Corrosion Process

- Four key elements required for corrosion to occur
  - Anode
    - Portion of the metal surface that corrodes where positive ions go into solution
  - Cathode
    - Portion of the metal surface where negative ions travel (not a corrosion location)
  - Metallic path
    - The pipeline
  - Electrolyte
    - Water
      - The higher the amount of chlorides (salts), the more electrolyte present

PHMSA – Pipeline Hazardous Materials Safety Administration

- 49 CFR part 192 Pertains to Gas Transportation

§ 192.475 Internal corrosion control: General

(a) Corrosive gas may not be transported by pipeline, unless the corrosive effect of the gas on the pipeline has been investigated and steps have been taken to minimize internal corrosion.

§ 192.477 Internal corrosion control: Monitoring

If corrosive gas is being transported, coupons or other suitable means must be used to determine the effectiveness of the steps taken to minimize internal corrosion.

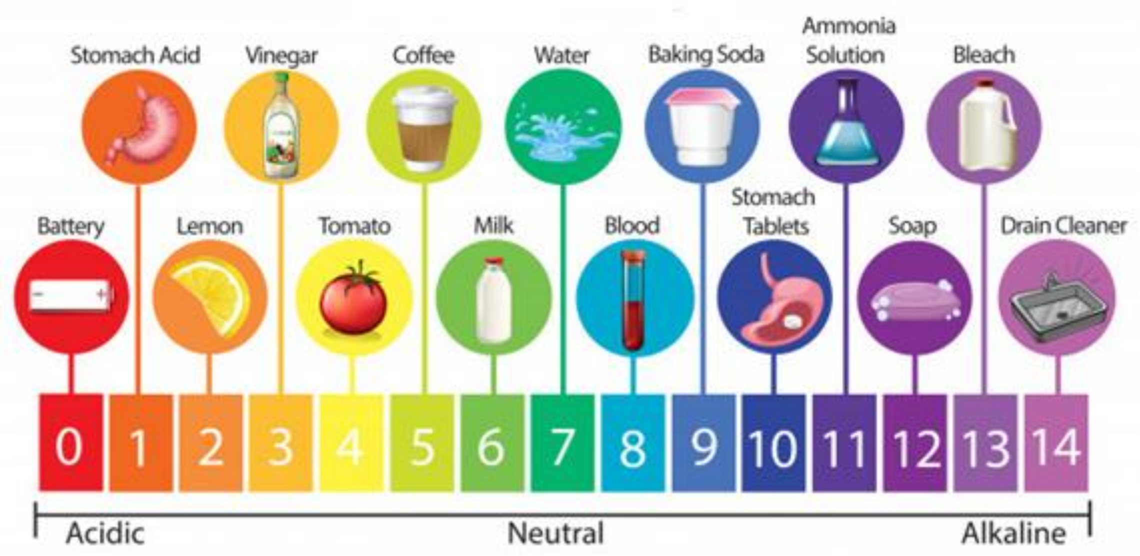
Water is a Major Influencing Factor in Internal Corrosion

Key Factors

- Water (Electrolyte)
  - Dew points in gas lines determine how much water is entering – lbs of H_2O/mmcf
  - pH
    - pH of 7 is neutral therefore less corrosive
    - May have higher scaling tendencies
    - pH 5.5 or below will have acid type of attack
  - Conductivity
    - Conductivity increases the corrosivity increases
    - TDS increases the corrosivity increases
  - Alkalinity is a measure of the waters ability to neutralize acids or resist changes that cause acidity, maintaining a stable pH

pH

- pH is the single, most influential factor in corrosion rate
  - Normal oilfield range = 6-8
  - Changes in pH are logarithmic: pH 8 = 10 X pH 7



Conductivity

- Higher conductivity indicates a greater presence of dissolved ions, which can facilitate the electrochemical reactions that drive corrosion processes, essentially making it easier for metals to oxidize and corrode in the water
- Generally speaking the higher the total dissolved solids (TDS) the greater the potential corrosion rate
- Total dissolved solids (TDS) that significantly increase conductivity in water include:
  - sodium, calcium, magnesium, potassium, chloride, sulfate, and other dissolved salts

Alkalinity

- Alkalinity is a measure of the capacity of water to neutralize acids. This is known as the buffering capacity of water, or the ability of water to resist a change in pH when acid is added.
- A measure of water's ability to neutralize acids or resist changes that cause acidity, maintaining a stable pH
  - Calcium, Magnesium and Iron are examples substances that can increase a waters alkalinity

