Corrosion & Fouling Control at Petrochemical Processes

Deepak Sharma
Regional Technical Manager - CPI
GE Water & Process Technologies

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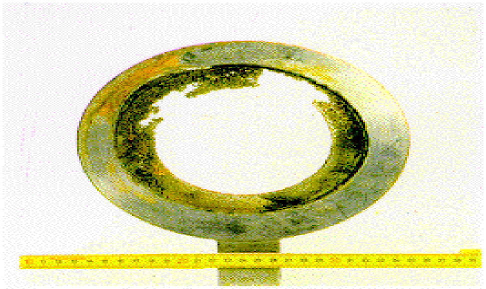

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- What Is Corrosion ?
- Corrosion Mechanism
- Filming Inhibitors
- Neutralizing Inhibitors
- Monitoring & Lab Testing Procedures
- Successful Corrosion Inhibition Treatment

Requirements for Corrosion to Occur

a) Anodic reaction

Corrosion reaction

b) Cathodic reaction

Uses the electrons produced at Anode

c) Metallic Path

Electrons flow from anode to cathode

d) Electrolytic Path

Flow for ions between anode and cathode

Corrosion?

Electrochemical Process in which metals react with their environment

Anode (oxidation):

- $Fe \longrightarrow Fe^{2+} + 2\,e^{-}$
- $Fe \longrightarrow Fe^{3+} + 3\,e^{-}$
- $Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$

Summary: The metal ionizes and produces electrons

Corrosion Chemistry

Cathode Reactions (Reduction)

Acidic Environment

- $2\,H^+ + 2\,e^- \longrightarrow H_2$
- $O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$

Basic or Neutral Environment

- $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$

Summary: Electrons are consumed, in any aqueous environment

Corrosion Chemistry

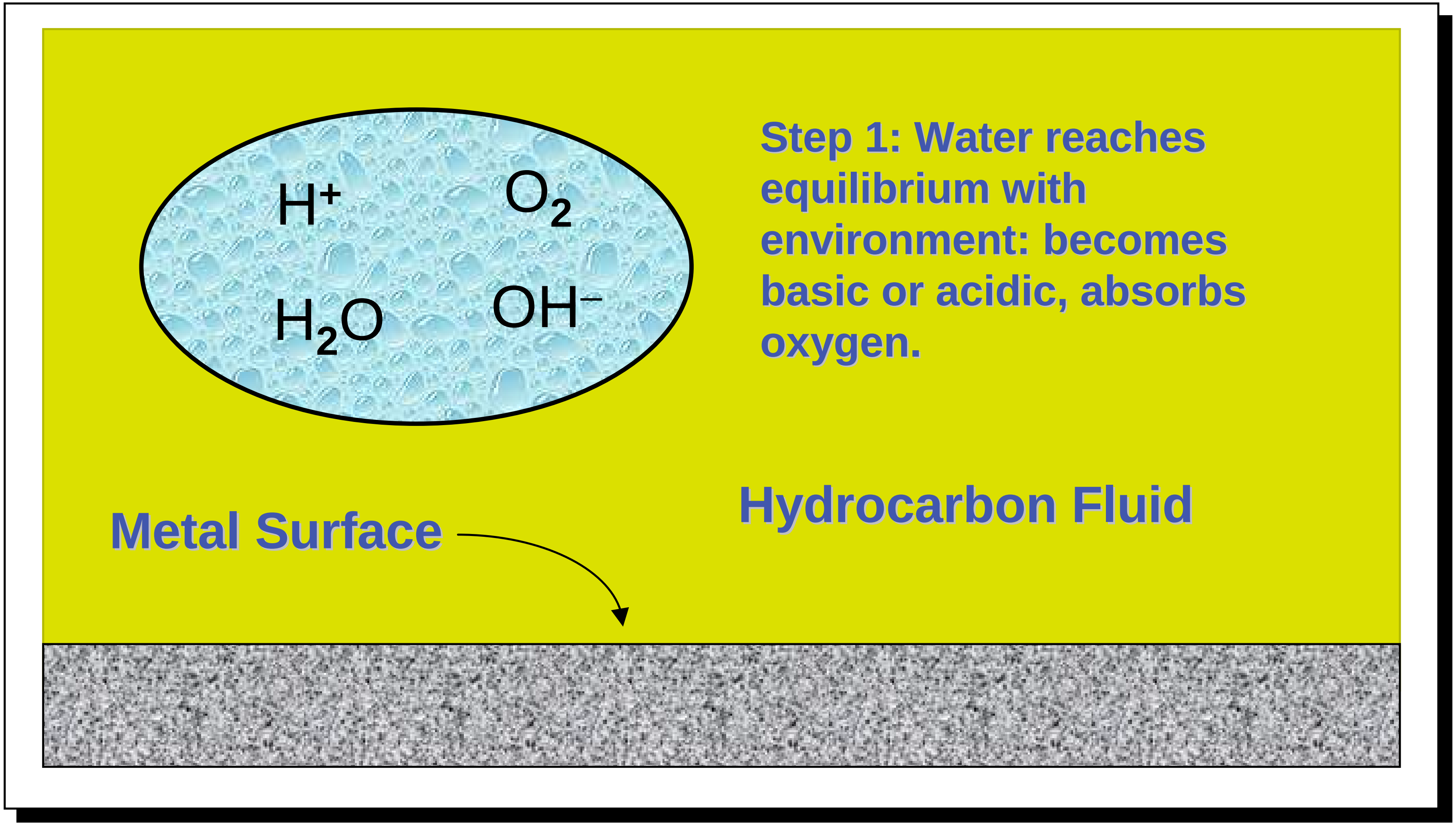
End Reactions

- $Fe^{3+} + OH^{-} \longrightarrow Fe(OH)_3$
- $Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$

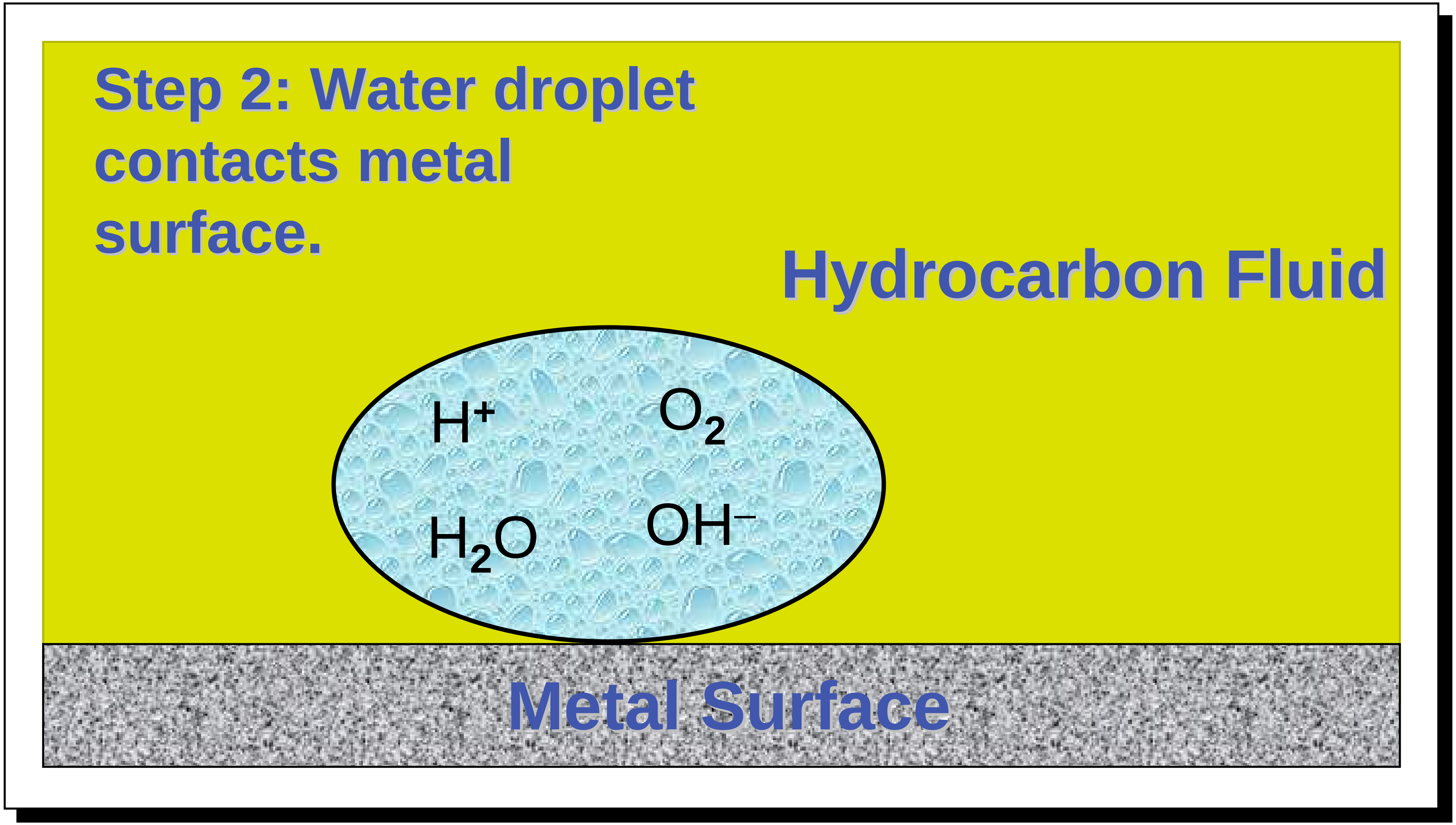
These are the distinctive brownish-red rust deposits

They are magnetic (good diagnostic tool)

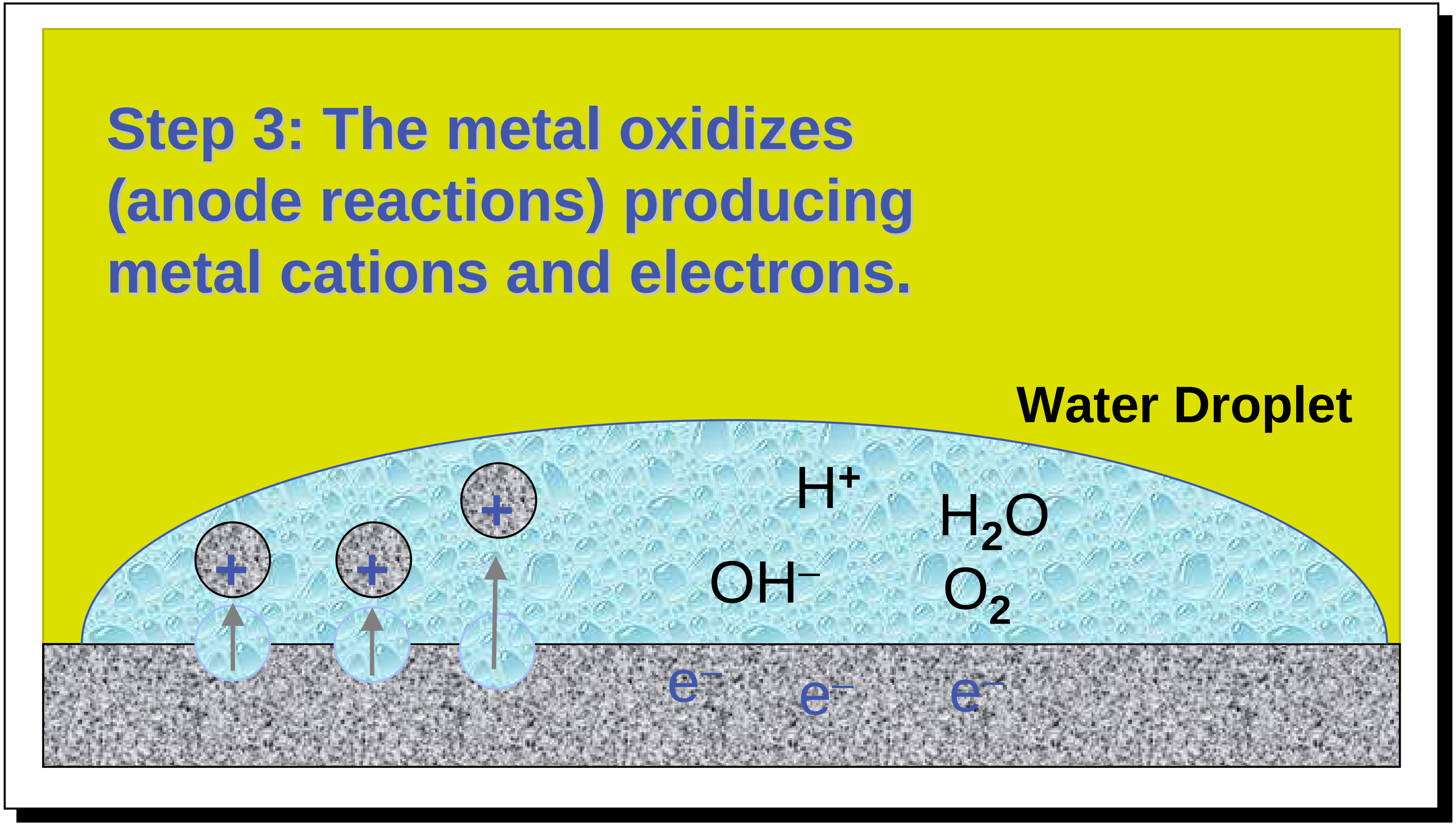
Visual Corrosion Picture (1)



Visual Corrosion Picture (2)



Visual Corrosion Picture (3)



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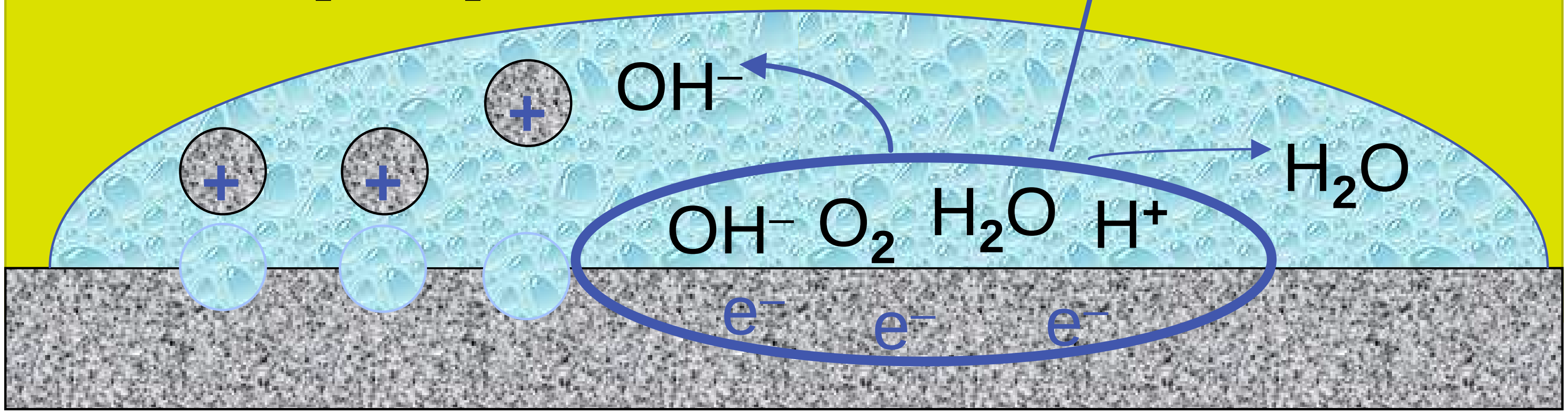
Visual Corrosion Picture (4)

Step 4: The electrons are consumed in the cathode reactions (reduction).

