Corrosion theory and mechanisms

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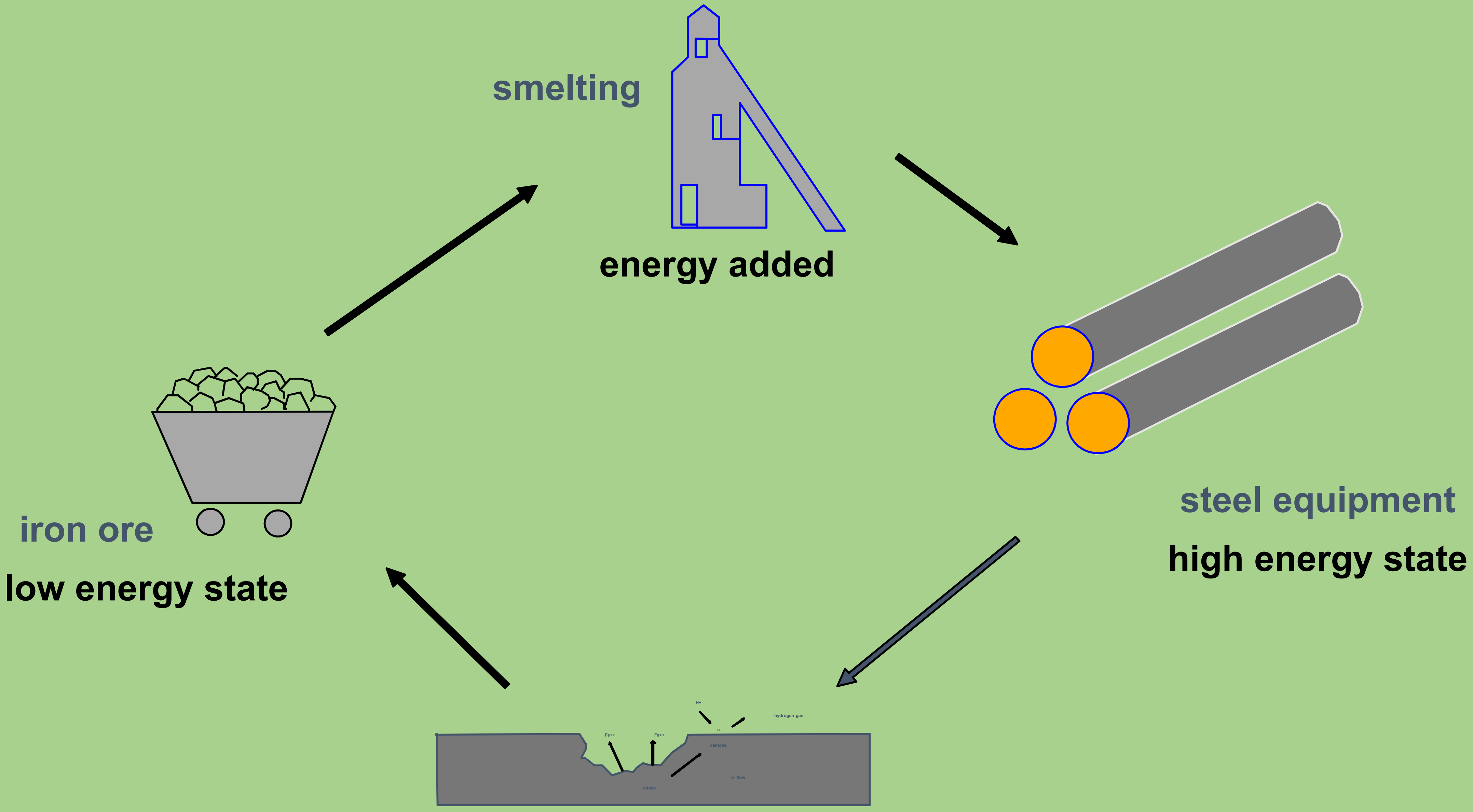
What is Corrosion?

According to the NACE definition -“*Corrosion is the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment.*”

Nature of Corrosion



smelting

energy added

steel equipment

high energy state

iron ore

low energy state

corrosion

energy released

ELECTROMOTIVE SERIES

Oxidation-Reduction Potentials

Reaction	Volts
$Au \longrightarrow Au^{+++} + 3\ e^{-}$	+ 1.5
$Pt \longrightarrow Pt^{++} + 2\ e^{-}$	+ 1.2
$Cu \longrightarrow Cu^{++} + 2\ e^{-}$	+ 0.34
$H_2 \longrightarrow 2H^{+} + 2\ e^{-}$	0.00
$Fe \longrightarrow Fe^{++} + 2\ e^{-}$	- 0.44
$Cr \longrightarrow Cr^{++} + 2\ e^{-}$	- 0.74
$Zn \longrightarrow Zn^{++} + 2\ e^{-}$	- 0.76
$Al \longrightarrow Al^{+++} + 3\ e^{-}$	- 1.7
$Na \longrightarrow Na^{+} + e^{-}$	- 2.7

The Corrosion Cell has Four Essential Elements

- ANODE

  portion of the metal that loses electrons

- CATHODE

  site where electrons are gained by corrodent.

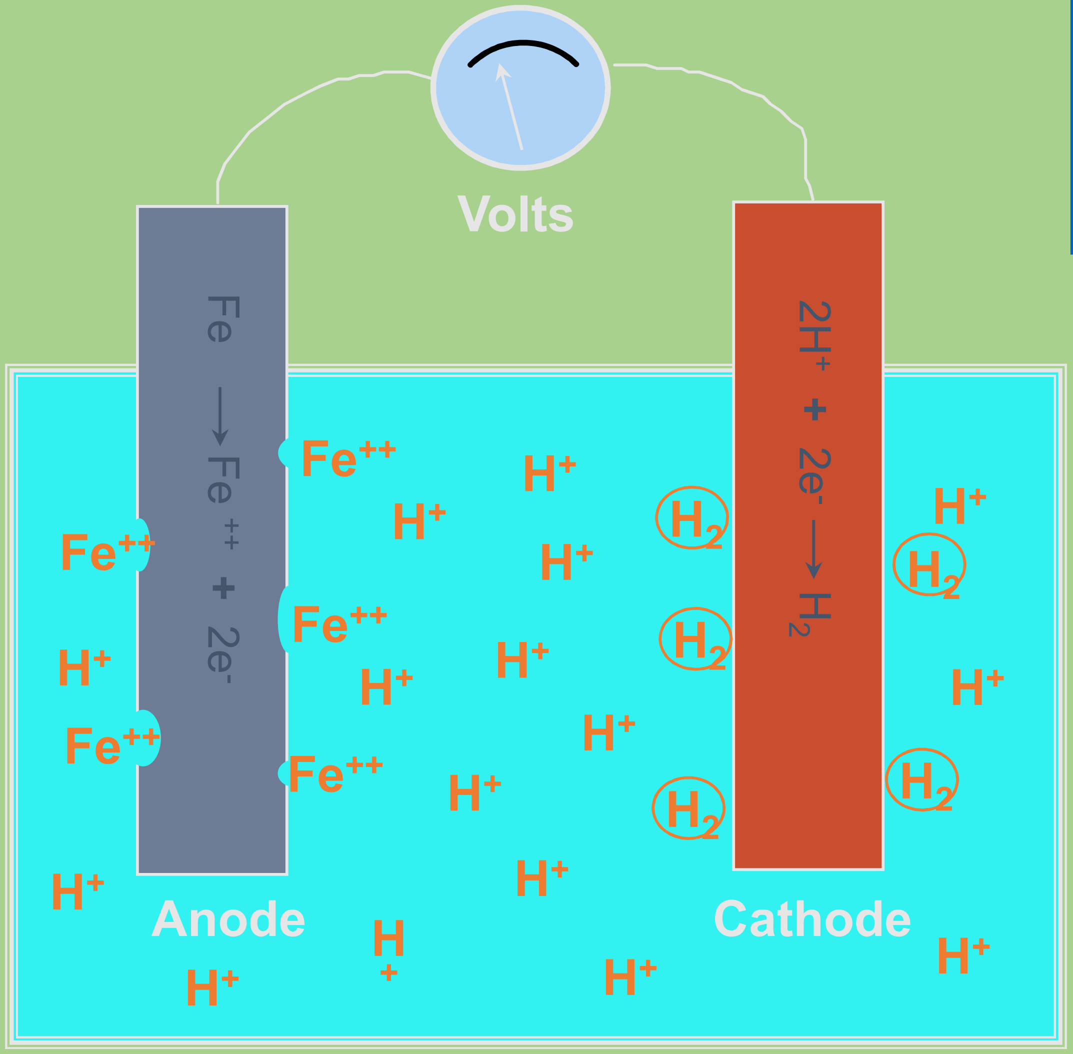
- ELECTRICAL CONDUCTOR

  pathway to carry electrons, usually the metal pipe in the oil field

- ELECTROLYTE

  solution containing conductive ions, brine in the oil field

Corrosion Cell



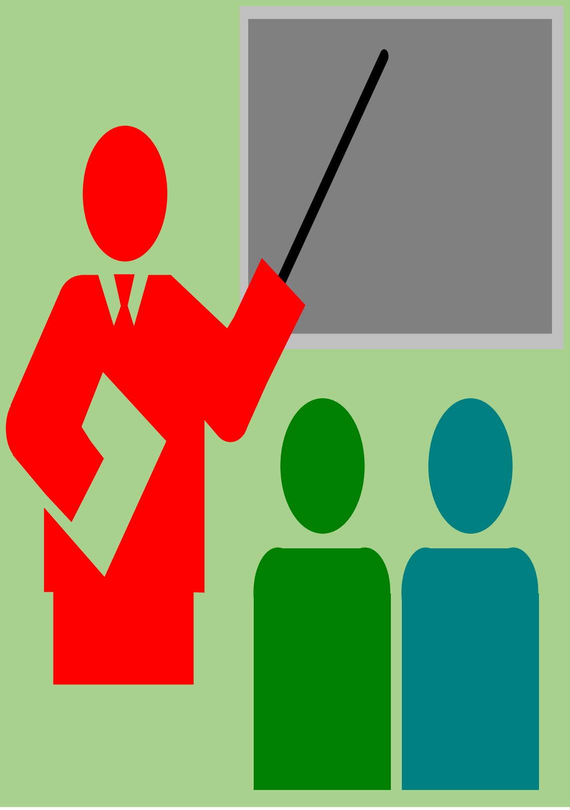
Oxidation Potential

Reaction	Volts
$Cu \rightarrow Cu^{++} + 2e^-$	0.34
$H_2 \rightarrow 2H^+ + 2e^-$	0.0
$Fe \rightarrow Fe^{++} + 2e^-$	-0.44

Oilfield Corrosion

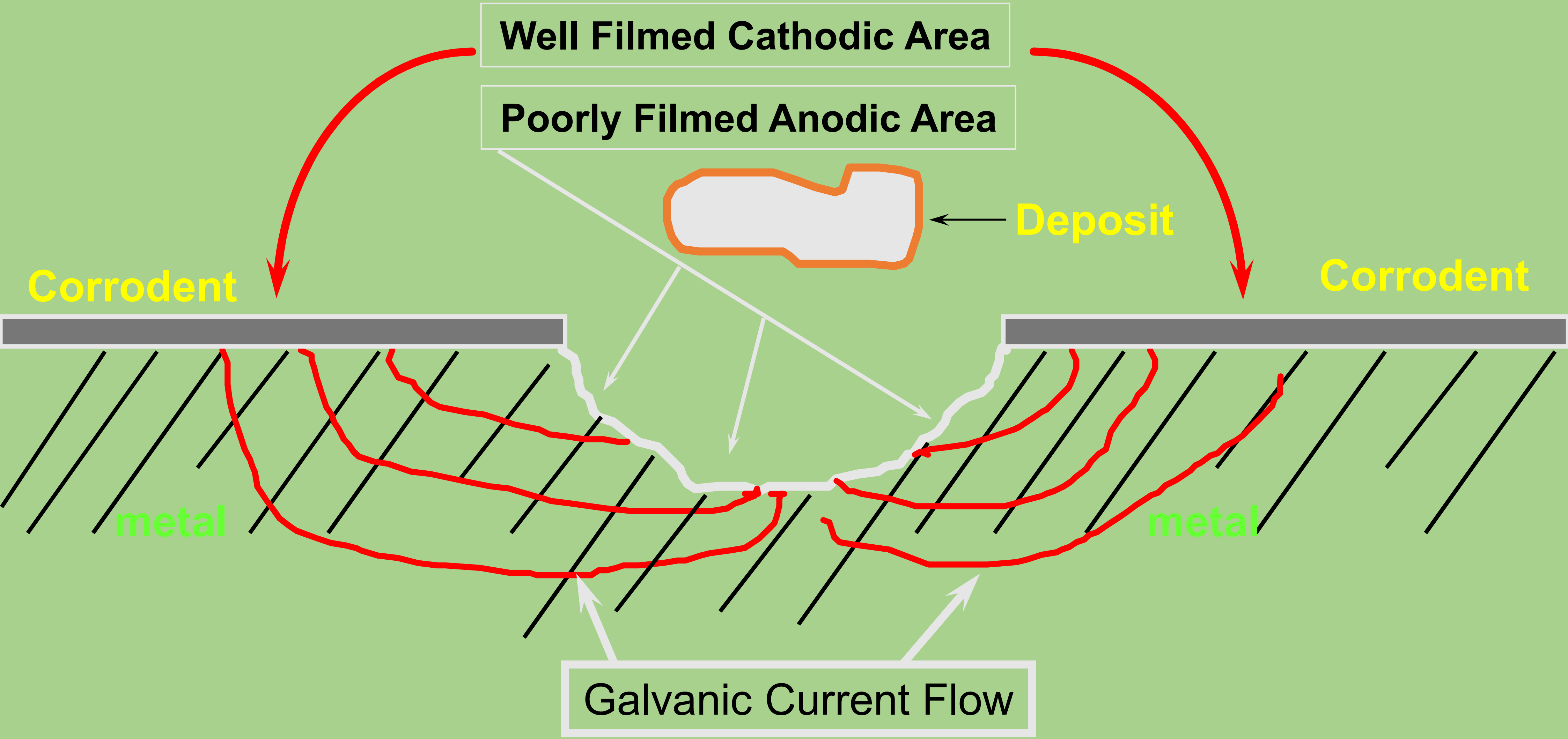
Anodic: $Fe \rightarrow Fe^{++} + 2e^-$

Cathodic: $2H^+ + 2e^- \quad 2H^o \rightarrow H_2 \rightarrow$



Oil Field corrosion is typically controlled by the cathodic reaction

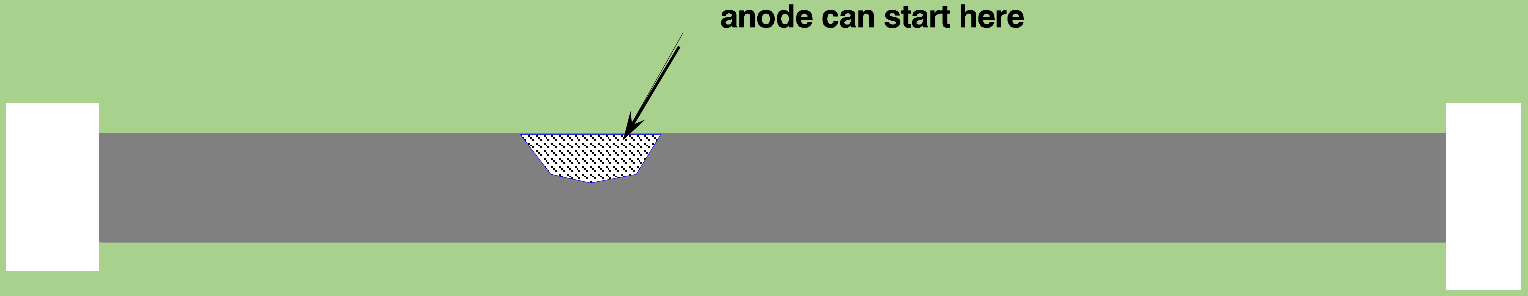
Diagram of Corrosion Cell



Initiation of Anodic Sites

Metal Microstructure

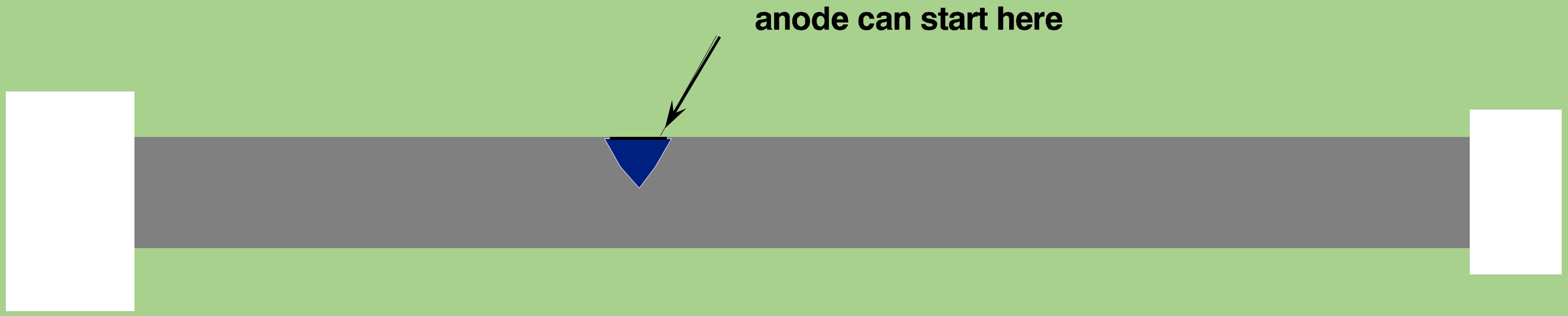
These are typically variations in the grain of the metal that occur during the manufacturing process. They can result from unequal heat treatment.



Initiation of Anodic Sites

Scratches or Abrasions

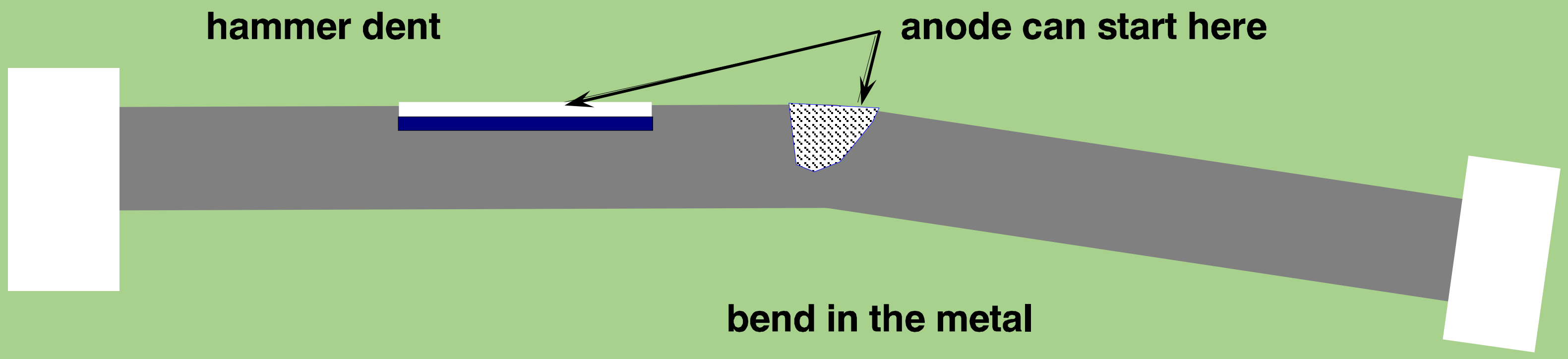
These can be any surface irregularity



Initiation of Anodic Sites

Differential Stress

These could be caused by hammer dents or bends or any strain that causes the metal to be different from the surrounding metal.



hammer dent

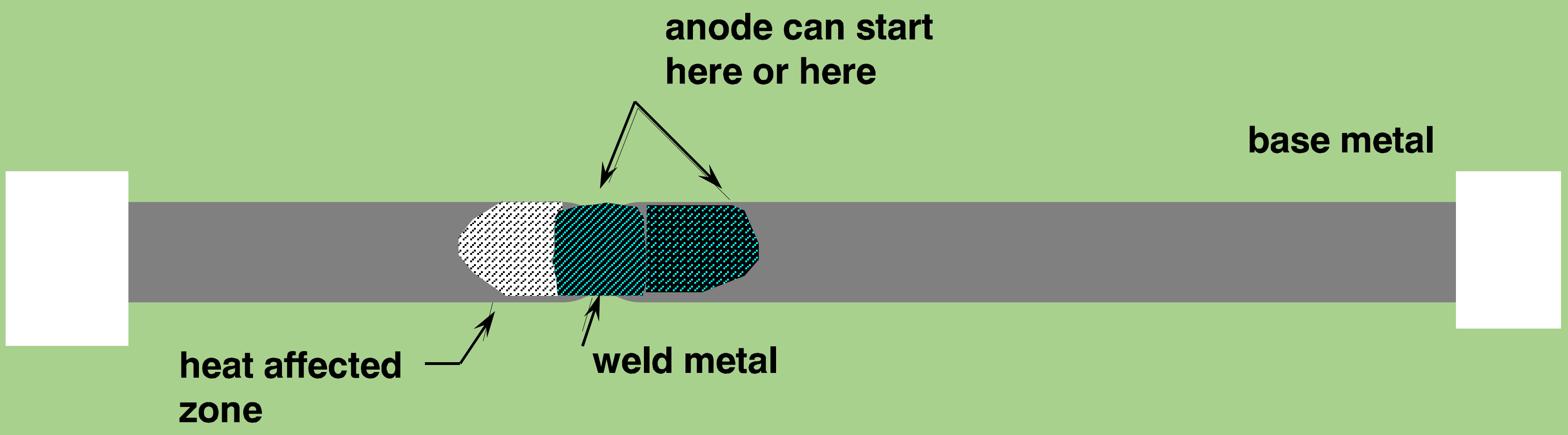
anode can start here

bend in the metal

Initiation of Anodic Sites

Welds

The heating that occurs during the welding process can produce a heat effected zone on both sides of the weld. Improper weld metal selection can cause a galvanic cell.



Oilfield Corrosive Agents

- CO_2 Carbon Dioxide
- H_2S Hydrogen Sulfide
- O_2 Oxygen
- Bacteria

Oilfield Corrosion Conditions

Working Definitions

- sweet ----any amount of CO_2, 5 ppm or less H_2S in fresh sample of water
- sour ----any amount of CO_2, 10 ppm or more H_2S in fresh sample of water
- oxygen influenced ----any amount of CO_2/H_2S, and 50 ppb or more oxygen in water

$$1+1=3$$

CO_2 Corrosion

Anodic: $Fe \rightarrow Fe^{++} + 2e^-$

Cathodic: $CO_2 + H_2O \rightarrow H_2CO_3$

$2H_2CO_3 \rightarrow 2H^+ + 2HCO_3^-$

$2H^+ + 2e^- \rightarrow H_2 \uparrow$

$Fe + 2H_2CO_3 \rightarrow Fe^{++} + 2HCO_3^- + H_2 \uparrow$

$Fe^{++} + HCO_3^- \rightarrow FeCO_3 + H^+$

CO_2 Corrosion

- Results from the removal of the protective iron carbonate scale
- Occurs in areas of high velocity or turbulence

CO_2 Corrosion

CO_2 Corrosion

Effects on CO_2 Corrosion

- CO_2 Pressure
- Temperatures
- Brine composition
- Type of hydrocarbon
- Oil/Water Ratio
- Metallurgy
- Velocities (Shear Stress)

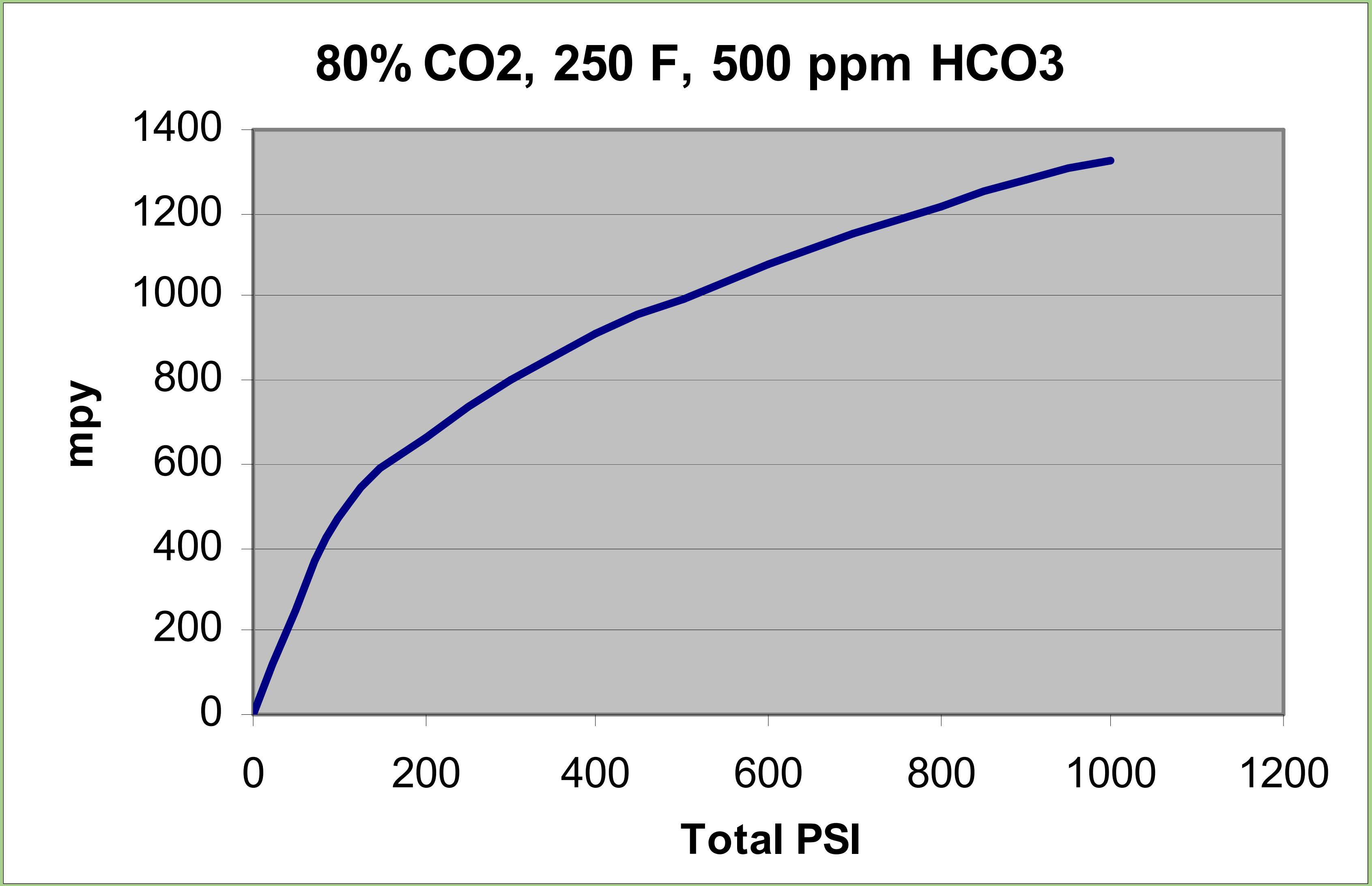
Corrosion Modeling

- Cassandra (BP-03)

Pressure	300 psi
CO2	80% (mole)
H2S	0 ppm
Temperature	250^{o}F
HCO_3^-	500 ppm

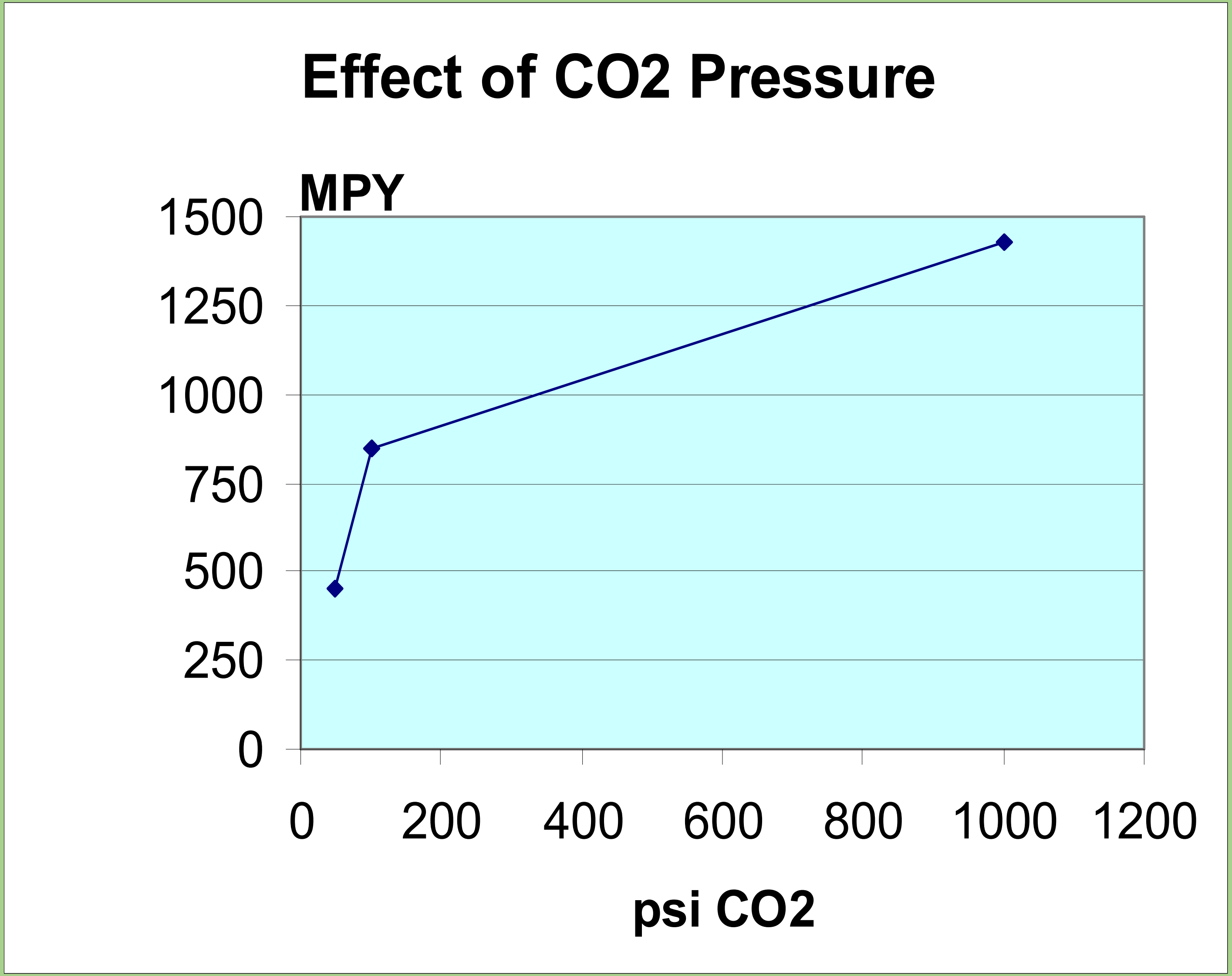
CO_2 Partial Pressure

(Cassandra Model)

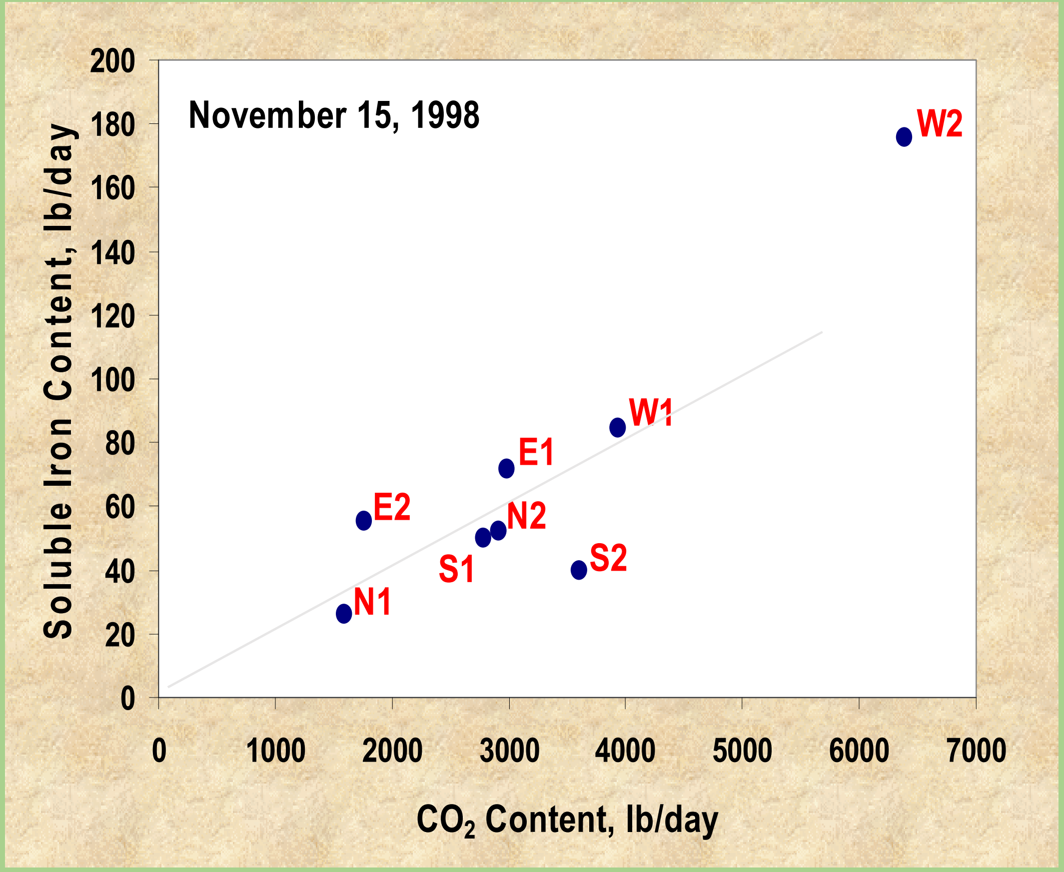


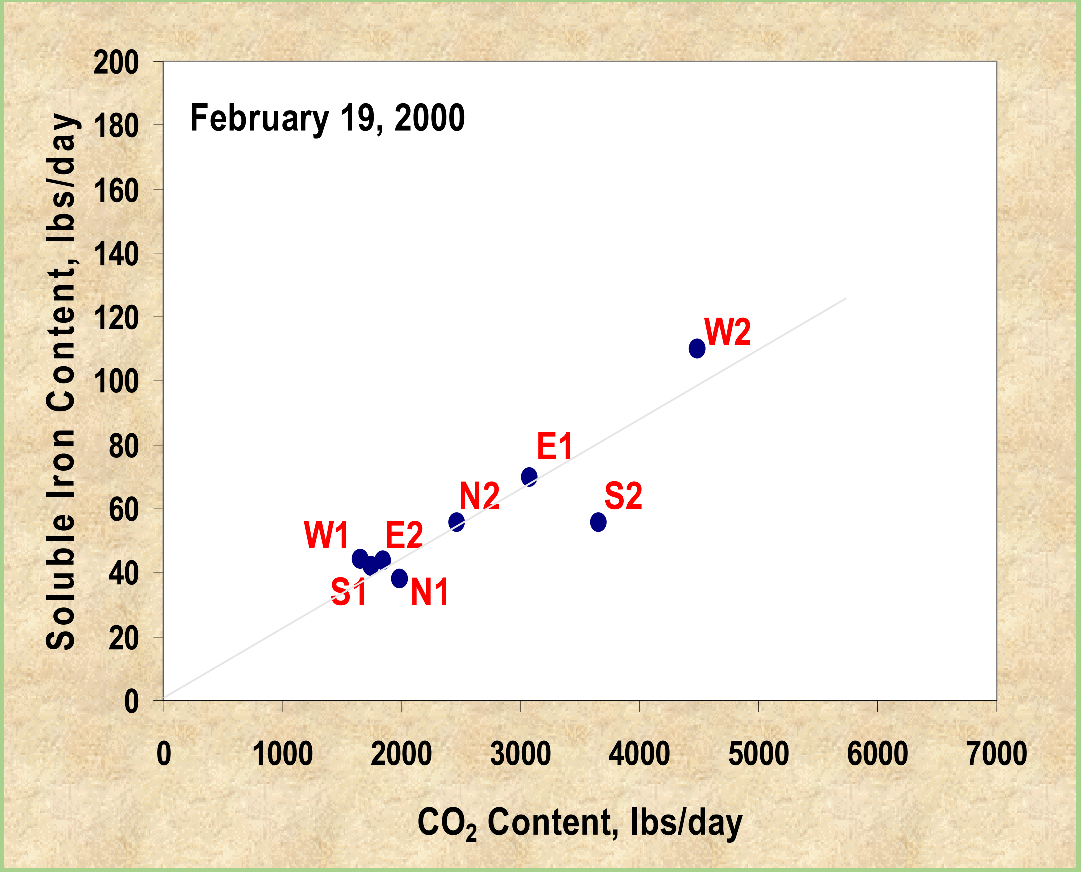
CO_2 Partial Pressure

(Laboratory Testing)



CO_2 Partial Pressure
(Field Results)



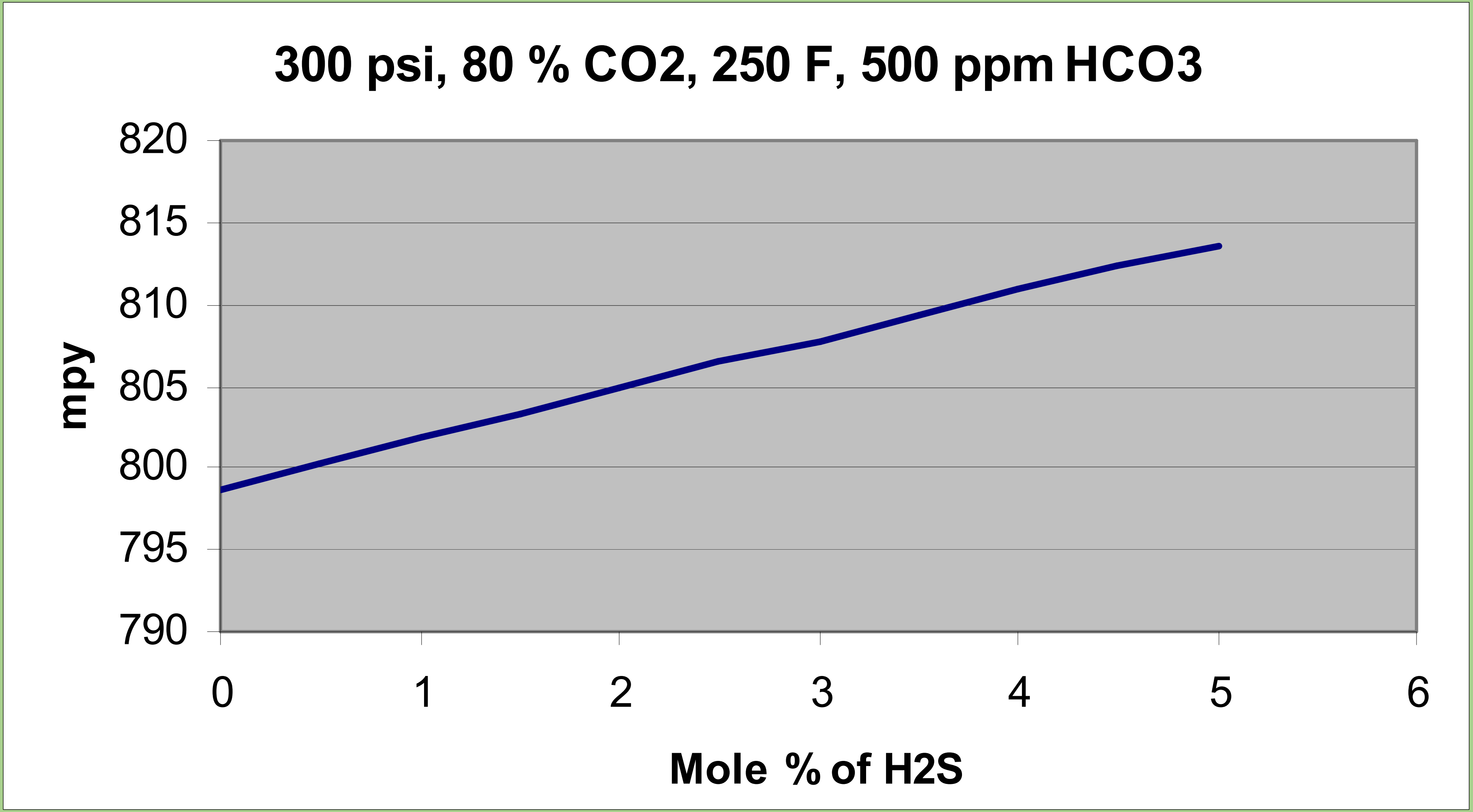


CO_2: 25,971 lb/day
Fe: 555 lb/day

CO_2: 20,954 lb/day
Fe: 459 lb/day

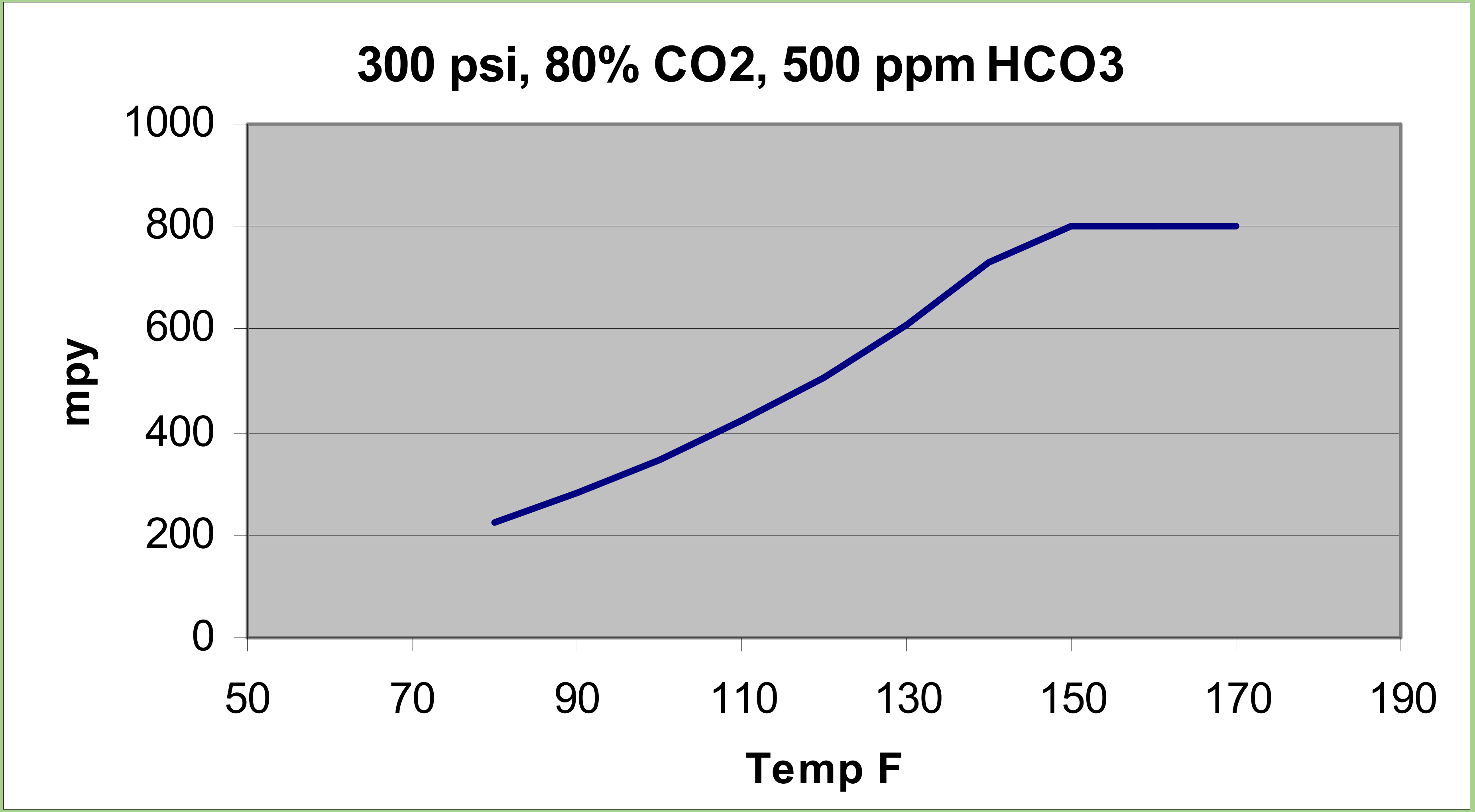
Oil Well Gathering Line Analysis

Effect of H_2S
(Cassandra Model)

