Water Reuse, a Boon or a Bane

Boundaries of Wastewater Treatment and Corrosion

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Water Reuse And Corrosion

- Water Reuse (The Boon)
  - Minimise: Increase productivity
  - Reuse: Decrease resource and energy consumption
  - Produce: New product bioplastic out of wastewater
- Corrosion (The Bane)
  - Forms of water corrosion
  - Practical examples

Agenda

- Benefit of Water Reuse
- Corrosion
- Cases

Case I -	Reuse of process condensate for desalter: Acidity
Case II -	RO permeate: Oxidation
Case III -	RO concentrate: Chloride induced Pitting
Case IV-	Cycle of concentration cooling tower: Crevice corrosion

Water Reuse

- Minimise: Increase productivity
- Reuse: Decrease resource and energy consumption
- Produce: New product bioplastic out of wastewater

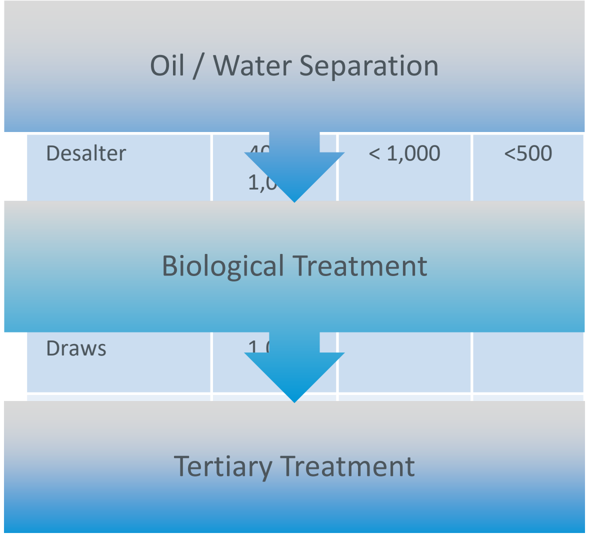
Minimise at Source

Reuse

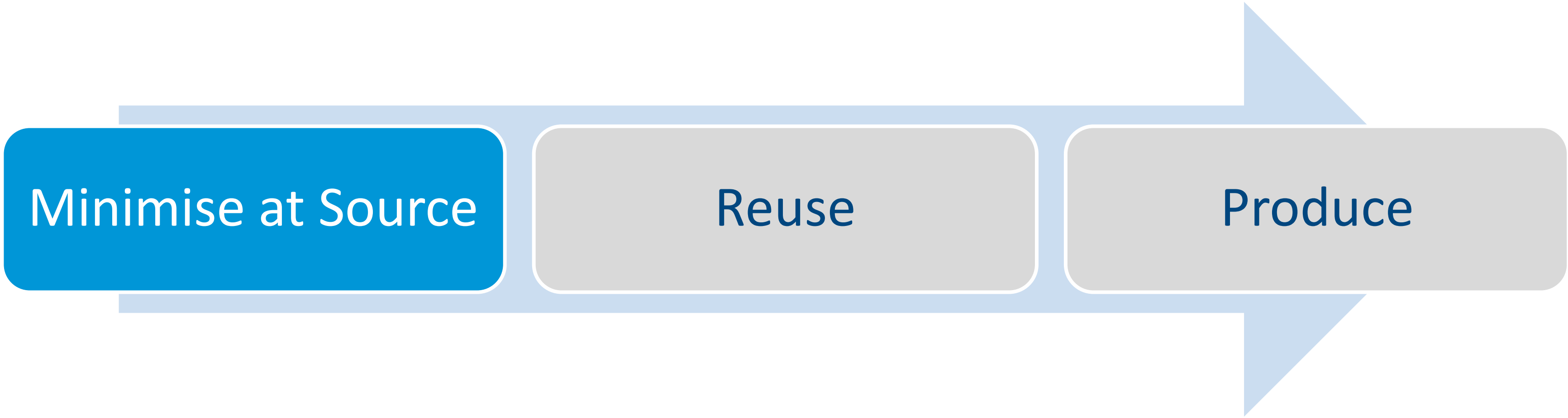
Produce

Introduction

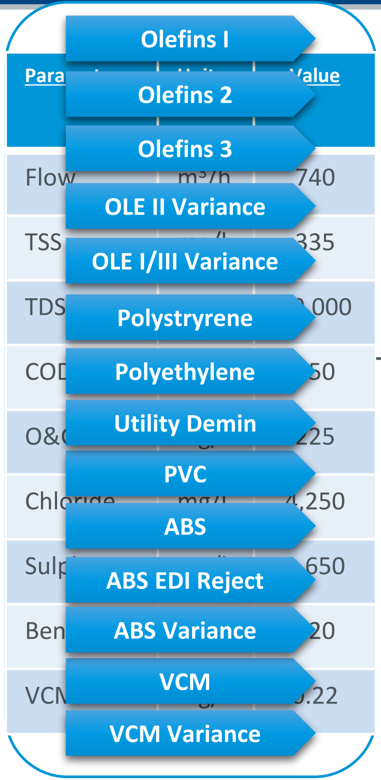
- Wastewater treatment or water reuse projects
  - **Current focus** on “End-of-Pipe” approach
- Why not take one step back?
- Pollutants
  - **Current mindset:** Something to get rid off
  - **Future mindset:** Potential resources

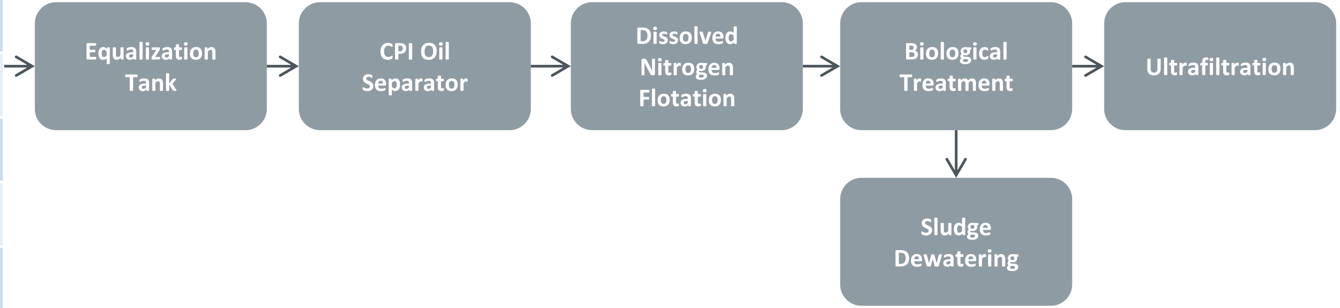


Minimise at Source



Minimise at Source





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Minimise at Source

- Olefins I
- Olefins 2
- Olefins 3
- OLE II Variance
- OLE I/III Variance
- Polystryrene
- Polyethylene
- Utility Demin
- PVC
- ABS
- ABS EDI Reject
- ABS Variance
- VCM
- VCM Variance

Low Total Dissolved Solids (TDS) and Moderate Total Organic Carbon (TOC)	Require Oil and Volatile Organic Carbon (VOC) Removal
Clean enough for disposal without any kind of treatment	No treatment
High TDS content that have little or no organic load	Require Salt Removal

