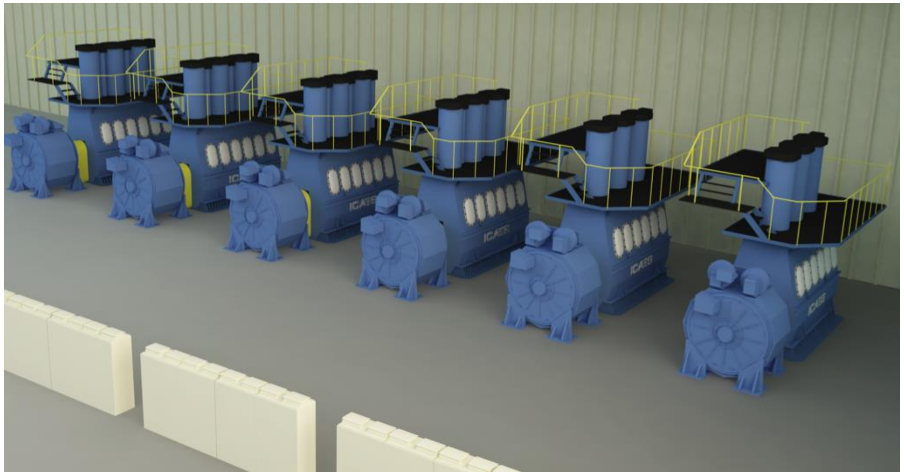
SustainX
SMARTER ENERGY STORAGE

ICAES

Corrosion Omnibus

Last update: 2014-03-19



Corrosion Overview

- Process Conditions
- Inhibitors
- Corrosion Fundamentals
- 2012 coatings testing
- Experience
  - Sunapee
    - P:\SUNAPEE\Corrosion\20140311_SPEMetalsCorrosion.pptx
    - P:\R&D\WaterManagement\2014-02-03 Corrosion Update.pptx
  - 2012 corrosion testing: \\10.233.152.26\Projects\Demo\R&D\CorrosionPrevention\WeeklyMeetings\20120730 CorrosionOverview.pptx

FYI

- Check notes for sources
- Wiki:

Date Added/Modified: 2014-03-19

Corrosion Prevention – 13 March 2014

- **SustainX process environment**: *compressor/expander using an air & water mixture*
  - Air ranging pressures: 0-3000 psi
  - Pressure cycling:
    - In high pressure storage: ~hourly, 850-3000 psig
    - In reciprocating piston cylinders: ~2Hz, 0-250 psig & 250-3000 psig
  - Elevated & cycling temperatures
    - 10°C to 70°C
    - High temp (70°C) and high pressure in air storage
  - A variety of wetted materials and metals → → →
  - Intermittent daily duty cycle – several of hours of operation, several hours of stand-by
  - Water and air migrate together:
    - *Compressions* push both into high pressure storage (water quality measurement & control become difficult)
    - *Expansions* vent air and push water into atmospheric storage (water quality measurement & control are much easier)
  - Every compression breathes in fresh air → oxygen and CO_2 replenished every compression cycle (scavenging will be difficult)
  - Water is chemically treated, some surfaces are coated or treated
- Current corrosion prevention: water treatment
  - Quaker's Quintolubric 807-WP (water hydraulic fluid: corrosion inhibitor & biocide) w/ Stepan's BioSoft D-40 (surfactant)

Wetted Metals and Locations

- Piping - A106 Gr B
- ANSI CS Flanges - A105
- MPV – A234 WPB
- Storage - SA-372
- LPC Head – 1050
- LPC Piston – anodized Al 6061
- LPC - chromed 1045
- HPC Head – 4340
- HPC Piston – 1050
- HPC Rod – 1050
- Bore – A106 C
- Valve Stem – Titanium, hardened
- Valve Poppets – Titanium
- Valve Seats – 4340

Cortec Inhibitor Corrosion Rate Data

Electrochemical Study of the Effectiveness of VCI-646, VCI-649 and S-69 Tap Water

Material	Corrosion rate (mpy)	Protection power (Z%)*	Corrosion Potential (mv)
Control (Tap water)	5.361	-	-630
VCI-649	0.3569	93	-375
VCI-646	0.2827	95	-303
S-69	1.007	87	-378

- Our Next Gen corrosion inhibitor: *Cortec VCI 649* (aka *VpCI-649 BD*)
  - We'll use it @ 1wt% concentration
- **0.36 mils/year** or **$7.62x10^{-3}$ mm/year**
  - Measured electrochemically by Cortec
  - Carbon steel and "tap water"
- For Sunapee, this means changing HP filters every 3 ½ days
  - At best! HP storage is an aggressive environment, the corrosion rate will be higher

Study of the performance of the formulations 2, 3, and 4 in tap water. Concentration level 0.1% by mass.