Evaluate the pipeline system

- What type of corrosion am I dealing with-Pitting/Uniform
- Where are my risks – High Consequence Areas
    - The Pipeline and Hazardous Materials Safety Administration (PHMSA) uses the term "High Consequence Area" (HCA) to identify areas where a pipeline leak or rupture could have a significant negative impact on the health and safety of the surrounding area. HCAs are often defined as a buffer zone that extends 660 feet (200 meters) on either side of a pipeline segment that passes through developed areas. The exact distance of the HCA depends on the pipeline's diameter and operating pressure.
- Corrosion occurring – Top, Bottom, Throughout the line
- How do I mitigate my internal risks

Evaluate the pipeline System

Dissolved Gases

- H_2S Hydrogen Sulfide – dissolved in water creates a weak sulfuric acid
- CO_2 Carbon Dioxide – dissolved in water creates a carbonic acid
- O_2 Oxygen – although not considered an acid gas, will exponentially accelerate H_2S and CO_2 corrosion and can be extremely corrosive by itself

Henry’s Law

At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

Simply Stated:

The solubility of a gas in a liquid is proportional to the pressure of that gas above the liquid.

Carbon Dioxide CO_2 Partial Pressure

- As the pressure of a line increases, the solubility of CO_2 increases.
- Therefore, corrosion rates go up as the partial pressure of CO_2 increases.

- $$CO_2 \text{ Partial Pressure} = \frac{\text{Total System Pressure psia} \times \text{mol \% } CO_2}{100}$$

- CO_2 partial pressure below 7 is unlikely for CO_2 pitting corrosion
- CO_2 partial pressure of 7 to 14 may indicate possible CO_2 pitting corrosion
- CO_2 partial pressure above 14 is probable for CO_2 pitting corrosion

Hydrogen Sulfide – H_2S (Sour Corrosion)

As the pressure of the line increases, the solubility of H_2S increases. Therefore, corrosion rates go up as the partial pressure of H_2S increases.

$$\textbf{H}_2\textbf{S Partial Pressure} = \frac{\textbf{Total System Pressure psia x mol \% H}_2\textbf{S}}{\textbf{100}}$$

NACE reference for H_2S pitting is a partial pressure that is at or above 0.0147

H_2S Partial Pressure with 20 ppm H_2S and 800 psia line pressure?

H_2S ppm to mol % is, (H_2S ppm / 10,000) = mol %   = 0.0160

Oxygen

- Oxygen highly corrosive
  - ppm / ppm oxygen most corrosive
- Oxygen Greatly Accelerates Corrosion
- Methanol injection – Good source of oxygen
- Corrosion by-product Iron Oxide, Fe_2O_3 - Rust

Line Velocity

- Line velocity will determine flow pattern – where water is likely in the pipe – where corrosion is most likely
- Low velocity lines will hold water in low spots
- Higher velocities can help sweep the line – wet the entire pipe wall
- Higher velocities >15 ft/sec can help break up bacteria colonies
- Higher velocities can create erosional effects and solids impingement
- Higher velocities may require DRA in crude lines

Velocities
Flow Pattern in Gas Pipelines

- Stratified flow: In horizontal flow, this flow regime typically occurs at low liquid and gas velocities and complete separation of the phases occurs in the pipe. The gas-phase travels at the top of the pipe and the liquid at the bottom and the phases are separated by an undisturbed horizontal interface. (At low velocities, gas and liquid phases separate with the gas on top and liquid below).

- Wavy flow: If the velocity of the gas phase in a stratified condition is increased, waves form on the interface and travel in the same direction as the direction of flow. As velocity increases, waves form at the liquid-gas interface. The crests of these waves tend not to reach the top of the pipe.