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Minimise at Source

- Minimize use of cooling water by shifting duty to air cooling
- Reducing Cooling Water Duty with Process Design Changes
- Eliminate Fresh Cooling Water Consumption
- Reduce Live Steam Injection

Minimise at Source

- Take ownership of water systems
- Identify and analyse the source
- Invest in improvement projects
  - Optimisation of factory processes
  - Increase of efficiency
  - Not creating needless waste

Reuse

Minimise at Source → Reuse → Produce

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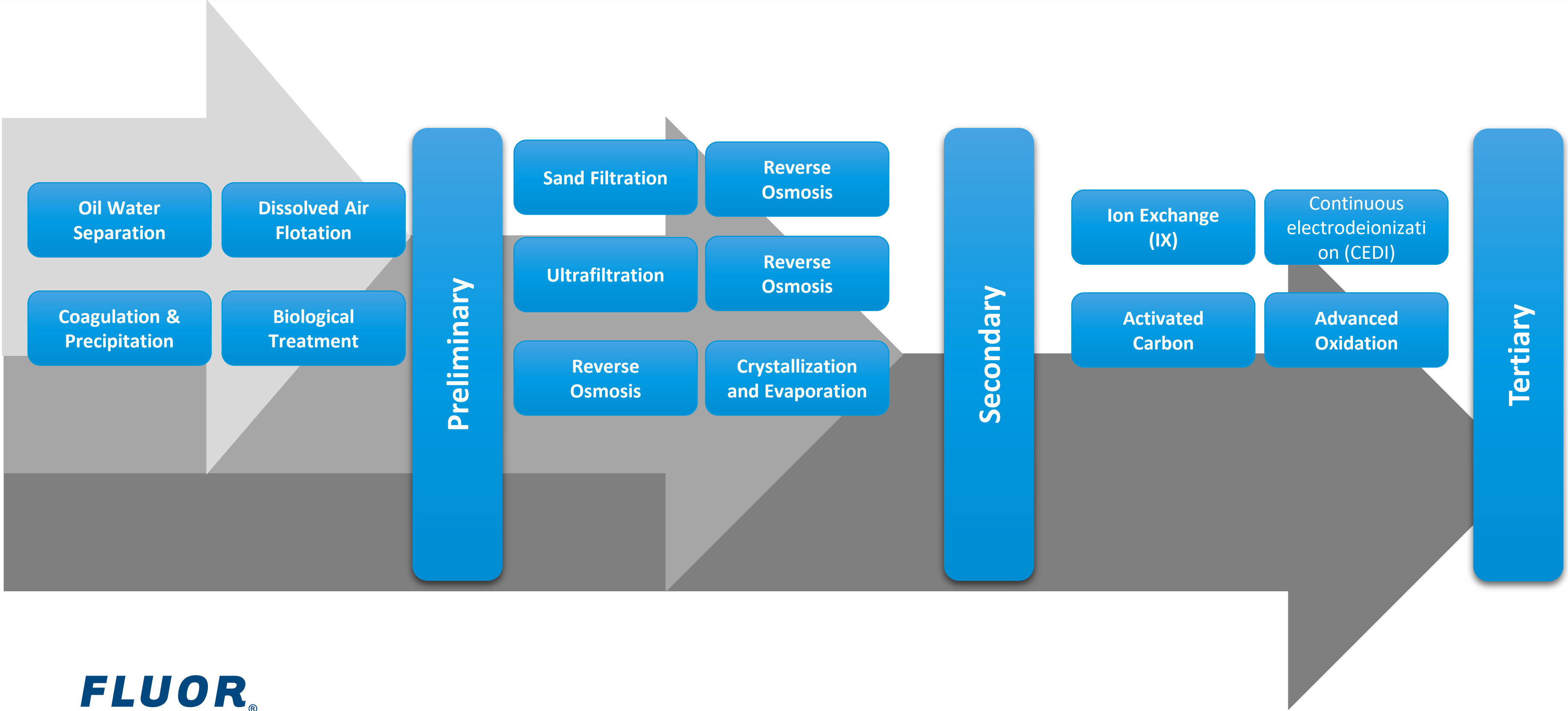
Reuse


Oil Water Separation
Dissolved Air Flotation
Coagulation & Precipitation
Biological Treatment
Preliminary
Sand Filtration
Reverse Osmosis
Ultrafiltration
Reverse Osmosis
Reverse Osmosis
Crystallization and Evaporation
Secondary
Ion Exchange (IX)
Continuous electrodeionization (CEDI)
Activated Carbon
Advanced Oxidation
Tertiary

Reuse

- Water Pinch Analysis
- Identify Source and Sink
- Analyse opportunities either with or without treatment

Produce

Minimise at Source

Reuse

Produce

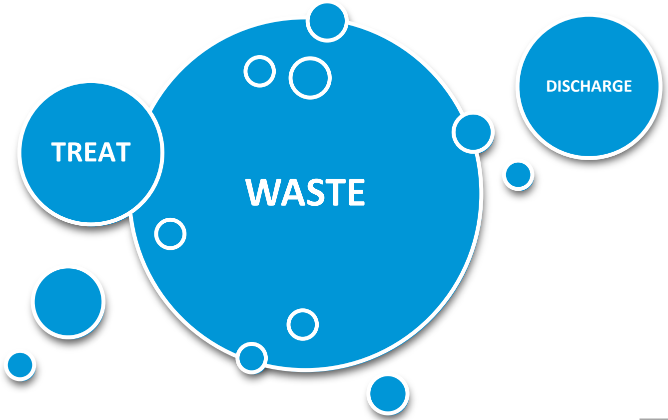
Produce

As a potential feedstock

- Biodegradable organic fraction present in wastewater
- Ways to produce value-added products
- Bioplastics : PHA - Polyhydroxyalkanoates

Remediation of Wastewater

- An energy-intensive process
- Increases the economic burden on industry
- The regulatory need for wastewater treatment before disposal