$2\ H^+ + 2\ e^- \longrightarrow H_2$ (Acidic)

$O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O$ (Acidic)

$O_2 + 2\ H_2O + 4\ e^- \longrightarrow 4\ OH^-$ (Basic)

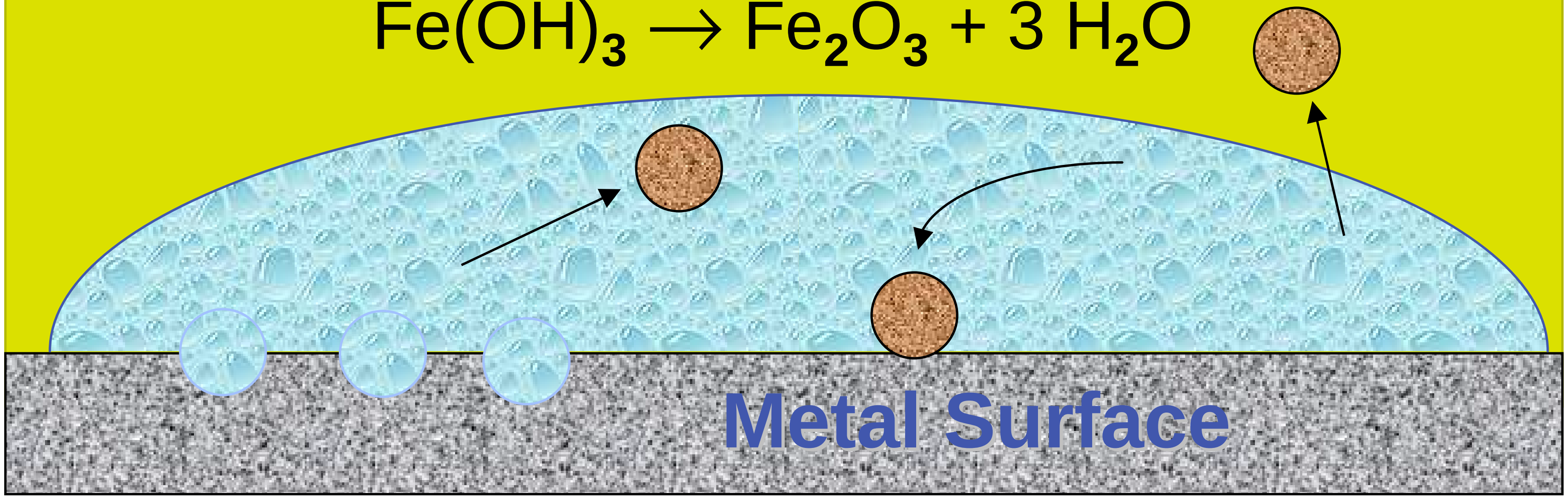


Visual Corrosion Picture (5)

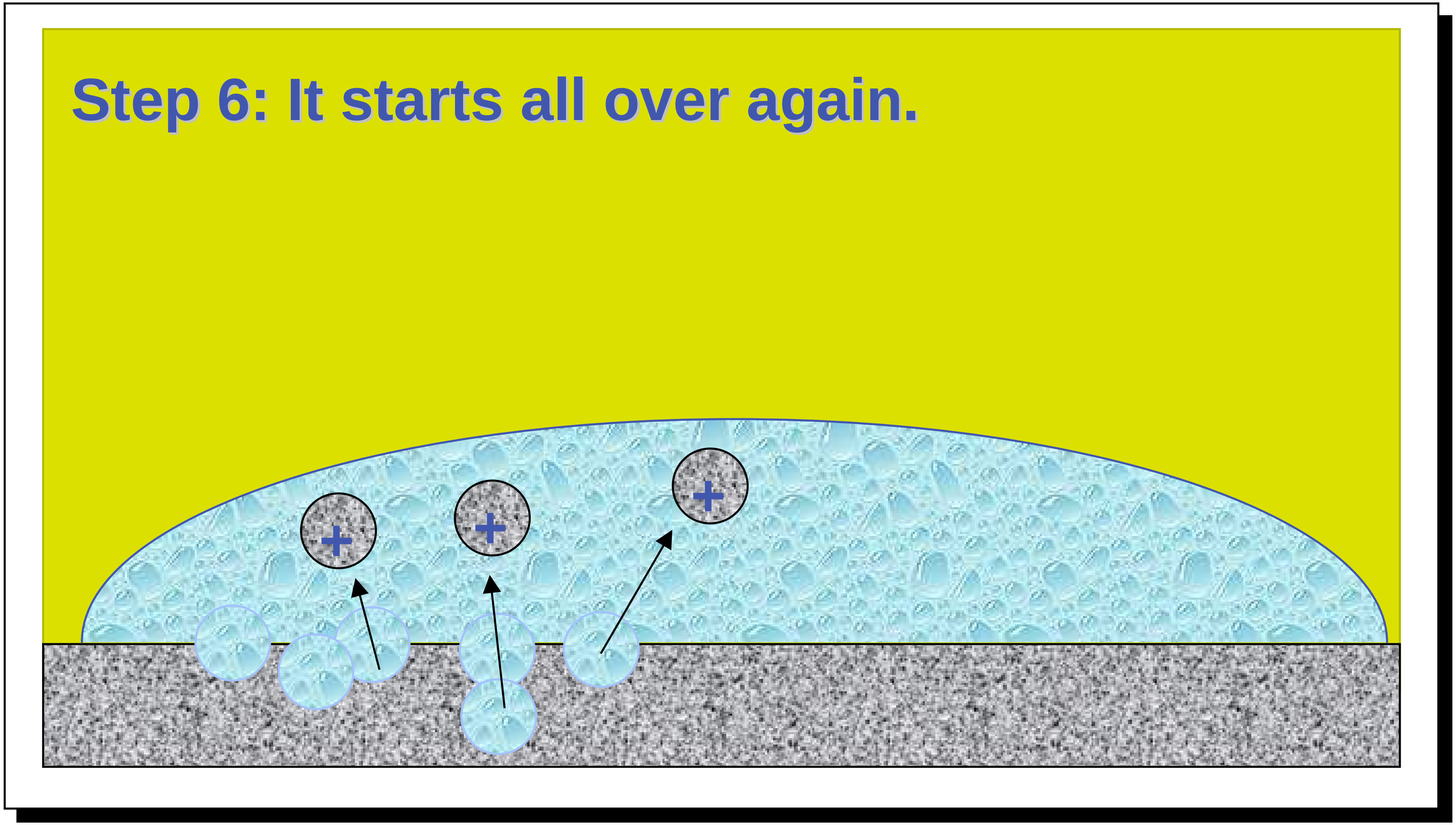
Step 5: The end reactions turn the metal ions into rust particles (Oxygen Corrosion Example).

$$Fe^{3+} + OH^{-} \rightarrow Fe(OH)_3$$

$$Fe(OH)_3 \rightarrow Fe_2O_3 + 3\ H_2O$$



Visual Corrosion Picture (6)



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Outline

Forms of Corrosion

a) General (Uniform)

b) Localized (pitting, under deposit & crevice)

c) Galvanic (bimetallic)

d) Velocity related (erosion & cavitation)

e) Intergranular corrosion (weld decay)

f) Dealloying (selective leaching)

g) Cracking (blistering, HIC, SCC)

h) High temp (oxidation, sulfidation, napthenic acid)

Corrosion Causes

Corrosives Species in Petrochemical Processes

a) Chlorides : inorganic - organic
b) Sulphur Compounds
   – H_2S
   – SO_x
c) Oxygen
d) CO_2 – Forming Carbonic Acid
e) Organic Acids – Acetic Acid, Propionic Acid, Formic Acid, etc.
f) Erosion Corrosion

HCl & Sulfur Corrosion

SWEET

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

No H2S

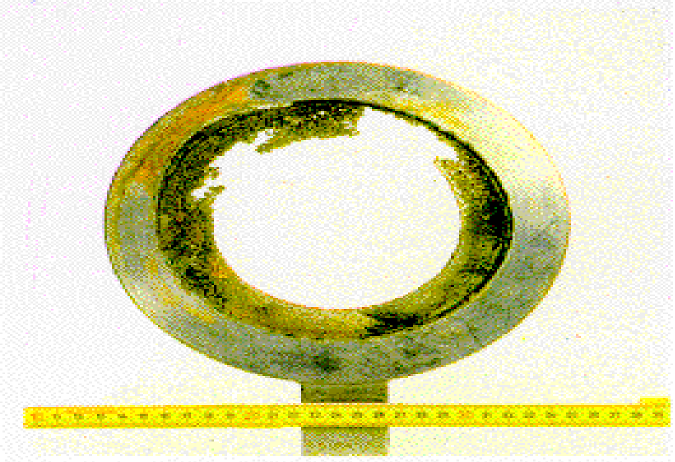
SOUR

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

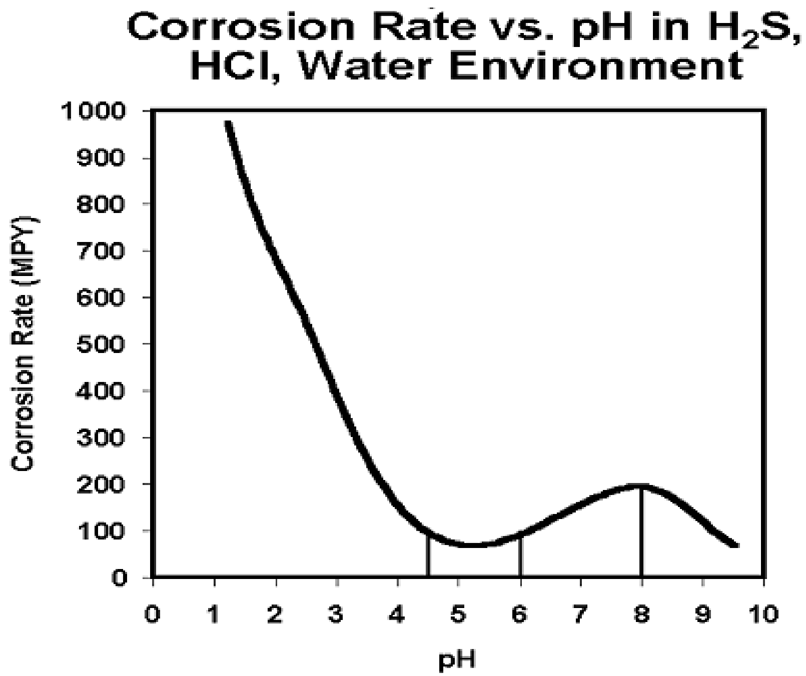
$$FeCl_2 + H_2S \longrightarrow FeS\downarrow + 2HCl$$

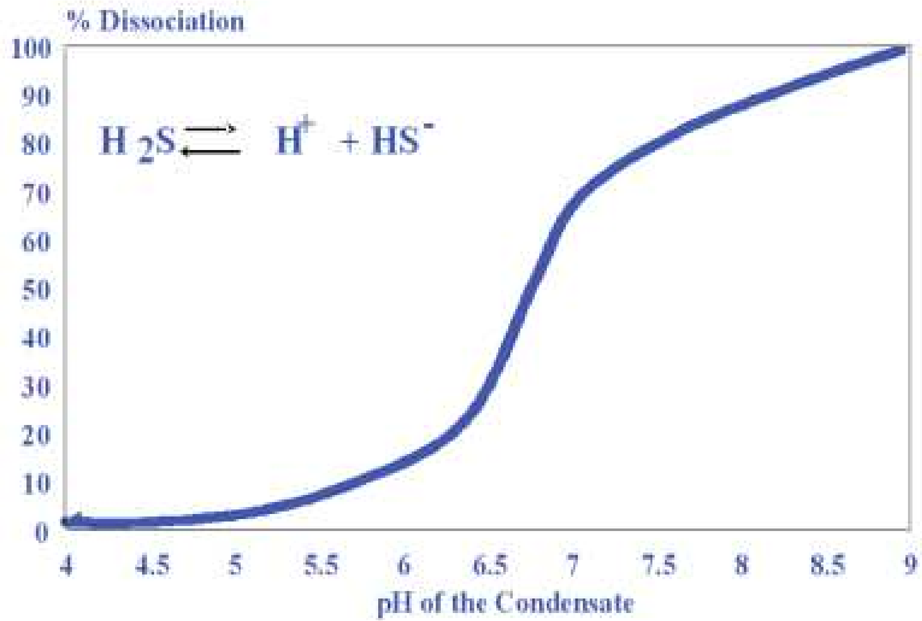
$$Fe + H_2S \longrightarrow FeS\downarrow + H_2\uparrow$$

With H2S



- Acid Dew Point Corrosion
- Aggressive corrosion at Initial Condensation Point





Oxidized Sulphur Species

Hydrogen Sulphide Dissociation

a) Sulphite :

SO2 + H2O → H2SO3 (acid condensation)

HS- + 3/2 O2 → HSO3- → SO32- + H+

(most severe at pH 6 – 7)

2H2S + SO2 → 3S + 2 H2O + O2 → HSO32- + H+

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GE Proprietary

Oxygen Corrosion

The presence of oxygen in the high temperature areas greatly increase the corrosion rates of the carbon steel equipment.