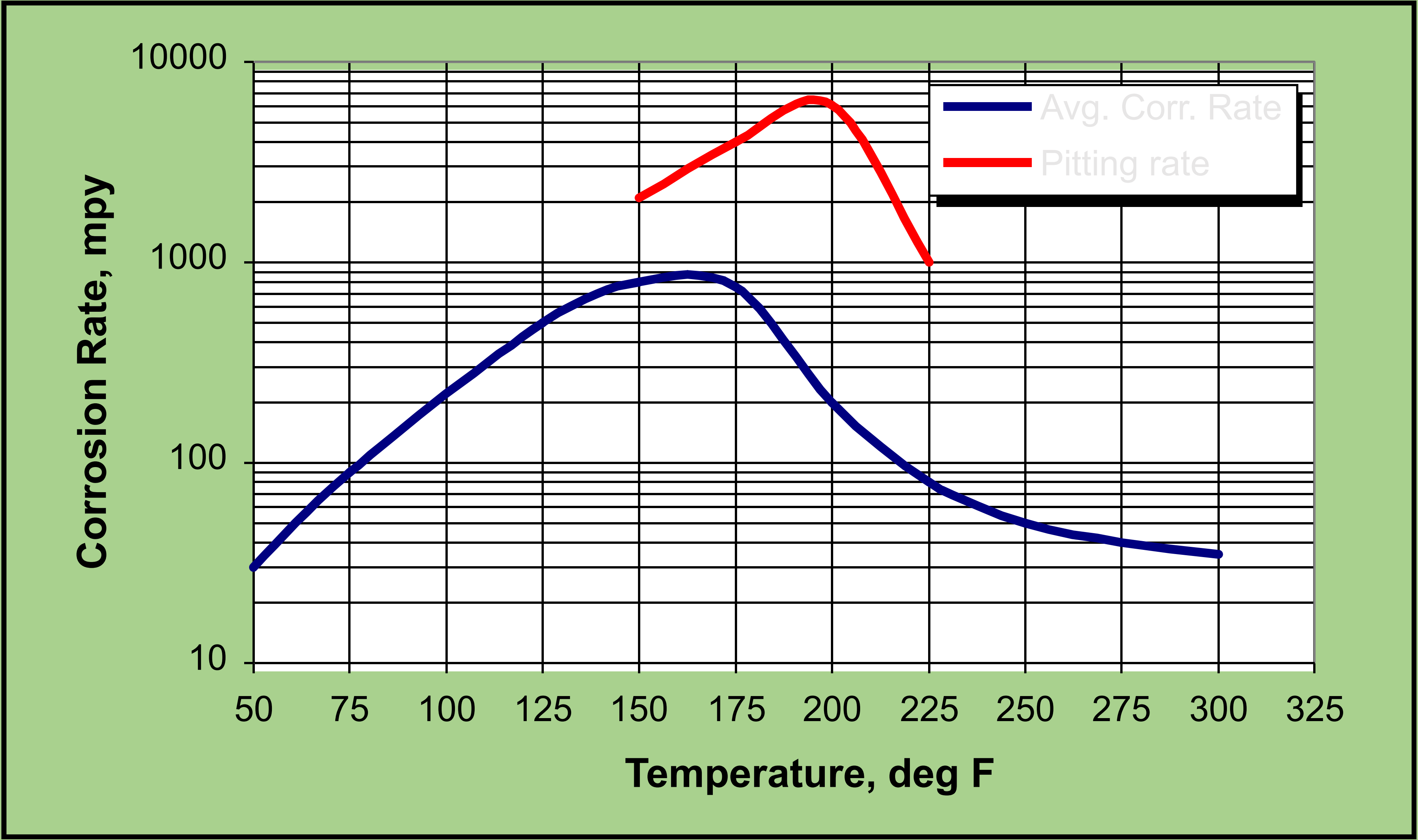


Effect of Temperature

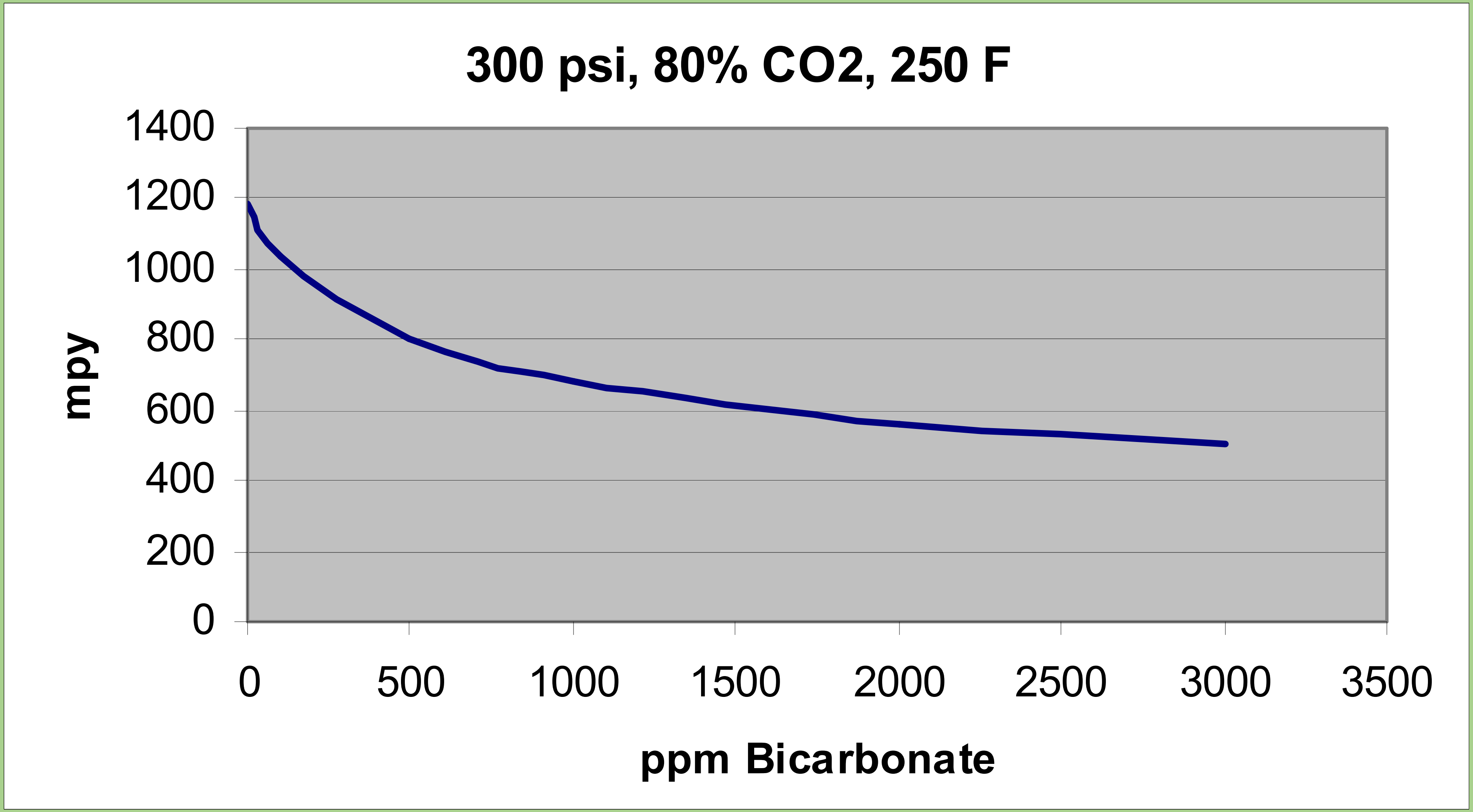
(Cassandra Model)



Effect of Temperature on CO_2 Corrosion (Lab Tests)



Effect of Bicarbonate Concentration
(Cassandra Model)



H_2S Corrosion

Anodic: $Fe \rightarrow Fe^{++} + 2e^{-}$

Cathodic: $H_2S \rightarrow H^{+} + HS^{-}$

$2H^{+} + 2e^{-} \rightarrow 2H^{0} \rightarrow H_2 \uparrow$

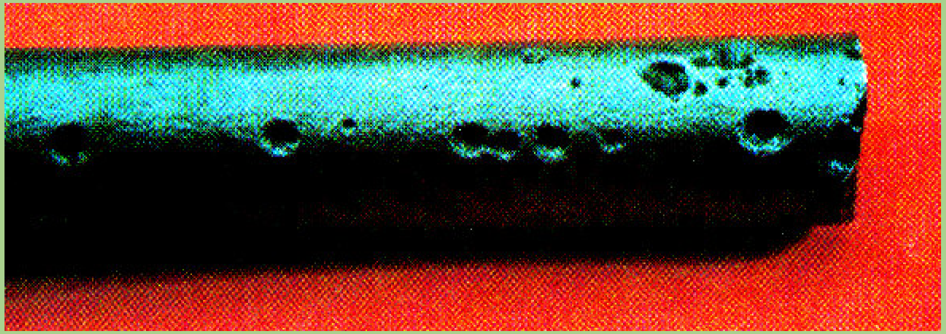
$HS^{-} \rightarrow S^{=} + H^{+}$

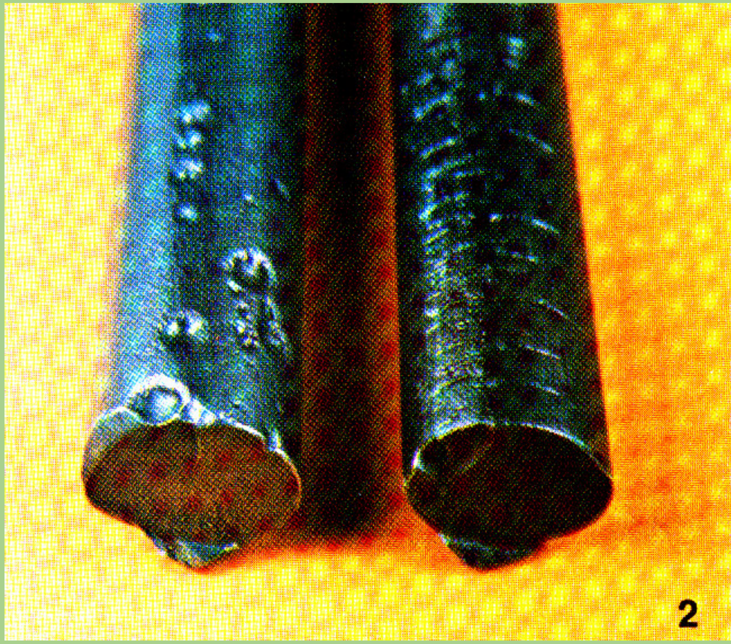
$S^{=} + Fe^{++} \rightarrow FeS$

$Fe + H_2S \rightarrow FeS + H_2 \uparrow$

H_2S Corrosion

- Underdeposit corrosion
- Stress cracking





Effect of H_2S

- The sulfide ions in the brine inhibit the formation of molecular hydrogen
  - $2H^o = H_2$(gas)
- The hydrogen atom enters the steel
- In high strength steel the hydrogen atom weakens the metal to metal bonds
  - Premature cracking under stress
- Hydrogen atoms can combine and form hydrogen molecules which become trapped in the steel
  - Blistering
  - Weaken the steel

Failures from Hydrogen Damage to Oilfield Steels

- Hydrogen cracking of high strength steels in tension
- Stepwise cracking or blister of non-stressed, medium strength steels
- Corrosion fatigue, alternating tensile stress

Environmental Cracking of Steels

- Failure from a brittle fracture which occurs below the rated tensile strength of the steel
- Not a result of a mechanical load on a area weakened by corrosion (stress-assisted cracking)
- It is the result of the steel being under a tensile stress in a specific corrosive environment over a period of time.

Types of Cracking

- SCC (Stress Corrosion Cracking)
- HIC (Hydrogen Induced Cracking)
- HE (Hydrogen Embrittlement)
- SSC (Sulfide Stress Cracking)
- CSC (Chloride Stress Cracking)
- Corrosion Fatigue

SCC (Stress Corrosion Cracking)

- Simultaneous presence of a tensile stress in a specific corrosion medium for a given metal.
    - Season cracking of brass
- Generally occurs where there is a low corrosion rate.
- It is an anodic process which can be controlled with cathodic protection.

HIC (Hydrogen Induced Cracking)

- Also called HE (hydrogen embrittlement)
- Results form H^o penetrating into the metal
  - Weakens the metal to metal bonds, making the metal more brittle
  - Hydrogen gas becomes trapped in the metal
    - $2H^o = H_2$ (gas)
- It is a cathodic process, which is accelerated by cathodic protection

HIC (Hydrogen Induced Cracking)

- Certain chemicals (poisons) stop the formation of hydrogen gas on the metal surface which results in an increase of atomic hydrogen penetrating into the metal
  - Hydrogen sulfide
  - Cyanides
  - Arsenic

Anodic: $Fe \rightarrow Fe^{++} + 2e^-$

Cathodic: $2H^+ + 2e^- \rightarrow 2H^o \rightarrow H_2 \longrightarrow$

SSC (Sulfide Stress Cracking)

- HIC in a wet hydrogen sulfide environment
- Methods of control
  - Metallurgical
    - (NACE MR-01-75)
    - Use a steels with a Rockwell hardness below C22
  - Reduce the tensile stress
  - Inhibit the corrosion reaction
  - Inhibit the entry of the H^o into the steel

CSC (Chloride Stress Cracking)

- It is one type of SCC (stress corrosion cracking).
- It occurs in austenitic (300 series) stainless steels under stress at temperatures above 200^{o}F in waters containing chlorides.
- The ferritic 13% chrome stainless steels (410) do not suffer from CSC but are effected by SSC.

Corrosion Fatigue

- It is the failure of the metal by cracking when subjected to cyclic stress
- The failure occurs below the tensile strength of the steel
- The endurance limit is the stress level at which no failures occur after a million cycles.

Oxygen Corrosion

Anodic: $Fe \rightarrow Fe^{++} + 2e^{-}$

Cathodic:

Acid conditions:

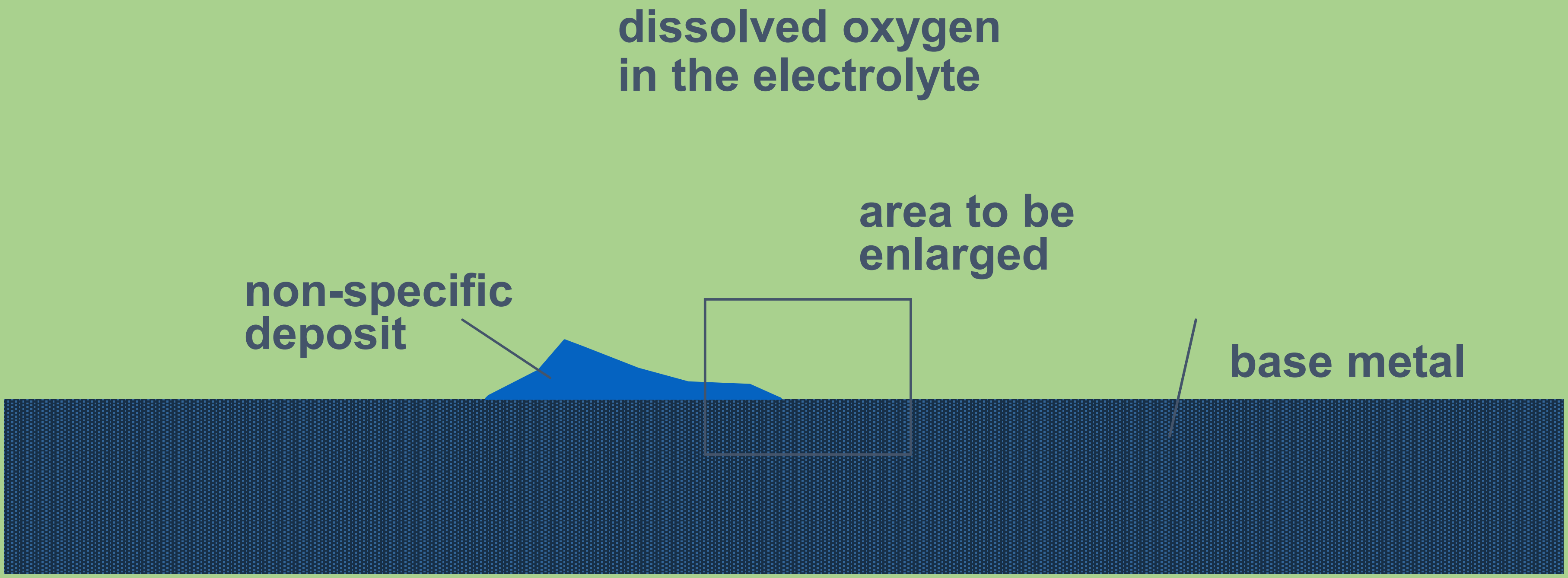
$1/2\ O_2 + 2H^{+} + 2e \rightarrow H_2O$

Basic conditions:

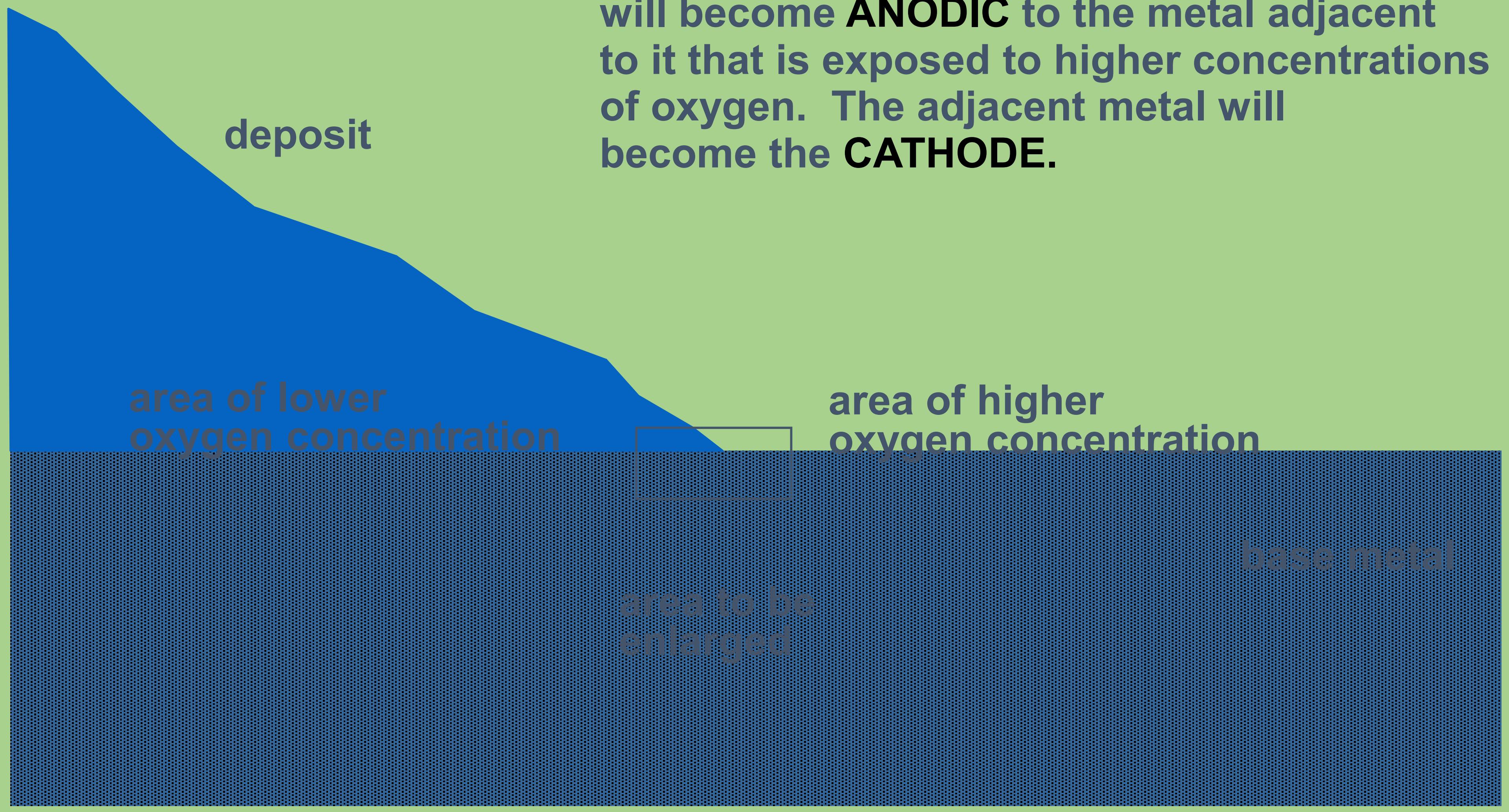
$O_2 + 2H_2O + 4e \rightarrow 4\ OH^{-}$

Oxygen Corrosion

This illustration shows a steel metal surface that is exposed to an oxygenated brine. The metal surface has a non-specific deposit attached to it.

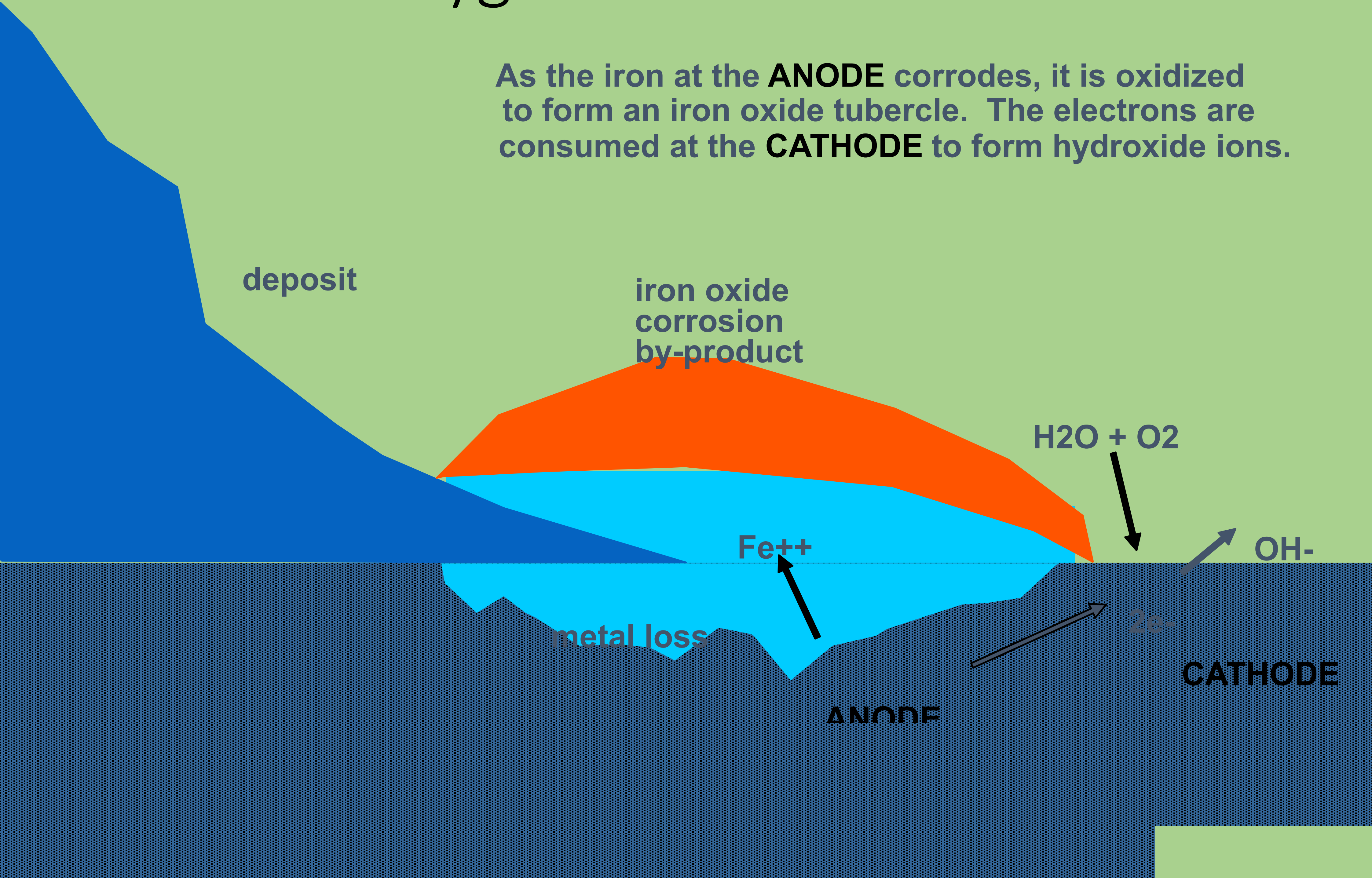


The portion of the metal that is exposed to the lower concentrations of oxygen will become **ANODIC** to the metal adjacent to it that is exposed to higher concentrations of oxygen. The adjacent metal will become the **CATHODE.**



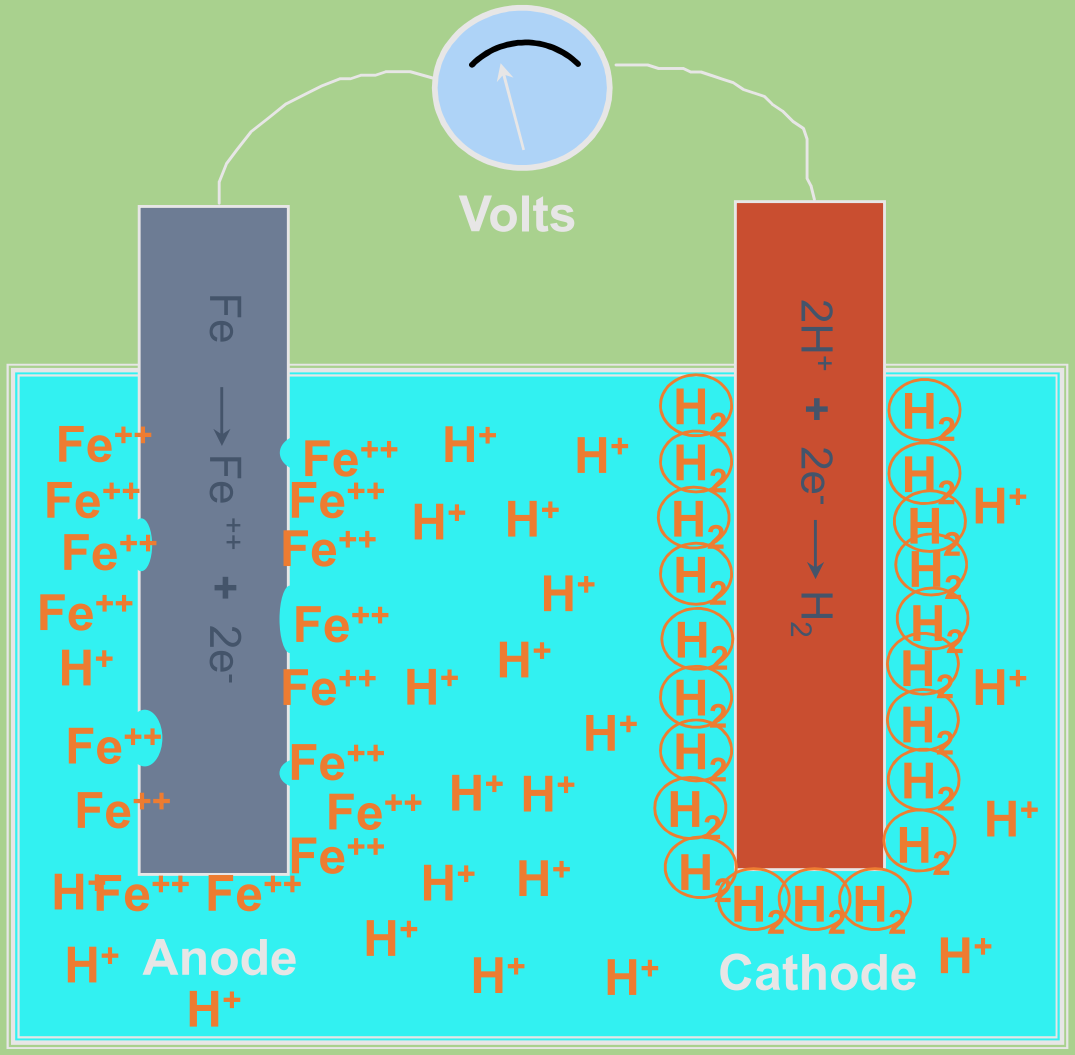
Oxygen Corrosion

As the iron at the **ANODE** corrodes, it is oxidized to form an iron oxide tubercle. The electrons are consumed at the **CATHODE** to form hydroxide ions.



Corrosion Cell

Cathodic Depolarization



Oxidation Potential

Reaction	Volts
Cu → Cu++ + 2e-	0.34
H2 → 2H+ + 2e-	0.0
Fe → Fe++ + 2e-	-0.44

Build up of H_2 gas on the cathode slows down the corrosion reaction

Effect of Oxygen

Anodic reaction: $Fe \longrightarrow Fe^{+2} + 2e^{-}$

Oxygen precipitates Fe^{+2} at the anode preventing anodic polarization, increasing the corrosion rate.

Cathodic reaction: $2H^{+} + 2e^{-} \longrightarrow H_2$

$2H^{+} + 2e^{-} \longrightarrow 2H^{o}$ (fast step)

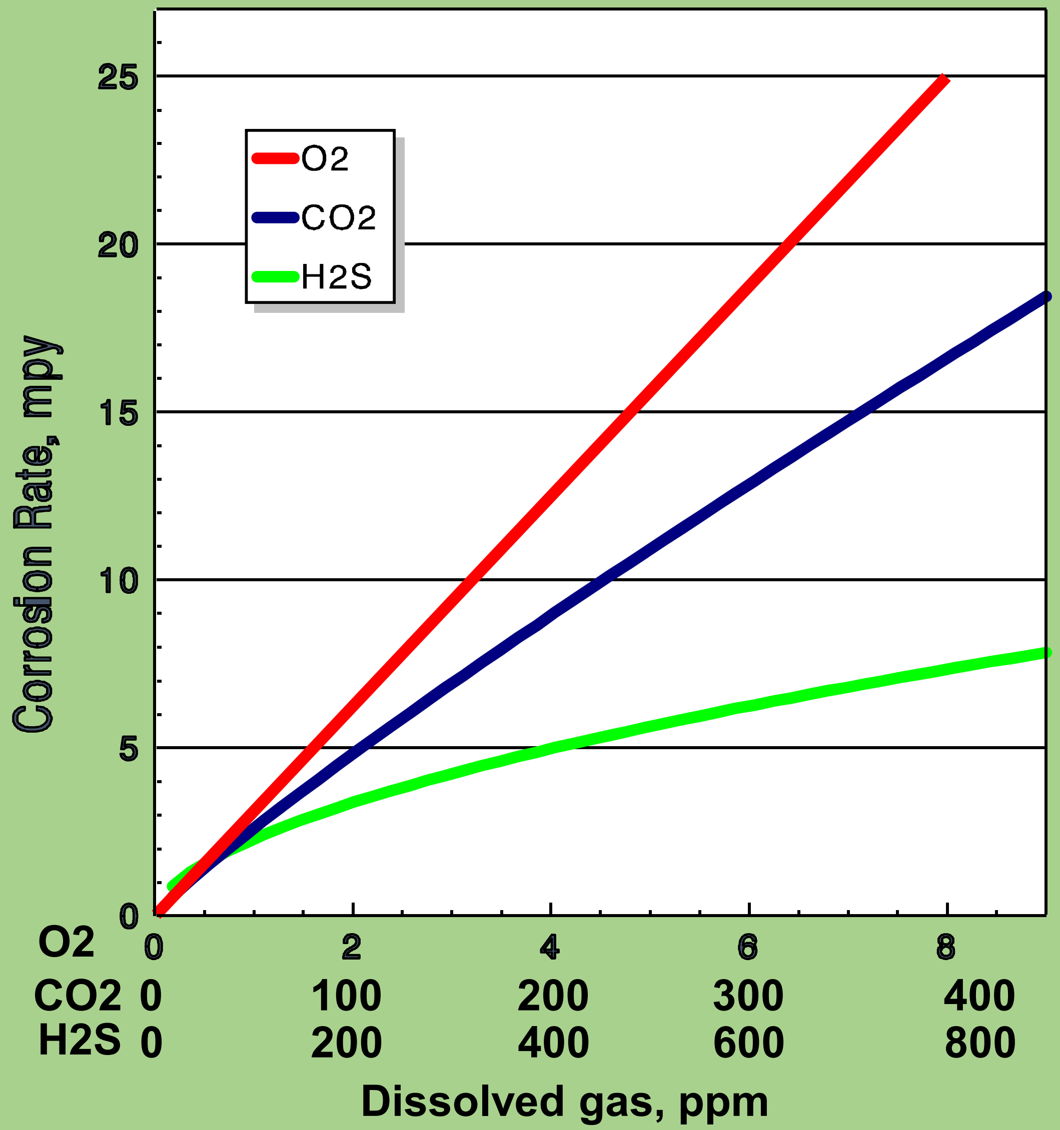
$2H^{o} + \longrightarrow H_2$ (slow step)

Gaseous H_2 films over and polarizes the cathodic electrode, slowing down the corrosion reaction.

$2H^{o} + {}^{1}/{}_{2}O_2 \longrightarrow H_2O$

With O_2 present the H_2 never forms, the cathode is not polarized, the corrosion rate remains high.

Comparison of Gases



Factors Involved in the Corrosion of Oilfield Steel

- pH (usually about 6.5 if from the reservoir)
- Chloride (influences inhibitors more than corrosivity)
- Temperature
    - Doubles for every 10°C increase
    - Decreases with the formation of protective scales
- Pressure
- Velocity (can be important, especially for sweet systems)
- Wear/abrasion (often involved as wear-accelerated corrosion)
- Galvanic acceleration (discussed later)
- MIC (discussed later)

Galvanic Corrosion

- Two different metals in contact
- Corrosion results from difference in oxidation potential
  - Anode: lower oxidation potential
  - Cathode: higher oxidation potential
- Corrosion rate effected by anode/cathode surface area ratio

Galvanic Corrosion

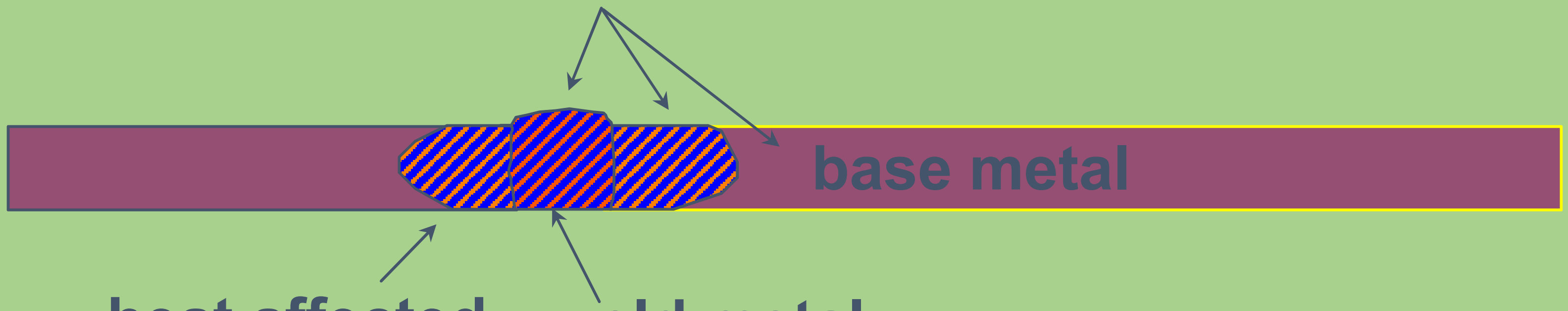
Reaction		Volts	
Cu	$Cu^{++} + 2e^-$	+0.34	Cathode
H2	$2H^+ + 2e^-$	0.00	
Fe	$Fe^{++} + 2e^-$	-0.44	Anode

Large anode/cathode ratio

Small anode/cathode ratio

Welds

The heating that occurs during the welding process will cause the weld metal and the heat affected zone around the weld to be physically different from the base metal.



The anode can form at any of these locations

base metal

heat affected zone

weld metal

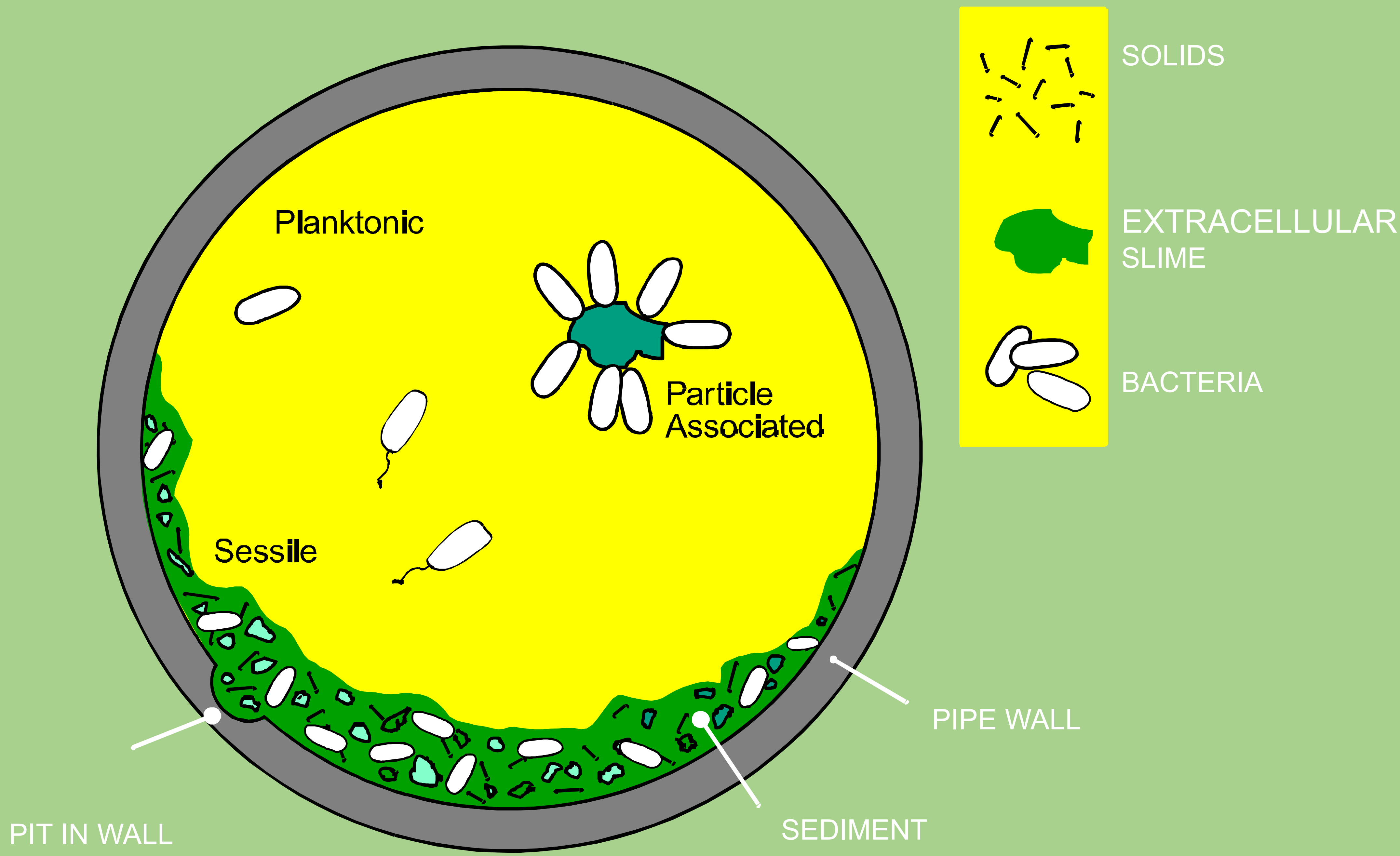
Maximum Corrosion Rates Resulting from Galvanic Couples in Sweet Brines

	Red Brass / MS		Type 410 SS /MS	
	Butted (mpy)	Surrounded (mpy)	Butted (mpy)	Surrounded (mpy)
22 deg. C Blank	54	90	70	450
22 deg. C Inhib.	1	5	2	40
90 deg. C Blank	70	260	90	860
90 deg. C Inhib.	2	20	4	80

Microbial Induced Corrosion (MIC)

- MIC is another recognized corrosion mechanism
- Results from bacterial activity
- Typically appears as under-deposit corrosion (pitting)
- Standard corrosion inhibitors are ineffective