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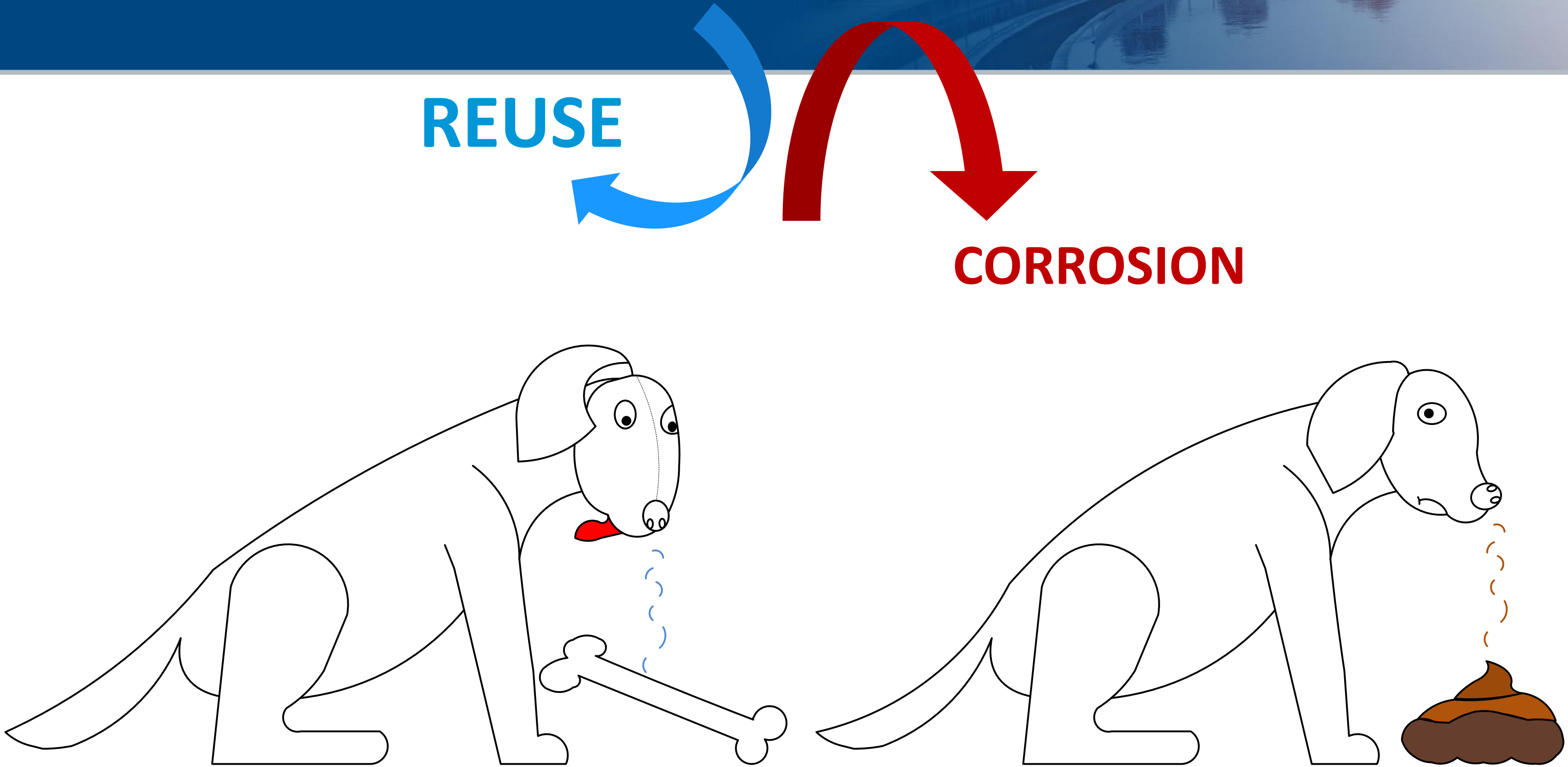
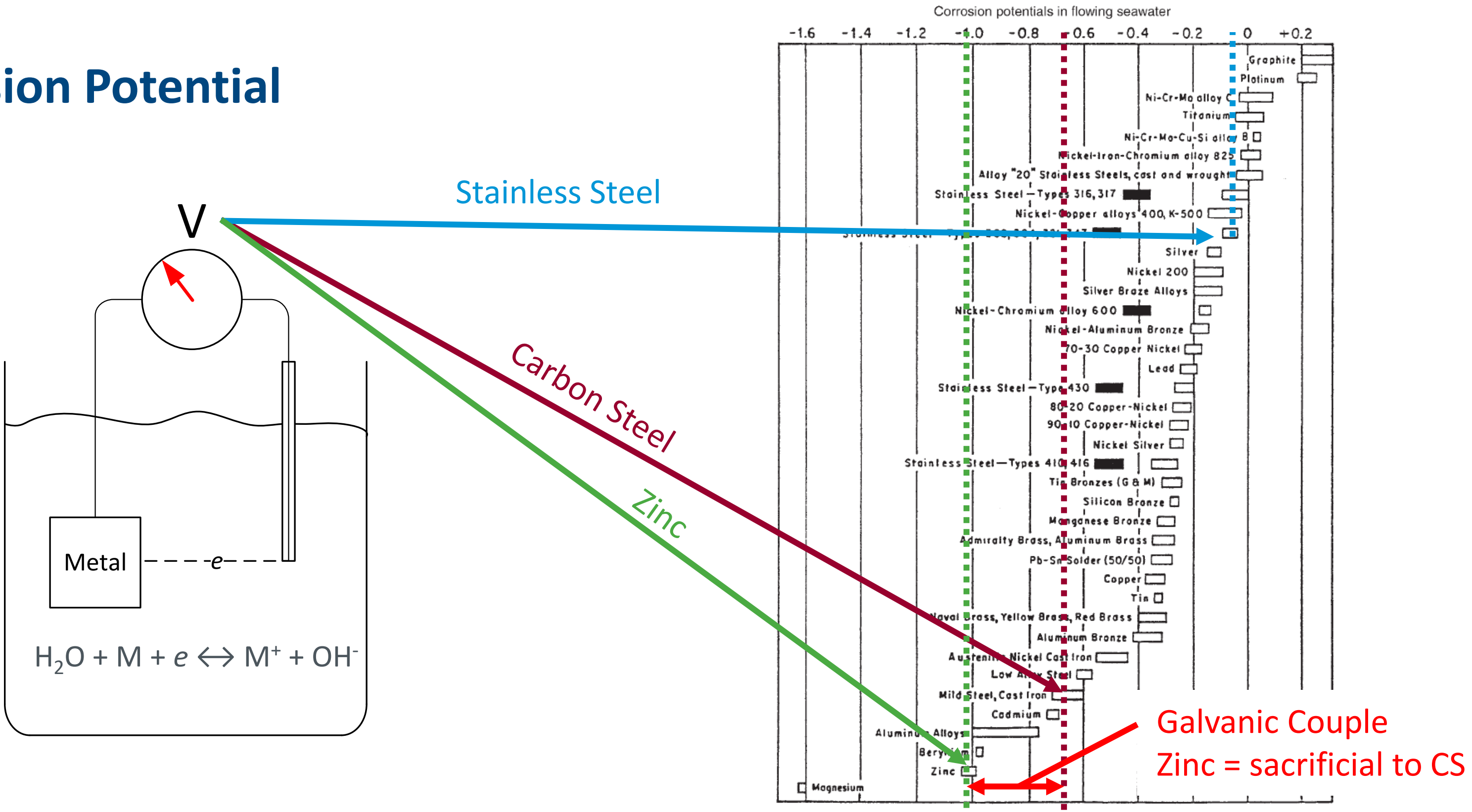

