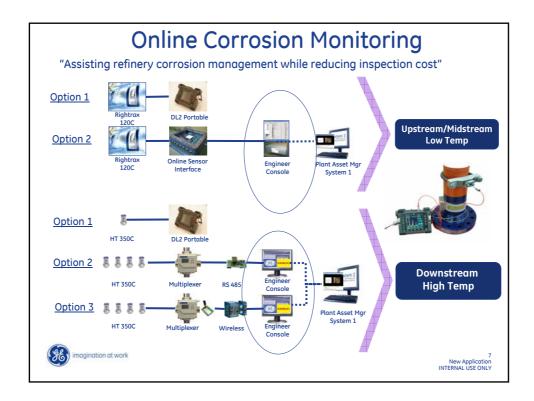
•Drive work orders through intelligent alarming

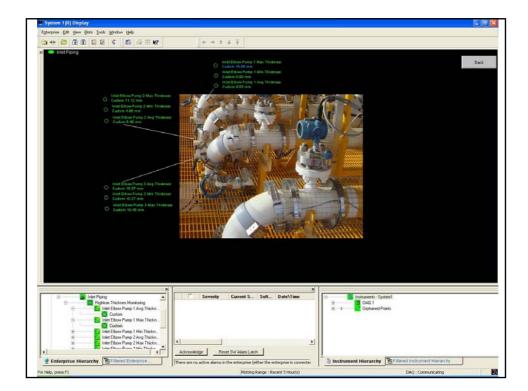
•Reduced overall per data point inspection cost through permanent installation and wireless technology