$4Fe + H_2O + O_2 \rightarrow 4Fe(OH)_3$

$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$ (time & temperature)

With water globes → corrosion
Underdeposit → PITTING

$Fe(OH)_3$ is insoluble leading to an increased corrosion rate as more iron is leached out from the metal to maintain the chemical equilibrium.

CO_2 Corrosion

Low pH carbonic acid corrosion

- Carbonic acid is formed when CO_2 dissolves in water and reacts with water:
  - $CO_2 + H_20 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$
  - pK_a of H_2CO_3 is 6.37
- $Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \uparrow$

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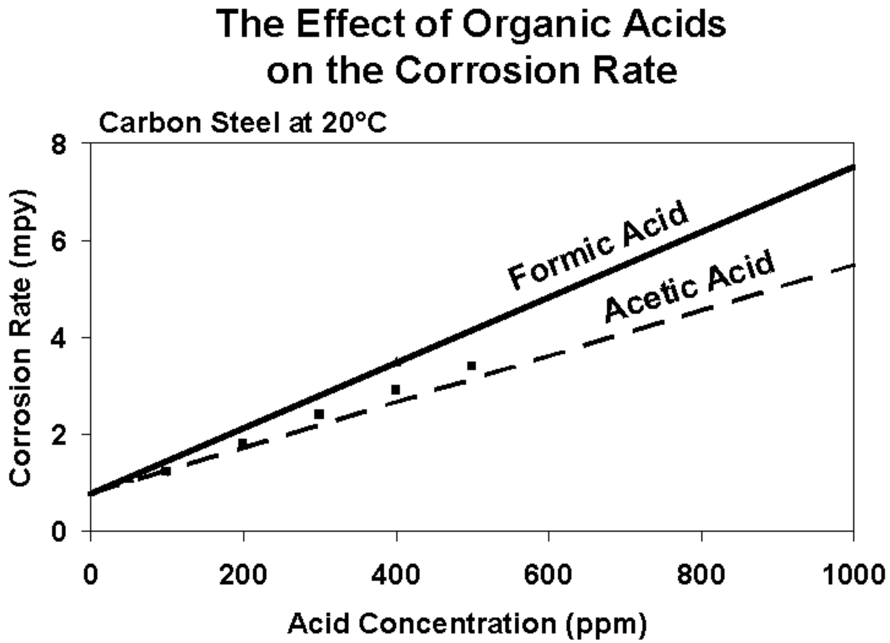
Organic Acid Corrosion

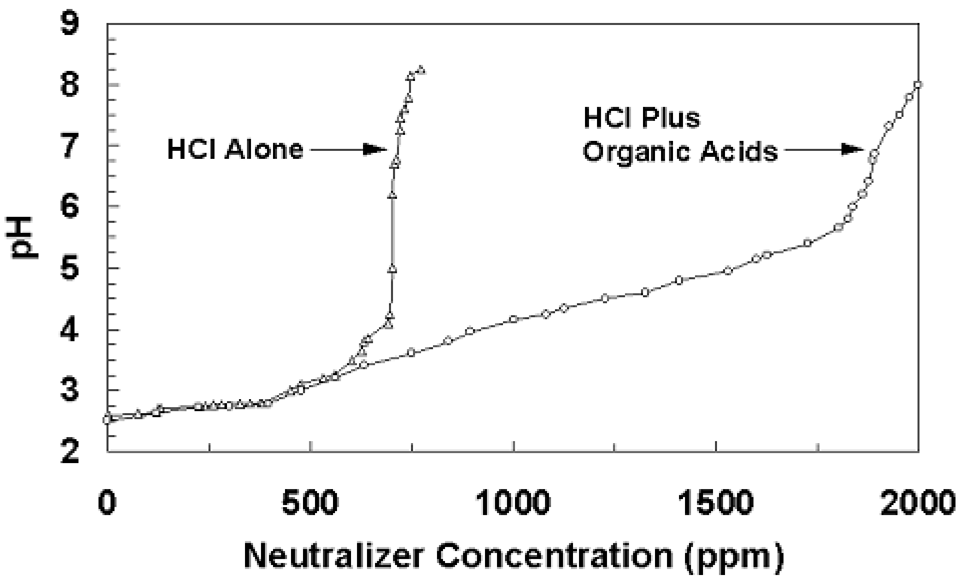
Contents naturally in the crude

- Oxidation of unsaturated compounds
- Weak acids (pKa: 3.8 to 4.5)

Figure 3.5-2



Neutralizer Titration Curves



Physical Properties of Organic Acids

Organic Acids	MW	B.P. °F	pKa	Solub. g/100 g H_2O	HCl Equiv
Formic	46	213	3.75	¥	0.79
Acetic	60	245	4.75	¥	0.61
Propionic	74	287	4.87	¥	0.49
Butyric	88	326	4.83	¥	0.41
Pentanoic	102	401	4.88	3.7	0.36

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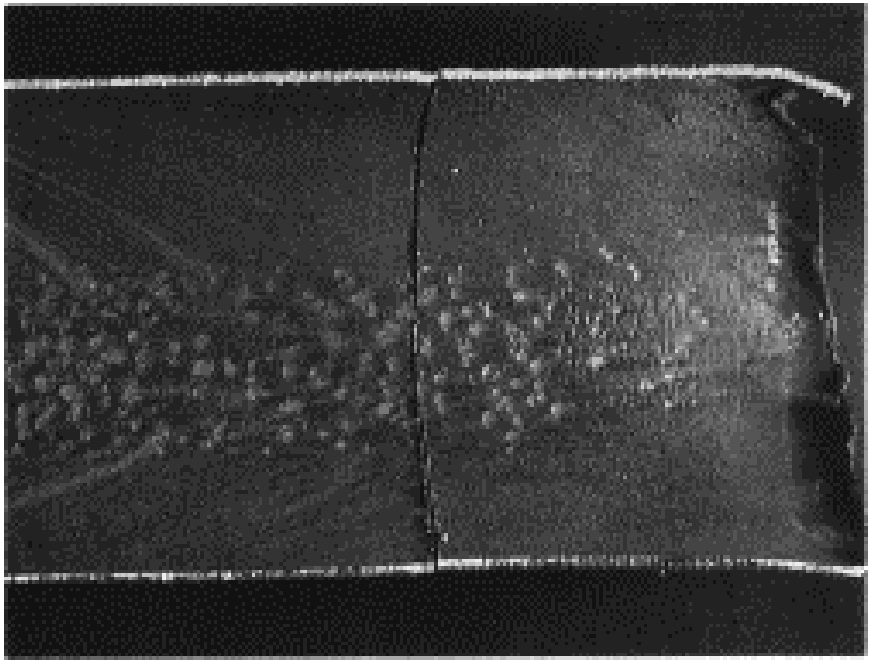
Erosion Corrosion

Factors effecting Erosion Corrosion

- Velocity
- Chemistry
- Geometry
- MOC



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Product Mechanisms

How does Chemical Technology work?

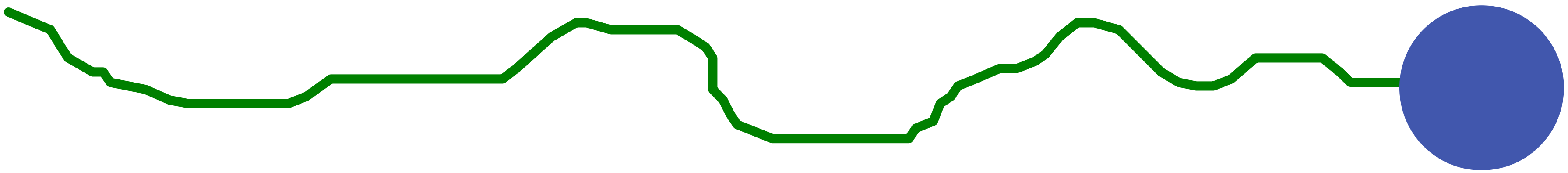
- Filmers – Forms Film
- Neutralizers – Neutralize the acidity

Filmers

1. Keep corrosive water off of metal surface
2. Bond to metal & to slough of the corrosion product scale
3. Disperse salts

