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NAVAL MATERIALS SCIENCE - VOL 1 OF 2

Main Category:	Naval Engineering
Sub Category:	-
Course #:	NAV-119
Course Content:	125 pgs
PDH/CE Hours:	8

OFFICIAL COURSE/EXAM
(SEE INSTRUCTIONS ON NEXT PAGE)

NAV-119 EXAM PREVIEW

Instructions:

- At your convenience and own pace, review the course material below. When ready, click "Take Exam!" above to complete the live graded exam. (Note it may take a few seconds for the link to pull up the exam.) You will be able to re-take the exam as many times as needed to pass.
- Upon a satisfactory completion of the course exam, which is a score of 70% or better, you will be provided with your course completion certificate. Be sure to download and print your certificates to keep for your records.

Exam Preview:

1. According to the reference material, in the corrosion cell, metal ions formed from metal oxidation migrate from the cathode to the anode through the electrolyte.
   a. True
   b. False
2. Using the Table CHEMICAL COMPOSITION OF SEAWATER, 19ppt Chlorinity, which of the following elements is NOT an anion?
   a. Chloride
   b. Sulfate
   c. Bromide
   d. Sodium
3. When metals are exposed in a more complex electrolyte such as seawater, the galvanic series may be used to help predict if corrosion of a metal is possible. Using the provided Galvanic Series table, which of the following elements has the greatest potential for galvanic corrosion?
   a. Titanium
   b. Lead
   c. Zinc
   d. Nickel 200
4. Steel structures exposed to seawater are normally protected if they are polarized to a potential of -0.85 volts versus a silver/silver-chloride or a copper/copper-sulfate reference electrode.
   a. True
   b. False

5. Using Chapter 5 in the reference material, which of the following corrosion types matches the description: is an extremely localized attack that eventually results in holes in the metal. It is one of the most destructive and insidious forms of corrosion?
   a. Pitting Corrosion
   b. Crevice Corrosion
   c. Galvanic Corrosion
   d. Erosion-Corrosion

6. Some interesting information can be gleaned from this diagram. The most striking thing is that if iron is kept at a potential of less than -1.2 v with respect to a hydrogen half cell, it should not corrode in a solution of any pH.
   a. True
   b. False

7. According to the reference material, the surface water temperatures varies from about -1.8 C at the poles to 30 C at the equator. The water in the deep ocean has a more constant temperature of about __ C except where thermal vents are active in the seabed.
   a. 2
   b. 4
   c. 10
   d. 12

8. Using the provided Penetration of Water by Visible Light figure, which of the following colors of visible light has the LEAST penetration in water?
   a. White
   b. Green
   c. Yellow
   d. Orange

9. According to the reference material, alloys containing chromium, iron, nickel, and titanium can become "active" in strong oxidizing solutions when they form protective surface films.
   a. True
   b. False

10. Materials used in ocean engineering have to withstand the physical conditions imposed on them by wind, waves and currents. Using the Beaufort Wind Scale and Sea State, which of the following descriptive term corresponds to winds in the 32-38 mi/h range?
    a. Moderate Breeze
    b. Storm
    c. Near Gale
    d. Strong Gale

CHAPTER 1:

MATERIALS THE MARINE ENVIRONMENT
(This chapter is adapted from Swain (1996) and Schultz (1997))

1.1 Characterization of Seawater
1.2 Organic Matter and Biology
1.3 The Physical Environment
1.4 Classification of Marine Environments
1.5 Corrosion factors for Carbon Steel in Marine Environments
1.6 Historical Perspective

Materials used in marine environments are subject to chemical, physical, and biological deterioration. These factors make materials selection, design, and protection critical to the effective and safe functioning of a structure, vessel, or component for its design life. An understanding of the marine environment and its impact on materials is essential to anyone working in these areas.

1.1 Characterization of Seawater

Seawater Composition
Seawater is a complex solution of inorganic, organic, and biological components. These can interact with materials to cause corrosion and to degrade their properties.

Inorganic Components
The typical composition of sea water is shown below, but it must be remembered that in tropical waters higher salinities may be experienced. And, in coastal waters, the complete spectrum from fresh to sea water is found. One must also account for temperature differences, redox potential, and physical activity.

CHEMICAL COMPOSITION OF SEAWATER, 19ppt Chlorinity
Salinity (ppt) = 0.03 + 1.805 Cl$^-$

Anions	g/kg of water	Cation	g/kg of water
Chloride	19.35	Sodium	10.76
Sulfate	2.70	Magnesium	1.29
Bicarbonate	0.14	Calcium	0.41
Bromide	0.067	Potassium	0.39
Borate	0.0044	Strontium	0.0079
Fluoride	0.0014		

Swain, G.W. (1996) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.
Schultz, M.P. (1997) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.

Specific Conductance of Seawater

The specific conductance of seawater relates to its ability to conduct electricity. This has implications to corrosion rates and cathodic protection. Specific conductance is a function of temperature and chlorinity. Resistance is the reciprocal of conductance.

Table of the Specific Conductance of Seawater ($\Omega^{-1}cm^{-1}$)

Chlorinity, ppt	Temperature, °C					
	0	5	10	15	20	30
1	0.001839	0.002134	0.002439	0.002763	0.003091	0.003431
2	0.003556	0.004125	0.004714	0.005338	0.005971	0.006628
3	0.005187	0.006016	0.006872	0.007778	0.008702	0.009658
4	0.006758	0.007845	0.008958	0.010133	0.011337	0.012583
5	0.008327	0.009653	0.011019	0.012459	0.013939	0.015471
6	0.009878	0.011444	0.013063	0.014758	0.016512	0.018324
7	0.011404	0.013203	0.015069	0.017015	0.019035	0.021121
8	0.012905	0.014934	0.017042	0.019235	0.021514	0.023868
9	0.014388	0.016641	0.018986	0.021423	0.023957	0.026573
10	0.015852	0.018329	0.020906	0.023584	0.026367	0.029242
11	0.017304	0.020000	0.022804	0.025722	0.028749	0.031879
12	0.018741	0.021655	0.024684	0.027841	0.031109	0.034489
13	0.020167	0.023297	0.026548	0.029940	0.033447	0.037075
14	0.021585	0.024929	0.028397	0.032024	0.035765	0.039638
15	0.022993	0.026548	0.030231	0.034090	0.038065	0.042180
16	0.024393	0.028156	0.032050	0.036138	0.040345	0.044701
17	0.025783	0.029753	0.033855	0.038168	0.042606	0.047201
18	0.027162	0.031336	0.035644	0.040176	0.044844	0.049677
19	0.028530	0.032903	0.037415	0.042158	0.047058	0.052127
20	0.029885	0.034454	0.039167	0.044114	0.049248	0.054551
21	0.031227	0.035989	0.040900	0.046044	0.051414	0.056949
22	0.032556	0.037508	0.042614	0.047948	0.053556	0.059321

Dissolved Gases

All gases present in the atmosphere are also found in seawater. They are, however, at a lower partial pressure due to their limited solubility in seawater. In general the only gases normally considered are nitrogen (because of its overwhelming percentage) and oxygen and carbon dioxide because of their importance in corrosion. Other gases, such as ammonia, hydrogen sulfide, and hydrogen also have important implications to materials performance.

Solubility of Oxygen in Seawater

SOLUBILITY OF OXYGEN IN WATER EXPOSED TO WATER-SATURATED AIR AT ATMOSPHERIC PRESSURE (101.3 kPA)[1]

| Temperature °C	Oxygen Solubility mg/L					
	Chlorinity: 0	5.0	10.0	15.0	20.0	25.0
0.0	14.621	13.728	12.888	12.097	11.355	10.657
1.0	14.216	13.356	12.545	11.783	11.066	10.392
2.0	13.829	13.000	12.218	11.483	10.790	10.139
3.0	13.460	12.660	11.906	11.195	10.526	9.897
4.0	13.107	12.335	11.607	10.920	10.273	9.664
5.0	12.770	12.024	11.320	10.656	10.031	9.441
6.0	12.447	11.727	11.046	10.404	9.799	9.228
7.0	12.139	11.442	10.783	10.162	9.576	9.023
8.0	11.843	11.169	10.531	9.930	9.362	8.826
9.0	11.559	10.907	10.290	9.707	9.156	8.636
10.0	11.288	10.656	10.058	9.493	8.959	8.454
11.0	11.027	10.415	9.835	9.287	8.769	8.279
12.0	10.777	10.183	9.621	9.089	8.586	8.111
13.0	10.537	9.961	9.416	8.899	8.411	7.949
14.0	10.306	9.747	9.218	8.716	8.242	7.792
15.0	10.084	9.541	9.027	8.540	8.079	7.642
16.0	9.870	9.344	8.844	8.370	7.922	7.496
17.0	9.665	9.153	8.667	8.207	7.770	7.356
18.0	9.467	8.969	8.497	8.049	7.624	7.221
19.0	9.276	8.792	8.333	7.896	7.483	7.090
20.0	9.092	8.621	8.174	7.749	7.346	6.964
21.0	8.915	8.456	8.021	7.607	7.214	6.842
22.0	8.743	8.297	7.873	7.470	7.087	6.723
23.0	8.578	8.143	7.730	7.337	6.963	6.609
24.0	8.418	7.994	7.591	7.208	6.844	6.498
25.0	8.263	7.850	7.457	7.083	6.728	6.390
26.0	8.113	7.711	7.327	6.962	6.615	6.285
27.0	7.968	7.575	7.201	6.845	6.506	6.184
28.0	7.827	7.444	7.079	6.731	6.400	6.085
29.0	7.691	7.317	6.961	6.621	6.297	5.990
30.0	7.559	7.194	6.845	6.513	6.197	5.896
31.0	7.430	7.073	6.733	6.409	6.100	5.806
32.0	7.305	6.957	6.624	6.307	6.005	5.717
33.0	7.183	6.843	6.518	6.208	5.912	5.631
34.0	7.065	6.732	6.415	6.111	5.822	5.546
35.0	6.950	6.624	6.314	6.017	5.734	5.464
36.0	6.837	6.519	6.215	5.925	5.648	5.384
37.0	6.727	6.416	6.119	5.835	5.564	5.305
38.0	6.620	6.316	6.025	5.747	5.481	5.228
39.0	6.515	6.217	5.932	5.660	5.400	5.152
40.0	6.412	6.121	5.842	5.576	5.321	5.078
41.0	6.312	6.026	5.753	5.493	5.243	5.005
42.0	6.213	5.934	5.667	5.411	5.167	4.933
43.0	6.116	5.843	5.581	5.331	5.091	4.862
44.0	6.021	5.753	5.497	5.252	5.017	4.793
45.0	5.927	5.665	5.414	5.174	4.944	4.724

Seawater pH
The pH of surface waters typically is in the range 7.8 to 8.4. This value is maintained by the effect of the carbonate equilibria and the presence of cations; Ca, Mg, Na, & K. The addition of CO_2, a decrease in temperature or an increase in pressure will cause the pH to fall. The removal of CO_2, an increase in temperature, or a decrease in pressure will cause the pH to rise. Seawater pH effects the corrosion rates of metals, and alters the calcareous deposits formed at metals cathodes.

Seawater Temperature
The surface water temperatures varies from about -1.8 C at the poles to 30 C at the equator. The water in the deep ocean has a more constant temperature of about 4 C except where thermal vents are active in the seabed. Higher temperatures will be found at heat exchangers and desalination plants

An increase in temperature increases seawater conductivity and decreases oxygen concentration. This effects corrosion rates. Increases in temperature also reduces the mechanical properties of thermoplastics.

A decrease in temperature may cause materials to become brittle and many failures of steel structures have been attributed to brittle fracture a low temperature.
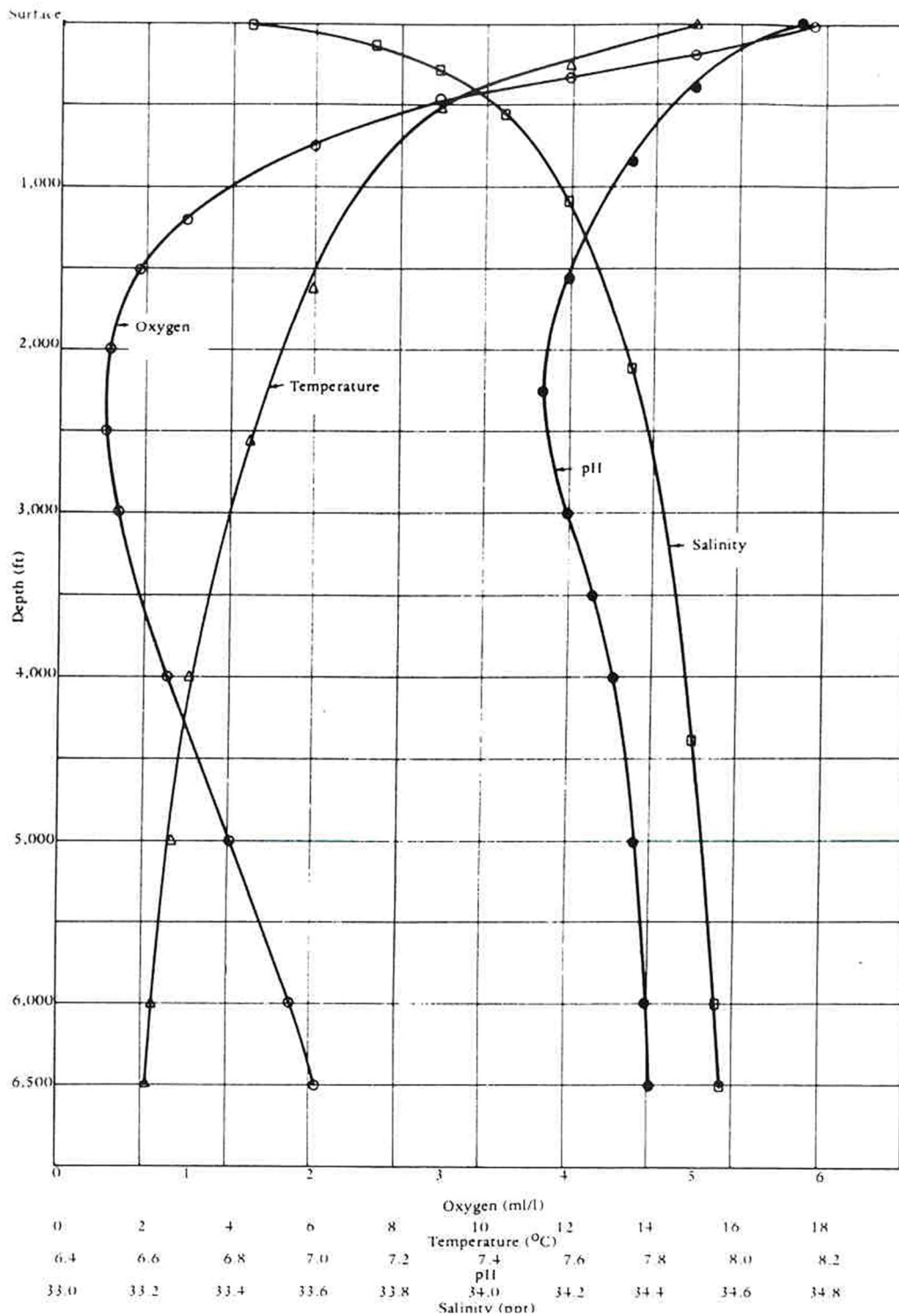
Typical Profiles of Oxygen, Temperature, and Salinity in the Ocean.

1.2 Organic Matter and Biology

Organic matter and marine organisms are generally more abundant in coastal areas. Their impact on materials may be due to biodegradation, microbial induced corrosion (MIC), wood boring, or biofouling. Their impact to the design life and operational efficiencies of structures is often underestimated, and materials selection or biological control may be necessary.

Penetration of Water by Visible Light.
This limits the Depth to which Plant Life can Grow

The Electromagnetic Spectrum and Transmission of
Visible Light in Water
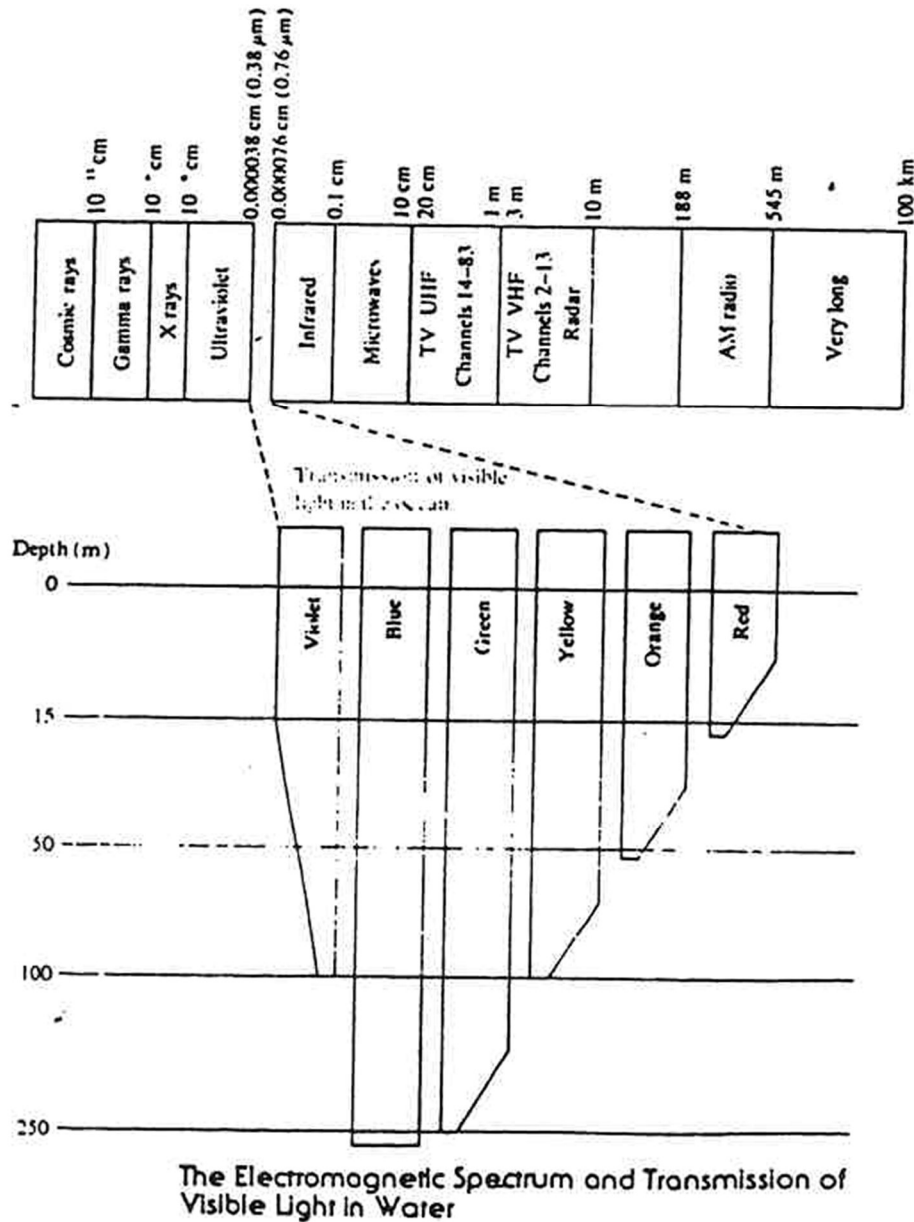
The Size and Shape of Typical Fouling Organisms

| Fouling type	Average size, mm	Illustration
BACTERIA	0·001	
ALGAL SPORES	0·01	
DIATOMS	0·1	
ANIMAL LARVAE Starfish larva Barnacle larva	1	
ANIMAL & PLANT FOULING TYPES Seaweed Tubeworm Barnacle	10	
Seaweeds Sea Anemone Mussel	100	
LARGE ALGAE Kelps	1000	

1.3 The Physical Environment

Materials used in ocean engineering have to withstand the physical conditions imposed on them by wind, waves and currents. These cause loading, stress, fatigue, scour, abrasion, and impact damage.

<u>Beaufort Wind Scale and Sea State</u>

Beaufort Number	Descriptive Term	Speed m/s	Speed mi/h	Appearance of the Sea
0	Calm	—	—	Like a mirror
1	Light air	0.3–1.5	1–3	Ripples with the appearance of scales; no foam crests
2	Light breeze	1.6–3.3	4–7	Small wavelets; crests of glassy appearance, no breaking
3	Gentle breeze	3.4–5.4	8–12	Large wavelets; crests begin to break; scattered whitecaps
4	Moderate breeze	5.5–7.9	13–18	Small waves, becoming longer; numerous whitecaps
5	Fresh breeze	8.0–10.7	19–24	Moderate waves, taking longer form; many whitecaps some spray
6	Strong breeze	10.8–13.8	25–31	Large waves begin to form; whitecaps everywhere, more spray
7	Near gale	13.9–17.1	32–38	Sea heaps up and white foam from breaking waves begins to be blown in streaks
8	Gale	17.2–20.7	39–46	Moderately high waves of greater length; edges of crests begin to break into spindrift; foam is blown in well marked streaks
9	Strong gale	20.8–24.4	47–54	High waves; dense streaks of foam and sea begins to roll. spray may affect visibility
10	Storm	24.5–28.4	55–63	Very high waves with overhanging crests; foam is blown in dense white streaks, causing the sea to take on a white appearance; the rolling of the sea becomes heavy visibility reduced
11	Violent storm	28.5–32.6	64–72	Exceptionally high waves (small and medium-sized ships might be for a time lost to view behind the waves); the sea is covered with white patches of foam; everywhere the edges of the wave crests are blown into froth. visibility further reduced
12	Hurricane	32.7–36.9	73–82	The air is filled with foam and spray; sea completely white with driving spray; visibility greatly reduced

Wind, Wave and Current Effects on Offshore Structures
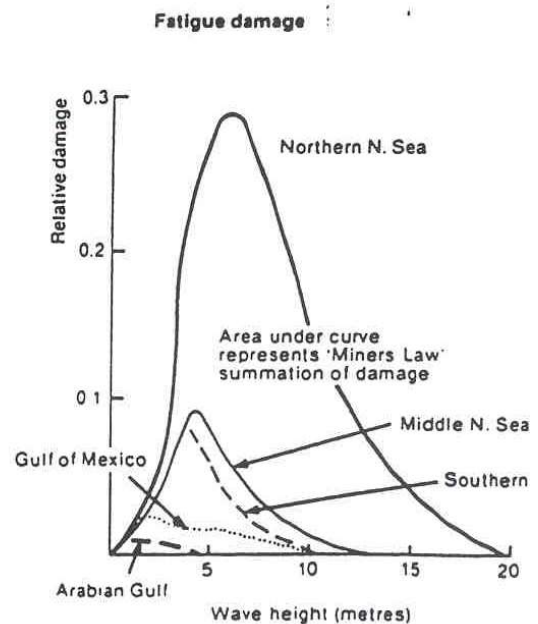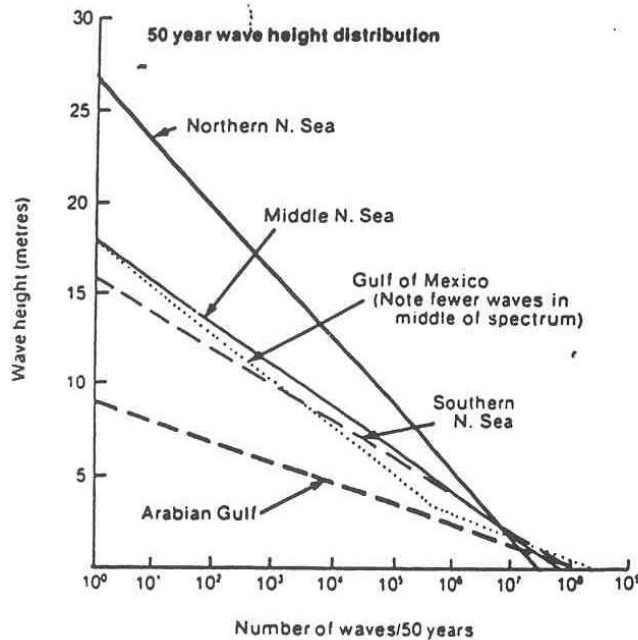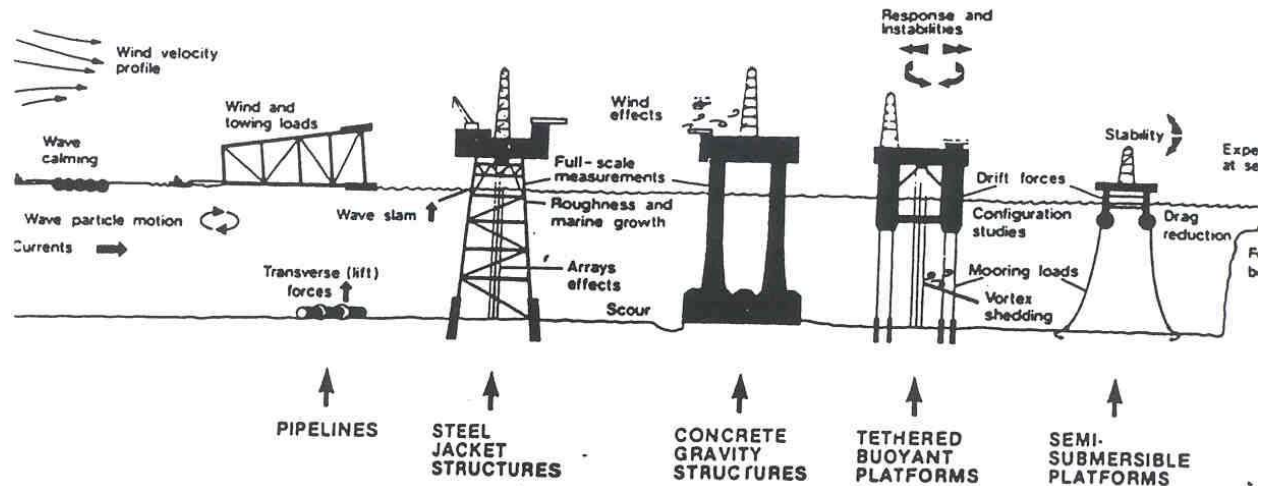
1.4 Classification of Marine Environments

For engineering and corrosion control purposes the marine environment may be divided into the following regions; atmospheric zone, splash zone, tidal zone, submerged zone, and mud or sediment line. These environments have been described with respect to their effect on steel.