New Application

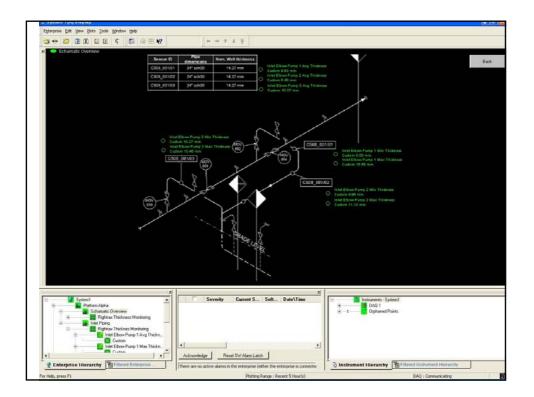


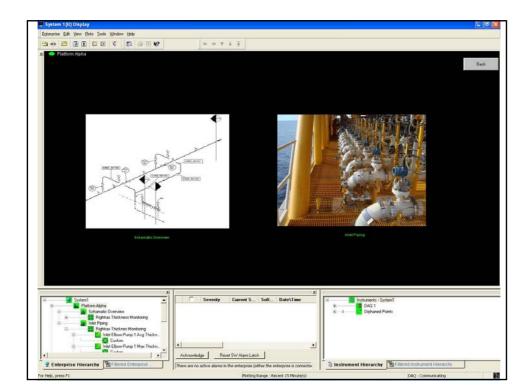




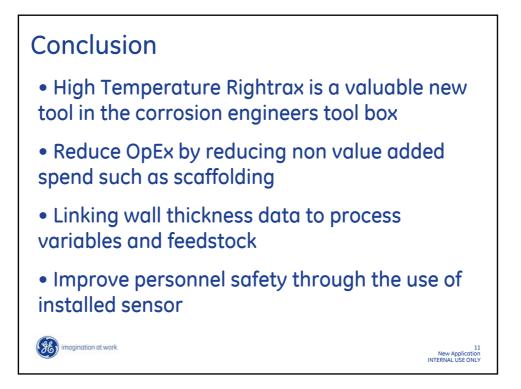


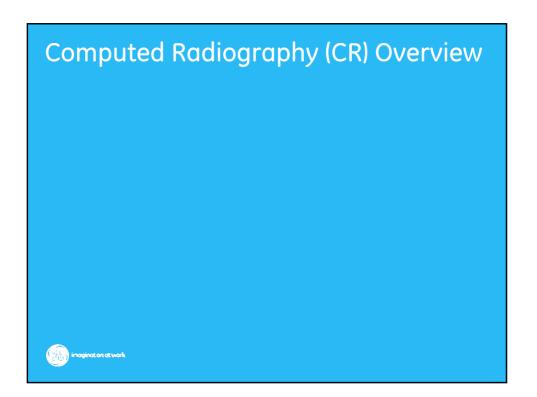




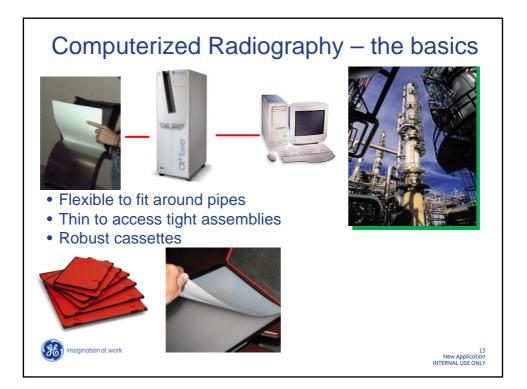


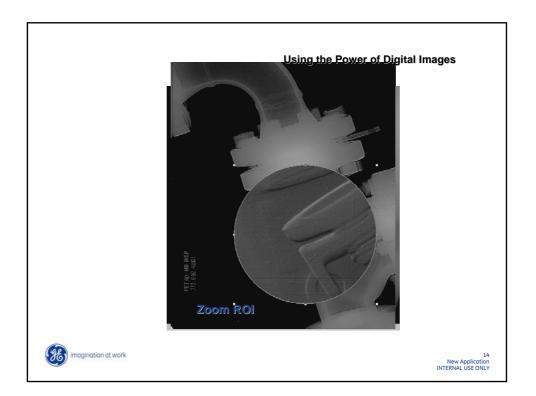




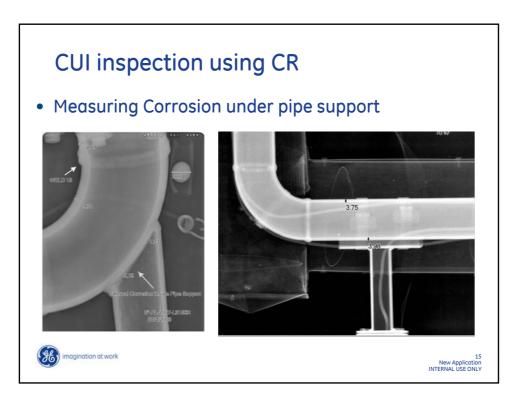


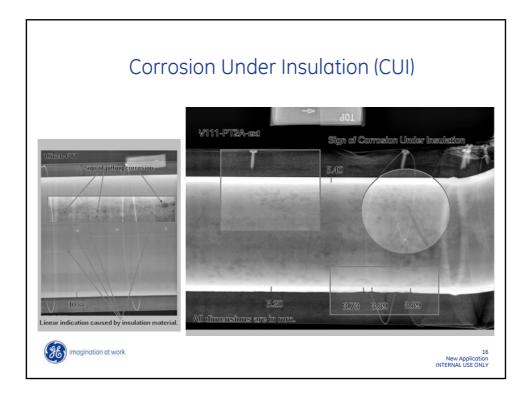




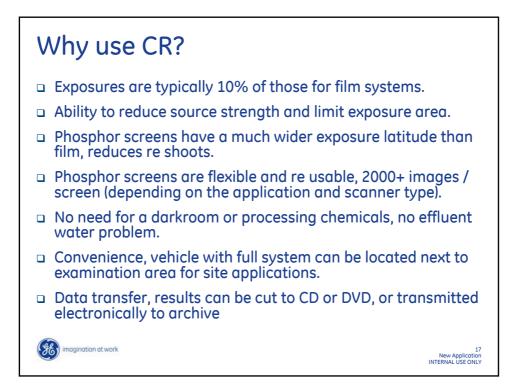


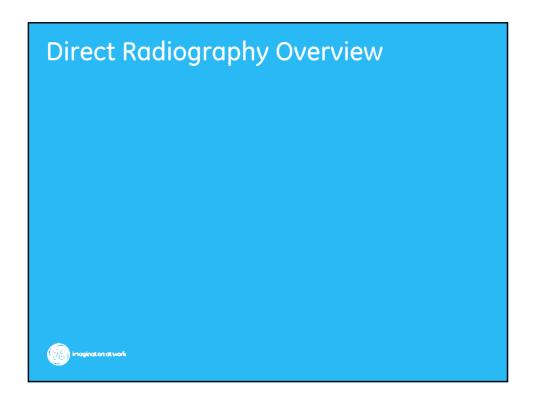




