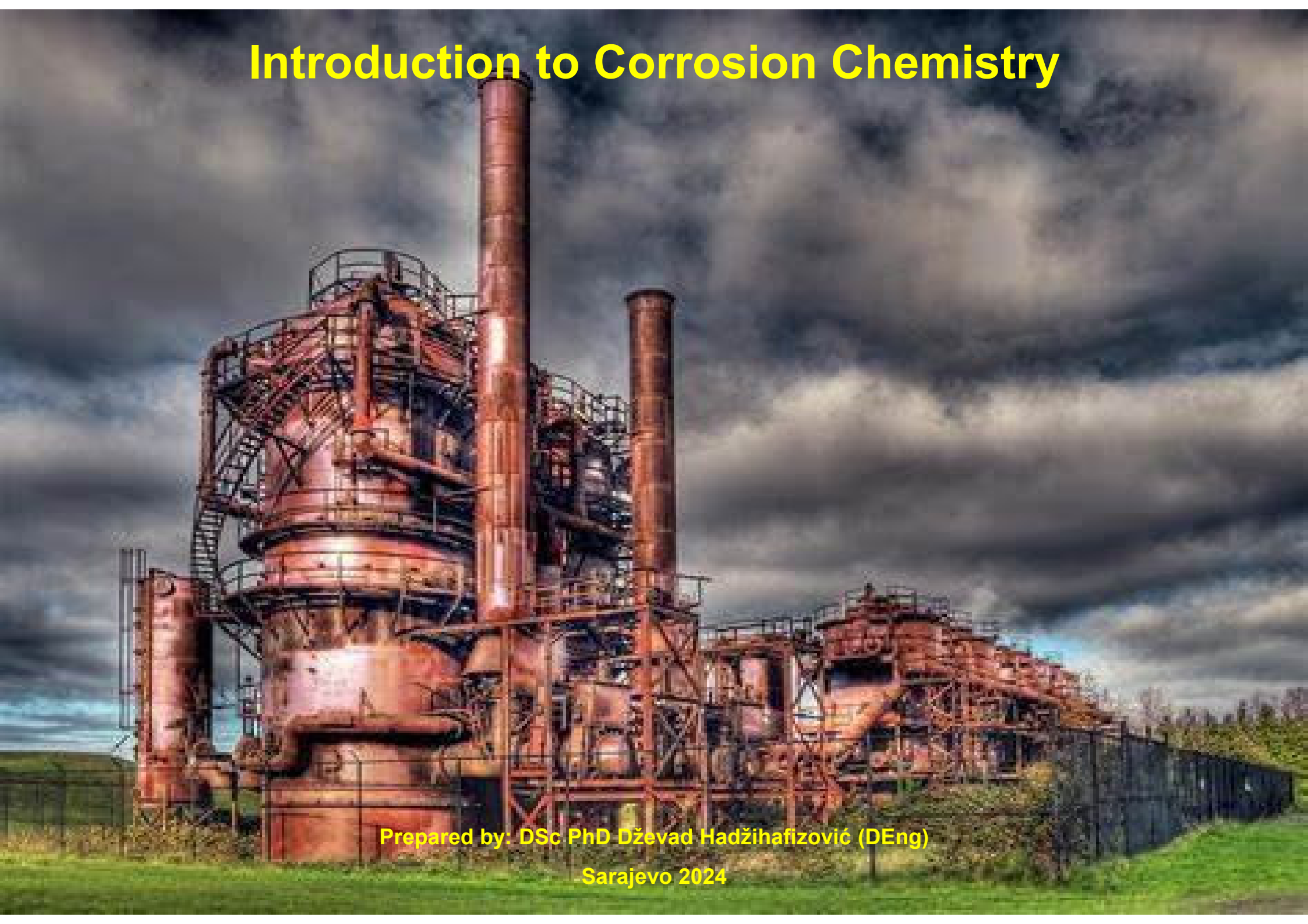


# Introduction to Corrosion Chemistry



Prepared by: DSc PhD Dževad Hadžihafizović (DEng)

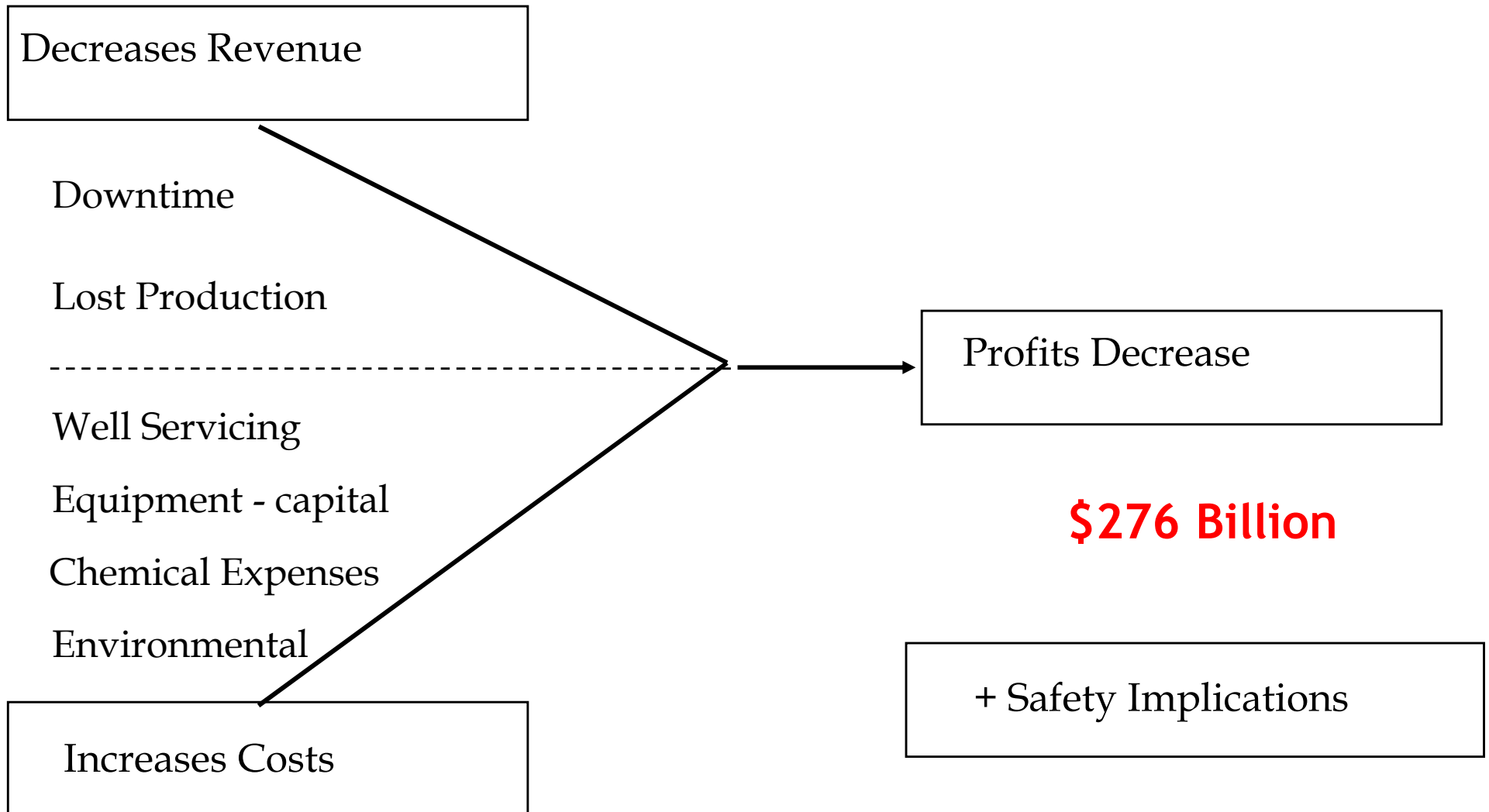
Sarajevo 2024

# Discuss Asset Integrity Related Issues

- Corrosion theory
- Corrosion inhibitor basics
- Corrosion inhibitor evaluation
- Corrosion monitoring
- Clean n Cor

A Greater Understanding of How Corrosion Takes Place And Can Be Mitigated

# Why is corrosion a concern ?

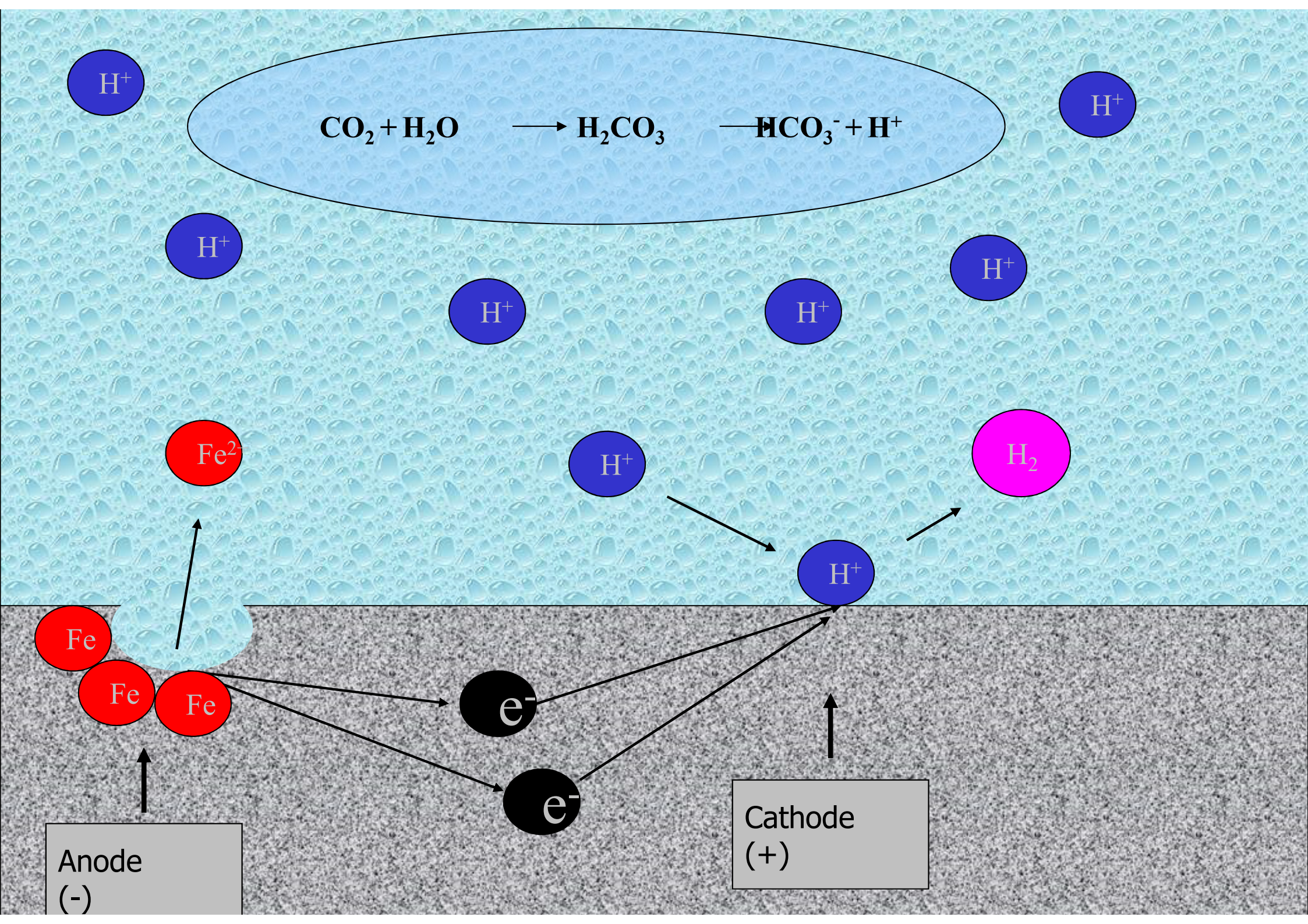


# What is Corrosion?

- Deterioration of a substance due to the reaction with its environment
- Corrosion problems are caused by presence of water and is an electrochemical process
- Energy is put into a metal by milling it, corrosion is the process of returning it to its lower state