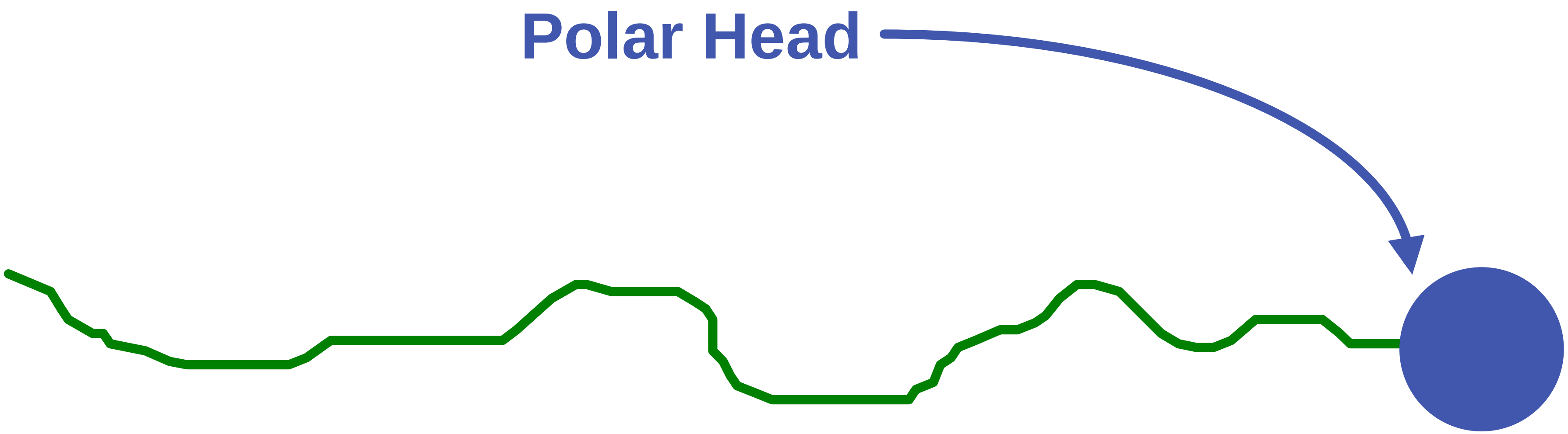
An Inside Look

This is a typical filming corrosion inhibitor molecule

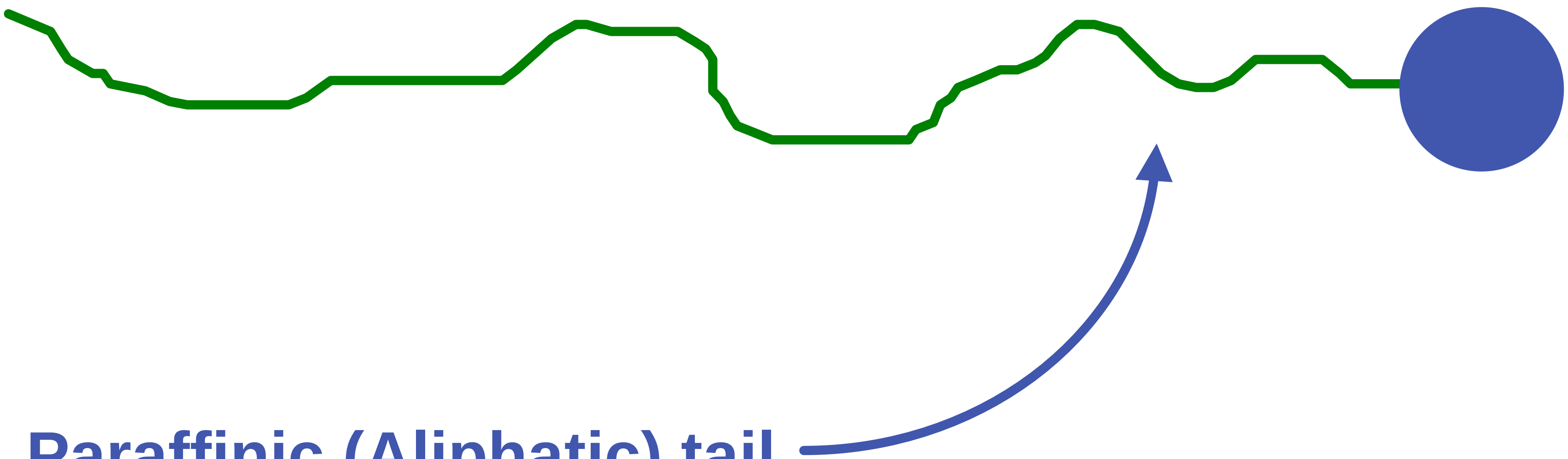


Two interesting features

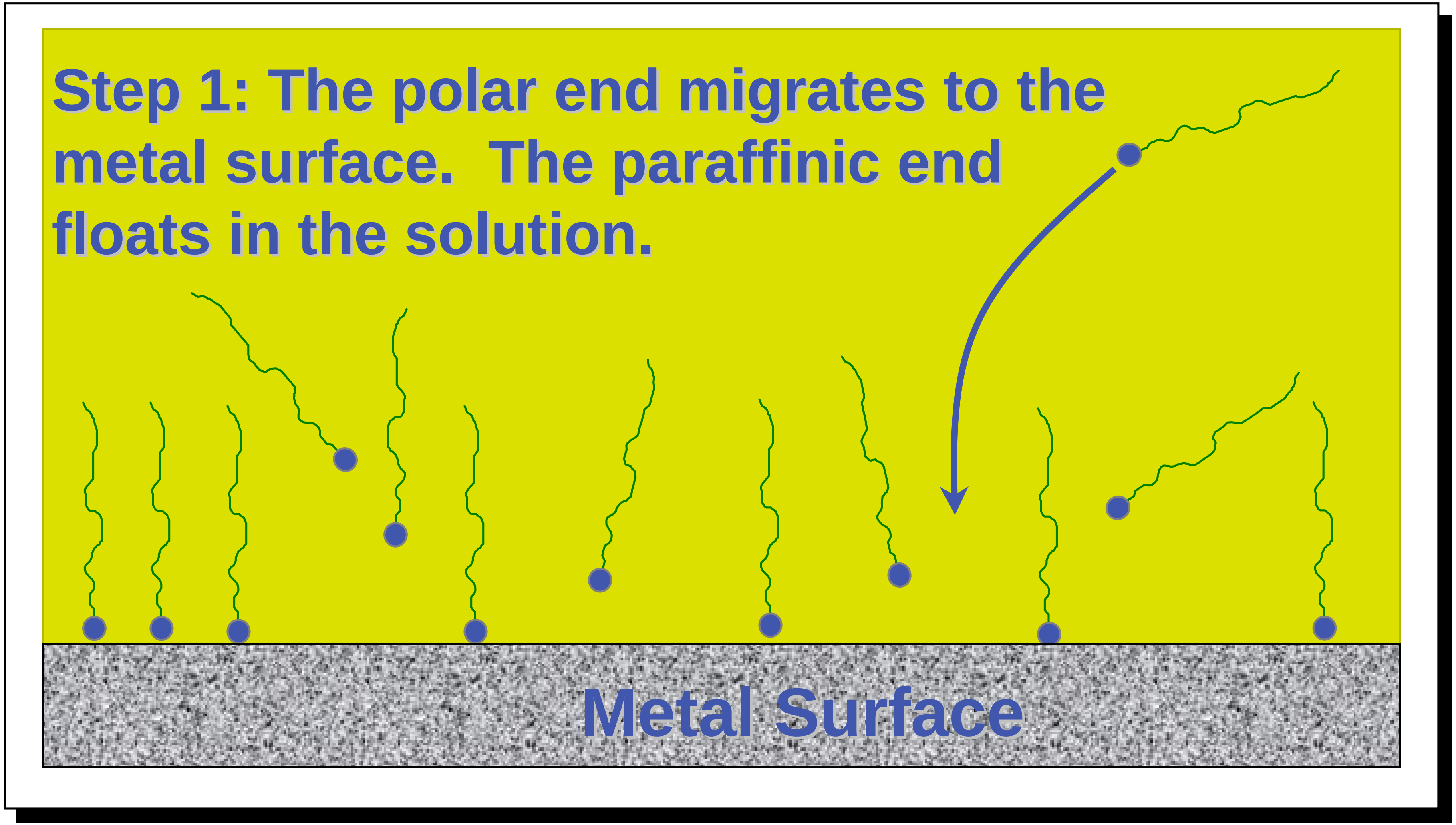
An Inside Look



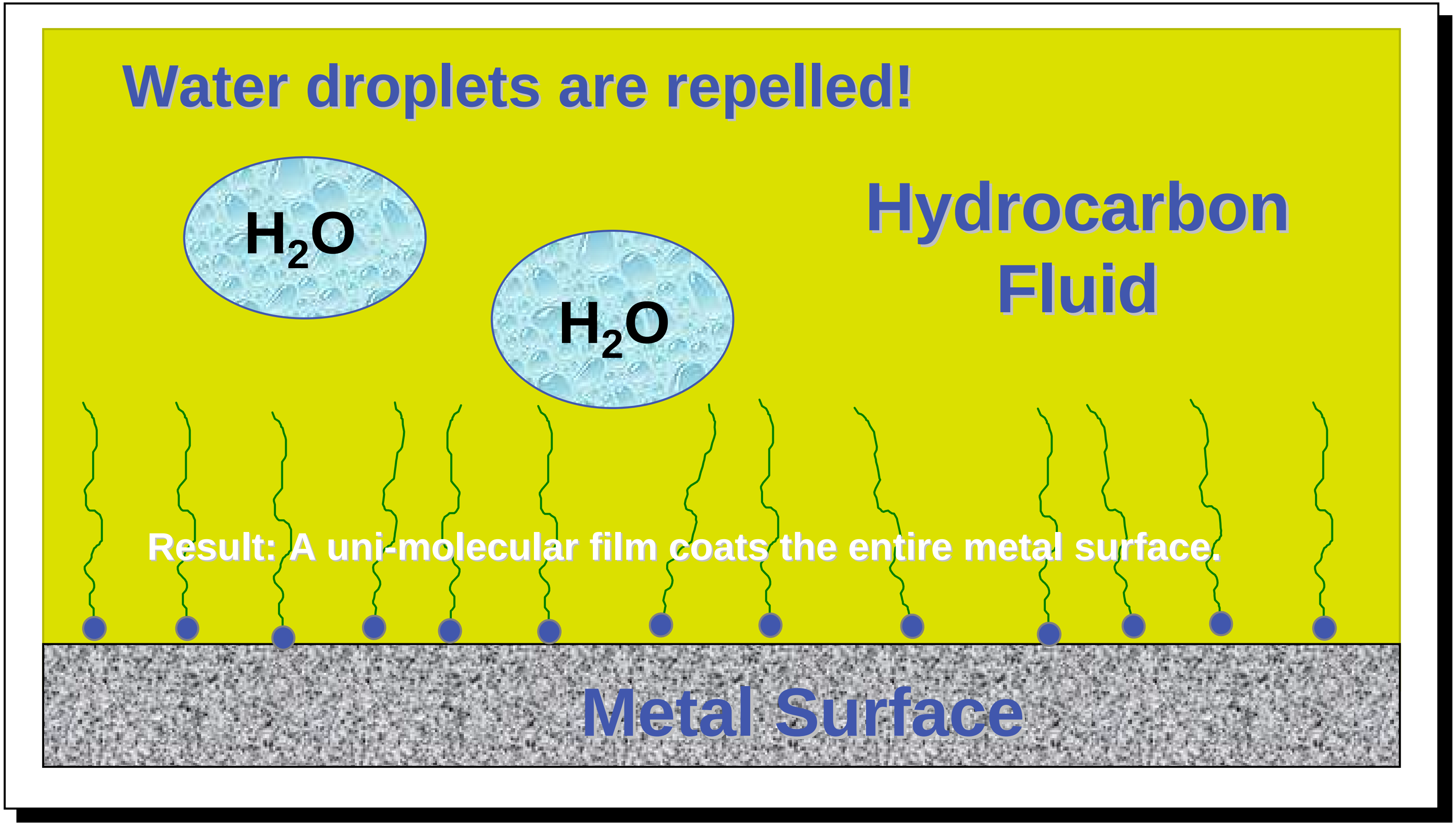
An Inside Look



How does it work (1)?



How does it work ?



Neutralizers

Neutralize Acids Condensing in Water Phase

- Low Molecular Weight Amines

Desired Neutralizer Features

1. Low oil/water partitioning coefficient

   Rekker Fragment Constant Method:

   - Estimates partitioning of amines
   - Expresses results as ppm amine in oil, for each ppm amine in water

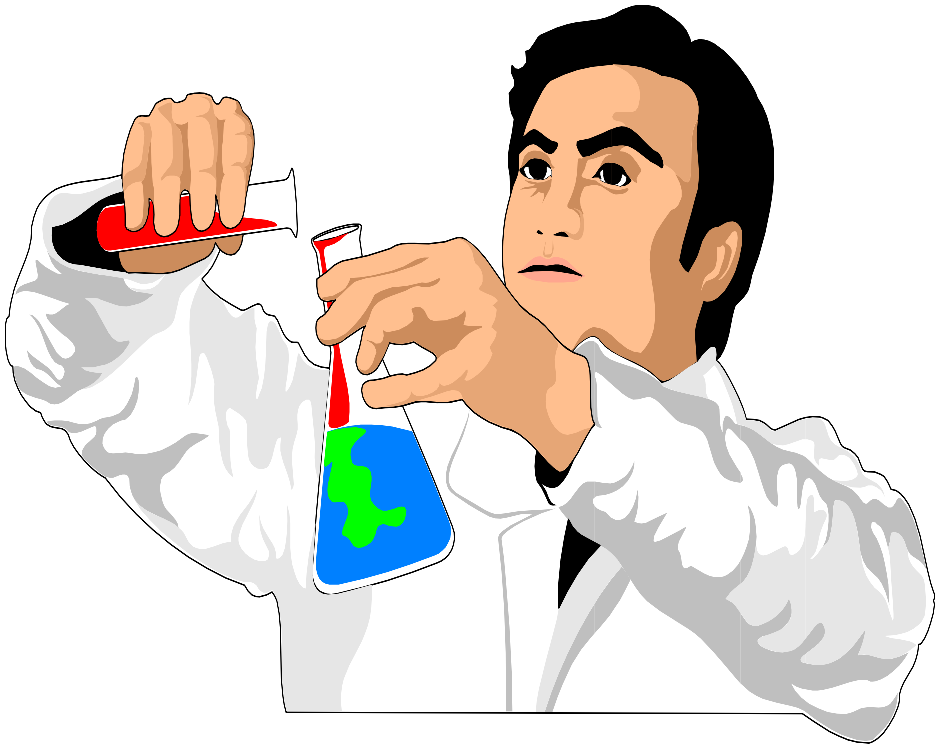
2. Low "Vapor-Aqueous" equilibrium ratio (Kva)

   a) In the Water, not the Vapor

$$Kva = \frac{\text{ppm amine in steam}}{\text{ppm amine in water}}$$

3. Cost effectiveness
4. Neutralizer Salt Properties

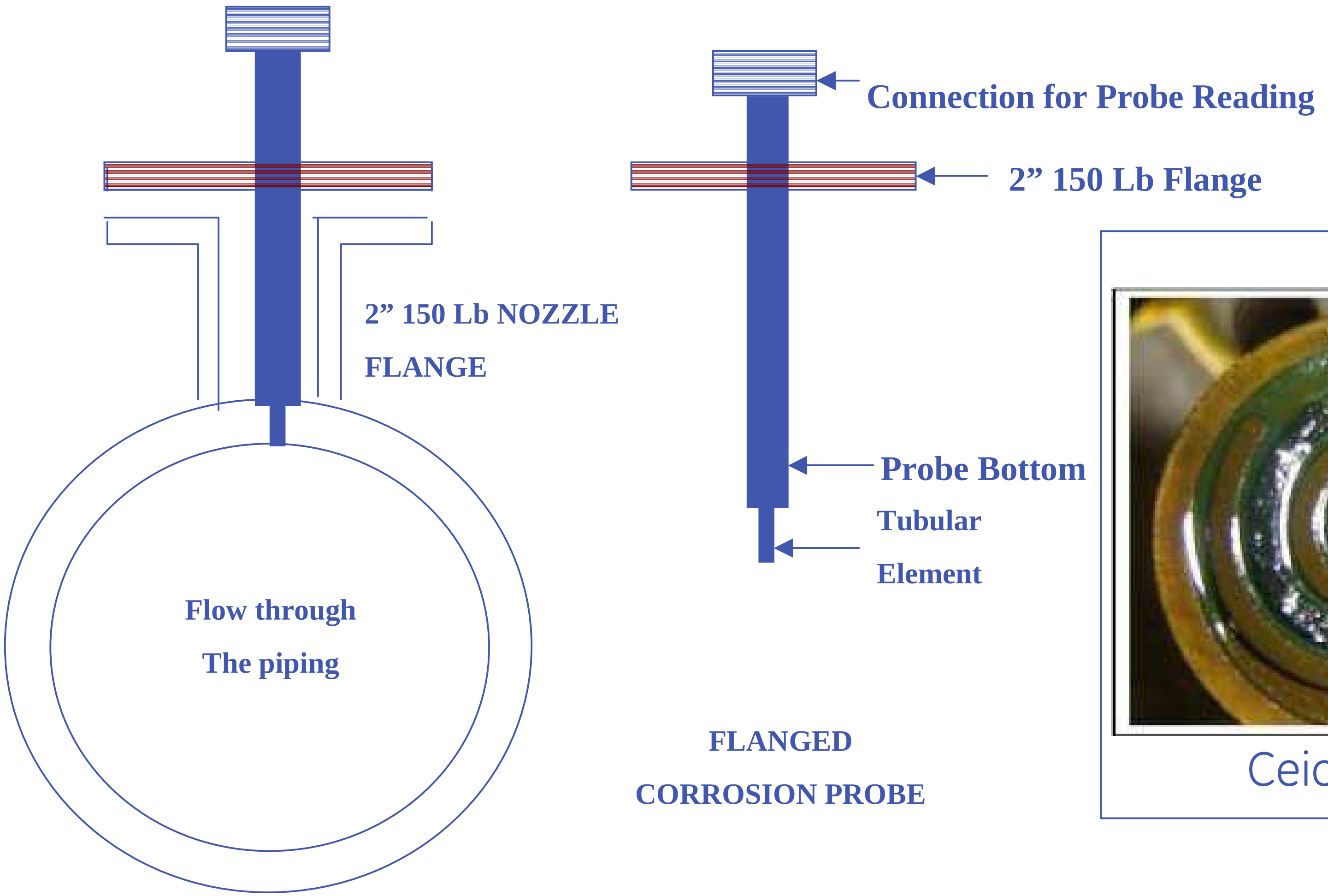
Monitoring & Lab Testing Procedures



Corrosion Monitoring

1) Water analyses
2) Hydrocarbon analyses
3) Corrosion rate measurement
   > ER Probes
   > Coupons
4) NDT