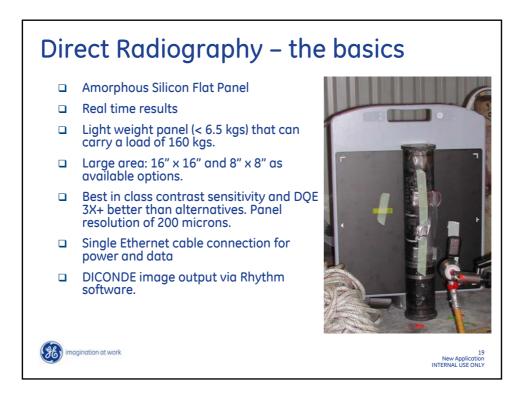






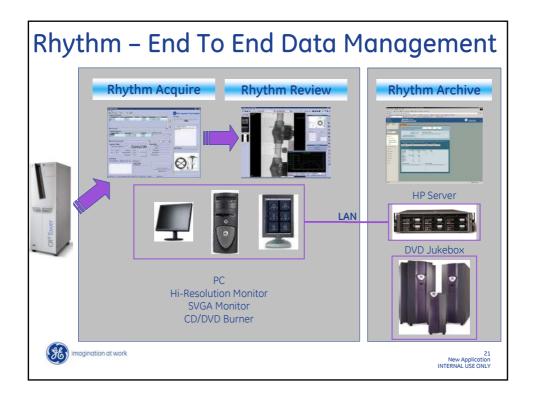


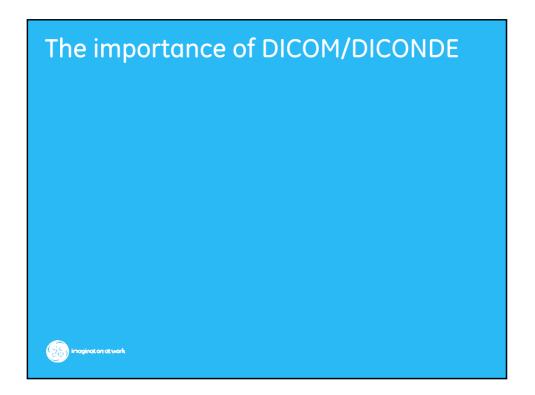














Digital Imaging and Communication in Medicine (DICOM)

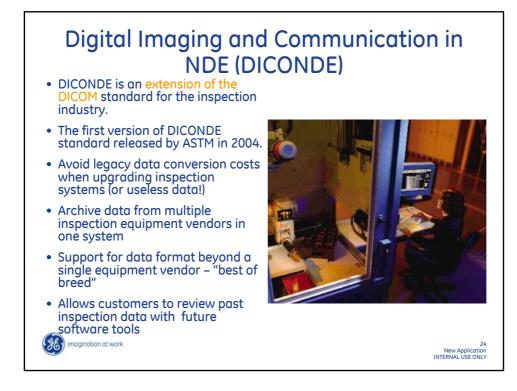
A standard that facilitates the interoperability of medical imaging equipment by network <u>communication protocols</u> and <u>data storage formats</u> for medical image data.