Here you will see a nice figure detailing the process of corrosion.  $\text{CO}_2$  is hydrolyzed to form carbonic acid which gives up a proton. The protons migrate to the surface of the metal where they are reduced to form hydrogen gas. The protons are reduced by electrons which are given up by the iron metal which is oxidized to form iron  $++$



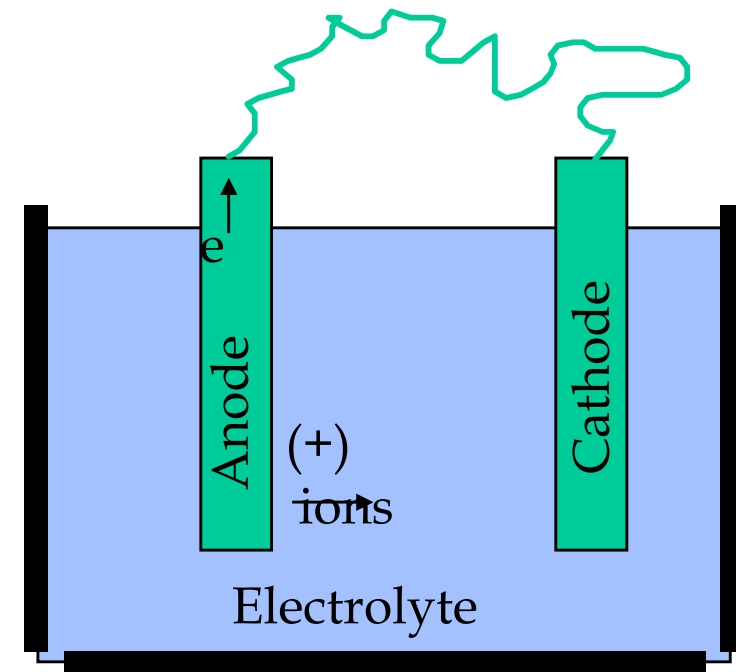
## Standard Electrochemical Series

*High Energy*

|    |         |
|----|---------|
| K  | -2.92 V |
| Mg | -2.34 V |
| Al | -1.67 V |
| Zn | -0.76 V |
| Cr | -0.71 V |
| Fe | -0.44 V |
| Ni | -0.25 V |
| H  | 0       |
| Cu | +0.35 V |
| Ag | +0.80 V |
| Pt | +1.20 V |
| Au | +1.68 V |

*Therefore Al more prone  
to corrosion than Fe*

*Low Energy*



## Four Requirements for Corrosion:

- *Anode*

*e.g. Al (-1.67 V) + Fe (-0.44 V)*

*Aluminium = Anode*

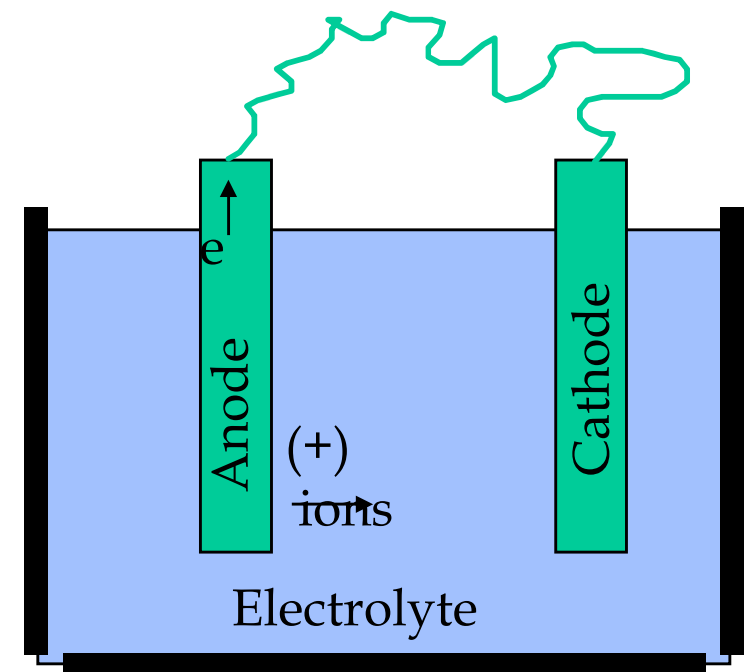
*Iron = Cathode*

*Potential = 1.67 - 0.44 = 1.23 V*

- *Cathode*

- *Metallic Path*

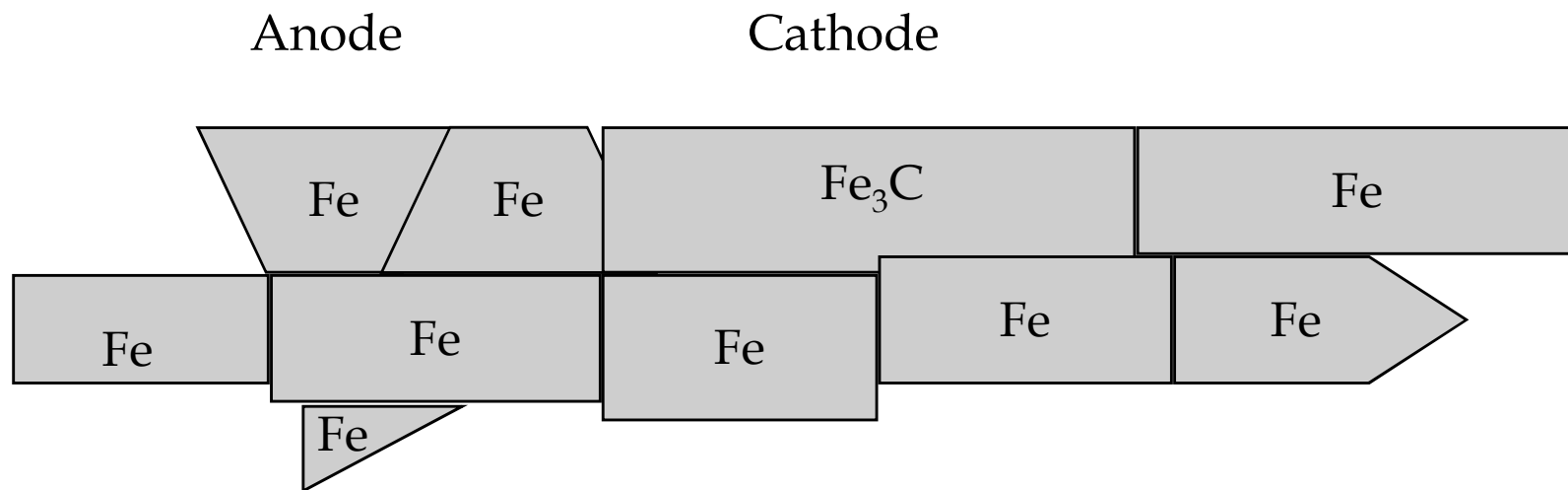
- *Electrolyte*



# Corrosion of Steel

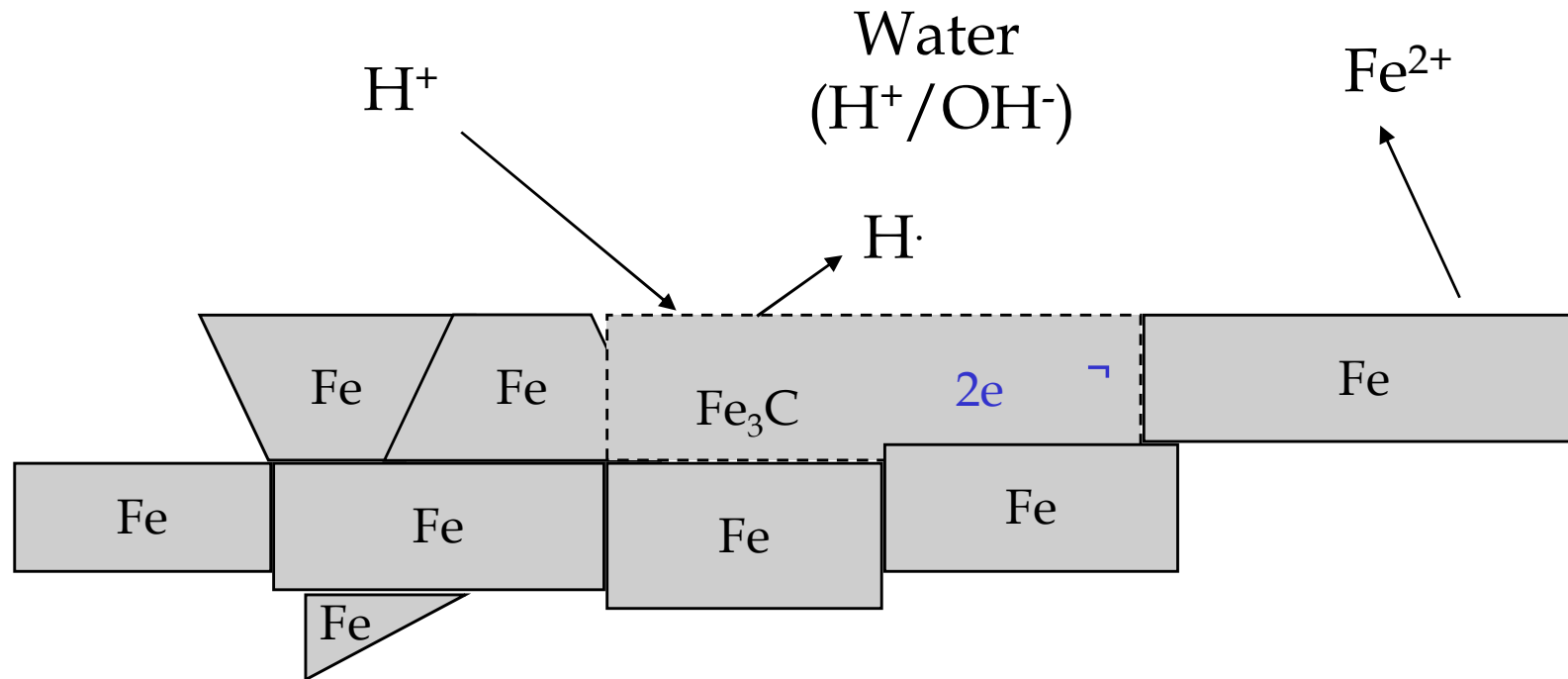
- Steel is primarily an alloy of iron and carbon
- Steel is inhomogeneous
- Composed of 2 materials: pure iron (Fe) and crystals of iron carbide ( $\text{Fe}_3\text{C}$ )
- Crystals of carbides are dispersed throughout the iron