MIC Cell



Planktonic

Particle Associated

Sessile

PIT IN WALL

SEDIMENT

PIPE WALL

SOLIDS

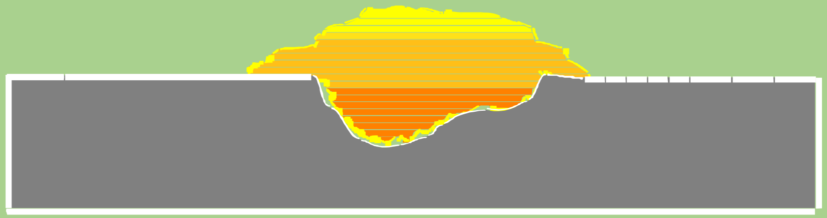
EXTRACELLULAR SLIME

BACTERIA

Recognition of MIC

- Stair-stepped: **SRB**

- Drill hole, cavernous or worm-hole: **APB**

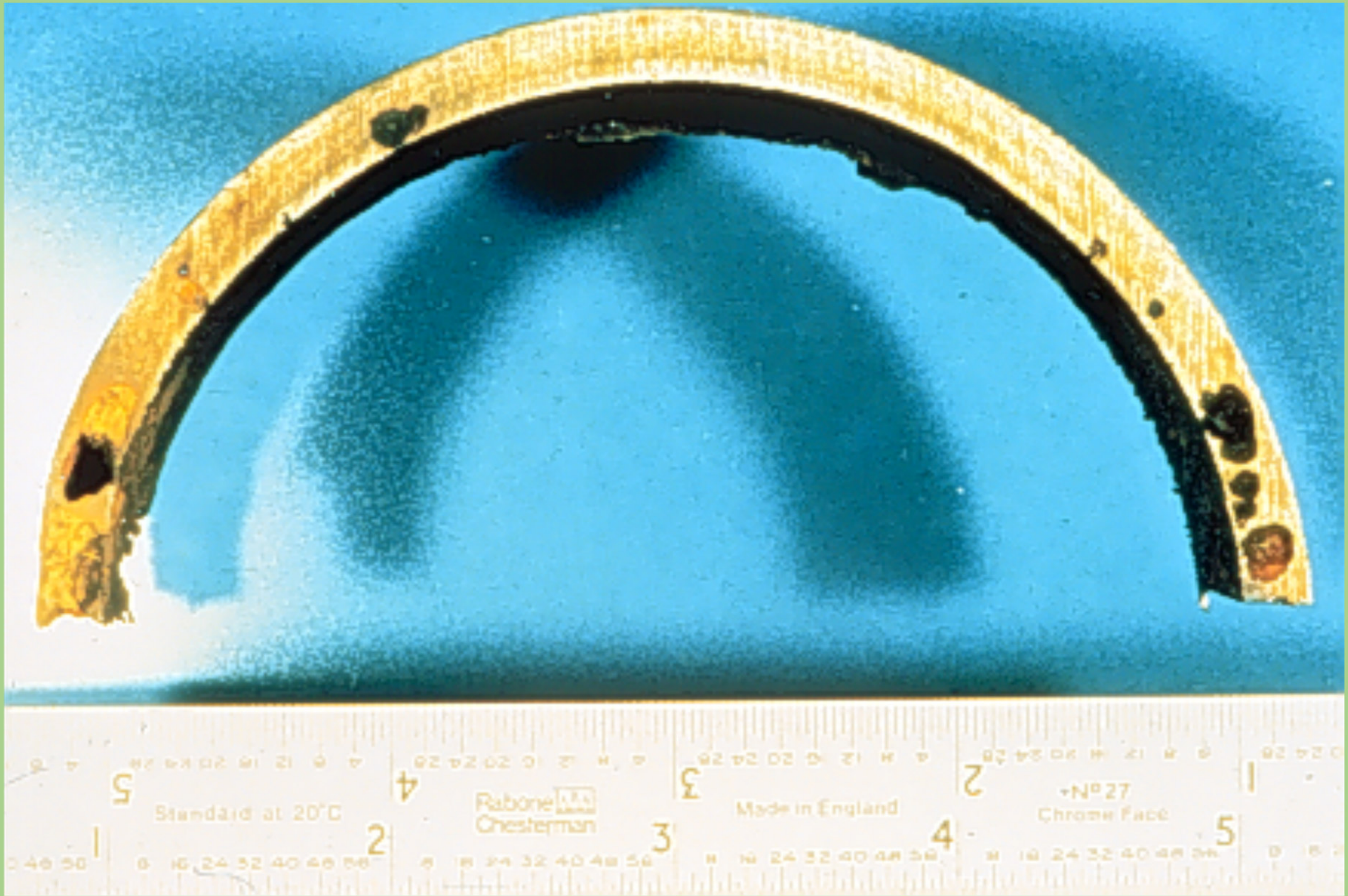


- Caped with solids

Bacterial Corrosion

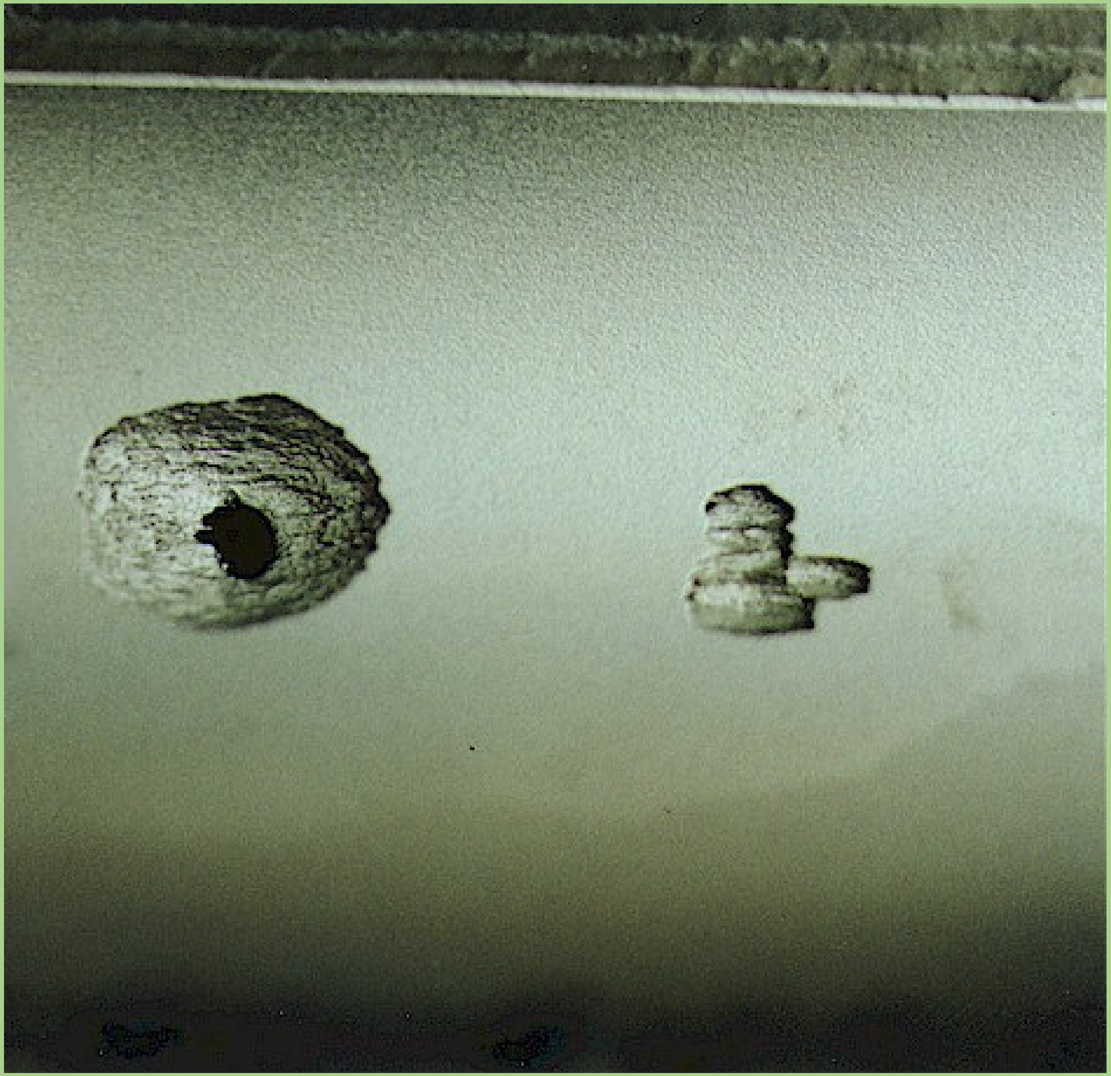
Corrosion from SRB (Sulfate Reducing Bacteria)

Bacterial Corrosion



Corrosion from APB (Acid Producing Bacteria)

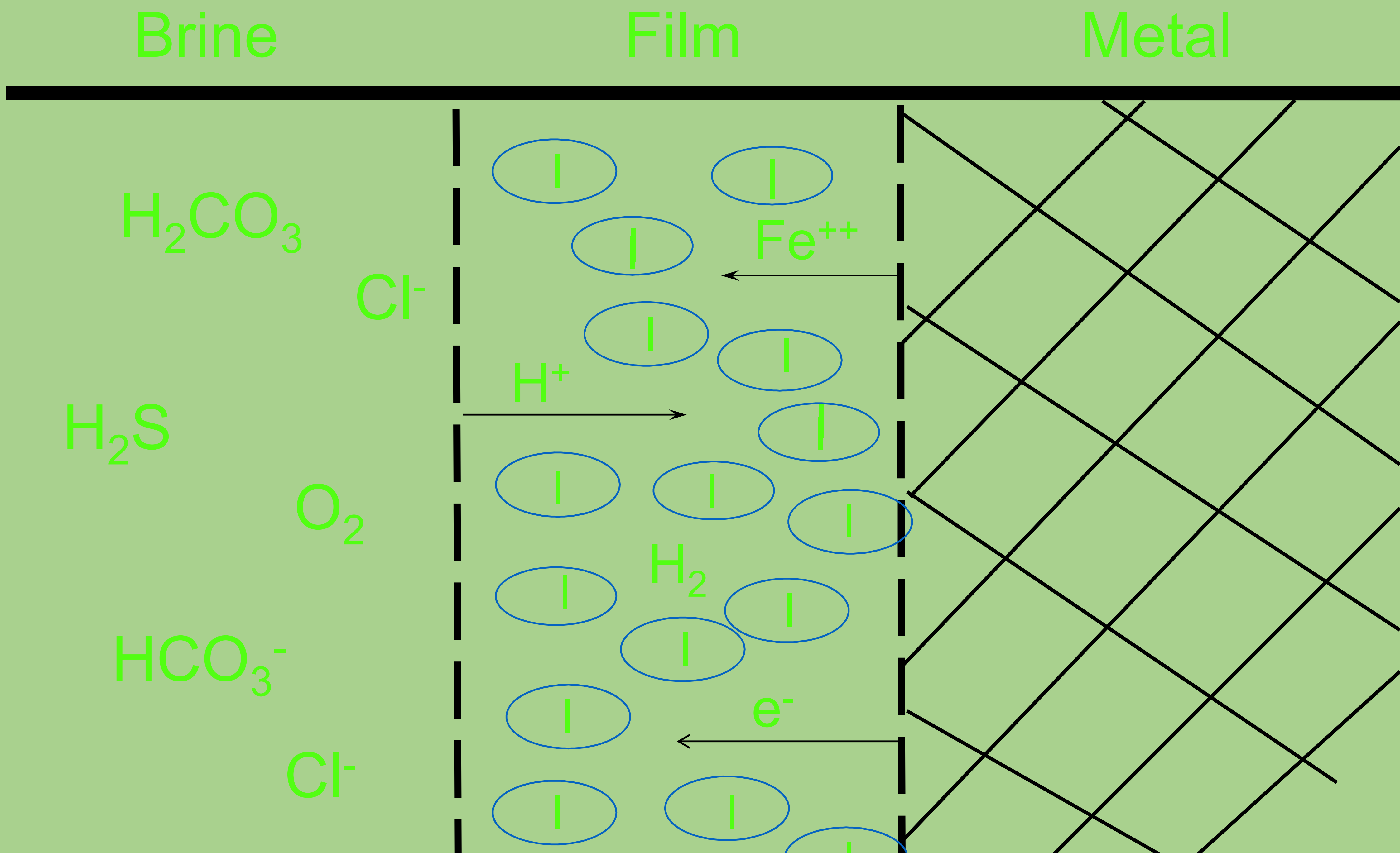
Bacterial Corrosion



Corrosion from APB (Acid Producing Bacteria)

Corrosion Inhibitor Characteristics and Chemistries

Corrosion Inhibition



Brine

Film

Metal

H_2CO_3

Cl^-

H_2S

O_2

HCO_3^-

Cl^-

Fe^{++}

H^+

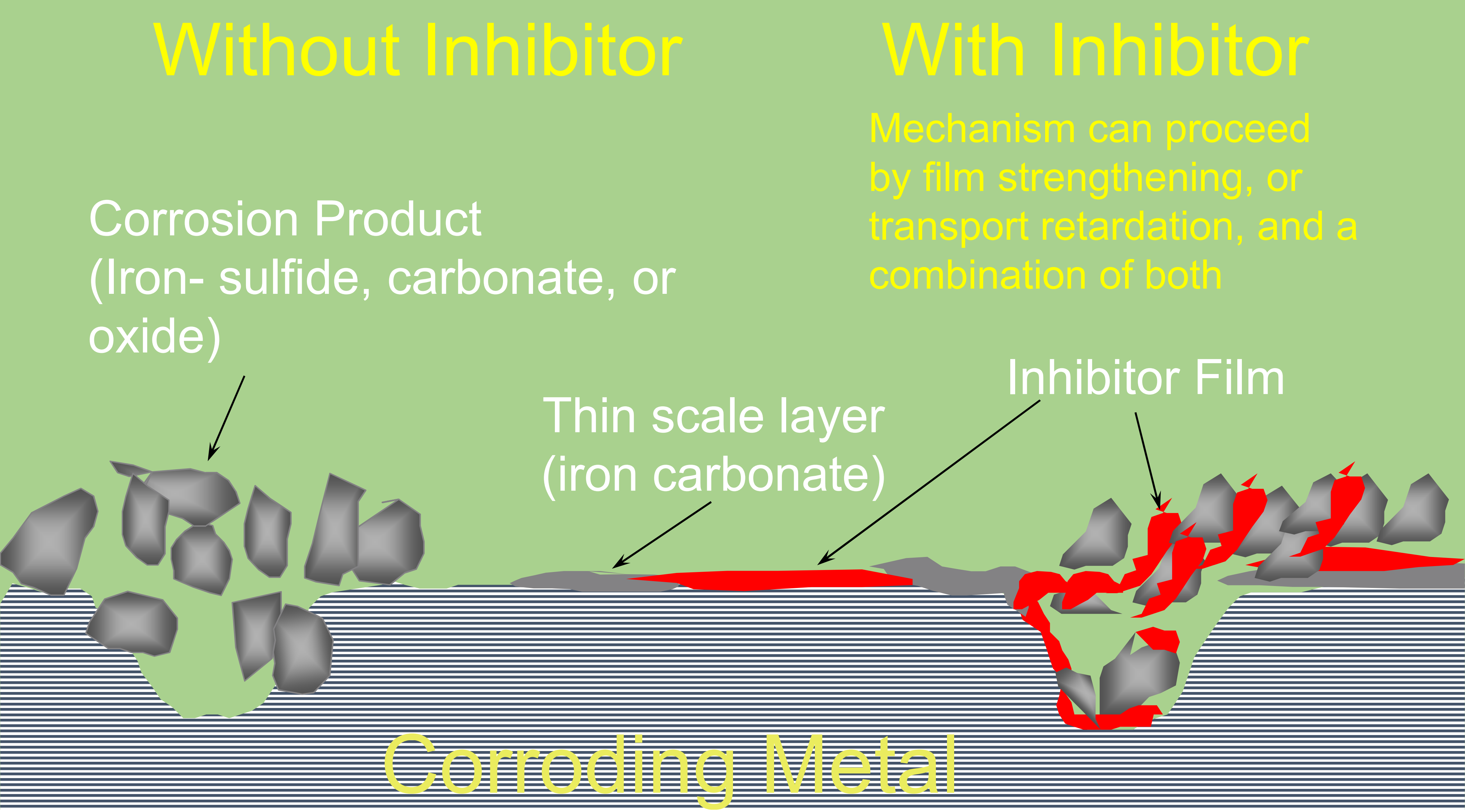
H_2

e^-

Mechanism of Inhibition

- Absorption onto corrosion product layer blocking transport of corrosive reactants
- Adsorption onto surface reaction sites (anodic or cathodic) slowing down metal dissolution and/or hydrogen evolution
- Changing transport and flow regime characteristics of production fluids

The Mechanism of Corrosion Inhibition



Without Inhibitor

With Inhibitor

Mechanism can proceed by film strengthening, or transport retardation, and a combination of both

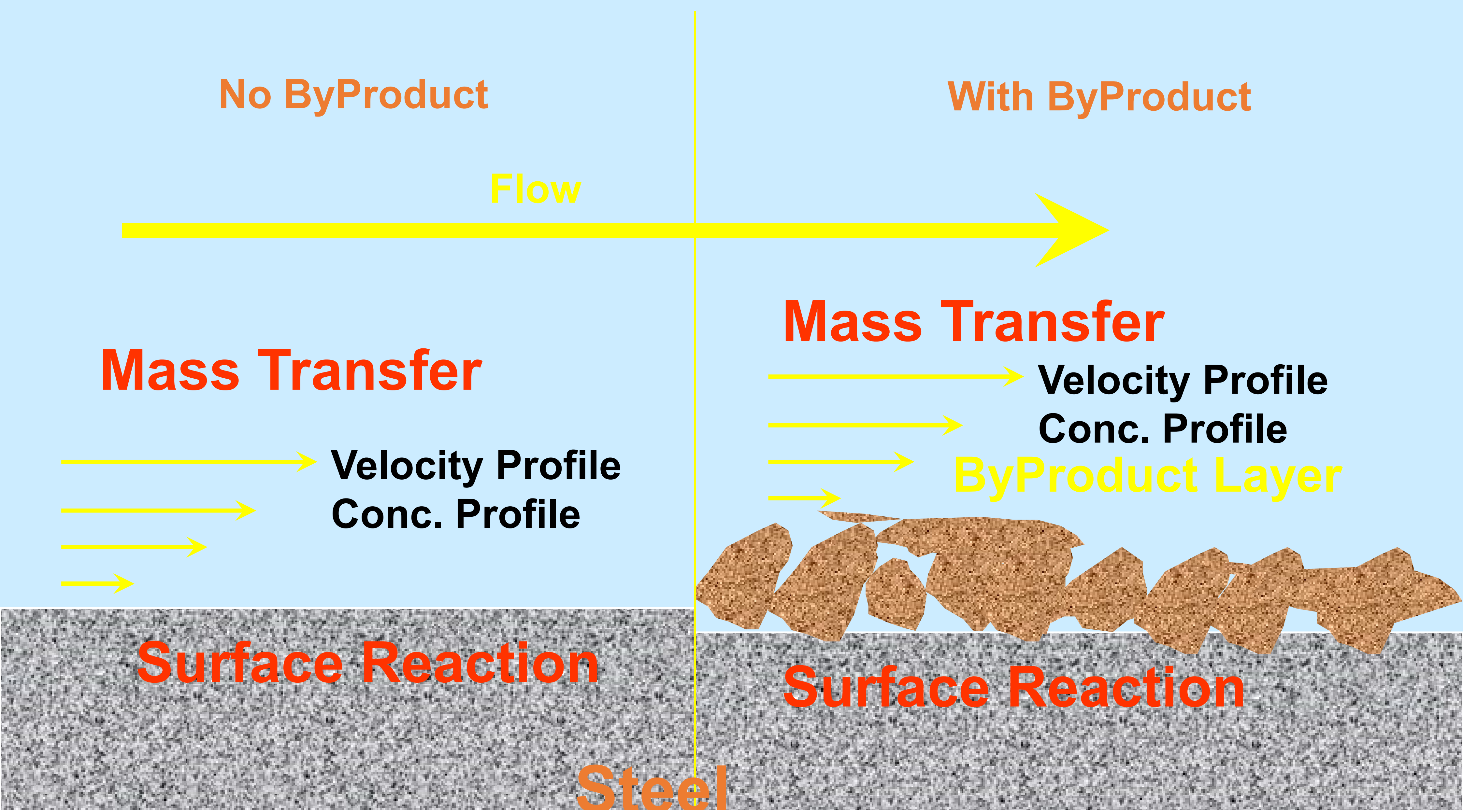
Corrosion Product (Iron- sulfide, carbonate, or oxide)

Thin scale layer (iron carbonate)

Inhibitor Film

Corroding Metal

CO2 Corrosion and the Role of Corrosion ByProduct Layers



No ByProduct

With ByProduct

Flow

Mass Transfer

Velocity Profile

Conc. Profile

Surface Reaction

Mass Transfer

Velocity Profile

Conc. Profile

ByProduct Layer

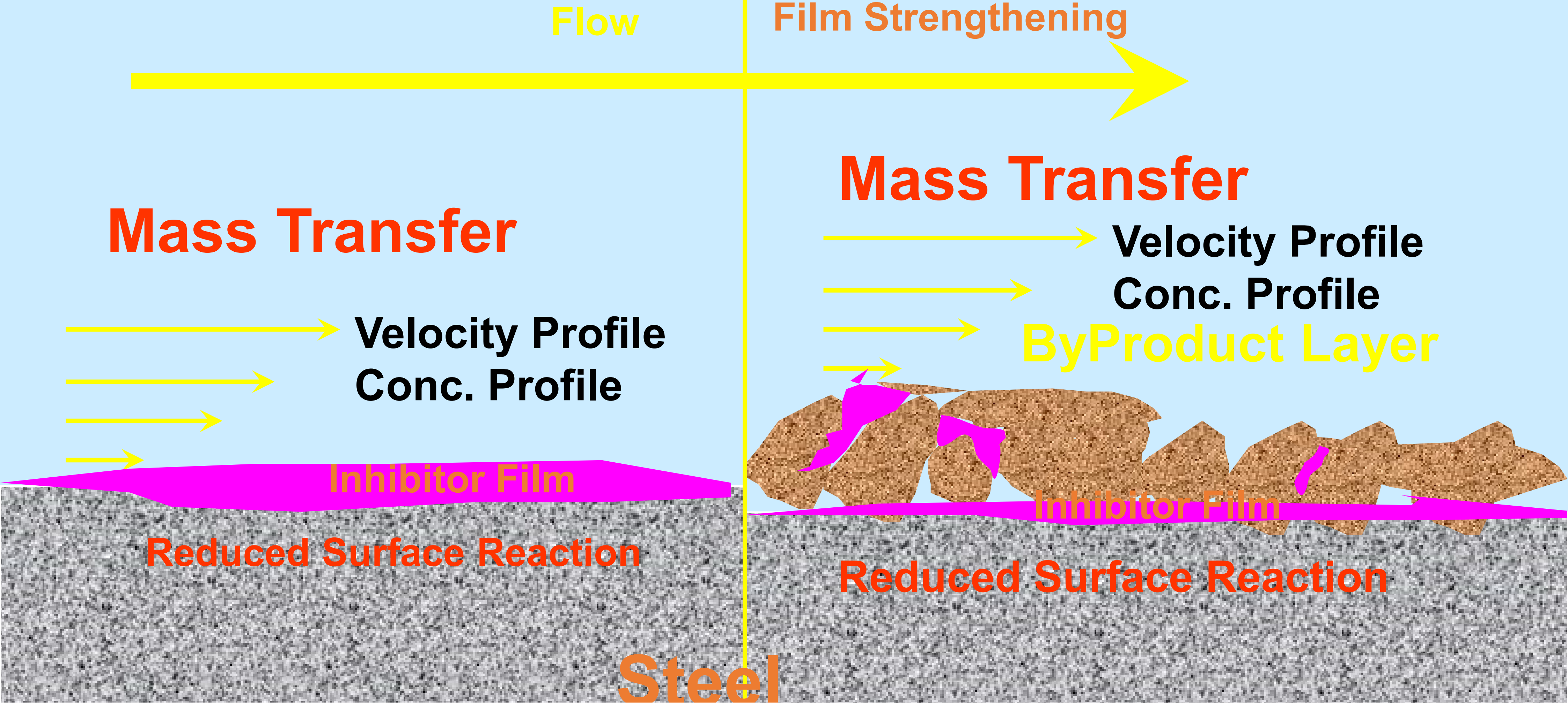
Surface Reaction

Steel

Role of Inhibitors

No ByProduct
Retardation of
Surface Reaction

With ByProduct
Retardation of Surface Reaction
Reduction of Porosity of ByProduct Layer
Film Strengthening



Flow

Mass Transfer

Velocity Profile
Conc. Profile

Inhibitor Film

Reduced Surface Reaction

Mass Transfer

Velocity Profile
Conc. Profile

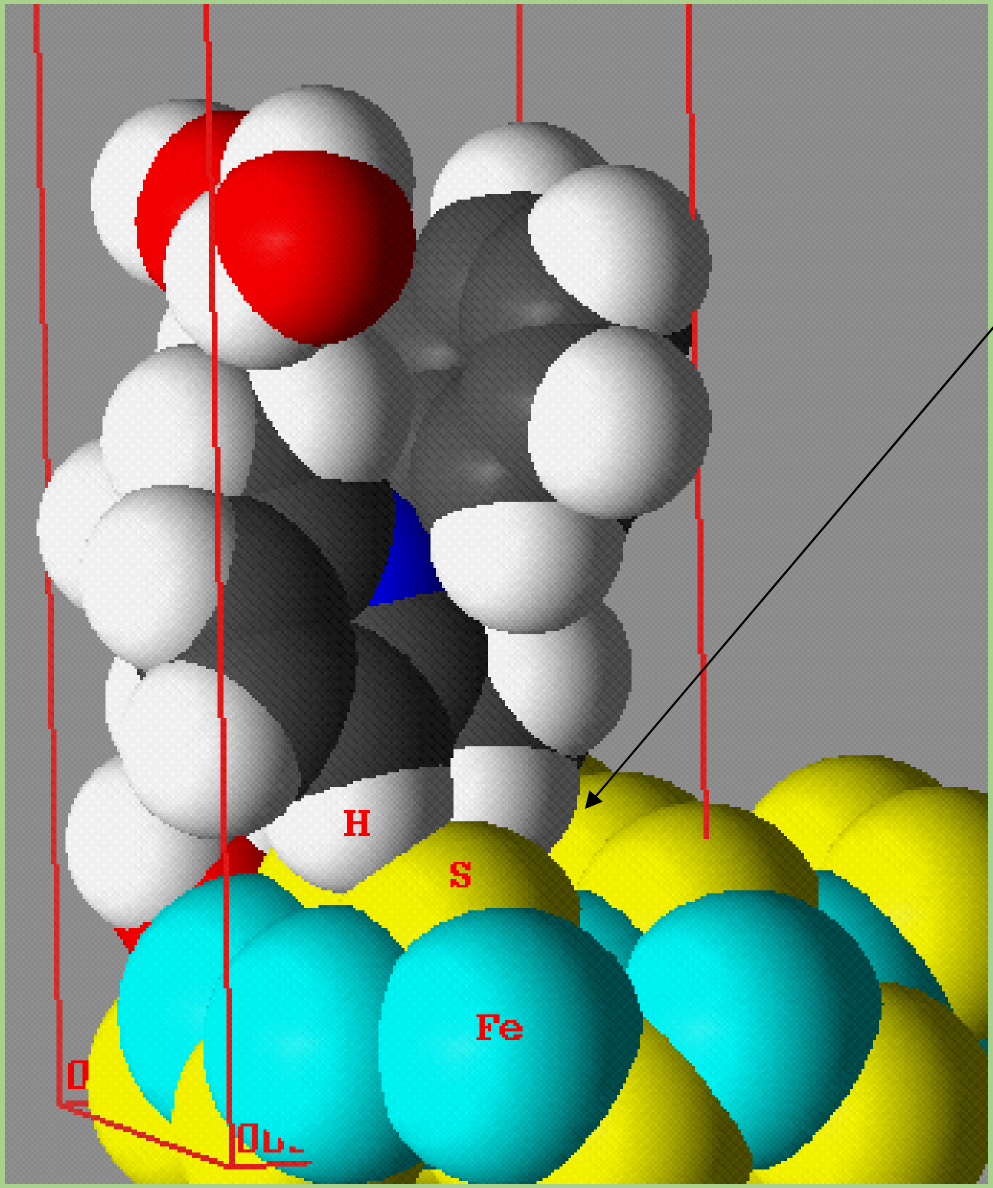
ByProduct Layer

Inhibitor Film

Reduced Surface Reaction

Steel

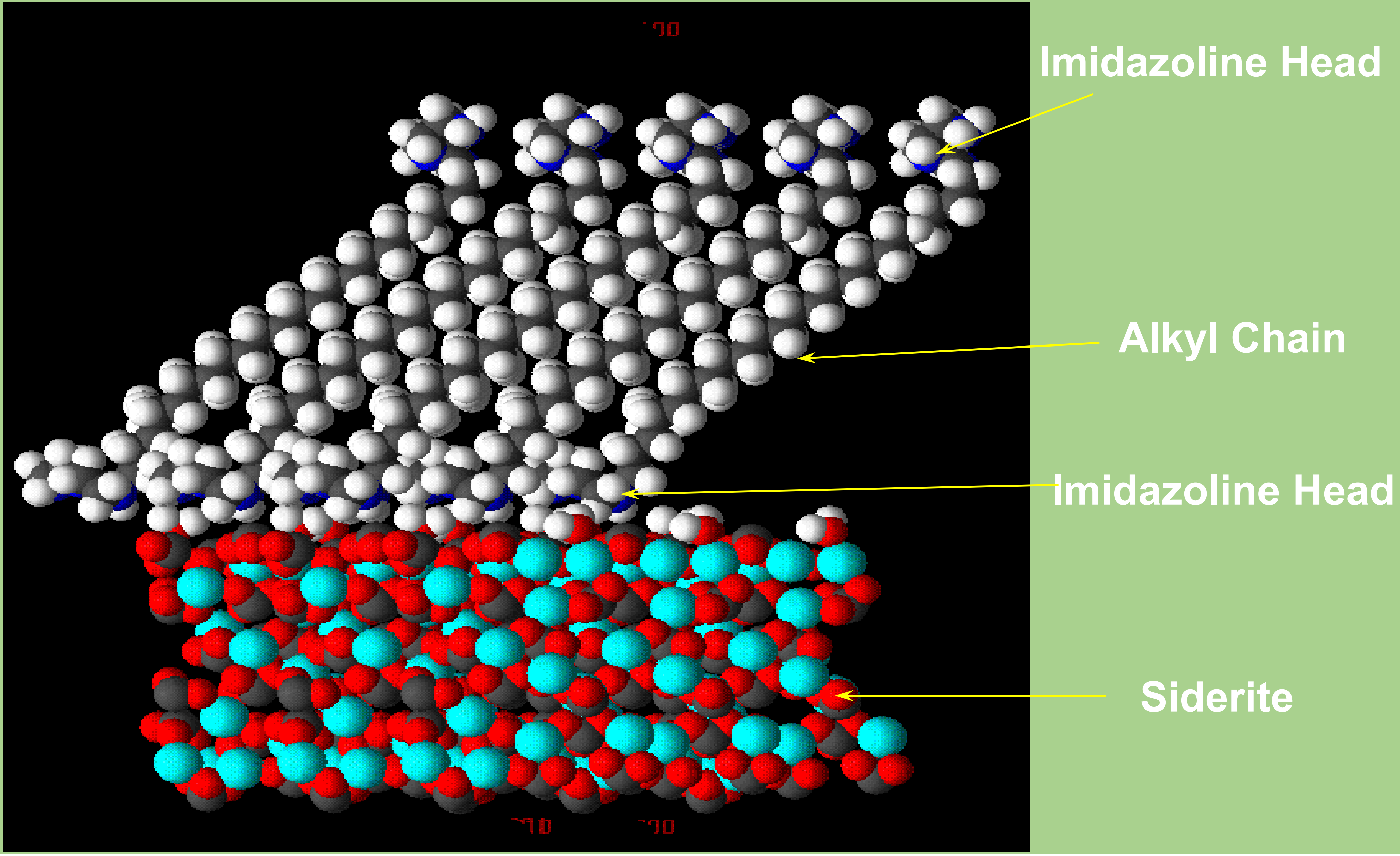
Binding of 1-benzyl-2,6 dimethylpyridinium chloride to mackinawite



70º degree
Angle with
the mackinawite surface

Modeling data provides information on how inhibitors adsorb on surfaces and the strength of the adsorption. This enables improvement in molecular design and chemical synergies to be sought.

Bilayer Film Formed on Surface



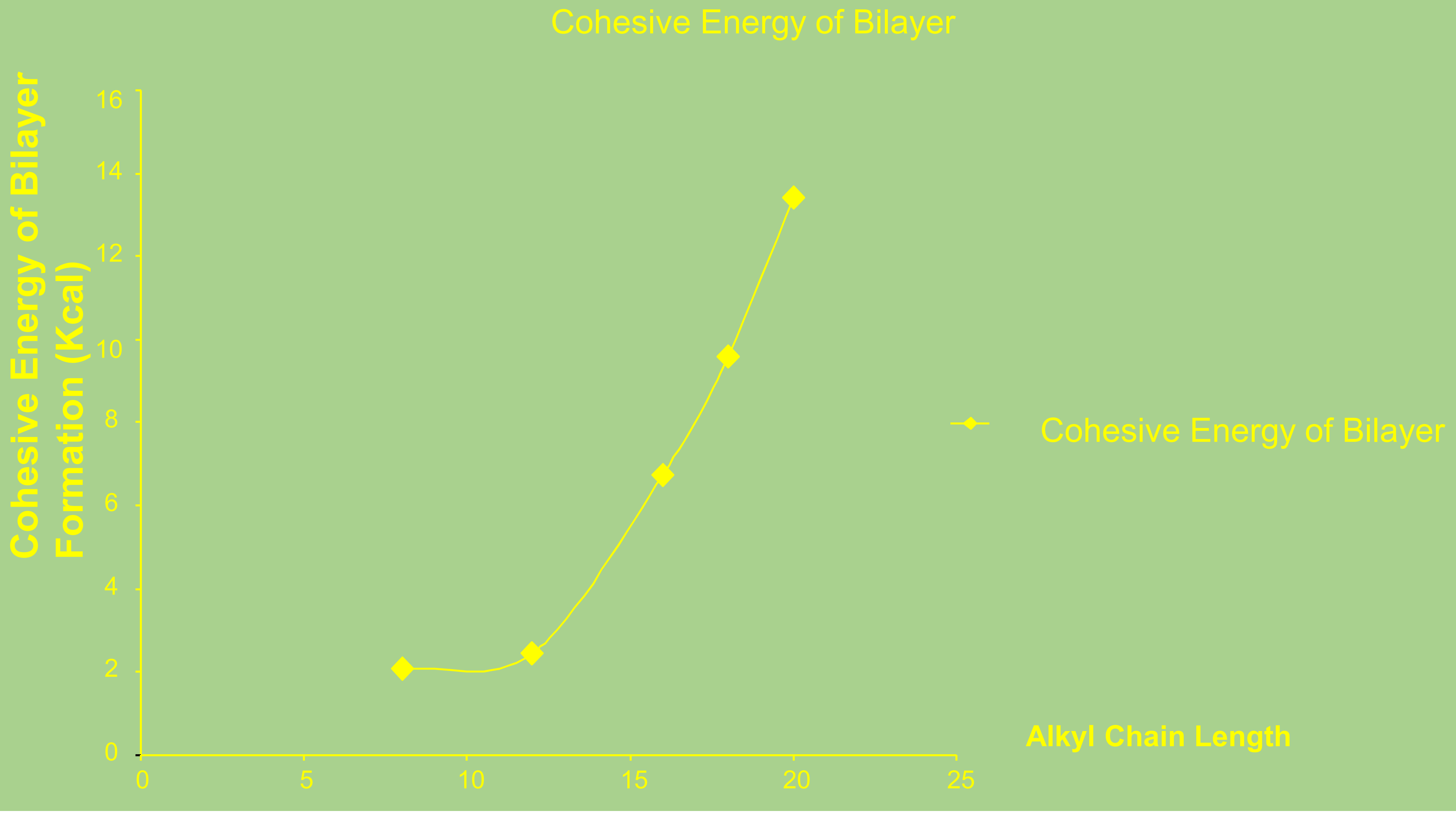
Imidazoline Head

Alkyl Chain

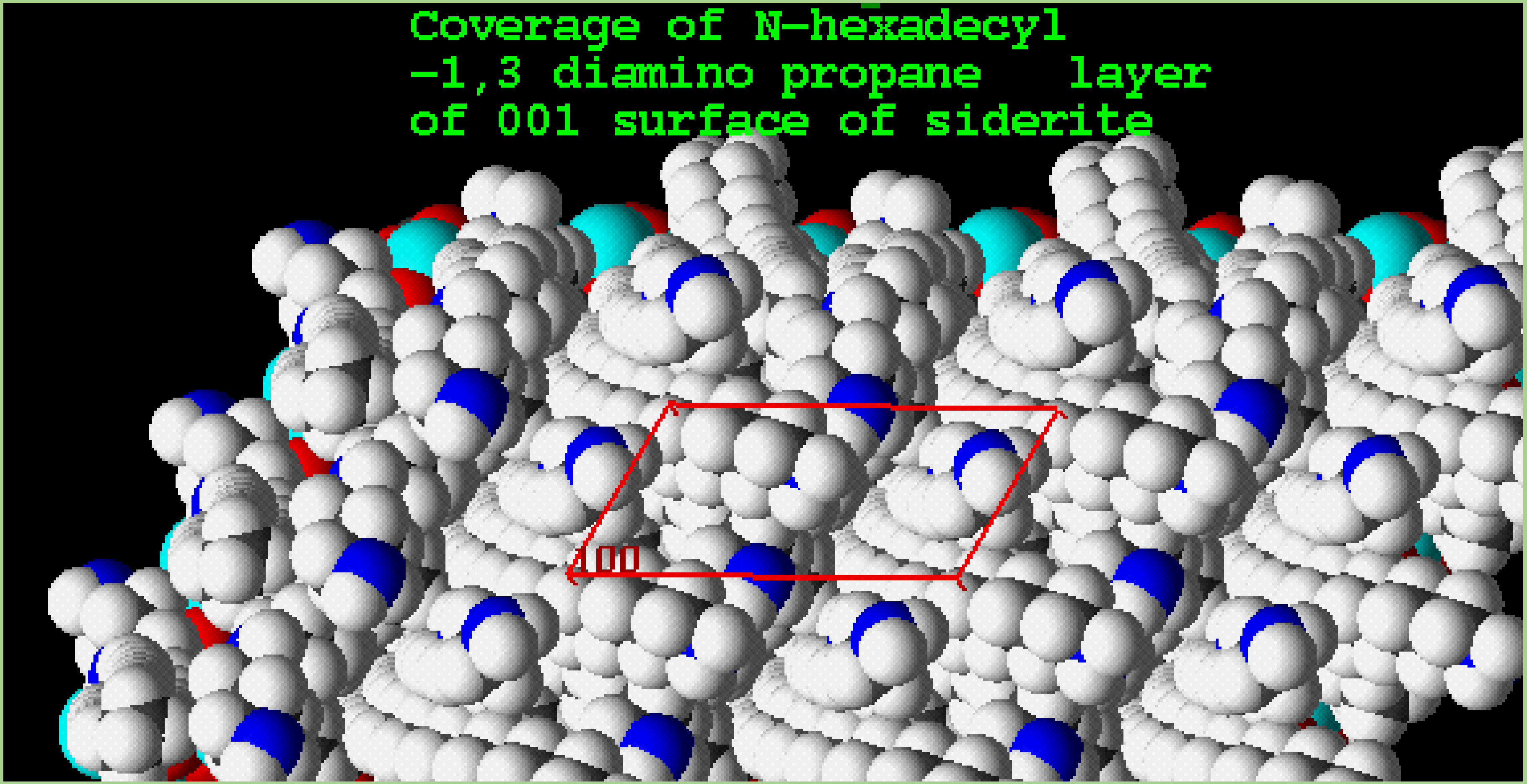
Imidazoline Head

Siderite

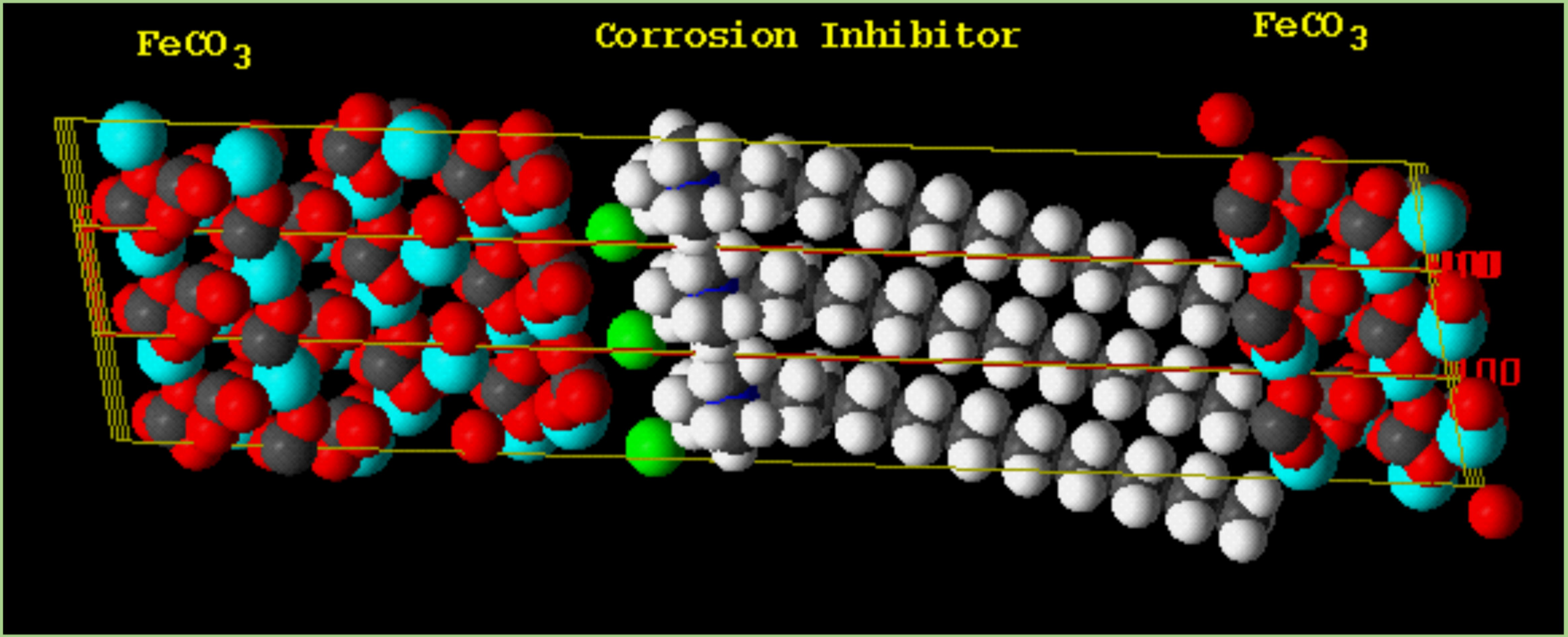
Film Formation Energy Dependence on alkyl chain length



Coverage of N-hexadecyl -1,3 diamino propane layer of 001 Surface of Siderite



Inhibitor Adsorbed in a Corrosion By-Product Layer



Oil Field Corrosion

- Fast acting
- Persistent film
- Low dosage
- Monolayer / bilayer film
- High shear resistant

Inhibitor Selection Criteria

- Application
  - Downhole
  - Surface
- Method of application
  - Batch
  - Continuous
  - Squeeze
- Concentration
  - Total fluids
  - Water production
  - Gas production
- Cost vs. Performance
  - Laboratory evaluation
  - Field test

Solubility

Soluble Dispersible Insoluble

Compatibility

Corrosion Inh.
+ Wetting Agent

Corrosion Inh.
+ Scale Inhibitor

Emulsion Tendency

E/T after 5 min.