Carbon Steel (Immersed)

	Time before corrosion (days)	
Material	Ambient Temperature	50°C
VCI-649	40+	40+
VCI-646	40+	40+
S-69	40+	40+

Carbon Steel (Half-immersed)

	Time before corrosion (days)	
Material	Ambient Temperature	50°C
VCI-649	40+	20+
VCI-646	40+	20+
S-69	40+	20+

Cortec VpCI & a galvanized steel cooling tower

Protection Ability Tested With Tafel Plots

Test Equipment

- Potentiostat/Galvanostat "Versastat" with corrosion software model 352/252 SoftCorr™
- Zinc working electrode
- Graphite counter electrode
- SSCE reference electrode

Test Parameters

- Tap water: pH = TDS = ppm, Conductivity = µS
- $CaCO_3$ in Tap water: pH = TDS = ppm, Conductivity = µS
- Polarization was applied 20 minutes after the working electrode was immersed in electrolyte

Sample	Corrosion Rate in Tap Water, mpy	Protection Ability, %	Corrosion Rate in 1000ppm $CaCO_3$ Solution, mpy	Protection Ability, %
100ppm VpCI additive	1.06	86.5	0.24	87.2
Control	7.8	-	1.8	-

Linear Polarization Resistance (LPR) Study

Test Parameters

- 1000ppm VpCI was added into two different types of water

90:10 Deionized : Tap water, pH 6.63; Conductivity 183µS			Tap water, pH 7.44; Conductivity 356µS		
Sample	Corrosion Rate, mpy	Protection Ability, %	Sample	Corrosion Rate, mpy	Protection Ability, %
Water with VpCI	0.2242	89	Water with VpCI	0.3924	98
Control Water	2.061	-	Control Water	17.74	-

Immersion Corrosion Test

Test Parameters

- Immersion at 40°C for 10 days

Test Solutions

- VpCI was added at 25wt% to two different water treatment program formulas (TF 1 and TF 2) both containing a blend of antiscalants (phosphates, maleates, phosphonates, acrylates) and azoles. These mixtures were then added to tap water at 2000ppm

Material	Protection Ability, %
TF 1 + VpCI additive	94.3
TF 2 + VpCI additive	94
TF 1	74
TF 2	31
Control (tap water)	-

Testing In Pilot Cooling Tower

Test Equipment

- RSD Towers, Model 005 Cooling Tower
- 16 GPM recirculation rate, 1.5 inch inlet and outlet diameter

Test Parameters

- 45-50°C tap water with 2.3-2.5 cycles of concentration
- pH = 8.6-8.8, TDS = 1250-1300ppm, Conductivity = 1850-2000µS
- Continuously treatment of 250ppm for 1 week, 100ppm for 1 week and then 50ppm during the following 6 weeks

Solution Tested	Corrosion Rate, mpy	Protection Ability, %
TF 1 + VpCI additive	0.59	89
TF 1	4.49	-

Qualitative Inhibited Corrosion Rates

Table 4: Qualitative Classification of Corrosion Rates in Recirculating Cooling Water—mpy

Metal/ Classification	Low Carbon Steel	Copper Alloys	Galvanized Steel	Aluminum	Stainless Steel
Excellent	<0.1	<0.1	< 2.0	<0.5	<0.1
Good	1.0-3.0	0.0-0.2	2.0-4.0	0.5-2.0	
Fair	3.0-5.0	0.2-0.3	4.0-8.0	2.0-5.0	
Poor	5.0-10.0	0.3-0.5	8.0-10.0	5.0-10.0	
Unacceptable	>10.0	>0.5	>10.0	> 10.0	>0.14