*$Fe_3C$  is a lower energy state than Fe  
therefore a potential difference exists with  
Fe as the anode and  $Fe_3C$  the cathode*



# Corrosion of Steel

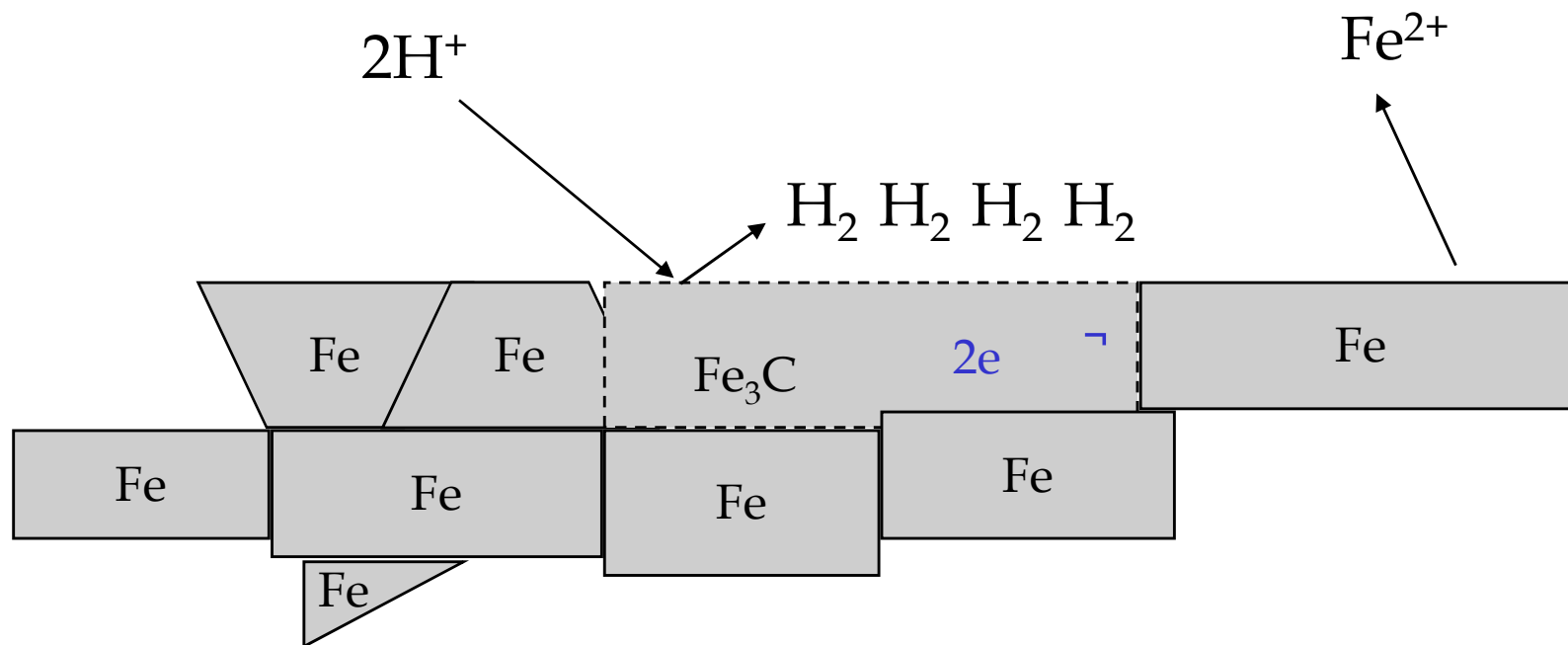
*Water comes in contact with steel completes the circuit*



*With the circuit closed by water the corrosion takes place spontaneously as electrons flow from iron to iron carbide*

## Cathodic Polarization

*If reaction products remain at cathode they slow the cathodic reaction, consequently anodic reaction also slows down.*

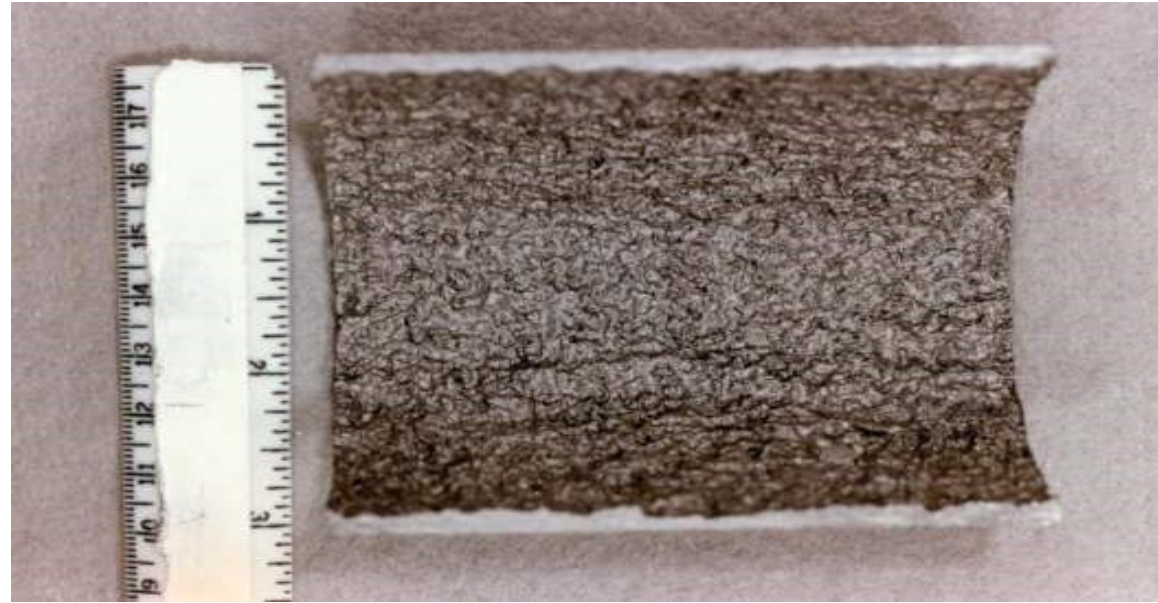


## Factors Which Affect Corrosion Rate

- Metallurgy – CS vs SS, 1018 vs. A-36
- Fluid chemistry
  - Water Chemistry – electrolyte composition, CO<sub>2</sub> solubility, pH unit basics
  - Oil chemistry – organic acids, naphthenic acids
  - Dissolved gases – CO<sub>2</sub>, H<sub>2</sub>S, (O<sub>2</sub>)
- Solids – sands, inorganic deposits, organic deposits
- Velocity – high vs. low
- Microbiological activity – what the bugs are producing
- Temperature & Pressure – high vs. low

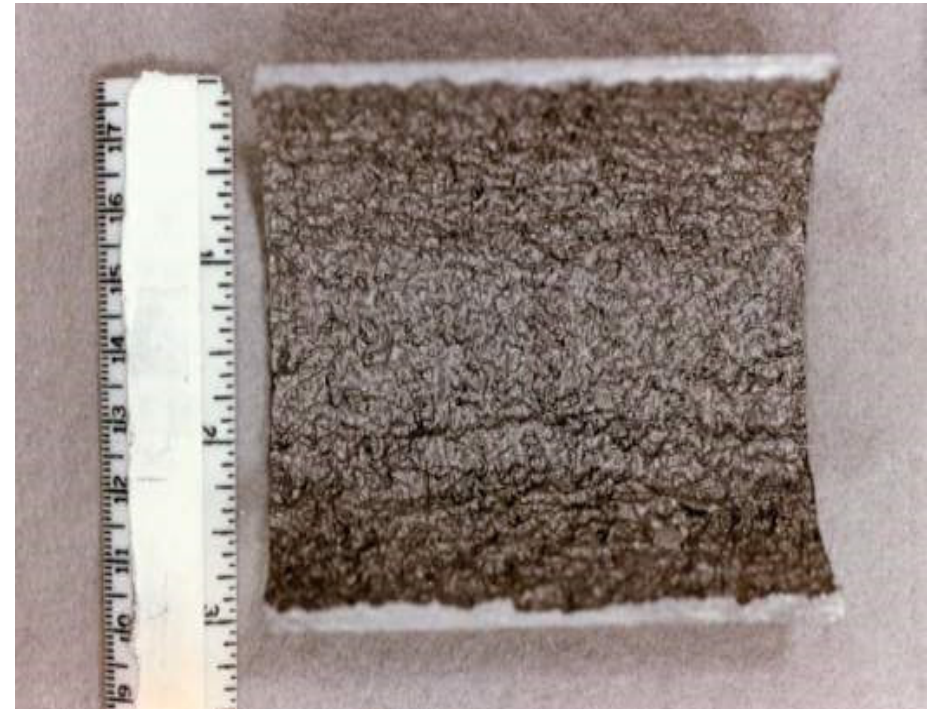
## Forms of Corrosive Attack

- General Corrosion
- Bimetallic
- Pitting
  - $\text{CO}_2$
  - $\text{H}_2\text{S}$
  - MIC

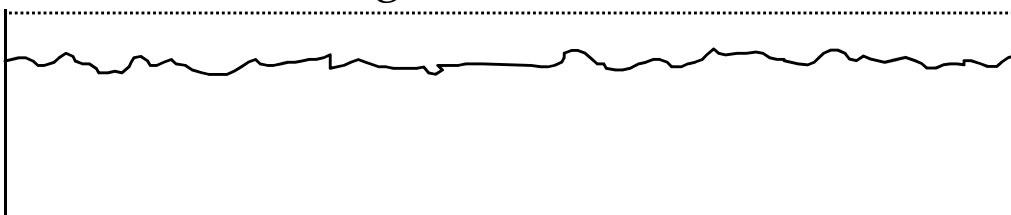


## General / Uniform Corrosion

- Occurs when anodic / cathodic areas shift frequently - corrodes surface 'uniformly'
- Removes largest quantity of metal however, least concern - lifetimes accurately estimated