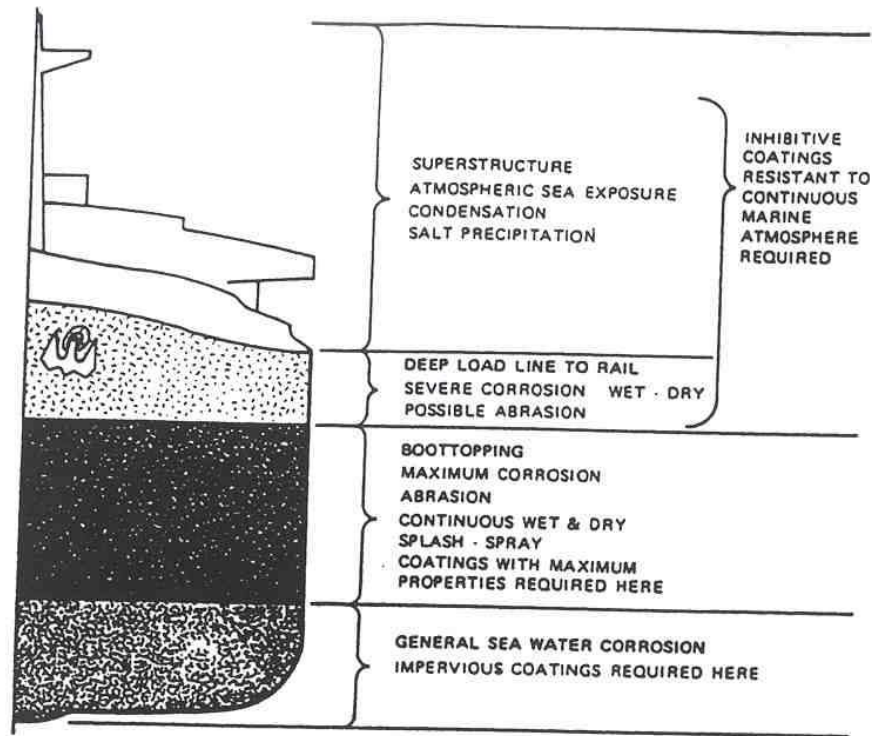| Marine Zone	Description of Environment	Characteristic Corrosion Behavior of Steel
Atmosphere (above splash)	Minute particles of sea salt are carried by wind. Corrosivity varies with height above water, wind velocity and direction, dew cycle, rainfall, temperature, solar radiation, dust, season, and pollution. Even bird droppings are a factor.	Sheltered surfaces may deteriorate more rapidly than those boldly exposed. Top surfaces may be washed free of salt by rain. Coral dust combined with salt seems to be particularly corrosive to steel equipment. Corrosion usually decreases rapidly as one goes inland.
Splash	Wet, well-aerated surface, no fouling.	Most aggressive zone for many metals, e.g., steel. Protective coatings are more difficult to maintain than in other zones.
Tidal	Marine fouling is apt to be present to high-water mark. Oil coating from polluted harbor water may be present. Usually, ample oxygen is available.	Steel at tidal zone may act cathodically (well aerated) and receive some protection from the corrosion just below tidal zone, in case of a continuous steel pile. Isolated steel panels show relatively high attack in tidal zone. Oil coating on surface may reduce attack.
Shallow water (near surface and near shore)	Seawater usually is saturated with oxygen. Pollution, sediment, fouling, velocity, etc., all may play an active role.	Corrosion may be more rapid than in marine atmosphere. A calcareous scale forms at cathodic areas. Protective coatings and/or cathodic protection may be used for corrosion control. In most waters a layer of hard shell and other biofouling restricts the available oxygen at the surface and thus reduces corrosion. (Increased stress on structure from weight of fouling must be provided for).
Continental-shelf depths	No plant fouling, very much less animal (shell) fouling with distance from shore. Some decrease in oxygen, especially in the Pacific, and lower temperature.	
Deep ocean	Oxygen varies, tending to be much lower than at surface in Pacific but not too different in Atlantic. Temperature near 0 C. Velocity low; pH lower than at surface.	Steel corrosion often less. Anode consumption is greater to polarize same area of steel as at surface. Less tendency for protective mineral scale.
Mud	Bacteria are often present, e.g., sulfate reducing type. Bottom sediments vary in origin, characteristics, and behavior.	Mud is usually corrosive, occasionally inert. Mud-to-bottom water corrosion cells seem possible. Partly embedded panels tend to be rapidly attacked in mud. Sulfides are a factor. Less current than in seawater is consumed to obtain cathodic polarization for buried part of structure.

SUPERSTRUCTURE
ATMOSPHERIC SEA EXPOSURE
CONDENSATION
SALT PRECIPITATION

INHIBITIVE COATINGS RESISTANT TO CONTINUOUS MARINE ATMOSPHERE REQUIRED

DEEP LOAD LINE TO RAIL
SEVERE CORROSION   WET · DRY
POSSIBLE ABRASION

BOOTTOPPING
MAXIMUM CORROSION
ABRASION
CONTINUOUS WET & DRY
SPLASH · SPRAY
COATINGS WITH MAXIMUM PROPERTIES REQUIRED HERE

GENERAL SEA WATER CORROSION
IMPERVIOUS COATINGS REQUIRED HERE

Figure 16-15.   Choice of coatings for different zones of off shore structures.

PLATFORM

PRECIPITATED SALT

CONDENSATION

ATMOSPHERIC SEA EXPOSURE

INHIBITIVE COATINGS RESISTANT TO CONTINUOUS ATMOSPHERIC MARINE CONDITIONS REQUIRED.

COATINGS

SEVERE CORROSION CONTINUOUS WETTING & DRYING

SUPERSTRUCTURE

SPLASH & SPRAY

COATINGS WITH MAXIMUM PROPERTIES REQUIRED IN THIS AREA

MEAN LOW TIDE   MAXIMUM CORROSION TIDAL AREA

GENERAL SEA WATER CORROSION

IMPERVIOUS COATINGS ARE REQUIRED HERE.

JACKET

MUD LINE

PILING   LITTLE CORROSION

Figure 16-16

1.5 Corrosion factors for Carbon Steel in Marine Environments

Atmospheric Corrosion
Atmospheres may broadly be divided into rural, industrial and marine. The most corrosive are the marine environments and if augmented by industrial pollution (acid rain) then severe corrosion will occur. A good local example is the problems associated with the HCl produced by the solid rocket boosters from the shuttle launch at Cape Canaveral. This has played havoc with corrosion of the steel rocket gantries which traditionally used zinc as a coating to protect the steel from the marine environment. The zinc is now dissolved by the acid fall-out.

Typical atmospheric corrosion rates for various locations

Test location	Average rate of corrosion in 2-year tests (in./year)[a]
Rural atmospheres	
Normal Wells, N.W.T., Canada	0.00001
Phoenix, Arizona	0.00037
State College, Pennsylvania	0.0019
Industrial atmospheres	
Detroit, Michigan	0.0012
Pittsburgh, Pennsylvania	0.0025
Newark, New Jersey	0.0041
East Chicago, Indiana	0.0068
London, England	0.009
Marine atmospheres	
Fort Amidor Pier, Panama Canal Zone	0.0011
Miraflores, Panama Canal Zone	0.0035
Limon Bay, Panama Canal Zone	0.005
Cape Kennedy—½ mile from ocean	0.007
Cape Kennedy—60 yd from ocean elevation 60 ft	0.011
Kure Beach, North Carolina—800 ft from ocean	0.012
Cape Kennedy—60 yd from ocean elevation 30 ft	0.013
Daytona Beach, Florida	0.024
Cape Kennedy—60 yd from ocean, ground level	0.036
Dungeness, England	0.039
Point Reyes, California	0.040
Kure Beach, North Carolina—80 ft from ocean	0.048
Galeta Point Beach, Panama Canal Zone	0.056
Cape Kennedy Beach, Florida	0.085

[a]Calculated from weight loss.

Splash Zone Corrosion
This is considered to be the most corrosive of all marine environments. Field data provides the following guidelines for different environments.

| Condition	Years Exposure	Rate, mpy
Quiet	5	20
Moderate	5	37
Rough	4	55

<u>Immersed Corrosion</u>
The factors affecting the corrosion of steel in the immersed condition are shown below

Factor in Seawater	Effect on Iron and Steel
Chloride ion	Highly corrosive to ferrous metals. Carbon steel and common ferrous metals cannot be passivated. (Sea salt is about 55 percent chloride.)
Electrical conductivity	High conductivity makes it possible for anodes and cathodes to operate over long distances, thus corrosion possibilities are increased and the total attack may be much greater than that for the same structure in fresh water.
Oxygen	Steel corrosion is cathodically controlled for the most part. Oxygen, by depolarizing the cathode, facilitates the attack; thus a high oxygen content increases corrosivity.
Velocity	Corrosion rate is increased, especially in turbulent flow. Moving seawater may (1) destroy rust barrier and (2) provide more oxygen. Impingement attack tends to promote rapid penetration. Cavitation damage exposes fresh steel surface to further corrosion.
Temperature	Increasing ambient temperature tends to accelerate attack. Heated seawater may deposit protective scale, or lose its oxygen; either or both actions tend to reduce attack.
Biofouling	Hard-shell animal fouling tends to reduce attack by restricting access of oxygen. Bacteria can take part in corrosion reaction in some cases.
Stress	Cyclic stress sometimes accelerates failure of a corroding steel member. Tensile stresses near yield also promote failure in special situations.
Pollution	Sulfides, which normally are present in polluted seawater greatly accelerate attack on steel. However, the low oxygen content of polluted waters could favor reduced corrosion.
Silt and suspended sediment	Erosion of the steel surface by suspended matter in the flowing seawater greatly increases the tendency to corrode
Film formation	A coating of rust, or rust and mineral scale (calcium and magnesium salts) will interfere with the diffusion of oxygen to the cathode surface, thus slowing the attack.

1.6 Historical Perspective

The marine environment has provided a challenge to engineers for thousands of years. The earliest surving boat is the Khufu Barge, discovered in a pit next to the great pyramid of Egypt, dated around 2500 BC. This boat was over 143 feet long, demonstrating the skill of Naval Architects over 4500 years ago. It was constructed out of Cedar, a rot-resistant wood that grew in Lebanon. The hull timbers were lashed together with rope. Part of this was because of the extreme expense of metal fasteners.
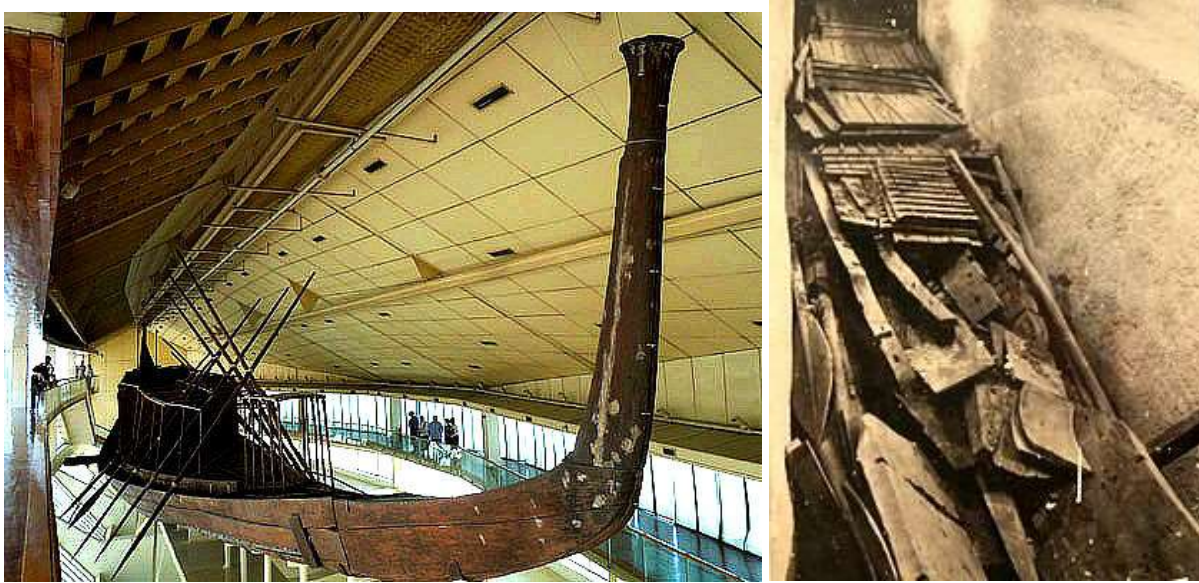
Khufu barge, Egypt, 2500 BC, Dimensions: 43.6 m x 5.9 m [143 ft. x 19.5 ft.] Material: wood

Bronze and Copper
The bronze age dates from around 2000-500 BC. Copper and Bronze found their way into marine design in terms of small nails (large nails were made of wood "tree nails" or "trunnels"), and in specialized castings. For instance, Greek Triremes used bronze rams to sink other ships.

Iron

Historically, Iron was in short supply. A knife found in the tomb of King Tut was determined by scientists to be of meteorite origin. The ability to process iron ore into tools and weapons was a major challenge. The "Iron age" began somewhere around 1000 – 500 BC depending on the locality. Iron weapons were of strategic importance, and there was significant geopolitical change during this period.

While iron was used in fasteners and reinforcements for ships for a very long time, wood was the most important building material for ships from pre-history until the 1800's when iron became available in large plates, and ships such as the *Great Britain* (1838 designed by I.K. Brunel) were constructed. This ship was 322' long, 50' 6" wide and displaced 3,680 LT. She had an iron keel 1" thick and 21" wide and hull plate 3/8 to 3/4" thick and riveted to frames of angle iron. The iron enabled larger ships to be built and supported the increasingly powerful steam ships.

Great Britian

The British Navy was slow to convert to iron for two reasons. Firstly a cannon ball fired at close range could easily penetrate 3/4" iron plate and yet 8" of oak would effectively stop it. Secondly, copper had successfully been used for many years as a means of preventing fouling. The corresponding loss in performance and the galvanic action between iron and steel, however, caused the steel to corrode and the copper to lose its antifouling qualities. This situation remained until satisfactory copper based antifouling coatings were produced.

Steel

Iron was eventually replaced by steel. Prior to the early 1940's most steels used in construction were low carbon steels (σ_y = 32 ksi). These performed well but there were occasions when the steel failed by brittle fracture. The most notable of these occurred in welded cargo ships and tankers built in the USA during the World War II. Of about 5,000 ships built, over 1,000 had experienced structural failures within three years of construction. About 20 ships actually broke in two. This lead to the American Bureau of Shipping or ABS (1948) specifying notch toughness

requirements for hull steel and specifying grades and steel making practices. The improvements to steel were furthered by submarine development which led to the use of high tensile strength (HTS) steels with yield strengths of 50 ksi, and now HY80, HY100 and HY120 steels are commonly used for offshore applications.

USS Virginia (SSN 774)

Other Alloys

Other alloys have been used for ship hull construction. Aluminum, discovered by Hans Oersted, University of Copenhagen, 1825, is commonly applied to marine structures. The first boat built out of aluminum was in 1890, *Zepher* a 17' launch. The early alloys used copper as an alloying agent and as such were unsuitable for marine service. However, the Washington Disarmament Conference, 1922, limited the total navy displacements and this revived interest in aluminum as a construction material. By 1940, aluminum was used in about 100 US warships as weight saving material, mainly for topside applications. For example the *USS Independence* (aircraft carrier) contains 2.25 million lbs of aluminum which saved 2 million lbs in weight. In 1951, the *USS United States* used 2,000 tons of aluminum, saving 8,000 tons in weight. Today aluminum is being used in many applications where weight savings are desired, such as the entire hull structure of the Littoral Combat Ships.

USS Independence (LCS 2)

Accompanying the development of the steam ship came requirements for hardware to support the engines, propulsion systems, piping, rigging, etc. The hardware had to be manufactured from

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materials that could withstand both the mechanical and corrosion abuse imparted by operating in the marine environment. Many of the parts were manufactured form cast and wrought irons, steels and aluminum; but others were made from copper based alloys and later stainless steels.

Copper based alloys were some of the first metals to be fabricated by man. About 400 BC Homer described the Trojan War where 1200 ships, 80' long with 50 oars were equipped with bronze beaks for ramming. The next copper alloys to find regular use were the brasses. Now there are a whole family of copper alloys that find regular application including the use of 90:10 copper-nickel hull plate for small boat construction.

Stainless steels were first developed around 1910 in England and Germany. By the 1920s, commercial production in the US was begun by companies such as Allegheny, Armco, Carpenter, Crucible, Firth-Sterling, Jessop, Ludlum, Republic, Rustless and US Steel. Production was, however, limited partially due to the problems of obtaining raw materials when civil unrest was active in Africa and Asia, which are traditional sources of nickel. The modern family of stainless steels show increasing use in marine engineering. They maybe divided into: martensitic, ferritic, austenitic, duplex, and precipitation-hardening stainless steels.

Continued Use of Wood
With the advent of the screw propeller problems arose with maintaining through hull stern bearings and glands. This was solved by the use of *Lignum vitae* (guaniacum tree) a tropical hardwood from the Caribbean which had excellent self lubrication properties and was also extremely hard. The wood is still used in the sterntube bearings of many ships currently operating, hence the title of a recent article, "Lignum Vitae: Wood So Bad-Ass, It's Used to Make Shaft Bearings for Nuclear Submarines (and More)"

During World War II, plywood was used extensively in high-speed, light weight patrol craft. Wood was also used in minesweepers because it is non-magnetic. Plywood still continues to be used today in small boat construction.

Offshore Structures
At the same time as shipping activities were increasing, so were the services required to support them on land and to ensure safe navigation and passage. Perhaps the earliest example of offshore structures were the lighthouses. Perhaps the most famous of these structures was the Eddystone light, built on some rocks about 15 miles south of Plymouth, England. The first structure was built by Winstanley in 1698 from wood and anchored to the bottom by iron rods. It was replaced in 1706 by a stone structure clad with wood and designed by John Lovett and John Rudyard. This burnt down in 1759, and John Smeaton designed a stone structure to take its place. In 1852 Trinity House decided that a taller lighthouse was required and moved Smeaton's structure to Plymouth and replaced it with the building that remains there to this day. In any event, the use of stone, wood, concrete, iron, and steel are commonplace for coastal and offshore facilities.

U.S. Navy R2 Tower

Offshore Oil Platform

U.S. Naval Base in Okinawa

New materials and material requirements are continually emerging at what sometimes seems an accelerating rate. The 1960's, 70's, and 80's saw the development of the offshore oil industry, which has led the way to improved structural materials and specifications and to the use of metals such as titanium and high nickel alloys for critical applications. The world's navies have continued to use and develop advanced materials for weapons, sonar, nuclear submarines, etc. Perhaps the greatest impetus for materials development and experimentation has come from racing sail and power boats. In these sports, the application of high strength to weight ratio composites provides the cutting edge to evaluate how these materials can withstand the marine environment.

Reference
Swain, G.W. (1996) "OCE 4518 - Protection of Marine Materials Class Notes", Florida Institute of Technology, Melbourne, FL.

CHAPTER 2

CORROSION AND ELECTROMOTIVE POTENTIAL

(from Swain (1996), Schultz (1997) and Dawson (2003))

2.1 Corrosion cell
2.2 Specific Examples of Electrochemical Reactions
2.3 Measurement of Potential
2.4 Standard Electromotive Force (Surface Potential)
2.5 Correction for Solution Concentration: Nernst Equation
2.6 Reference electrodes
2.7 Galvanic series
2.8 Passivating films
2.9 Concentration Cells
2.10 Effect of Alloying
2.11 Pourbaix, or pH Diagrams

What is corrosion?
- Webster's Dictionary - corrode (v.) To eat away or be eaten away gradually, especially by chemical action.
- NACE Corrosion Basics - corrosion may be defined as the deterioration of a material (usually a metal) because of a reaction with the environment.

Why do metals corrode?
Most metals are found in nature as ores. The manufacturing process of converting these ores into metals involves the input of energy. During the corrosion reaction the energy added in manufacturing is released, and the metal is returned to its oxide state.

$$\text{Metal Ore} \xrightarrow{\text{reduction (add electrons)}} \text{Metal} \xrightarrow{\text{oxidation (strip electrons)}} \text{Corrosion Products}$$

In the marine environment, the corrosion process generally takes place in aqueous solutions and is therefore electrochemical in nature.

Corrosion consequences
Economic - corrosion results in the loss of $8 - $126 billion annually in the U.S. alone. This impact is primarily the result of:
1. Downtime
2. Product Loss
3. Efficiency Loss
4. Contamination
5. Overdesign

Safety / Loss of Life
Corrosion can lead to catastrophic system failures which endanger human life and health. Examples include a 1967 bridge collapse in West Virginia which killed 46. The collapse was attributed to stress corrosion cracking (SCC). In another example, the fuselage of an airliner in Hawaii ripped open due to the combined action of stress and atmospheric corrosion.

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2.1 Corrosion cell

Corrosion occurs due to the formation of electrochemical cells. In order for the corrosion reaction to occur five things are necessary. If any of these factors are eliminated, galvanic corrosion will not occur. THIS IS THE KEY TO CORROSION CONTROL! The necessary factors for corrosion to proceed are:

1. ANODE - the metal or site on the metal where oxidation occurs (loss of electrons). The anode has a more negative potential with respect to (wrt) the cathode and is termed less noble wrt the cathode.
2. CATHODE - the metal or site on the metal where reduction occurs (gain of electrons). The cathode has a more positive potential wrt the anode and is termed more noble wrt the anode.
3. ELECTROLYTE - the electrically conductive medium in which the anode and cathode reside.
4. ELECTRICAL CONNECTION - the anode and the cathode must be electrically connected.
5. POTENTIAL DIFFERENCE - a voltage difference must exist between the anode and the cathode.
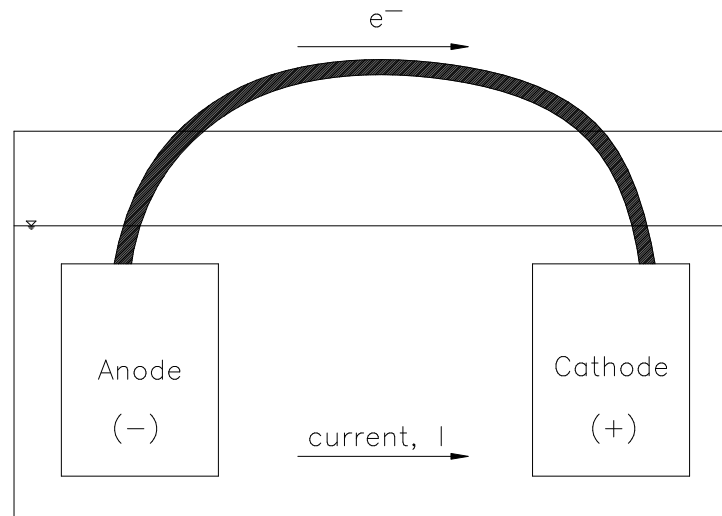


Schematic of the corrosion cell

The electrochemical cell is driven by the potential difference between the anode and the cathode. This causes a current to flow, the magnitude of which will be determined by the resistance of the electrochemical circuit (i.e. Ohm's Law, I=V/R). The three main types of electrochemical cells are:

- Concentration Cells - this is where the anode and the cathode are the same material, but concentrations of reactants and therefore potential differ at the electrodes. These can be oxygen concentration or metal ion concentration cells.
- Bimetallic Cells - where the anode and cathode are different materials.
- Thermo-galvanic Cells - where the anode and the cathode are of the same material and the composition of the electrolyte is the same but the temperature at the electrodes are different.

In the corrosion cell, metal ions formed from metal oxidation (cations) migrate from the anode to the cathode through the electrolyte. The electrons given off by this oxidation reaction move from the anode to the cathode through the electrical connection. Current flows from cathode to the anode through the electrical connection and from the anode to the cathode in the electrolyte.