A: Diesel + Brine

B: Diesel + Brine
+ 100 ppm Inh. A
(Good E/T)

C: Diesel + Brine
+ 100 ppm Inh. B
(Poor E/T)

Inhibitor Types

- Oil Soluble
  - Good filmers
- Water Soluble
  - Get to where corrosion is occurring
- Oil Soluble / Water Dispersible
  - Features of oil soluble and water soluble
- Volatile
  - Vapor phase (gas pipelines)

Corrosion Inhibitor Chemistries

- Amines and Amine Salts
- Quaternary Amines
- Fatty Acids
- Acid/Amine Reaction Products
- Alkyl Pyridine (Salted or Quaternized)
- Phosphorous Chemistry
- Sulfur Compounds

Corrosion Inhibitor Chemistries

- Amines - Typically vapor phase inhibitors for gas pipelines
- Amine Salts - Very water soluble, some provide good protection against MIC
- Quaternary Amines - Very water soluble, good protection against general corrosion as well as MIC

Corrosion Inhibitor Chemistries

- Fatty Acids - Typically used in batch oil soluble inhibitors
- Acid/Amine Reaction Products - Same as above but can be made water dispersible or soluble by salting

Corrosion Inhibitor Chemistries

- Alkyl Pyridine (Salted) - Typically used in water systems, hydrotesting or packer fluids
- Alkyl Pyridine (Quaternized) - Water dispersible, typically used continuously in wet transmission lines, especially effective against sour corrosion

Corrosion Inhibitor Chemistries

- Phosphorous Chemistry - Water soluble, continuous applications, especially effective against oxygen corrosion
- Sulfur Compounds - proprietary BPC additives suitable for any type of corrosion inhibitor, boost performance

Corrosion Inhibitor Formulation

- Active Chemistries
  - Often a combination of several chemistries
- Solvent System
- pH Adjustment
- Surfactant
- EB Package

Formulation

pH Adjustment

A: Imidazoline in water

B: Imidazoline in water
+ acetic acid

Formulation

<u>Effect of Surfactant</u>

A: APQ in water
(Insoluble)

B: APQ in water + surfactant
(Clear Solution)

Formulation

Effect of EB

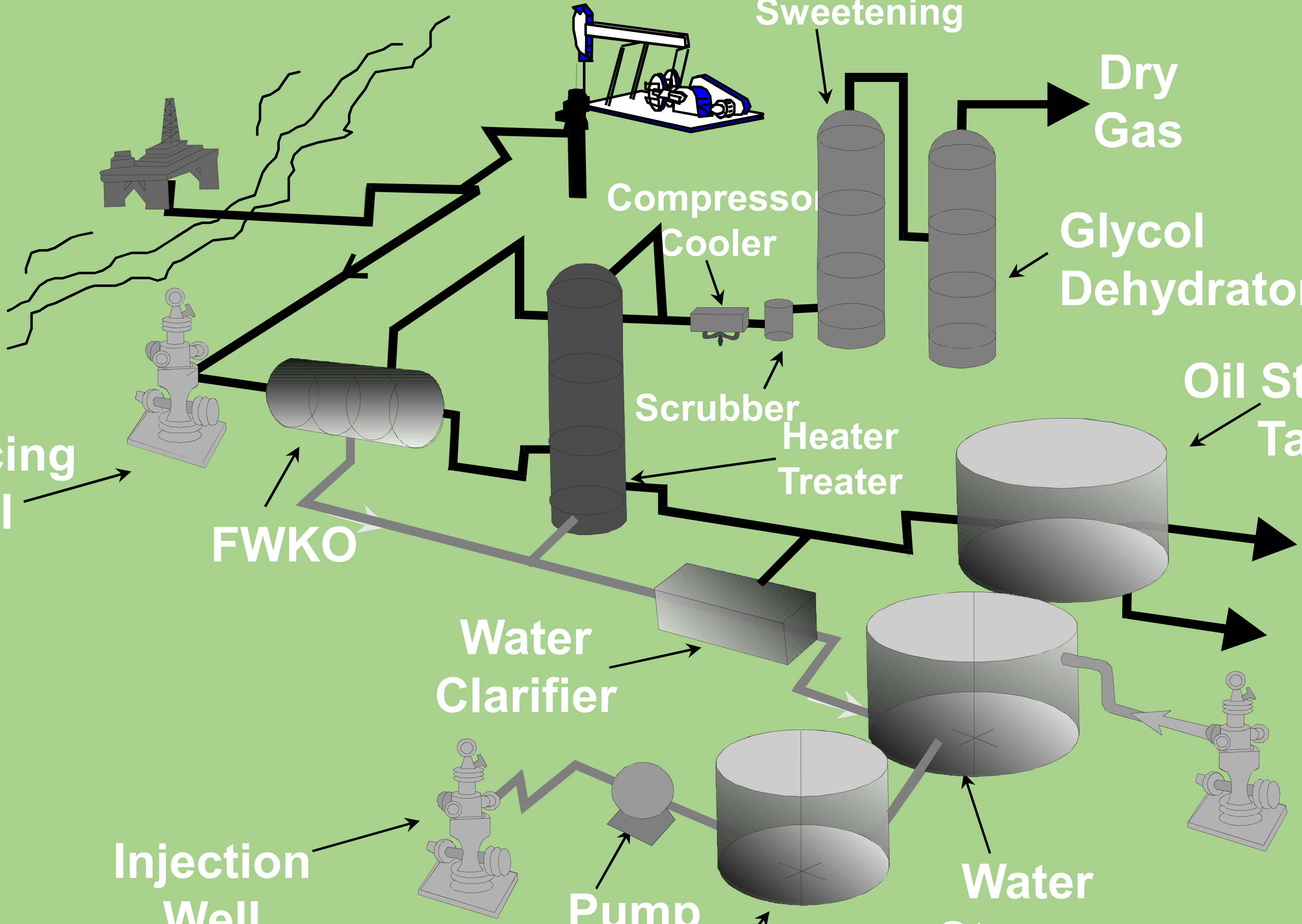
A: Diesel + Brine

B: Diesel + Brine

+ 100 ppm Inh. A

C: Diesel + Brine + 100 ppm Inh. A (w/o EB Package)

Corrosion Inhibition in the Oil Field



Amine Sweetening

Dry Gas

Compressor Cooler

Glycol Dehydrator

Scrubber

Oil Storage Tank

Heater Treater

Producing Well

FWKO

Water Clarifier

Source Water

Injection Well

Pump

Water Storage Tank

Surge Vessel

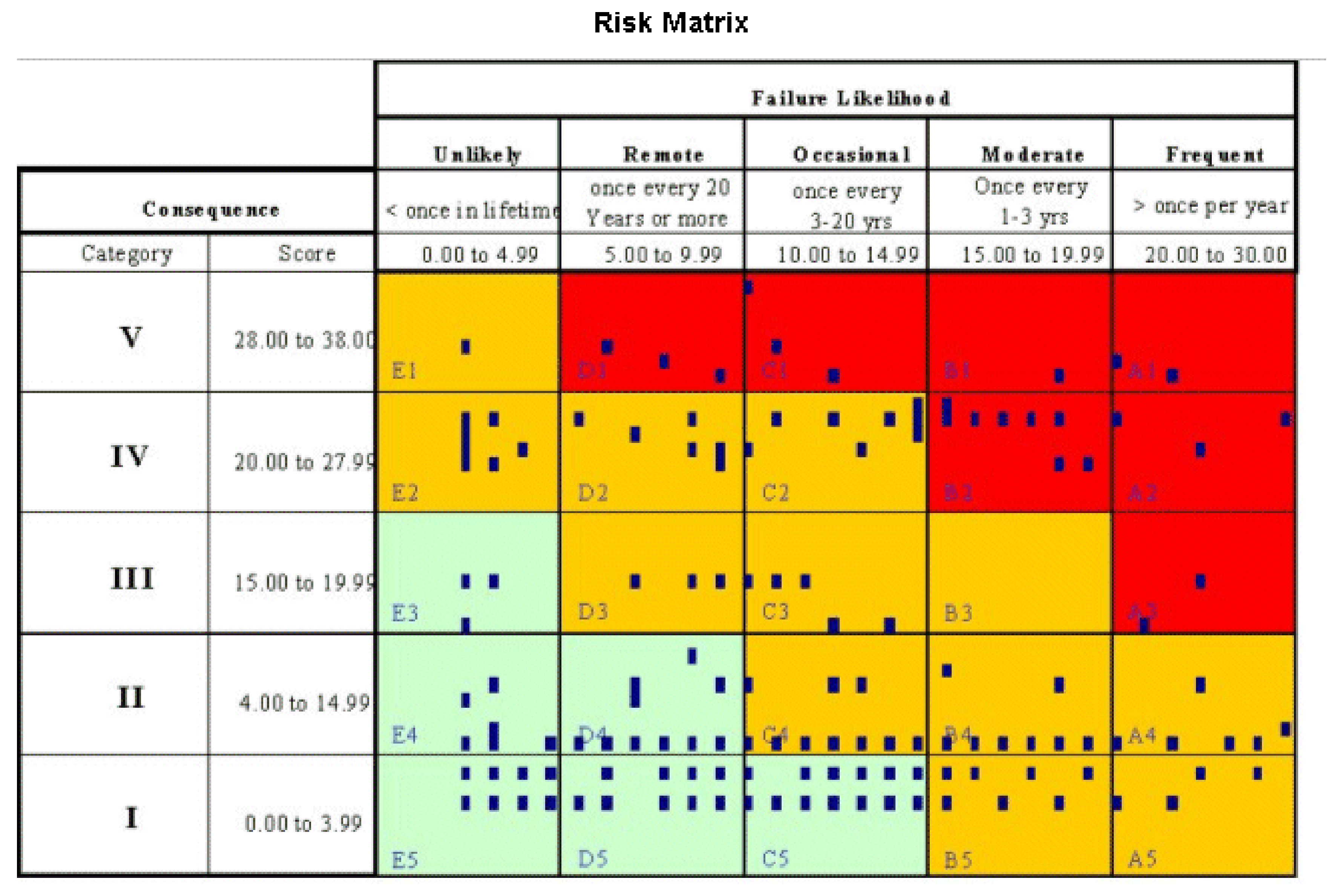
Areas of Corrosion and Inhibitor Applications

- Wells
  - Oil
  - Gas
- Flow lines and transmission lines
- Production and water treatment facilities and the injection system

Internal Corrosion Risk

- <u>Risk = (likelihood) x (consequence)</u>
  - Likelihood of internal corrosion
    - Water movement through the system
      - Elevation profile
      - Shear stress of the gas or hydrocarbon liquid on the water (velocity and pressure)
    - Corrodant concentration (CO2, H2S, Oxygen, Bacteria, & Solids)
  - Consequence
    - High consequence areas (HCAs)
    - Company designated risk factors
      - Safety
      - Environmental impact
      - Business loss
      - Corporate reputation

Commit Resources to Problem Areas



Risk Matrix

		Failure Likelihood				
		Unlikely	Remote	Occasional	Moderate	Frequent
Consequence		< once in lifetim	once every 20 Years or more	once every 3-20 yrs	Once every 1-3 yrs	> once per year
Category	Score	0.00 to 4.99	5.00 to 9.99	10.00 to 14.99	15.00 to 19.99	20.00 to 30.00
V	28.00 to 38.00	E1	D1	C1	B1	A1
IV	20.00 to 27.99	E2	D2	C2	B2	A2
III	15.00 to 19.99	E3	D3	C3	B3	A3
II	4.00 to 14.99	E4	D4	C4	B4	A4
I	0.00 to 3.99	E5	D5	C5	B5	A5

Oil Field Corrosion

- Identify the corrosive agent
  - H_2S
  - CO_2
  - O_2
  - Bacteria
- Treat for identified problem

Oil Well Corrosion in Sour H_2S Environments

- Method of Failure
  - Pitting and underdeposite corrosion
  - Hydrogen embrittlement
    - SSC
    - Fatigue
- The corrosion product layer is an iron sulfide which is not very protective.

Oil Well Corrosion in a Sweet CO_2 Environment

- The corrosion product layer is $FeCO_3$ which can give significant protection
- Mode of failure is severe pitting where the $FeCO_3$ is removed
- Pitting is the worst where there is CO_2 gas breakout. Often down stream of the rod boxes

Oil Well Corrosion in a Oxygen Environment

- Oxygen is not in the produced fluids, it is introduced on the surface
  - Leaking stuffing box: corrosion of top several rods and flowlines
  - Leaks into casing: corrosion right above the pump
- Fresh water leaks into casing
- Try a mechanical fix before an inhibitor treatment
- Standard corrosion inhibitors lose effectiveness at about 50 ppb oxygen.

Oil Field Corrosion Resulting from MIC

- Souring of the produced fluids
- Standard corrosion inhibitor program is not effective against MIC
- Need to start a biocide program
- Keep the system clean

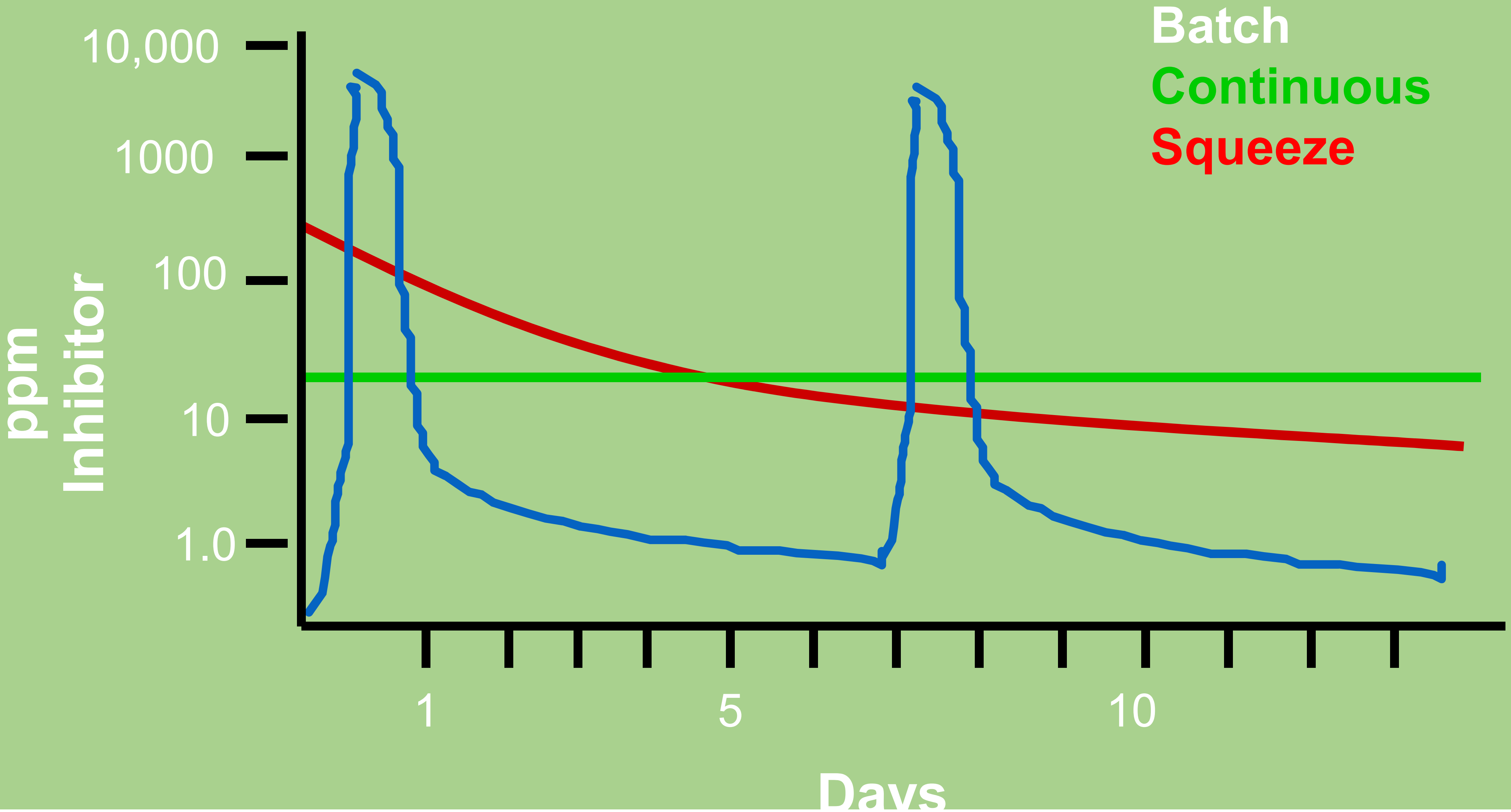
Surface condition of the metal is crucial for a successful corrosion inhibitor program

- Inhibitors work much better on a clean surface
- May need to clean the well
  - Surfactant
  - Magnatreat M
- May need to clean the pipeline
  - Pigging
  - Surfactant
  - Magnatreat M

Methods for Applying Corrosion Inhibitor

- Batch
  - Oil and gas wells
  - Pipelines
- Continuous
  - Oil and gas wells
  - Production facilities
  - Water Systems
  - Pipelines
- Squeeze
  - Oil and gas wells

Rate of Inhibitor Feedback

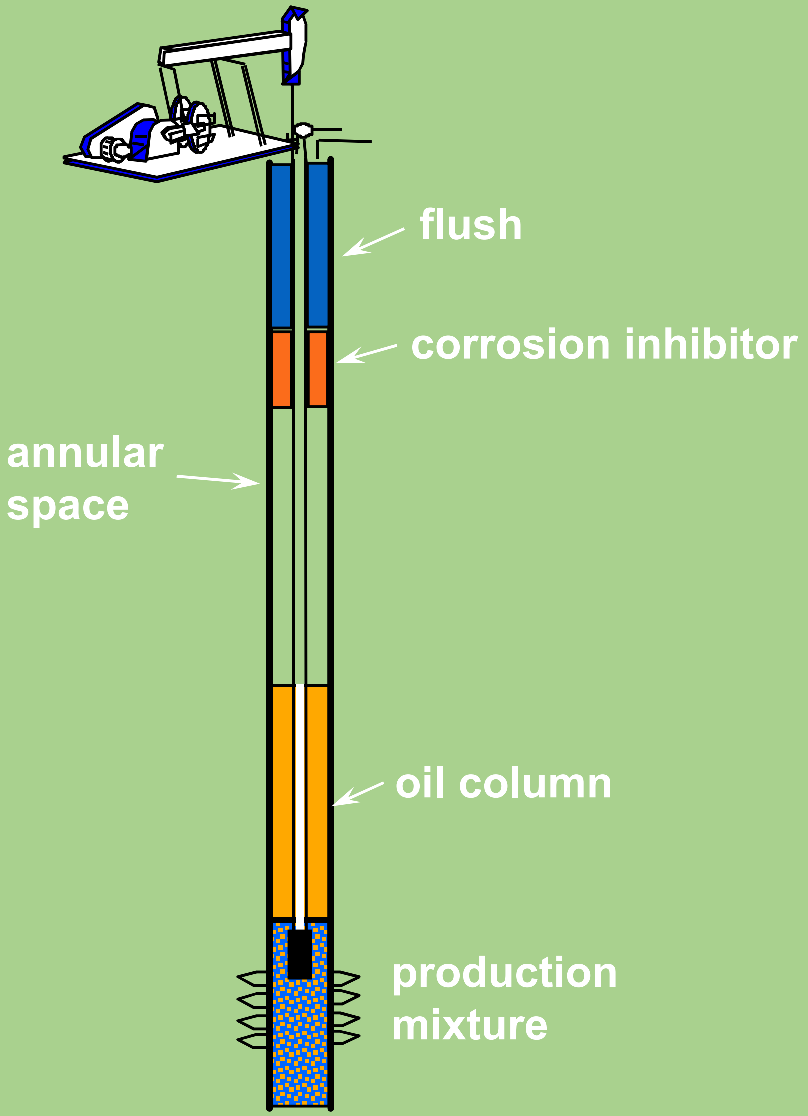


Corrosion Inhibitor Application to Oil Wells

- Batch and Flush
- Batch and Circulate
- Continuous
- Squeeze

Oil Well Inhibitor Applications
Batch and Flush

- Open Annulus (No Packer)
- Weekly or biweekly application of inhibitor with flush water
- Flush water volume based on fluid level
- Dosage based on production and corrosion severity (25 ppm total fluids)



Batch Inhibitor Application

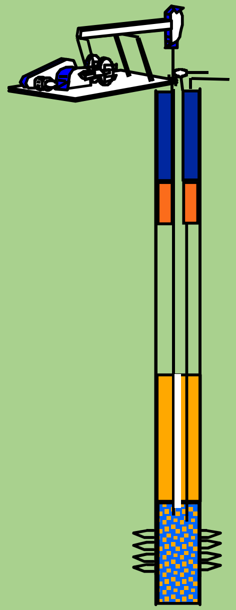
As a starting point use 25 ppm of inhibitor (based on total production) once per week. Use a minimum of 0.5 gal. per 1000 feet of depth per week.

Batching Inhibitors Through Fluid Levels

Fluid Level, F.O.P	Best Inhibitor Type
0-500’	Oil soluble, non-dispersible
500-1500’	Oil soluble, water dispersible
1500+	Water soluble

Truck Treating Flush Volumes

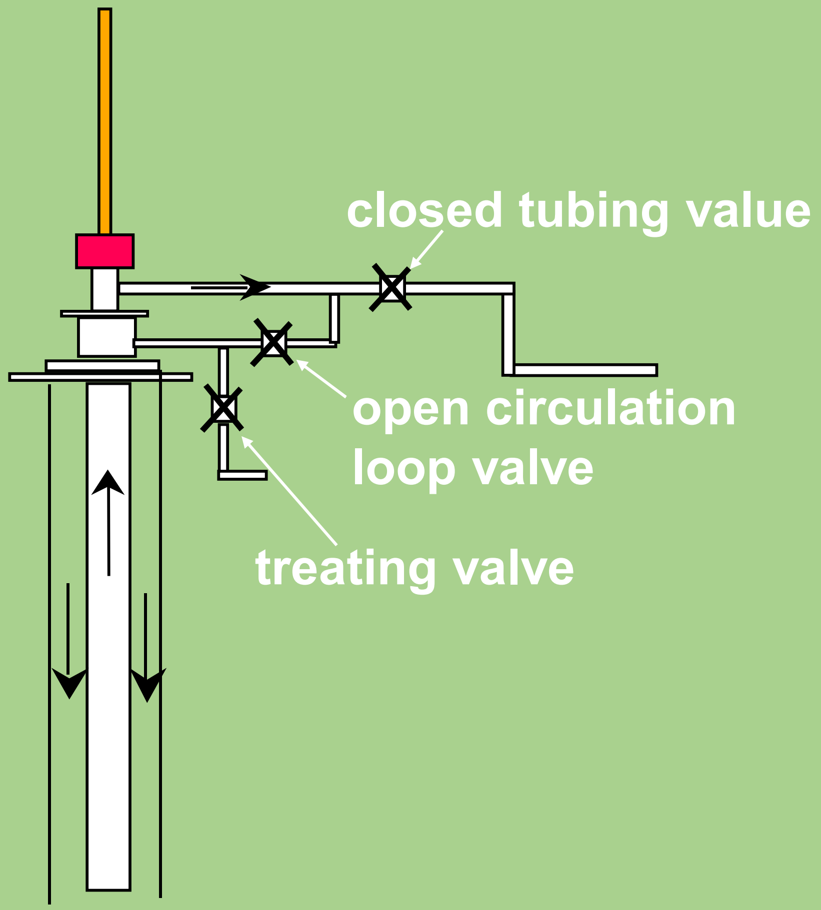
Feet of Fluid Over Pump	Minimum Flush In Barrels
0	1
1000	3
2000	5
3000	7



Oil Well Inhibitor Applications
Batch and Circulate

- Open Annulus (No Packer)
- Weekly or biweekly application of inhibitor with flush water
- Flush water volume based on fluid level
- Dosage based on production and corrosion severity

  (25 ppm total fluids)
- Good for wells with high fluid levels

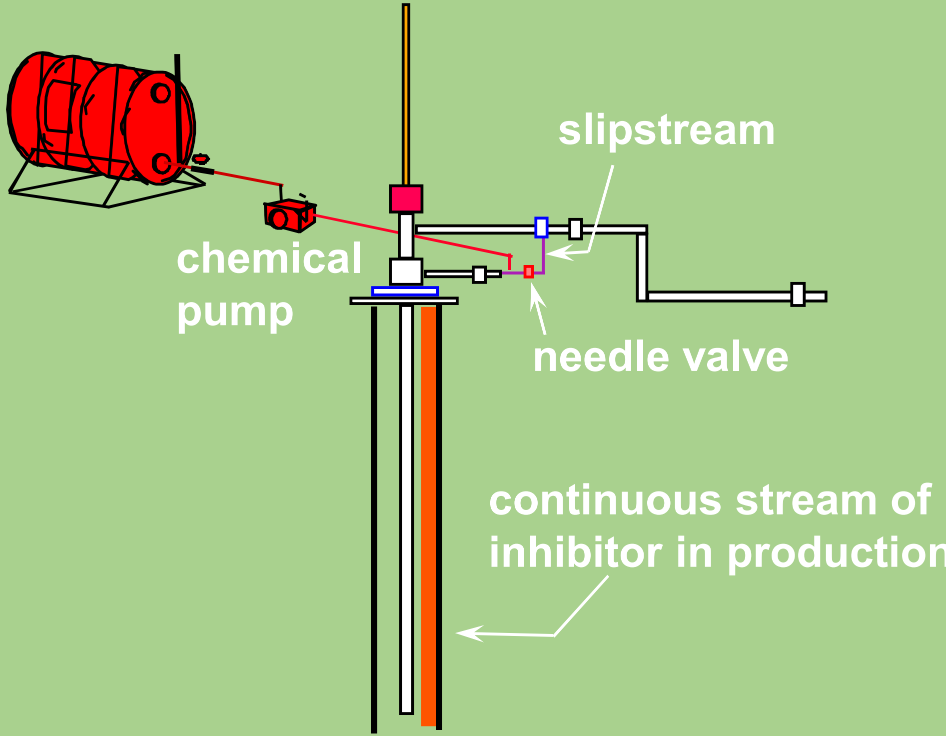


Batch Treating Recirculation Times

Feet of Fluid Over Pump	***Recirculation Time in Minutes***			
	100 b/d	*250 b/d*	*500 b/d*	*1000 b/d*
0	**14**	**6**	**3**	**2**
1000	**40**	**20**	**10**	**5**
2000	**70**	**30**	**15**	**7**
3000	**120**	**50**	**25**	**10**

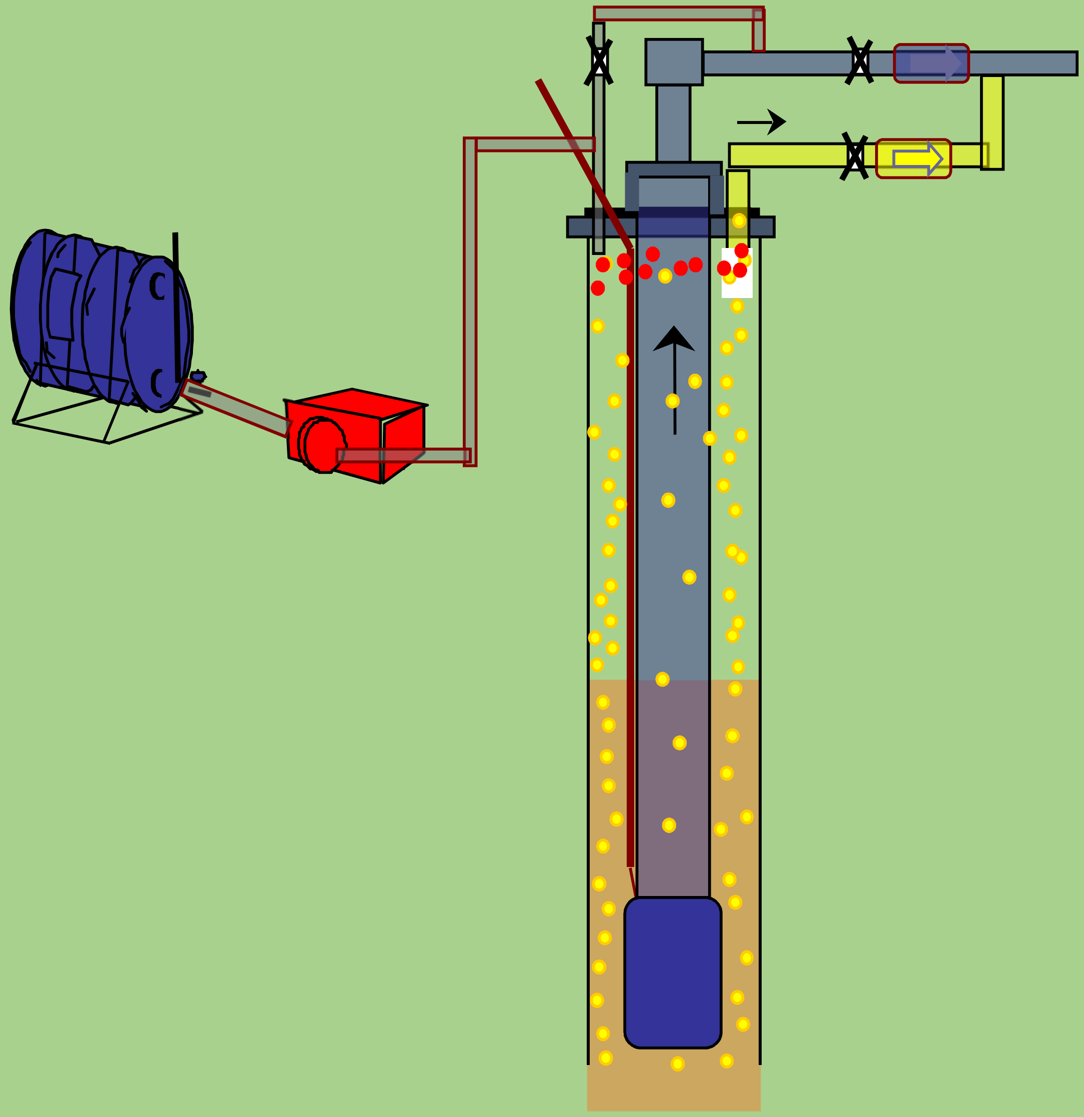
Oil Well Inhibitor Applications Continuous

- Slipstream application
- Dosage based on production and corrosion severity (25 ppm total fluids)
- Water soluble or oil soluble/ water dispersible inhibitor most commonly used
- Good for wells with high fluid levels



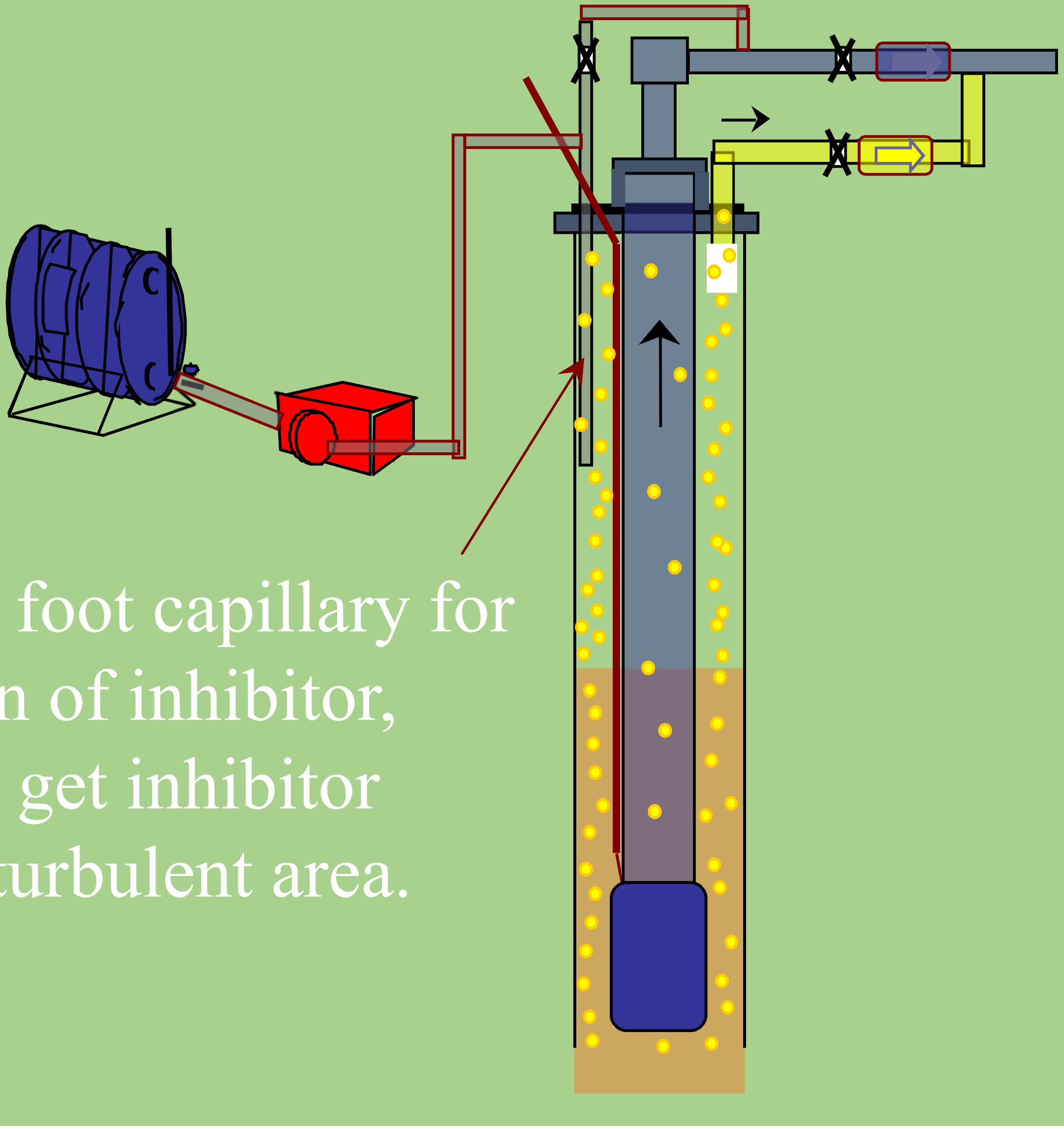
Continuous Injection into the Annulus

- Turbulences at the well head can keep the inhibitor from falling
- Inhibitor can go directly into gas flowline



Continuous Injection into a Short Capillary

- The inhibitor must fall through the
  - rising gas
  - liquid column

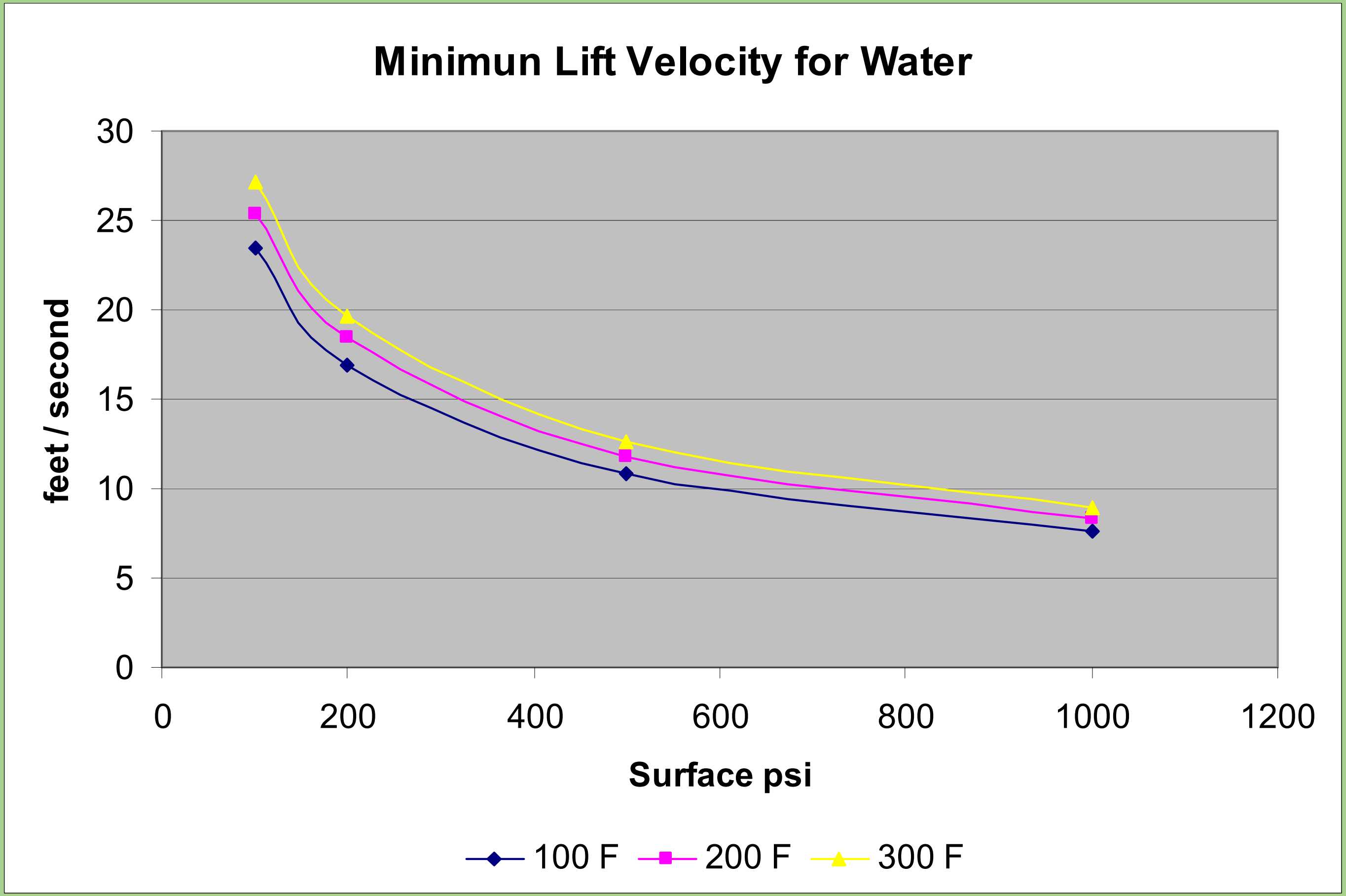


20 - 40 foot capillary for addition of inhibitor, used to get inhibitor below turbulent area.

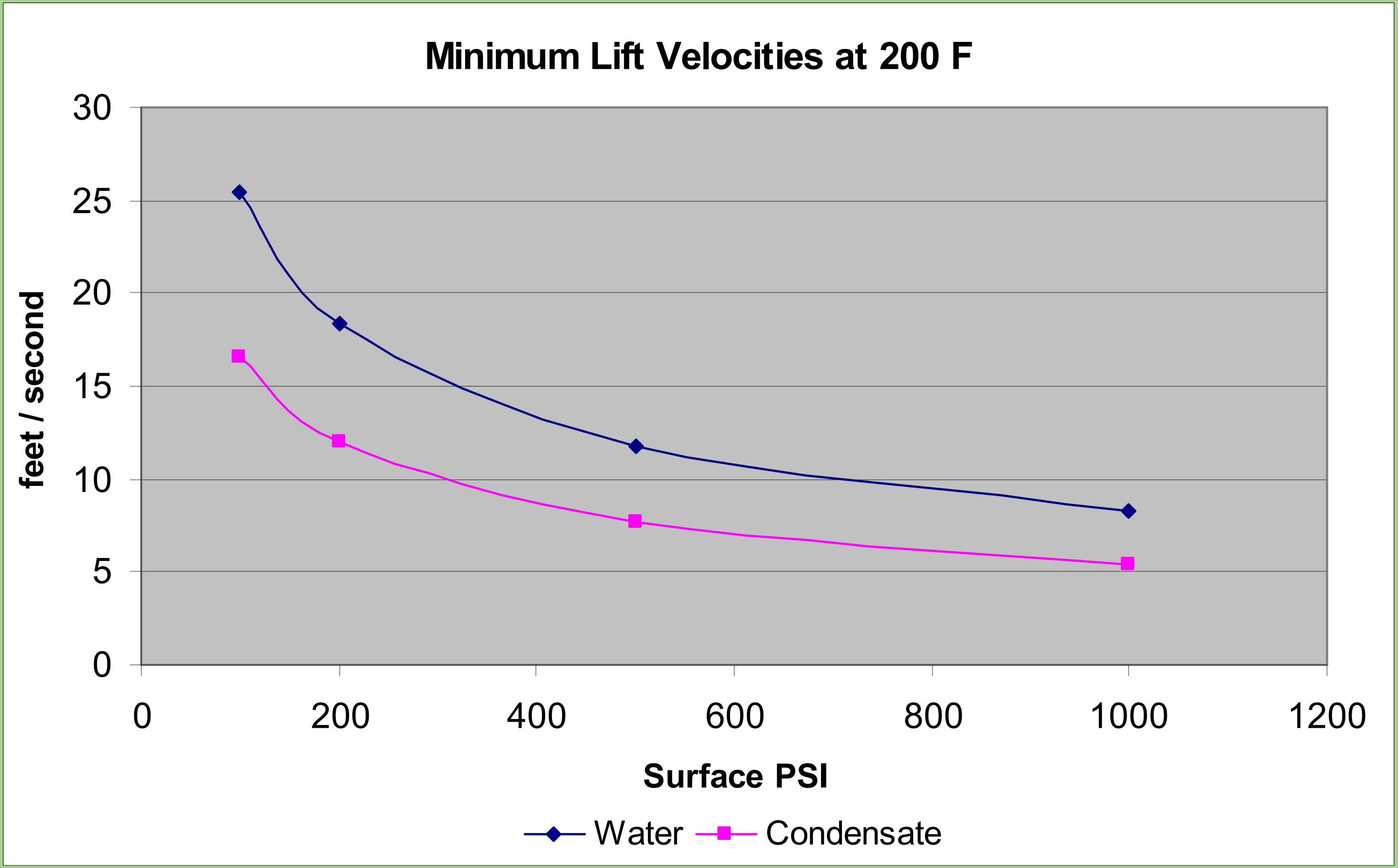
Liquid Drop - Gas Velocity Calculations

- Liquid drop model
  - Minimum gas velocity to lift largest liquid droplet in a vertical gas stream
  - M.S. Bizanti, Assistant Professor and A. Moonesan, Doctoral Candidate, Louisiana Tech University, Ruston, La. World Oil, Sept. 1989