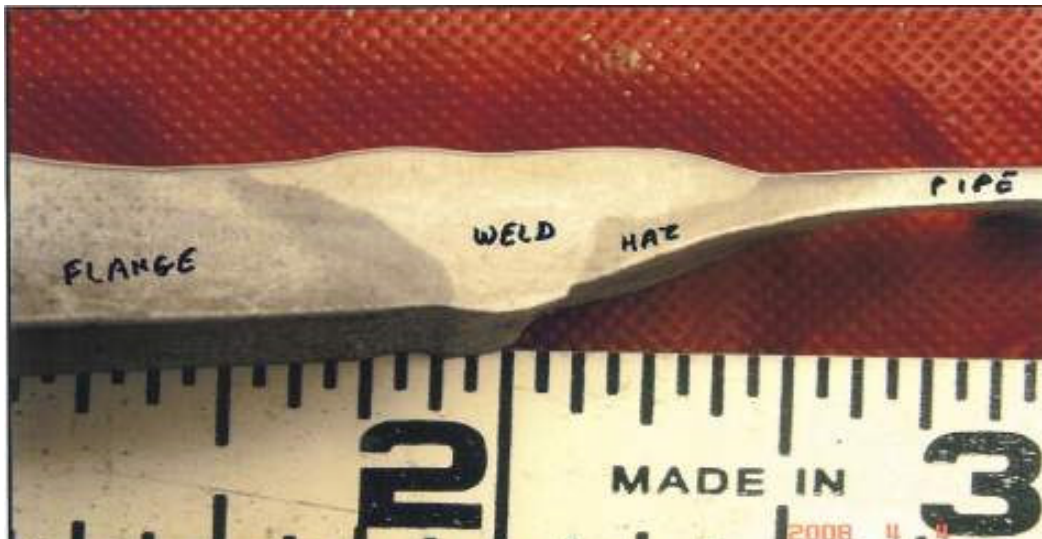
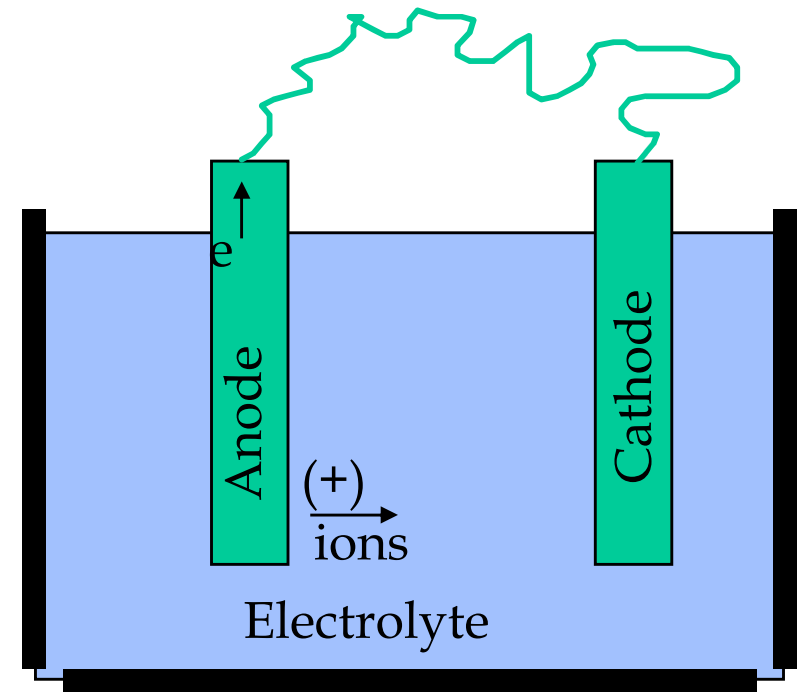
original surface



# Types of Corrosion - Bimetallic

## Bimetallic Corrosion

- Dissimilar metals in an electrolyte - different potentials
- More reactive metal = anode
- Localized corrosion
- Example: Weld lines



## Pitting Corrosion

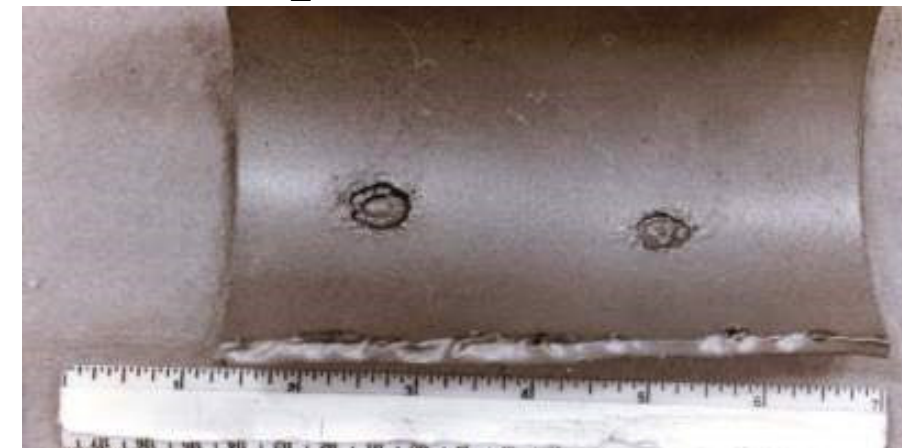
- Most difficult to predict - most severe - failures in days
- Anodes remain relatively fixed - concentrated corrosion - localized corrosion rate  $\gg$  general rate
- Caused by concentration cells where anode area becomes progressively  $\ll$  cathode area during reaction
- Occurs in non-homogeneous iron sulfide, oxide and hydroxide films



CO<sub>2</sub> Pitting



H<sub>2</sub>S Pitting



MIC Pitting

# Options for a Corroding System:

- Mechanical/Operational
  - Materials of construction
  - Equipment design
  - Cathodic protection
  - Process control
- Chemical
  - Neutralizers
  - Filming corrosion inhibitors
- Let the system corrode...

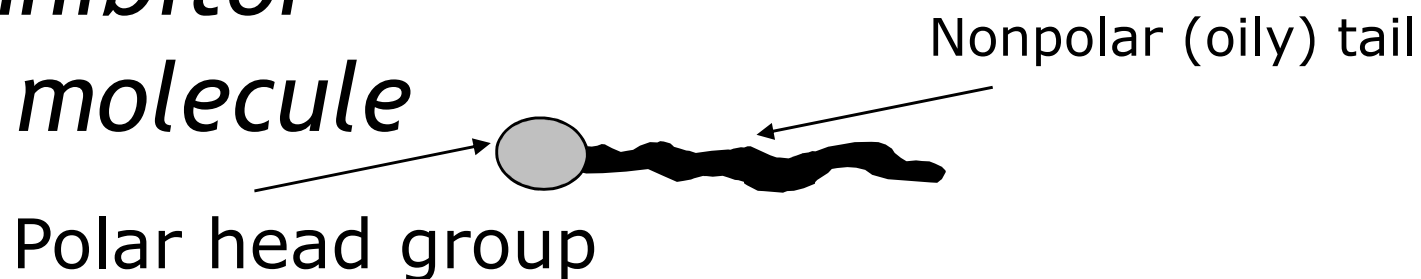


# ***Introduction to Corrosion Inhibitor Chemistry***

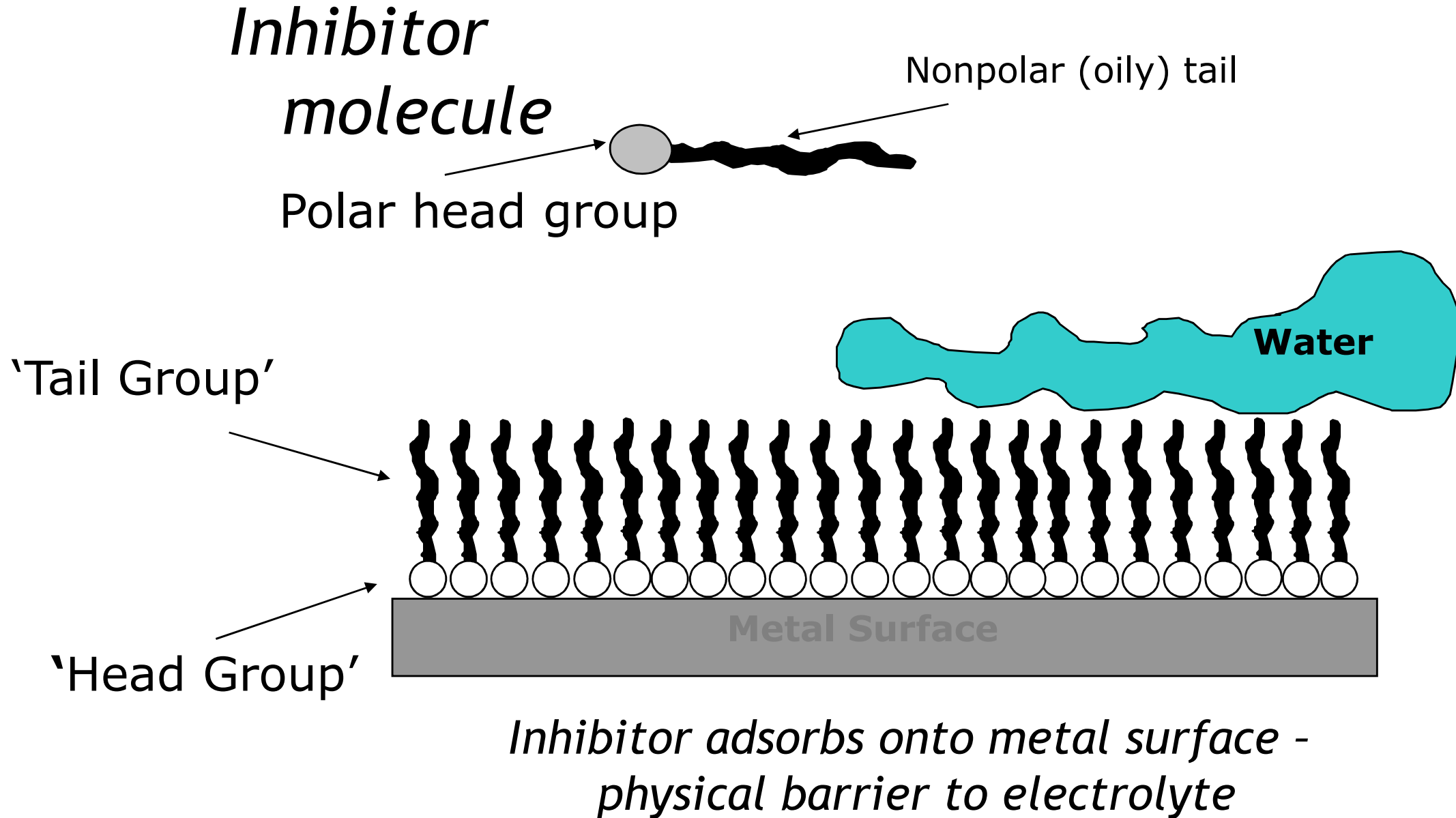
## Oilfield corrosion inhibitor mechanisms

- Adsorption as a thin protective film (organic inhibitors)
- Changing the environmental characteristics (neutralizers)