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Anode half-cell reaction
Oxidation of the metal at the anode may be expressed by the following half-cell reaction:
$$M \rightarrow M^{n+} + ne^-$$
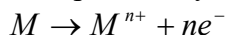
Cathode half-cell reaction
The reduction half-cell reaction at the cathode depends mainly on environmental conditions. The following six reactions represent common cathodic reactions along with the conditions in which they generally occur:

1. $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ aerated neutral to alkaline water
2. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ aerated acidic solutions
3. $2H^+ + 2e^- \rightarrow H_2 \uparrow$ hydrogen evolution (in acids)
4. $M^{n+} + ne^- \rightarrow M$ metal deposition
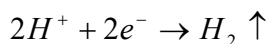5. $M^{n+} + e^- \rightarrow M^{(n-1)+}$ metal reduction

Example: *Magnesium is submerged into a bath of HCl. What would the predominate anodic and cathodic reactions be?*
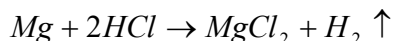
Solution:
Anodic $Mg \rightarrow Mg^{2+} + 2e^-$
Cathodic $2H^+ + 2e^- \rightarrow H_2 \uparrow$
Overall reaction $Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$

## 2.2 Specific Examples of Electrochemical Reactions

Keeping in mind the definition of corrosion as a destructive electrochemical process, resulting in material wastage, we examine here the basic concept of a corrosion cell and its associated reactions.

Iron Bar in Hydrochloric Acid
To begin, we consider a simple idealized case where a perfectly homogeneous bar of iron (every part the same as every other part) is placed in a container of hydrochloric acid (Hcl). On placing the bar in the acid, some of the iron will initially tend to go into solution as ferrous iron (Fe $^{++}$) as a result of attractive forces exerted by the ionized acid solution. Such a situation will, however, leave the departure points on the bar with electrons, causing negative charge so the tendency for ion formation is thus counteracted by local electrostatic attraction from these fixed electrons, i.e. the reaction stops. If the bar is perfectly homogeneous, as assumed, there will accordingly be no loss of metal to the solution and therefore no corrosion of the bar.

Iron and Copper in Hydrochloric Acid
Suppose, however, that we now place a second metal bar, say a copper, in the acid and connect a wire between them as indicated in the figure below:
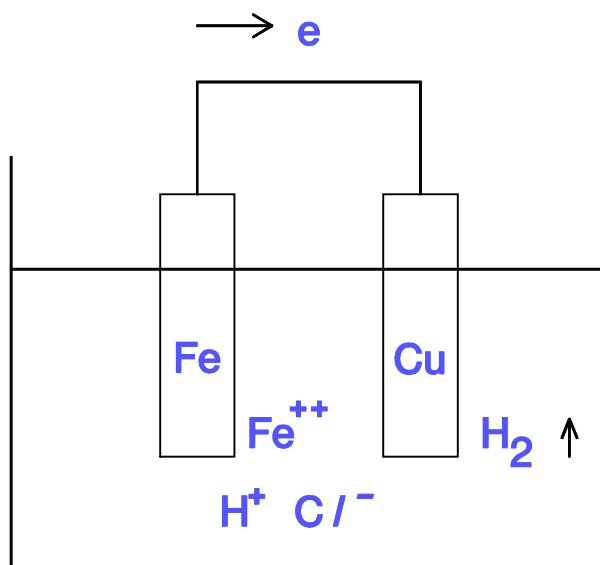
Iron and Copper in Hydrochloric Acid

In this case, we have what is called a corrosion, or galvanic cell. Again, there is a tendency for the iron to be drawn into solution as ferrous ions and leave behind electrons. But now, these electrons will no longer be fixed in place at the departure sites of the ions. They will, in fact, be drawn through the iron bar and connecting wire by the natural potential difference existing between the two metals. In this way, the iron ions are thus fully drawn into solution because the freed electrons are drained away rather than remain at the departure sites to attract the ions back to the metal. Of course, when the electrons reach the copper bar, they must be used in some way if the process is to continue. This happens because the electrons can combine with the hydrogen (H^+) ions in solution to form hydrogen (H_2) gas on the surface of the bar which then bubbles off. In addition, the Fe^{++} ions can combine with the Cl^- ion in solution to form ferrous chloride. Thus, as long as the above conditions exist, corrosion of the iron bar will continue.

In the above example, oxidation occurs at the anode according to the reaction:

$$Fe \rightarrow Fe^{++} + 2e^-$$
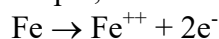
Reduction occurs at the cathode according to the reaction:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow (gas)$$
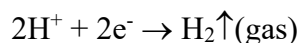
A compound also forms as described by:

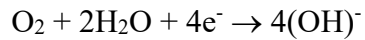$$Fe^{++} + 2Cl^- \rightarrow FeCl_2$$

Which is ferrous chloride. (Note how the reaction is balanced, so remember your chemistry).

Iron and Copper in Water
Suppose now that we place the iron and copper bars in water rather than HCl. In this case, the anode reaction is still:
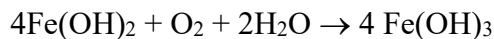
$$Fe \rightarrow Fe^{++} + 2e^-$$

2 - 4

The cathode reaction is, however, now mainly

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$

that is the production of hydroxide ions. The additional reaction in the electrolyte is

$$Fe^{++} + 2(OH)^- \rightarrow Fe(OH)_2$$
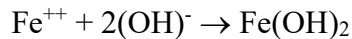
which is ferrous hydroxide. This compound in the presence of oxygen is converted to ferric hydroxide according to the reaction

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\ Fe(OH)_3$$

Ferric hydroxide is orange to red-brown in color and compromises <u>most of ordinary rust</u>.

<u>Non-Perfect Bar</u>
The above discussion assumed a homogeneous iron bar such that if placed alone in an electrolyte, no corrosion would occur. In reality, though, no bar is perfectly homogeneous, and when placed alone in an electrolyte, a part of it will act as an anode and a part as a cathode, thus giving rise to a <u>local corrosion cell</u> as indicated in the figure below
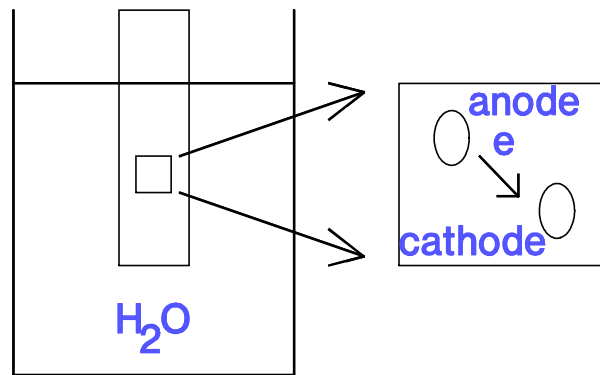
Local Anodes and Cathodes
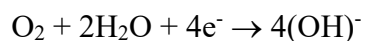
As corrosion proceeds, the location of the anode and cathode regions will shift around on the bar and the bar will corrode more or less uniformly. This is the basis for the uniform corrosion (rusting) of an iron bar immersed in water. At the anode region, the reaction as before is

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

At the cathode region

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$

2 - 5

As discussed above, ferric hydroxide is formed from the Fe^{++} and OH^- ions and this compound (rust) precipitates out of solution. Of course, if a non-perfect bar of iron is connected to a copper bar, as described earlier, the cathodic behavior of the copper bar will generally override that of any regions of the iron bar itself, and the entire iron bar will act as an anode.

When two bars are placed in an electrolyte and connected, the question of which one acts like the anode and which like the cathode is determined by the potential difference existing between them. The same is also true regarding regions of a non-perfect bar.

2.3 Measurement of Potential

Consider again the iron and copper bars discussed earlier. To fix ideas, we now suppose the iron to be immersed in a solution of iron ions (Fe^{++}) with a concentration of 1 mole/liter. Similarly, we suppose the copper is immersed in a solution of copper ions (Cu^{++}) with a concentration of 1 mole/liter. We also suppose a voltmeter connected between the two bars as indicated in the figure below:
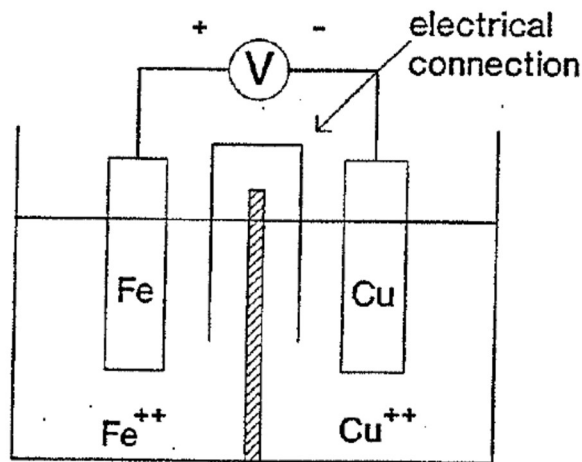
Iron and Copper Bars with a Voltmeter Connection

If we measure the potential difference when no current exists, we find with the voltmeter hook-up indicated that

$$\Delta V = V_{Fe} - V_{Cu} = -0.789 \text{ volts}$$

Since this shows the potential of the copper to be greater (i.e. less negative), the direction of the current, externally will be from the copper to the iron when the (open circuit) voltmeter is replaced by a connecting wire. By convention, the current direction is opposite to the flow of electrons. The electrons would therefore flow from the iron to the copper through the connecting wire and the iron would thus act as the anode and corrode and the copper would act as the cathode and would not corrode. This, of course, is consistent with what we assumed earlier when discussing the iron and copper bars.

Standard Hydrogen Electrode

It is useful to use a standard hydrogen electrode to measure the potentials of the various metals for comparative purposes. The hydrogen electrode consists of a platinum tube immersed in a 1 mole/liter solution of H^+ ions through which hydrogen gas is bubbled, as shown below:
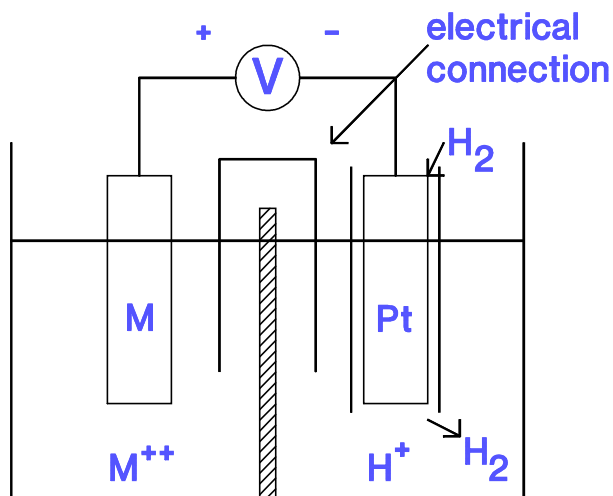
Hydrogen Half-Cell Electrode, As connected to Measure Potential

Note: With the wire in place, it is equivalent to not having a barrier between the 1 mole/liter ion solutions. The potential reaction of the hydrogen half-cell is

$$1/2 \ H_2 \leftrightarrow H^+ + e^-$$

the potential reaction being to the right when the half-cell is anodic to the sample and to the left when it is cathodic.

2.4 Standard Electromotive Force (Surface Potential)

The surface potential of a metal is a measure of its activity. When a metal is immersed in an aqueous environment, both oxidation and reduction reactions occur until some equilibrium is reached. These reactions tend to create an electrical double layer at the surface which establish an electrical potential. The more positive metals are said to be more noble and less reactive, while the more negative metals are called base metals and are highly reactive. The standard potential of metals are given in the following table termed the standard electromotive force series. It should be made clear however that a metal's actual potential can be greatly altered by its environment.

Standard EMF Series Table [from Jones (1996)]
(Note, these potentials are in a solution of 1 mole/liter of their own ions, measured against a
standard hydrogen electrode)

	Reaction	Standard Potential, $e°$ (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 2e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)a	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.342
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 7)[a]	−0.413
	$Fe^{2+} + 2e^- = Fe$	−0.447
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.762
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 14)	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.372
	$Na^+ + e^- = Na$	−2.71
	$K^+ + e^- = K$	−2.931
Active		

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Consider the potential difference between iron and copper. We have

$$\Delta V = V_{Fe} - V_{Cu} = -0.447 - 0.342 = -0.789 \text{ volts}$$

as before. The iron would thus act as an anode in a corrosion hook-up and corrode.

Next consider potential difference between iron and zinc.

$$\Delta V = V_{Fe} - V_{Zn} = -0.447 - (-0.762) = +0.315 \text{ volts}$$

Hence, in this case the zinc would act as the anode and corrode while the iron would act as the cathode in a corrosion hookup. If we put the (+) probe on the iron and the (-) probe on the zinc, we would read +0.323 volts on the voltmeter. This means that the current would be from the iron to the zinc and hence that the electrons would flow from the zinc to the iron in accordance with our previous discussion.

It should be noted that any metal listed in the electromotive series table will act as an anode when connected to one above it in the series and hence will corrode.

For example, if tin (Sn) and zinc (Zn) are connected in a corrosive cell, the tin will act as the cathode and be protected and the zinc will act as the anode and corrode. Similarly, if iron is placed in a solution of nickel ions, the iron will corrode and the nickel will plate out at the local cathode regions. This is known as a DALIC process. The nickel plating of steel is a common process for the restoration of dimensions on shafts and the mating surfaces of press fittings. It is also important to note that given time, as ΔV increases, the rate of reaction also increases.

2.5 Correction for Solution Concentration: Nernst Equation

The potential values listed in the electromotive series table are for a unit concentration (1 mole/liter) of the metal ions in solution. For other concentrations, we may calculate the potential using the Nernst equation, which simplifies to:

$$E = E_o + (0.0592/Z) \log_{10}(c)$$

where E_o is the potential at unit concentration, Z is the valence of the ion (Z = 2 for iron, 3 for aluminum, etc.) and c is the concentration (moles/liter).

Example: As an example, we may calculate the electrode potential of iron in contact with a solution of 10^{-3} moles/liter of Fe^{++} ions. We have from Table 1, E_o = -0.440 V and

$$E = -0.440 + (0.0592/2)\log_{10}(10^{-3})$$

or

$$E = -0.529 \text{ V}$$

2 - 9

2.6 Reference electrodes

Half-cell reference electrodes are used in corrosion measurements to determine the potentials of specific metals in selected aqueous environments. The hydrogen half-cell provides the basic standard, but in practice is awkward to use. For this reason, several other types of half-cells have been developed. Some of these reference cells are listed in the following table along with their potential with respect to the hydrogen half-cell and location of use.

Commonly used half-cells [from Swain Classnotes (1996)].

Half-Cell	Potential Ref. SHE (v)	Environment
Copper : Copper Sulfate	+0.3160	Soil
Tenth Normal Calomel	+0.3337	Laboratory
Normal Calomel	+0.2800	Laboratory
Saturated Calomel	+0.2415	Laboratory
Silver : Silver Chloride (0.1M KCl)	+0.2880	Seawater
Silver : Silver Chloride (Seawater)	+0.2222	Seawater
Silver : Silver Chloride (3.8M KCl)	+0.1990	Seawater
Hydrogen	0	Laboratory
Zinc	-0.7600	Seawater

The following sub-sections present more details on the construction of Saturated Calomel, Saturated Copper-Copper Sulfate and Silver-Silver Chloride half cells.

Saturated Calomel Reference Electrode
In establishing the galvanic series of metals and alloys in seawater, use is generally made of the saturated calomel half-cell, which derives its name of calomel from one of its ingredients, mercurous chloride (Hg_2Cl_2). The potential reaction is

$$2Hg + 2Cl^- \leftrightarrow Hg_2Cl_2 + 2e^-$$
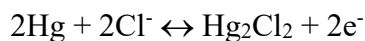
The potential of the saturated calomel half-cell relative to the hydrogen half-cell is + 0.246V. The cell is illustrated below.
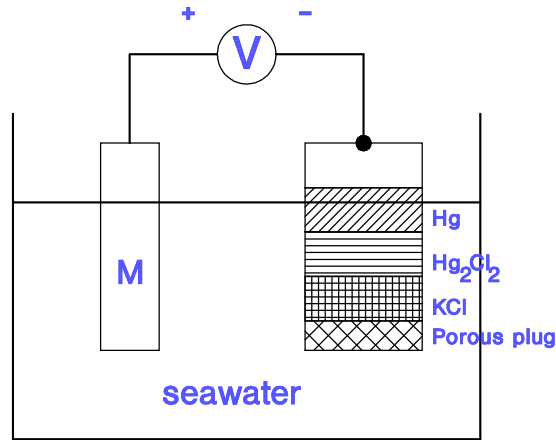
Figure: Saturated Calomel Reference Electrode

Saturated Copper-Copper Sulfate Reference Electrode

The saturated copper-copper sulfate half-cell is an equally useful cell for corrosion measurements. A sketch of the cell is illustrated below. When used, it is immersed in seawater where the porous plug makes the connection to the cell. The half-cell potential reaction is $Cu \leftrightarrow Cu^{++} + 2e^-$ and its reverse. The potential of the copper-copper sulfate half-cell, relative to the hydrogen electrode is +0.316 V
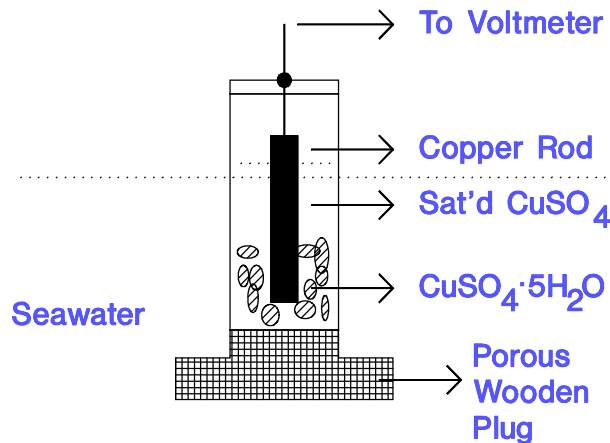
Silver-Silver Chloride Half-Cell

This electrode consists of silver chloride covering a silver plated platinum wire sealed in a glass tube, as indicated below. When the electrode is immersed in a chloride solution (such as seawater), the potential reaction is:

$$Ag + Cl^- \leftrightarrow AgCl + e^-$$

The potential of the silver-silver chloride electrode relative to the hydrogen half-cell is +0.266V.

2 - 11
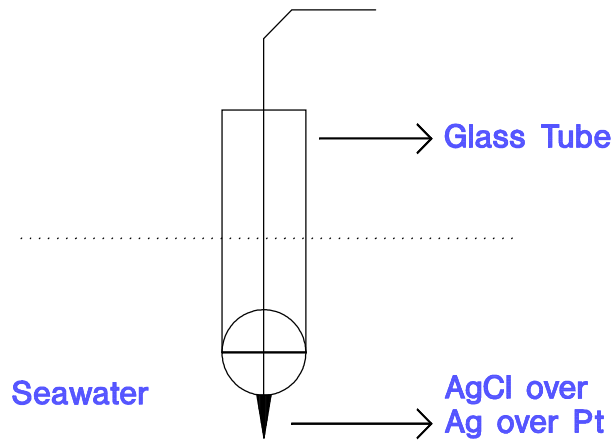
Figure: Silver-Chloride Half Cell

2.7 Galvanic series

In marine applications, we are obviously not so much interested in the potential of a metal immersed in a solution of its own ions as we are in the relative potentials of metals placed in seawater. Such a ranking is known as the **galvanic series**.

The electrochemical series presented earlier can only be applied to oxide free surfaces at ion concentrations for which the standard potentials are valid. When metals are exposed in a more complex electrolyte such as seawater, the galvanic series may be used to help predict if corrosion of a metal is possible. The galvanic series for many commonly used metals is given in the table on the next page. It should be noted that for some metals, such as the stainless steels, there are significant differences in the potential they are likely to exhibit. These differences are generally owed to the condition of the metal surface. For example, 316 stainless steel has a potential of about -0.1v ref saturated calomel when it is passive (protected by a thin oxide film). If the oxide layer is compromised, the potential may shift to -0.4v and corrode. In service, severe localized attack may occur at active sites.
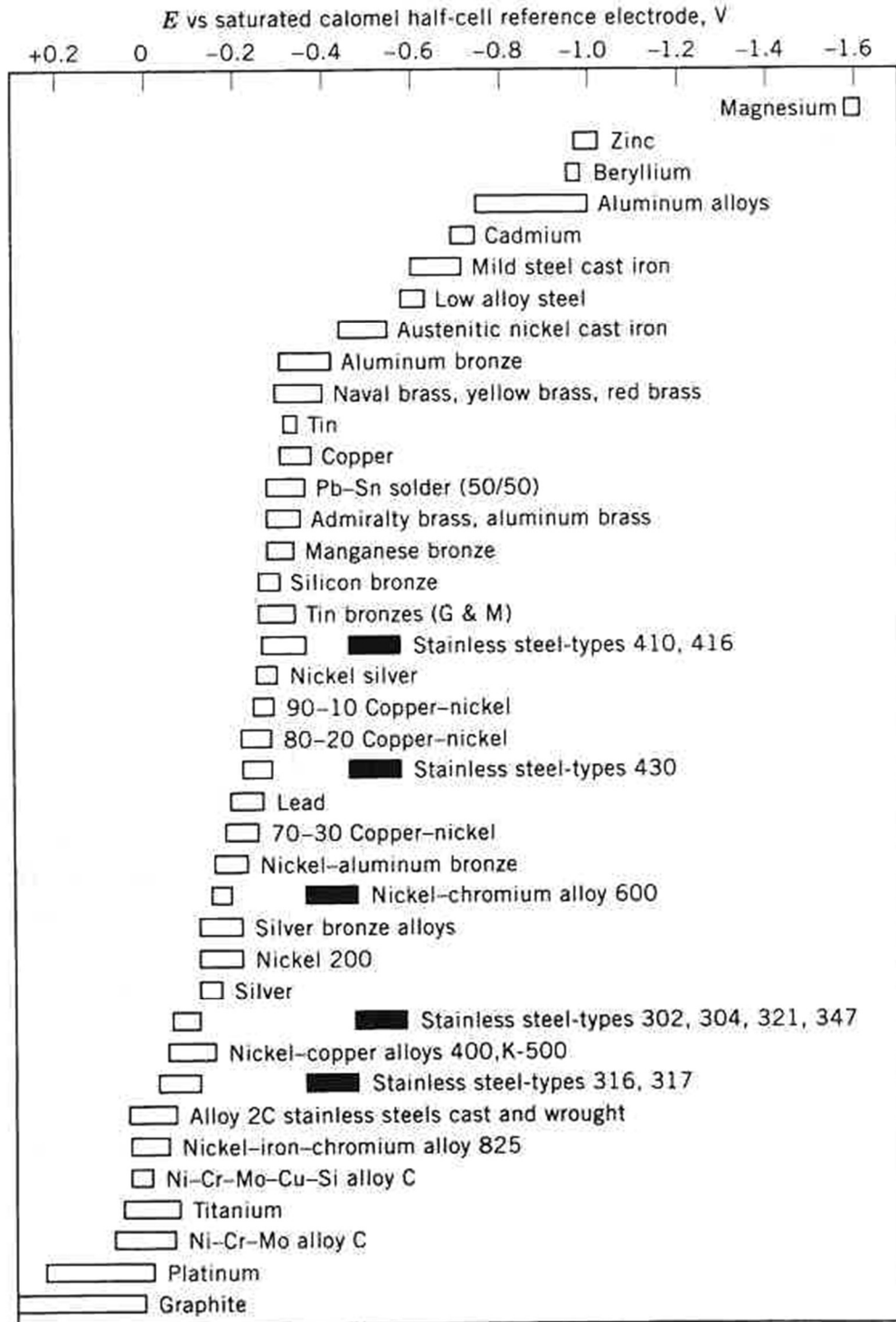
Galvanic Series [from Fontana (1986)].

2 - 13

2.8 Passivating films

Passivity can be defined as the loss of chemical reactivity exhibited by certain metals under specific environmental conditions. In some cases, oxide films which form on the surface of a metal exposed in an electrolyte can have a marked effect on its corrosion behavior. This is notable with metals near the top of the electromotive series. Aluminum, for example, would corrode rapidly in seawater if it were not protected by a thin oxide surface film.

Alloys containing chromium, iron, nickel, and titanium can become "passive" in strong oxidizing solutions when they form protective surface films. In this state, they may have a resistance to corrosion which is orders of magnitude greater than the unfilmed or "active" metal surface. The stainless steels can often exhibit this behavior. The passivating film is usually of the order of only 3 nm in thickness, however. This means that the film can be quite delicate. The ability of the surface film to adhere or self heal if compromised by turbulence or mechanical effects can be the determining factor in their corrosion rate. It is in cases which the surface film does not remain intact that stainless steels can undergo severe localized attack.
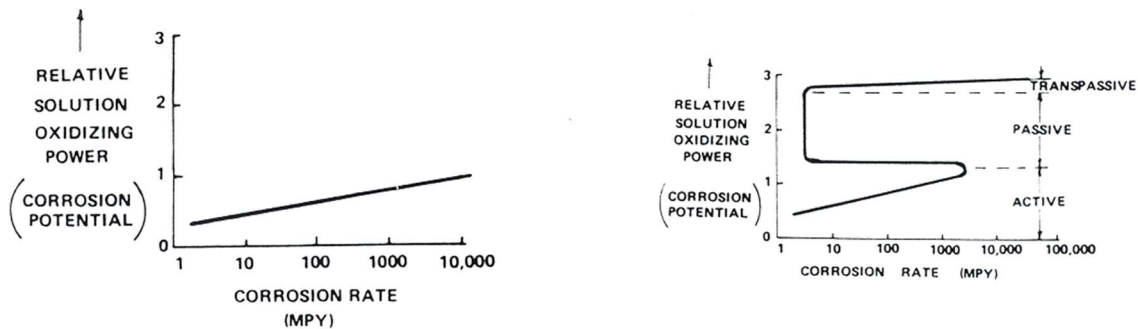
Nonpassivating (left)/ passivating metal (right) [from Corrosion Basics (1984)].