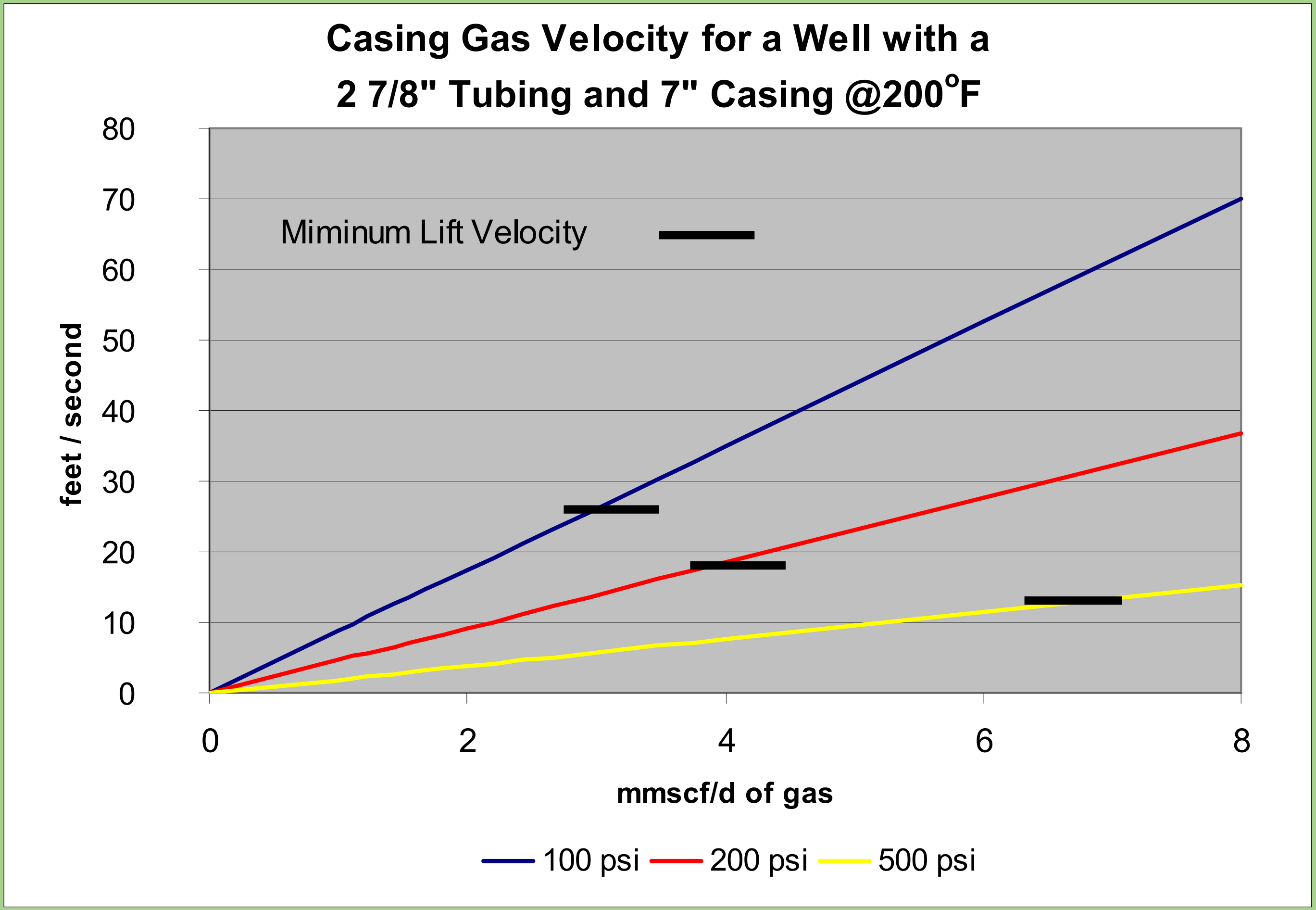
Liquid Drop - Gas Velocity Calculations



Liquid Drop - Gas Velocity Calculations

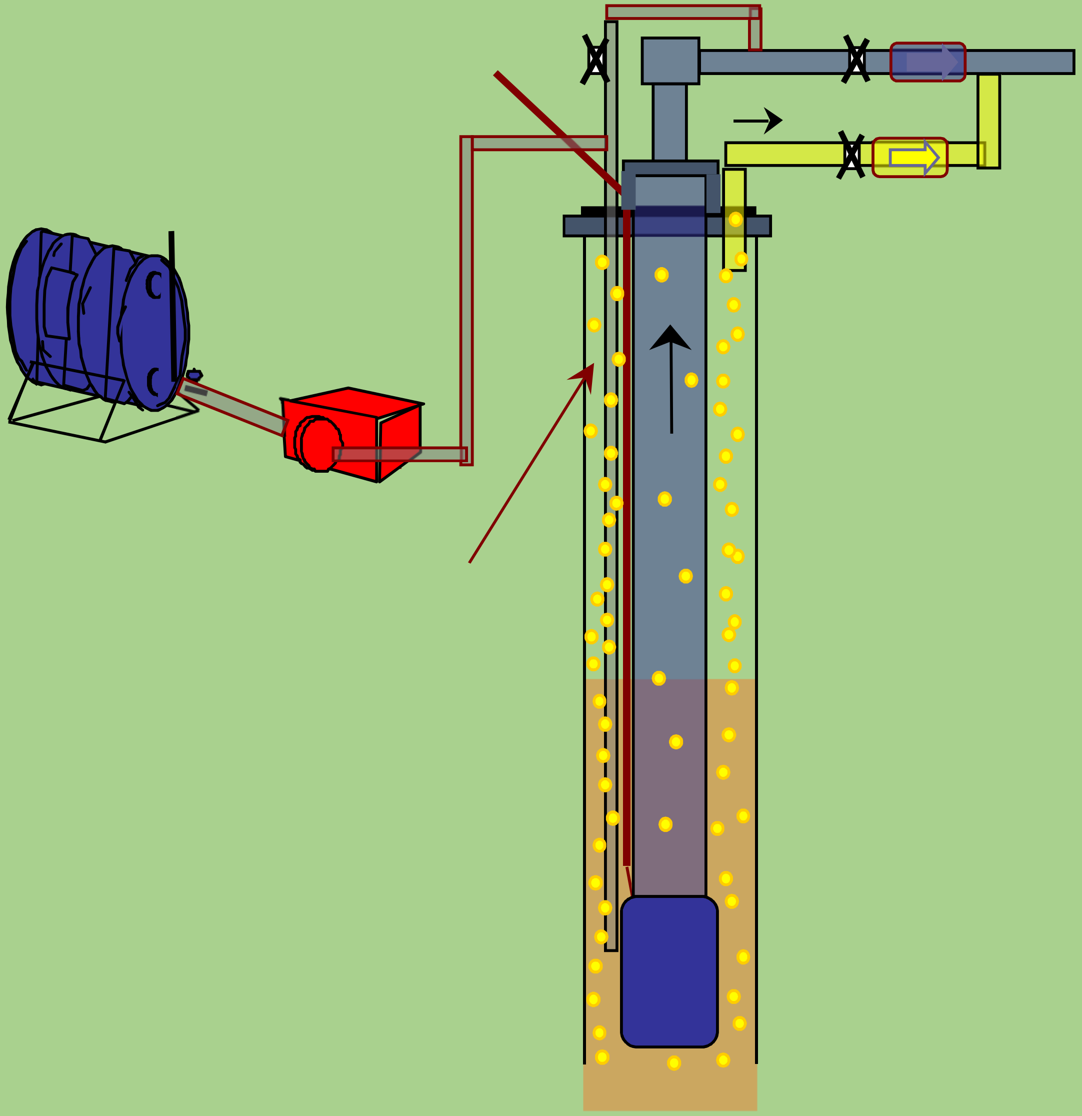


Liquid Drop - Gas Velocity Calculations



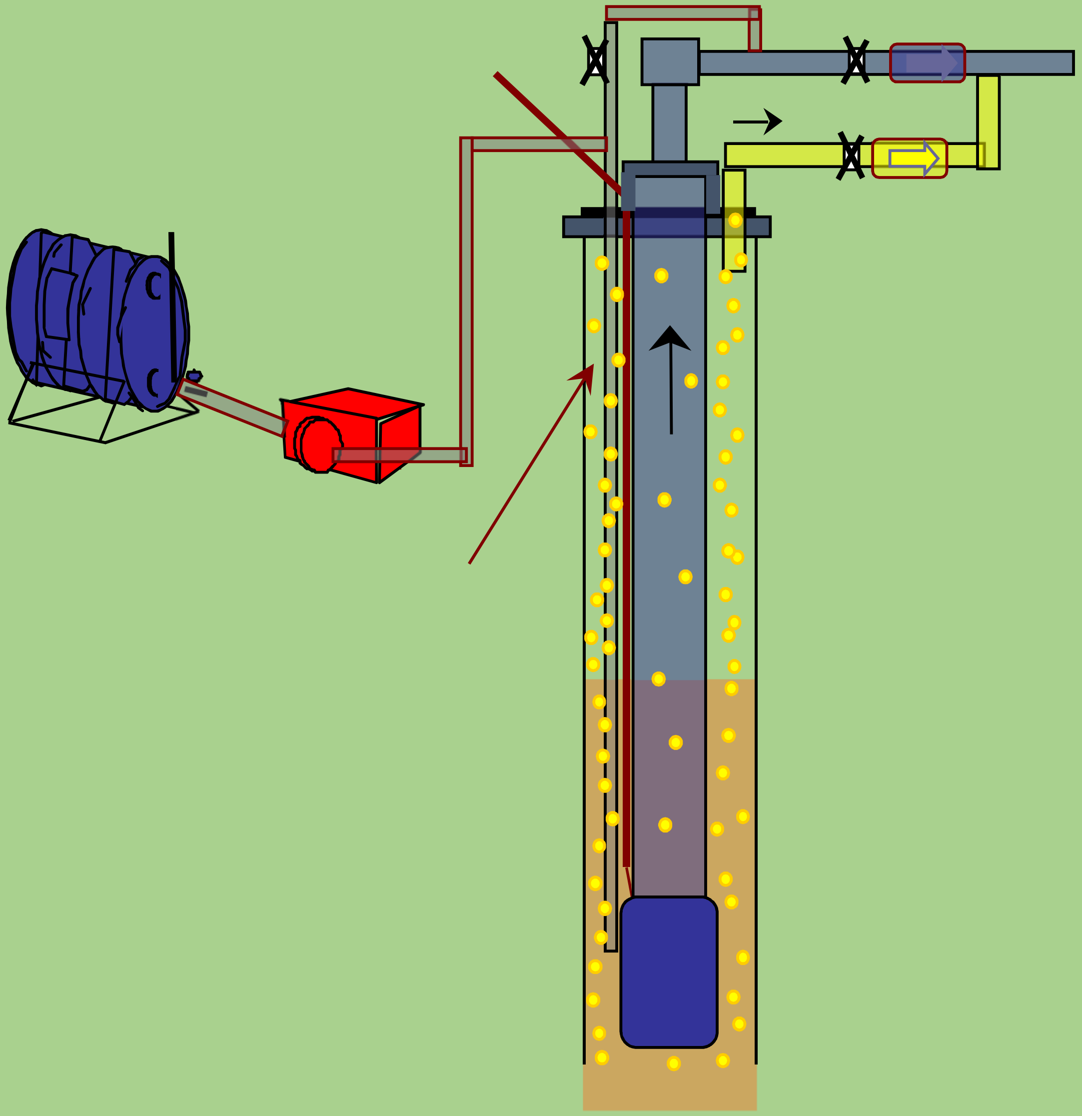
Continuous Injection into a Full Capillary

- Inject neat inhibitor
- Insures inhibitor get to the pump
- Casing left unprotected for corrosion



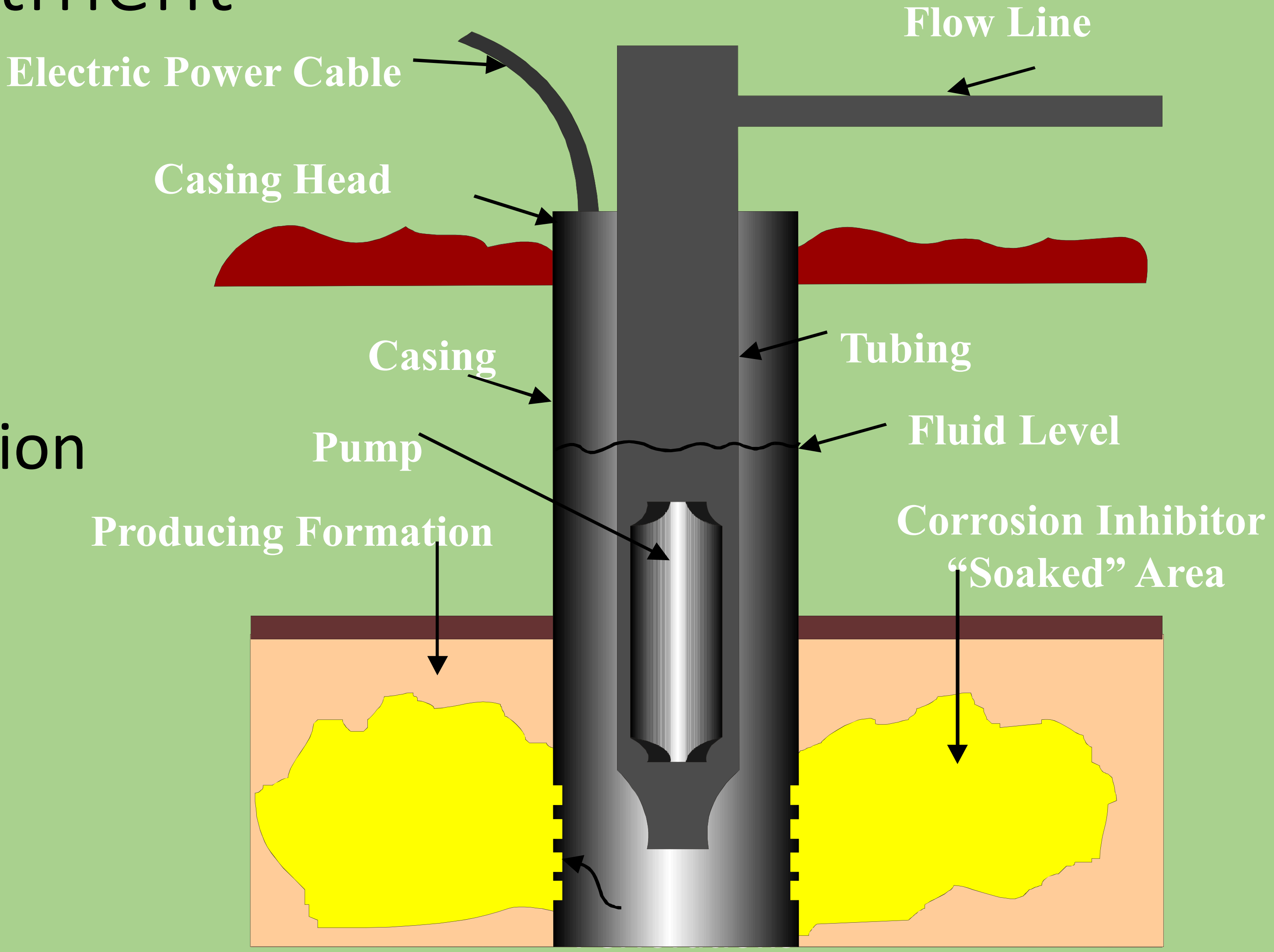
Casing Inhibition with a Full Capillary

- Secondary inhibitor application into the casing
- Install a packer
    - Gas flows up tubing
    - May be able to remove pump



Oil Well Inhibitor Applications
Squeeze Treatment

- Use oil soluble inhibitor
- Treatment based on total production
- Good for wells with packer



Inhibitor Squeeze Rules

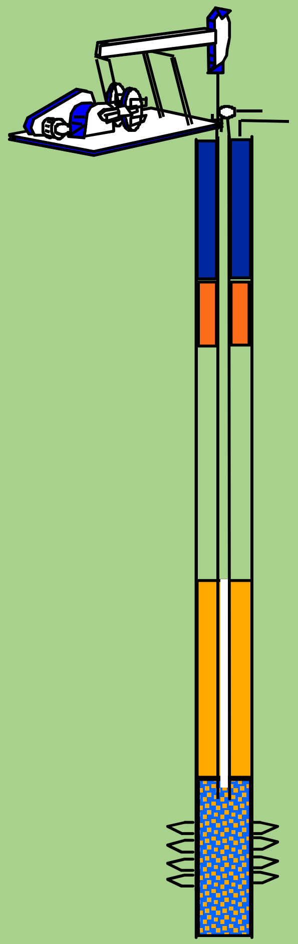
- Use 1-3 drums diluted in 50 bbl of clean lease crude
- Make sure that Step #1 results in a true solution
- Size inhibitor batch based on 50-75 ppm of total production for expected treatment life
- Push the solution to the bottom with clean lease crude or clean lease brine
- Overflush with one day’s production volume of clean lease crude or brine; minimum of 50 bbl
- Re-assemble well and begin production (no delay necessary)
- Monitor results!

Approximate Squeeze Lives in Oil Wells

Total Daily Production (bbl/day)	Approximate Expected Life
0-50	1 year
50-100	8 months
100-250	6 months
250-500	4 months
500-750	3 months
750-1000	1 month

Types of Oil Wells

- Rod Pumped
- ESP
- Gas Lift
- Hydraulic Pumped
  - Power Oil
  - Power Water
- Flowing



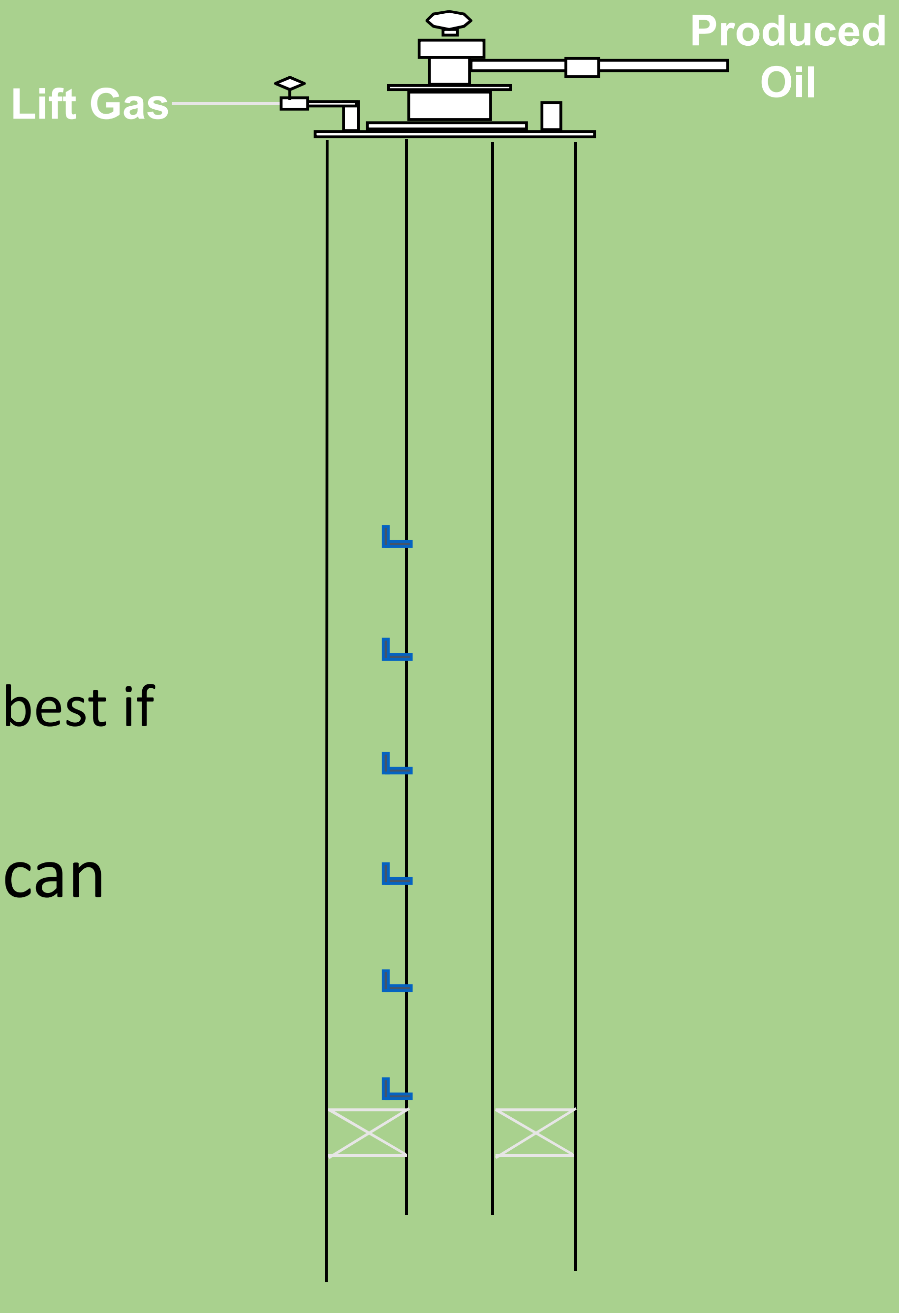
Treating ESP or Rod Pumped Wells

- With and open annulus (no packer)
  - batch and flush
  - batch and circulate
  - continuous
- With a packer
  - continuous through a capillary tubing
  - squeeze

Treating Methods

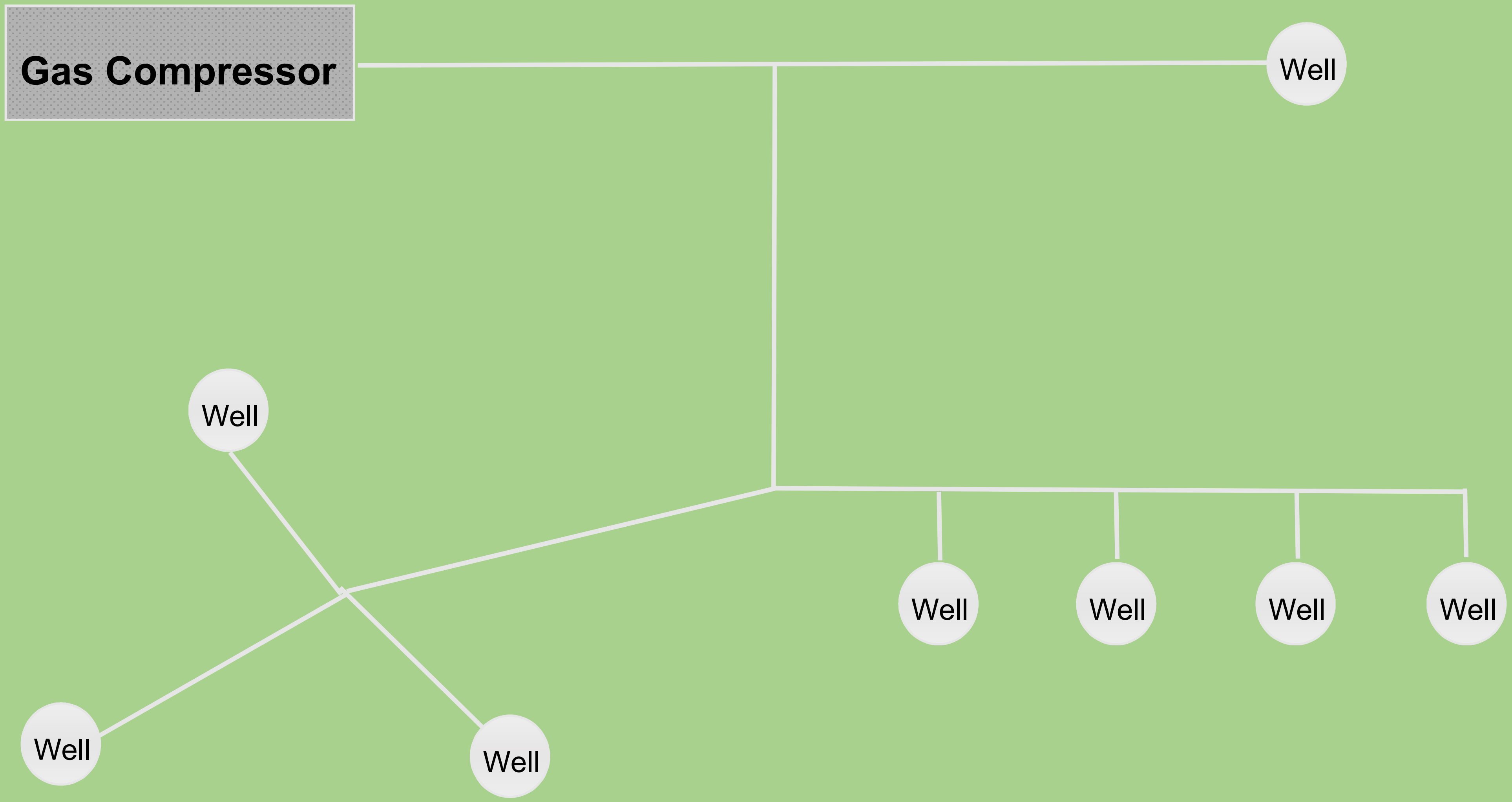
- Batch (Truck Treating)
- Continuous Injection
  - At well head with flush
  - Through a capillary
    - Full capillary to pump
    - Short capillary (40 feet)
- Squeezes (Corrosion & Scale)

Gas Lift Oil Wells



- Through Capillary Tubing
- Into Lift Gas
  - Wet Lift Gas
  - Dry Lift Gas
  - Inhibitor will not distribute evenly through a header system, it’s best if added to each well
- Corrosion of the lift gas flow lines can be a problem if wet gas is used.

Lift Gas Manifold System



Gas Compressor

Well

Well

Well

Well

Well

Well

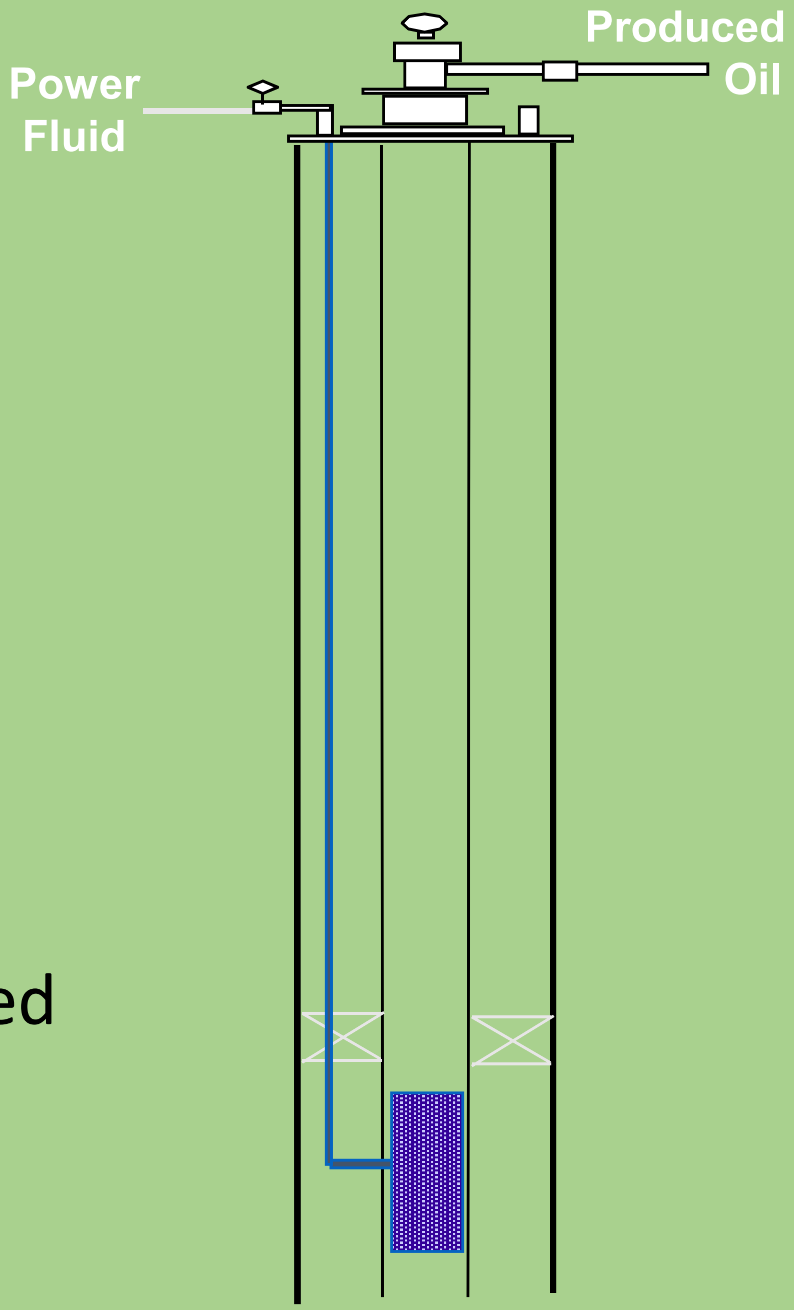
Well

Well

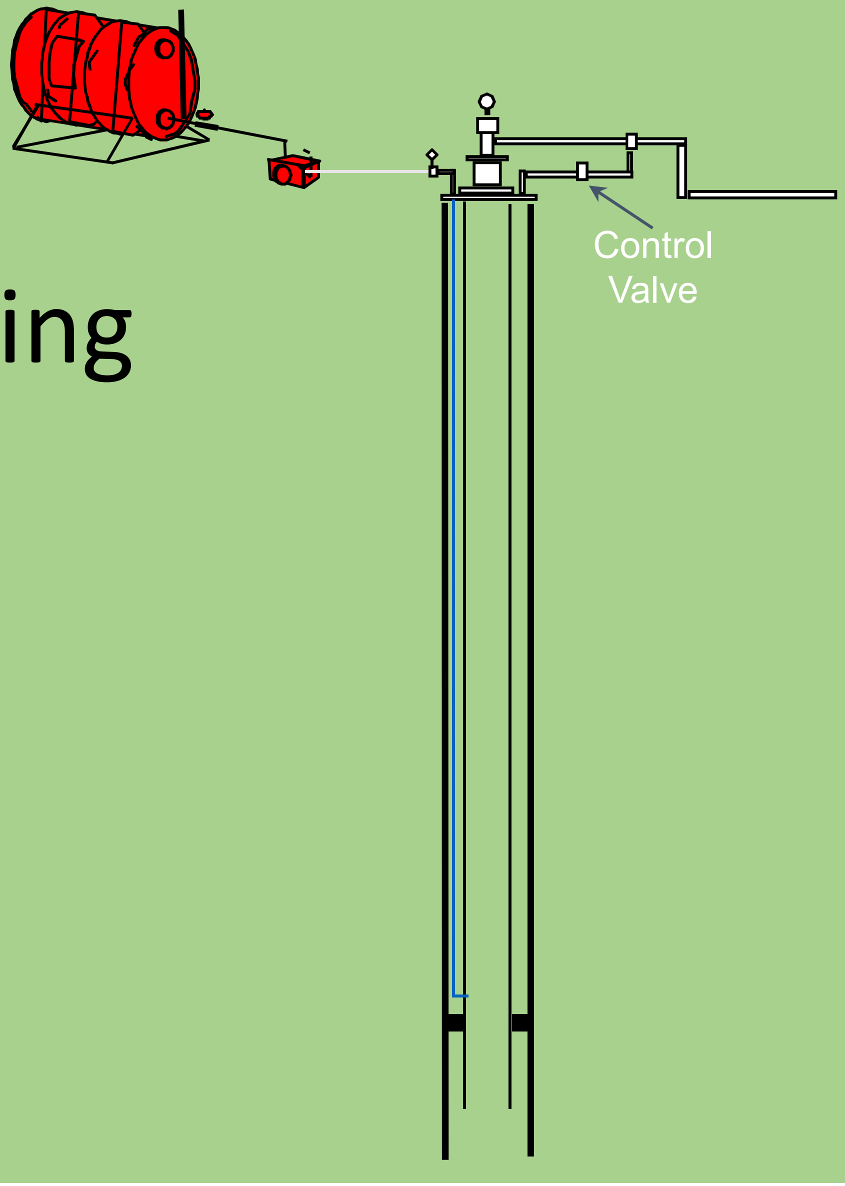
Well

Hydraulic Wells

- Power Oil
  - Oil Soluble
  - Oil Soluble / Water Dispersible
- Power Water
  - Water Soluble
- Inhibitor added to the power fluid
  - 25 ppm average starting point
- Another method of treating will be needed if the power fluid is not mixed with the production

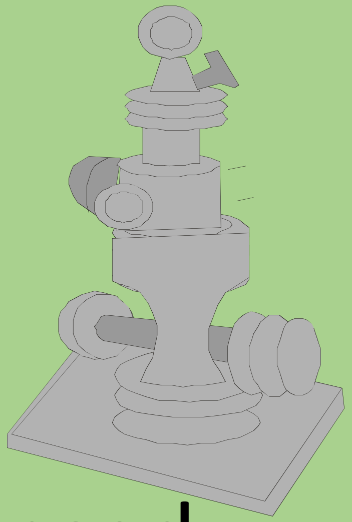


Flowing Oil Wells



- Through Capillary Tubing
- Squeeze

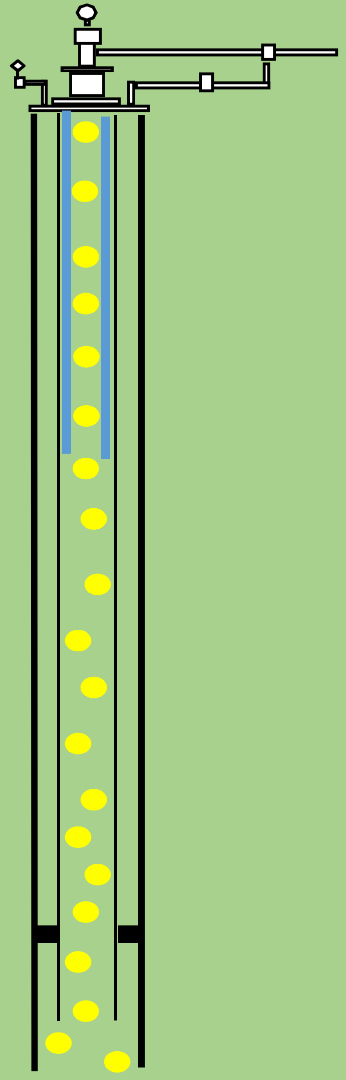
Corrosion in Gas Wells



- Identify the corrosive agent
  - H_2S
  - CO_2
- Is the well producing connate or condensed water
  - Connate water: corrosion bottom to top of the well
  - Condensed water: corrosion from the condensation point up

Corrosion in Gas Wells

- Models are used
    - To predict where vapors condense to a liquid
    - To estimate the corrosion rate at a point in the well as a function of the depth
    - To predict the type of flow



What Effects the Corrosion Rate in Gas Wells

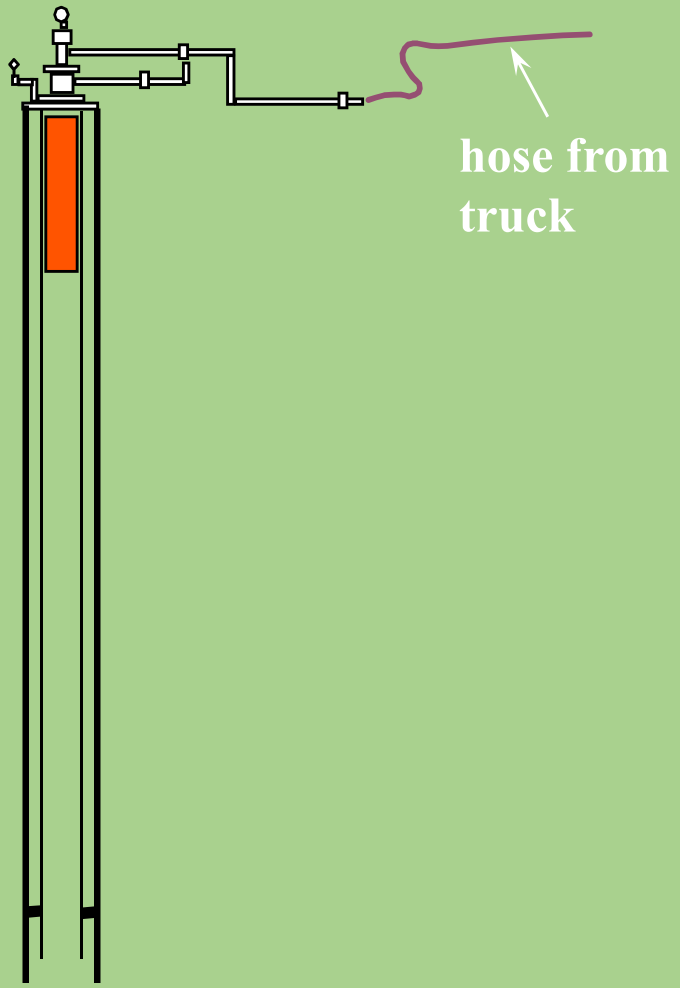
- CO_2 and H_2S partial pressures
- Velocity (production rates)
  - Erosion corrosion
    - Droplets of liquid (down stream of flow upset)
    - Sand
- Temperature
  - Condensation of liquids

Corrosion Inhibitor Application for Gas Wells

- Simple Batch
- Tubing Displacement
- Continuous
- Squeeze

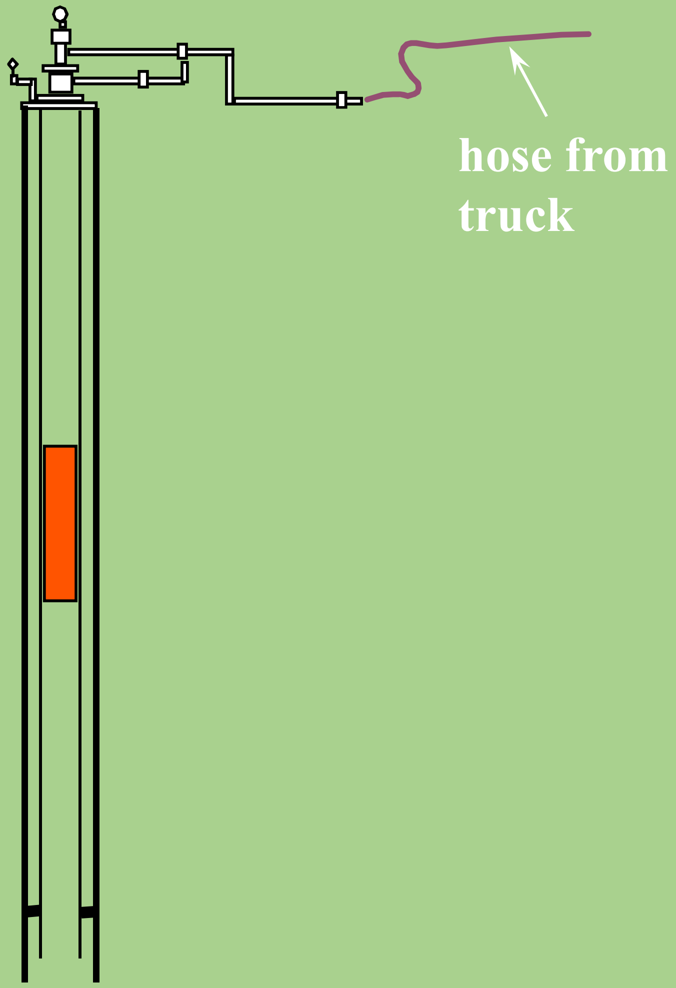
Inhibitor Applications
Gas Wells

- Simple Batch Treatment
  - Most widely used method of gas well treatment. Treatment life varies from two weeks to six months, averaging about four weeks. There are limitations on pressure, tubing size, and liquid production.
  - Corrosion inhibitor in carrier fluid is pumped into the production string and allowed to fall



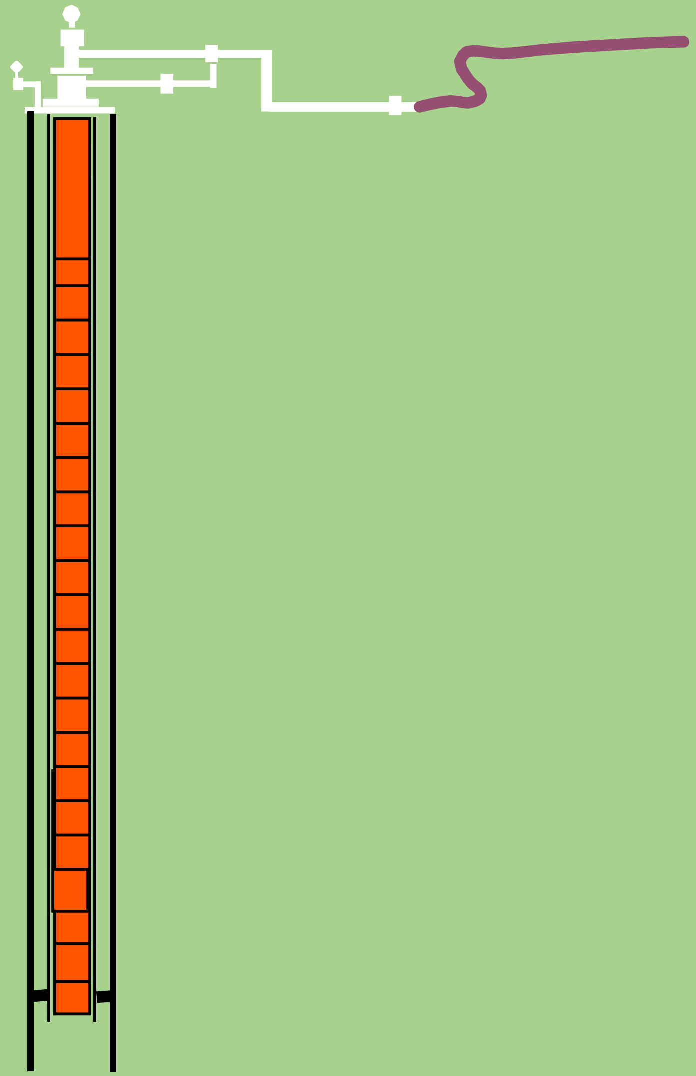
Inhibitor Applications
Gas Wells

- Simple Batch Treatment
  - Chemical amount based on depth of well, diameter of production string, production and corrosion severity.
  - Inhibitor type based on acid gas, corrosion severity and downhole temperature.

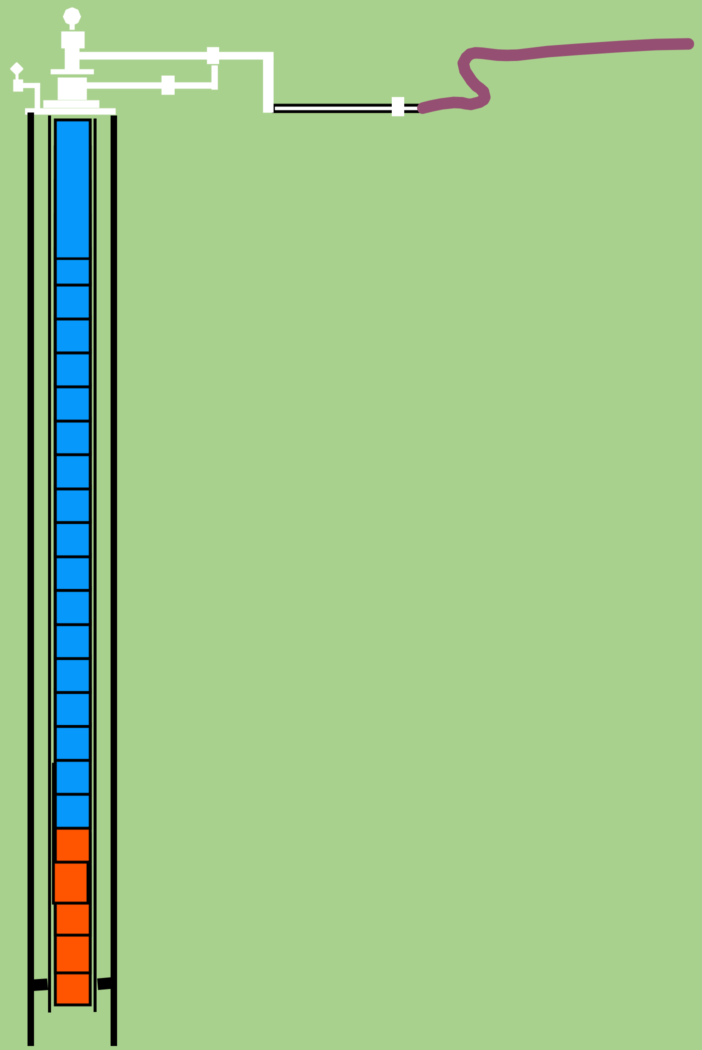


Inhibitor Applications
Gas Wells

- Tubing Displacement
  - Fill the entire string, with inhibitor in diluent
  - Can be applied to most wells.
  - The well must have enough bottom hole pressure to unload
  - Treatment life varies from two weeks to two months.



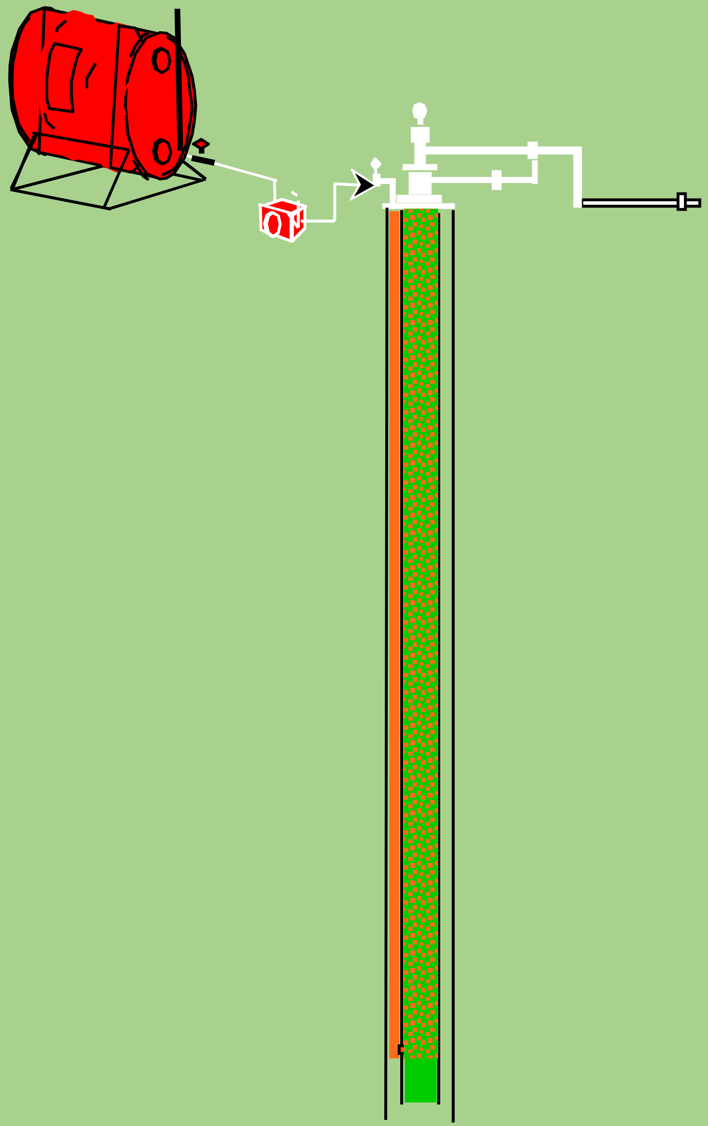
Inhibitor Applications
Gas Wells



- Tubing Displacement
  - Displace diluted inhibitor with nitrogen
  - Used for low pressure wells

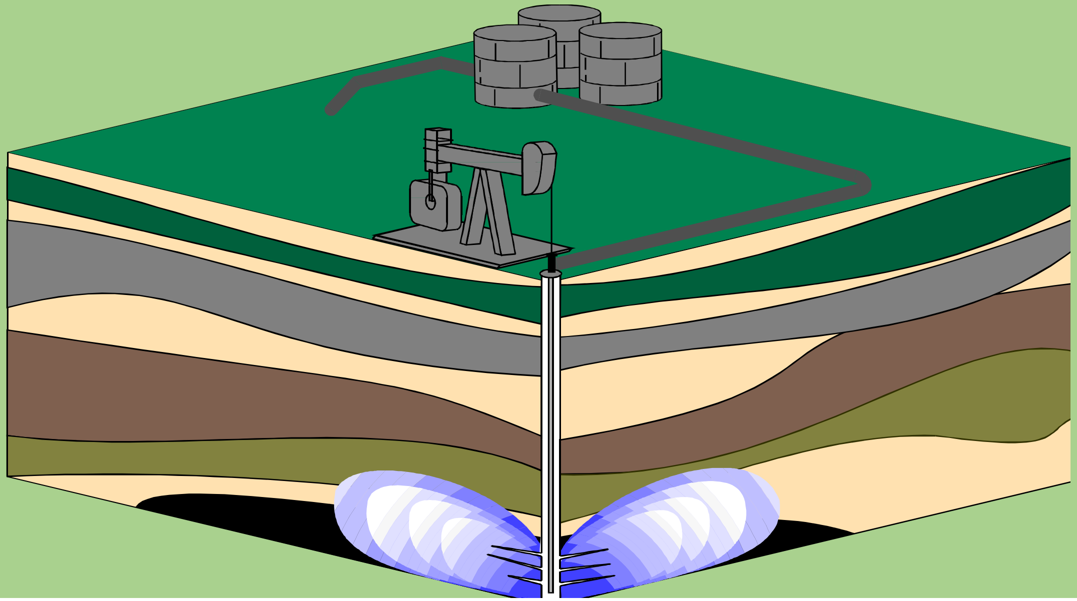
Inhibitor Applications
Gas Wells

- Continuous Injection
  - Into open annulus
  - Into annulus through ported sub above packer
  - Via small capillary tubing through packer (1/4” I.D. or larger)



Inhibitor Applications
Gas Wells

- Squeeze Treatment
  - Corrosion inhibitor in diluent is pumped into the well and displaced into the formation.
  - Must produce a connate liquid phase



Treating Flowlines

What’s Needed for Internal Corrosion of Flowlines ?