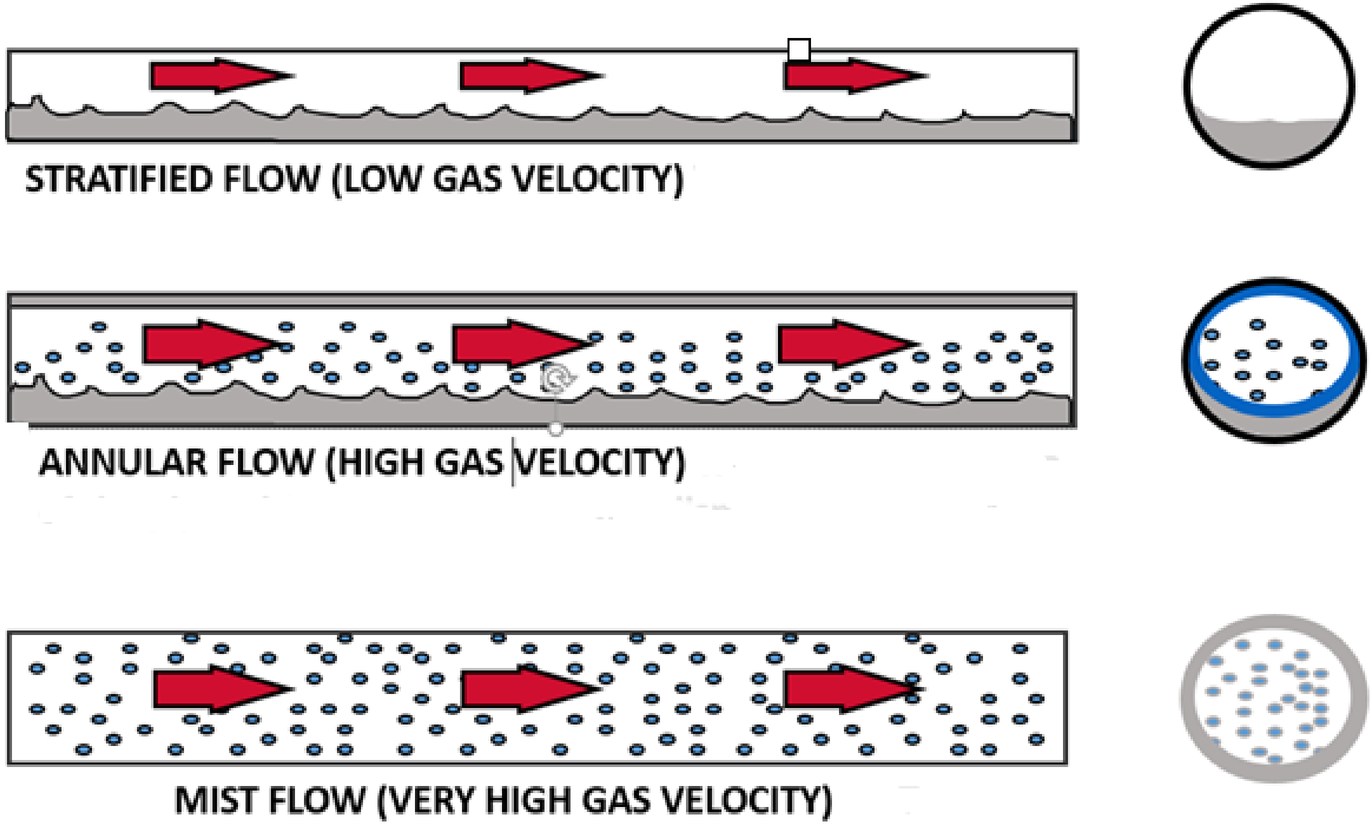
- Plug Flow: As the gas velocity is increased further, the interfacial waves become larger and can wash to the top of the pipe. Liquid plugs are separated by elongated gas bubbles.

- Slug flow: At higher velocities larger gas bubbles (slugs) alternate with liquid slugs, causing potential pipeline vibrations.

- Annular flow: At very high velocities, liquid forms a thin film on the pipe wall with gas flowing in the center, carrying liquid droplets.