*Inhibitor  
molecule*



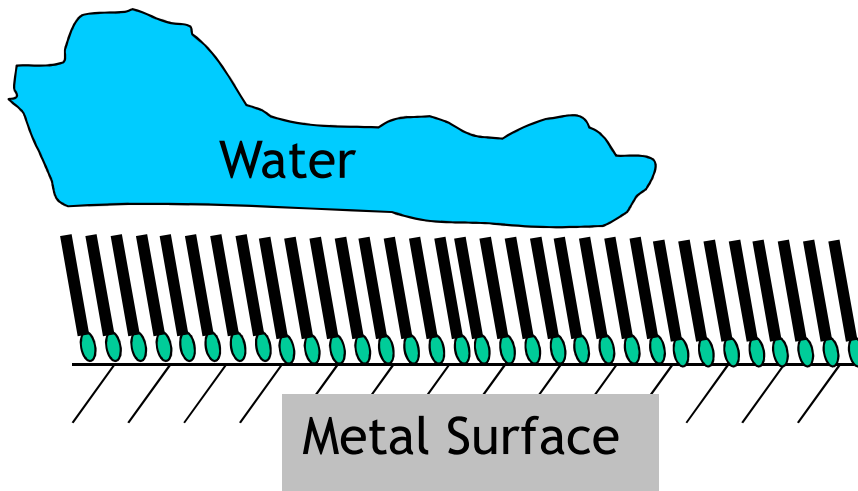
# Filming Corrosion Inhibitors



## Batch vs. Continuous

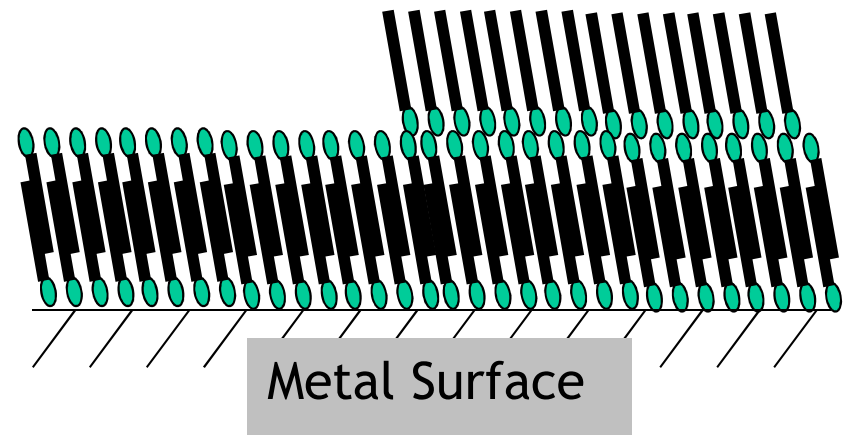
- Continuous

- Continuous film replenishment
- Film persistency, adsorption kinetics and coherency are key properties
- Typically water soluble



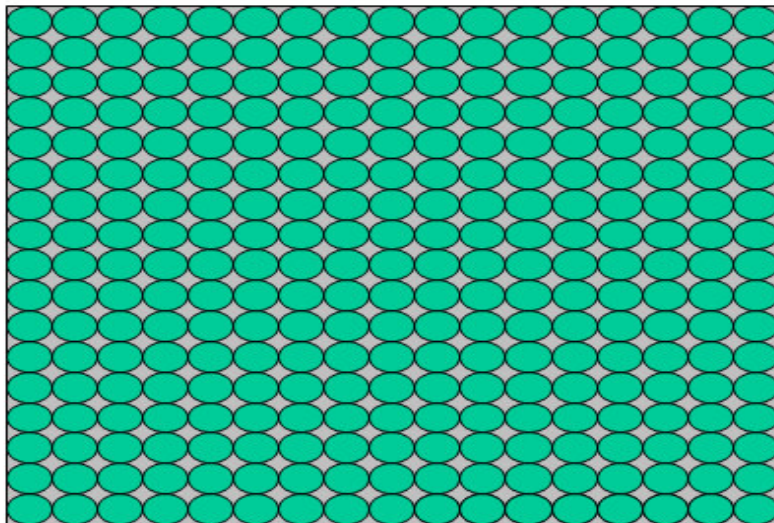
- Batch

- Product applied via a batch process
- Film thickness, film persistency are key properties
- Typically oil soluble

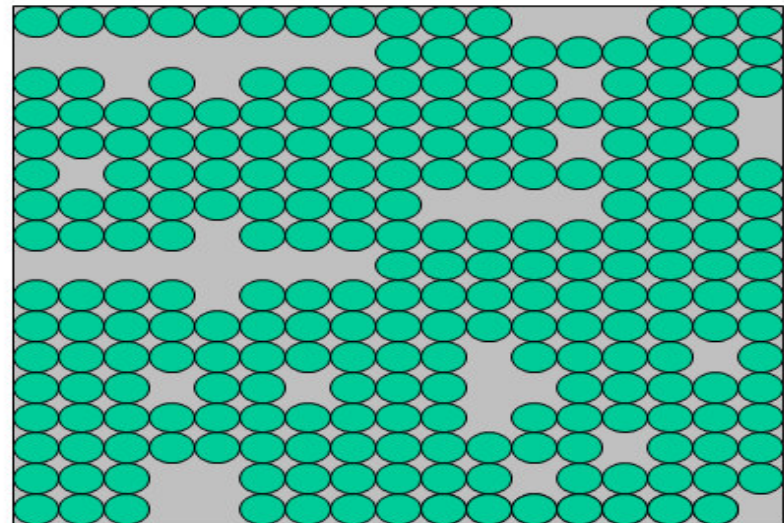


## Filming

- Form a film on the metal surface to protect from electrolytes
- Desirable properties
  - Favorable adsorption kinetics
  - Film coherency
  - Film persistency



**Coherent Film**



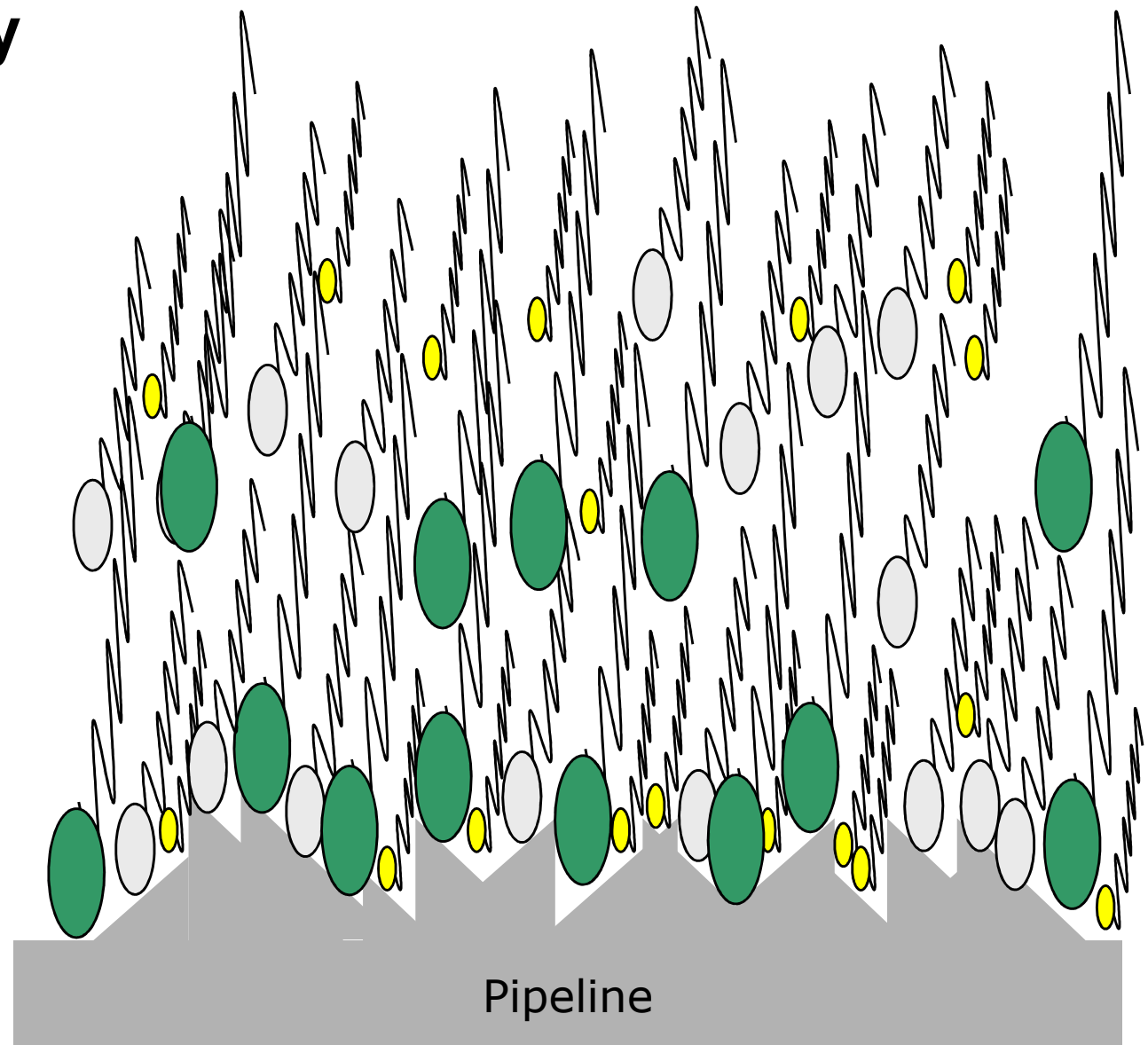
**Non-coherent Film**

### Continuous Application

- Typically water soluble oil dispersible
- Favorable water partitioning
- High adsorption kinetics to metal wall
  - Replaced by CI in bulk solution phase

## Batch inhibitor chemistry

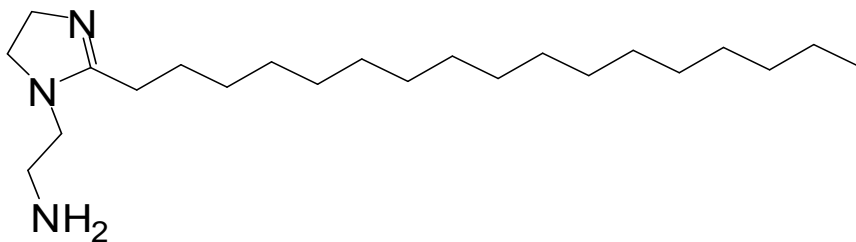
- Form a strong persistent film
- Typically oil soluble
  - > 18 carbon fatty acid chain
  - High molecular weight
- Oil wet surface to film effectively



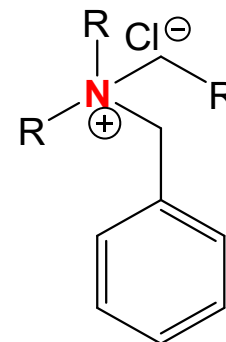
# Corrosion Inhibitors - Formulation

## Formulation factors to consider

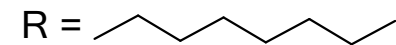
- Solubility and dispersibility
- Neutralizing acid
- Compatibility of other production chemicals
- Solvents to desired pour point
- Demulsifiers
- Stability
- Cost



*Imidazolines*



Example



*Quats*

## Corrosion inhibitor qualification

### Performance testing

- Partitioning
- High shear/velocity performance
- Film persistency
- High temperature/high pressure