(%) imagination at work

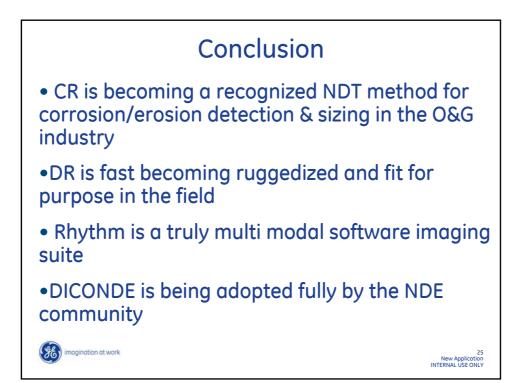


New Application

Not just an image









Appendix 10

High temperature corrosion – a comparative over view of CUI protective coating systems Steve Reynolds (Performance Polymers)



Performance Polymers HI-TEMP COATINGS TECHNOLOGY

High Temperature Corrosion Protection

A Comparative Overview Of CUI Protective Coating Systems

Steve Reynolds Steve Fenton <u>www.pp-bv.com</u>

 Corrosion under insulation is one of the costliest problems attacking the industry today. According to one specifier from a major oil company, CUI problems account for more unexpected downtime than all other possible causes combined.

Corrosion under insulation is a unique problem. A CUI protective coating in this environment needs to be able to withstand multiple abuses and also have certain application characteristics in order to make it a viable solution. Deficiencies Associated with Generic High Heat Coatings

- Thin film resulting in pinpoint rusting / corrosion
- Ineffective Corrosion Under Insulation
- Inability to be applied while the unit is online & hot
- Limited thermal shock capabilities
- The need for high levels of surface preparation
- Heat cure issues
- Short recoat windows in often hostile conditions
- High VOC
- Sacrificial coatings (aluminum or zinc based)

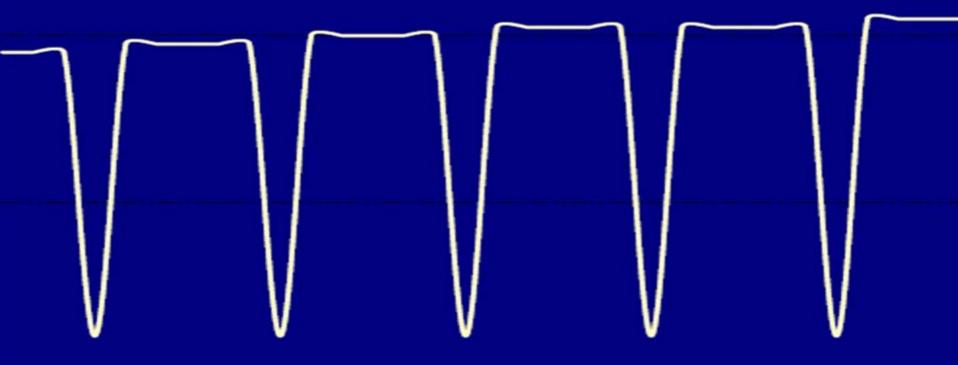
Properties a CUI Coating Must Have In Order To Be Successful

1) Resistance to Boiling Water 2) Heat and Thermal Shock Resistance 3) Application to Hot Steel (site maintenance) 4) Application to Ambient Steel (OEM, fabrication) 5) High Film Build Capability, Direct to Hot Steel 6) Simple to Use 7) VOC and Environmental Compliance

	Inert Multi- polymeric Matrix	Thermal Spray Aluminum	Traditional Elevated Temperatur e Silicones	Multi- polymer Primer	Inorganic Zinc	Novalac Elevated Temperature Epoxies
Max Operating Temp	750ºC	630ºC	540ºC	425⁰C	400°C	220ºC
Max DFT per Coat (in Microns)	150	200	37	150	75	100
Recoatable with self	Yes	No	Yes	Yes	No	Yes
						200 Max
Max DFT (in microns)	500 +		112	200		Recoat interval is critical
Single Component	Yes	n/a	Yes	No	No	No