Table 5: Qualitative Classification of Corrosion Rates in Closed Cooling Water—mpy

Metal/ Classification	Low Carbon Steel	Copper Alloys	Stainless Steel
Excellent	< 0.2	<0.1	<0.1
Good	0.2-0.5	0.1-0.3	
Fair	0.5-1.0	0.3-0.5	
Poor	> 1.0	>0.5	>0.1

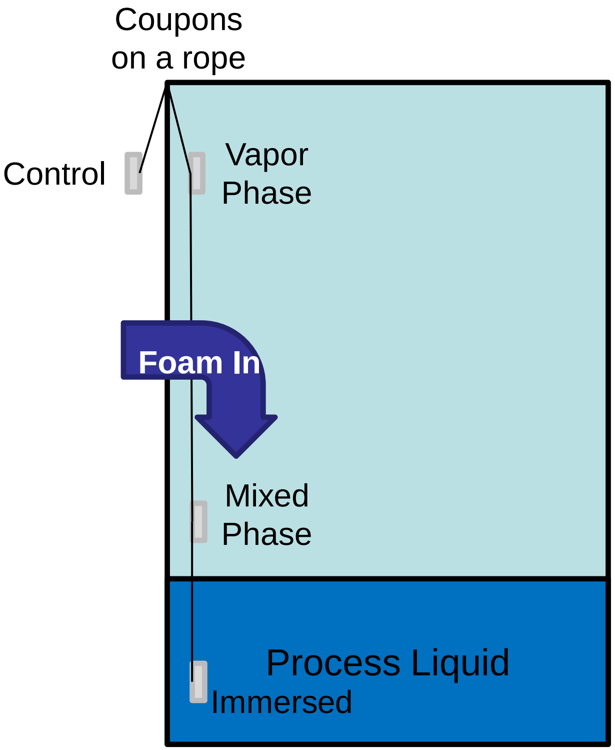
Table 6. Qualitative Classification of Corrosion Rates of Carbon Steel in a Cooling Water System

Corrosion Rate (mm/Year)	Mils /Year	Classification
<0.03	1.2	Excellent
0.03 – 0.08	1.2 – 3.2	Very good
0.08 – 0.13	3.2 – 5.2	Good
0.13 – 0.20	5.2 – 8	Moderate
0.20 – 0.25	8 – 10	Poor
>0.25	>10	Very poor

Metal	*Corrosion rate (mpy)*	*Comment*
Carbon Steel	0—2	Excellent inhibition
	2—3	Generally acceptable for all systems
	3—5	Fair
	5—10	Unacceptable, migrating corrosion products may cause fouling
Copper	0—0.1	Excellent inhibition
	0.2—0.5	Generally acceptable
	0.6—1.0	Fair
	>1	Unacceptable
Admirality	0—0.2	Generally safe for HX tubing and mild steel
	0.2—0.5	High rate and may enhance corrosion of mild steel
	>0.5	Unacceptably high, significantly affects mild steel

- **Generally, the best inhibitors limit corrosion to around 1 mil/year or less**

Racetrack & VpCI-649 BD Corrosion



- Pictured: After 10 days, process liquid of 1% VpCI-649 BD & 1% Biosoft D-40 in carbon filtered tap water.
- For reference, the previous process liquid, Quintolubric 807-WP & Biosoft, did not exhibit any visual level of corrosion i.e. liquid did not change color, for over 6 months
- X70 steel coupons hanging inside process tank on plastic twine
  - Coupons blasted, cleaned then rinsed with fresh VpCI-649BD based process liquid before testing

Racetrack & VpCI-649 BD Corrosion

Control – In lab air, outside of process tank

Vapor Phase – In "dry" top half of process tank

Mixed Phase – In splash zone of process tank

Immersed – In liquid zone of process tank

- Pictured above: After 10 days, coupons in a fresh process liquid solution of 1% VpCI-649 BD & 1% Biosoft D-40 in carbon filtered tap water. Vapor & Mixed Phase coupons exposed to foam cycles – foam filling tank during test then receding during down times

Corrosion Prevention – 30 July 2012

Purpose: evaluate protection provided by coatings (epoxies, polyurethanes, etc.)