2.9 Concentration Cells

As stated previously, the electrochemical cell may be the result of differing concentrations of reactants on a metal surface. This can be in the form of either oxygen or metal ion concentrations. In both the case of the oxygen concentration cell and the metal ion concentration cell, the surface potential is lowered at the site of lower concentration. Our earlier example of the rotating copper disk was a metal ion concentration cell. In this case the higher velocity on the periphery of the disk led to a turbulent boundary layer. This is much more diffusive than its laminar counterpart. The metal ions produced at the surface move more rapidly from the surface on the periphery. A lower ion concentration at the metal surface is established, and corrosion occurs on the outer part of the disk. Copper and its alloys are the most susceptible to setting up a metal ion concentration cell.

If we this time look at a rotating iron disk placed in aerated seawater, it is observed that the corrosion attack occurs near the center of the disk. Why is this? In this case, an oxygen concentration cell is established on the iron surface. The oxygen on the metal surface is able to reach a higher concentration at the periphery of the disk, where turbulent flow allows higher diffusion. At the center, oxygen concentrations at the metal surface are lower. This causes attack at the center of the iron disk. Iron and its alloys are the most susceptible to forming an oxygen concentration cell.

Both the metal ion and oxygen concentration cell can also be established in metal crevices. In the case of the metal ion cell, corrosion occurs just outside the crevice. In the oxygen concentration cell, attack occurs in the crevice. In all these cases, if the concentrations are known, the driving potential can be predicted with the Nernst equation.

2.10 Effect of Alloying

The graphs depicting the change in corrosion rate with increasing corrosion potential show how the amount of oxidizing agent in solution can have a great effect on the corrosion rate of a metal. Choosing proper alloying metals for a given metal can have a similar effect. Not only can alloying reduce the amount of oxidizer needed to make the metal go "passive", but it can also reduce the corrosion rate of the metal while it is in the passive state. A good example would be adding 18% chromium to iron. This produces what is termed a ferritic stainless steel. The corrosion rates are shown in the following graph.

2 - 15
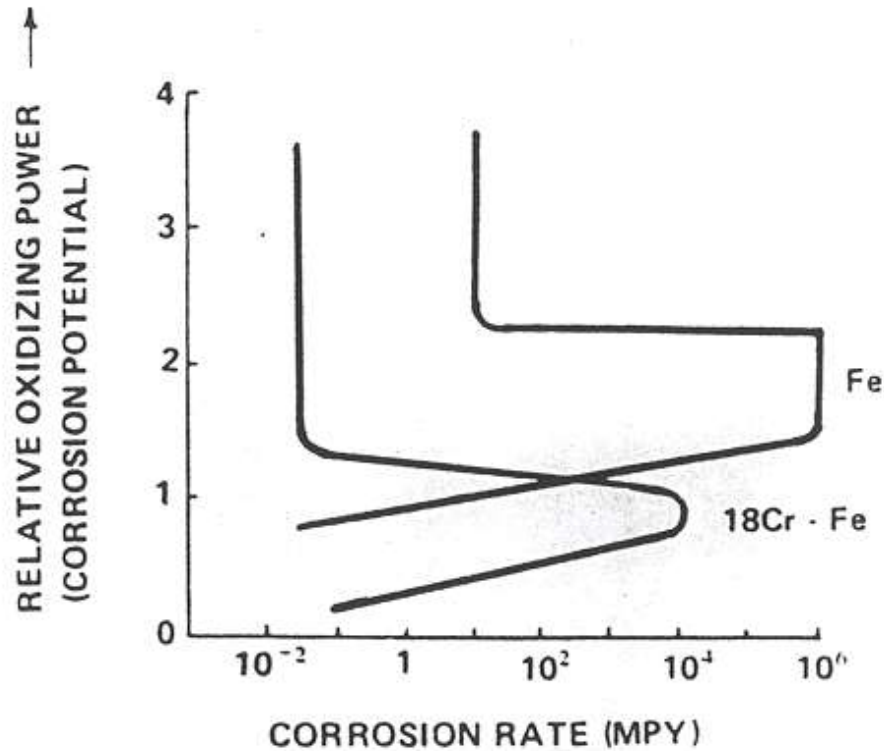
Effect of alloying on corrosion rate [from Corrosion Basics (1984)].

It can be seen that the stainless steel reaches passivity at a much lower corrosion potential and its corrosion rate in its passive state is much lower than that of iron.

2.11 Pourbaix, or pH Diagrams
A plot for a given metal which expresses its potential versus pH, is termed a Pourbaix diagram. The diagrams are generally constructed using equilibrium constants, solubility data, and a form of the Nernst equation which includes a pH term. These diagrams are some very important uses. These include:
- Predicting if corrosion will occur.
- Finding what the corrosion products may be.
- Forecasting what effect environmental changes may have on corrosion.

The following is a Pourbaix diagram for iron immersed in water.

2 - 16
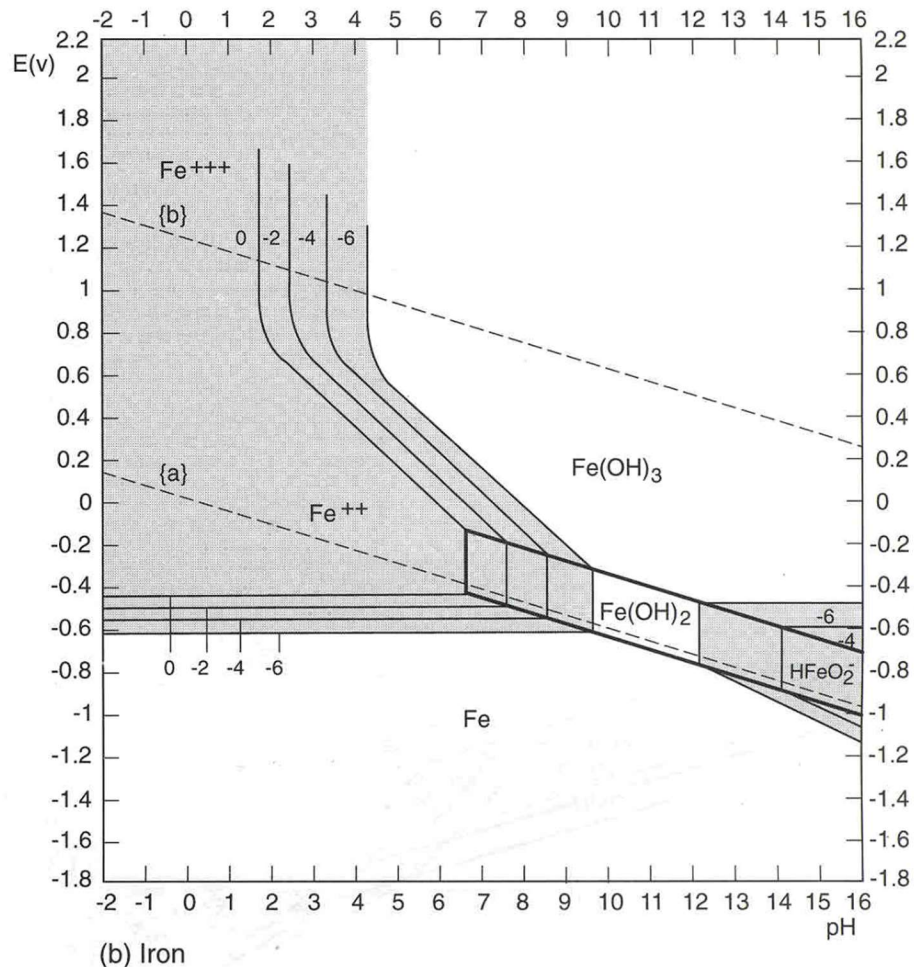
Pourbaix diagram for iron [from Jones (1996)].

Some interesting information can be gleaned from this diagram. The most striking thing is that if iron is kept at a potential of less than -1.2 v with respect to a hydrogen half cell, it should not corrode in a solution of any pH. To keep the iron protected, however, and external voltage would be required. This is the basis of cathodic protection, which we will discuss later in more detail. It can also be observed that in a potential range of about 0.7 v and -0.6 v and pH below 9, the corrosion product will be the ferrous ion. At more positive potentials, the ferric ion would be produced. In other cases, ferric or ferrous hydroxide and complex iron ions may be formed.

References

Corrosion Basics: An Introduction (1984) National Association of Corrosion Engineers, Houston.

Fontana, M.G. (1986) *Corrosion Engineering*, 3rd Edition, McGraw Hill, New York.

Jones, D.A. (1996) *Principles and Prevention of Corrosion*, 2nd Edition, Prentice Hall, Upper Saddle River, NJ.

2 - 17

Schultz, M.P. (1997) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.

Swain, G.W. (1996) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.

Dawson, T. (2003) "EN380 Course Notes" United States Naval Academy.

CHAPTER 3

CORROSION THERMODYNAMICS

3.1 Gibb's Free Energy
3.2 Nernst Equation
3.3 Electrochemical kinetics of corrosion
3.4 Corrosion rates

As we have observed, corrosion reactions inevitably involve electron transfer. For this reason, the reactions may be considered electrochemical in nature. Thermodynamics can provide a basis for the understanding of the energy changes associated with the corrosion reaction. It can, in general, predict when corrosion is possible. Thermodynamics cannot predict corrosion rates. The rate at which the reaction proceeds is governed by kinetics.

3.1 Gibb's Free Energy

The Gibb's free energy, given by the following equation, provides us a tool with which to predict if a corrosion reaction is thermodynamically possible:

$$\Delta G = -nFE$$

$$where : \Delta G = \text{Gibb's free energy (Joules)}$$

$$n = \text{electrons transfered in oxidation reaction (mol e}^-)$$

$$F = \text{Faraday's constant (96,500 J/v - mol e}^-)$$

$$E = \text{Standard emf potential} = E_{ox}^{\,0} + E_{red}^{\,o} \text{ (volts)}$$

$$E_{red}^{\,o} = \text{Standard potential for cathode half cell (volts)}$$

$$E_{ox}^{\,0} = \text{Standard potential for anode half cell (volts)}$$

If ΔG is positive, the reaction will not proceed. If ΔG is negative, the reaction is possible.

Example: *Steel is placed in aerated seawater with a neutral pH. Is corrosion of the steel possible, why? (Assume valence of 2)*

Solution:

Anodic	$Fe \rightarrow Fe^{2+} + 2e^-$	$E_{ox}^o = 0.447\ v$
Cathodic	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$E_{red}^o = 0.820\ v$
Overall reaction	$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$	

$$E = E_{ox}^o + E_{red}^o$$
$$E = 1.267\ v$$
$$\Delta G = -nFE \quad \text{(see variable definitions above)}$$
$$\Delta G = -(2\ \text{mol e}^-)(96,500\ \text{J/v - mol e}^-)(1.267\ v)$$
$$\Delta G = -244,531 \text{J}$$
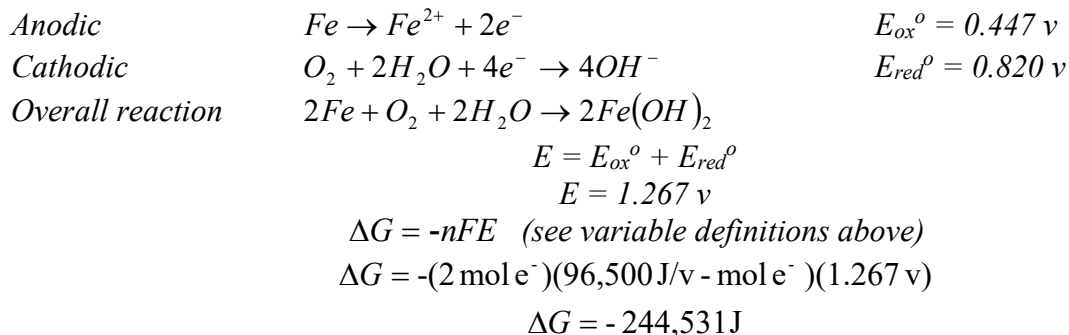
negative sign indicates corrosion reaction, as written, is possible

3.2 Nernst Equation

As mentioned earlier, the potential values of a metal are modified by the environment. Concentrations of anodic and cathodic reactants will alter the balance between the oxidation and reduction reactions. The **Nernst equation** allows us to calculate metal potentials under differing metal ion or oxidation/reduction conditions. The Nernst equation may be stated as follows:

$$E_{cell} = E^o + 2.3\frac{RT}{nF}\log_{10}\frac{[oxid.]}{[red.]}$$

$where : E_{cell} =$ Cell potential under environmental conditons (volts)

$E^o =$ Standard reduction potential @ 25^0C and unit activity (volts)

$R =$ Universal gas constant (8.3143 J/mol °K)

$T =$ Absolute temperature (degrees Kelvin)

$n =$ electrons transfered in the reaction (mol e$^-$)

$F =$ Faraday's constant (96,500 coulombs/mol e$^-$)

$[oxid.] =$ activity of oxidized species (M)

$[red.] =$ activity of reduced species (M)

At standard temperature and pressure (25°C and 760mm Hg) this may be simplified to the following (shown earlier):

$$E_{cell} = E^o + \frac{0.059}{n}\log_{10}\frac{[oxid.]}{[red.]}$$

The Nernst equation can also be written for each half cell as is shown in the following metal ion concentration cell example.

Example: A circular copper coupon is rotated in seawater. A gradient in the metal ion concentration is set up on the disk surface. On periphery of the disk copper ion concentration is 0.001 M. Near the center of the disk the copper ion concentration is 10 M. What are the potentials of anodic and cathodic sites on copper? Where will the metal loss occur? Assume STP.

Solution: In this case we find the standard EMF for the following equation:
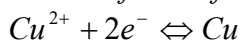
$$Cu^{2+} + 2e^- \Leftrightarrow Cu$$
$$E^o = 0.342 \text{ volts}$$

$$E_{outside} = E^o + \frac{0.059}{n}\log_{10}\left(\frac{[10^{-3}]}{[1]}\right)$$

$$E_{center} = E^o + \frac{0.059}{n}\log_{10}\left(\frac{[10^1]}{[1]}\right)$$

3 - 2

$$E_{outside} = 0.342\text{v} + \frac{0.059}{2 \text{ mol e}^-} \log_{10}\left(10^{-3}\right) = 0.2535\text{v}$$

$$E_{center} = 0.342\text{v} + \frac{0.059}{2 \text{ mol e}^-} \log_{10}\left(10^{1}\right) = 0.3715\text{v}$$

Metal will be lost from the outside of the disk (it is more negative)

$$E_{overall} = E_{center} - E_{outside} = 0.118\text{v}$$

3.3 Electrochemical kinetics of corrosion

We now have a tool to predict if the corrosion reaction is possible, but it would also be handy to predict how fast the reaction will proceed. In theory, Faraday's law can be used do this. Faraday's law may be stated as follows.

$$m = Izt$$

$where: m =$ mass of metal lost to corrosion (grams)

$I =$ corrosion current (amps)

$z =$ electrochemical equivalent $= \dfrac{a}{nF}$ (g/A - s)

$a =$ atomic weight of corroding metal (grams)

$n =$ electrons transfered in oxidation reaction (mol e$^-$)

$F =$ Faraday's constant (96,500 A - s/mol e$^-$)

$t =$ time of reaction (seconds)

3 - 3

Example: A steel coupon with an anode surface area of 1000 cm² is placed in an electrolyte. The corrosion current is measured to be 1 mA. What mass of steel will be lost in 6 hours? What is the corrosion rate in µg/cm²/day? In mpy? Assume valence of 2.

Solution:

$$m = Izt$$

$$I = 0.001\text{A}$$

$$z = \frac{a}{nF} = \frac{55.847\text{g}}{(2 \text{ mol e}^-)(96,500 \text{ A - s/mol e}^-)} = 2.89\text{x}10^{-4}\text{g/A - s}$$

$$t = (6 \text{ hr})\left(\frac{60\text{min}}{1\text{hr}}\right)\left(\frac{60\text{s}}{1\text{min}}\right) = 21,600 \text{ s}$$

$$m = (0.001\text{A})(2.89\text{x}10^{-4}\text{g/A - s})(21,600\text{s})$$
$$m = 6.255\text{x}10^{-3}\text{g}$$

To find the corrosion rate in µg/cm²/day, first divide by anode area and time.

$$\text{rate} = \frac{m}{At} = \frac{6.255\text{x}10^{-3}\text{g}}{(1000\text{cm}^2)(21,600\text{s})}\left(\frac{10^6\text{ }\mu g}{1\text{g}}\right)\left(\frac{3600\text{s}}{1\text{hr}}\right)\left(\frac{24\text{hr}}{1\text{day}}\right) = 25.02\mu g/\text{cm}^2/\text{day}$$

To find the corrosion rate in mpy, divide by the metal density.

$$\text{rate} = \frac{25.02\mu g/\text{cm}^2/\text{day}}{\rho} = \frac{25.02\mu g/\text{cm}^2/\text{day}}{7.20\text{x}10^6\text{ }\mu g/\text{cm}^3}\left(\frac{365\text{days}}{\text{yr}}\right)\left(\frac{1\text{mil}}{2.54\text{x}10^{-3}\text{cm}}\right)$$
$$\text{rate} = 0.499 \text{ mpy}$$

3.4 Corrosion rates

The rate of corrosion (or current density) is determined by the potential difference beween the anode and the cathode and the resistance of the corrosion cell. The corrosion current is therefore:

$$I = \frac{V}{R}$$

The resistance of the cell may be as a result of electrical resistance or electrode polarization. The greater the resistance the lower the corrosion current and from Faraday's law the lower the mass loss. A high resistance within the corrosion cell is beneficial for control. This resistance may result from one or more of the following factors:
- Resistance of the electrical connection between anode and cathode.
- Resistance of the electrolyte.

- High concentration of anode metal ions in solution.
- Reactant build-up at the cathode.
- Lack of reactants at the cathode.

The action of these resistances may be expressed in a polarization diagram. These diagrams plot potential difference versus current (or log current). The slope of the curve represents the resistance.

The following table gives density, atomic mass, valence, and corrosion rate for various metals.

Corrosion data for various metals [from Swain Classnotes (1996)].

Element	Atomic Mass (g/mole)	Valence	Electrochemical Equivalent (g/coulomb)	Corr. rate equivalent to 1 $\mu A/cm^2$ (mm/yr)	Density (g/cm^3)
Magnesium	24.31	2	1.26E-04	0.023	1.74
Zinc	65.38	2	3.39E-04	0.015	7.13
Aluminum	26.98	3	9.30E-05	0.011	2.72
Iron	55.85	2	2.89E-04	0.013	7.20
Iron	55.85	3	1.93E-04	0.087	7.20
Copper	63.54	1	6.58E-04	0.023	8.94
Copper	63.54	2	3.29E-04	0.012	8.94
Nickel	58.71	2	3.04E-04	0.011	8.89

CHAPTER 4

POLARIZATION

4.1 Activation and Concentration Polarization
4.2 Scaling of Corrosion Measurements
4.3 Determination of Corrosion Current for Single Metals
4.4 Mixed Potential Theory
4.5 Alternate construction of Polarization Diagrams

Previously, our consideration of potentials has dealt with equilibrium considerations when no current actually existed between the cathode and the anode. When a net current to or from an electrode exists, the electrode is no longer in equilibrium and the measured potential is altered. The alteration being such as to oppose the current. The extent of the potential change caused by the current is known as polarization. Such change is caused by various physical and chemical factors at the electrodes.

Polarization may be defined the shift in electrode potential which results from the effects of current flow w.r.t. the zero current flow potential. All corrosion reactions involve current flow and will alter the potential of the metal surfaces involved. The degree of polarization will be determined by the resistance of the corrosion cell. The higher the cell resistance, the larger the shift in potential.

$$V = IR$$

Anodic and cathodic polarization can be measured using the cell illustrated below
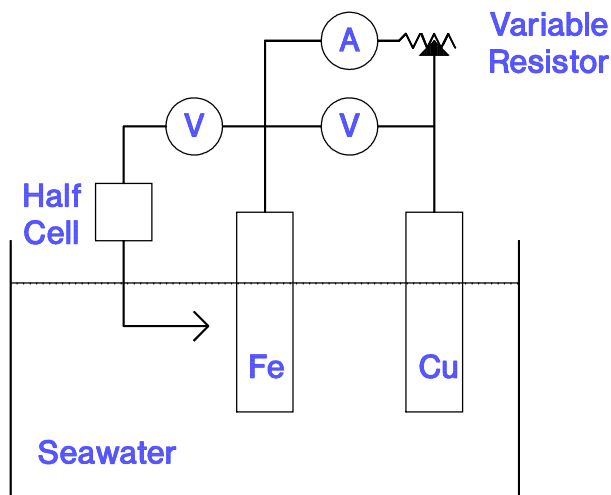
Laboratory Polarization Cell

As the current is allowed to develop through the variable resistor, the potential difference between the two metals will decrease as illustrated in the graph below. This decrease in potential difference is due to the polarization of the two electrodes. Note that the potential is plotted on a linear scale while the current is plotted on a logarithmic scale, plotted on semi-log paper. This causes the data to plot approximately as straight lines.
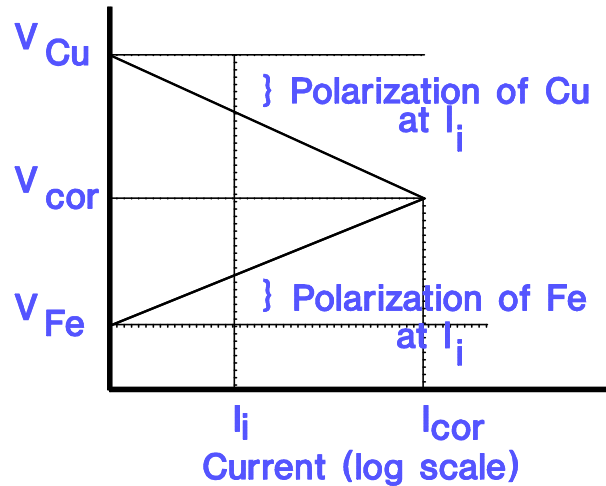
Polarization Graph for Iron-Copper Corrosion

At I_I in the figure above, the polarization of the cathode (copper) and the anode (iron) is as indicated and the potential difference (ΔV) between the two is reduced from its open-circuit value (V_{Cu} - V_{Fe}). Finally, when the resistor is completely shorted out of the circuit, I_{cor} is the maximum corrosion current and V_{cor} is the corresponding voltage. Note that the potential difference will not be zero even when the resistor is shorted since there is internal resistance in the electrolyte.

When the potential change caused by current (polarization) occurs mostly at the anode, the corrosion is said to be anodically controlled. When polarization occurs mostly at the cathode, it is said to be cathodically controlled. These conditions are illustrated in the figure below.
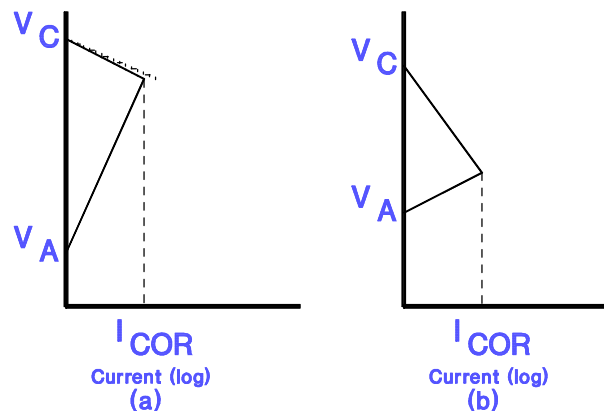
System Corroding under (a) anodic and (b) cathodic control

4.1 Activation and Concentration Polarization

There are two different types of polarization, that is, two ways that electrochemical reactions of corrosion are retarded. These are referred to as activation and concentration polarizations.

Activation polarization is used to indicate retarding factors inherent in the reaction itself. Thus, for example, with a metal corroding in acid, a finite time is required to form hydrogen gas at the cathode regions even when an ample supply of electrons exist.

In contrast, <u>concentration polarization</u> refers to the retardation of an electrochemical reaction of corrosion resulting from concentration changes in the solution next to the metal surface. A good example is provided by the cathode region of a metal corroding in seawater, that is,

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$
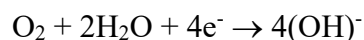
which is known as the hydroxyl reaction. Because of its low solubility in seawater, the amount of oxygen in contact with the cathode areas is small and readily consumed by the reaction. For the reaction to continue, additional oxygen must therefore diffuse to these areas. <u>The diffusion of oxygen is a relatively slow process and accordingly gives rise to concentration polarization of the cathode</u>.