	Inert Multi- polymeric Matrix	Thermal Spray Aluminum	Traditional Elevated Temperature Silicones	Multi- polymer Primer	Inorganic Zinc	Novalac Elevated Temperature Epoxies
Anodic Metal sacrifices in Electrolyte	No	Yes	Yes	Yes	Yes (Zinc)	No
			(Aluminum)	(Aluminum)		
Immersion in Salt Water	Yes	Fails	Fails	NR	Fails	Yes
Hot Apply ºC	Yes	Yes	Yes	Yes	No	Yes
	260ºC		93ºC	120ºC		150ºC
Surface Tolerant	Yes	No	No	No	No	No
	SSPC SP-2					
Stainless Steel	Yes	No	No	Yes	No	Yes
Easy repair with Self	Yes	No	Yes	Yes	No	Yes
Protects at Ambient	Yes	Yes	No	Yes	Yes	Yes
Cryogenic Service	Yes	Yes	No	Yes	No	Yes

Surfaces at Elevated Temperatures Cyclic (all) or continuous



Service is all Cyclic over TIME ->



Novalac Epoxy After 3 months service Originally White Cracking Excessive DFT in places.

Overheated Epoxy

4

Consequences of Leaking

Insulation

Insulation Leaks Eventually











New Interest In High Temperature Coating Systems

many older refineries and chemical plants

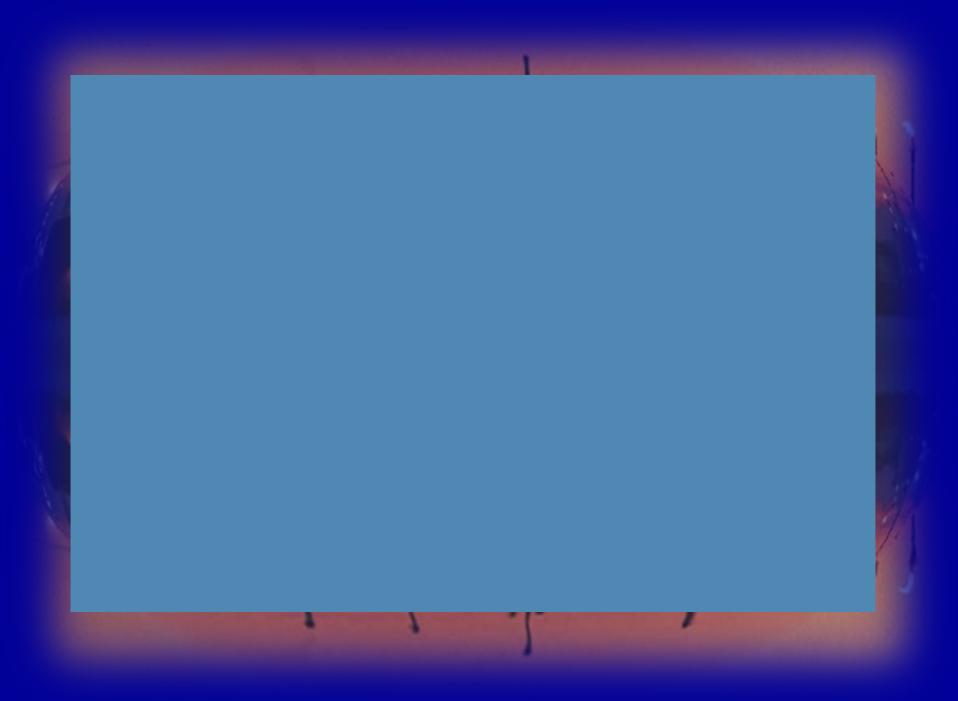
 upgrade for higher quality products
 improved efficiency
 or simply expand,

In doing so they raise operating temperatures

End User Cost / Benefit Analysis

- The economics of rehabilitation and repair are mainly driven by the cost of the labour, access costs and the <u>down time</u> that is associated with making repairs.
- Extended maintenance cycles also dramatically reduce whole life cycle costs, as does taking CUI programs out of essential shutdown processes. – they can form ongoing schedules to further reduce costings.





Thank you for your attention

Questions?