### Subsea certification

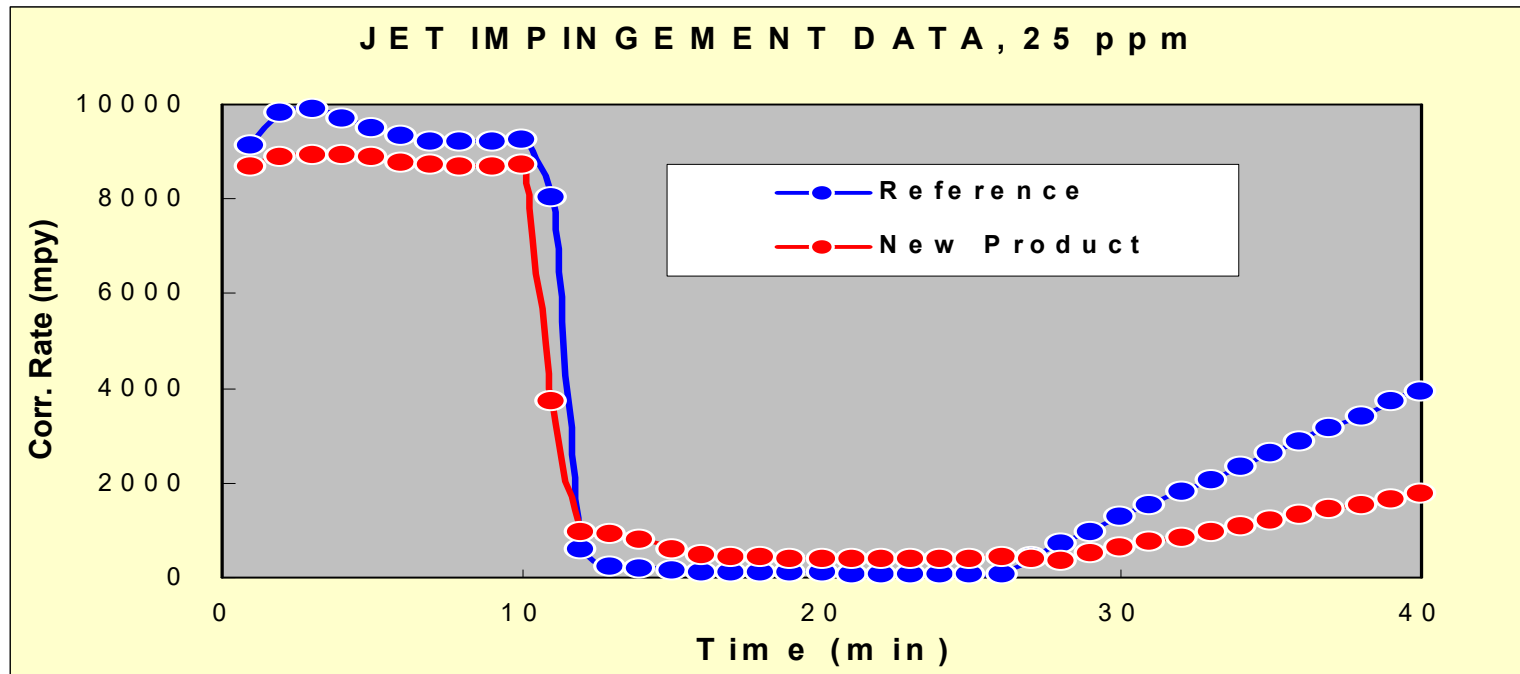
- Physical stability
- Thermal stability
- Pumpability
- Compatibility
- Cleanliness

## **CI performance testing should consider**

- Fluid composition (Oil/Water/Gas)
- Velocities/Shear
- Temperature
- Gas composition
- Compatibility
- Cost-effectiveness
- Environmental implications
- Application requirements

## Performance Tests

- A set of required tests are developed before a product can be taken to a field trial
- Provide a relative measurement of how a product will perform in the field
- Corrosion rates provide a direct comparison of new products to incumbents



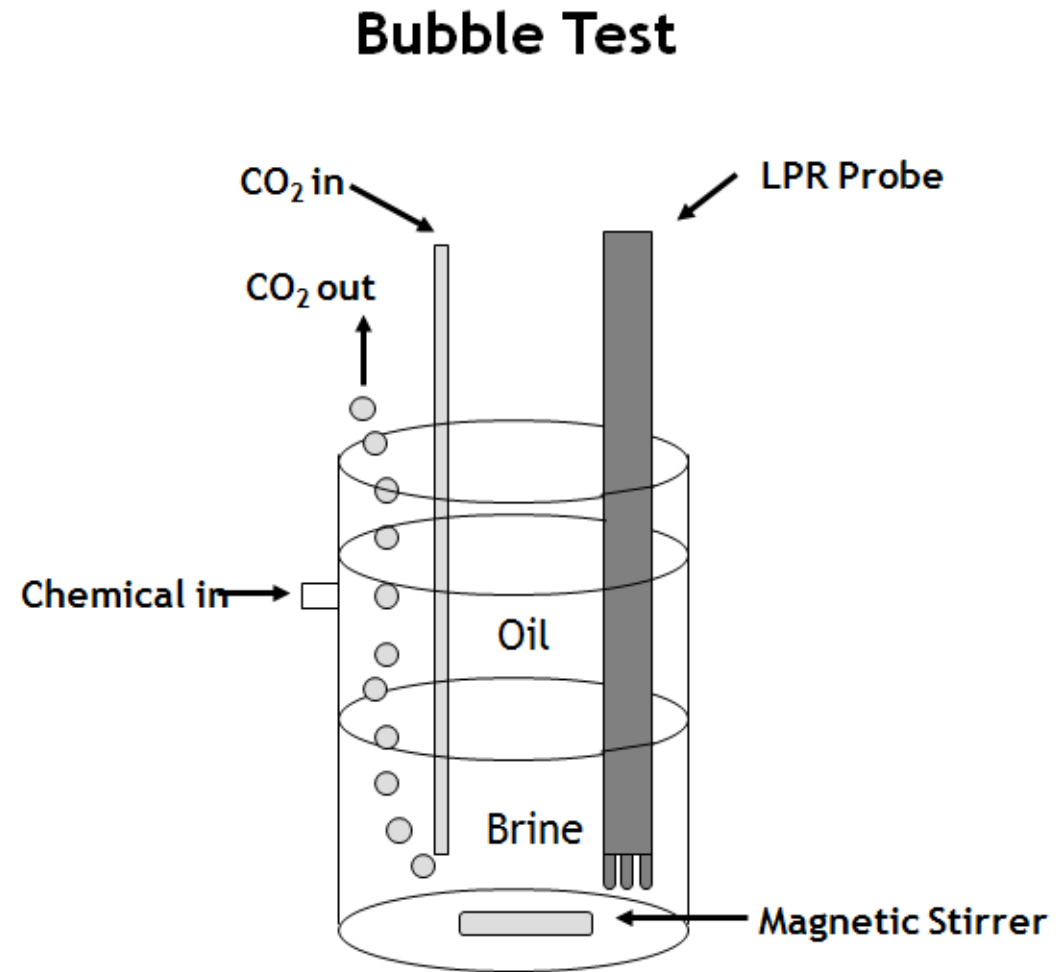
## Laboratory Evaluation

- Bubble test
- Wheelbox test
- Flow loop test
- Jet impingement
- Autoclave testing
- Surface profilometry



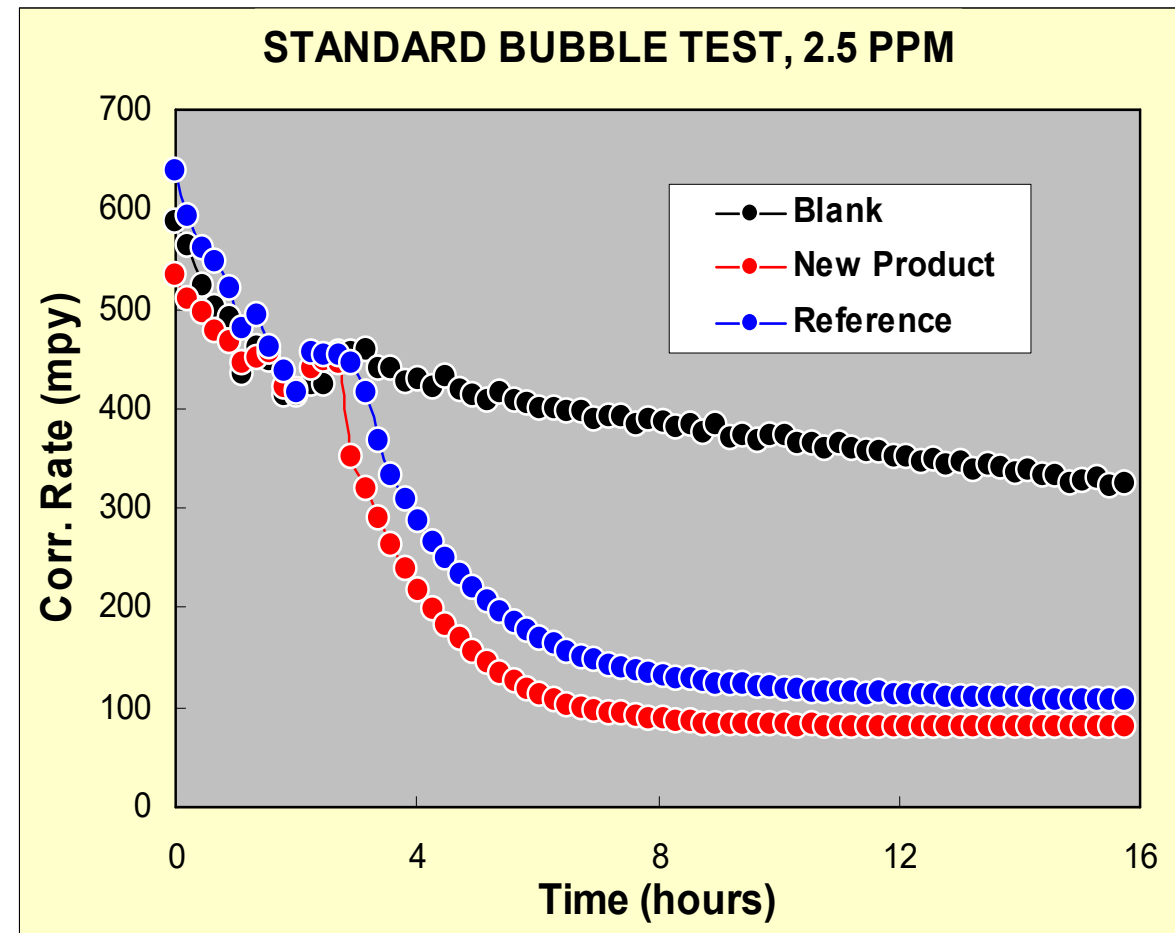
## Bubble Test

- Evaluates partitioning of chemical
- Field crude desired
- Wide range of water cuts
- Temperatures up to 90°C, 14.7 psi CO<sub>2</sub>
- LPR measurements; short term test
- Low dosage rate



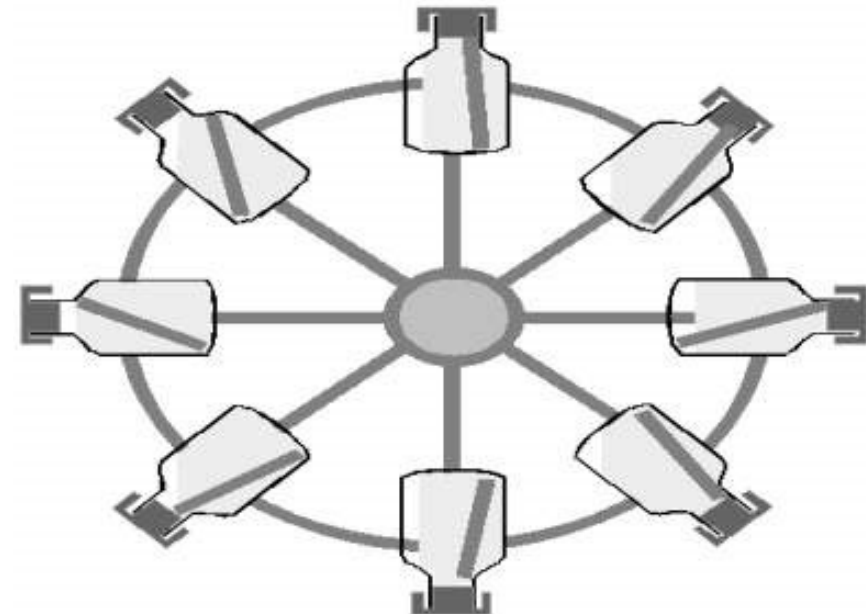
# Corrosion Inhibitors - Testing

## Bubble Test



## Wheel Box Test

- Quick screening of chemicals typically pass/fail rating
- Low shear
- Sweet or sour
- Coupons of desired metallurgy
- Film persistency or continuous inhibitor evaluation
- Cost effective and versatile testing
- Typically 24 hours but longer durations common
- Temperature up to 400°F