Procedure of Coating Corrosion Test Stand

- Preparing Coupons/Test Stand
  - Add coupons to holders, load into the test stand chamber
  - Bolt on end flanges
- Water Fill
  - Fill halfway with 3L of distilled water
- Air Fill
  - Fill the chamber with 2500 psi every weeknight
- Rotate
  - Chamber is rotated overnight every weeknight
- Vent
  - Chamber vented in the morning
- Examination
  - Coupons taken out and examined on Fridays
  - Removed from racks, photographed

- **Results & Conclusions**
  - Some coatings bubble, not from corrosion underneath, but from expanding permeated air aka decompression causes disbondment of the coating

Corrosion Prevention – 30 July 2012

- 4 failures after 5 weeks

Manufacturer	Coating	Description	Chemical Class	Tensile Strength	Compressive Strength	Permeability	Elongation	Hardness
Specialty Polymer Coatings	SP-2889		Epoxy/Erethane	42.7 MPa	1.56*10^4 PSI	<0.003 (perm-in)	9.00%	85 (Shore D)
Specialty Polymer Coatings	SP-9888		Novolac (Phenol Formaldehyde Resin)					84 (Shore D)
Specialty Polymer Coatings	SP-2888		Epoxy/Erethane	44.86 MPa	1.56*10^4 PSI	<0.003 (perm-in)	4.20%	85 (Shore D)
Madison Chemical Industries	CorroPipe 3000 AM		Polyurethane			.20 Metric Perms		75 +/- 5 (ASTM D-2240 Shore D)
Madison Chemical Industries	MG120AM 3000 AM		Epoxy-Polyurethane					80 (ASTM D-2240 Shore D)
Carboline	Plasite 7159		Epoxy Coating, Polymerized with a polyamine curing agent					7159 of 113 seconds (ASTM Method D4366-84)
Tnemec	Polyurethance Spray Elastomer	No other information given	Polyurethane Spray Elastomer					
Tnemec	Elasto-Shield	Series F400 (polyurea)	Polyurea					
Tnemec		Series F061	Cycloaliphatic Amine Epoxy					
Tnemec		G340	Modified Polyamine Epoxy					
Tnemec	Series 1E77							
Tnemec	(Expoxoline Series 22)	Series 1E74	Modified Polyamine Epoxy					
Akzo Nobel	Corvel ECA-1660	GREEN 10-6051	Modified Epoxy					

Corrosion Prevention – 30 July 2012

Madison Chemical Industries

Failed Week 1

CorroPipe 3000 AM (Polyurethane)

Madison Chemical Industries

Failed Week 1

CorroPipe 3000 AM (Polyurethane)

Tnemec: Discontinued

Failed Week 1

Elasto-Shield: Series 400 (Polyurea)