With metals corroding in seawater, the main retarding effect on the corrosion is generally the concentration polarization resulting from the slow diffusion of oxygen to the cathode areas. The "bottleneck" in the corrosion process is therefore the cathode reaction, and any situation which would increase the rate of the oxygen diffusion would increase the rate of corrosion. Thus, for example, water flowing past a steel pipe is more corrosive than still water because of the increased oxygen supply. Conversely, de-oxygenated water is far less corrosive than ordinary. This is the prime reason that steam plant feedwater and reactor coolant water is "deaerated" prior to use.

Because corrosion of metals in seawater is cathodically controlled, the relative size of the anode and cathode has an important effect on the corrosion. The larger the cathode, relative to the anode, the faster the corrosion since more surface area on the cathode is in contact with the seawater and thus in contact with the oxygen. In seawater, small steel (or iron) rivets in a large copper plate would fail quickly by accelerated corrosion. If the reverse was used, ie steel plates riveted together with copper rivets, the corrosion would be greatly reduced. These effects can be illustrated by a polarization diagram.
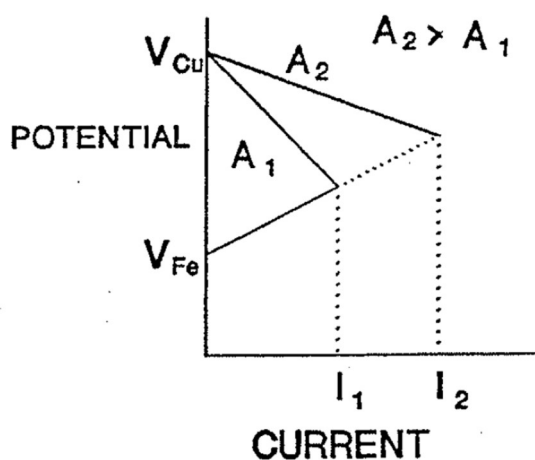
Effect of Area on Polarization

With the larger cathode area, A_2 the polarization (potential change caused by current) of the cathode is reduced and the corrosion current is increased, thereby accelerating the corrosion of the anode. These polarization diagrams may also be plotted as a function of current density, below:

Polarization diagram [from Jones (1996)].
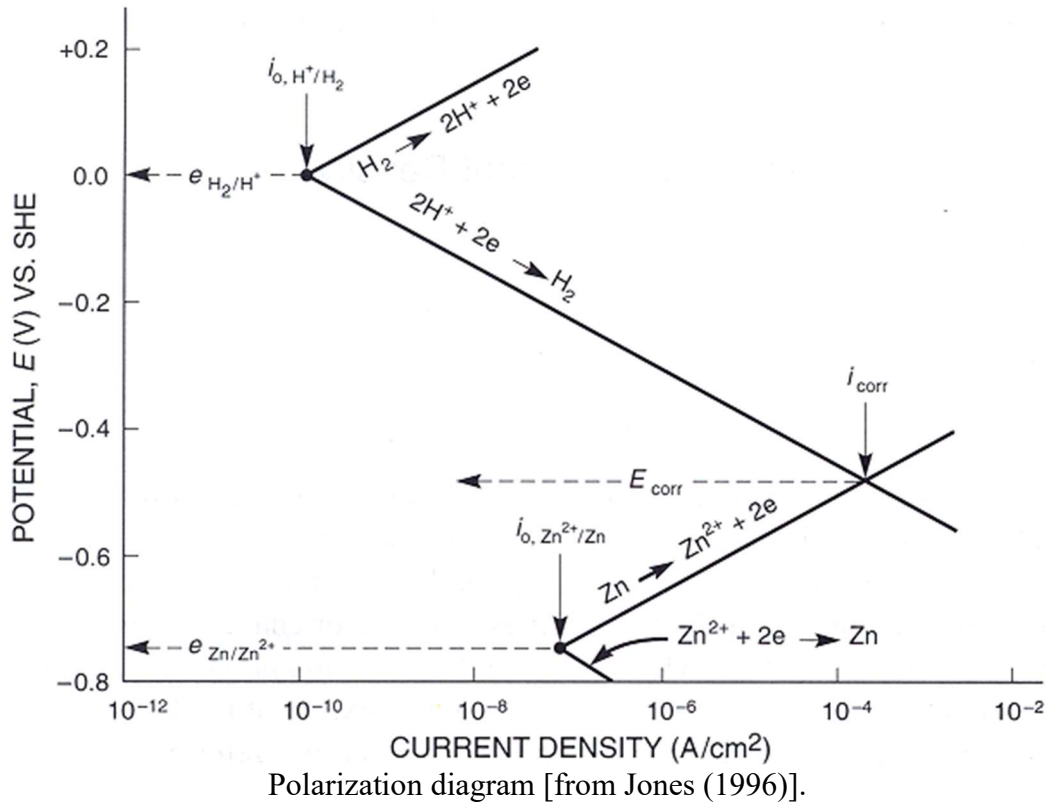
4.2 Scaling of Corrosion Measurements

We may use laboratory scale polarization cells such as illustrated earlier to determine the corrosion current for two small metal samples. <u>Under appropriate conditions</u> (such as flow of the electrolyte or bio fouling), we may then scale this measurement to predict the corrosion current for the same metals when attached to a full scale field set-up.

The procedure is based on the fact that the corrosion current per unit of (wetted) anode area is a function of the types of metals, the ratio of the area of anode to cathode, and the type and condition of the electrolyte. Thus, we have

$$\frac{I}{A_A} = F(\frac{A_A}{A_C}, electrolyte, metals)$$

Now, if we fix all the dependent variables in this equation, the independent, I/A_A, will be fixed. Thus, if we keep the same anode and cathode metals, duplicate the electrolyte, and require

$$(\frac{A_A}{A_C})LAB = (\frac{A_A}{A_C})FIELD$$

Then $(\frac{I}{A_A})LAB = (\frac{I}{A_A})FIELD$?? $(\frac{I}{A_C})LAB = (\frac{I}{A_C})FIELD$

Example: We wish to find the corrosion current existing in a field (ocean) structure when 50 ft² of steel (anode) is attached to 25 ft² of copper (cathode). Laboratory data for a steel bar of 5 in² and a copper bar of 2.5 in² give corrosion current (in seawater) of 5 ma (5 x10⁻³ amps).

Solution: First, since the ratio of anode to cathode area is equal to 2, we can directly scale the lab data.

Therefore,

$$(\frac{A_A}{A_C})_{LAB}=2, (\frac{A_A}{A_C})_{FIELD}=2$$

$$\frac{(I)_{LAB}}{(A_A)_{LAB}}=\frac{(I)_{FIELD}}{(A_A)_{FIELD}}$$

$$(I)_{FIELD}=\frac{(A_A)_{FIELD}}{(A_A)_{LAB}}(I)_{LAB} \ \ or \ \ I_{FIELD}=\frac{50 \ x \ 144}{5} \ x \ (5 \ x \ 10^{-3})= 7.2 \ amps$$

Thus, so long as the conditions of the seawater in the lab approximate these in the ocean, the expected current in the field is 7.2 amps.

4.3 Determination of Corrosion Current for Single Metals

When two metals are in electrical contact in an electrolyte such as seawater, we can determine the corrosion current and potential using the polarization cell illustrated in Figure 8. When a single bar or object is placed in seawater, however, the anodes and cathodes will be located at small, continually changing areas of the bar. As discussed earlier, an indirect method for determining the corrosion current and potential must be used. Consider the set-up shown below consisting of a specimen.
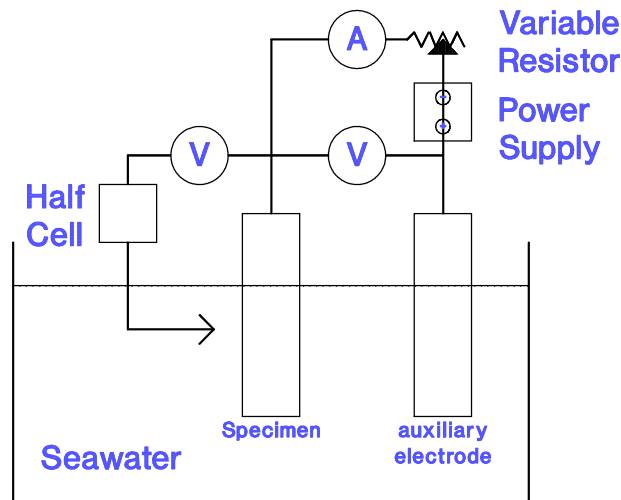
Cell for study of polarization of a single metal

If the specimen is attached to the negative side of the power supply, electrons will be drawn from

4 - 5

the auxiliary electrode and supplied to it. Thus the specimen will be made to act as a cathode even if it is naturally anodic to the auxiliary electrode. Similarly, if the specimen is attached to the positive side of the power supply, it can be made to act as an anode, with electrons being drawn from it and supplied to the auxiliary, regardless of its natural tendency toward the auxiliary electrode.

Using this cell, we thus first make the specimen act as an anode and determine current and potential data for a number of power supply settings. Next we repeat the process when the specimen is made to act as a cathode. On dividing the current measurements by the specimen area in contact with the seawater, we obtain <u>current density</u> measurements which are independent of the particular size of the specimen used in the test. In this way we can then construct the polarization diagram shown below.
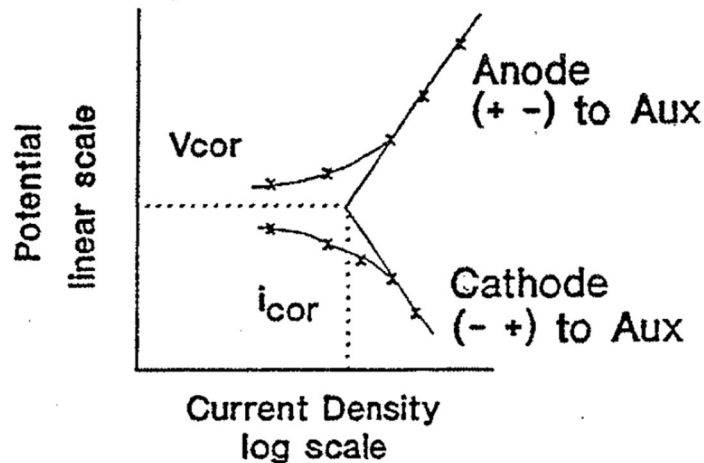
Polarization Diagram for a Single Specimen in Seawater

When the potential approaches the corrosion potential V_{cor}, certain areas of the specimen will act as anodes and cathodes regardless of the polarity setting of the power supply. Thus, the polarization curve will no longer reflect total anodic or cathodic behavior, as indicated by the portion of the curves in the figure above near V_{cor}.

By extrapolating the pure anodic and cathodic curves, we can estimate the corrosion potential and the corresponding net corrosion current density existing for the specimen. With the corrosion current density known we can then calculate the corrosion current for a given surface area in contact with the seawater simply as the product of the current density and the wetted area.

<u>Example</u>: Listed below are <u>potential - current density</u> polarization data for a metal A in seawater. Use this data to determine the corrosion current existing for 20 ft² of metal A in contact with seawater.

Metal A			
Pot (v)	*i (ma/in^2)*	*Pot (v)*	*i (ma/in^2)*
-0.70	0.100	-0.52	0.087
-0.74	0.158	-0.40	0.110
-0.80	0.251	-0.32	0.138
-0.85	0.400	-0.20	0.190

Solution: *The data is plotted as shown with log$_{10}$(i) as the horizontal axis. The corrosion current density is read as log$_{10}$(i) = -1.22 or i - 0.06. The corrosion current for the 20 ft^2 area is I = 0.06 x 20 x 144 = 173 ma.*
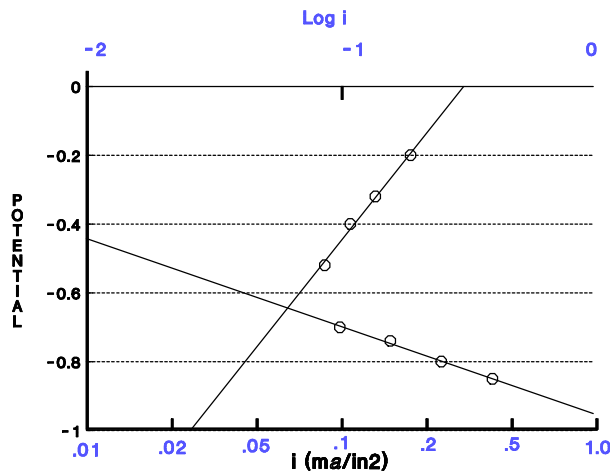
4.4 Mixed Potential Theory

Polarization diagrams such as shown above "Polarization Diagram for a Single Specimen in Seawater", if determined for two dissimilar metals, can be used to estimate the corrosion current and mixed corrosion potential when the two are connected together in a galvanic cell. The method is based on the requirement that the magnitude of the current must be the same for the anode and the cathode. Thus, the current densities in the polarization diagrams for each metal must be converted into actual currents for the given area of metal in contact with the electrolyte (the product of the current density and respective areas). When plotted together, the intersection of the two polarization (potential vs current) curves will indicate where the current is the same for both metals, and thus, the corrosion current. This method is illustrated in the figure below. In this figure, the corrosion current I$_{cor}$ and mixed potential V$_{cor}$ are determined as shown. For the two metals, it is also seen that metal B acts as the anode and metal A as the cathode.
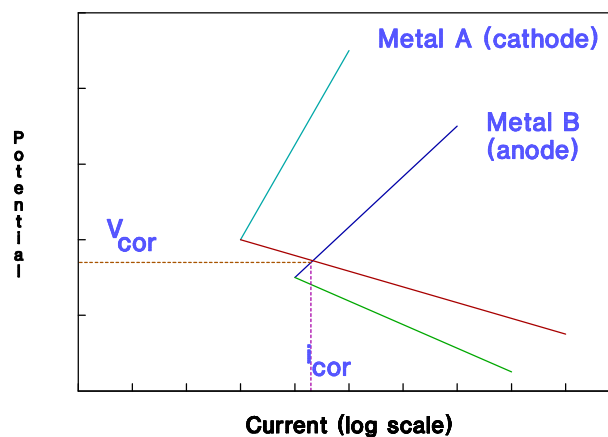
Example: Listed below are potential-<u>current density</u> data for metals A and B in seawater.

Metal A   Metal B

Pot (v)	i (ma/in^2)		Pot (v)	i (ma/in^2)
-0.66	0.075		-0.54	0.300
-0.74	0.090		-0.70	0.215
-0.86	0.120		-0.86	0.150

Use this data to estimate the corrosion current existing for 20 ft^2 of metal A in contact with 12 ft^2 of metal B in a Galvanic cell.

<u>Solution:</u> *The current densities of A are multiplied by the area, 20 x 144 = 2880 in^2, to get the total current. Potential vs $\log_{10}(I)$ is then plotted as indicated. Similarly, the current densities of B is multiplied by its area, 12 x 144 = 1728 in^2 and its potential-current relationship plotted. B is seen to act as the anode and metal A as the cathode. The corrosion current is read from the intersection of the two lines as $\log_{10}(I)$ = 2.47, or I = 295 ma.*
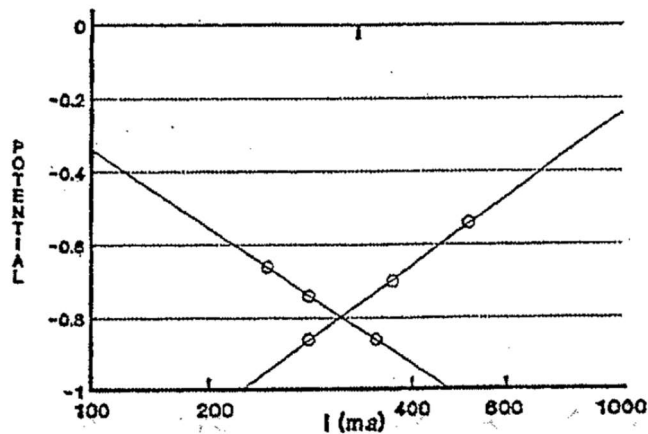
Example: Polarization diagrams for two metal specimens A and B are shown below. Using these, determine the corrosion current (in amps) for a submerged structure having 45 ft^2 of metal A in contact with 90 ft^2 of metal B.
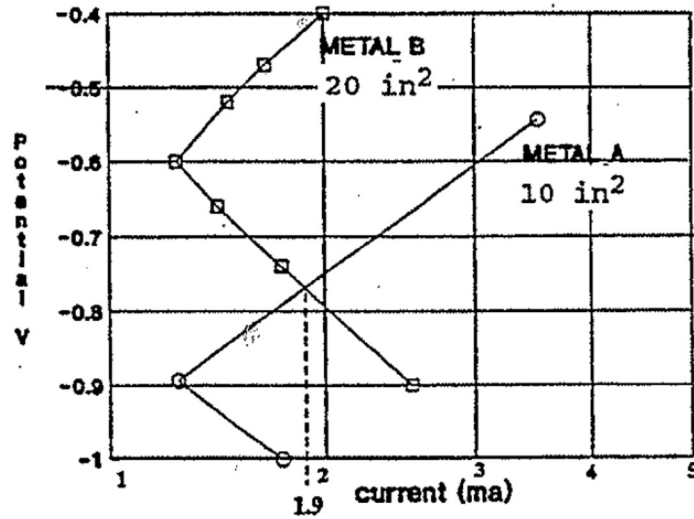
Solution: This diagram is for 20 in² of metal B in contact with 10 in² of metal A. Since the ratio of these areas (20/10 = 2) is the same as that of interest (90/45 = 2), we may find the corrosion current by directly scaling the value found from the data. The corrosion current from the data is I = 1.9 ma. Hence since the ratio of I/AA is the same for the lab and the field under the conditions of direct scaling,

$$\frac{(I)_{LAB}}{(A_A)_{LAB}} = \frac{(I)_{OCEAN}}{(A_A)_{OCEAN}} \ or \ (I)_{OCEAN} = I_{LAB}\frac{(A_A)_{OCEAN}}{(A_A)_{LAB}}$$

we have

$$I = 1.9 \ x \ 45 \ x \ 144/10 = 1231 \ ma \ (1.23 \ amps)$$

4.5 Alternate construction of Polarization Diagrams

The polarization diagrams discussed above refer to the case where the anode reaction is that of a metal changing to its ion and the release of electrons, and the cathode reaction is that typical of seawater where the electrons are used to make hydroxyl ions, as indicated the figure "Polarization Diagram for a Single Specimen in Seawater" a few pages back. An alternate diagram may be determined for which the anode reaction is still the formation of the metal ion, but the cathode reaction is the plating out of the ion from an ion-rich solution. (Such as in an acid bath). The measurement thus involved is an experimental polarization cell, except that the seawater is replaced with an electrolyte rich in the metal ion. The figure below illustrates the polarization diagram obtained by this procedure.
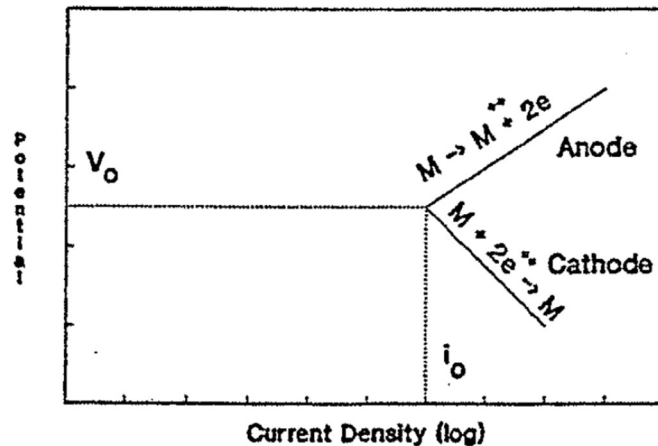
Polarization diagram for case where cathode reaction is the plating out of the metal ion.

An interesting interpretation of this diagram is that the intersection of the anode and cathode curves gives, not the corrosion current, but instead the equilibrium exchange current where as many ions are going into solution as are coming out. If we superimpose on the polarization diagram of Fig. 15, the corresponding diagram for the reaction $O_2 + H_2O + e^- \leftrightarrow OH^-$ we then have the diagram shown below.
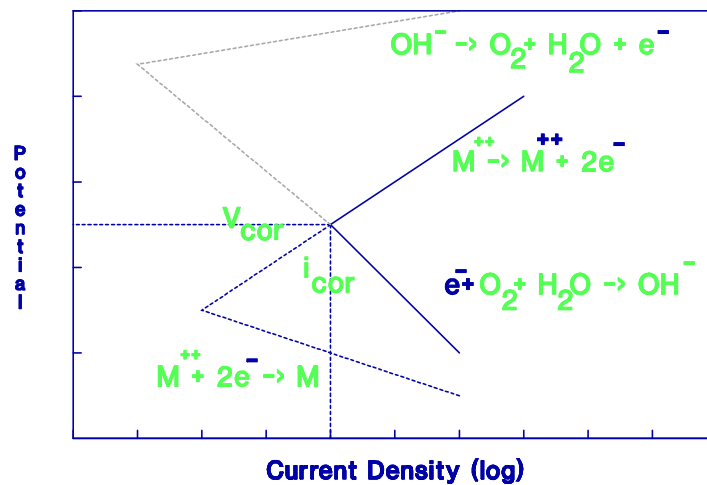
Superimposed Polarization Diagrams for metal/seawater reaction

The solid line in the figure above is seen to correspond to the polarization diagram shown earlier. The intersection represents the corrosion potential V_{cor} and the free corrosion current density i_{cor} of the metal in seawater. This alternate method for polarization diagrams is thus seen to be one-step more detailed than that of our earlier discussion.

CHAPTER 5

CORROSION TYPES

5.1 Uniform Corrosion
5.2 Galvanic Corrosion
5.3 Crevice Corrosion
5.4 Pitting Corrosion
5.5 Other Localized Corrosion
5.6 Selective Leaching aka Dealloying
5.7 Erosion-Corrosion
5.8 Stress-Corrosion-Cracking (S.C.C.)
5.9 Intergranular Corrosion
5.10 Fretting
5.11 Biological corrosion
5.12 Stray current corrosion

The diagram on the following page illustrates the main types of corrosion which will be discussed in this chapter.
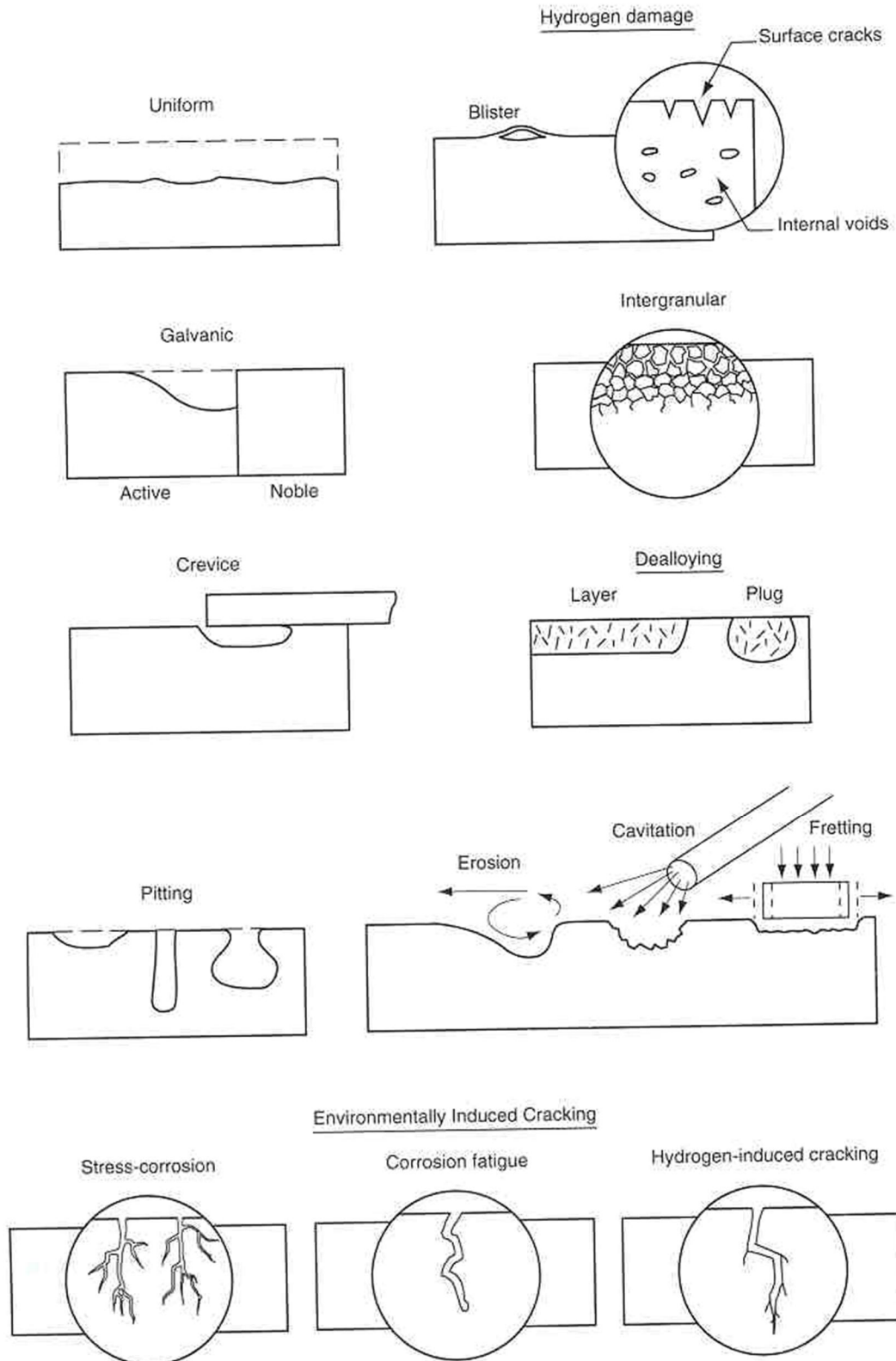
Corrosion types [from Jones (1996)].