ER CORROSION PROBE SCHEMATIC



FLANGED
CORROSION PROBE

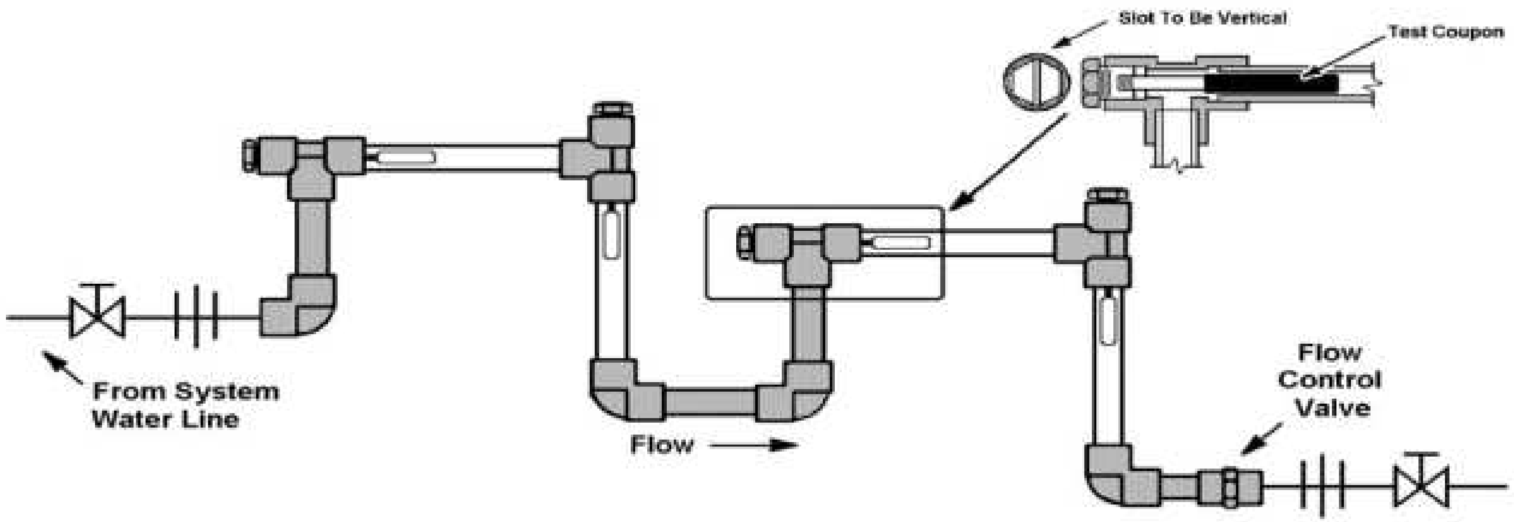
Ceion Probes

BLACK IRON CORROSION RACK

The Black Iron Corrosion Rack is recommended for corrosion monitoring in high temperature and/or high pressure installations such as steam condensate,high temperature water, hydronic heating, recirculating process systems, etc.

•Maximum Pressure: 200 psig (13.8 bar)

•Maximum Temperature: 160° F (71° C)



Corrosion Simulation Testing

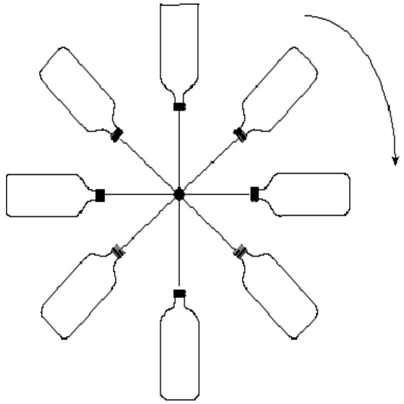
NEW TEST METHODS PROCEDURES

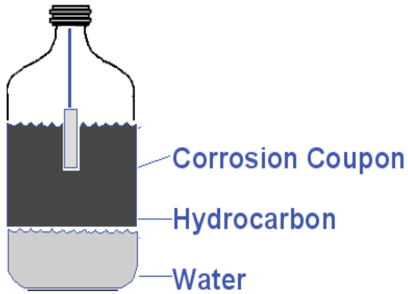
High Temperature and Velocity Autoclaves

- Coupon weight loss
- Realistic velocity effects
- Realistic oil/water ratio and coupon contact
- Realistic Aqueous Chemistry

Rotating Cylinder Electrode (RCE)

- Electrochemical Method
- Realistic velocity, well defined flow regime
- Allows multiple dosages per test
- Test film persistency
- Easy to simulate low pH excursions (pH upset)





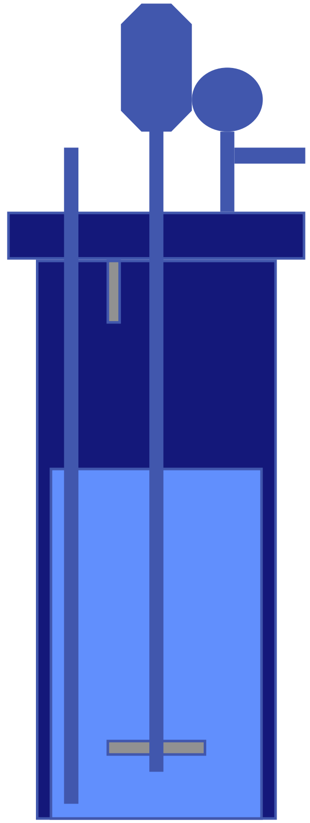
Coupon Wt. Loss, Good for Low Velocity & Temperature; Simple

Diagnostics - On Stream Monitoring

- Electrical Resistance (ER) Probes
- Coupons
- VTCP (Variable Temp Corrosion Probe)
- COLA (Condensate On-Line Monitor)
  - Simulates Dewpoint
- Continuous pH
- UT / X-Ray
- Water Analysis

Dew Point Corrosion Simulator

- Capabilities
  - Constructed of 316SS
  - Temp = 350ºF
  - Velocity = 50 ft/sec
  - Realistic chemistry
  - Can add appropriate gas (CO2)
  - Can vary oil/water ratio
  - Various metallurgies
- More Time Consuming Test



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Metallurgical Lab Capabilities

Failure/Corrosion Mechanisms

Deposit Analysis

Photography

Visual Analysis

Alloy Verification

Metallography

Hardness/Non-Destructive Testing

Fig.6 Microstructure of tube L at 100x magnification

Successful Corrosion Inhibition Treatment

Corrosion Location-CGC Interstage Coolers

Neutralizer Amine treatment at the CGC Inter-stage coolers to reduce the corrosion in the system due to acid loading in the system.

RESULTS ACHIEVED:

The injection of neutralized amines resulted in effectively mitigating the risk of corrosion of the intercoolers. Table III below illustrates a representative pH and iron content before and after the chemical treatment was initiated in the process gas compressor intercoolers.

Table-III: Summary of results before and after chemical treatment in the intercoolers.

Intercoolers	Condensate Sample [Before the Chemical Treatment]		Condensate Sample [After the Chemical Treatment]	
	pH	Iron (ppm)	pH	Iron (ppm)
1st Stage Suction Drum	4.2	10.35	5.01	0
2nd Stage Suction Drum	3.9	5.5	5.05	0.4
3rd Stage Suction Drum	3.8	7.8	5.1	0.98
4th Stage Suction Drum	4.2	11.74	4.95	1.1
5th Stage Suction Drum	9.1	2.5	5.85	0.5

Corrosion Location-Benzene Column

The major cause of corrosion is hydrochloric acid

- Chemical should be benzene soluble as there is very little water in the benzene column overhead
- Should be non-volatile under process conditions
- Should contain no nitrogen as nitrogen will poison zeolite alkylation catalyst

Technical Paper @ Badger Conference 2005 - "Addressing Process Corrosion Problems in EB/SM Plants"

J. Link - Park, Y.W. - Kim, C. - Yang, H.G.

Major Applications....

Ethylene Units

- Oil Quench/Water Quench Overhead Lines & Process Circulation
- Process Water Stripper
- DSG
- CGC Interstage Coolers
- Depentanizers, Dehaxenizers Overhead

Acrylonitrile Units

- Water Section – Quench Tower, Absorber Column
- Purification Section – Recovery Column

EDC- VCM Units

- Oxy-Clorination Water Quench
- Drying Column
- Light ends removal Column

EB & Styrene Units

- Dehydro Effleuent Condensors
- EB/SM Splitter Overhead
- BT Column Overhead
- Bz Recovery Column Overhead

Fouling & Inhibition

- What Is Fouling ?
- Fouling Mechanism
- Various Fouling Areas at Petrochemical Ind.
- Fouling Inhibitors
- Monitoring & Lab Testing Procedures
- Successful Antifouling Treatment

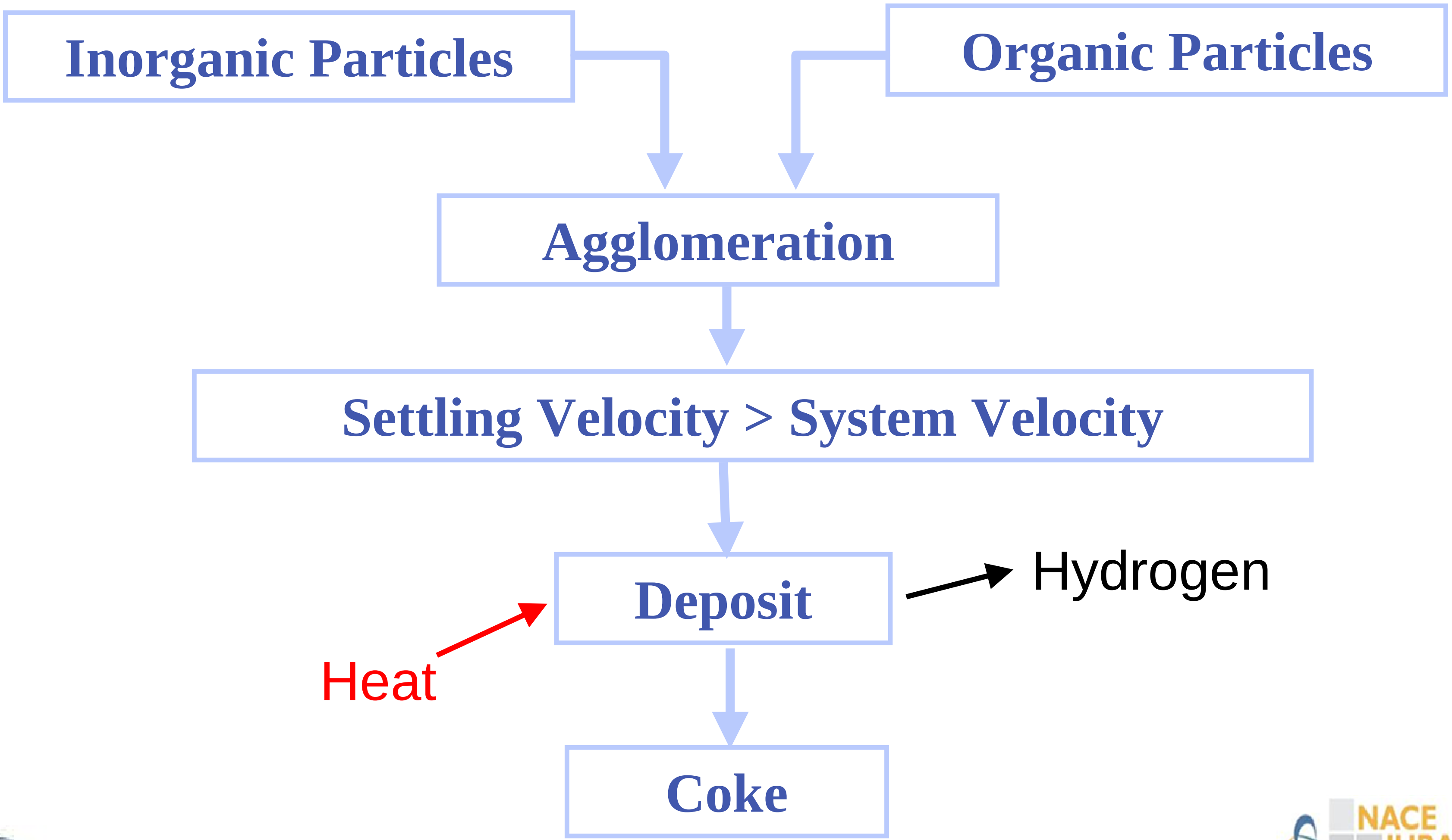
Fouling

- **Definition of Fouling**
  - Deposition/accumulation of unwanted material in process equipments.