REUSE
CORROSION

Corrosion

Electrochemical Corrosion

Free Corrosion Potential



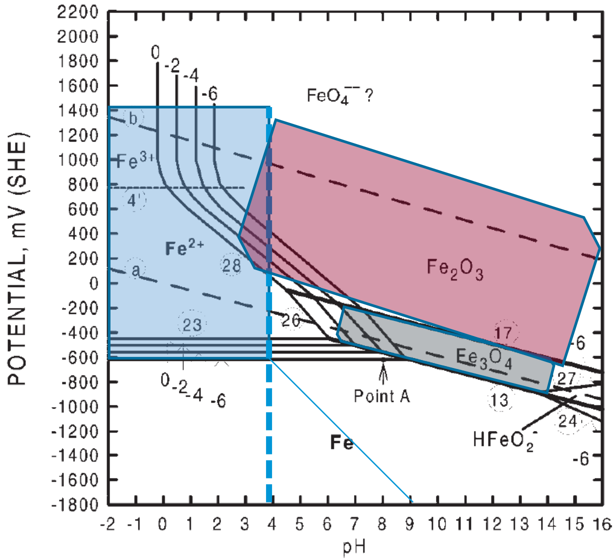
Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

Corrosion reactions

Aqueous oxidation reactions

- Ferric hydroxide
  $xFe + yH_2O\ z(+O_2) + we \rightarrow qFe^{2+} + rOH^-$
- Rust (Hematite)
  $2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$
- Black scaling (Magnetite)
  $3Fe^{2+} + 4H2O \rightarrow Fe_3O_4 + 8H^+ + 2e$

Pourbaix diagram



Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

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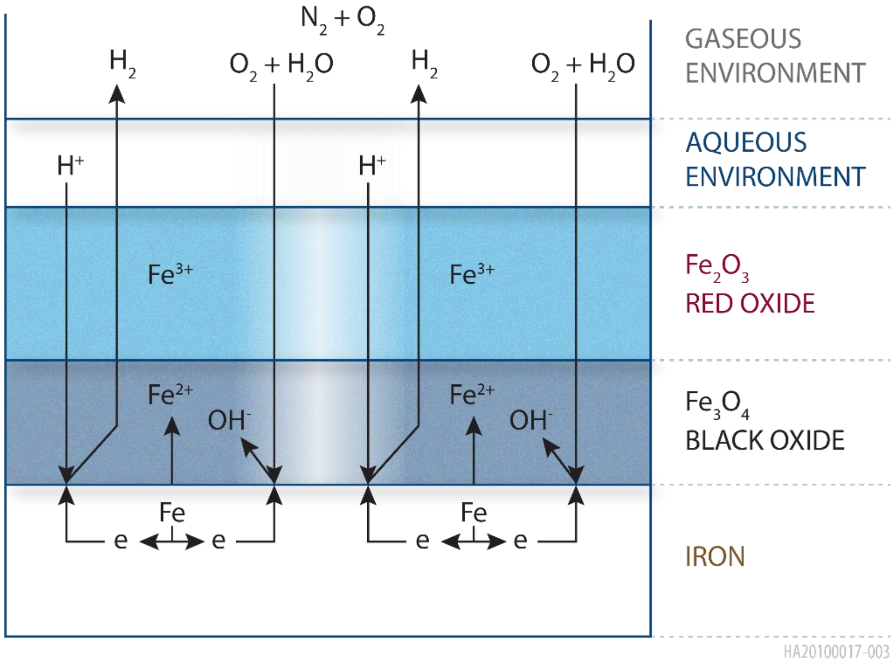
Oxide film

Stable Oxides

- Fe_3O_4 Black Oxide
- Chromium-Oxide
  Stainless Steel
- Titanium- and Aluminum -Oxide

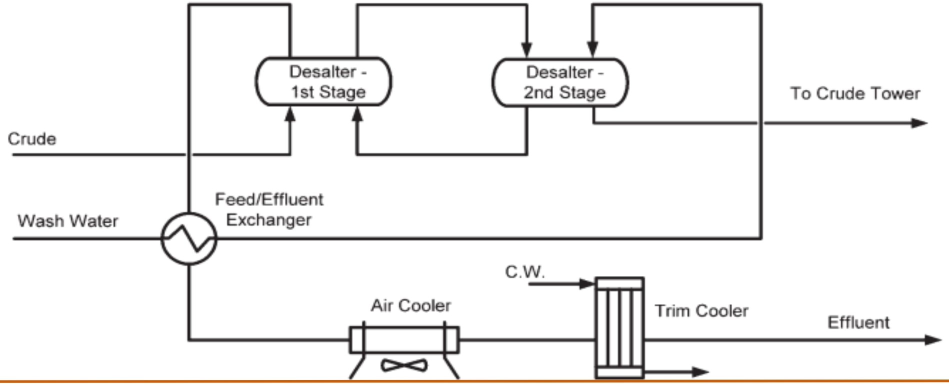
Unstable Oxides

- Fe_2O_3 Red Rust
- Sacrificial dissolving zinc anode



Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

Case I - Reuse w/o Treatment
Reuse of process condensate for desalter Acidity



Desalter Wash Water

Fresh water

Recycled crude tower overhead

Recycled vacuum tower overhead

Recycled stripped sour water

NH_4

H_2S / HCl

HC's

Phenol

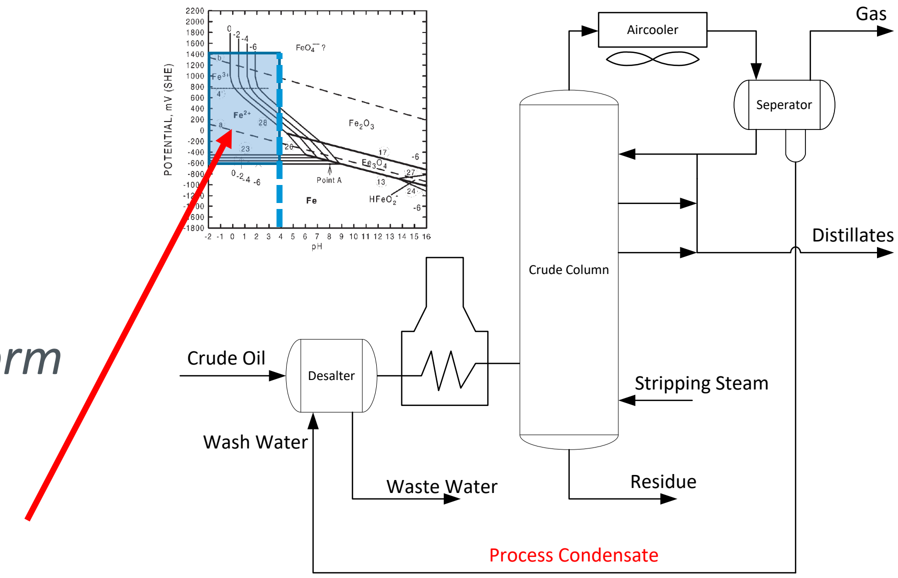
Case I - Reuse of Process Condensate

Acidification

- Beneficial to reuse process condensate for wash water
- Normal pH>4 = No Corrosion

- Insufficient desalting → HCl
  Thermal cracking of hydrogen form HCl gas
- Acidic condensate = Corrosion