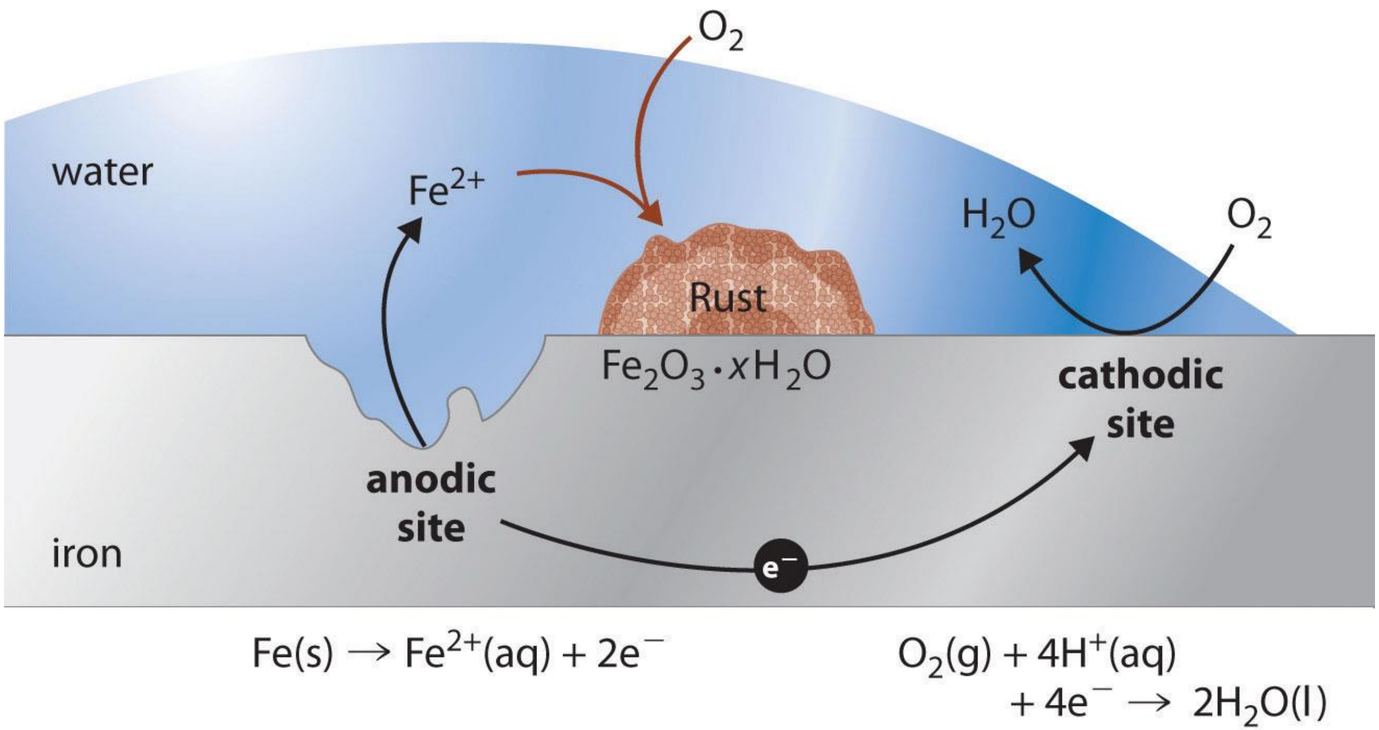
Tnemec

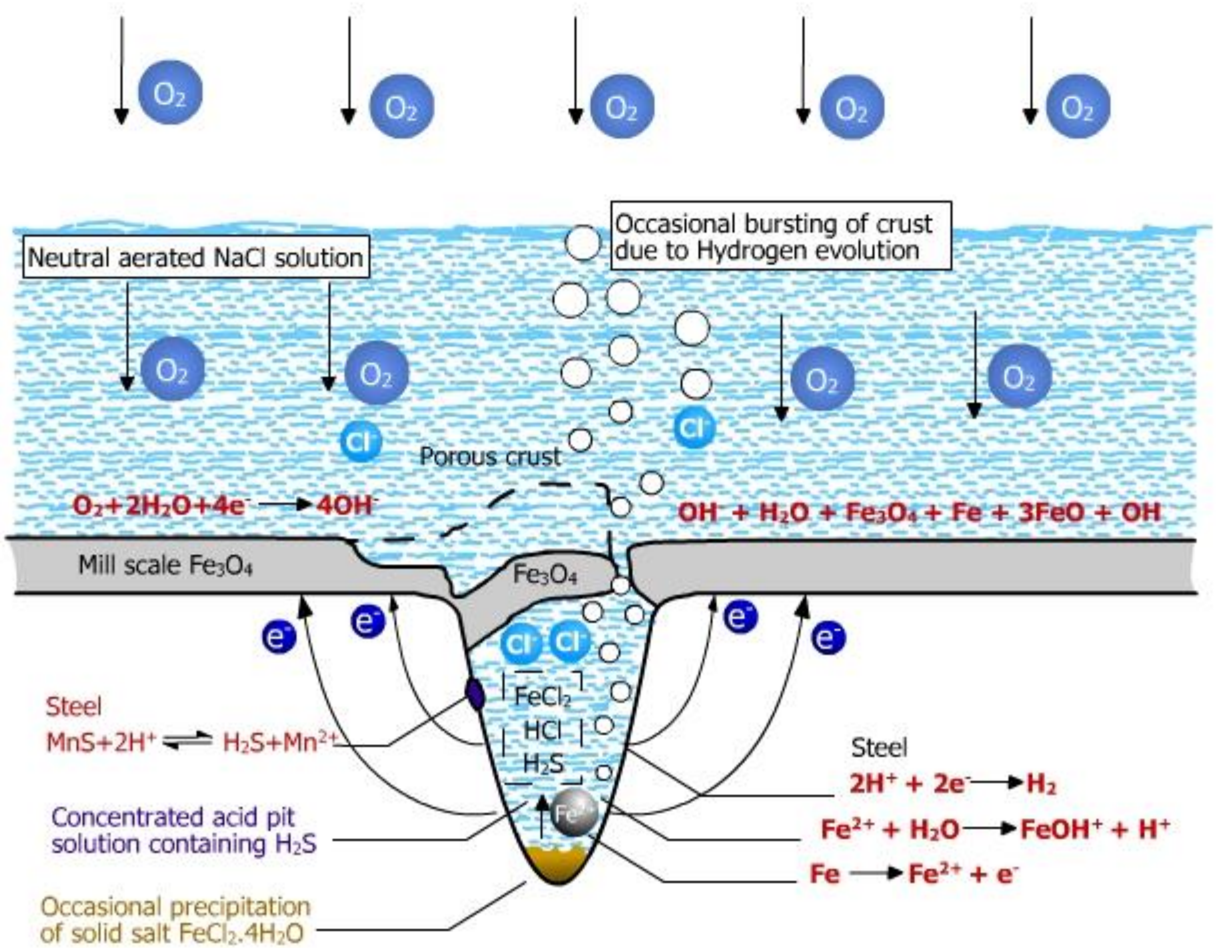
Failed Week 5

Series F061(Cycloaliphatic Amine Epoxy)

- Pitting corrosion
  - Passive films failure – local corrosive cell forms
    - Chlorides are main aggressor
  - Does Q807WP act as a film?
  - Will VpCI649BD?
    - Why did ours have chlorides in it?

  - http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s23-06-corrosion.html