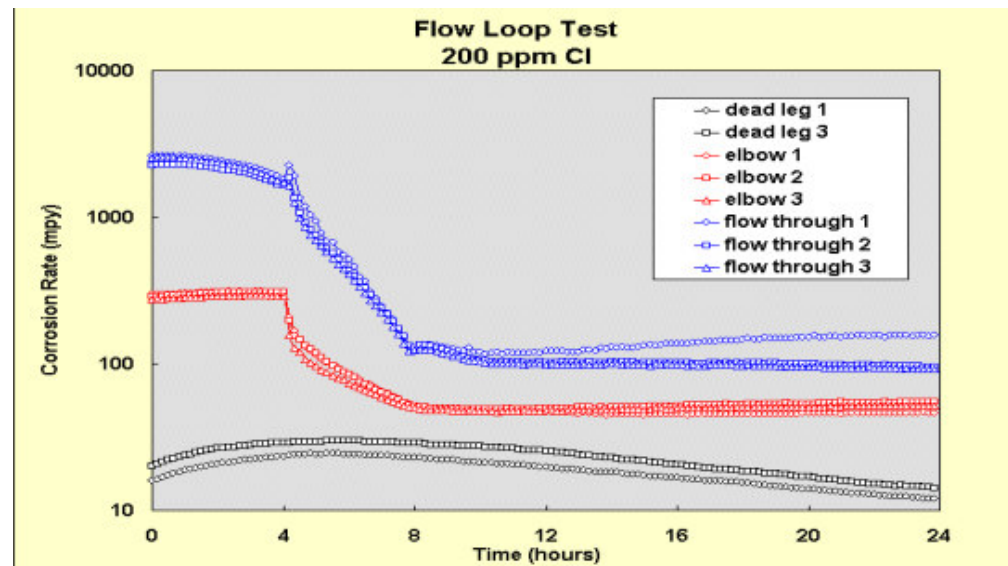
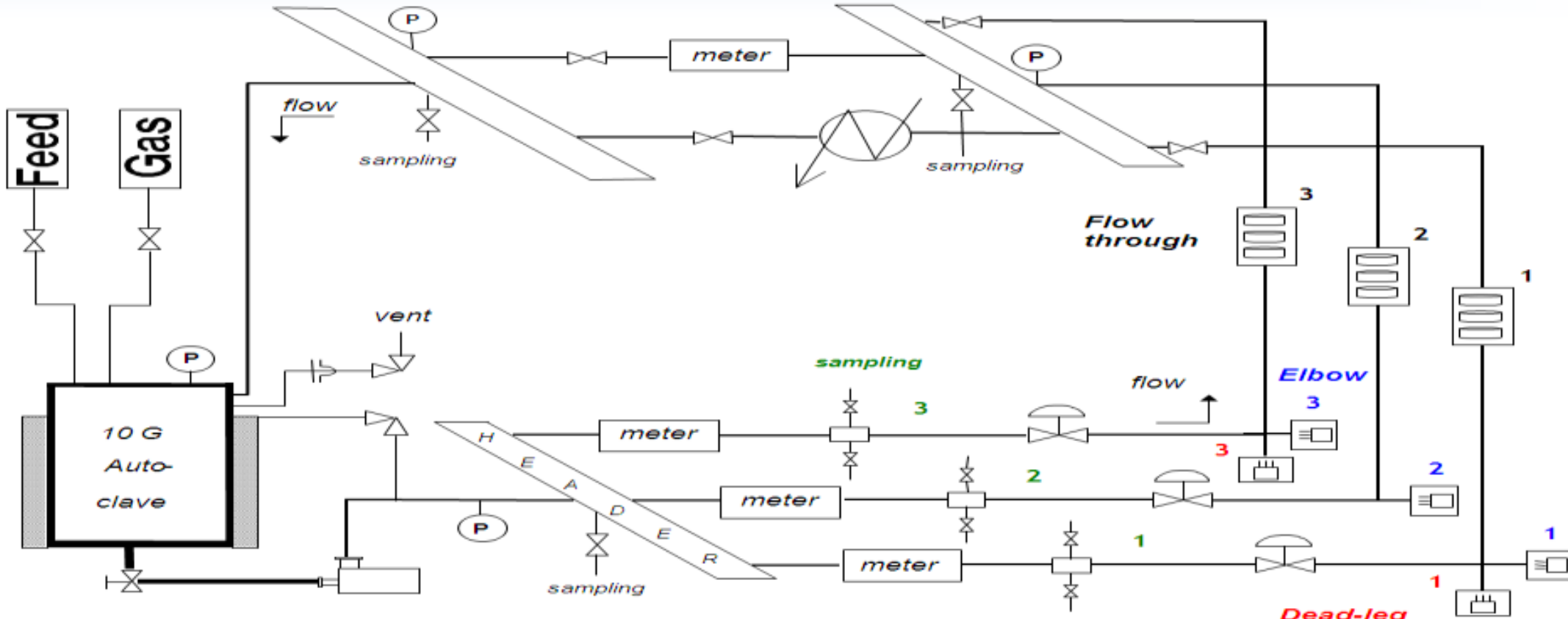


## Flow Loop Test

- Recirculated system
- Brine/hydrocarbon mixtures can vary
- Synthetic hydrocarbon
- Temperature – up to 95°C (176°F)
- Total pressure – up to 300 psi
  - ▶ CO<sub>2</sub> partial pressure – up to 100 psi
- Test duration – typically 3 days
- Inhibitor concentration 25 - 250 ppm
- LPR probes
- 3 flowing regions evaluated – up to 1000 Pa
- Desired electrode material



# Flow Loop Test



# Corrosion Inhibitors - Testing

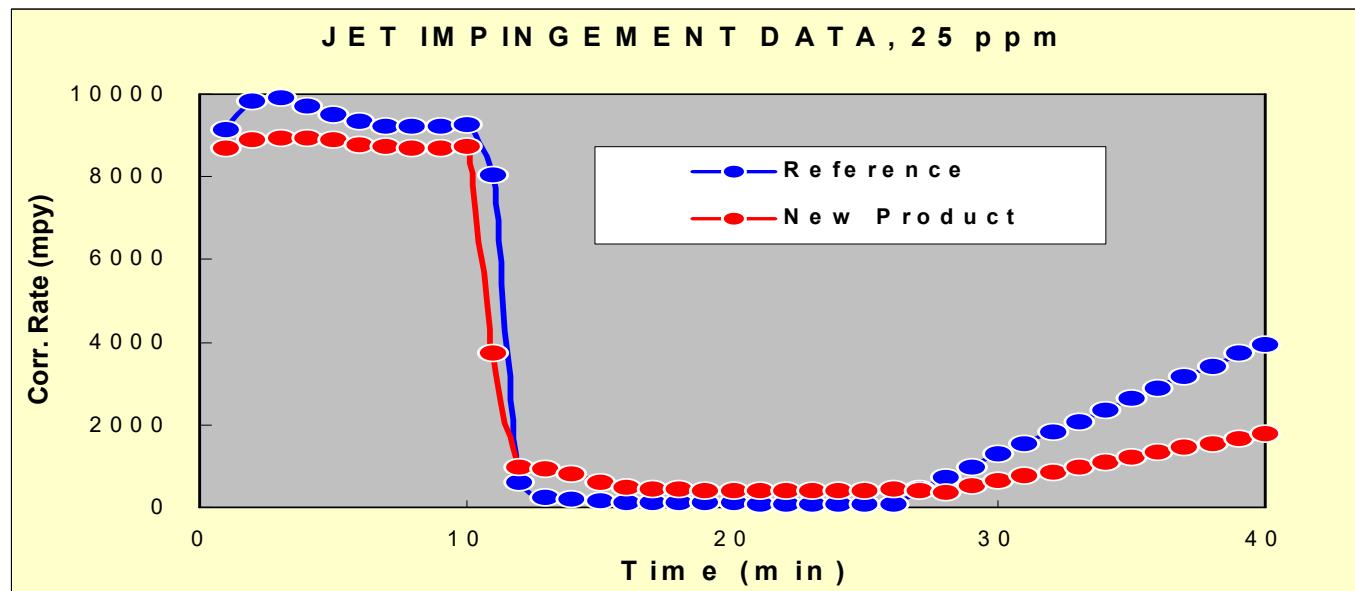
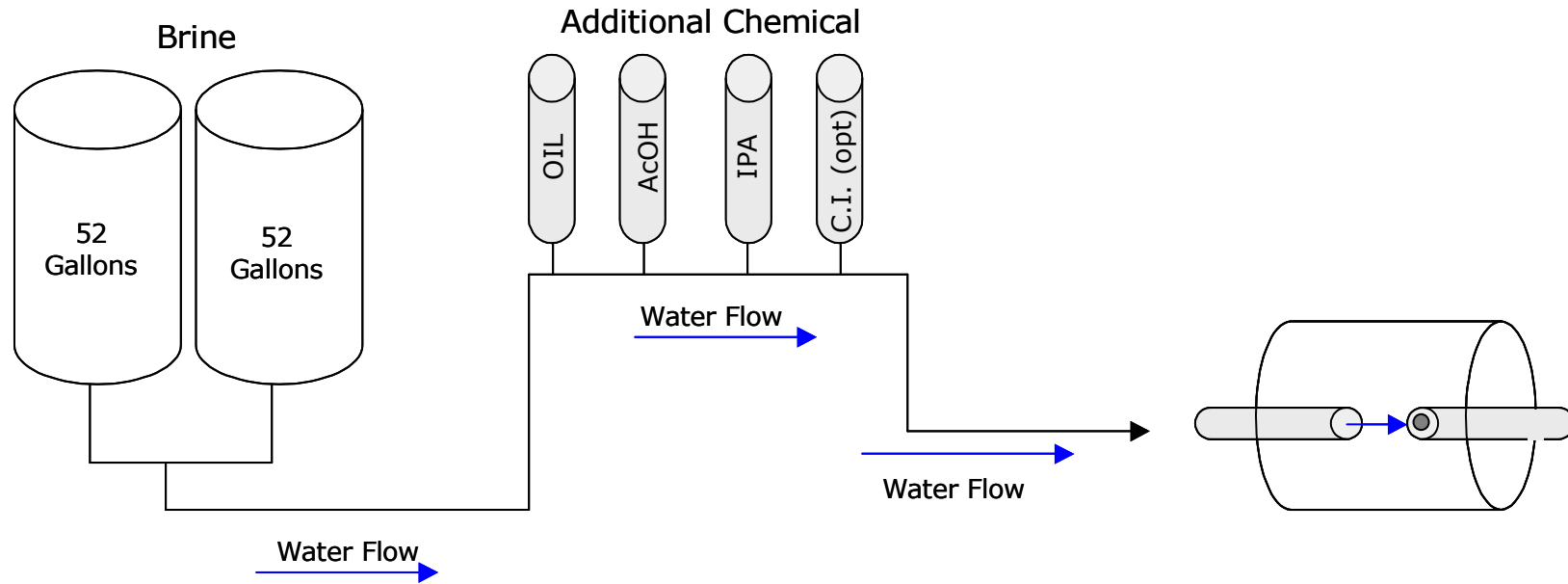
## Jet Impingement Test