Reuse of sour water for desalination



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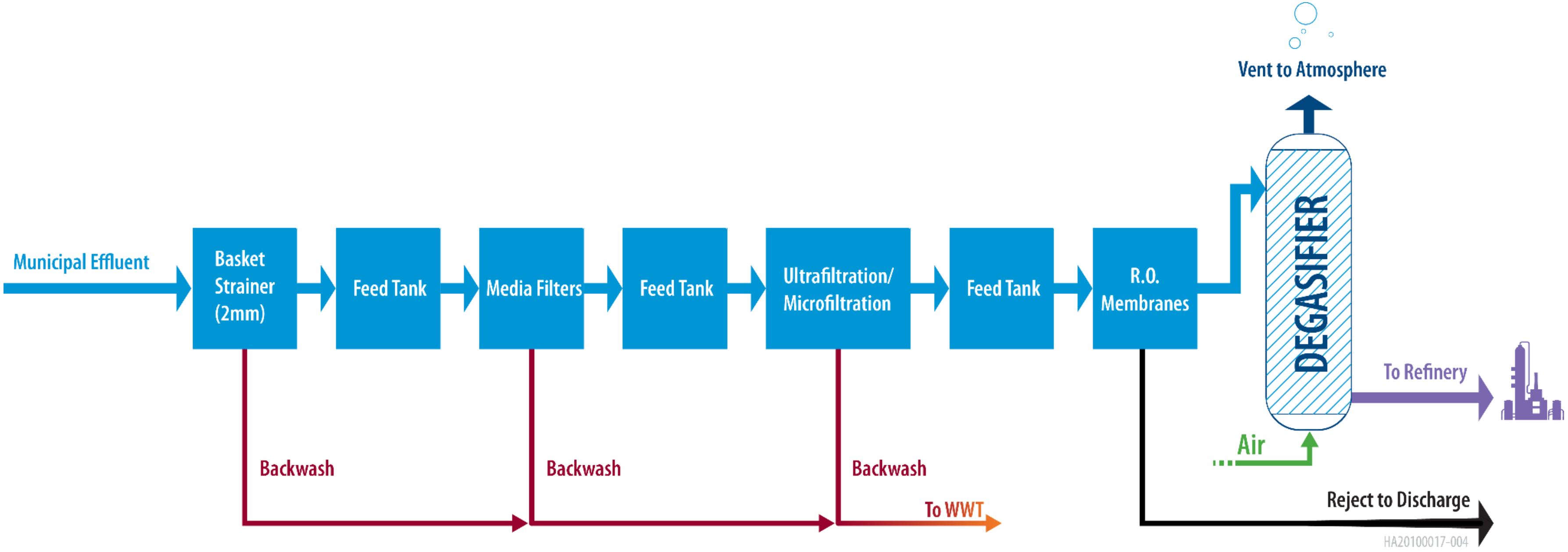
Case II - Reverse Osmosis Permeate



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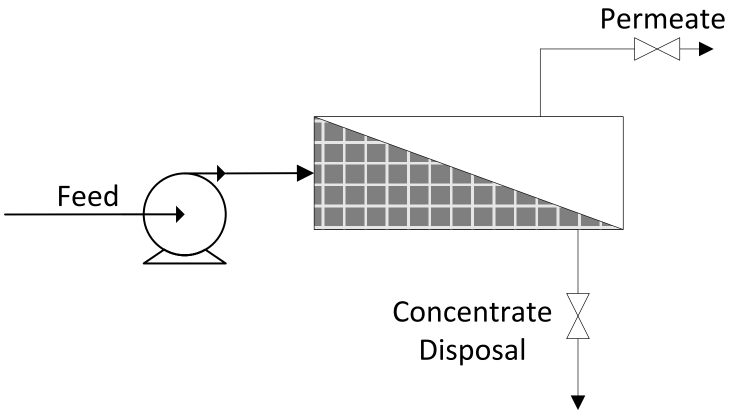
Case II - Reverse Osmosis Permeate
Oxidation



Permeate

Recycled as Cooling Tower Make up

Recycled as Process Water

Traces of NH_4

CO_2

O_2

Aggressive (no Ca and Mg)

Reverse Osmosis (RO) Permeate Water

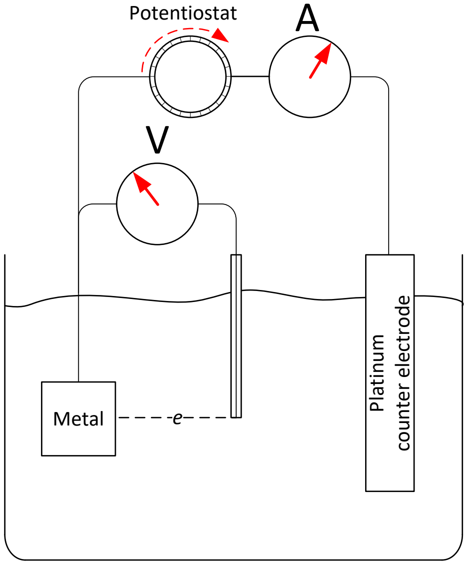
- Extreme low in dissolved ions (*Low TDS / hungry water*)
- Aerated water
- Very corrosive to carbon steel

Corrosion prevention by

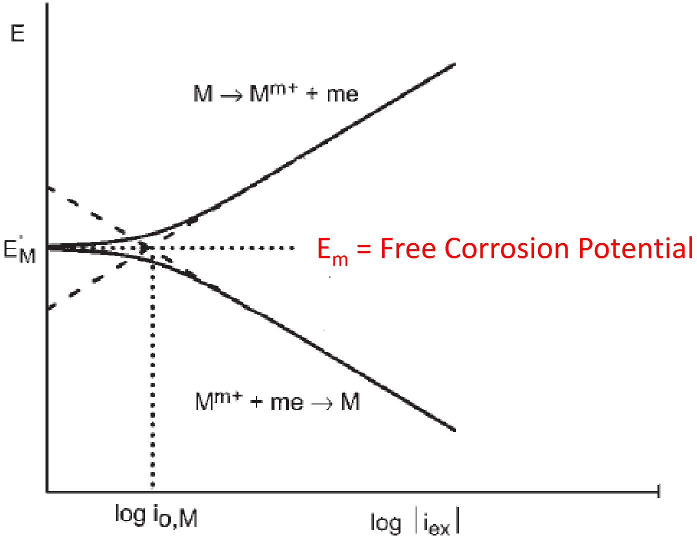
- Deaerating, or
- Saturate with Calcium Carbonate (*Limestone, Langelier Index*)