5.1 Uniform Corrosion

This corrosion results from the continual shifting of anode and cathode regions of the surface of a metal in contact with the electrolyte and leads to a nearly uniform corrosive attack on the entire surface. An example of such corrosion is the rusting of steel plate in seawater.
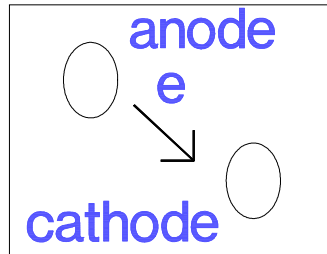
If the rate of metal loss is known, allowances can be made in design and maintenance to accommodate the corrosion. Although it is termed uniform corrosion, it is characterized by the average surface loss.

Uniform corrosion of storage tanks [from Jones (1996)].

5.2 Galvanic Corrosion

When two different metals are exposed to a corrosive environment, an electrical potential difference will exist. If the two metals are electrically connected, the more active metal will become the anode in the resulting galvanic cell and its corrosion will be increased. An example of such a corrosion cell is the use of steel bolts to hold copper plates together

Not all galvanic corrosion is detrimental. Zinc coated steel, or galvanizing, is used to protect steel, not because the steel is resistant to corrosion, but because the zine, being anodic to the steel, corrodes preferntially. Hence, the steel is protected cathodically by making any exposed areas of steel into cathodes.

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It is generally good practice not to use dissimilar metals unless it is necessary, but if it is, the following precautions should be used:

- Attempt to electrically isolate the metals.
- Use protective coatings on the metal surface(s), generally the cathode
- Cathodically protect the less noble metal.
- Put corrosion inhibitors into the system.
- Use design in which anodic part may be replaced easily.
- Keep out moisture.
- Use metals that are close to one another in the galvanic series.
- Design so that the anode/cathode area ratio is high.
- Use design allowances to account for the corrosion.

5.3 Crevice Corrosion

Crevice corrosion is a localized attack which occurs when crevices, formed by lapped joints, or areas of partial shielding, are exposed to corrosive environments. Such resulting cells are referred to as concentration cells. Two common cases are oxygen cells and metal-ion cells.

Oxygen concentration cells occur when the shielded area becomes depleted in oxygen and the area acts as an anode relative to the oxide region. As illustrated in Figure 24, the corrosion becomes quite rapid because of the small shielded area as compared to the unshielded area. Do not get confused with the concentration polarization that we previously discussed. In the case of an oxygen cell, we have an oxygen "gradient" that forces the formation of the anode and cathodes with respect to the oxygen levels.

5 - 4
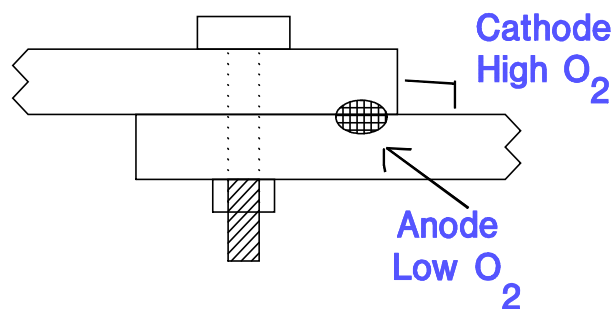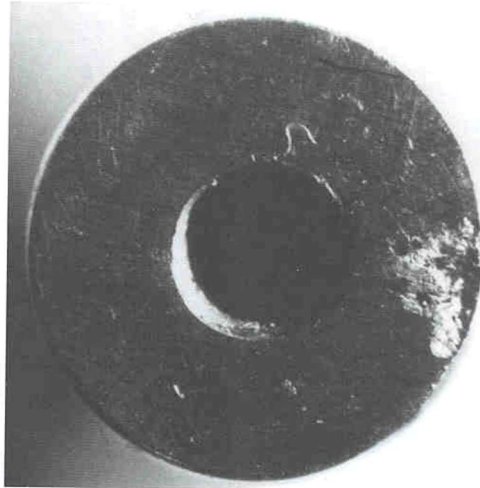
Crevice corrosion of stainless steel [from Jones (1996)].

The initial driving force of such corrosion is the oxygen cell. The continued growth is fostered by the accumulation (often caused by the same factors that produced the low oxygen level) of acidic, hydrolyzed salts within the crevice. Alloys, such as 18-8 stainless steels, are subject to oxygen cell crevice corrosion.

Metal-ion cells are formed mainly with copper alloys. The shielded area accumulates corrosion products and becomes cathodic to the regions outside of the crevice where corrosion products are kept washed away. The figure below illustrates this type of concentration cell.
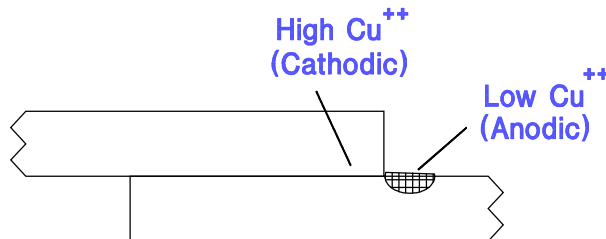
Another example of metal-ion cell corrosion occurs when relative speeds of electrolyte over the metal surface are greater at one point than at another, thus resulting in metal-ion crevice corrosion. A good example is where a disc of metal is rotating at high speed in seawater. Corrosion occurs near the edge where linear velocities ($v = \omega r$) are the highest and the metal-ion concentration is low (since the ions are repeatedly swept away). The high velocity, higher than in regions closer to the hub of the disc, sweeps away the metal-ions, thus forming anode regions. At the center of the disc, where velocities are lower, the metal acts as a cathode and is protected (Do not confuse this with the discussion on "immunity" from corrosion where the low ion concentration was one of the entering arguments. That was an equilibrium concentration. In this case, metal ions continue to form because we can't reach an equilibrium concentration).

However, the two concentration cells corrode at different regions of the crevice. The oxygen cell corrodes under the shielded area while the metal-ion cell corrodes outside of the area. As stated before, the initial driving force behind the corrosion is either the oxygen or the metal-ion cell. Its continued growth is governed by the accumulation of corrosion products, clacareous deposits, and salts within the crevice.

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5.4 Pitting Corrosion

Pitting is an extremely localized attack that eventually results in holes in the metal. It is one of the most destructive and insidious forms of corrosion. Basically, the alloys subject to pitting are those that rely on an oxide film for protection, such as stainless steels. The initiation of a pit can be the result of any of the following:

a) Chemical attack, such as ferrous chloride or aerated seawater on stainless steel.

b) Mechanical attack such as an impact or scratching that removes small areas of the protective film.

c) Crevice corrosion resulting from tiny deposits on the surface, especially in stagnant seawater.

Some theories state that pitting is just a special case of crevice corrosion.

Localized pitting of stainless steel [from Jones (1996)].

5.5 Other Localized Corrosion

In addition to the pitting and the crevice corrosion, the following are also localized corrosion:

- Poultice corrosion - attack which occurs at the edge of a damp fabric.
- Deposition corrosion - corrosion process in which a more noble metal deposits on a less noble metal and causes attack due to a bimetallic cell. It is common in copper/aluminum systems
- Filiform corrosion - localized attack of a metal surface beneath a coating due to oxygen concentration cells.

5.6 Selective Leaching aka Dealloying

Selective Leaching corrosion results from areas of a metal surface being different metallurgically from other, adjacent areas. Brass, for example, is an alloy with zinc and copper in a "solid solution". It can corrode with the zinc being selectively removed from the alloy, leaving behind the copper. It makes the alloy porous and compromises its mechanical properties. In brass it may be identified when its yellow natural color turns reddish or coppery in appearance. It is helpful to add a small amount of tin to the alloy to prevent dealloying.

Such selective leaching is known as "dezincification". Cast irons can corrode in such a matter that the iron is selectively corroded away, leaving behind a soft graphite layer. This is referred to as "graphitization". Other examples are referred to as dealuminification, denickelification, decobaltification, etc. where the terms refer to the metallic element that is selectively corroded away.

The mechanism of selective leaching has been explained as follows for a brass alloy:
       A. the brass corrodes
       B. the zinc ions stay in solution
       C. the copper plates back on as a solid layer

The problem with this theory is that the corrosion occurs even under high electrolyte flow velocities when one would surmise that the copper ion would be swept away before they could plate out.

A second theory, again for brass, is that the zinc corrodes preferentially, leaving behind copper in a lattice structure. A corrosion process in which the less noble metal in an alloy is attacked preferentially and replaced in the matrix by cathodic products. The most common example of this occurs with brass and is termed dezincification. In the dezincification of brass, the zinc in the alloy's matrix is attacked and copper remains.
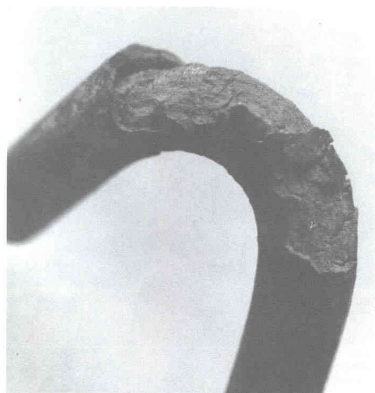
Dealloying of brass [from Jones (1996)].

5.7 Erosion-Corrosion

Erosion-Corrosion results from a high velocity electrolyte flow whose abrasive action accelerates the corrosion. This corrosion is especially severe when the electrolyte contains solids in suspension. The effect is to remove a protective oxide from the film surface, thus exposing fresh alloy to corrode. Erosion-Corrosion could be thought of as pitting on a much larger scale.

There is, in fact, a limit to what electrolyte velocities can be tolerated by specific metals. Copper-nickel alloys are selected for seawater service based on their resistance to erosion-corrosion (amongst other requirements). This table illustrates these limitations.

<u>Recommended Maximum Velocity to Reduce</u>
<u>Impingement/Velocity Effects in Seawater</u>

<u>Alloys</u>	<u>Maximum velocity, fps</u>
<u>Copper</u>	3
90 Cu/10 Ni (with 1.25% Fe)	12
70 Cu/30 Ni (with .5% Fe)	15
85 Cu/15 Ni (with .5% Cr)	>15
<u>Titanium</u>	>15

In addition to Erosion, other forms of attack related to velocity effects are:
- Cavitation - the deterioration of a surface caused by the sudden formation and collapse of bubbles and voids due to the turbulence in the liquid. It is generally marked by a pitted or rough metal surface.
- Impingement attack - localized corrosion caused by turbulence or impinging flow. Generally there is a critical velocity below which no impingement occurs and above which attack increases rapidly.

It should be stated that in many cases these three corrosion processes occur simultaneously.
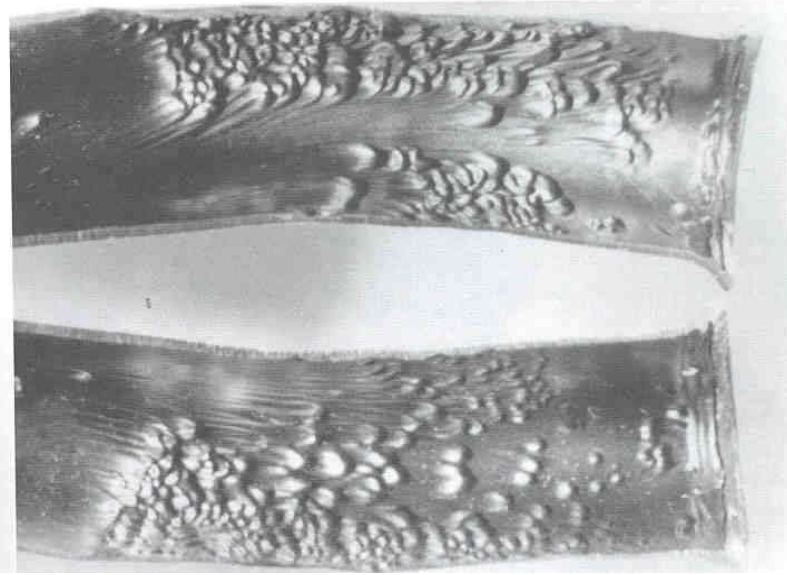
Erosion corrosion [from Jones (1996)].

5.8 Stress-Corrosion-Cracking (S.C.C.)

Stress-corrosion-cracking occurs with specific alloys under the following threshold conditions:
   a) Specific corrosive environment solution composition
   b) Minimum tensile stress levels
   c) Temperature
   d) Metal composition
   e) Metal structure

Some examples of scc are the brass and stainless steel alloys. Specific brass alloys will crack in ammonia containing environments when a minimum threshold tensile stress is reached. Stainless steel alloys do not crack in ammonia environments, but will crack in chloride solutions.

The interplay of the conditions leading to scc is not well understood. It is believed that the corrosion causes a pit or surface discontinuity to form on the metal which then functions to act as a stress concentrator. The presence of a minimum threshold tensile stress, coupled with the corrosion, causes the crack to propagate. Additionally, during the initial corrosion, the tensile stresses could cause the protective films on the surface to rupture, thereby exposing the metal to the corrosive environment.

This particularly dangerous corrosion type can be the result of environmental factors or cyclic stresses. The following are the major types of cracking attack:
- Corrosion fatigue - the accelerated failure of a metal which undergoes cyclic loading due to its presence in a corrosive environment.
- Stress corrosion cracking (SCC) - the corrosion induced cracking which occurs in alloys under high tensile stress. The cracks start on the surface and go inward. It should be noted that the stress can be the result of cold working, forming, or external loading.

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- Hydrogen embrittlement - the loss in ductility of a metal due to the saturation of atomic hydrogen in the grain boundaries. It occurs at local cathodic sites and is aggravated by stress and compounds such a hydrogen sulfide.
- Liquid metal cracking - metals subjected to simultaneous tensile stress and certain molten metals can undergo this type of cracking. It is most common in mercury/copper alloy systems.
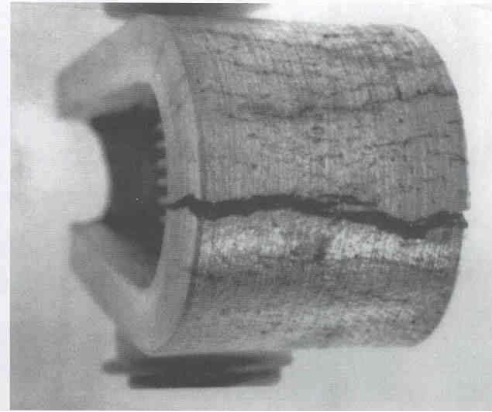
Stress corrosion cracking [from Jones (1996)].

5.9 Intergranular Corrosion

On a microscopic level, metals and there alloys have small, distinguishable regions called grains. Within an individual grain the orientation of the atomic arrangement (called a lattice) is the same. Individual grains have different orientations and the boundary between the grains is called the grain boundary. Normally, grain boundaries are no more reactive in corrosion than the grain itself. Under certain conditions, however, the grain boundaries are altered from the grain itself by impurities and/or enrichment (or depletion) of one of the alloying elements.

Heat treatment and welding can lead to changes metal composition which may incite intergranular corrosion. In severe cases, intergranular corrosion can lead to a marked decrease in mechanical properties and can, in extreme cases, turn the metal into a pile of individual grains.

One of the most common examples of intergranular corrosion occurs in stainless steels. During welding of the alloy, or heating in the temperature range of 950°F to 1450°F, the alloy becomes sensitized or susceptible to intergranular corrosion as illustrated in Figure 26. The chromium carbide ($Cr_{23}C_6$) is not soluble in this temperature range and preciptates out of the grain into the grain boundary. As a result, the area of the grain adjacent to the grain boundary is depleted of the chromium and becomes anodic to the rest of the grain and to the grain boundary. The corrosion of this depleted grain boundary area is very severe and occurs in environments and acids where the alloy would not normally corrode. The simplest solution to the stainless steel intergranular corrosion problem is to cast alloys with carbon contents below 0.03%. (This prevents the formation of the chromium carbide and the chromium stays in solution).
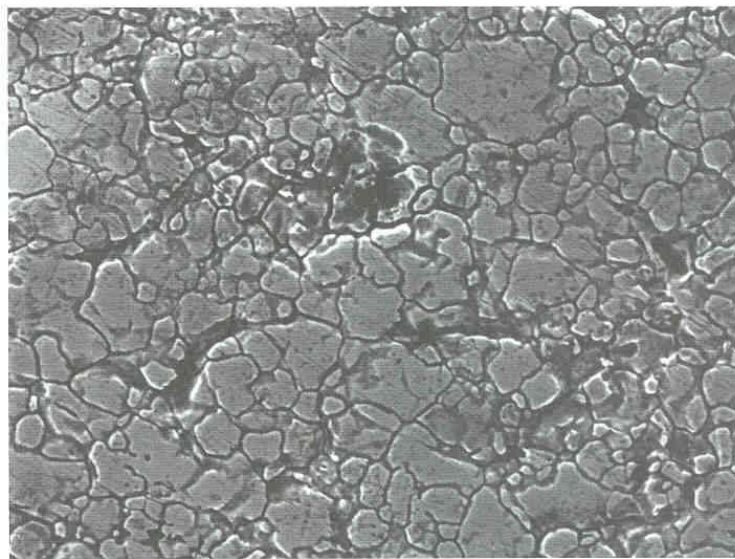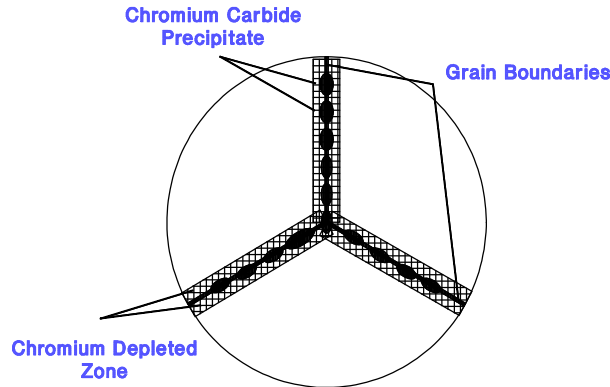
Intergranular attack [from Jones (1996)].

5.10 Fretting

A rapid localized attack which occurs on mated surfaces under load when a small amount of slip is allowed to occur. It is often observed on bearings, shafts, and gears in mounted in vibrating machinery. Not only is mechanical damage of the surface possible, but the protective surface film of the metal is also removed. This in turn hastens electrochemical corrosion processes.

5.11 Biological corrosion

Biological organisms can play a major role in metal attack. This attack is usually categorized in the following two headings:

- Microbially induced corrosion (MIC) - aerobic and anaerobic bacteria and other microorganisms contain enzymes and can produce metabolites which accelerate corrosion. This can manifest itself in pitting type corrosion of the metal surface.
- Macrofouling effects - barnacles, oysters, and other macrofoulers produce by-products that are often acidic and can accelerate corrosion. These organisms also create crevices at their attachment points that can lead to crevice corrosion.

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5.12 Stray current corrosion

Corrosion can be accelerated by the action of electrical currents entering a metal from some external source such as a generator or a battery and leaving the metal to continue its flow in whole or part through the seawater electrolyte. As an example of stray current corrosion, consider the bilge pump illustrated below. The electrical connections were made such that the current found a path from the pump and its through-hull connection to the seawater and back through the propeller shaft and engine to the battery.
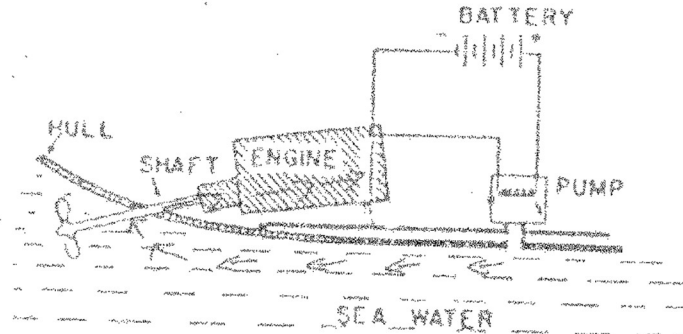
To prevent such corrosion, all metal surfaces exposed to bilge water or projecting through the hull should be electrically connected (bonded) to the negative side of the battery as shown in the following figure:
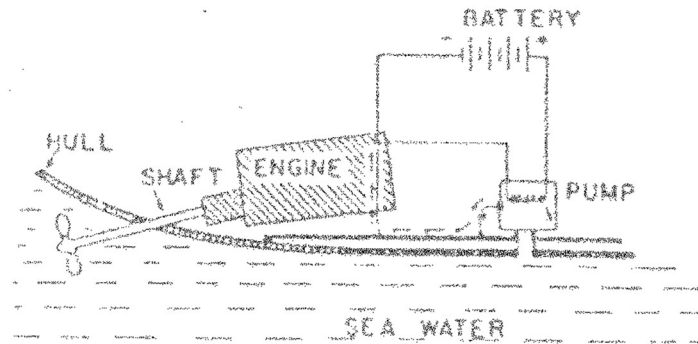
Another example of stray current corrosion damage to a ship is through the use of an onshore welding generator below. If the return leads to the onshore generator do not have ample current carrying capacity, some of the current will find its way back through discontinuities in the paint on the submerged hull, resulting in corrosion of the hull. To avoid such corrosion, the generator should have been placed on the ship's deck and its AC lines could have been run from shore. Any AC stray current to shore would have caused little damage.
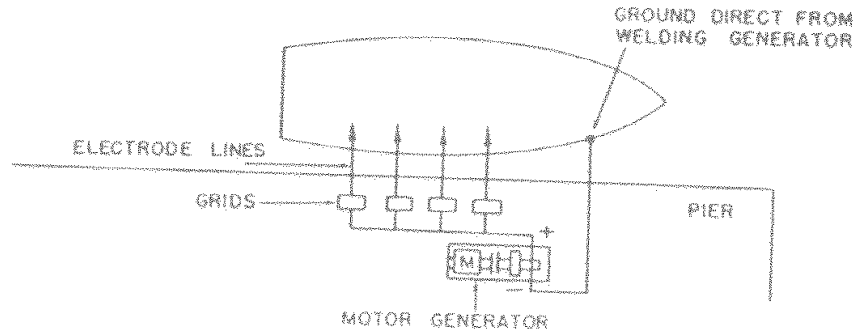
Stray current corrosion can also occur when the current from a cathodic protection system passes from the anode to a metal object which was not designed to be protected before going to the object which was intended to be protected. The result can be severe local attack on the unprotected metal where the current exits. It can also attenuate the current to a point that the object to be protected is underprotected.
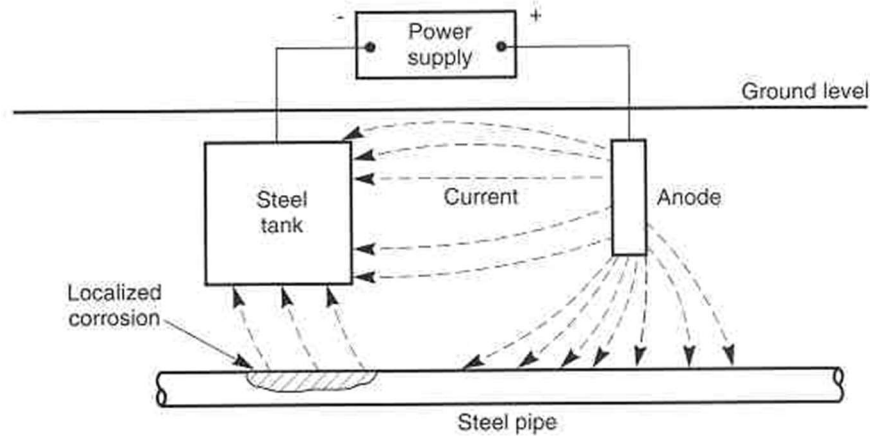
Stray current corrosion [from Jones (1996)].

References

Jones, D.A. (1996) *Principles and Prevention of Corrosion*, 2nd Edition, Prentice Hall, Upper Saddle River, NJ.

Schultz, M.P. (1997) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.

Swain, G.W. (1996) "OCE-4518 Protection of Marine Materials Class Notes", Florida Institute of Technology.

Dawson, T. (1993) "EN380 Engineering Aspects of Materials Class Notes", United States Naval Academy

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CHAPTER 6

CORROSION PROTECTION AND MONITORING

6.1 Cathodic Protection: Sacrificial Anodes
6.2 Cathodic Protection: Impressed Current
6.3 Measures of Corrosion Rate (Weight Loss and Strength Tests)
6.4 Corrosion Allowance Calculations

As inferred during the previous discussion of the Pourbaix diagram, corrosion may be prevented by introducing electrical currents from external sources to counteract the normal electrochemical reaction. There are two basic types of so-called cathodic protection systems, namely, sacrificial anodes and impressed current. Sacrificial anodes consist of expendable electrodes, usually zinc, aluminum or magnesium, or their alloys, whose natural potentials provide adequate protective current to a structure. Impressed current systems are those that employ a direct current (DC) power source to provide the necessary current.