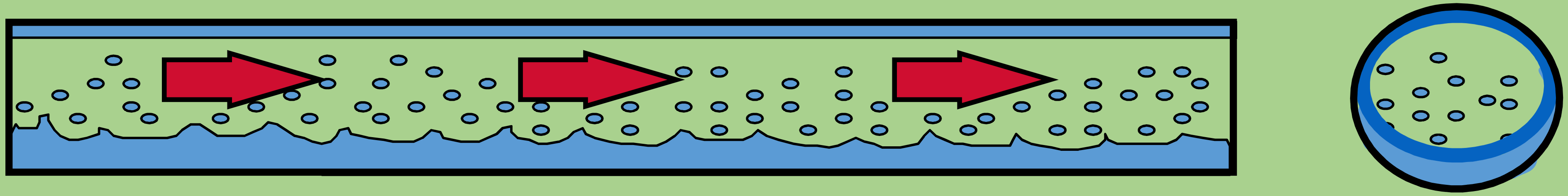
- Corrosion will occur where there is water (one of the 4 parts of the corrosion cell)
  - Produced water
  - Condensed water vapor
  - Produced water carry-over
  - System upsets
- If water is not present corrosion will not occur

Water Movement In Oil and Gas Pipeline Systems

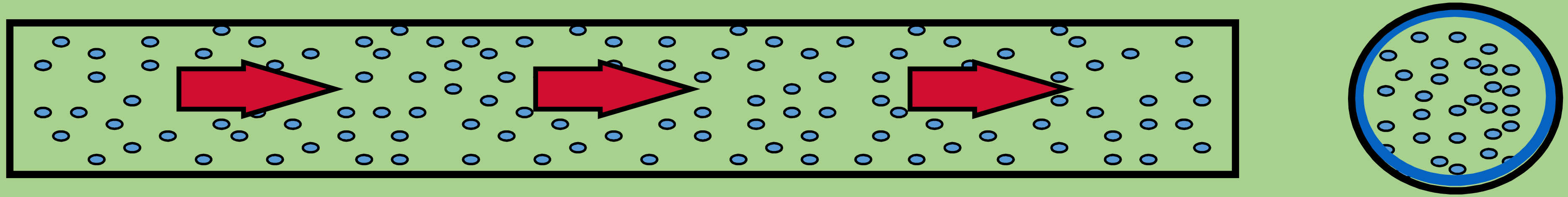
- Understanding the way water moves through a production or pipeline system is extremely important to:
  - Prediction of internal corrosion
  - Corrosion inhibition
  - Monitoring

Liquid Movement in Pipelines

STRATIFIED FLOW
(LOW GAS VELOCITY)



TRANSITIONAL FLOW
(INTERMEDIATE GAS VELOCITY)

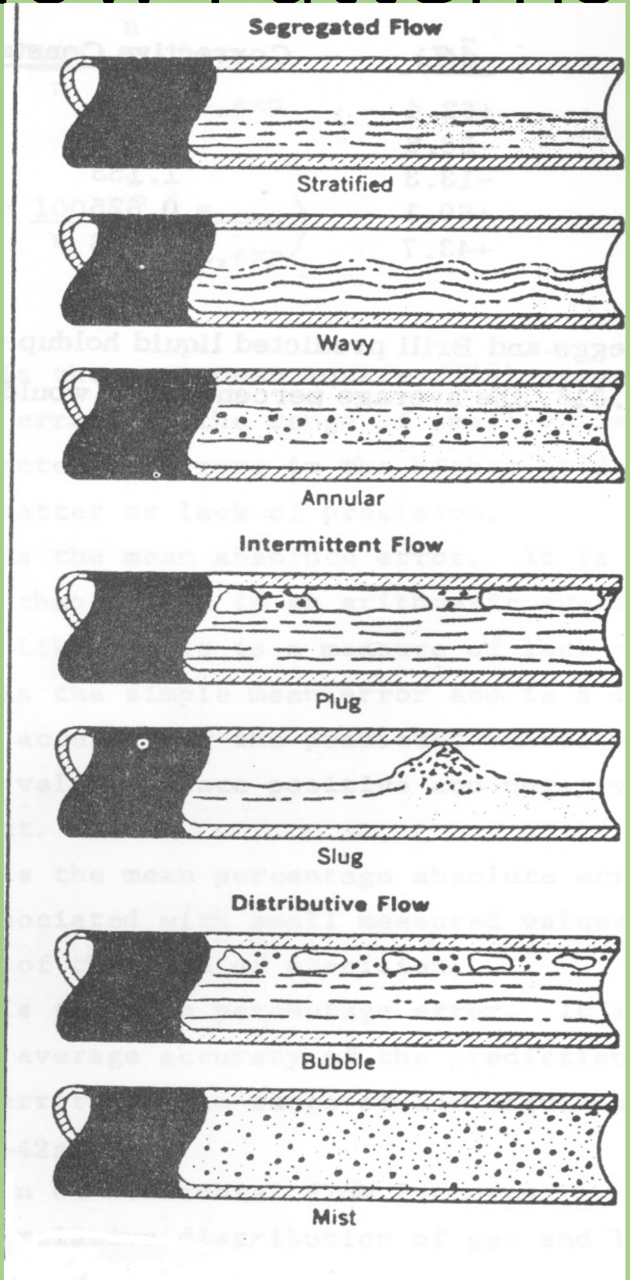


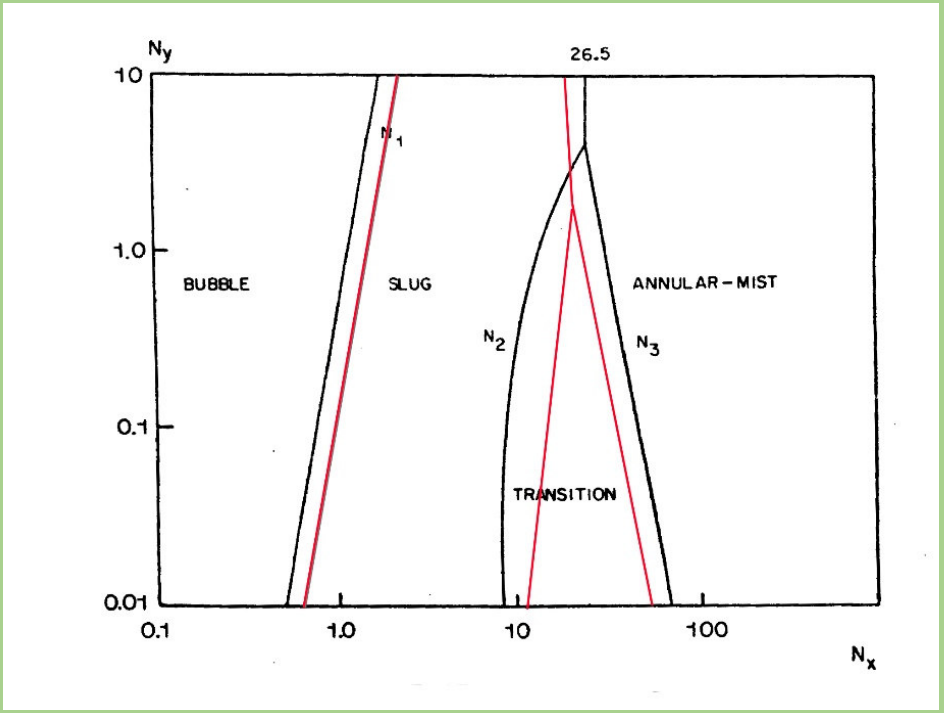
ANNULAR FLOW
(HIGH GAS VELOCITY)

Flow Regime Influences the Inhibitor and Application

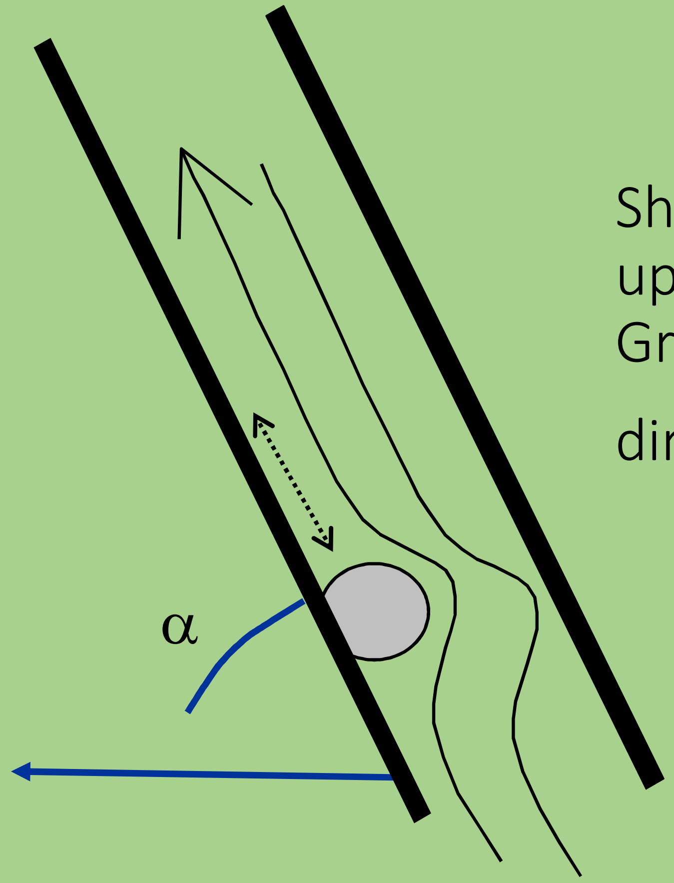
- Knowing the type flow regime in the pipeline is critical to designing a successful corrosion inhibitor program
  - Stratified
  - Wavy
  - Turbulent
  - Slug
  - Mist
  - Annular
- Type of inhibitor
- Method of application

Flow Patterns





Water Movement Up An Incline



Competing Forces

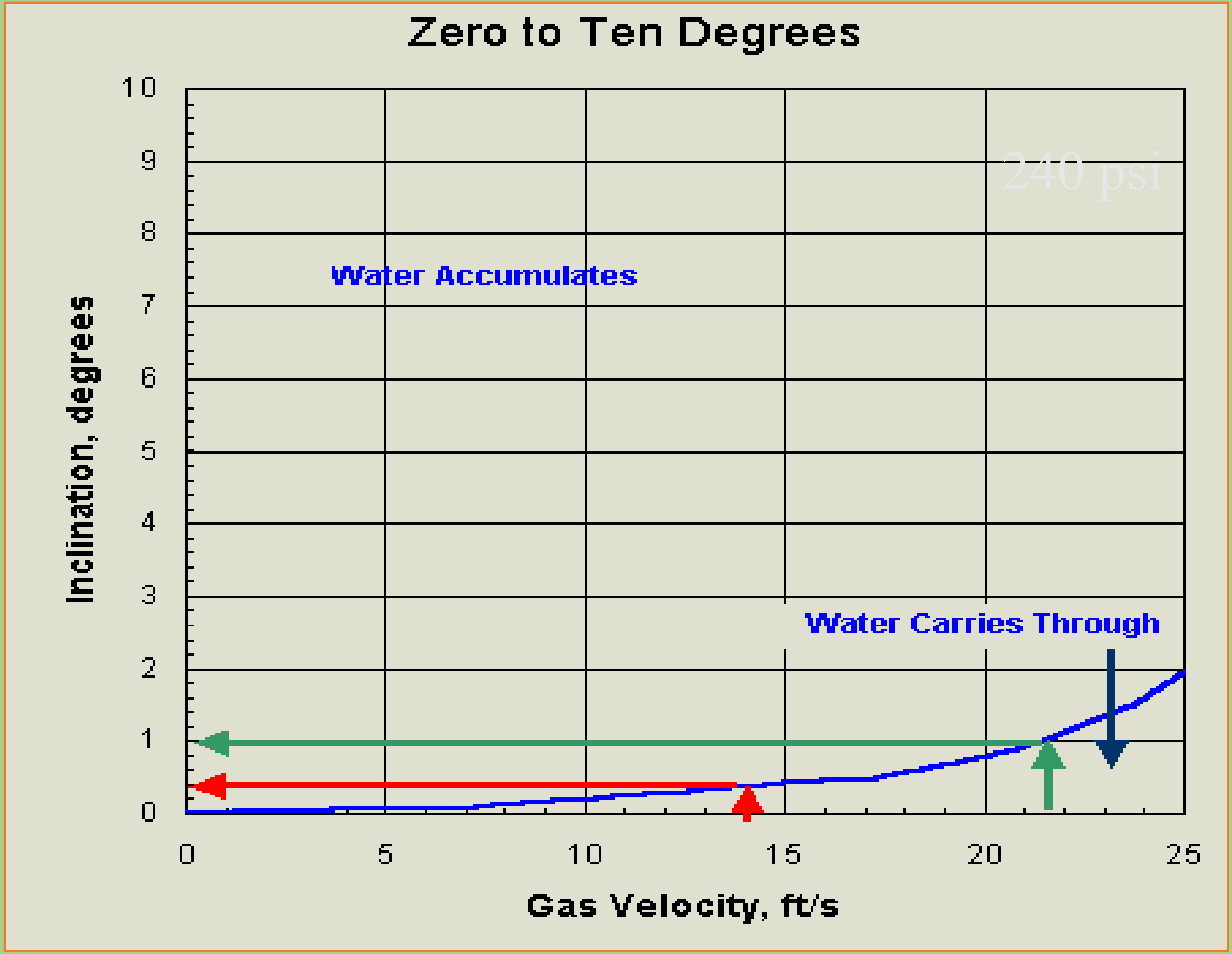
Shear stress tries to move the water in an upward direction
Gravity pulls water in a downward

direction

Determination Of The Critical Inclination Angle to Move Water

Critical Inclination Angle @ 14 ft/sec = **0.40** degrees for 6-inch pipeline, 240 psi

Critical Inclination Angle @ 22 ft/sec = **1.00** degrees for 6-inch pipeline, 240 psi



Gas - Water Movement / Terrain

- Small angle of inclination can greatly affect ability of gas to carry liquids
- Pressure and velocity dependent
- Water holdup areas susceptible to corrosion
  - Corrodent concentrations
  - Bacterial growth
  - Length of time water remains

Modeling of Flowlines by BPC

- Pipesim
- Cassandra
  - Corrosion Prediction
- Hysis
- USL (now ULL)
- Tulsa
  - Erosion
- Technical Contacts
  - Sunder Ramachandran

Pipeline Evaluation Model by PMG

- Obtain Digital Elevation Mapping (DEM) and geo-referenced system maps
- Segment gathering system lines
- Elevation data and system maps used to determine inclination angles for each segment
- Production data used to determine gas / crude and liquid flows
- Output tabulated on summary sheets and graphs

Understanding Water Movement

- Modeling pinpoints specific locations where internal corrosion is likely to occur.
    - Elevation profile
    - Transit time
    - Water fraction
    - In-situ water volume
- Basis for direct assessment techniques to verify system integrity

Pipeline Evaluation Model

- Internal corrosion occurs where water accumulates
- Specific locations can now be predicted
    - From flow conditions
    - Elevation profile
- Competing forces control the movement of water:
    - Gravity causes liquid to drain backwards
    - While the shear stress attempts to move the water forward.
- The water inventory of a pipeline increases DRAMATICALLY when gas / fluid velocity drops below a critical threshold

Pipeline Treatment Considerations

- Liquid Hold-up
- Solids / underdeposit corrosion
- Production / piping bottlenecks
- Integrity Management
  - Intelligent Pigging
  - Pipeline topography
  - Monitoring
  - Direct Assessment

Internal Corrosion of Flowlines

- Detrimental flow conditions
  - Liquid movement
  - Water hold-up
- Potential corrodants
  - CO_2
  - H_2S
  - Oxygen
  - MIC
- Solids

Pigging

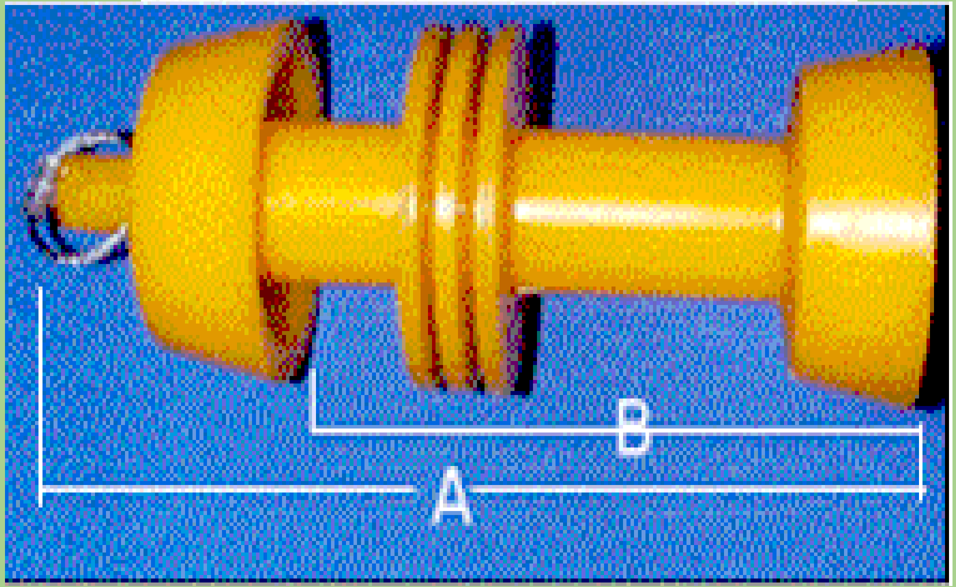
- Removal of liquids
  - Increase flow through pipeline
  - Can remove corrosion inhibitor
    - From liquid traps
    - From pipe wall
- Removal of solids
  - Reduces underdeposit corrosion
  - Reduces bacterial corrosion
  - Solids absorb corrosion inhibitor

SurfSweep^{TM} Pipeline Cleaning

- Chemicals to remove pipeline deposits
- Baker Petrolite can provide turn-key services
    - Contact George Carlisle

SURFSWEEP

Types of Pigs



Disk and Cup pigs are used for batching chemicals and removing liquid hold-up

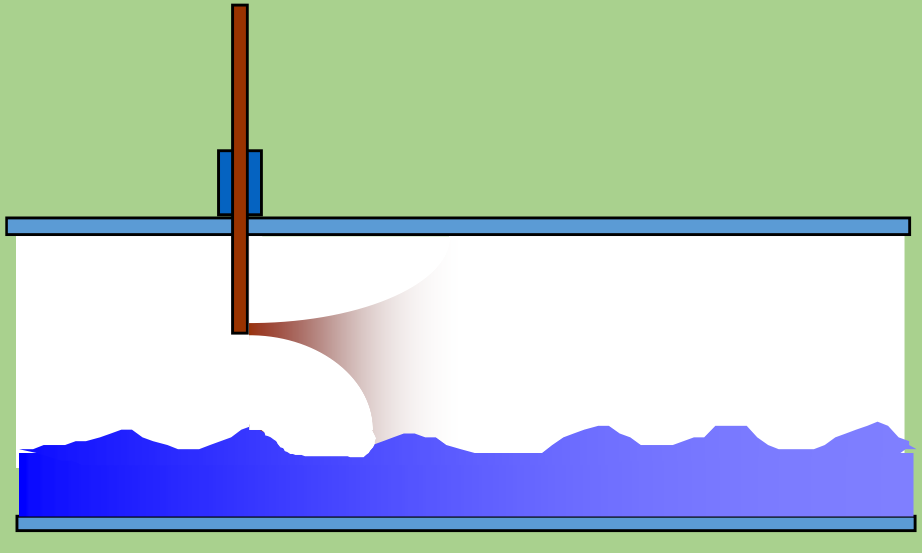
Scraper and brush pigs are used to remove solids from a pipeline

Pipeline Inhibitor Applications

- Continuous Injection
- Batch
  - Slug of diluted inhibitor
  - With the aid of pigs

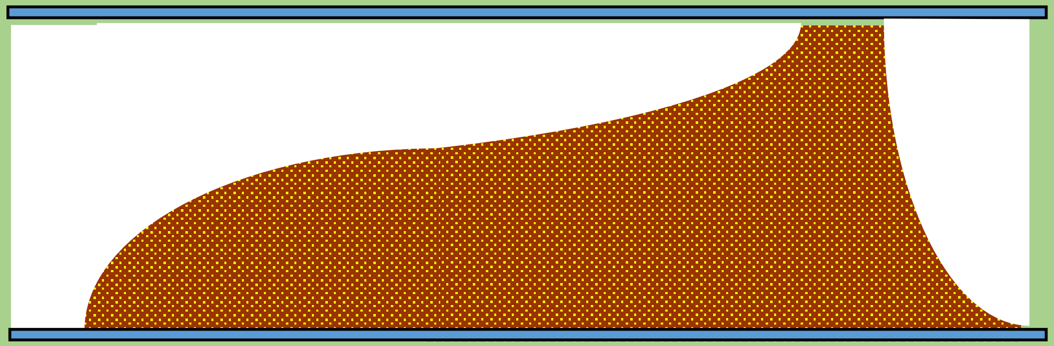
Continuous Application

- Oil soluble/water dispersible or water soluble used depending on flow regime
- Best if concentration based on water volume, can be based on gas volume
- Residual analysis may be needed



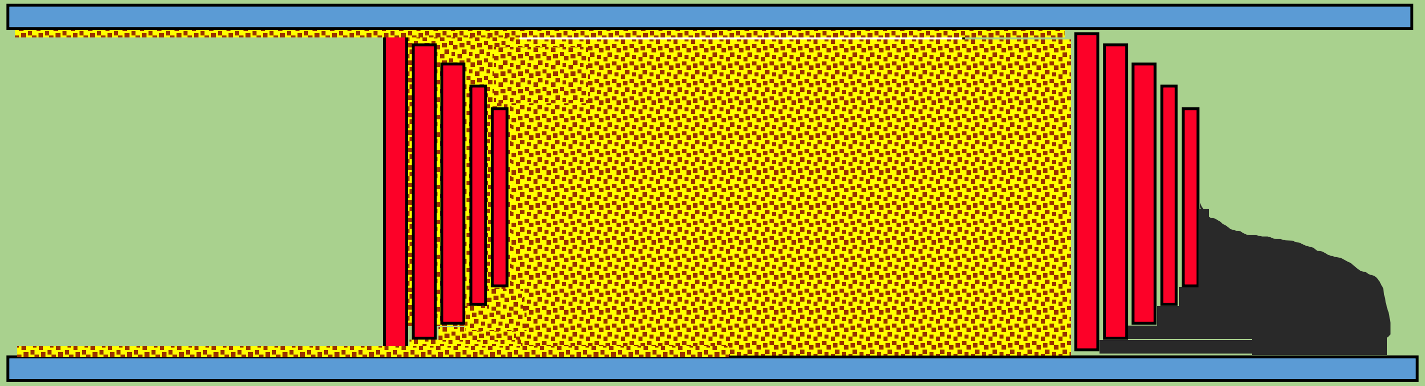
Batch Treatment with Slug

- Oil soluble or oil soluble/water dispersible generally used
- Minimum superficial gas velocity necessary for proper distribution
- Treatment volume based on diameter and length



Batch Treatment with Pigs

- Oil soluble or oil soluble/water dispersible generally used
- Removes liquids and solids from the line
- Treatment volume based on diameter and length of flowline
- Preferred application is between 2 pigs, but can be applied using one pig in some applications



Types of Pipelines

- Production flowlines and gathering systems
    - Produced fluids
- Oil or gas transmission lines
    - Finished products

Flowlines From Oil Wells

- Flow back of corrosion inhibitor from batch or continuous well treatments may not be enough to protect flowlines
  - Reasons: solubility characteristics, low fluid velocities
- <u>Rule of Thumb:</u> Recommend continuous injection of a water soluble or highly dispersible inhibitor at the well head. Initially use 25 -100 ppm, based on water volume, and optimize based on monitoring.
- Monitoring will be required to determine best program

Wet Gas Flowlines and Gas Gathering Systems

- Low spots in the flowline (water traps)
- Drips
  - Remove corrosion inhibitor with the water removal
- Top of line corrosion
  - Acid gas (CO_2 & H_2S)
  - Oxygen
- Effect of pigging

Wet Gas Flowlines

Batch treatments

- Rule of Thumb: This application requires an oil soluble corrosion inhibitors. The treatment rate is 2 gallons, multiplied by the pipeline diameter in inches, multiplied by the length in miles, diluted to 10-20% in a suitable hydrocarbon solvent.
  - This represents a 2 mill thickness. Use 3 gallon multiplier of a 3 mill thickness is needed.

Wet Gas Flowlines

Continuous Treatment

- Continuous treatment may not protect the top of the flowline
- Transport of the corrosion inhibitor through the flowline must be verified
- If the system is subsea the corrosion inhibitor must pass all specifications for the umbilicals or capillaries being used
    - Compatibly with all components of the umbilicals
    - Solids –must insure that plugging does not occur
- Rule of thumb: Use a water soluble corrosion inhibitor at 25-100 ppm based on water volume or 1-2 pints per mmscf of gas, adjust with monitoring

Oil Pipelines

(less than 5% free water)

- Low velocity corrosion will occur in low spots where water drops out and collects
- Pigging can be used to minimize liquid hold-up and remove solid deposits
- High velocity (high shear) conditions require specific products
- Rule of Thumb: Continuous injection of a water soluble corrosion inhibitor, at 100-200 ppm based on the water volume

Dry Gas Pipelines

- No corrosion will occur as long as there is no liquid water (stay above dew point)
- Corrosion can occur when
  - Drop below dew point
  - Water carry over for dehydrator
  - System upset
- Treat with corrosion inhibitor formulated with a carrier for dry gas
- <u>Rule of Thumb:</u> Continuously treat with 1 pint / mmscf of gas

Monitoring for Internal Corrosion

- Detrimental flow conditions
  - Model liquid movement
  - Identify water traps (hold-up areas)
  - Locate monitoring stations
- Gas analyses
  - CO_2, H_2S, oxygen, & moisture
- Water analyses
  - pH, iron, sulfide, & bacteria
- Solids analyses
  - Corrosion products – iron sulfide, iron carbonate, iron oxide?
- Corrosion rate
  - Coupons & probes

Monitoring : Types of Tests

- Gas Phase Testing
  - CO_2 : gas analysis or stain tubes
  - H_2S : gas analysis, hand held meter, or stain tubes
  - Moisture (dew point): gas analysis or stain tubes
  - Oxygen: may require continuous monitoring: inline monitor or portable monitor

Monitoring : Types of Tests

- Water Phase Tests
  - Bacteria
    - SRB using modified sulfate API broth,
    - APB using phenol red dextrose broth,
    - Anaerobic bacteria including APB using thioglycollate broth,
  - pH
  - Sulfide
  - Inhibitor and bactericide residuals
    - Sample towards the end of flowline to ensure transport through flowline

Sampling for Water

- Getting a water sample from a gas flowline can be difficult
  - Valve in low spot
  - May need a collection pot
  - From a drip
  - At a separator

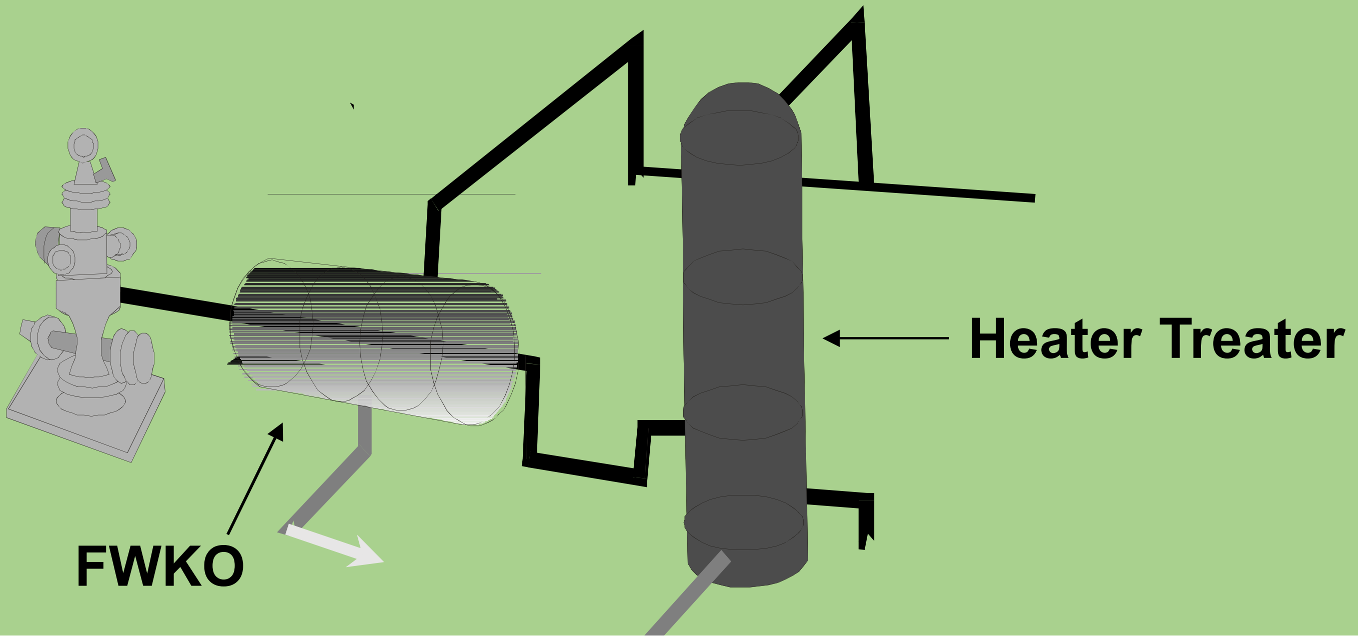
Internal Flowline Corrosion Summary

- Detrimental flow conditions
  - Water must be present
  - Liquid traps
- Corrodants:
  - Acid gases
    - CO_2 & H_2S
    - Partial pressures
  - Oxygen
    - Very aggressive
    - Accelerates other types of corrosion
  - Solids
  - Bacteria
    - SRB & APB
    - Localized attack

Production and Water Treatment Facilities

Flow of inhibitor

- Oil and water separation
- Inhibitor solubility (<u>do not use CRO or CRW to determine</u>)
  - Oil
  - Oil soluble water dispersible
  - Water



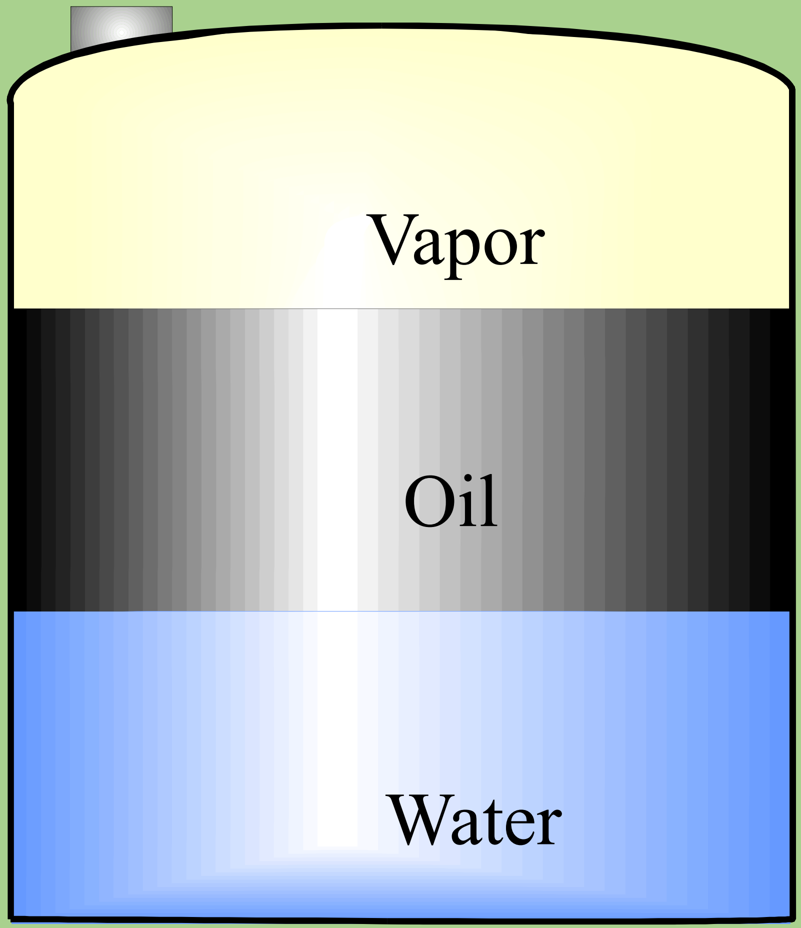
Possible Causes of Corrosion in Treatment Facilities

- H_2S
- CO_2
- Oxygen
- Bacteria
- Solids

Produced Gas

- Gas is separated at
  - Separators
  - Free water knock outs
- Concentration of dissolved CO_2 and H_2S should decreases through the system
- Decrease in temperature
- Fluids should become less corrosive

H_2S Concentration: Relative Amounts



100 ppm

1 ppm

10 ppm

Oxygen

Enters the produced fluid on the surface, can be controlled with good operating procedures.

- Vented Tanks
- Pumps (leaking seals)
- Wemcos need a gas blanket
  - Make sure the doors stay closed
- Make up water
  - From another field
  - From another aquifer

Oxygen Relationship

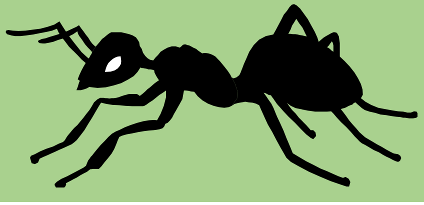
oxygen — aerobic

some oxygen — facultative anaerobic

no oxygen — anaerobic

Bacteria

- Bacterial corrosion is not controlled by standard oil field inhibitors
- SRB bacteria will increase the H_2S levels across the system
    - The H_2S will increase the general corrosion in addition to the bacterial corrosion
- Monitor for bacteria and if found treat with a biocide (FCT group)

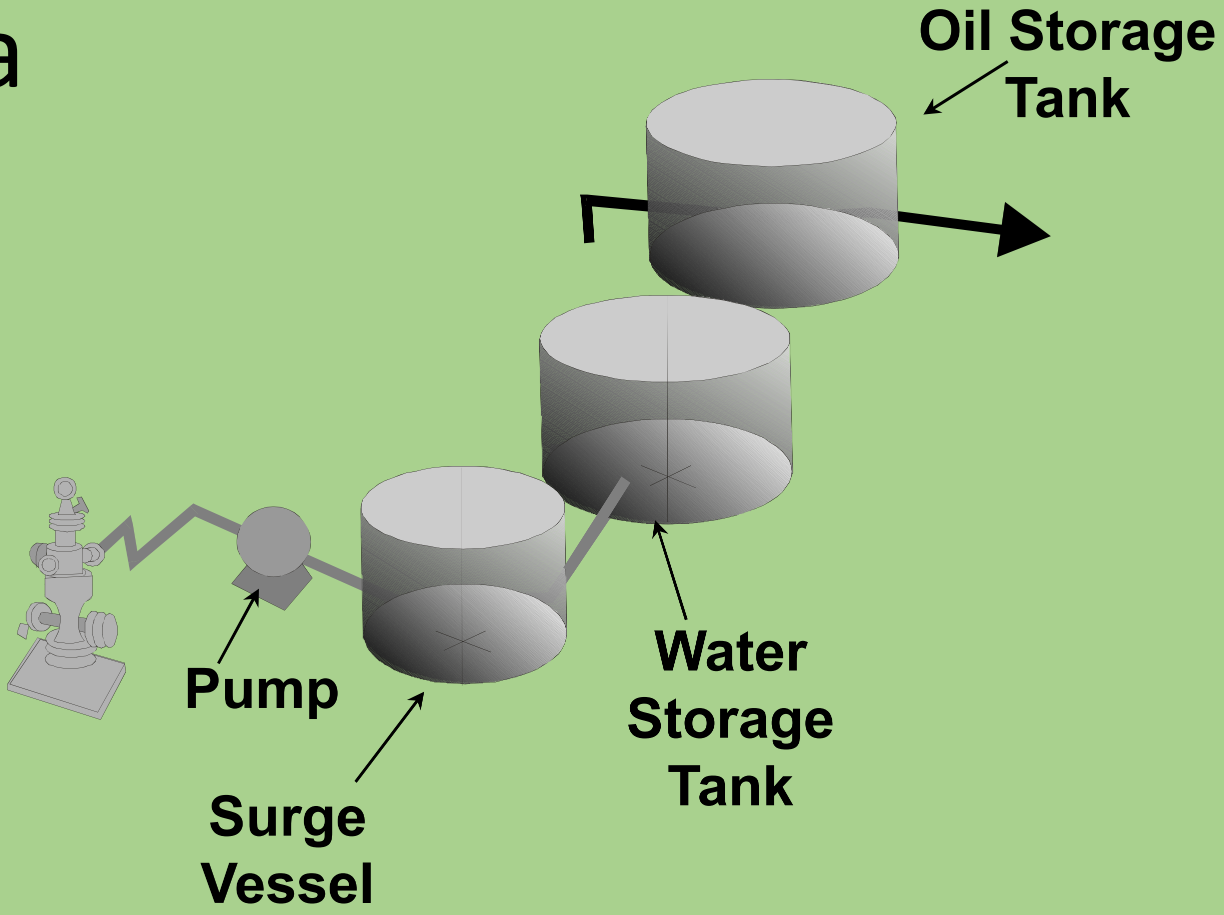


Solids

- Prevent inhibitors from reaching the metal surface were corrosion is occurring
- Soak up corrosion inhibitor making less available to treat corroding areas
- Promote underdeposit corrosion
- Home for Bacteria
- <u>RULE OF THUMB: Clean systems are easier to inhibit</u>

Tanks

- Oxygen
- Bacteria
- Solids



Consideration for Inhibitor Selection in Water Systems

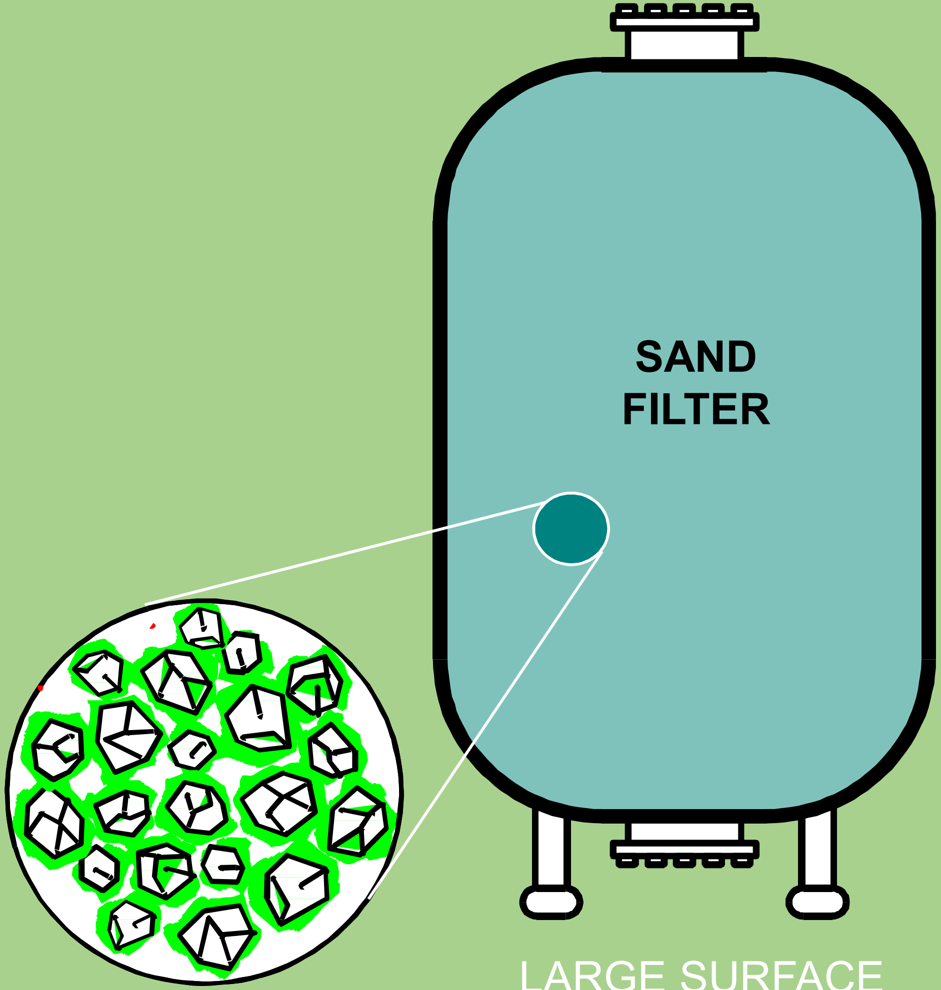
- Pipe/pump/tank material of construction
- Flow amounts and pipe sizes
- Sweet or sour
- Any possibility of oxygen contamination (tank tops, leaking pumps, pit water)
- Clean or dirty
- Final disposal (disposal well, secondary recovery, surface discharge, sea)

Corrosion Protection in Treatment Facilities

- Corrosion inhibitors
  - Residuals in produced fluids – some inhibitors carry through downstream better than others
  - Batch or Continuous injection
- Biocides
- Materials of construction

Filters

- Filters can remove corrosion inhibitors
- May need to retreat down stream of filters
- Corrosion inhibition will reduce solids and extend filter life



LARGE SURFACE AREA

Water injection wells

- Typically corrosion from bacteria
- Acid gas corrosion
  - Inhibitor carried through system
  - If removed by filters may need to retreated downstream of filters
- Removal of oxygen from makeup water

Corrosion Monitoring

Corrosion Monitoring

- Goals of Monitoring
- Methods of Monitoring
- Location of Monitoring

Reasons for Monitoring the Corrosion Program

- To demonstrate the effectiveness of the corrosion mitigation program
- To optimize inhibitor program
- To detect operational changes in the system which alter asset lifetime
- <u>NEVER MONITOR WITHOUT A PURPOSE</u>

Target Corrosion Rates

- Based upon corrosion allowance and asset lifetime
- "Availability" of inhibitor
- May need to be a minimum number to prevent localized attack
- Typical numbers may be 1 mpy for production wells and 2 for surface equipment

Inhibitor Availability

- Total system corrosion rate as a function of availability:

  Total CR = $\%T_{inhb} * CR_{inhb} + \%T_{uninhb} * CR_{uninhib}$

- Down time of the inhibitor pumps can significantly effect the life of the equipment

Target Corrosion Rates

- Based upon corrosion allowance and asset lifetime.