Corrosion Kinetics

Electrochemical Polarization



Charge-Transfer Polarization Curve

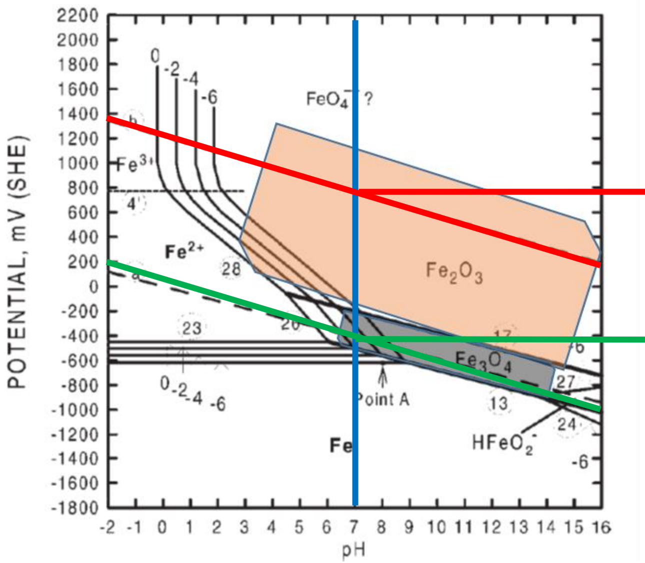


Current Density measured = Corrosion velocity

Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

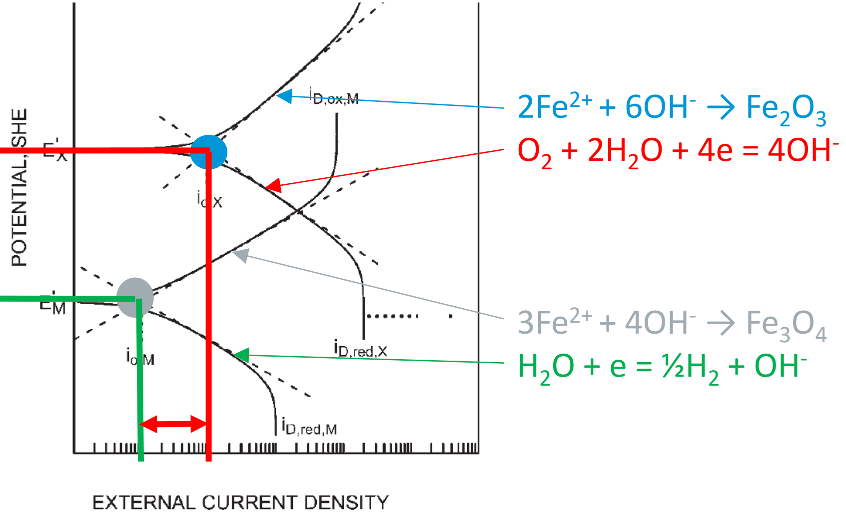
Aeration

Aerated vs. Deaerated



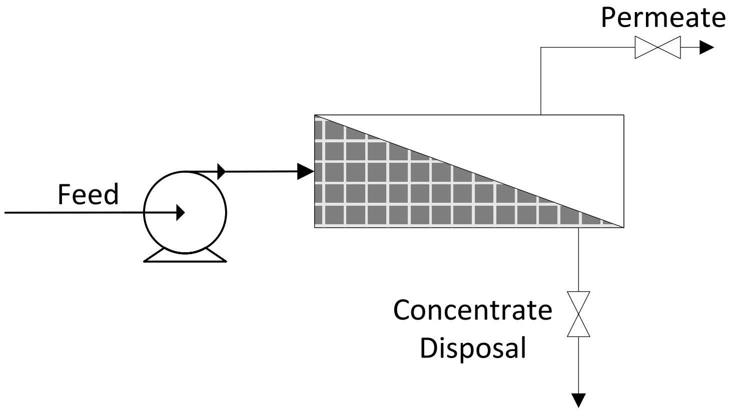
Indicative difference corrosion activity

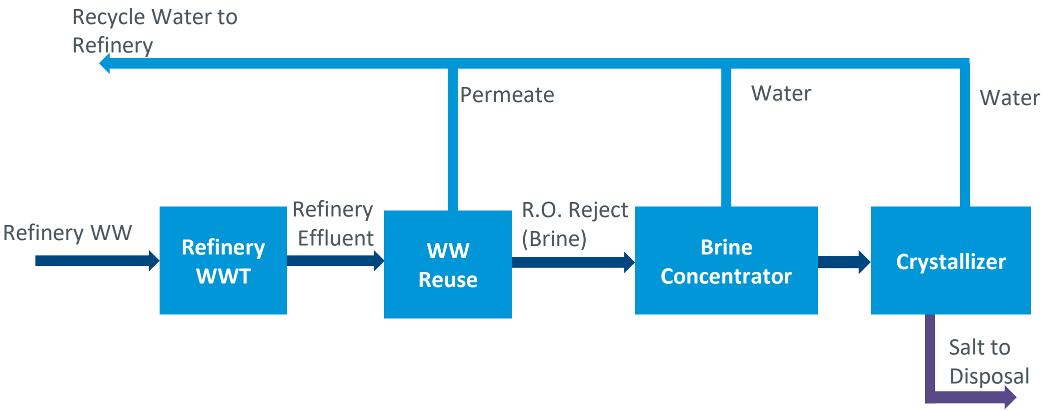
Hematite vs. Magnetite



Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

Chloride induced pitting





Concentrate

Disposal

Evaporators and Crystallizers

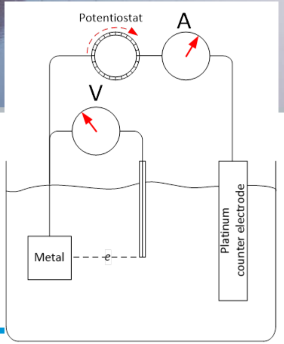
Chloride

High Total Dissolved Solids

Reverse Osmosis Concentrate

- Chloride induced corrosion
- Chlorides require expensive alloys
  - Especially for the evaporator of zero liquid discharge installations

Stages of Oxidation



Transpassive - Dissolving

Passive - (Stable)Scaling

Reducing area

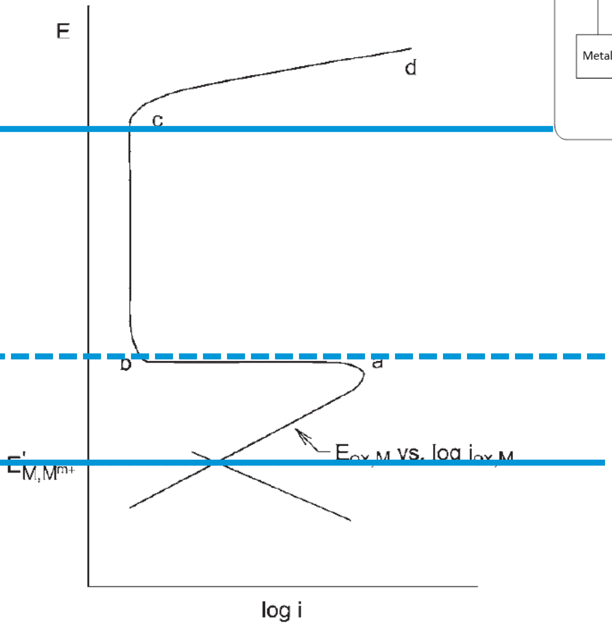


Fig. 3.3 Anodic polarization curve representative of active/passive alloys. Oxide films forming in the potential range a to c cause a decrease in current density.