6.1 Cathodic Protection: Sacrificial Anodes

When iron and copper are attached in a galvanic cell, we have seen that the result is the corrosion of the iron, with electrons flowing out of the iron (the anode) and into the copper (the cathode). Suppose that we now place a zinc bar in the cell as illustrated below:

Sacrificial Zinc Anode
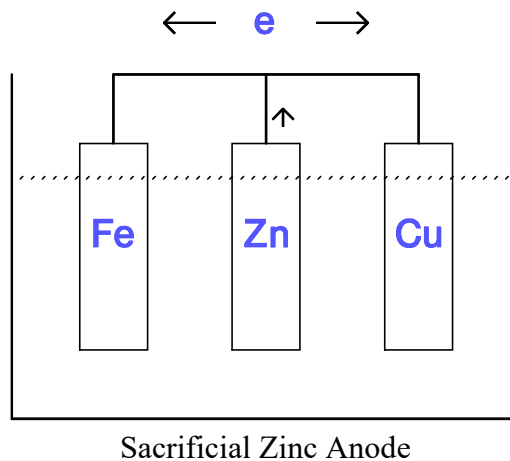
In this case, we now find, that because of the potentials involved, that electrons flow out of the zinc and into both the iron and copper. Thus the zinc corrodes and the iron and copper, which now both function as cathodes, do not. This is the basis for sacrifical anode protection, namely, the use of an expendable anode to protect another metal from corrosion. Two examples of this type of corrosion protection are shown in Figure 28. The first is the protection of an ordinary hot-water heater with a magnesium anode and the second is the protection of a ship's hull in the vicinity of the bronze propeller by zinc anodes. Without the protection, the steel hull of the ship is, of course, subject to galvanic corrosion because of the presence of the bronze material used for the propeller.

6 - 1

Hot Water Heater   Ship Hull & Rudder
Example Sacrificial Anodes
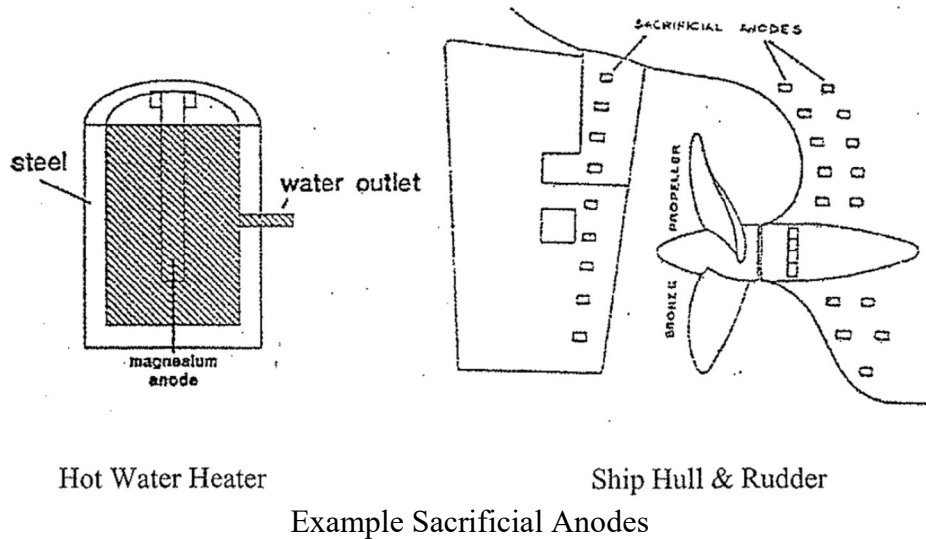
To determine the amount of material needed for sacrificial anode protection of a structure, we use Faraday's Law together with an estimate of the current density needed for protection (typically in the range of 10-15 ma/ft^2).

Example: If an aluminum alloy is 100% efficient as a sacrificial anode (i.e. it follows Faraday's Law exactly) determine the number of pounds of aluminum needed to protect a steel structure with 80 ft^2 of surface area in seawater for 18 months. Assume a current density of 10 ma/ft^2 is needed for current protection.

Solution

$$W = \_CI$$

From Faraday' Law we have

$$C = \frac{\frac{27}{3}}{96,500} = 9.33 \times 10^{-5} \text{ grams/amp\_sec}$$

where

$$w = -7.45 \times 10^{-5} \text{ grams/sec}$$

Hence

$$w = (7.35 \times 10^{-5})(2.205)(10^{-3})(3600)(24)(365) = 5.19 lb/year$$

in lbs/yr

For total consumption in 18 months, we must have (for 100% efficiency)

$$w = (5.19)(1.5) = 7.7 \text{ lbs}$$

6 - 2

Example: *A chemical company advertises aluminum-alloy sacrificial anodes with an average current output of 1176 amp-hours/lb. Calculate the efficiency.*

Solution: *From Faraday's Law we have the consumption given as*

$$C = \frac{\frac{27}{3}}{96,500} = 9.33 \times 10^{-5} \text{ grams/amp-sec}$$

hence, the current output is
        $C^{-1} = 1.07 \times 10^4 \text{ amp-sec/gm}$
or
        $C^{-1} = 1350 \text{ amp-hours/lb}$

The efficiency of the advertised anodes is therefore 1176/1350 = 0.87 or 87%.

Example: *An offshore structure has 10,000 ft^2 of submerged area to be protected for 20 years with aluminum-alloy anodes (85% efficient) weighing 150 lbs each. Determine the number of anodes required if 15/ma ft^2 is needed for protection.*
Solution:

Again, from Faraday's Law we have

$$C = \frac{\frac{27}{3}}{96,500} = 9.33 \times 10^{-5} \text{ grams/amp\_sec}$$
and

        $I = 150 \text{ amp}$

so that

$w = -0.014 \text{ gm/sec} = 973 \text{ lbs/year}$

Hence, w = 973 x 20 = 19463 lbs if the anodes were 100% efficient. Since they are only 85% efficient, 19463/.85 = 22,900 lbs are required and 22,900/150 = 152.6 or 153 anodes.

6.2 Cathodic Protection: Impressed Current

In an impressed current system of cathodic protection, the current can be supplied from such sources as storage batteries, rectifiers, or generators depending on convenience and the amount of current required. The anodes used in an impressed current systems can be expendable, being made of ordinary steel. Such steel anodes would require periodic replacement, since they are destroyed at a rate of about 20 pounds/ampere-year by the passage of the protective current. It is common to use permanent impressed current anodes which are not destroyed or are destroyed very slowly by the passage of the protective current. These anodes are platinum; platinum sheathed titanium, tantalum, or niobium. Steel structures exposed to seawater are normally

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protected if they are polarized to a potential of -0.85 volts versus a silver/silver-chloride or a copper/copper-sulfate reference electrode.

A description of such a system follows. Consider again the case of iron and copper attached together in a galvanic cell, with the iron corroding and the copper protected. Instead of using a sacrifical anode to supply electrons to the steel and protect it, we use a DC power supply. In this case, we have the cell described in the figure below.
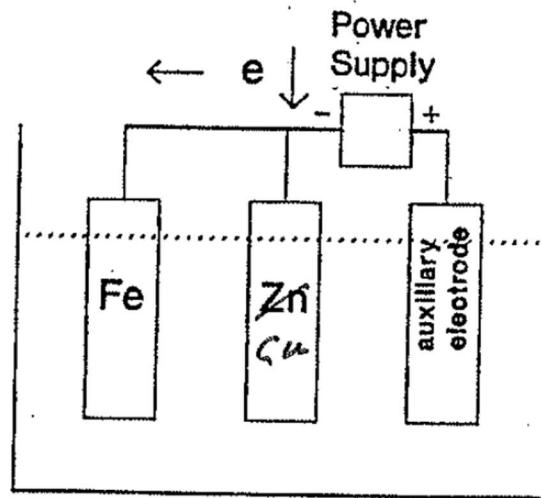
Impressed Current Cathodic System

By proper choice of the power supply voltage, we can over-ride the potential difference between the iron and copper and make each act as a cathode (receive electrons) and be protected. In selecting the proper potential, it must be the same as the open-circuit potential of the local anode. This means that the voltage is chosen such that current is neither entering or leaving the iron, nor is it flowing between the local anode and cathode regions on the iron. By use of a standard half-cell, as in Figure 29, a polarization diagram can also be produced. The open circuit potential and applied current can be determined in this manner. Thus, the rule for selecting the proper voltage setting of the power supply is to <u>adjust the power supply until the potential of the iron (and copper) relative to a standard half-cell is equal to the open circuit potential of the local anode regions, which was determined experimentally</u>. Some examples of impressed current protection are shown below .
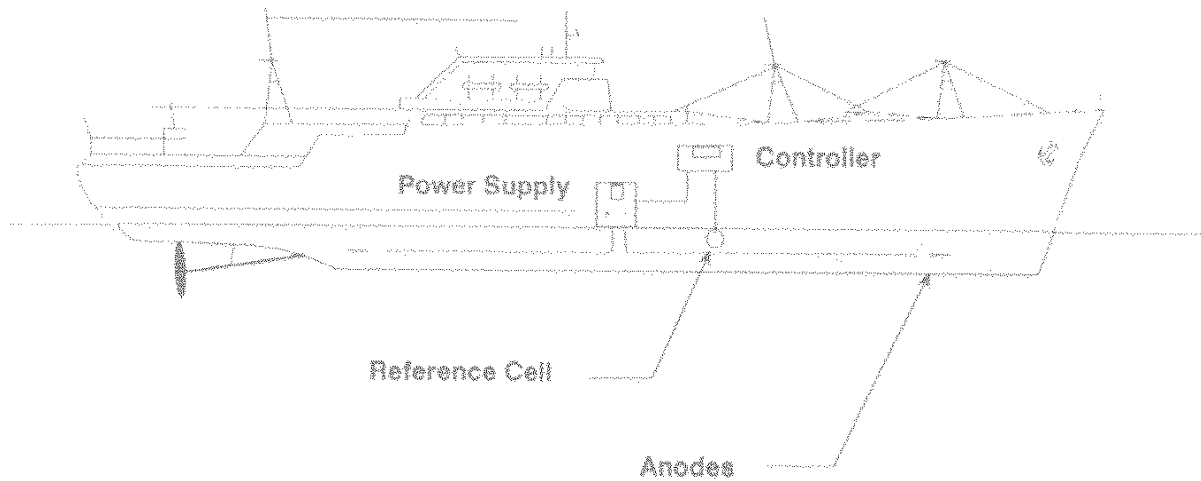
Example: Use the Nernst equation to establish the potential of steel (iron) relative to the copper/copper-sulfate half-cell needed for protection from corrosion.

Solution: We assume a concentration of 10^{-3} ions/liter in the electrolyte adjacent to the steel to indicate essentially negligible corrosion activity. From the Nernst equation, we then have relative to the hydrogen half-cell,

$$E = -0.44 + (0.0592/2)Log_{10}10^{-3}$$

or

$$E = -0.53 \ v$$

The potential of the copper/copper-sulfate half-cell relative to the hydrogen is +0.32V. Hence

$$E = V_{Fe} - V_{H2} = V_{Fe} - V_{Cu} + V_{Cu} - V_{H2}$$

or

$$-0.53 = V_{Fe} - V_{Cu} + 0.32$$

or

$$V_{Fe} - V_{Cu} = -0.85 \ v$$

6.3 Measures of Corrosion Rate

The Galvanic Series gives us information on which metals will corrode when connected with others in seawater, but it does not tell us anything about the rate of corrosion. Polarization experiments can give us information on the rate of corrosion of metals connected together or freely corroding. When time permits, field tests can provide the simplest and most reliable way to obtain corrosion-rate data.

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<u>Weight-Loss Tests.</u> These experiments are conveniently made using flat plates, as shown in the figure below.

h/a ⟨⟨ 1
h/b ⟨⟨ 1
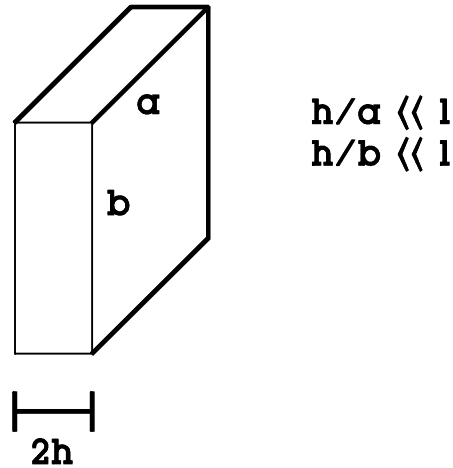
Sample for Weight Loss Test

The weight of the plate is given in terms of geometry of the figure above and the specific weight γ of the material as

$$2\gamma abh = W$$

and the rate of weight loss is given by differentiation as

$$2\gamma(abh + abh + abh) = \overset{o}{W}$$

or with

$$h \; = \; \frac{a}{2} \; = \; \frac{b}{2}$$

denoting the corrosion rate, as

$$2\gamma abh(\frac{2h}{a} + \frac{2h}{b} + 1) = \overset{o}{W}$$

For thin plates, this expression yields

$$\overset{o}{h} \; = \; \frac{\overset{o}{W}}{2\gamma ab}$$

Writing A = 2ab = total surface area of plate and $\overset{o}{W}$ = Δw/Δt, where Δw denotes weight loss in time Δt, we have

$$\overset{o}{h} \; = \; \frac{\Delta w}{\gamma A \Delta t}$$

The corrosion rate may vary with time under various circumstances, but for purposes of calculation we may generally assume it to be constant. In examining test data, it is usual to replace Δw and Δt by w and T where w denotes the total weight loss in time T, so that the equation becomes

$$\overset{o}{h} \; = \; \frac{W}{\gamma A T}$$

These two equations are of course equivalent only if the rate of weight loss is constant.

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Example. *A steel plate of dimensions 3 x 6 x (1/8) inches is known to suffer a weight loss of 0.025 lb when exposed in seawater for 6 months. Determine the corrosion rate.*

Solution: *We have A = 2(3 x 6) = 36 in², γ = 0.28 lb/in³, T = 0.5 years and W = 0.025 lbs. Hence the equation gives*

$$h = \frac{0.025}{(0.28)(36)(0.5)} = 0.005 \ inches/year = 5 \ MPY$$

If, in place of the thin plate, we have a specimen of arbitrary shape, we may construct a weight-loss formula similar to that for the flat plate. Consider, in particular, the effect of corrosion on the cross section shown in the figure below.
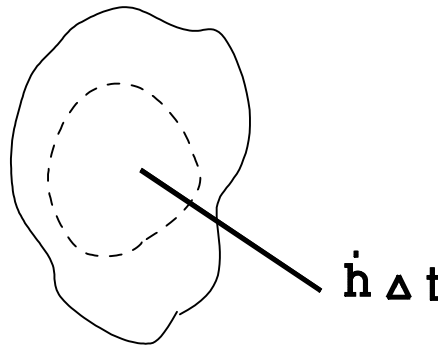
During a time Δt, the surface of the solid will move inward an amount $\underline{h}\Delta t$. If S denotes the lateral surface area of the solid, the volume loss will be $\underline{h}\Delta tS$ and the weight loss $\Delta w = \gamma\underline{h}\Delta tS$, where γ denotes the specific weight. Hence, solving for h we have

$$h = \frac{\Delta w}{\gamma S \Delta t}$$

If we take S to be the initial lateral surface area of the solid and write W = Δw, T = Δt, we have

$$h = \frac{W}{\gamma ST}$$

Because the lateral surface area changes with time, this equation will be only valid only as long as the lateral area change is small.

Example. *A cylindrical steel test rod of 0.50 inches in diameter and 2 inches in length is exposed in seawater for 3 years. The measured weight loss is 0.0165 lbs. Find the corrosion rate.*

Solution:

We have $\gamma = 0.28$ lb/in³, T = 3 years
and
$S = (\pi \times .5 \times 2) + (2 \times \pi \times 0.25^2) = 3.53$ in²

$$h = \frac{0.0165}{(0.28)(3.53)(3)} = 0.0055 \ inches/year = 5.5 \ MPY$$

Note: This is not a particularly good example of our assumption of the total area, S, staying constant. If one recalls that corrosion occurs through the wetted surface area, it can be shown that since 12% of the area is at the ends of the cylinder, 12% of the corrosion must have occured there. The remaining 88% of the corrosion occured through the cylinder walls.

Strength Reduction Test. Instead of using the weight loss test to determine the corrosion rate, we may use a strength- reduction test. Suppose we have a thin plate with a failure (breaking) force F applied over area 2ha, as shown in the figure below:
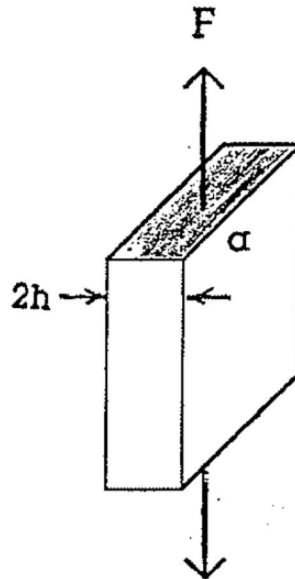
We assume the failure stress Y is the same, regardless of the amount of corrosion so that

$$\frac{Y}{Y_o} = \frac{\frac{F}{A}}{\frac{F_o}{A_o}} = 1$$

where the subscript o denotes initial value. Solving for A/A_o, we have

$$\frac{A}{A_o} = \frac{F}{F_o}$$

now the area A is given by A = 2ah where (neglecting corrosion of the edges as is permissible

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for thin plates)

$$h = h_o - ht$$

hence we have

$$\frac{A}{A_o} = \frac{2ah}{2ah_o} = 1 - \frac{h}{h_o}t$$

so that <u>h</u> may be determined as

$$h = \frac{(1-\frac{F}{F_o})h_o}{T} = \frac{\Delta Fh_o}{F_oT}$$

where T denotes the duration of exposure.

Example: A thin-plate of 1/8 inch thickness is exposed for 6 months in seawater. The initial yield strength of the plate was 28,000 lbs. After exposure the strength is 25,000 lbs. Determine the corrosion rate <u>h</u>.

$$h = \frac{\Delta Fh_o}{F_oT}$$

$$hdot = \frac{(3000)\ (0.0625 inches)}{(28000)\ (0.5 years)} = 0.0134 inches/year = 13.4\ MPY$$

Solution:
Suppose that a standard cylindrical tensile specimen is used in place of the flat-plate specimens in the above scheme. In this case, we have as before

$$\frac{A}{A_o} = \frac{F}{F_o}$$

But now,

$$\frac{A}{A_o} = (\frac{R}{R_o})2 = (1 - \frac{hdot}{R_o}t)2$$

so that

$$h = (\frac{1 - \sqrt{\frac{F}{F_o}}}{T})R_o$$

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Example: A standard 0.5 inch diameter tensile specimen is found to suffer a 15% loss in strength when exposed in seawater for 2 years. Determine the rate of corrosion.

$$\Delta\frac{F}{F_o} = \frac{F_o - F}{F_o} = 1 - \frac{F}{F_o} = 0.15$$

$$\frac{F}{F_o} = 0.85$$

$$h = (1 - \sqrt{.85})(\frac{0.25}{2})$$

h = 0.0099inches/year = 9.9MPY

6.4 Corrosion Allowance Calculations

The following examples illustrate engineering calculations associated with corrosion allowances.

Example: A submerged pipeline is corroding on the outside with a corrosion rate of 15 MPY and on the inside with a rate of 5 MPY. Find the design wall thickness of the pipe if the design life is 30 years.
Solution: The inside radius is denoted by r_1, and its initial value by r_{1o}. If the corrosion rate is $\overset{o}{h}_1$, then

$$r_1 = r_{1o} + h_1 T$$

where T = life of the pipe. Similarly, with r_2 denoting the outside radius and r_{2o} its initial value. If the corrosion rate is $\underline{h}_2$, then

$$r_2 = r_{2o} - h_2 T$$

From a corrosion standpoint we require that $r_1 = r_2$ at T = 30 years. Hence the initial wall thickness required is

$$r_{2o} - r_{1o} = (h_1 + h_2)T$$
$$r_{2o} - r_{1o} = (.20)(30) = 0.6inches$$

From a true design standpoint, we would also need to account for the fact that this pipeline is going be carrying a fluid at a design flow rate and that it is going to be exposed to both internal and external pressures. At T = 30 years there will some required wall thickness to withstand this pressure, p = absolute value of ($p_{external}$ - $p_{internal}$) and at T = 0, there will be a minimum r_1 to allow for the rated flow at the design pumping pressure. Since we know which material is going to be used, we also know its shear strength τ. We can now solve for the required wall thickness and subsequently the outside radius.

$$r_2 - r_1 = \frac{pr_1}{\sigma} + (h_1 + h_2)T$$

Example: *A steel cable is to be used as an underwater guide wire in an off shore structure. In the absence of corrosion, a section area of 1 in² is recommended. If tests show the rate of corrosion at the site and for this material to be 25 MPY, what initial area of cable should be used for a design life of 20 years.*

Solution: *With R_o denoting the initial cable radius and R its radius after T years, we have*

$$R = R_0 - \dot{h}T$$

where h is the corrosion rate. Now $\pi R^2 = 1$ and $R_o = 0.564$ inches.

$$0.564 = R_o - (0.025)(20)$$

or

$$R_o = 1.06 \text{ inches, and the required initial area is } 3.53 \text{ in}^2.$$

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APPENDIX

CATHODIC PROTECTION DESIGN

from Swain Classnotes (1996)

STRUCTURE
Metal, Design Life, Dimensions, Coatings, Other

LOCATION
Environmental Conditions, Other Structures

C.P. CRITERIA
Potential for Cathodic Protection

C.P. CURRENT DEMAND
Initial, Mean, Final

C.P. TYPE
Impressed Current, Sacrificial Anode

ANODE AND HARDWARE SELECTION
Current Output, Design Life, Placement

COST AND IMPLEMENTATION

Appendix: Cathodic Protection Design - 1

Table of Contents

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1.0   INTRODUCTION

Metallic structures in contact with water, soil, concrete, and moist air are subject to corrosion. Cathodic protection (CP) is one of the few methods that successfully mitigates corrosion. It can be applied in any situation where the environment surrounding the metal acts as a conductor for electric current. It has been successfully applied to offshore structures, ships, boats, propellers, moorings, pipelines, storage tanks, piers, jetties, bridges, aquaria, instrumentation etc.

This handout is designed as an introduction to CP design. As such, it does not cover all aspects of the subject. Therefore, the student should realize the limitations of his/her knowledge and consult other literature or experts in the field when necessary.

2.0   STRUCTURE

CP design begins with a thorough understanding of the structure to be protected. This includes the following information:
- Metal type(s)
- Operating conditions
- Dimensions and surface area
- Coatings
- Data from previous structures and CP systems
- Design life

3.0   LOCATION

The environmental conditions are determined by the location of the proposed installation. Factors such as climate, electrolyte conductivity and chemistry, physical loading, and biological activity, all impact CP requirements. These factors are generally allowed for in the CP current demand and polarization potential criteria.

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4.0   CP CRITERIA

Potential measurements are the most commonly used criteria to ascertain the level of CP afforded to metals and alloys. CP potential values vary according to the metal and the environment. Corrosion is likely to occur at potentials which are more positive than the protected value. Damage may also occur if the metal is overprotected (i.e. the potential too negative). The most common error associated with potential measurements is a result of IR drop. This is the displacement of measured metal potential due to current flow through the electrolyte. High electrolyte resistivity and high current densities can cause significant differences between the measured and actual metal potential.

4.1   Potential Values

The measurement of potential with respect to a standard reference electrode is probably the most common method of evaluating the degree of cathodic protection afforded to a structure. Typical cathodic protection potentials for commonly used metals ref. Ag/AgCl reference electrode (seawater) are provided in Table 4.1. A more detailed summary of protection potentials for steel in seawater is provided in Table 4.2.

Table 4.1   Approximate freely corroding and protected potentials of metals in seawater (may vary according to velocity and conditions).

Metal or Alloy	Freely Corroding Potential (V) ref. Ag/AgCl	Protected Potential (V) ref. Ag/AgCl
316,304 Stainless (passive)	-0.10	-0.75
Copper Alloys	-0.35	-0.70
316,304 Stainless (active)	-0.50	-0.75
Steel	-0.60	-0.80
Aluminum Alloys	-0.75	-1.00
Zinc/Aluminum Anodes	-1.05	
Magnesium Anodes	-1.50	

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Table 4.2   Potential values for corrosion and protection of steel in seawater

V ref. Ag/AgCl	Condition	V ref. Zn
	Heavy Corrosion	
-0.60	Freely Corroding Steel	+0.50
-0.70	Some Protection	+0.40
-0.80	Cathodic Protection	+0.30
-0.90	Some Over	+0.20
-1.00	Protection	+0.10
-1.10		0.00
-1.20	Over Protection	-0.10
-1.30	May Cause	-0.20
-1.40	Paint Blistering and Flaking	-0.30
-1.50		-0.40

4.2   300 mV Shift

The NACE Standard, RP-02-85 states that a minimum negative (cathodic) voltage shift of 300mV, produced by the application of protective current should provide CP to iron and steels. The voltage shift is measured between structure surface and a stable reference electrode contacting the electrolyte. This criteria does not apply to structures in contact with dissimilar metals.