- **Fouling Material**
  - Inorganic particles
    - Metal Oxides, Catalyst fines, Corrosion products, Salts, dirt , other insoluble contaminants and Volatile salts.

  - **Organic particles**
    - Polymers, Coke fines

Fouling Mechanism



Polymerization Mechanism

- Free Radical Polymerization
  - Free Radical
    - An Atom or Atomic group which lacks an electron of electron pair
    - Due to the lack of one electron
      - tries to be stable by obtaining an electron
      - unstable and reactive
  - 3 steps of Free Radical polymerization
    - Initiation
    - Propagation
    - Termination

Free Radical Polymerization

Thermal/Peroxide Radicals

Initiation

R-H $\xrightarrow{\Delta}$ R˙ + H˙

ROOH $\xrightarrow[\text{metals}]{\Delta}$ RO˙ + OH˙

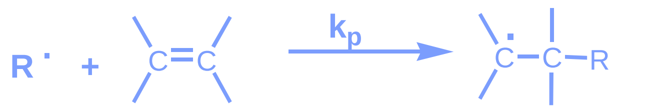
Propagation

Autooxidation

R˙ + O_2 ⟶ ROO˙

ROO˙ + R-H ⟶ ROOH + R˙

Polymerization



Inhibition

R˙ + In $\xrightarrow{k_i}$ R-In

RO˙ + In ⟶ RO-In

ROO˙ + In ⟶ ROO-In

- Radicals initiate polymerisation
- Dissolved oxygen or oxygen containing organic molecules
- Fast generation of peroxide radicals at low temperature
- At somewhat higher temperatures further chain propagation reactions
- Inhibition method depends on type of radicals

- < 85 ℃ : Slow
- 85 - 95 ℃ : Moderate
- 95 – 120 ℃ : Fast

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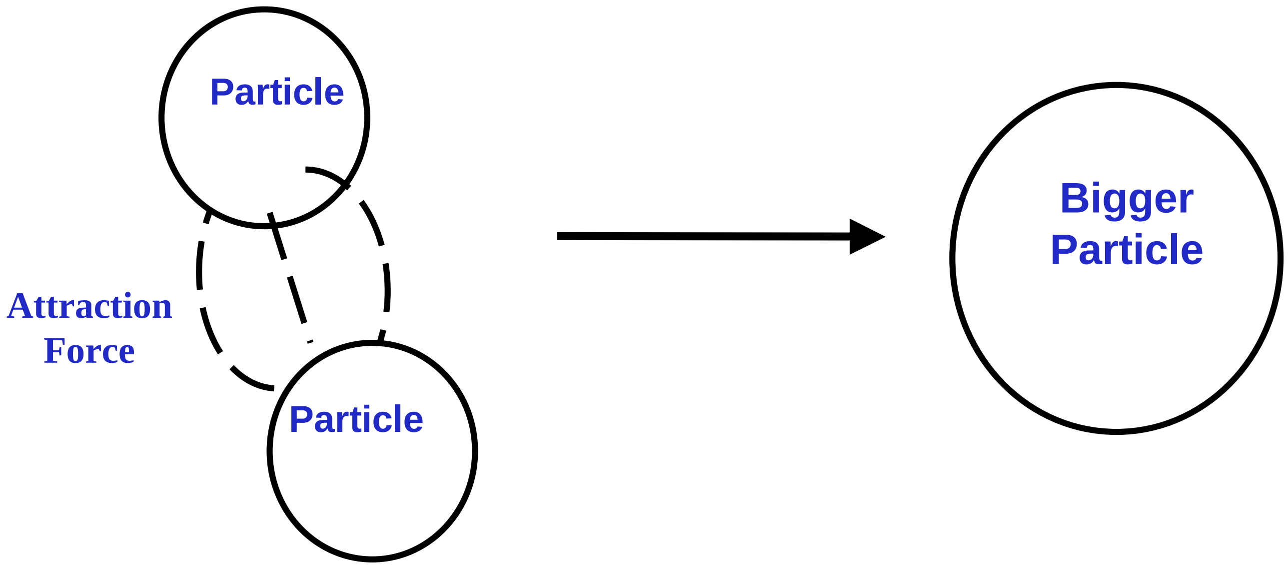
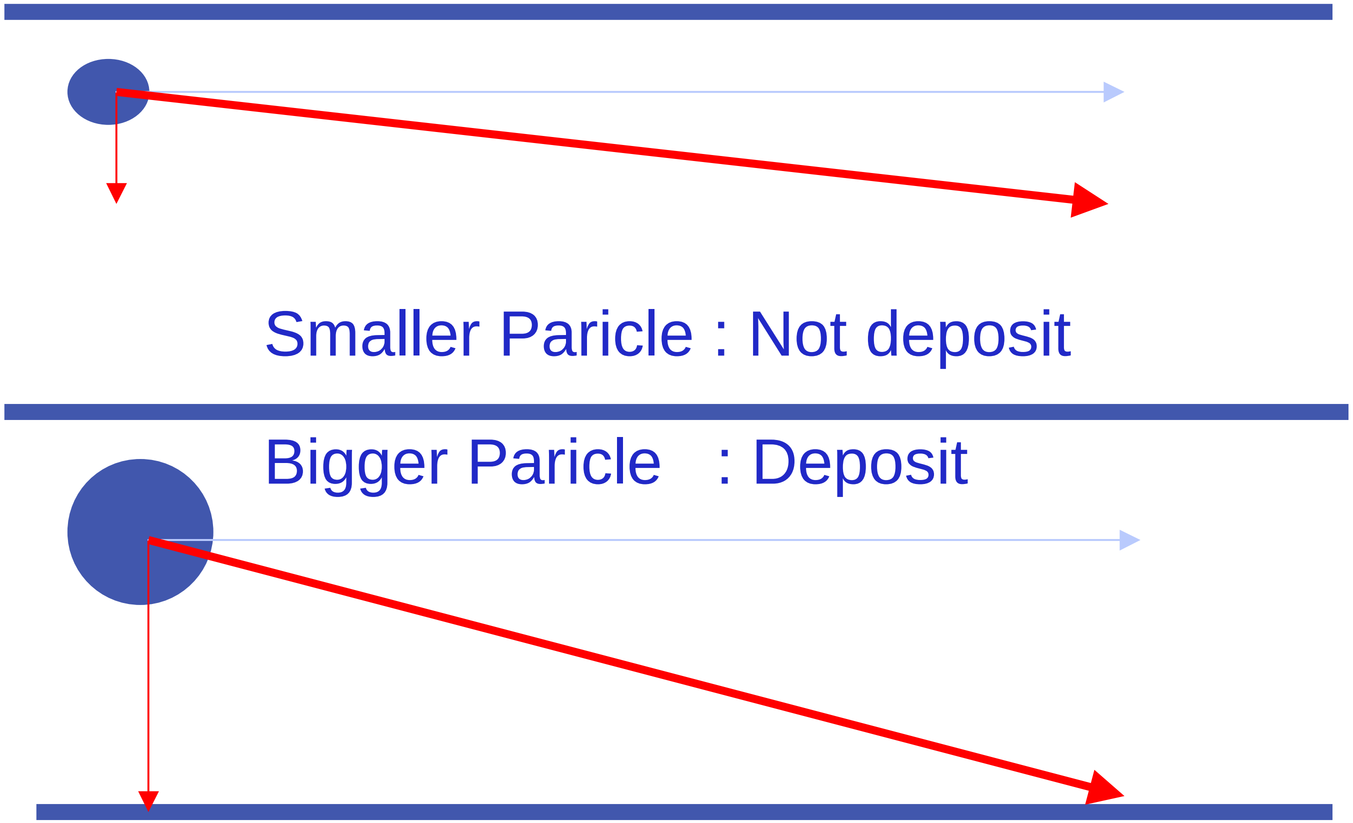
Agglomeration of Particles



Diameter increases Easily settles (Stokes law)

Fouling Mechanism

- Fluid Velocity V/s. Settling Velocity



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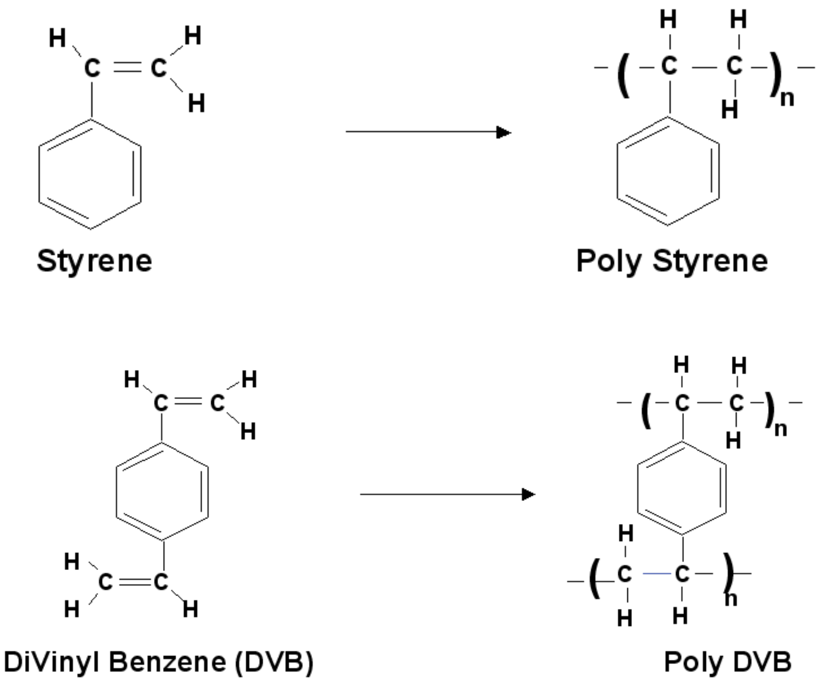
Concern Areas …

Oil Quench …

- Free Radical Polymerization of:
    - Styrene
    - Indene
    - Divinylbenzene
    - Naphthalenes



- Precipitation of naphthalenes and asphaltenic compounds
- Complex Hetero-polymeric material consisting of Butadiene, Isoprene, Styrene, Indene, DVB, & Vinylnaphthalenes

Caustic Tower & CGC ...

- Formation of “red oil” from polymerization of carbonyls (acetaldehyde and ketones (acetone))---which are formed in furnaces.

- Acetaldehyde forming reaction is furnace is as follows:

  Ethylene + $H_2O \rightarrow$ Acetaldehyde + H_2

  Acetylene + $H_2O \rightarrow$ Acetaldehyde (CH_3CHO)

- When acetaldehyde enter the caustic tower, caustic catalyzes the Aldol condensation reaction, resulting “aldol” (β-Hydroxyaldehyde)

- The unsaturated Aldol can further polymerize with another acetaldehyde or another aldol molecule to form higher MW oligomers and polymers which are water insoluble and dark red in color

DSG …

- Entrained oil from the Quench System coming to the DSG degrades and the deposit dehydrogenates over time into a coke-like material
- Heat Induced polymerization of water soluble organics
- Corrosion product (iron) agglomeration acting as a catalyst
- Oxygen initiated polymerization

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Ethylene Fractionation Train …

- Free Radical Polymerization of di-olefins like Butadiene, Isoprene, Propadiene, Cyclopentadiene
- Contamination of feedstock with oxygenated compounds such as ethanolamines will result in peroxide formation, which initiates fouling when heated
- Transition metals, iron and copper, catalyze polymerization and increase fouling potential
- High residence time leads to high fouling potential
- High Unit utilization

Acrylonitrile ...

- Anionic mechanism
  - HCN polymer
  - Cyanide polymer typically found in Heads column

- Free Radical mechanism

  AN polymer

  a) Recovery Column Overhead

  b) Heads column bottoms and reboiler

  c) Dryer column and reboiler

EDC/VCM …

- ➢Polymerization of Chloroprene in light still overhead

- ➢Cracking of EDC and other chlorinated organics due to heat and catalyzed by Ferric Chloride

- ➢Precipitation or loss of solubility of high molecular weight organics in tar still and/or vacuum column bottoms

- ➢Water contamination during distillation causes severe organic fouling

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Styrene …

➢ SM polymerization due to high operating temperature

➢ DEB will readily dehydrogenated to DiVinyl Benzene (DVB) which polymerizes readily via free radical mechanism resulting into a cross-linked polymer

➢ Dehydro Effluent Condenser
➢ Process Water Stripper
➢ Off (Vent) Gas Compressor
➢ SM Distillation Section

Product Mechanisms

GE W&PT offers a complete line of antifoulant products

Types of antifoulant products:

- Dispersants
  - Low temperature
  - High temperature
- Inhibitors
  - Free radical inhibitors
  - Condensation inhibitors
  - Metal passivators
  - Antioxidants