Mean CR = corrosion allowance / design life

- ideally should use maximum pitting rate

- "Availability" of inhibitor model

$$\%\ \text{wall loss} = \frac{(\text{uninhibited CR x time}) \text{ x } (\text{inhibited CR x time})}{\text{wall loss corrosion allowance}} \text{ x } 100$$

- Typical target corrosion rate $\leq$ 5 mpy for localized corrosion and general corrosion rate

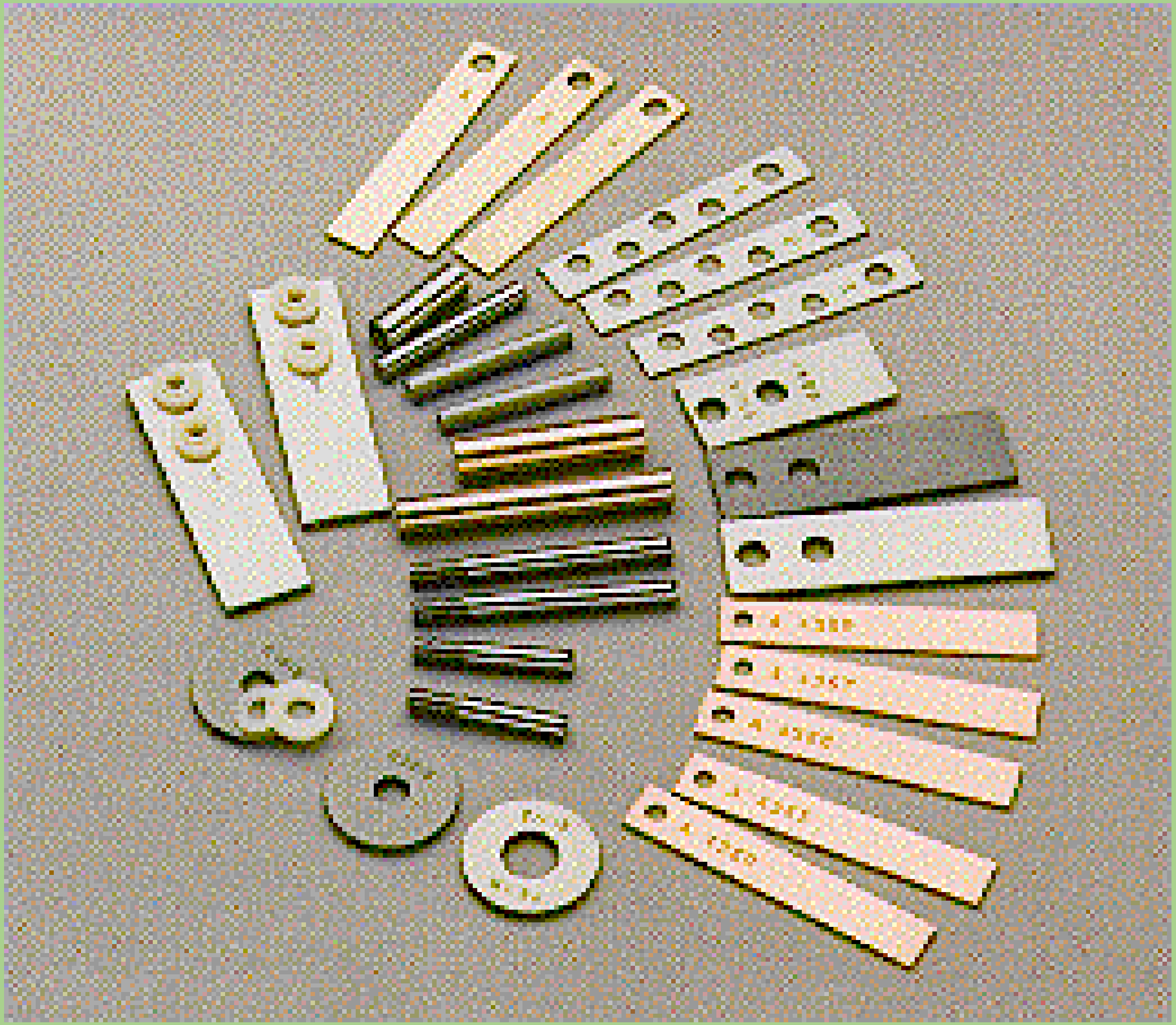
Methods of Measuring Corrosion

- Indirect methods
- Direct methods

Indirect Methods

- Weight loss coupons
- LPR (Linear Polarization Resistance)
- ER (Electrical resistance)
- Noise
- Hydrogen probe
- Metal ion analysis (Iron Counts)
- Copper ion displacement (CID)
- Residuals

Weight Loss Coupons



Weight Loss Coupons

Advantages

- Measures actual metal loss
- Visual
  - Pitting
  - Erosion
  - Deposits
- Can be used in all systems
- Low cost
- Easy installation

Disadvantages

- Measurement at location only
- Slow response
- Analytical Balance or Lab Required

Weight Loss Coupons

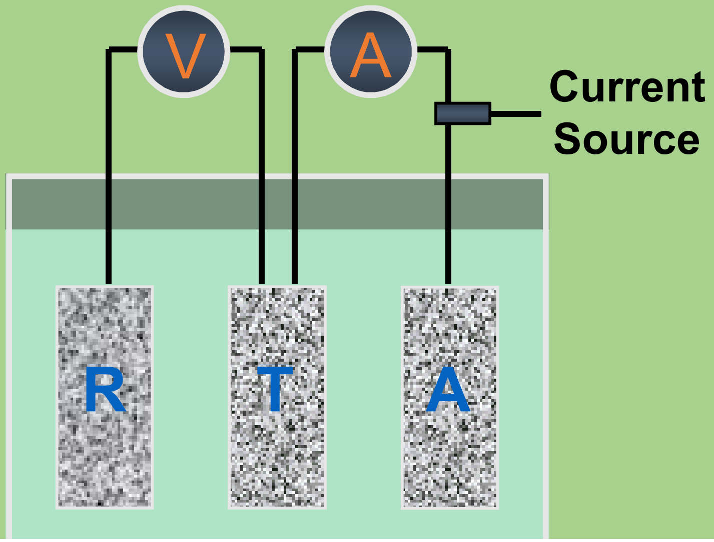
$$\textbf{MPY} = \frac{\text{gm wt. loss} \quad \text{X} \quad 22{,}270}{(\text{area sq. in.})\ (\text{days})\ (\text{density*})}$$

***Density in gm/cc metal**

Carbon Steel.....7.87 g/cc
Stainless Steel..7.92 g/cc (Type 304)

Linear Polarization Resistance

- Based on Ohm's Law E = IR
- 2 or 3 electrode systems
- A current is applied to shift the potential 10 millivolts
- The current flow is measured
- By knowing the current flow and the potential shift a corrosion rate can be calculated
- PAIR meter



Types of LPR Equipment

- Field models
    - Portable or Field Mount
- Lab models
- Potentiodyne
- Suppliers
    - Rorhback Cosaco (RCS)
    - Caproco
    - Cormon
    - Cortest

Linear Polarization Resistance (LPR)

Advantages

- Easy to install and interpret
- Real-time measurement
- Direct corrosion rate measurement
- Pitting rate with Potentiodyne

Disadvantages

- Needs minimum conductivity between electrodes (brine)
- Susceptible to fouling
- Needs expensive electronic equipment

Electrical Resistance Probe

- A small wire or strip of metal is exposed to the corrosive environment
- The resistance through the wire or metal strip is measured
- The loss of metal changes the electrical properties of the metal which can then be converted into corrosion rate

$$\text{MPY} = \frac{(\text{Reading \#2} - \text{Reading \#1}) \times (\text{Factor for probe})}{\text{Elapsed time between the two readings}}$$

Electrical Resistance Probe

Advantages	**Disadvantages**
Easy installation	Can foul in sour environment
Does not need to be in contact with brine	High sensitivity provides short lifetime
Slow to moderate measurement speed	Not sensitive to pitting
Immediate result upon reading	

Noise Measurements

Advantages	**Disadvantages**
Needs only thin conductive layer • Work in moist gas phase	Interpretation of data controversial
Indicates localized corrosion	Direct measurement of corrosion rate not accurate
Real time measurement	New and not readily available
Good for looking at trends	

Hydrogen Probe

- Electrical chemical hydrogen patch probe
- Hydrogen pressure finger probe
- Vacuum hydrogen probe

Ion Science “Hydrosteel 6000”

Features

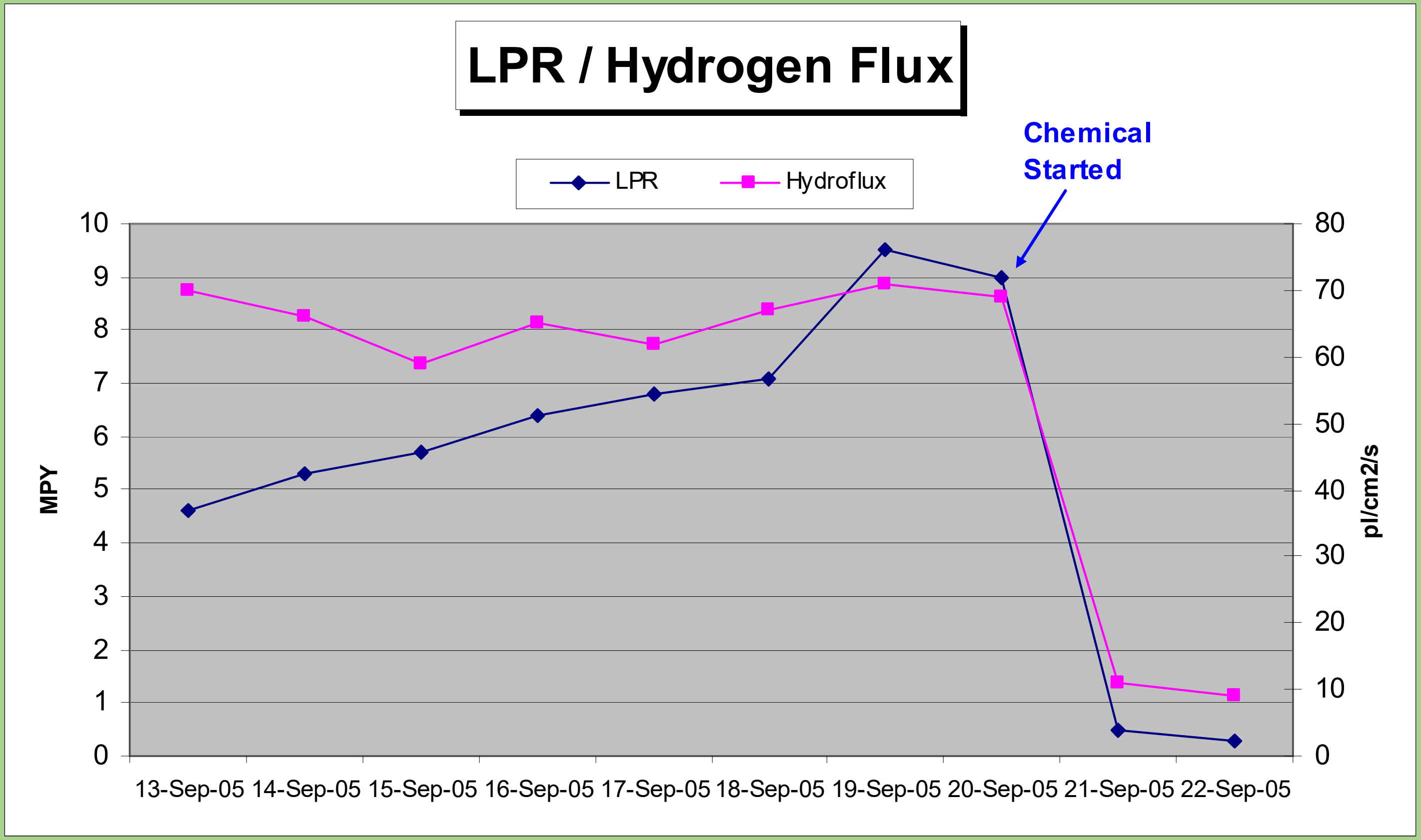
- Rapid, reliable and repeatable measurement of hydrogen flux
- Operates on steel up to 500 °C
- Accommodates surfaces from 2" diameter to flat
- Operates in any orientation, e.g. at base of pipe and vessels where corrosion commonly occurs
- Portable, light-weight
- Simple to use
- Intrinsically safe
- Totally non-intrusive
- Little or no test surface preparation needed

No consumables such as adhesives, liquids or greases required

Hydrosteel Unit and Probe

Non-Intrusive

Comparative Data
LPR / Hydrogen Flux



Field Experience with Hydrogen Flux

- Ability to measure active SRB related corrosion sites
- Have had success in measuring corrosion where H_2S was less 2 ppm
- Does not work in sweet corrosion systems
- Using it along with UT line inspection to determine if anomalies are corrosion sites

Hydrogen Probe

Advantages

- Measures H^o tendency to go into the steel
  - SSC (Sulfide Stress Cracking)
  - Hydrogen Blistering
- No hole required in pipe or vessel with some models

Disadvantages

- Only measures relative effects. Can not measure corrosion rate directly
- Difficult to use
- Expensive

Metal Ion Analyses

- Iron counts (generally used)
- Manganese counts
- Chromium counts (extremely rare)

Generalized Formulas for Metal Ion Analyses

# of Fe per day = ppm of Fe x 0.00035 x BWPD

$$\text{MPY} = \frac{\text{ppm Fe X BWPD X 11.931}}{\text{Diameter X Length}}$$

- **Diameter in inches**
- **Length in feet**

$$\text{MPY} = \frac{\text{Lb. of Fe per day X } 1.29 \text{ X } 10^6}{\textbf{Factor x Depth in Feet}}$$

# of Fe per day = ppm of Fe x 0.00035 x BWPD

TUBING SIZE	FACTOR FOR ROD PUMPED WELLS	FACTOR FOR OTHER WELLS
2 Inches	97	61
2 3/8 Inches	109	73
2 7/8 Inches	127	89
3 1/2 Inches	148	108
4 Inches	173	131

Iron Counts Measurements

Advantages

- Measures all corrosion upstream from sample site
- Simple field equipment
- Slow response
- Low resolution

Disadvantages

- Cannot be used in sour systems
- Need to know surface area of steel to relate to mpy
- Includes produced iron from formation
- Fluid sample handling

Copper Ion Displacement (CID)

- Film Coupon
  - Multi-coupon chuck can be used to measure time to film or film life.
- Rinse coupon in gasoline to remove oil
- Immerse in a 10% copper sulfate solution for 1 minute
- Record % area copper plated (this is the area that does not have an inhibitor film)

Copper Ion Displacement (CID)

Advantages

- Low cost
- Easy to use
- Fast
- Measures the filming effectiveness of the inhibitor

Disadvantages

- Fouling
- Provides no corrosion rate information

CHEMICAL RESIDUALS

- Fluid sampling (must be representative)
- Testing for inhibitor
  - Need a baseline
  - Dye Transfer (Field Method)
    - Methyl Orange
    - Bromophenol Blue
  - Chromatography (Laboratory Method)
- Measures the treatment life
  - Batch treatment
  - Squeeze treatment
- Determines chemical delivery

Residuals

Advantages

- Easily accepted by customer
- Determines lifetime
- Confirms inhibitor transport to entire systems

Disadvantages

- Low accuracy
- Subject to interference
- Difficult to run
- Does not predict performance
- Unavailable for some inhibitors
- Fluid unavailable

Direct Methods

- Failure records
- Spools
- Caliper survey
- Smart pig
- Ultrasonic Testing (UT)
- X-ray

Failure Records

Advantages

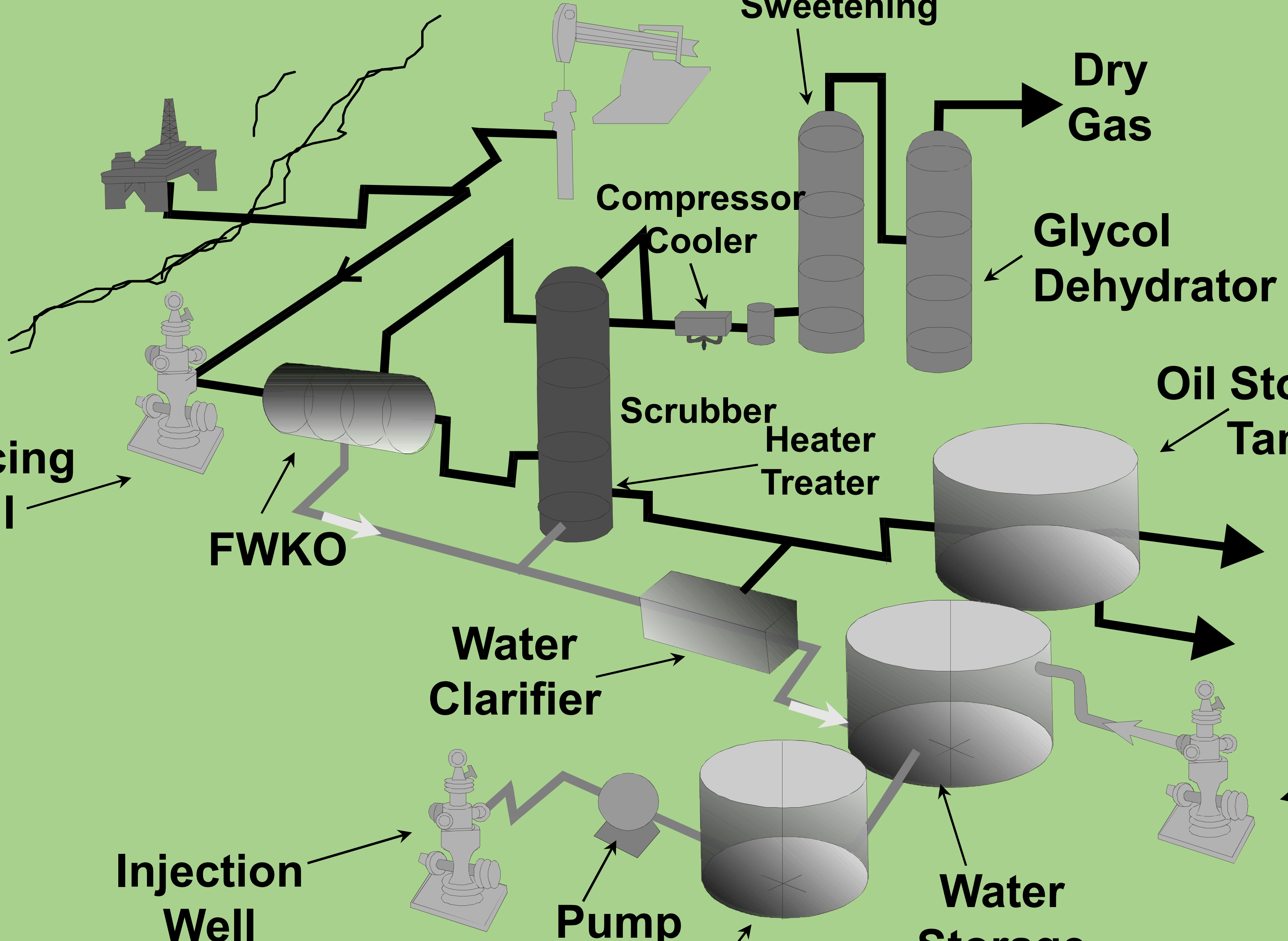
- Provides system history
- Identifies trends
- TCO tool
- Verifies KPI achievement

Disadvantages

- Not in our control
- Not always accessible
- May be incomplete
- Failure has already occurred

Corrosion Monitoring

Where and How



Amine Sweetening

Dry Gas

Compressor Cooler

Glycol Dehydrator

Scrubber

Heater Treater

Oil Storage Tank

Producing Well

FWKO

Water Clarifier

Source Water

Injection Well

Pump

Water Storage Tank

Surge Vessel

Applications

- Oil wells
- Gas wells
- Flowlines
- Productions facilities
- Injection or disposal wells
- Transmission pipelines

Oil Wells

- Failures per well per year always tracked
- Identify problems before a failures occur
- Optimize inhibitor program

Oil Wells

- Batch treatment
  - Is the inhibitor coming around
  - Film life
  - General corrosion rate (life of equipment)
- Continuous treatment
  - Is the flush bringing the inhibitor around
  - General corrosion rate (life of equipment)

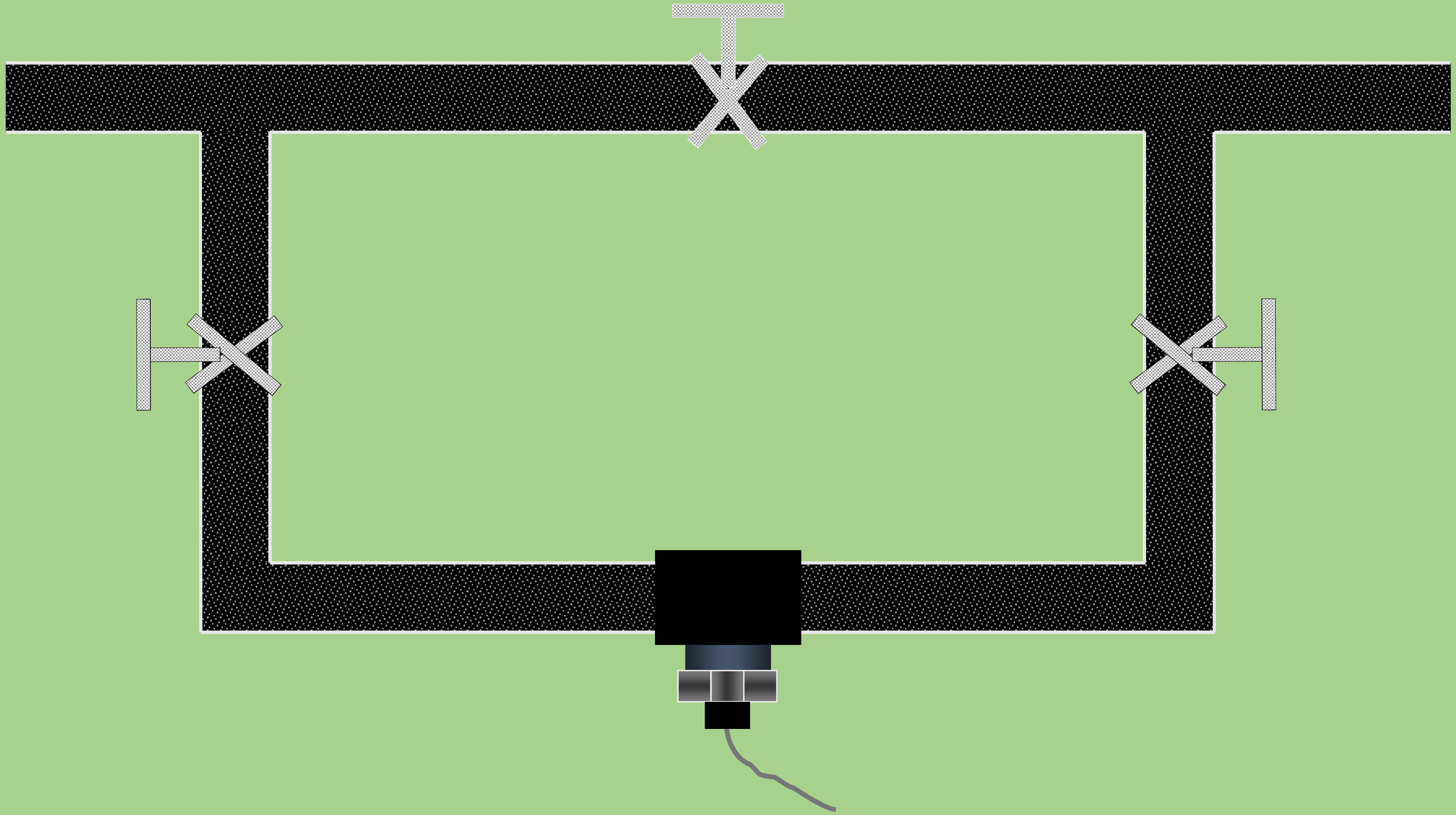
Oil Wells

- Monitor at the well head
- Types of monitoring
  - Weight loss coupons
  - LPR (high water cuts)
  - ER (low water cuts)
  - Copper ion displacement
  - Iron counts (sweet systems)

Oil Wells

- RULE OF THUMB: monitor 10% of the wells
- Pick problem wells
- Pick different types of wells
    - High - low volume wells
    - Rod pumped - ESP wells
- As wells are optimized, relocate monitoring to optimize entire field.

Test Loop



Gas Wells

- Well head measurements may not correlate with down hole corrosion
  - May be only the option
  - Will indicate if the inhibitor is circulating through the well
  - Use modeling
- Downhole corrosion coupons or subs may be a possibility
- Iron counts may represent down hole corrosion in sweet systems if no iron produced

Gas Wells

- Common methods of monitoring
    - Weight loss coupons
    - Iron counts
    - ER probes

Gas Wells - Modeling

- Monitor
  - Temperature
  - Pressure
  - Flow rates
  - Water chemistry
- Calculate expected corrosion rate

Flowlines

- Flow regime
- In stratified flow, corrosion will be in the 6:00 position
- Weight loss coupons are the most commonly used
- Place coupon towards the end of the line and at high risk locations
  - This is to insure inhibitor is transported the length of the line.

Production Facilities

- Monitor the incoming production
- Monitor downstream of water oil separation
- Monitor downstream of oxygen entry points
  - Tanks
  - Water clarifiers
  - Pumps
- Monitor downstream of filters, which can remove the corrosion inhibitors

Production Facilities

- Weight Loss coupons used for performance valuation
- LPR or ER used to look for system upsets
  - LPR is used for
    - High water cuts
    - Quick time response
- Monitor oxygen and bacteria

Injection or Disposal Wells

- Weight loss coupons at well head
- Monitor close to injection pumps
- Monitor at farthest edge of injection system
- Monitor for oxygen and bacteria

Transmission Pipelines

- Weight loss coupons most common
  - DOT requirements
- Low water volumes - ER probes
- Flush mounted probes and coupons
  - Do not disturb flow
  - Representative of corrosion on pipe wall
  - Do not have to be pulled when pigged
  - Batch inhibitor will coat
- Also check for bacteria and oxygen

Corrosion Monitoring

“Never rely on any single method of monitoring corrosion. Use several techniques simultaneously if possible,

and keep complete records.”

Corrosion Control in Petroleum NACE

Selection of the Corrosion Inhibitor

Inhibitor Selection

- Local knowledge
- Case histories
- Laboratory testing
- Field testing

Local knowledge

- What corrosion inhibitors are working in similar application in your location
  - This will help identify field proven products
  - Products already in local inventory
  - Reduce the amount of testing for a new application
- The is the probably the most common method of inhibitor selection

Case Histories

- Aids in selecting an inhibitor
    - Other similar field located in the area
    - Other areas with similar production
- Use to reduce the number of inhibitors to be tested
    - Laboratory
    - Field

Laboratory Inhibitor Testing

Laboratory Testing

Reproduce field conditions

- Fluid composition
  - Produced field fluids
  - Synthetic fluids (brine made from H_2O analysis)
- Temperature
- Pressure
- Gas composition
- Flow or velocity
- Partitioning effects

Laboratory Testing

Reproduce field operating parameters

- Understand the failure mechanism
  - High velocity
  - Underdeposit corrosion
- Method of application
  - Continuous
  - Batch
  - Squeeze
- Inhibitor transport through the system
  - Amount of mixing
    - Does it change through the system
  - Fluid level in wells
  - Liquid or vapor phase corrosion

Laboratory Testing

- Corrosion inhibitor properties
  - Can take several test to understand how an inhibitor will perform in the field
    - Temperature & pressure
    - Velocity effects
- Secondary properties

Corrosion Testing

- Wheel test
- Atmospheric sparge test
  - Beaker
  - Kettle
  - Rotating cylinder
- High pressure bombs or wheel test
- Autoclave testing
  - Standard stirred vessel
  - Rotating cage (high velocity)
- High Velocity
- Flow loops
- Jet Impingement
- Evaluation of pitting

Testing Secondary Properties

- Emulsion Tendency
- Foaming Tendency
- Solubility / Partitioning
- Thermal Stability
- Rack Gunking
- Capillary/Umbilical Stability
- Materials Compatibility
- Viscosity
- Pour Point
- Flash Point
- Ecotoxicity

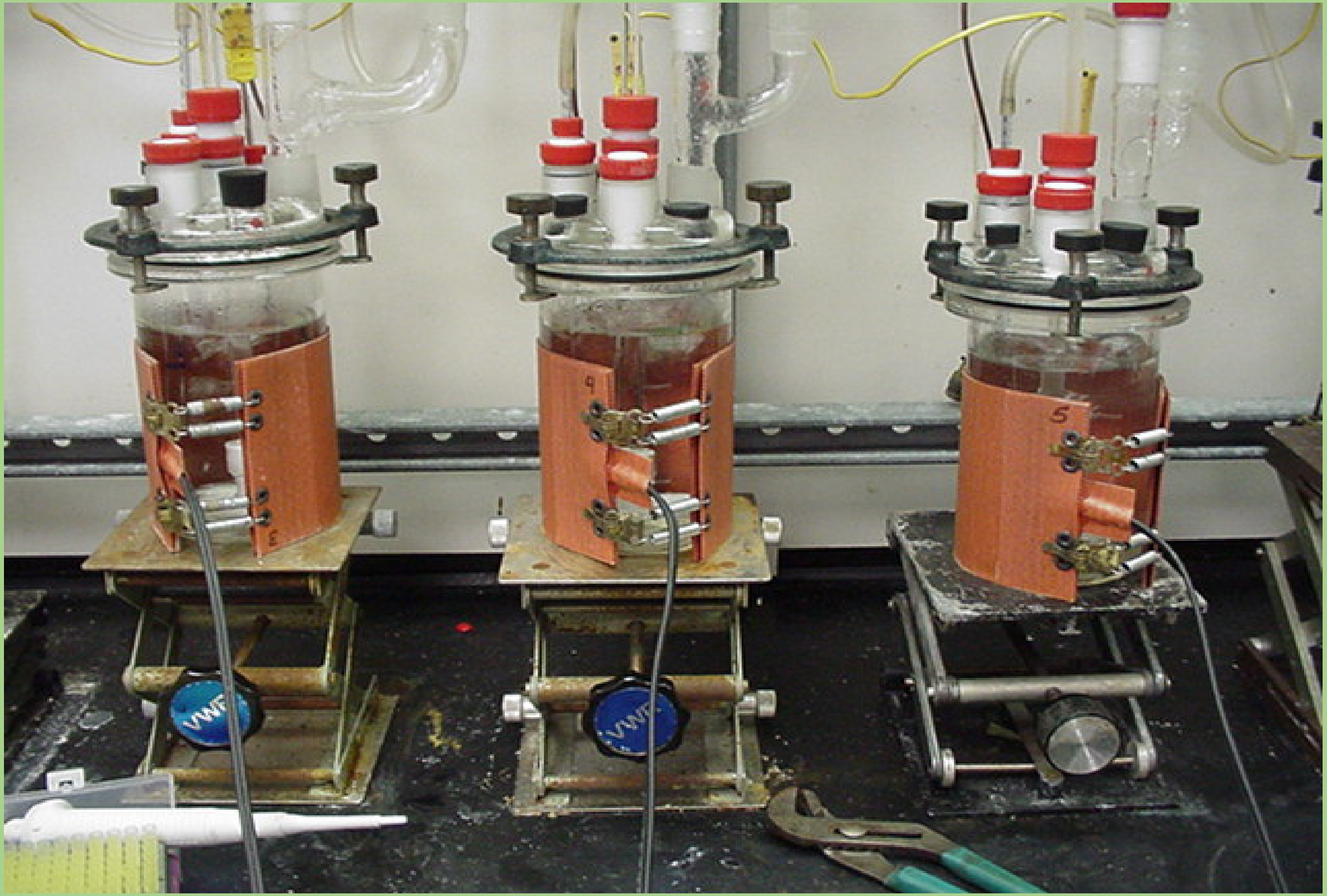
Wheel Test

Wheel Test

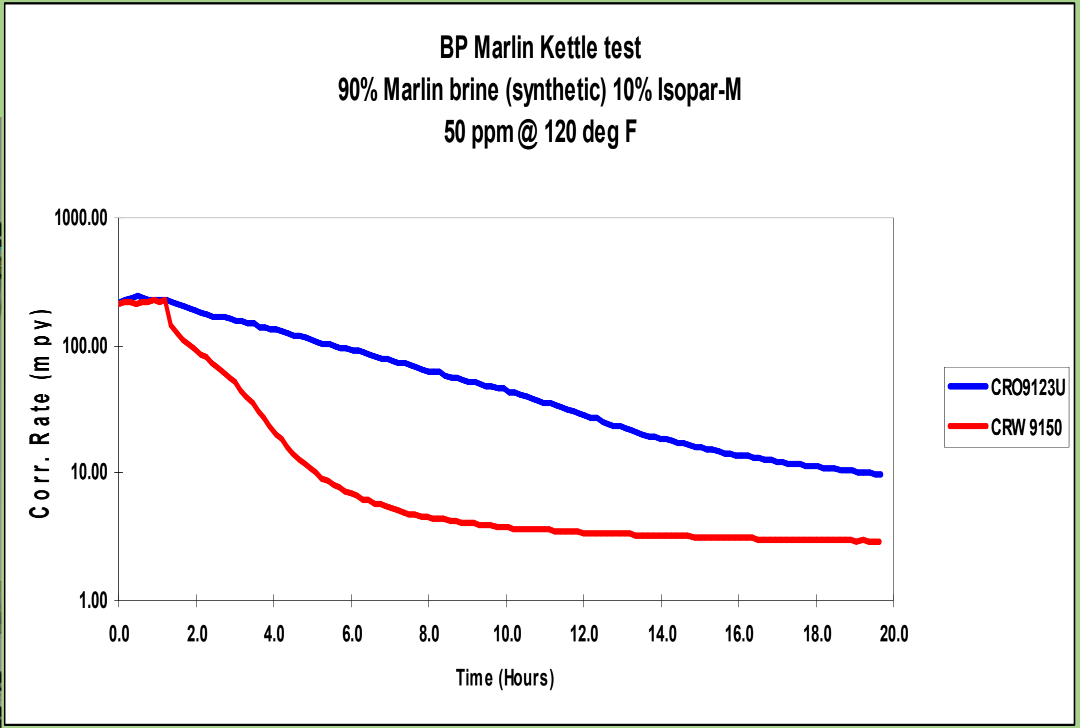
- Advantages
  - Run a very large number samples
  - Sweet or sour
  - Can run film persistency type test
  - Easy to run and vary conditions
  - Simulates rod-pumped wells

- Disadvantages
  - Mild agitation
  - Low pressure
  - Constant fluid inventory
  - Constant gas inventory
  - Uses coupons rather than electrodes

Kettle Test



Kettle Testing (LPR)



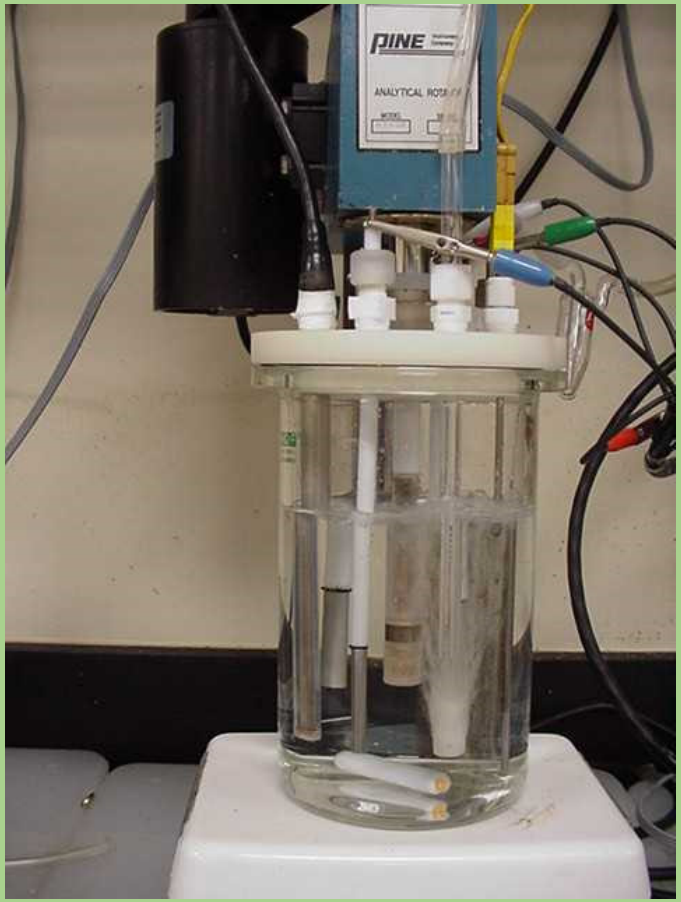
BP Marlin Kettle test
90% Marlin brine (synthetic) 10% Isopar-M
50 ppm @ 120 deg F

Beaker/Kettle Test

- Advantages
  - Sweet or sour
  - Gas replenishment
  - Weight loss and LPR
  - pH can be controlled
  - Easy to run and vary conditions

- Disadvantages
  - Mild agitation
  - Atmospheric pressure
  - Constant fluid inventory

RCE Test


PINE
ANALYTICAL ROTA

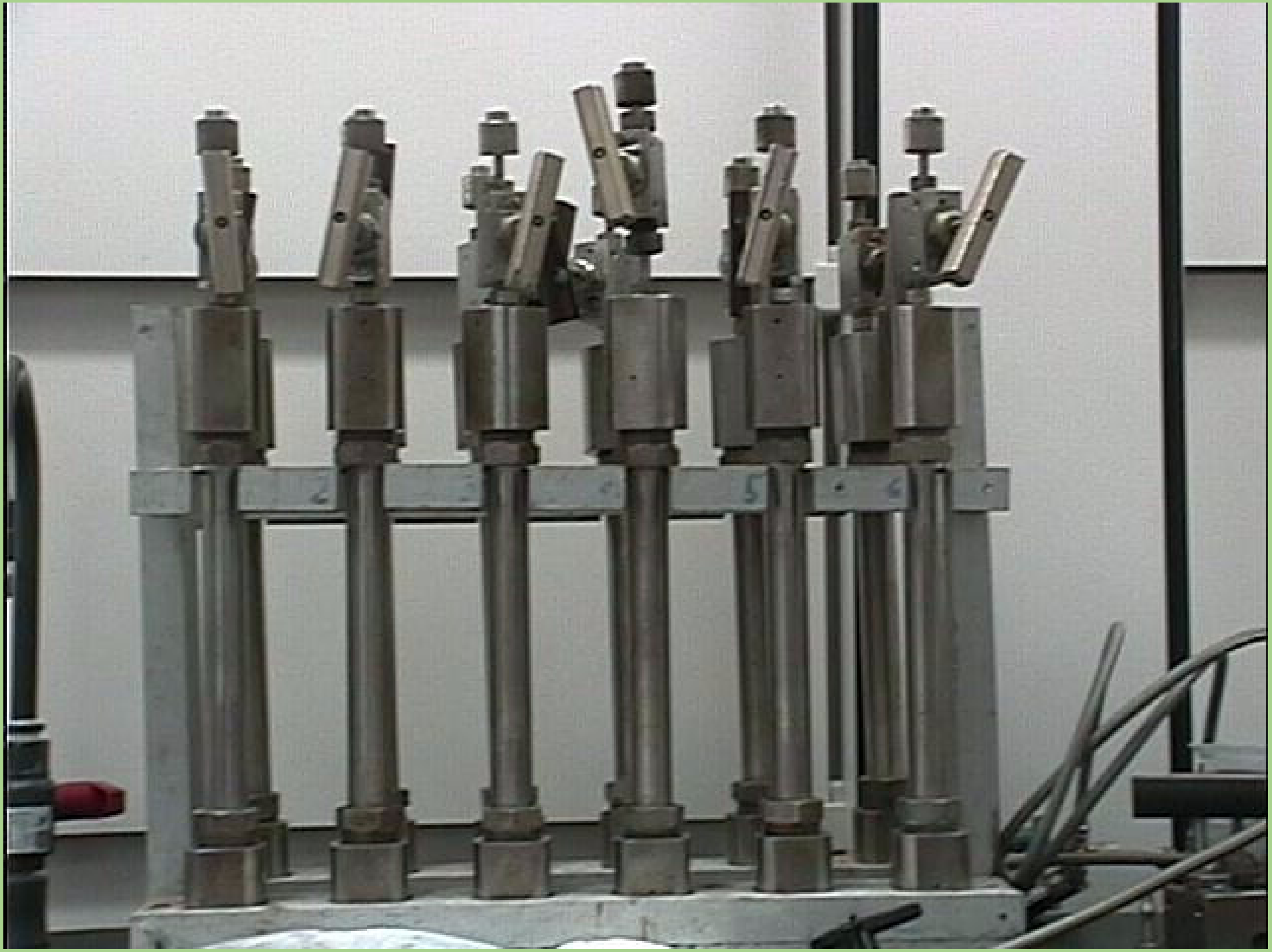

MONOGRAM
66
PINE
INSTRUMENT
COMPANY
ASR SPEED CONTROL
1000 RPM PER TURN
POWER
INPUT
COMMON
OUTPUT
1V/1KRPM
1V/1KRPM

Rotating Cylinder Electrode (RCE) Test

- Advantages
  - High velocities
  - Gas replenishment
  - Constant pH possible
  - Weight loss and LPR
  - Easy to run and vary conditions

- Disadvantage
  - Mainly sweet
  - Low pressure
  - Constant fluid inventory
  - Undisturbed Flow

High Pressure Wheel Test Bombs



- Weight loss test
- Cells rotated on a "wheel" to agitate fluids
- 1500 psi, 400°F

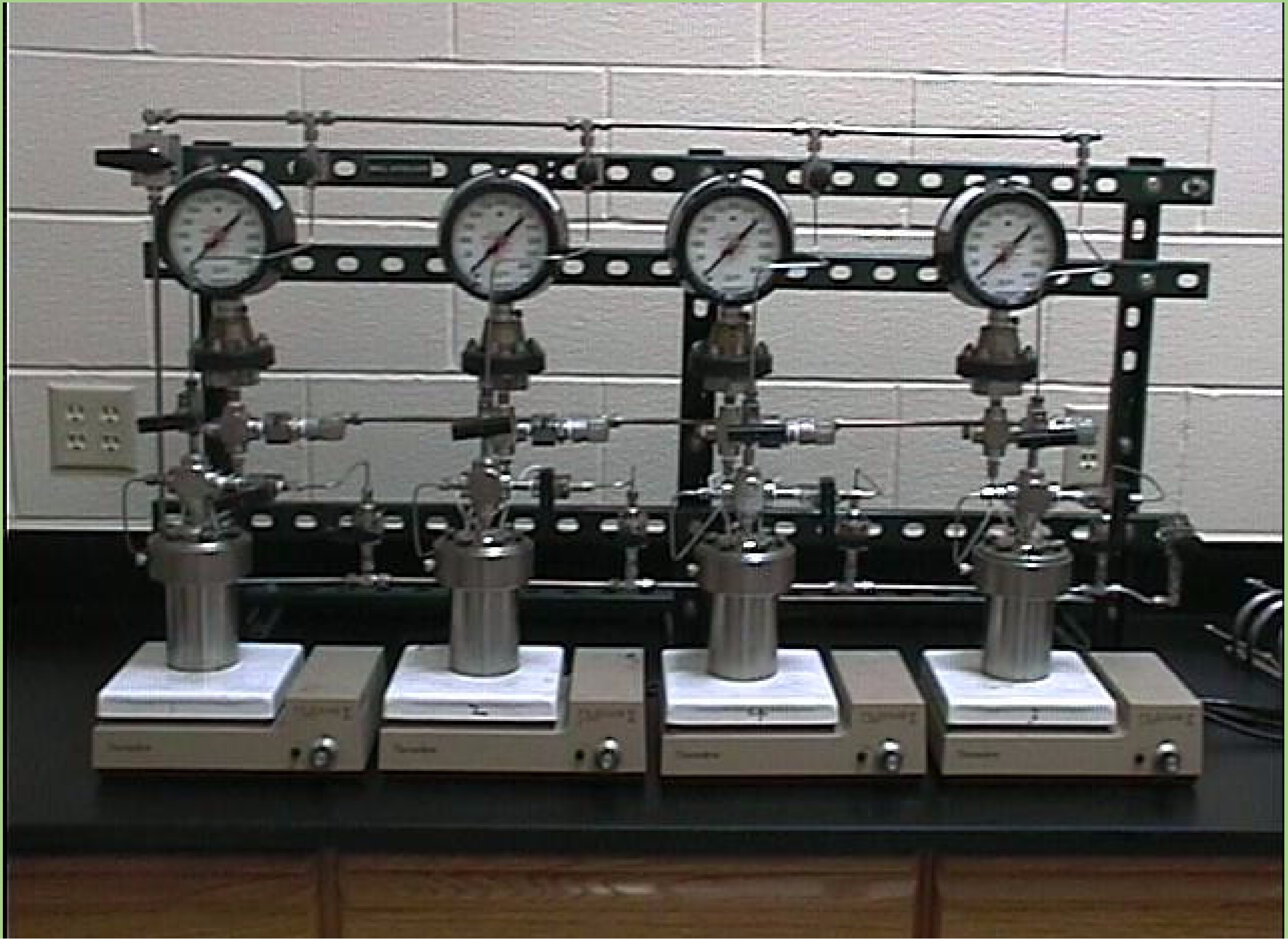
High Pressure Wheel Test

Laboratory Bomb or High Pressure Wheel Test

- Advantages
  - High pressure
  - High temperature
  - Sweet or sour
  - Weight loss