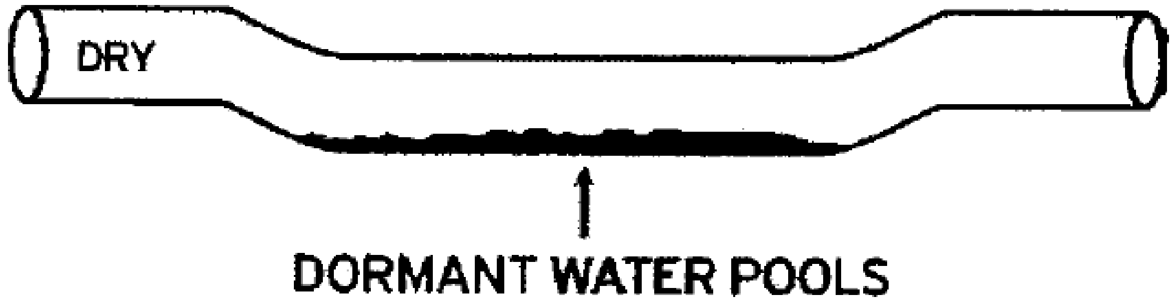
Flow Regimes

- Stratified
- Annular
- Mist Flow



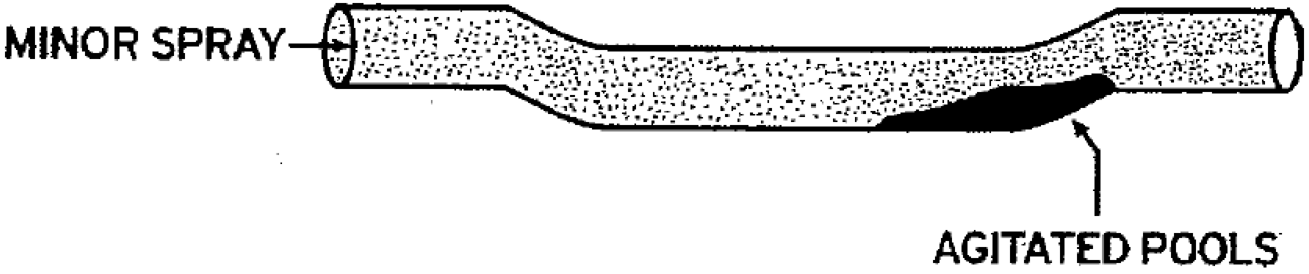
Stratified " Laminar"

- Most of the water drops out very quickly and pools
- Flow regime exist normally between 0 to 7 ½ feet / second
- Often significant corrosion threat and can be difficult to treat



Annular or “Slug” Flow

- This flow regime exist between velocities of 7 ½ - 15 ft / second.
- Pipelines with velocities in this flow regime experience water wetting of the entire pipe wall.
- Water will form a continuous line as it is pushed along the bottom of the pipeline, It will accumulate in pools at deflections in topography.



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“Annular-mist”

- Flow regime exist at Velocities between 15 ft/ second and 25 ft/second

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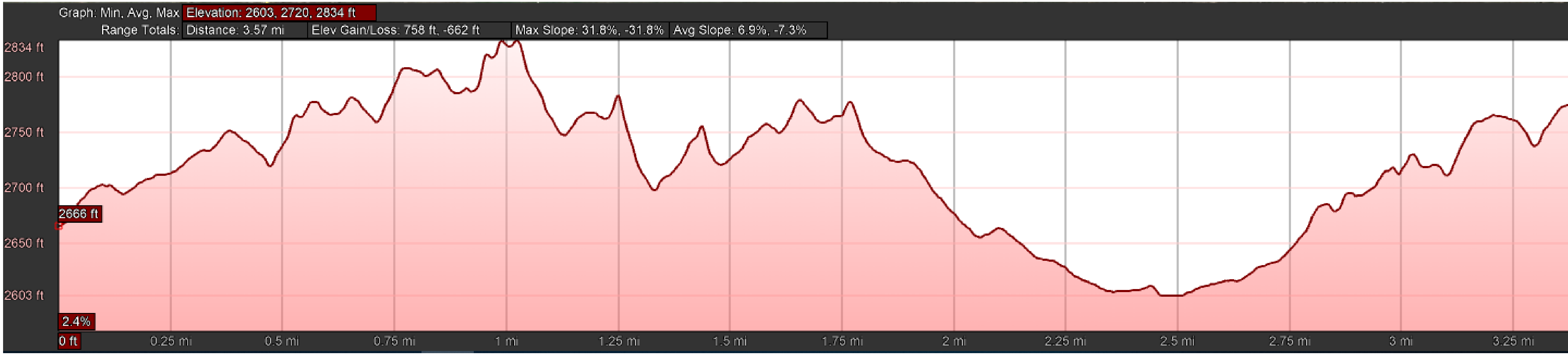
Topography

- Elevation changes increase the potential for water hold up
  - Increases as velocity decreases
- Velocity review is key
- Increase pigging frequencies on lines where water hold-up potential is greatest
  - Dewatering chemicals can be utilized when pigging is not applicable

Topography



Graph: Min, Avg, Max
Elevation: 2603, 2720, 2834 ft
Range Totals:
Distance: 3.57 mi
Elev Gain/Loss: 758 ft, -662 ft
Max Slope: 31.8%, -31.8%
Avg Slope: 6.9%, -7.3%
2834 ft
2800 ft
2750 ft
2700 ft
2650 ft
2603 ft
2666 ft
2.4%
0 ft
0.25 mi
0.5 mi
0.75 mi
1 mi
1.25 mi
1.5 mi
1.75 mi
2 mi
2.25 mi
2.5 mi
2.75 mi
3 mi
3.25 mi

Bacteria

- Sulfate Reducing
  - Generate H_2S
  - Generate solids – iron sulfide, biofilms (under-deposit corrosion)
  - Typically Anaerobic
  - Pitting type corrosion