Polarization curves of different metals

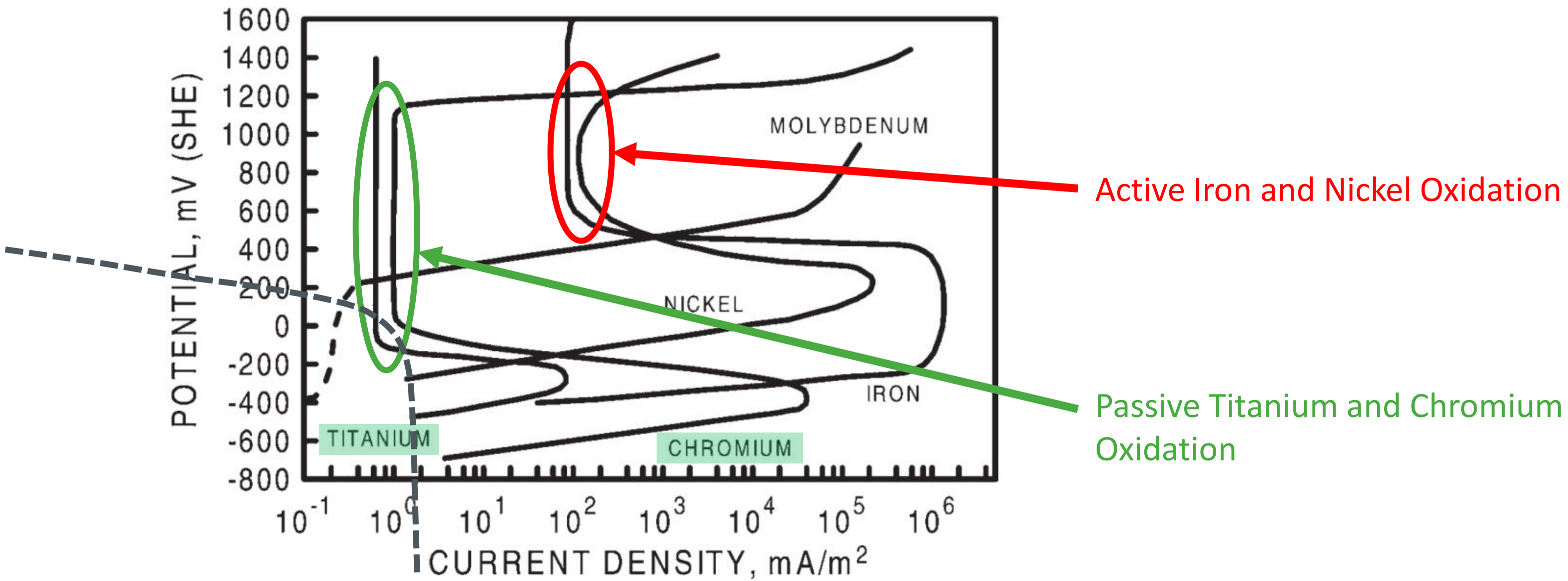
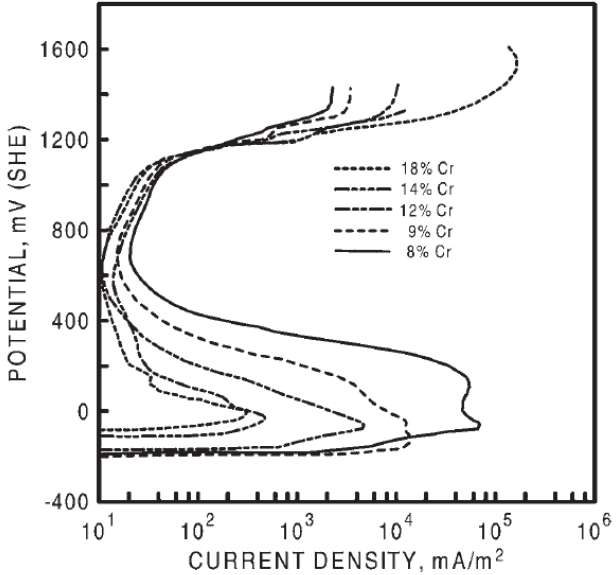


Fig. 5.20 Representative anodic polarization curves for indicated pure metals in 1 N H_2SO_4, pH = 0.56. Linear sections at lower potentials are representative of Tafel behavior. Redrawn from Ref 5, 10–14

Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

Polarization of Stainless Steel

Effect of alloying Chromium to Steel



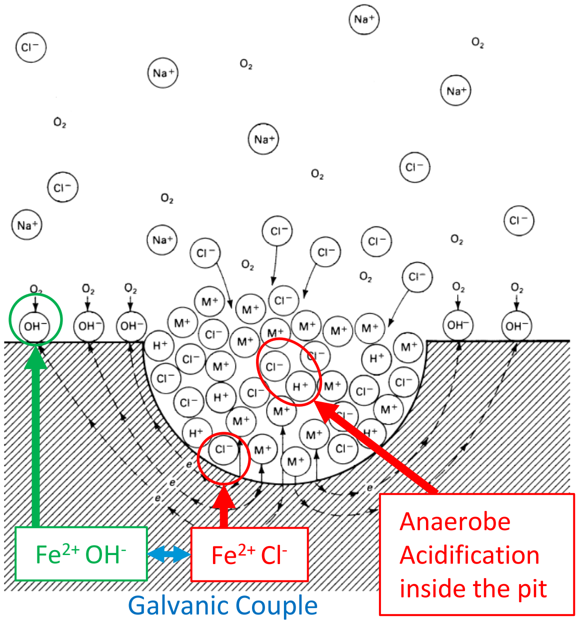
Ref. ASM, E. Stansbury, fundamentals of electrochemical corrosion

Stainless

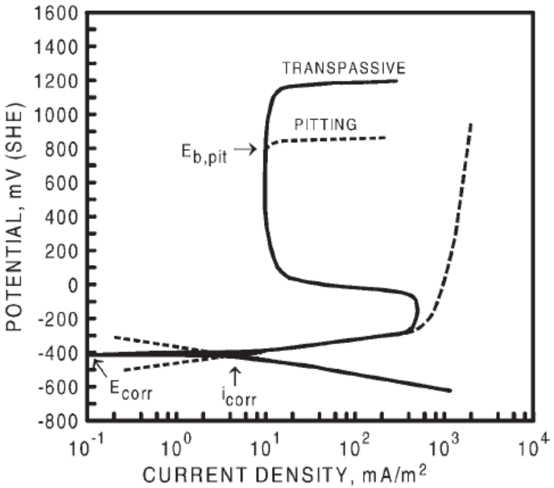
- ≥12wt% Chromium
  - Ferrite *(magnetic), or*
  - Martensite *(hard & brittle)*
  - 400 series
- ≥18wt% Chromium min. 8wt% Nickel
  - Austenite *(ductile not magnetic)*
  - 300 Series
- ≥21wt% Chromium min. 4wt% Nickel
  - Duplex *(50/50 - ferrite/austenite)*
  - Economical *(strong, low in expensive Ni)*

Chloride Induced Pitting

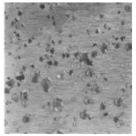
Localized breakdown of passive oxide scaling