- Disadvantages
  - Low agitation
  - Constant fluid inventory
  - Constant gas inventory

SMALL AUTOCLAVES



- Stratified tests under pressure (H2S or CO2)
- Gently stirred
- Electrochemical probes

Standard Autoclave Test

- Advantages
  - High pressure
  - High temperature
  - Sweet or sour
    plus CH_4 or other gases
  - Weight loss and LPR
- Disadvantages
  - Constant fluid inventory
  - Constant gas inventory
  - Limited turbulence

High Speed Autoclave


2003 8 28

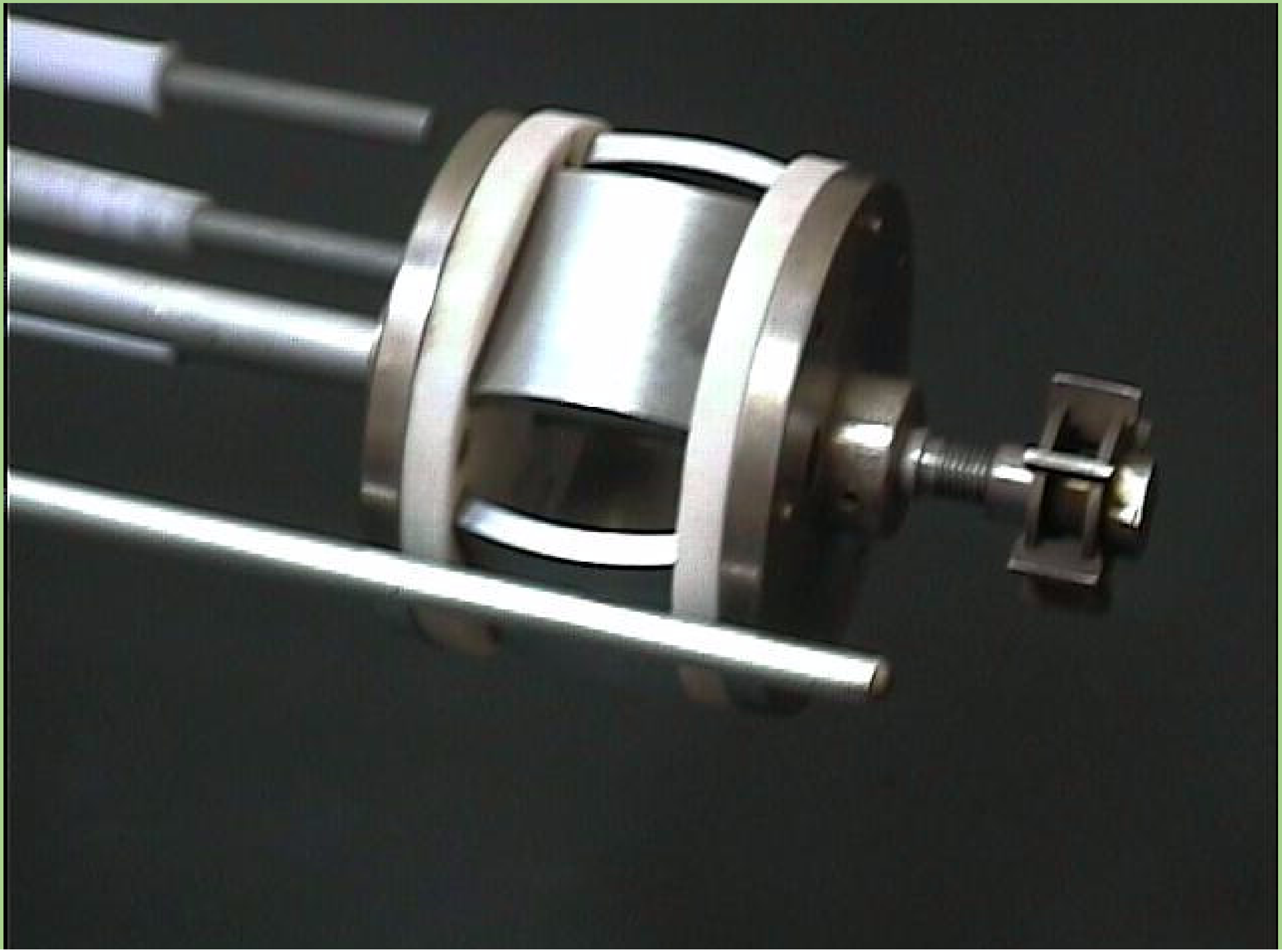
- Rotating cage design designed to produce shear stresses >400 Pa
- 400°F, 6000 psi
- H_2S or CO_2

High Speed Autoclave

Uninhibited

Inhibited

High Speed Autoclave (HSAT)

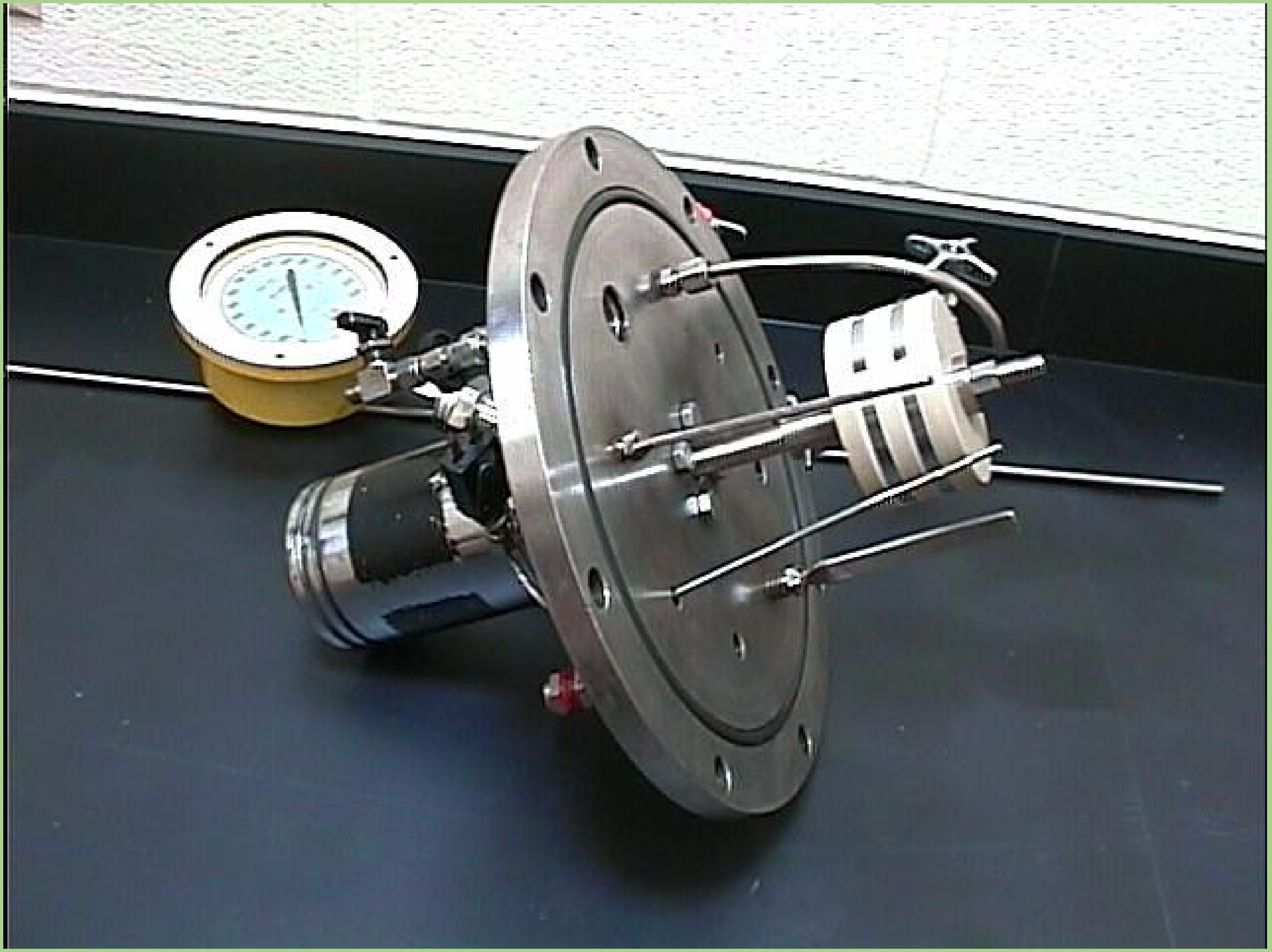


- Rotating “Cage” design on coupons
- Generates very high shear stresses (>400 Pa)
- 400°F, 6000 psi
- H_2S or CO_2

High Speed Autoclave Test

- Advantages
  - High pressure
  - High temperature
  - Sweet or sour plus CH_4 or other gases
  - Weight loss
  - High turbulence
- Disadvantages
  - Constant fluid inventory
  - Constant gas inventory
  - No LPR data

ROTOCLAVE



- Cylindrical shaped coupons
- Sweet or sour tests
- Adjustable speeds (200 Pa max)
- 220°F, 500 psi

Rotoclave

- Advantages
  - Medium pressure
  - High temperature
  - Weight loss
  - High velocities

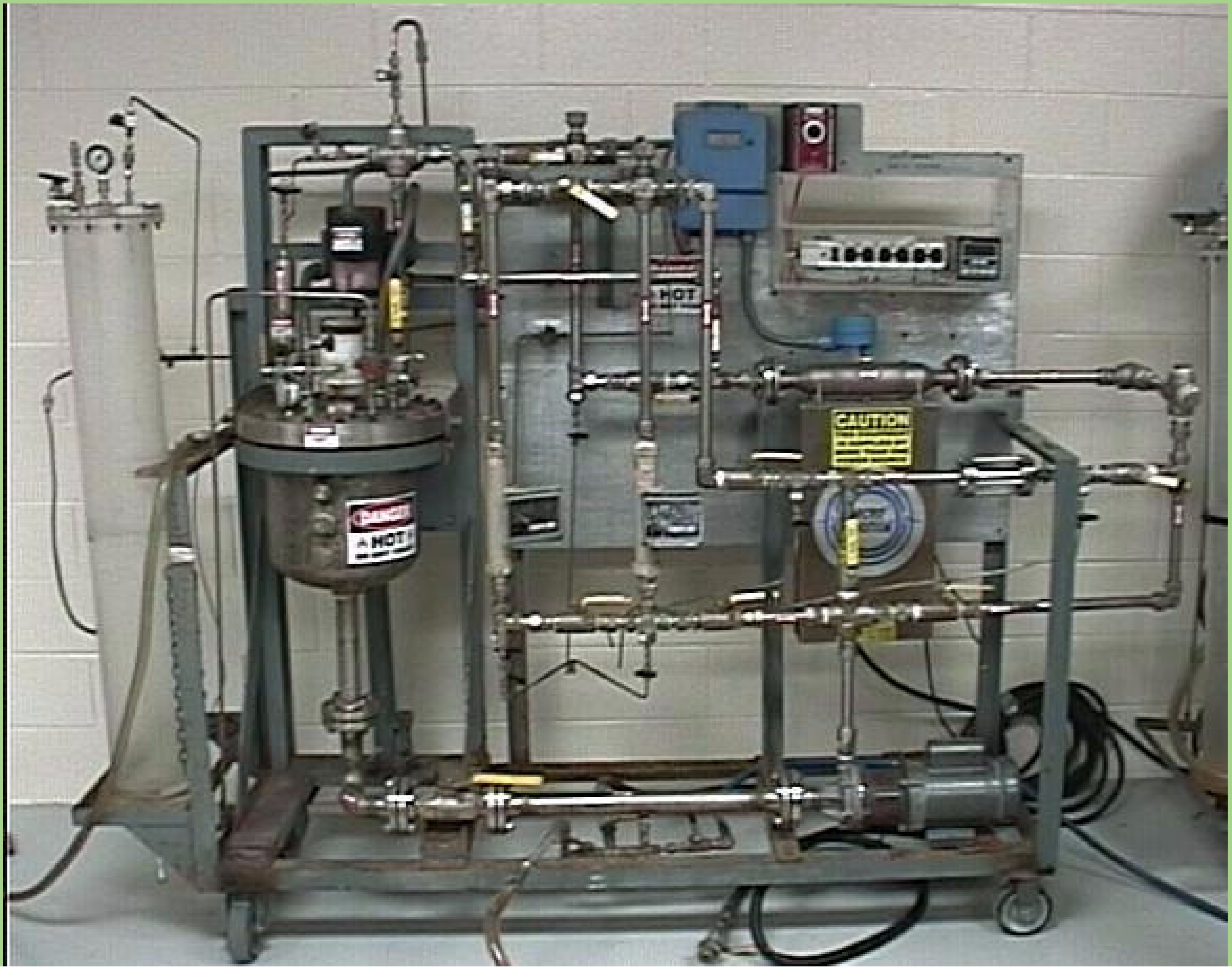
- Disadvantages
  - Constant fluid inventory
  - Constant gas inventory
  - Sweet only
  - No LPR data

Flow Through Autoclave

- Advantages
  - High pressure
  - High temperature
  - Gas replenishment
  - Fluid replenishment
  - Weight loss and LPR
  - High turbulence

- Disadvantage
  - Only Sweet

FL0W LOOPS (Old Design)

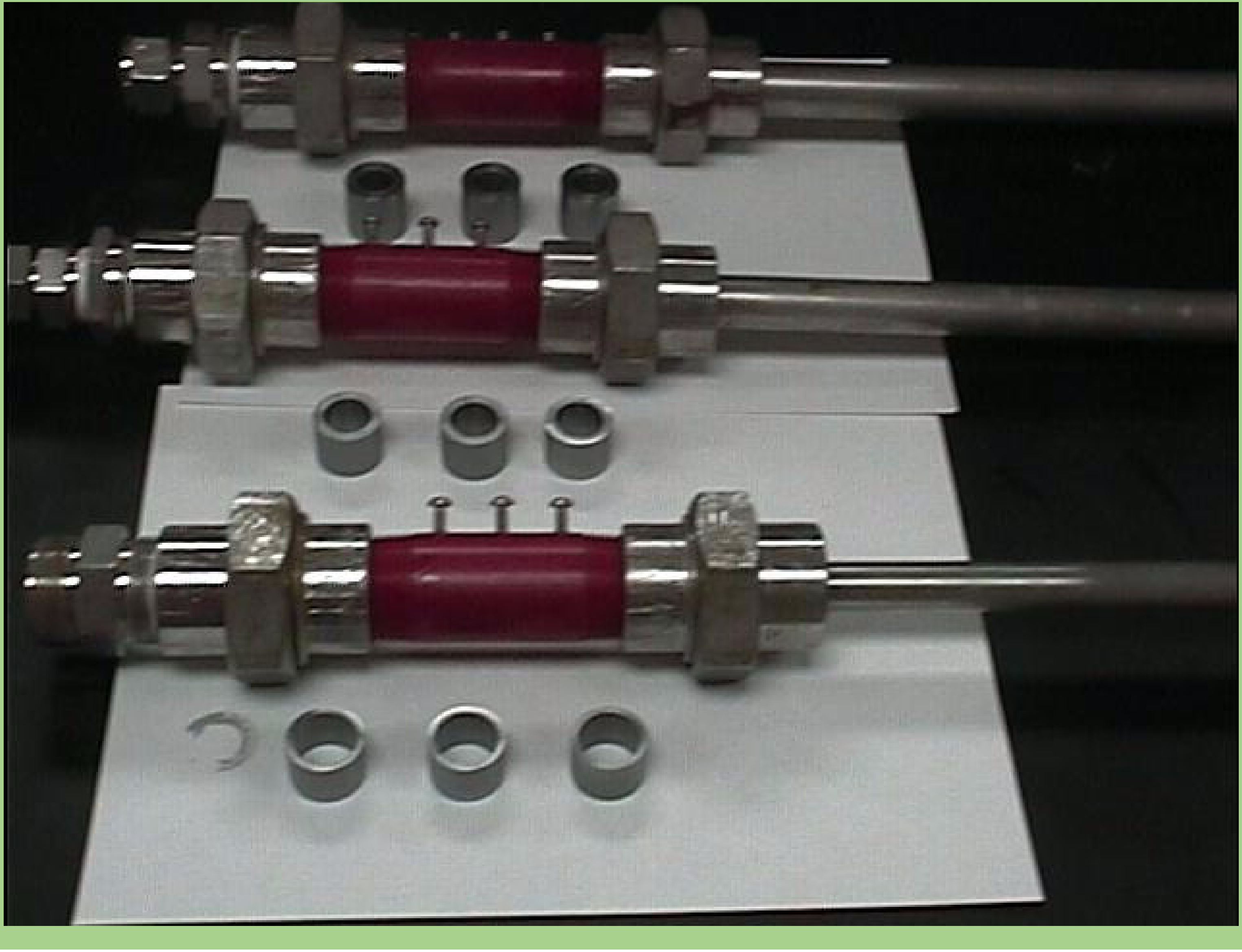


- Recirculating system for brine and HC
- 3 Weight Loss Probes and LPR Probes
- Velocities -- 4.2, 9.3, 13.8 ft/sec (48 Pa)
- 200 psi, 220 °F
- 22 L capacity

FLOWLOOPS (New Design)

- 3 LPR Cells in Series
- 3 Velocities up to 32 ft/sec max
- Continuous P, T, mpy, and flow rate monitoring on each loop
- Bypass between loops
- 200 psi and 220 °F

Corrosion Monitoring Probes for New Flow Loop

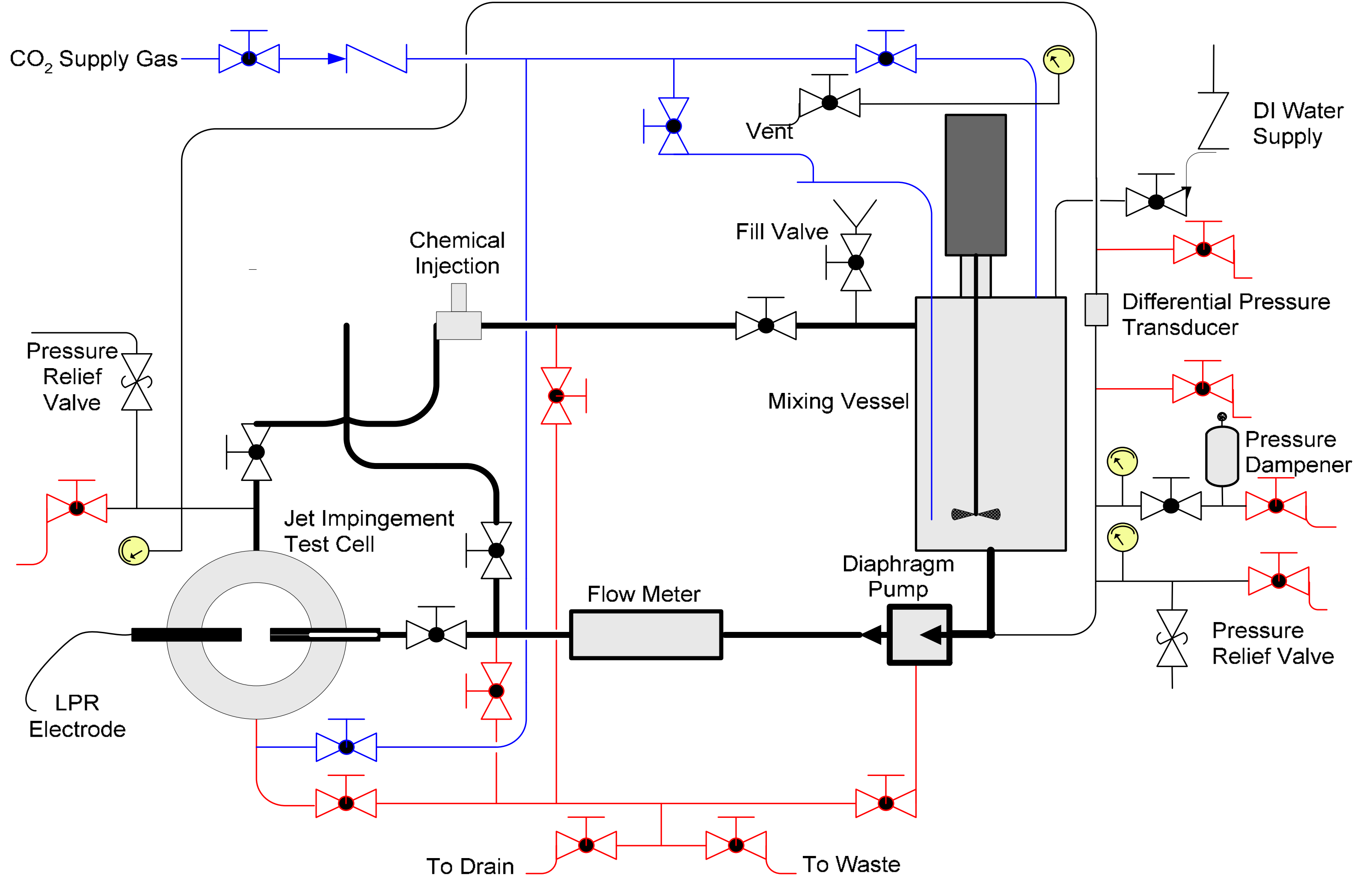


- Velocity controlled by tubing diameter
- 3 coupons per probe
- Weight loss and electrochemical

Flow Loops

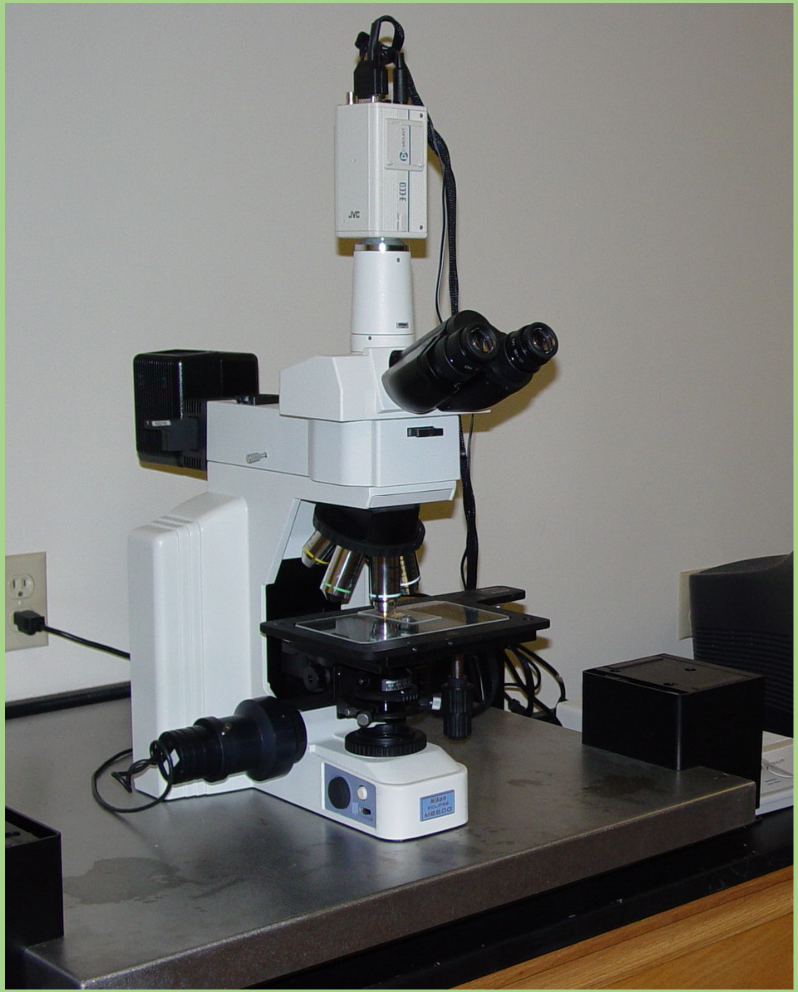
- Advantages
  - High velocities
  - Gas replenishment
  - Large liquid volume to coupon surface area ratio
  - Weight loss and LPR
- Disadvantage
  - Only Sweet
  - Medium pressure
  - Constant fluid inventory

Jet Impingement Test

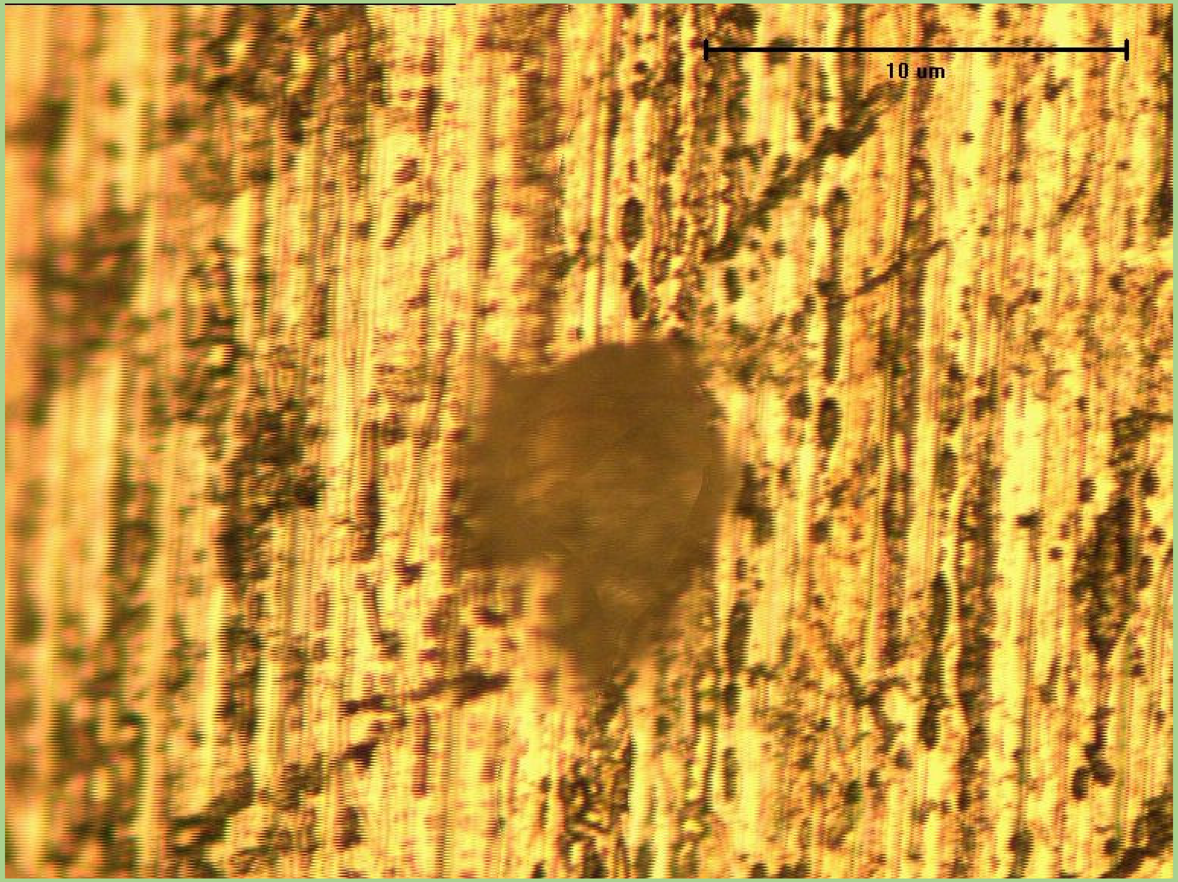


BAKER HUGHES Baker Petrolite	**Jet Impingement Test Apparatus**	Black: Liquid test system Blue: Sparge gas system Red: Drain system	Drawing: # 1.0 2/28/02

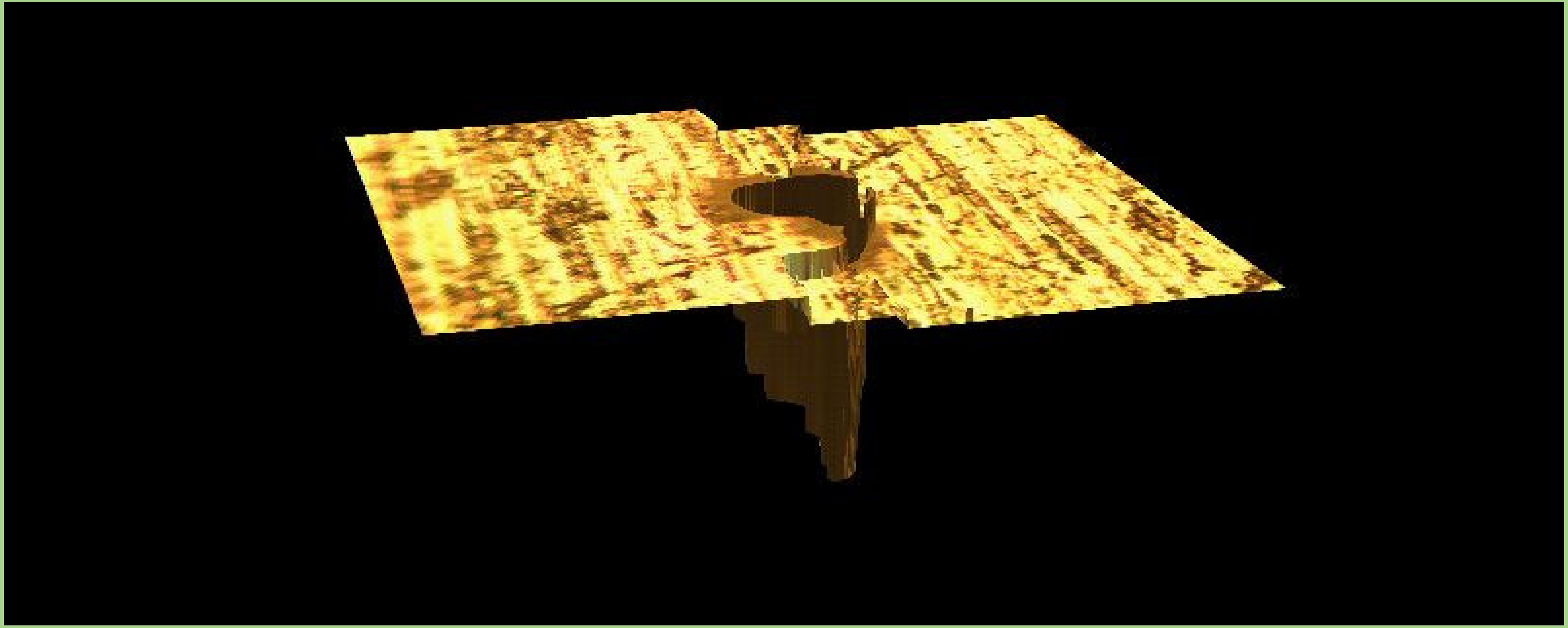
Metallurgical Microscope



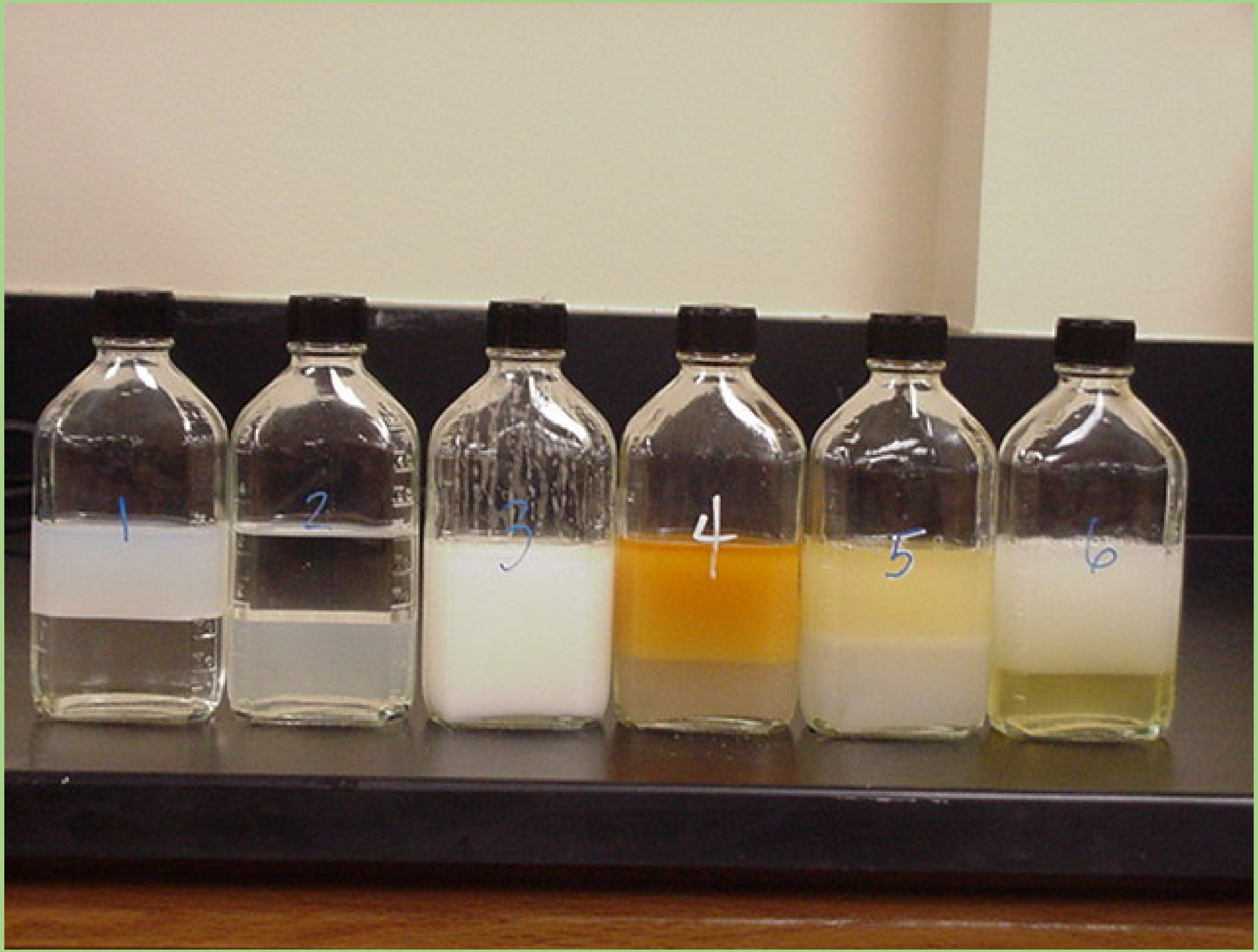
Microscopic View of a Pit



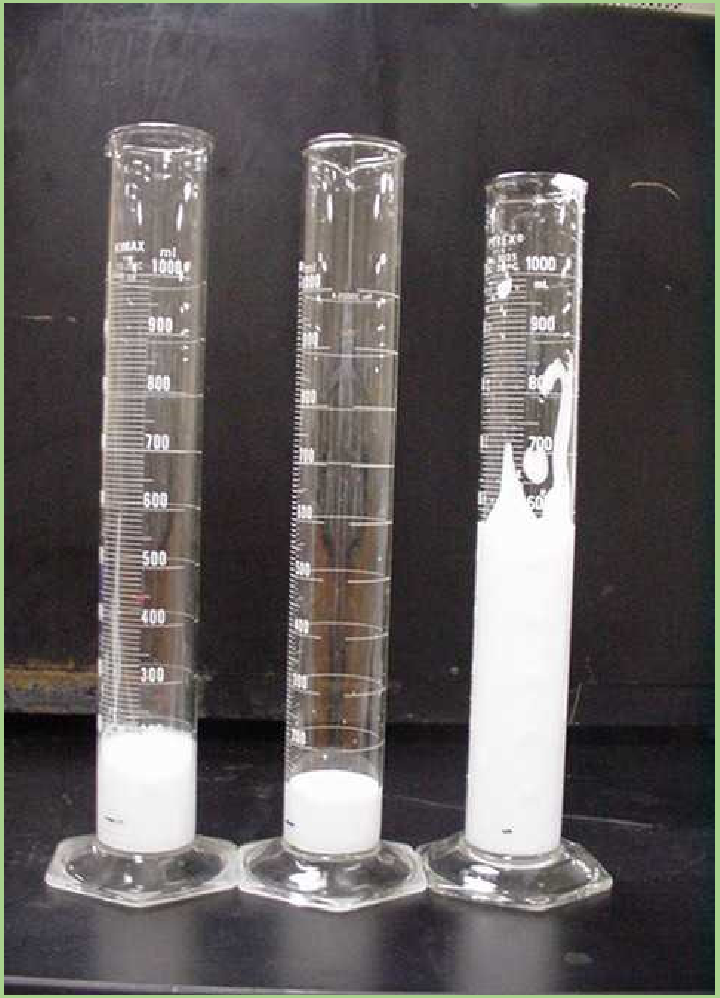
Software 3D Rendering of Pit



Fluids Compatibility

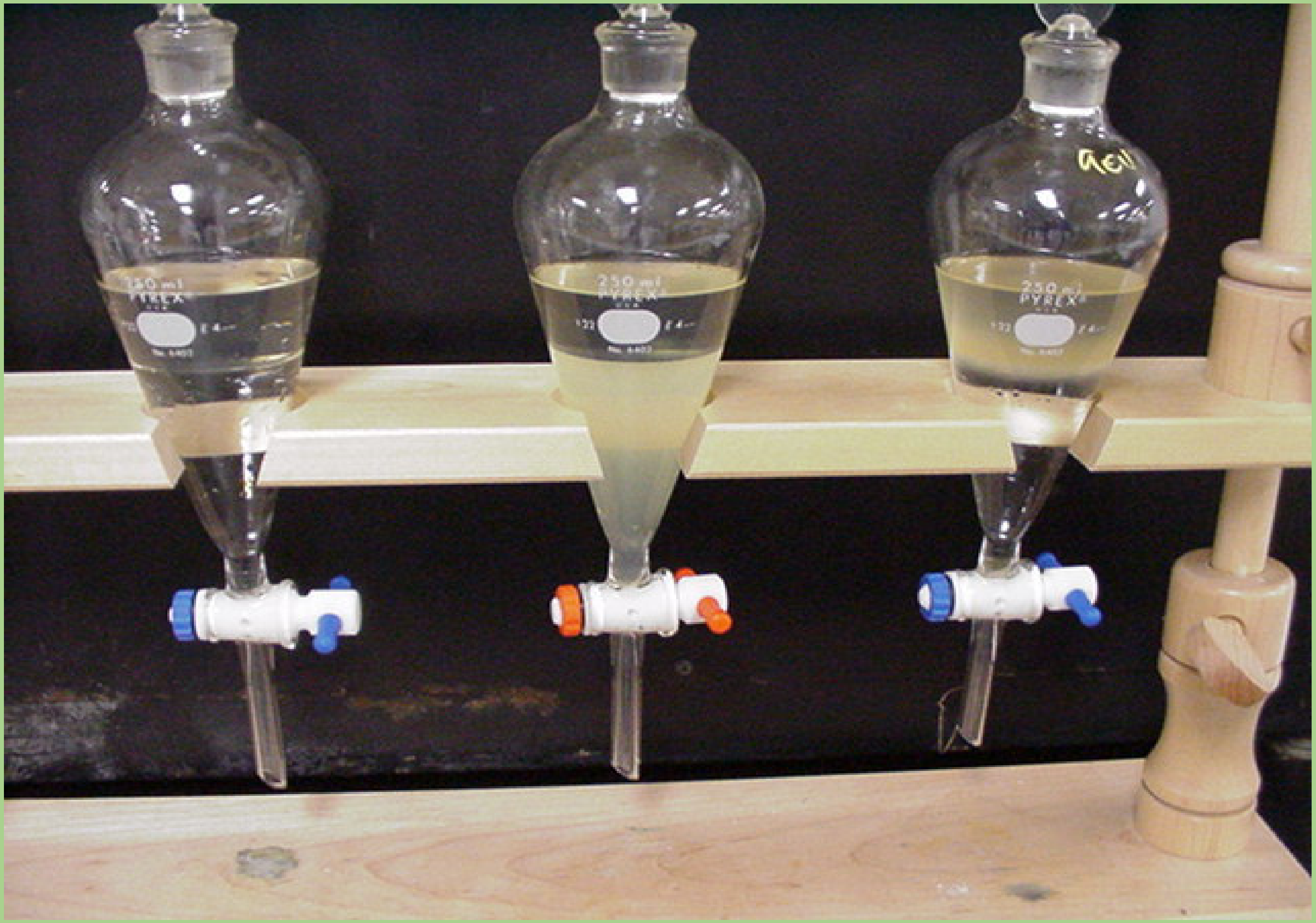


Emulsion Tendency test



Foaming test

Partitioning of Inhibitors



Laboratory Testing

- Select the best overall inhibitor
- Establish concentration vs. performance profile
- Establish how the inhibitor moves through the system
  - Solubility
  - Partitioning
- Secondary properties
  - Emulsion and foaming tendencies
  - Flash point
  - pour point
- Compatibility
  - System
  - Other treating chemicals

Laboratory Testing

- The dose rate determined in the laboratory should be optimized in the field
    - It is very difficult to determine the treatment concentration with laboratory testing
- The field corrosion monitoring must be effective and reliable

Laboratory Testing

- Check the compatibility of a corrosion inhibitor with the materials, linings, seals, and other oil field chemicals with which it is to come into contact with.
- Environmental concerns are becoming increasingly more important in the selection of oil field chemicals.

Field Screening Tests

Field Testing

- Inhibitor selection
- Optimize the program
  - Inhibitor concentration
  - Treatment interval
- Establish effectiveness of the program

Field Testing

Inhibitor Selection

- Compatibility in field fluids
- Inhibitor selection (corrosion performance)
    - Rotating jar test
    - Side stream test
- Secondary properties
    - Emulsions
    - Foaming

Compatibility Testing

- Solubility
- Emulsion tendency
- Foaming
- Downstream operations - sweetening, dehydration

Solubility Testing

- Can be run using water or water and oil
- Should use actual field fluids
- Run at use concentration and higher
- Look at solubility and dispersibility

Emulsion Tendency Test

- Shaker bottle
- Seltzer bottle
- Blender

Shaker Bottle

- Mildest - most basic form of testing
- Mix oil and water at specific ratio
- Shake 50 - 100 times
- Observe water drop, interface and oil quality versus blank standard

Seltzer Bottle

- More severe test than shaker bottle
- Simulates shear going through a pump or choke
- Best test when looking at oil quality in high flow, velocity systems

Blender

- Most severe shear test
- Typically mix oil, water and inhibitor for one minute at high speed
- Has been used effectively to gauge water quality in velocity, offshore applications

Foaming Tendency

- Looking for effect of inhibitor on glycol or sweetening operations
- Foaming may also affect dehydration of oil
- Test can be run using blender or gas sparging
- Should be run at use concentration and higher