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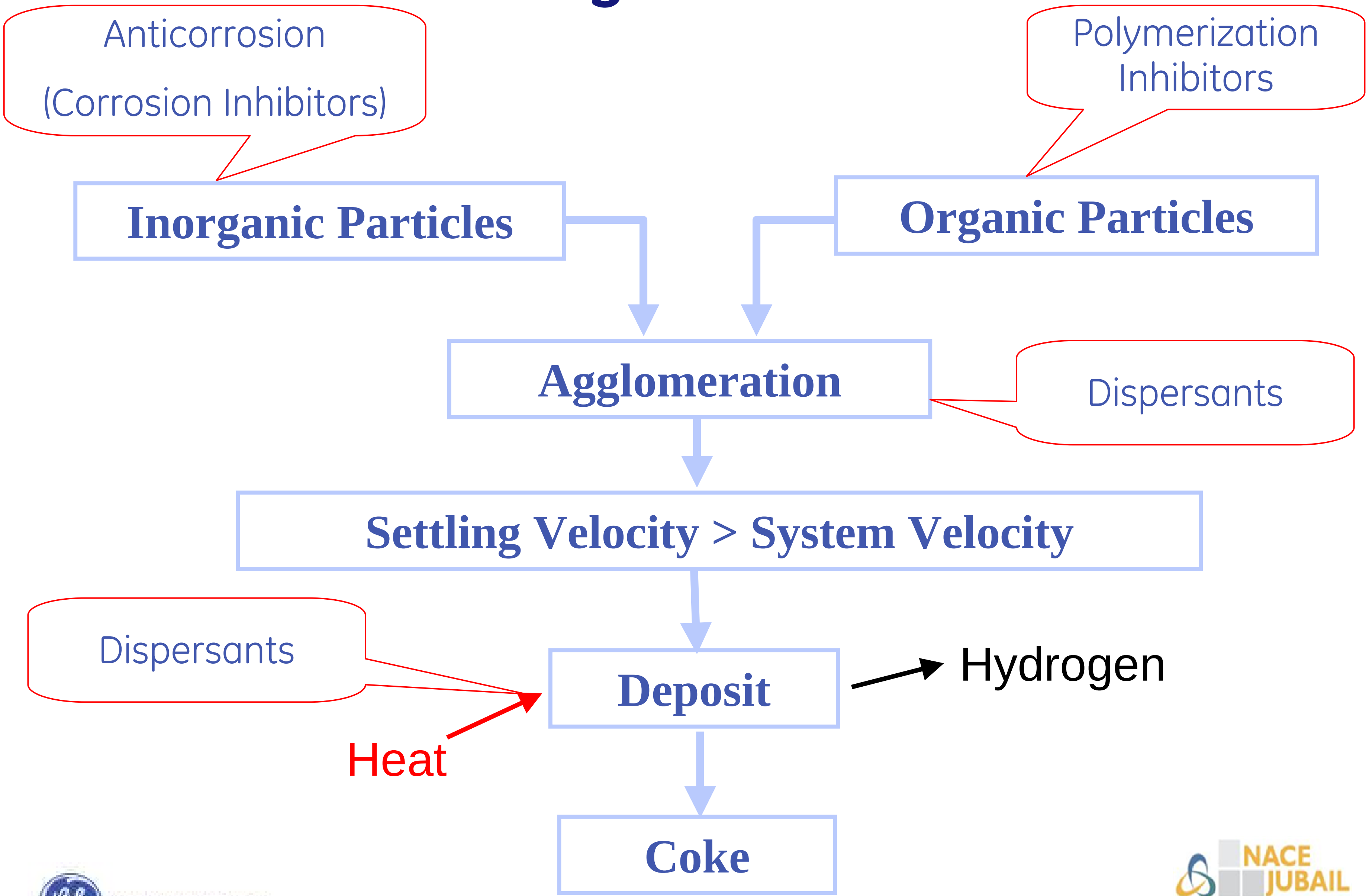
Fouling Mechanism



Antifoulants/Antipolymerants

Antifoulants are chemical additives (one or more functional chemicals) used to protect equipment from loss of heat transfer efficiency.

Inhibition

$$R^{\cdot} + In \xrightarrow{k_i} R\text{-}In$$

$$RO^{\cdot} + In \longrightarrow RO\text{-}In$$

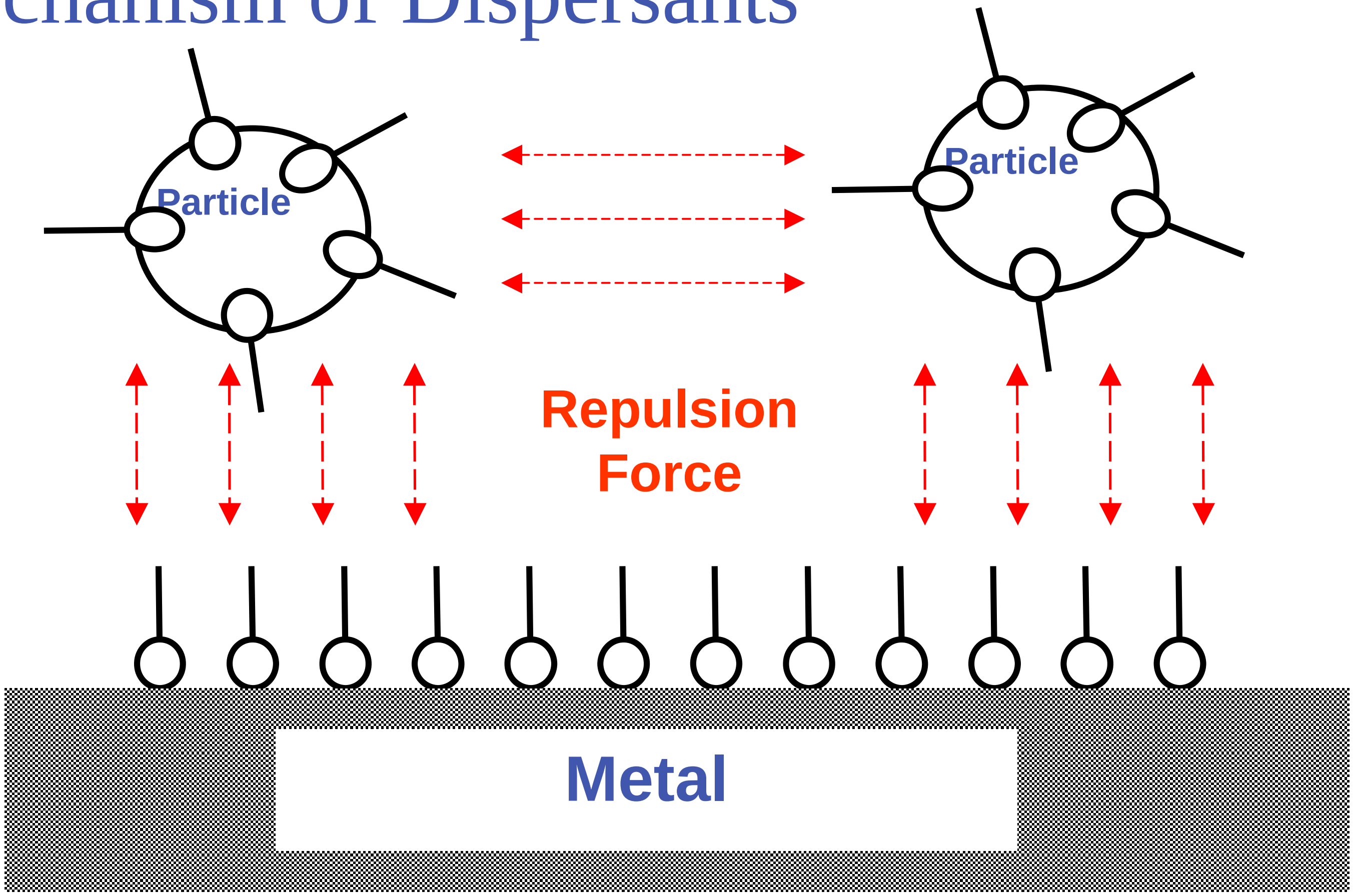
$$ROO^{\cdot} + In \longrightarrow ROO\text{-}In$$

$$R\cdot + A\text{-}In \longrightarrow R\text{-}In + A$$

R· = Reactive polymer, monomer radical
A-In = Hydrogen donating chain-stopper
R-In = Short chain, terminated radical
A· = Stable Chain-stopper radical

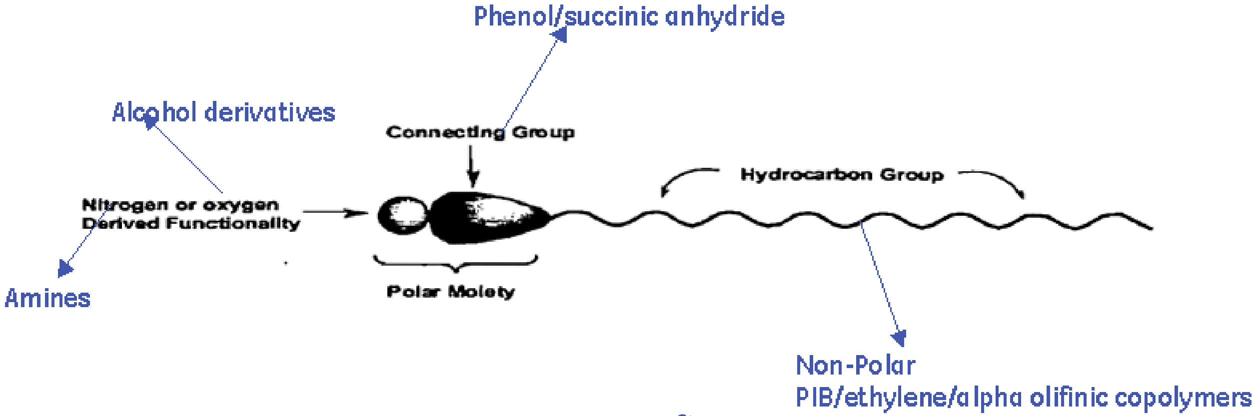
Dispersants

- Mechanism of Dispersants



Prevents Particles from Deposition on Metal Surface

Dispersant Functionality



Features

- Highly surface active chemistry
- Inorganic and Organic dispersant functionality
- Prevents the agglomeration of solids
- At high dosages may exhibit cleanup capability
- Formulated for process compatibility

Benefits

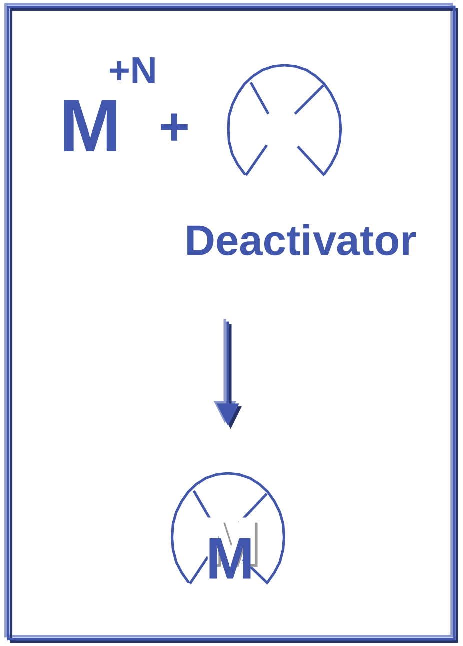
- Prevents deposition of solids
- Effective fouling control of both salt deposition and entrapped hydrocarbons
- Protection for downstream equipment.
- Avoids downstream problems
- Provides ability to respond to upsets
- Eliminates concerns for product or downstream contamination

Metal Deactivator/ Chelant

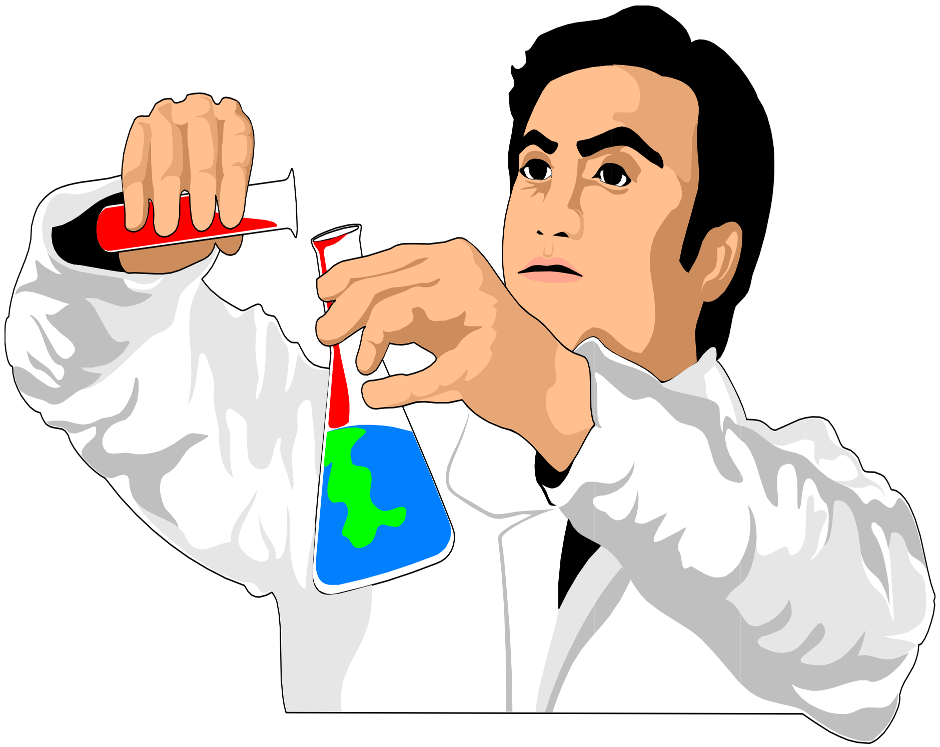
Modification of Metal Ion Activity

Reduces Catalytic Activity

Reduces Initiation of
Polymerization



Monitoring & Lab Testing Procedures



Monitoring Processes

Operating Conditions

- Flows
- Pressures
- Exchanger temperature
- Heater tube temps
- Compressor vibrations
- Furnace firing rates
- Open bypasses
- Cleaning frequency
- Corrosion rates

- Reboiler and vaporiser U-coefficients
- Multiple Regression Analysis (MRA) and Statistical Process Control (SPC) of heat transfer calculations
- Data plots of other appropriate process data