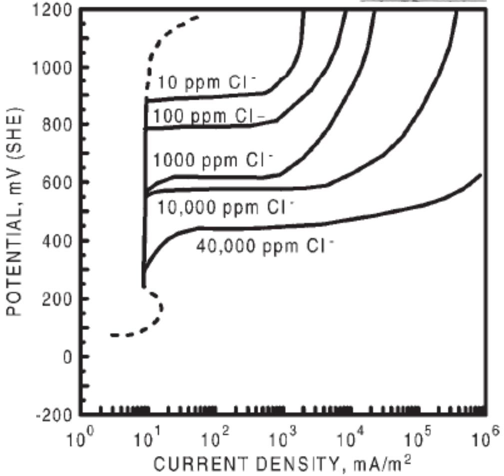


Ep = Pitting Potential



Effect Cl^- onSS 304





Ref. ASM, S. Lampman, Corrosion in the petrochemical industry & ASM, E. Stansbury, fundamentals of electrochemical corrosion

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Pitting Resistance Stainless Steel

PREN = Pitting Resistance Index

PREN = Cr + 3.3Mo + 16N (wt%)

SS 304	PREN = 18
SS 316	PREN = 24
SS 317	PREN = 28
Duplex 2205	PREN = 35
Super Duplex	PREN = 43
254SMO	PREN = 43

Pitting resistance vs. Temperature

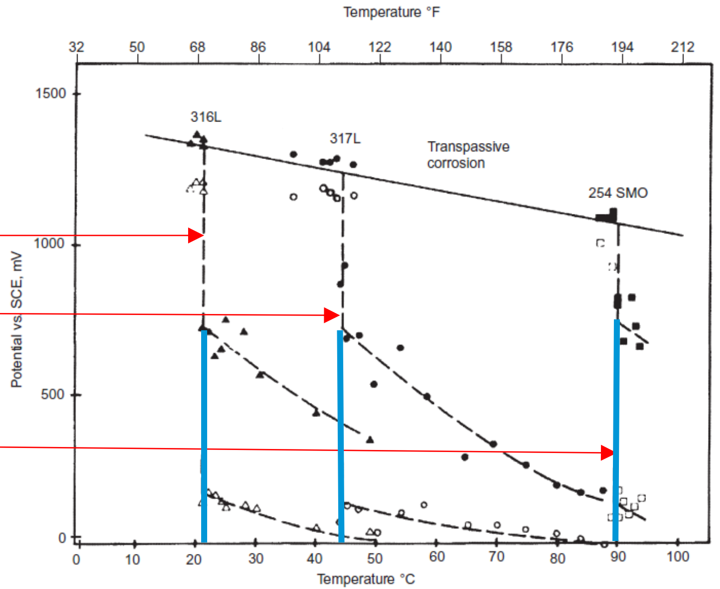
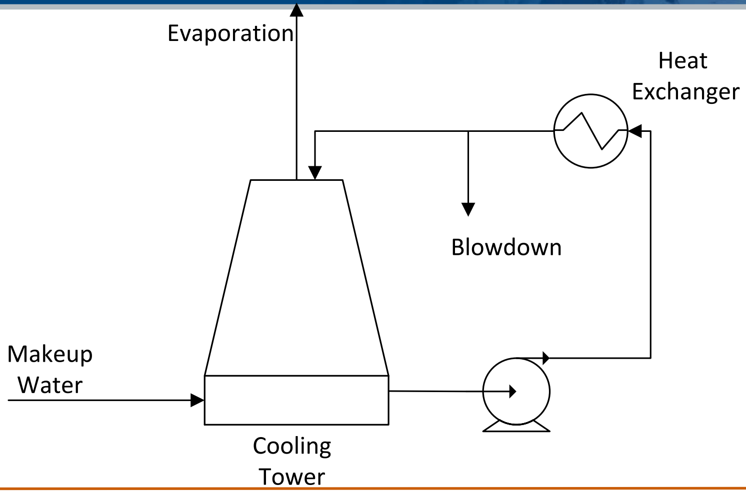


Fig. 4 Pitting (filled symbols) and repassivation (open symbols) in 1 *M* NaCl as a function of temperature for different grades of stainless steel. SCE, saturated calomel electrode. Source: Ref 40

Ref. ASM, S. Lampman, Corrosion in the petrochemical indust

Case IV – Cooling Tower Max. Cycle of Concentration

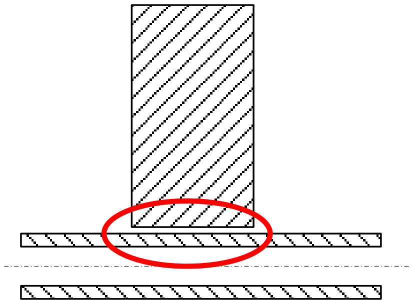


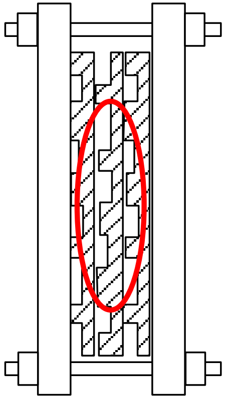
Recycled as Cooling Tower Make up

Chloride
Calcium Content
Aggressive anions
PO_4
Alkalinity

Cooling Tower Water and increased cycle of concentration

- Increased Chloride concentration
- Creates problems in areas of crevices, such as:
  - Plate and Frame Heat exchangers
  - baffle-tube protrusions of Shell and Tube Heat exchangers





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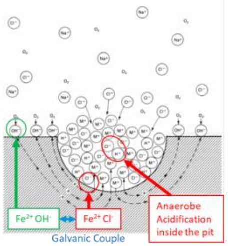
Crevice Corrosion

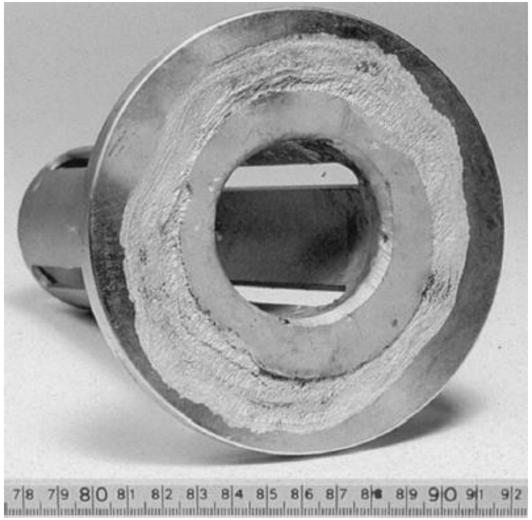


Accelerated pitting / transpassive corrosion

- <<Temperature than pitting
- Anaerobe electrochemical cell
- Acidification because of water dissociation causing H^+ formation

Preventive measures

- Cooling Water Channel Side
- Upgrade to Super Duplex, 254SMO or Ti



Crevice corrosion under seal in type 316 stainless steel sieve from steam condenser cooling water system exposed to flowing seawater for two years at less than 40 °C (104 °F). Source: Ref 3

Ref. ASM, S. Lampman, Corrosion in the petrochemical industry

Summary, Water Reuse, The Bane of Corrosion

1. Reuse of process condensate for desalting and acid corrosion
2. RO permeate and general oxidation
3. RO concentrate and chloride induced pitting
4. Cycle of concentration cooling tower and crevice corrosion

Thank you

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