Bacteria

- Acid Producing
  - Produce acids – fatty acids, acetic acid, formic acid and other organic acids
  - Can coexist with other types of bacteria
  - Can cause rapid pitting
  - Aerobic and or Anaerobic
  - Pitting type corrosion

Bacteria

- Slime Forming
  - Produce slime that sticks to deposits
  - Can coexist with other types of bacteria
  - Aerobic and or Anaerobic
  - Slim can form a shielding layer (protective layer)

Bacteria

- Iron Reducing
  - Form tubercles – Iron deposits
  - Create concentration cells – crevice corrosion
  - Can coexist with other types of bacteria
  - Typically Aerobic
  - Pitting type corrosion

Under Deposit Corrosion

- Under deposit corrosion occurs where sand, clays, scale, corrosion by-products, biological growth or other deposits accumulate in the pipeline.
- Water trapped under the deposit becomes the electrolyte and sets up concentration cells which accelerate corrosion – Pitting.
- Frequent pigging schedule will help reduce deposits and help control under deposit corrosion.
- If the line cannot be pigged, then a penetrating type of inhibitor can be used to slow down the corrosion process.

Deposit Analysis

What caused the corrosion anomaly?

- Pitting morphology – shape and characteristics
- pH of the pit.
- Deposit Analysis – What does it tell us?

Simple Deposit Analysis

- Iron Sulfide – Formed by H_2S and soluble iron, possible SRB’s
- Iron Carbonate – Formed by CO_2 and soluble iron, possible APB’s
- Iron Oxide – Formed by oxygen and soluble iron, possible methanol injection
- Calcium Carbonate, Calcium Sulfate, Barium Sulfate, Strontium Sulfate, ect
    - Water formed scales that may precipitate with temperature changes, or mixing of incompatible waters
- Sand, Silt, Clay – Formation fines that come from producing wells.

Know your system

- Transmission - Gas
  - Typically larger lines moving larger volumes
  - Typically Dry = $\leq$ 7 lbs / mmcf
  - Coupon placement is intentional?
- Gathering
  - Lines are typically wet
  - Velocities change
- Storage
  - On demand or seasonal
  - Injection and withdrawal can be same well
- Distribution
  - Always dry
  - Rarely internal issues

Know your system

- Transmission Lines
  - Typically will fall under ***PHMSA*** (Pipeline Hazardous Materials Safety Administration) "regulated lines"
    - Smart pigged or hydro tested periodically – 7 to 10 yrs
    - *chemical batch* and pigging to clean pipe before running in-line inspection tool
- Gathering
  - Lines are typically water wet with corrosive conditions that *need chemicals*
  - Run CO_2, H_2S partial pressure, look for O_2
- Storage
  - Typically wet with varying degrees of corrosivity – *need chemicals*
- Distribution
  - Rarely internal issues – *no corrosion chemicals*
  - *https://www.ksn.com/news/local/ntsb-shares-update-on-hutchinson-gas-explosion-investigation/*
  - *https://www.youtube.com/watch?v=QEsHkF5QxCc*

Know Your System

- Identify the corrosive constituents and environment of the product your moving – **Oil / Condensate, NGL**
  - Sulfur content - <0.5 wt% classified as sweet
  - TAN total acid number - >1.0 mg is considered high for crude oil
    - A measure of the corrosiveness of the crude due to acids, mostly naphthenic acids
    - Based on the mg of potassium hydroxide required to neutralize one gram of crude
  - Paraffin/Asphaltene content
  - BS&W content
  - Bacteria
  - Continual or intermittent flow
  - Flow velocities when pumping
  - General topography – where are the low spots
  - History of leaks
  - Solids Analysis

Know Your System

- Identify the corrosive constituents and environment of the product your moving – **Gas**
  - CO_2, H_2S, O_2 content
  - Water content – lbs/mmcf
  - Bacteria
  - Flow velocities = Flow pattern (where’s the water)
  - General topography – where are the low spots – water and deposits
  - History of leaks / cut-outs
  - Solids analysis

Know The System

- Maps of the system with topographic
- Line origin
- Inlets – Laterals feeding the line
- Line sizes and lengths
- Flow rates
- Pressures
- Delivery points

Monitor at a Minimum

Chlorides

- Periodic check of the salinity of the water

pH

- Corrosivity of the water

Deposits

- Periodic analysis of deposits tell us what the corrosion by-products are

Bacteria

- Planktonic and Sessile

Coupons

- Corrosion rates – general mpy and pitting mpy