Tools to Design an Effective Treatment Program

Experience / Case Histories

Knowledge of Unit History

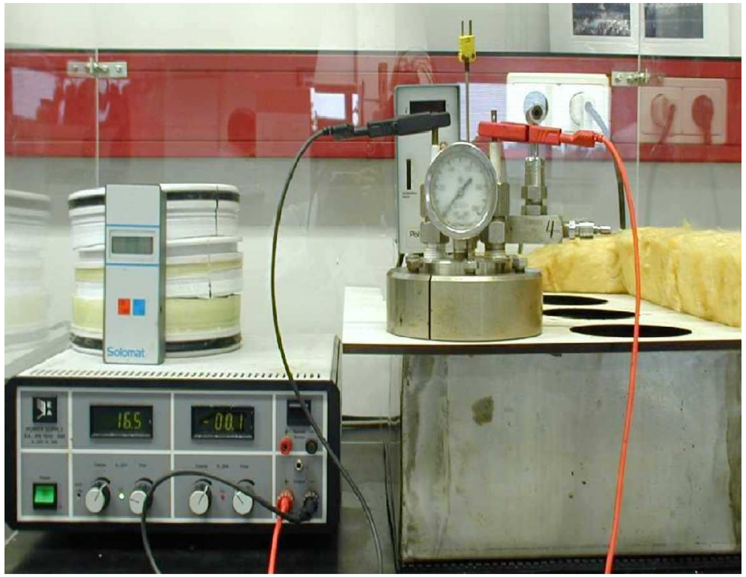
Fluid Characterisation

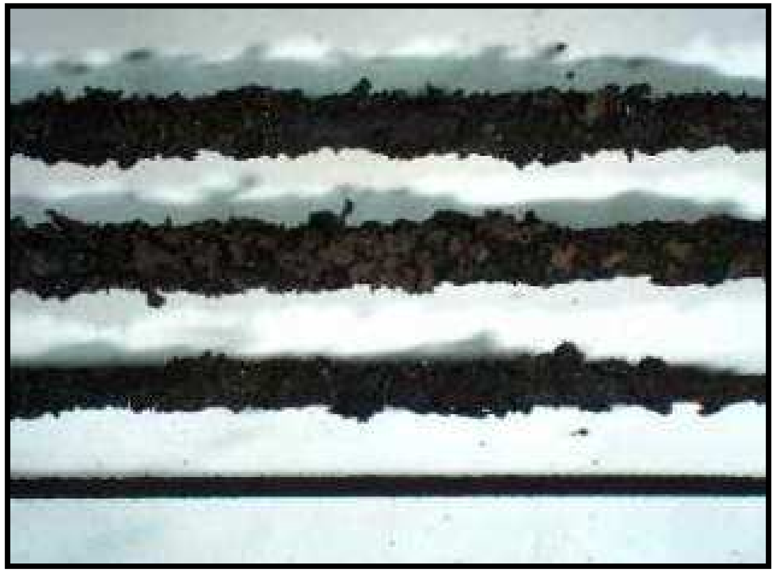
Deposit Analysis

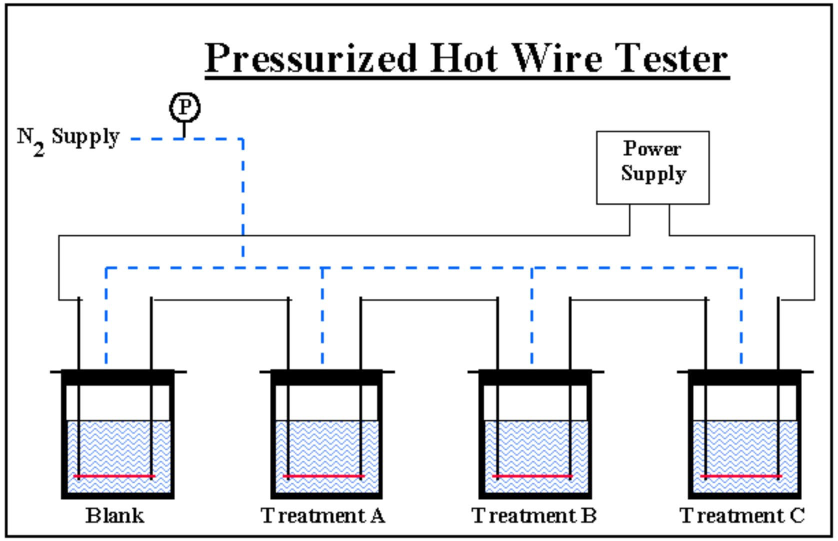
Lab Simulation

Field Tests

Pressurized Hot Wire (HWT) Apparatus

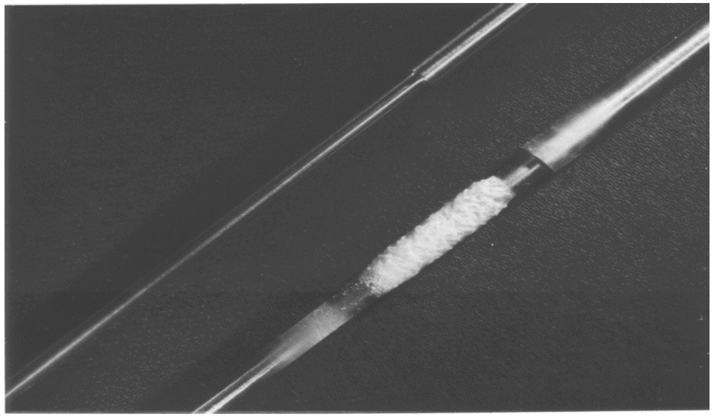


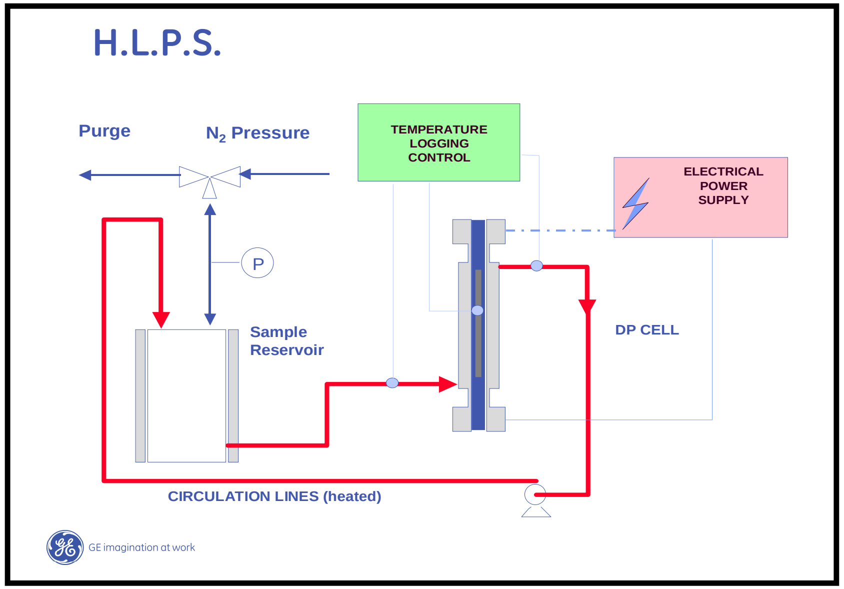




Dynamic Lab Test - Hot Liquid Process Simulator (HLPS)

- Thermal Fouling Mode
- Rod temperature constant at 260 C
- Oil outlet temp. started at 210 C
- Fluid under 600 psi nitrogen purge
- 5 hour run





Deposit Analysis Capabilities

Loss on Ignition	Organics and Volatile Inorganics
Ash (100-LOI)	Non-volatile Inorganics
Dichloromethane Extractables	Lower Molecular Weight Organics Including Entrained Hydrocarbons
Non-Extractables	Coke and Inorganic Content
Inorganic Analysis	Elemental Composition of Ash (Fe, Cu, Ni, etc...)
Organic Analysis	Carbon, Hydrogen, Nitrogen Content of Non-Extractables

Deposit Analysis

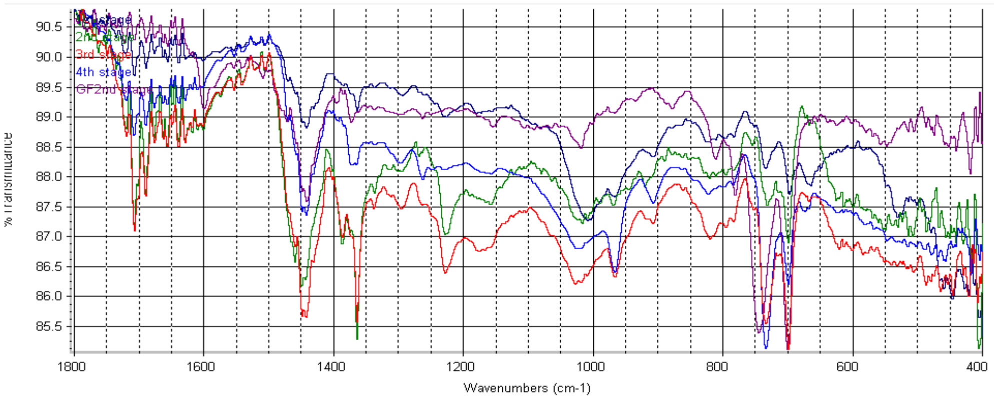
LOI analysis

Sample	% Loss on Ignition @		
	105 °C	550 °C	840 °C
1st Stage Intercooler	0	98.8	98.9
2nd Stage Intercooler	0.7	93.7	93.4
3rd Stage Intercooler	1.1	99.2	99.5
4th Stage Intercooler	0.8	99.2	99.1
Gasoline fractionator	5.7	99.5	99.8

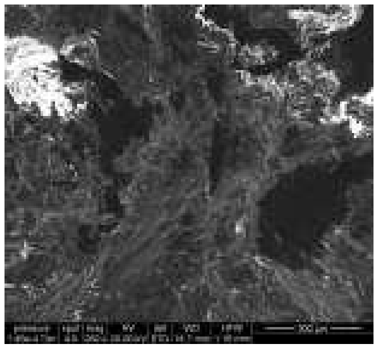
Metals- ICP-AES analysis

Sample	Metals (ppm)					
	Na	K	Ca	Mg	Al	Zn
1st Stage Intercooler	373	34	315	73	197	14
2nd Stage Intercooler	1058	99	282	527	47	66
3rd Stage Intercooler	35	7	101	29	42	49
4th Stage Intercooler	55	17	74	19	72	14
Gasoline fractionator	345	11	72	68	29	3
Total	1866	168	844	716	387	146

FTIR spectra of DCM insoluble fraction



SEM-EDX Analysis



Element	Weight%	Atomic%
C K	71.37	76.92
O K	28.43	23.00
S K	0.20	0.08
Totals	100.00	

Element	Weight%	Atomic%
C K	74.47	79.66
O K	25.14	20.19
S K	0.39	0.16
Totals	100.00	

Successful Antifoulant Treatment

EDC-VCM Plant in Gulf Region

EDC Furnace Convection Section

- Before treatment run length 3 to 4 months
- After treatment run length 12 to 13 months

HCl Column

- Reboiler run length before treatment 3 to 4 months
- After treatment – 22 to 24 months
- Column run length 4 - 5 yrs after treatment without any limitation

Head & Vacuum Column

- Reboiler run length before treatment – 3 to 4 months
- After Treatment 22-24 months

Caustic Unit at Europe

Sampling on strong & weak caustic loop

Feb. 9th / PF 20Y15 Injection pump failure

Feb. 10th/ 1 day after 20Y15 re-injection

Feb. 12th/ 3 days after 20Y15 re-injection

Feb. 16th/ 6 days after 20Y15 re-injection

Major Applications….

Ethylene Units

- Oil Quench/Water Quench
- DSG
- CGC & Interstage Coolers
- Caustic Tower
- Cold Trains
- GHU

Acrylonitrile Units

- Water Section – Heads,Dryer, Product & Rerun Column
- Purification Section – Recovery Column, Absorber column

EDC- VCM Units

- Oxy-Clorination Water Quench
- Drying Column
- Light ends removal Column

EB & Styrene Units

- Dehydro Effleuent Condensors
- EB/SM Splitter Overhead
- BT Column Overhead
- Bz Recovery Column Overhead

GEWPT Corrosion Inhibitors & Antifoulant Technology

1. Petroflo 21Y.. series as Neutralizer Amines
2. Petroflo OS.. series as Filming Amines
3. Petroflo 21Y..series as non Amine based Filmers
4. Styrex series for Styrene plant on Neutralizers & Antifoulants
5. Petroflo20Y... series as Antifoulants, Dispersants, Surface Modifiers, Metal Deactivators, Antioxidants, etc...
6. Petroflo20Y... Non N based antifoulants

GE WPT Application Global Running Experience

1. 24 applications in Oil Quench Tower for fouling & corrosion control
2. >32 applications in Quench & Dilution Steam Generation System for fouling & corrosion
3. 25 applications in CGC for fouling & corrosion control
4. 19 applications in Caustic Scrubber for fouling control
5. 36 applications in fractionation train for fouling control
6. 24 applications in G.H.U. / Py-Gas stabilisation for fouling and corrosion control
7. 13 applications in crude butadiene for fouling control
8. 10 applications on butadiene for fouling control on EDS & Purification Sections
9. >30 applications on EDC/VCM for fouling control
10. >36 applications on Styrene for corrosion & fouling control

Thank you very much for your attention

Deepak Sharma
GE Power & Water
Water & Process Technologies
T: +973 17408650
F: +973 17408691
M: +973 39418041
E: deepak.sharma.s@ge.com

P.O. Box 10252, Bldg. 1503,
Road 1161, Al Musalla 411, Manama
Kingdom of Bahrain

imagination at work

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