- Once through system
- Synthetic brine + 1000 ppm kerosene
- Temperature up to 176°F
- CO<sub>2</sub> partial pressure - 14.7 psi
- Shear stress up to 1000 Pa
- Inhibitor concentration - 10, 25, 50 ppm
- Test duration - 40 min
- Electrode material - 1018 carbon steel



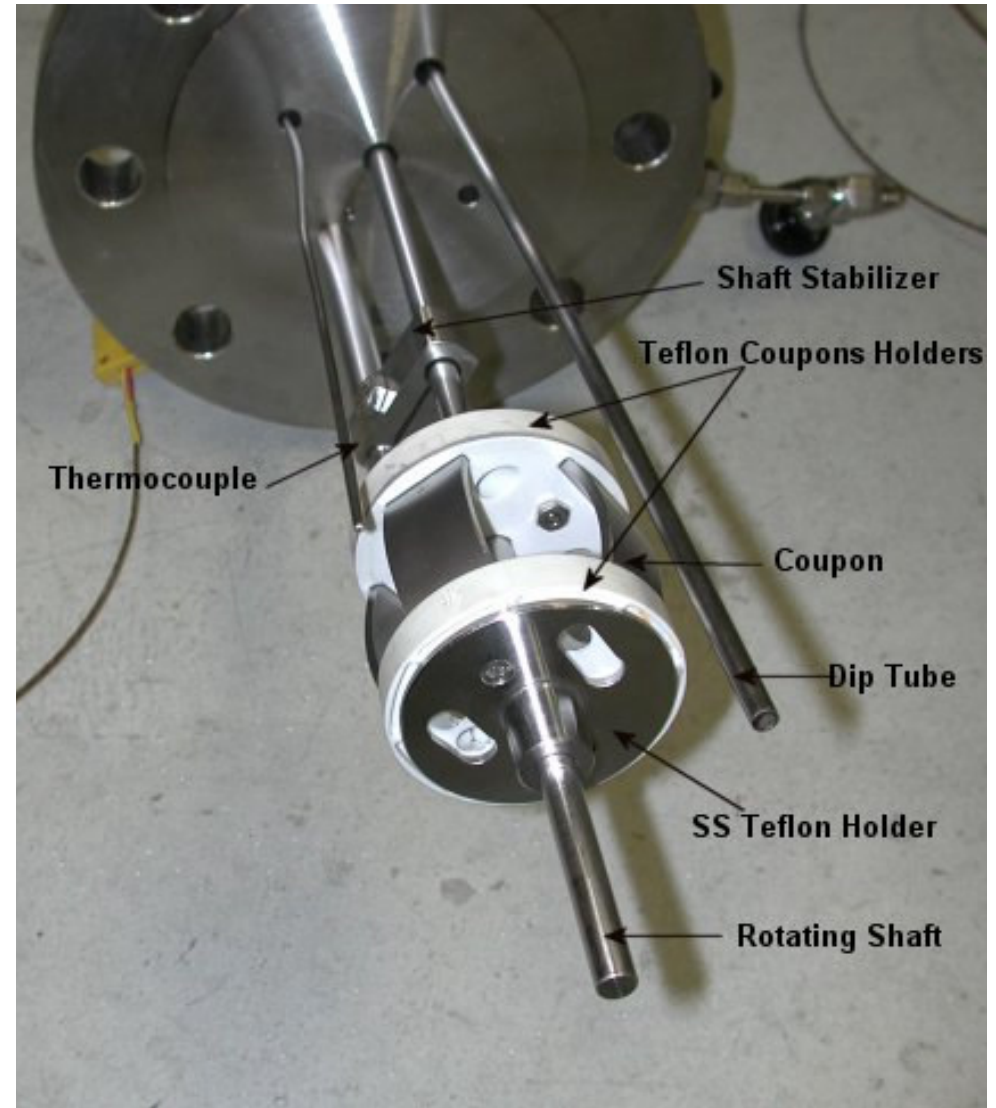
# Corrosion Inhibitors - Testing

## Jet Impingement Test



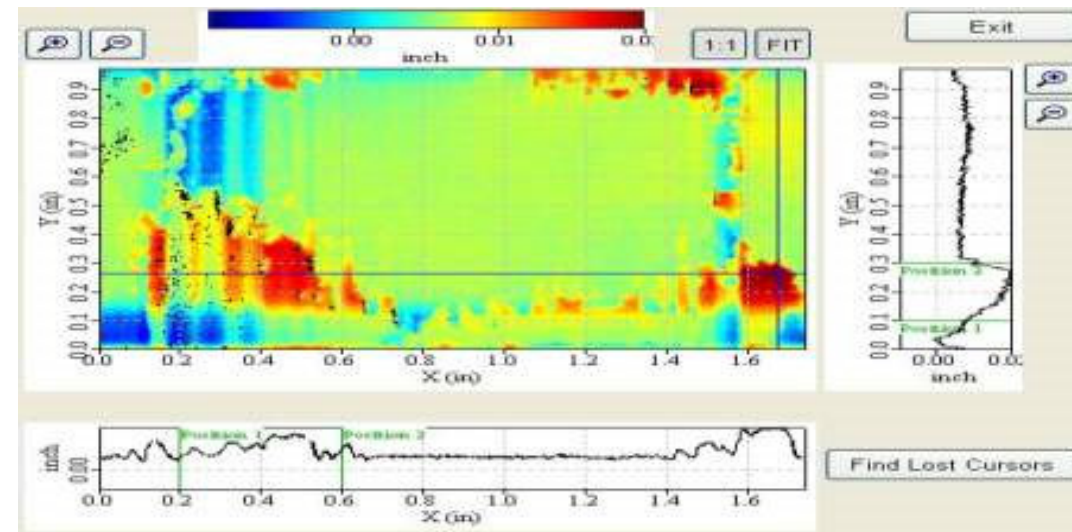
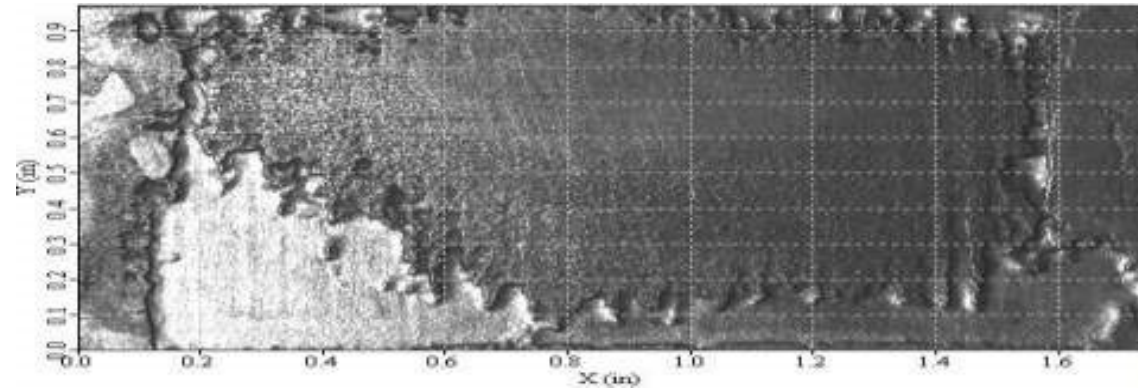
## Rotating Cage Autoclave Test

- Tests high shear conditions
- Weight loss coupons
- Sweet or sour conditions
- Variable water cut
- Temperature up to 350°F
- Pressure up to 300 psi
- CO<sub>2</sub> pressure up to 100 psi
- Test duration typically 3-7 days
- Shear stress up to 1000 Pa



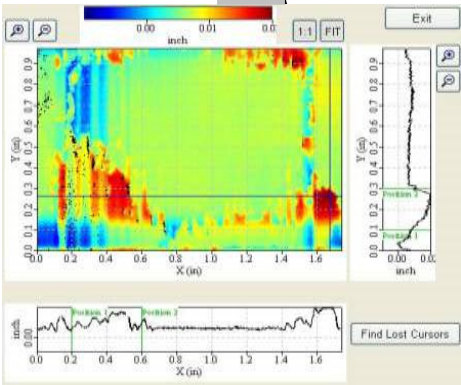
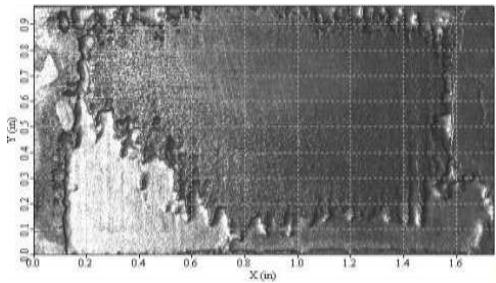
## Laser Surface Profilometry

- Evaluates surface profile by LASER light scan
- Eliminates subjectivity in pitting analysis
- Inhibitors can be differentiated by pitting protection

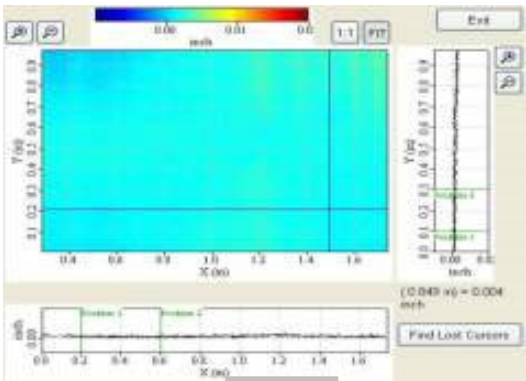
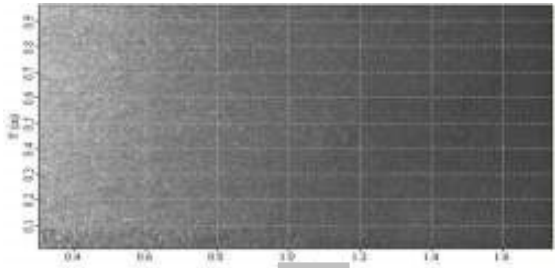


# Blank vs. Treated

Coupon A



Coupon B



| Coupon |           | Average Depth (mils) | Max Depth (mils) | General CR (mpy) | Pitting CR (mpy) | General % Protection | Pitting % Protection |
|--------|-----------|----------------------|------------------|------------------|------------------|----------------------|----------------------|
| A      | Untreated | 6.5                  | 20.0             | 39.8             | 743.7            |                      |                      |
| B      | Treated   | 1.7                  | 6.0              | 1.9              | 226.1            | 95.2%                | 69.6%                |

# Summary of Performance Testing

- Laboratory testing allows an operator to make an informed decision when choosing a corrosion inhibitor
- Implementation of a chemical program should be verified by field testing when possible
- Performance testing should be validated a robust monitoring program