Electrochemical reactions that occur when a pit is initiated at sulphide inclusion in a carbon steel.

LPR & Tafel Plots

- http://www.cosasco.com/corrosion-rate-instrument.html
- http://www.alspi.com/lprprobemenu.htm

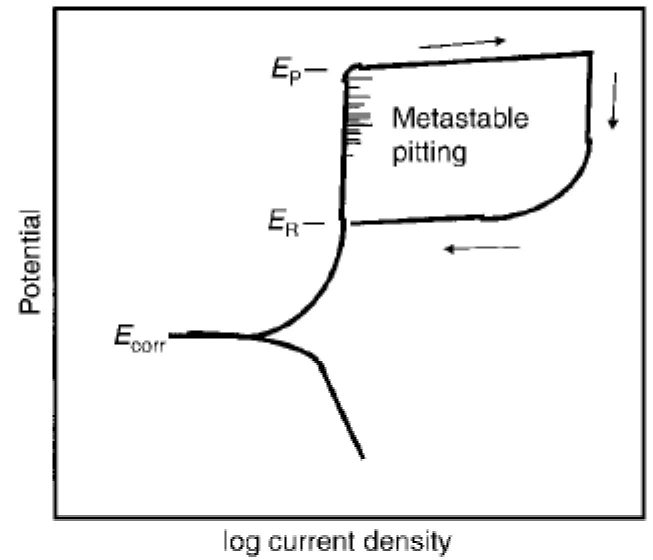


Fig. 3 Schematic of a polarization curve showing critical potentials and metastable pitting region. E_P, pitting potential; E_R, repassivation potential; E_{corr}, corrosion potential. Source: Ref 1

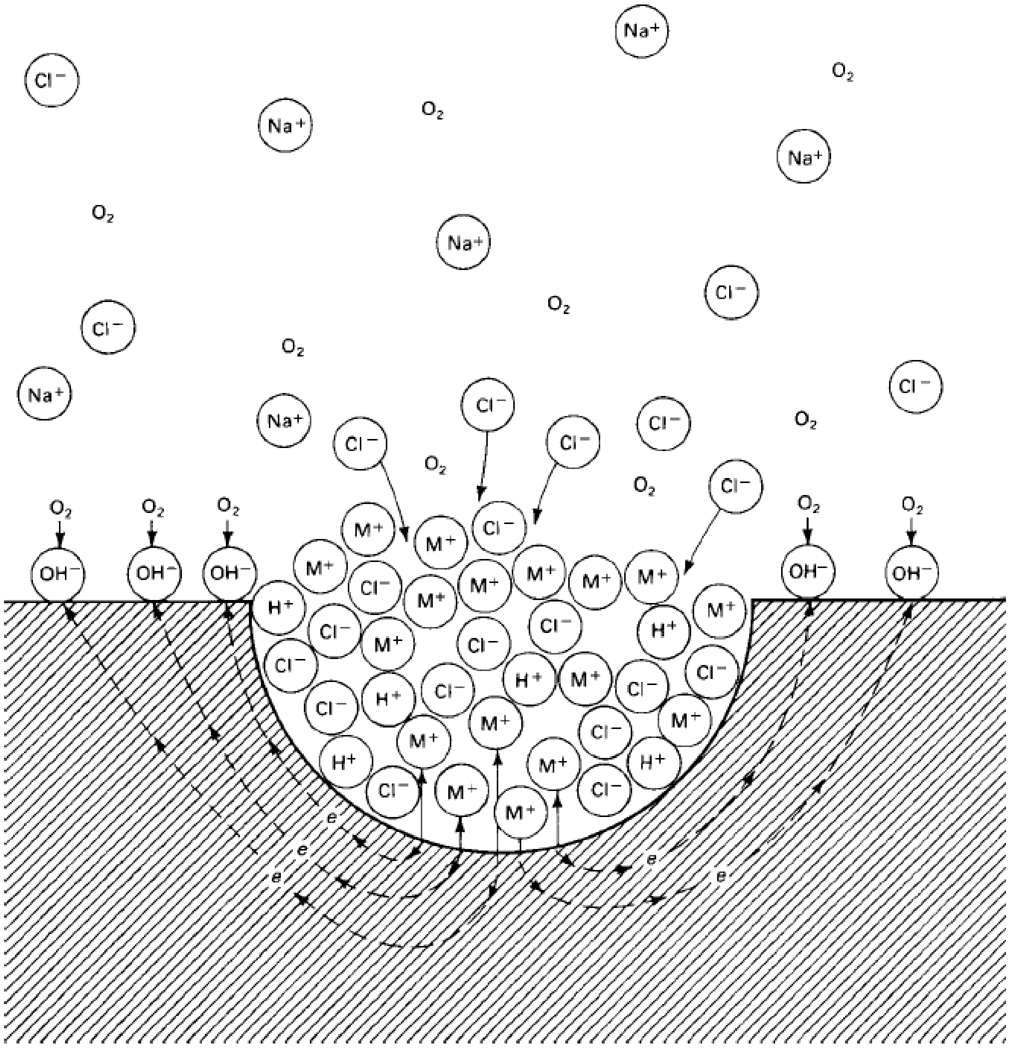


Fig. 2 Autocatalytic process occurring in a corrosion pit. The metal, M, is being pitted by an aerated NaCl solution. Rapid dissolution occurs in the pit, while oxygen reduction takes place on the adjacent metal surfaces.

Corrosion Filtration

- Sunapee Storage Bottles & Header
  - 900m^2 of internal surface area
- HP filters, FLT-620 & FLT-591
  - 360g dirt holding capacity & rust density ~ 5.5 g/cm^3
    - 65 cm^3 holding capacity

→ 7.3x10^{-5} mm layer from storage of rust needed to load filter

- <u>Rate Estimates</u>
- Month: total time for corrosion
  - HP Filter changes on 10/23, 12/3, 1/14
  - 720 hours to fully loaded filter
  - 0.00089 mm/year estimated corrosion rate
- Week: filters loaded much sooner than we changed them
  - HP Filter changes on 10/23, 12/3, 1/14
  - 168 hours to fully loaded filter
  - 0.0038 mm/year estimated corrosion rate

- Example corrosion rates (oil pipelines)
  - 0.4-10.9 mm/year, uninhibited
  - 0.05-0.1 mm/year, inhibited
  - Conflicting Views: CO2 Corrosion Models, Corrosion Inhibitor Availability Philosophies, and the Effect on Subsea Systems and Pipeline Design

- Supposing we had an inhibited 0.05 mm/year corrosion rate, we would need to change filters every 12 hours