4.3   100 mV Shift

The NACE Standard, RP-02-85 states that a minimum negative (cathodic) voltage shift of 100mV measured between the structure surface and a stable reference electrode contacting the electrolyte should provide CP to iron and steel. This polarization voltage shift is determined by interrupting the protective current and measuring the instant off and polarization decay. The instant off value is obtained immediately following the interruption of the CP current. The voltage shift is equivalent to the IR drop created by the CP current and electrolyte resistance. The polarization decay is measured as the change in potential over a period of time from the instant off value.

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4.4   E-log-I Curve

The NACE Standard, RP-02-85 states that a structure-to-electrolyte voltage at least as negative (cathodic) as that originally established at the beginning of the Tafel segment of the E-log-I-curve should provide CP to iron and steel. This structure-to-electrolyte voltage shall be measured between the structure surface and a stable reference electrode contacting the electrolyte at the same location where voltage measurements were taken to obtain the E-log-I curve.

4.5   Anodic Current Discharge Points

The NACE Standard, RP-02-85 states that a net protective current from the electrolyte into the structure surface as measured by an earth current technique applied to predetermined current discharge (anodic) points of the structure should provide CP to iron and steel.

5.0   CATHODIC PROTECTION CURRENT DEMAND

The cathodic protection current demand is the amount of electricity required to polarize the structure to a level that meets the criteria described in Section 4. This may be obtained from a trial polarization of the structure at the installation site, a trial polarization of a metal test coupon at the installation site, or from conservative estimates obtained from historical information obtained from previous structures operating under the prescribed conditions.

For planning and design purposes, it is often possible to rely on conservative estimates provided by recommended practice. There are several sources for this information. The most current one is Recommended Practice RP B401, Cathodic Protection Design, Det Norske Veritas Industri Norge AS, 1993.

5.1   Recommended Practice RP B401, Det Norske Veritas

The CP current densities are calculated for different environmental conditions and conditions of the steel (i.e. uncoated, coated, concrete reinforcing steel, pipeline).

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5.1.1 Uncoated Steel

Three design current densities are given: initial, final, and average.

Initial This is the current density required to effect polarization of the initially exposed bare steel surface. It assumes some atmospheric rusting and/or millscale. The initial current density is higher because of lack of calcareous scales (cathodic chalks). A proper initial current density enables rapid formation of protective calcareous scales.

Final This is the current density required to protect the metal surface with established marine growth and calcareous layers. It takes into account the current density required to repolarize the structure in the event of removal of these layers by storms, cleaning operations etc.

Average This is the anticipated current density required once the cathodic protection system has reached its steady state. The average or maintenance current density is used to calculate the minimum mass of anode material required to protect the structure throughout the design life.

Table 5.1 **Initial, final, and average current densities for various climatic conditions and depths (climatic conditions are based on yearly range of average surface water temperatures).**

	Design Current Densities (A/m^2)											
	Tropical >20ºC			Sub-Tropical 12º-20ºC			Temperate 7º-12ºC			Arctic <7ºC		
Depth (m)	Initial	Final	Average	Initial	Final	Average	Initial	Final	Average	Initial	Final	Average
0 - 30	0.150	0.090	0.070	0.170	0.110	0.080	0.200	0.130	0.100	0.250	0.170	0.120
>30	0.130	0.080	0.060	0.150	0.090	0.070	0.180	0.110	0.080	0.220	0.130	0.100

5.1.2 Coated Steel

The use of coatings on steel dramatically reduces the current demand on the cathodic protection system. This can save on the cost and structural weight associated with sacrificial anode systems. The CP current demand of a coated offshore jacket may be estimated by multiplying the bare steel current demand by a coating breakdown factor (f_c). The coating breakdown factor does not allow for mechanical damage to paint

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coatings. These areas are treated as bare metal surface. For CP design purposes the average and final coating breakdown factors for a design life of t_r years are as follows:

$$f_c(average) = k_1 + k_2 \frac{t_r}{2}$$

$$f_c(final) = k_1 + k_2 t_r$$

When the design life of the CP system exceeds that of the coating system then f_c (average) is calculated as follows:

$$f_c(average) = 1 - \frac{\left(1 - k_1^2\right)}{2 k_2 t_r}$$

If the calculated value exceeds 1, then $f_c = 1$ shall be applied to the design.

Table 5.2   **Constants (k_1 and k_2) for calculation of paint coating breakdown factors.**

Category	Description	k_1	k_2 0-30m	k_2 >30m
I	One layer of primer coat, about 50 μm nominal DFT.	0.10	0.10	0.05
II	One layer of primer coat, plus minimum one layer of intermediate top coat, 150 - 250 μm nominal DFT.	0.05	0.03	0.02
III	One layer of primer coat, plus minimum two layers of intermediate/top coats, 300 μm nominal DFT.	0.02	0.015	0.012
IV	One layer of primer coat, plus minimum three layers of intermediate/top coats, 450 μm nominal DFT.	0.02	0.012	0.012

5.1.3 Pipeline Coatings

The coating breakdown factors as shown in table 5.2 apply equally to both buried and non-buried pipelines. It is assumed that coatings and field joint systems have been chosen to be compatible with the maximum design temperature of the pipeline.

For pipelines with the following coating systems, another coating breakdown factor is calculated.

$\Rightarrow$ asphalt + concrete weight coating

$\Rightarrow$ fusion bonded epoxy + adhesive + polyethylene or polypropylene

$\Rightarrow$ polychloroprene rubber

$\Rightarrow$ equivalent coating systems based on an inner layer dedicated to corrosion protection and one or more outer layers for mechanical protection.

This is as follows:

$$f_c(average) = 0.05 + 0.002(t_r - 30)$$

$$f_c(final) = 0.07 + 0.004(t_r - 20)$$

5.1.4 Concrete

It is now recognized that cathodic protection of concrete reinforcing steel is necessary to ensure the long term integrity of the structure. Also, any CP system designed to protect metallic appendages and components must be designed to allow for current drain from CP to the reinforcement. The cathodic current density is determined by transport of oxygen to the steel by capillary action of pore water driven by evaporation in the atmospheric zone and internal dry compartments. The current densities are, therefore, dependent on depth and climatic conditions.

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Table 5.4   Design current densities for concrete reinforcing steel.

(NOTE: design currents refer to the area of the reinforcing steel)

Depth (m)	Design Current Densities (A/m^2)			
	Tropical >20°C	Sub-Tropical 12°-20°C	Temperate 7°-12°C	Arctic <7°C
5 to -10	0.0030	0.0025	0.0015	0.0010
<-10	0.0020	0.0015	0.0010	0.0008

5.2   Current Requirements for Pipelines in Soils of Different Types

The current demands for steel pipelines are determined by the soil type (conductivity, pH, moisture, temperature) and the condition of the steel (coating type). An example of typical CP current demand for a pipeline with different coating conditions is presented as follows.

Table 5.3   Range of current required to protect 10 miles of 36" diameter pipe in soil with average resistivity of 1000 ohm-centimeters. Current required is that needed to cause a 0.3 Volt drop across the effective resistance between pipeline and remote earth. [from A.W.Peabody, Control of Pipeline Corrosion,NACE, 1967]

Effective Coating Resistance in Ohms for One Average Square Foot	Current Required, Amps
Bare Pipe (minimum 1 mA/ft^2)	500
10,000	14.91
25,000	5.964
50,000	2.982
100,000	1.491
500,000	0.2982
1,000,000	0.1491
5,000,000	0.0298
Perfect Coating	0.000058

5.3 Current Requirements for Ship Protection

Information with regard to current density requirements for ship hull protection is limited. One source of information is the Technical and Research Report R-21, Fundamentals of Cathodic Protection for Marine Service, The Society of Naval Architects and Marine Engineers, January 1976. It must be remembered that this was compiled before the development of modern day bottom coatings. It may, therefore, be better to use the DNV practice for coated steel and to include an allowance for damaged surfaces.

Table 5.5   Protective current densities for ships. [from Technical and Research Report R-21, Fundamentals of Cathodic Protection for Marine Service, The Society of Naval Architects and Marine Engineers, January 1976]

Specific Area	Current Density, mA/m^2
External Hull	22-54
Rudders (Coated and for velocities not exceeding 5 knots. Current demand maybe 3 or more times greater underway)	490
Propellers (For velocities not exceeding 5 knots. Current demand maybe 3 or more times greater underway)	150 -170
Coated Tanks	11
Segregated Ballast	150
Washed Cargo / Clean Ballast	130
Dirty Ballast Tanks	86

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6.0   CP TYPE

The CP type determines how the cathodic current is supplied to the structure. CP can be applied by either an impressed current system or by a sacrificial anode system. Impressed current CP systems use an external DC current source and a variety of anode materials to supply the cathodic current. Sacrificial anode CP systems generate the cathodic current from the corrosion of metals less noble than the metal to be protected.

The choice between impressed and sacrificial cathodic protection depends many factors and may be just personal preference. There are, however, situations where one or the other provides the correct choice. The advantages and disadvantages of each type of CP system are described in Table 6.1.

Table 6.1   Advantages and disadvantages of impressed current and sacrificial anode CP systems.

Impressed Current	Sacrificial Anodes
Advantages	
Variable control of current and potential	Self contained
Can be automated	Can be self adjusting
Light weight and fewer anodes	Polarity of connections always correct
Varied anode geometry	Needs no supervision
Long life with inert anodes	Simple to install
Disadvantages	
Complex installation and maintenance	Expensive method of generating electricity
Requires external power source	No variable control
Anodes require dielectric shields	Anodes add weight
Anodes may be damaged	Anodes have finite life
Probability of stray current corrosion	Small lead resistance reduces current

7.0 ANODE SELECTION

Anodes, for both impressed current and sacrificial anodes, are selected according to their size and chemical composition. This determines the current output and design life. Specifications for impressed current anodes are provided in Table 7.1 and for sacrificial anodes in Tables 7.2 and 7.3.

Table 7.1 Impressed current anodes.

Anode Material	Recommended Current density A/m^2	Maximum Voltage, V	Consumption Rate, g/A-yr	Comments
Scrap Steel	Varies	-	200 - 9,000	Difficult life prediction
Graphite	10	-	30 - 450	Very brittle
Silicon-Chromium-Cast Iron	10 - 100	-	90 - 250	Very brittle
Lead-Silver	250 - 500	-	30 - 90	Heavy, Poor mechanical properties
Lead-Platinum	100	-	2 - 60	
Magnetite	10 - 500	-	40	Very Brittle
Platinized Titanium	250 - 700	9	0.01	5 μm thick Pt film provides 10 year life
Platinized Tantalum	500 - 1000	100	0.01	5 μm thick Pt film provides 10 year life
Platinized Columbium	500 - 1000	100	0.01	5 μm thick Pt film provides 10 year life
Lithium-Ferrite Ceramic	15 - 2000	9.7	1-2	Lightweight and tough

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Table 7.2   Sacrificial anode types and use.

Anode	Preferred Use	Approx. Potential Volts ref. Ag/AgCl
Magnesium, High Potential	Soils with resistance > 2000 Ω-cm	-1.75
Magnesium, Standard	Soils with resistance < 2000 Ω-cm, and in aqueous environments with controllers if necessary	-1.50
Zinc, Hi-Amp	Seawater, brackish water, saline mud. Temps < 60°C	-1.05
Zinc, Hi-Purity	Underground, fresh water, and saline environments > 60°C	-1.05
Galvalum I	Submerged seawater, max. temp 25 °C	-1.05
Galvalum II	Saline mud	-1.04
Galvalum III	Seawater, brackish water, saline mud	-1.10
Reynode		-1.05
Al-Sn-In Alloy		-1.05

Table 7.3   Sacrificial anode properties.

Property	Anode Material Type				
	Magnesium	Zinc	Galvalum 1	Galvalum II	Galvalum III
Density, kg/m^3	1940	7130	2700	2700	2700
Electrochem Equiv, g/coulomb	0.126E-3	0.339E-3	0.093E-3	0.093E-3	0.093E-3
Theoretical Ah/Kg	2,205	819	2,987	2,987	2,987
Current Efficiency %	0.55	0.95	0.95	0.57	0.85
Actual Ah/Kg	1,212	780	2,830	1,698	2,535
Actual Kg / Amp / Year	7.95	11.25	3.10	5.16	3.46
Potential V, ref. Ag/AgCl	-1.75	-1.05	-1.05	-1.04	-1.10

Table 7.4   Sacrificial Anode Composition.
Percent of Total Weight

	Mg	Zn	Al	Cd	Cu	Fe	Hg	In	Mn	Ni	Pb	Si
Magnesium, High Potential	rem		0.01		0.02	0.03			0.50 - 1.30	0.001		
Magnesium, Standard	rem	2.5 - 3.5	5.3 - 6.7		0.05	0.003			0.15	0.003		0.30
Zinc, Hi-Amp		rem	0.1 - 0.4	0.025 - 0.060		0.005					0.006	
Zinc, Hi-Purity		rem		0.003		0.0014					0.003	
Galvalum I		0.35 - 0.48	rem				0.035 - 0.048					0.14 - 0.21
Galvalum II		3.5 - 5.0	rem				0.035 - 0.048					
Galvalum III		2.8 - 3.5	rem					0.01 - 0.02				0.08 - 0.12

Appendix: Cathodic Protection Design - 15

7.1 Anode Resistance to Ground

The current output from an anode is determined by its shape, electrolyte resistance, and driving potential. The shape and electrolyte resistance determine the anode resistance to ground which is calculated from standard anode resistance formulae. The most commonly used formulae are presented in Table 7.4 and seawater conductance values in Table 7.5.

Table 7.4   Anode resistance to ground formulae.

Anode Type	Resistance Formula
Long Slender stand-off L ≥ 4r	$R = \dfrac{\rho}{2\pi L}\left(\ln\left(\dfrac{4L}{r}\right) - 1\right)$ (Modified Dwight)
Long Slender stand-off L < 4r	$R = \dfrac{\rho}{2\pi L}\left[\ln\left\{\dfrac{2L}{r}\left(1 + \sqrt{1 + \left(\dfrac{r}{2L}\right)^2}\right)\right\} + \dfrac{r}{2L} - \sqrt{1 + \left(\dfrac{r}{2L}\right)^2}\right]$
Long flush mounted L ≥ 4 x width and thickness	$R = \dfrac{\rho}{2S}$ (Lloyds)
Short flush-mounted, bracelet and other flush mounted shapes	$R = \dfrac{0.315\rho}{\sqrt{A}}$ (McCoy)

where: R   is anode resistance, ohms

ρ   is electrolyte resistivity, ohm-cm

L   is anode length, cm

S   is the mean of the anode sides $= \dfrac{a + b}{2}$

r   is equivalent radius, cm, $= \sqrt{\dfrac{\text{anode cross - sectional area}}{\pi}}$

A   is the exposed surface area of anode, cm^2

Appendix: Cathodic Protection Design - 16

Table 7.5   Specific Conductance of Seawater

Note: Resistivity, ρ, is the reciprocal of conductance. Tabled values are expressed in in

$(\Omega^{-1}\text{-cm}^{-1})$.

Chlorinity, ppt	Temperature, °C					
	0	5	10	15	20	30
1	0.001839	0.002134	0.002439	0.002763	0.003091	0.003431
2	0.003556	0.004125	0.004714	0.005338	0.005971	0.006628
3	0.005187	0.006016	0.006872	0.007778	0.008702	0.009658
4	0.006758	0.007845	0.008958	0.010133	0.011337	0.012583
5	0.008327	0.009653	0.011019	0.012459	0.013939	0.015471
6	0.009878	0.011444	0.013063	0.014758	0.016512	0.018324
7	0.011404	0.013203	0.015069	0.017015	0.019035	0.021121
8	0.012905	0.014934	0.017042	0.019235	0.021514	0.023868
9	0.014388	0.016641	0.018986	0.021423	0.023957	0.026573
10	0.015852	0.018329	0.020906	0.023584	0.026367	0.029242
11	0.017304	0.020000	0.022804	0.025722	0.028749	0.031879
12	0.018741	0.021655	0.024684	0.027841	0.031109	0.034489
13	0.020167	0.023297	0.026548	0.029940	0.033447	0.037075
14	0.021585	0.024929	0.028397	0.032024	0.035765	0.039638
15	0.022993	0.026548	0.030231	0.034090	0.038065	0.042180
16	0.024393	0.028156	0.032050	0.036138	0.040345	0.044701
17	0.025783	0.029753	0.033855	0.038168	0.042606	0.047201
18	0.027162	0.031336	0.035644	0.040176	0.044844	0.049677
19	0.028530	0.032903	0.037415	0.042158	0.047058	0.052127
20	0.029885	0.034454	0.039167	0.044114	0.049248	0.054551
21	0.031227	0.035989	0.040900	0.046044	0.051414	0.056949
22	0.032556	0.037508	0.042614	0.047948	0.053556	0.059321

7.2   Anode Ground Beds

Anode ground beds are used to increase the anode current output in soils. They typically comprise an excavation which is filled with low conductance carbonaceous material into which the anode(s) are placed. The total resistance of the system then becomes the resistance of the anode to the carbonaceous backfill plus the resistance to earth of the backfill itself. The anode resistance is reduced by the low resistance of the backfill (typically 50 ohm-cm for coke breeze), and the resistance of the backfill to earth is reduced by the large surface area of the backfill in contact with the soil. Standard anode to ground resistance formulae are used to obtain the resistance values.

Because of the variables involved in ground bed sites, experience is invaluable in attaining competence in their design. They are designed with regard to the current demand of the structure to be protected, to the soil resistance, and to other structures and stray current effects.

7.3   Anode Current Output

Anode current output is calculated using Ohm's Law:

$$I = \frac{V}{R}$$

This is where V is the driving potential, and R is the anode resistance. The driving potential is determined by the anode type. The driving potential for sacrificial CP systems is determined by the environment (Table 7.2), but for impressed current systems it is determined by the rectifier and controller voltage output (Table 7.1). The anode resistance to ground is found from the anode resistance formulas (Table 7.4).

7.4   Anode Size, Weight, Number, Distribution and Design Life

The CP system must be designed to provide the required current to every part of the structure for the required design life. This requires determining anode size, weight, number, and distribution.

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The calculations for impressed current CP systems are relatively simple. In this case, it is only necessary to match the number of anodes of known current output to the total current demand of the structure, and to be sure that the anode distribution insures an even and well balanced current distribution.

The calculations for sacrificial CP systems are a little more complex. Not only must the number of anodes satisfy the current demand of the structure, but they must also have sufficient mass to provide electricity for the design life of the structure.

Anode size and shape are determined by the following factors:
- Requirements for minimum and maximum current output
- Requirement for mounting and attachment
- Requirement for streamlining
- Requirement for weight of anode material (sacrificial)
- Commercial availability

The minimum and maximum current outputs are calculated as described in sections 7.1 and 7.2. The types of mounting methods range from welding steel cores, cast into the anode materials, directly to the structure, to mounting complex dielectric shields with screw in platinized titanium impressed current anodes. Where streamlining is required, recesses may be built into the structure to house both impressed and sacrificial anode types.

Sacrificial CP design requires that the weight of anode material is sufficient to supply current for the design life of the structure. This is calculated by the following formula:

$$W = \frac{\left(8760\frac{h}{yr}\right)YC}{ZU}$$

where :

W = weight of anode material

Y = design life (yrs)

C = current demand (Amps)

Z = anode capacity

U = utilization factor (0.9 for aluminum and zinc)

Finally, due to practical considerations, anode selection may ultimately be determined by commercial availability. It is often too expensive to customize anode size and geometry for one job. Therefore, except for large and specialized requirements, CP design centers around standard, commercially available anode types.

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8.0   COST AND IMPLEMENTATION

There are many permutations possible in CP design, however to be successful it must satisfy economic constraints and be easy to install and operate.   Examples of CP designs are presented for an oil platform and ship.

8.1   Oil Platform Example

8.1.1 Structural Details

Water Depth	110m
No. of Legs	4
No. Horizontal Frames	5
No. of Nodes Below Surface	75
Total Submerged Surface Area	63,000 m^2
Total Pile Surface Area in Mud	6,000 m^2
Allowance for Risers, Conductors, Wells	220 Amps
Design Life	35 years

8.1.2. Current Demand

$Total = (\text{submerged S. A.})(\text{CP current density}) + (\text{pile S. A.})(\text{CP current density}) + \text{allowance}$

	Submerged Steel (A)	Piles (A)	Allowance (A)	Total (A)
North Sea				
Initial	11,340	150	220	11,710
Mean	5,670	120	220	6,010
Final	7,560	90	220	7,870
Gulf of Mexico				
Initial	6,930	150	220	7,300
Mean	3,780	120	220	4,120
Final	5,040	90	220	5,350

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The following design current densities were used for calculating the current demand shown in the previous table:

	Submerged Steel (mA/m²)	Piles (mA/m²)
North Sea		
Initial	180	25
Mean	90	20
Final	120	15
Gulf of Mexico		
Initial	110	25
Mean	60	20
Final	80	15

Example calculation (for North Sea, Initial)

CP current for submerged steel = (submerged S. A.)(CP current density) = $(63,000 \text{m}^2)(0.180 \frac{A}{m^2})$

CP current for submerged steel = $11,340 A$

CP current for piles = (pile S. A.)(CP current density) = $(63,000 \text{m}^2)(0.025 \frac{A}{m^2})$

CP current for piles = $150 A$

Total CP current = $11,340 A + 150 A + 220 A$

Total CP current = $11,710 A$

8.1.3. Sacrificial Anode Design for Uncoated Structure

The following table is the weight required for 35 year CP design life (using mean current density)

Location	Zinc, kg	Aluminum, kg
NORTH SEA	2,624,880	723,462
GULF OF MEXICO	1,799,419	495,953

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Example calculation for the weight of zinc required, North Sea:

$$W = \frac{\left(8760\frac{h}{yr}\right)YC}{ZU}$$

$$W = \frac{\left(8760\frac{h}{yr}\right)(35\,yr)(6,010\,A)}{\left(780\frac{Ah}{kg}\right)(0.9)}$$

$$W = 2,624,880\,kg$$

Number of Anodes Required to Provide Initial Current Demand to Polarize the Structure

Assume the following anode dimensions:

2,500 mm long

250 mm width

207 mm thick

	NORTH SEA	GULF OF MEXICO
Seawater Resistivity, ohm-cm	30	20
Anode Resistance, Ohms	0.0641	0.0427
Anode Current Output, Amps	3.900	5.855
Number of Anodes for Initial Current Demand	3003	1247
Mass of Zinc Anodes, kg	2,768,766	1,149,734
Mass of Aluminum Anodes, kg	1,048,047	435,203

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The previous table was created using the following methodology:

Find Mass of One Anode, Zinc

$$m = \rho_{zinc} \forall$$
$$m = (7{,}130 \tfrac{kg}{m^3})(2.5m)(0.25m)(0.207m)$$
$$m = 922kg$$

Find Mass of One Anode, Aluminum

$$m = \rho_{Al} \forall$$
$$m = (2{,}700 \tfrac{kg}{m^3})(2.5m)(0.25m)(0.207m)$$
$$m = 349kg$$

Find the Resistance of the Anode Using Table 7.4 (example for North Sea)

$$R = \frac{\rho}{2\pi L}\left(\ln\left(\frac{4L}{r}\right) - 1 \right)$$

$$R = \frac{30\Omega cm}{2\pi(250cm)}\left(\ln\left(\frac{4(250cm)}{\sqrt{\dfrac{(25cm)(20.7cm)}{\pi}}} \right) - 1 \right)$$

$$R = 0.0641\Omega$$

Calculate single anode current output (example for North Sea):

$$I = \frac{V}{R}$$
$$I = \frac{(-0.800V - (-1.05V))}{0.0641\Omega}$$
$$I = 3.90A$$

Find the # of Anodes Necessary to Produce the Initial Current (example for North Sea):

$$\# \text{ of anodes} = \frac{\text{Initial current demand}}{\text{current output per anode}}$$

$$\# \text{ of anodes} = \frac{11{,}710\text{A}}{3.90 \frac{A}{anode}} = 3002.5 \text{ anodes} = 3003 \text{ anodes}$$

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Find the Mass of the Anodes (example for zinc anodes, North Sea):

Total Mass of Zinc Anodes = (# of anodes)(mass per anode)

Total Mass of Zinc Anodes = (3003 anodes)(922 $\frac{kg}{anode}$) = 2,768,766 kg

Let us then compare the mass of anodes required for the design life and the mass required for the initial polarization of the structure:

	NORTH SEA	GULF OF MEXICO
Mass of Zinc to protect the structure for 35 years, kg	2,624,880	**1,799,419**
Mass of Zinc required to provide the initial current, kg	**2,768,766**	1,149,734
Mass of Aluminum to protect the structure for 35 years, kg	723,462	**495,953**
Mass of Aluminum required to provide the initial current, kg	**1,048,047**	435,203
# of Zinc Anodes Needed	3003	1952
# of Aluminum Anodes Needed	3003	1421

Anode Distribution and Spacing

For sacrificial anodes this maybe based on the current demand of the structure and the maximum current output of the anode.

NORTH SEA

Maximum Current Output   3.900 Amps

Maximum Current Demand   180 mA/m^2

Maximum Area Protected   3.900 A/(0.180A/m^2) = 21.7m^2

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GULF OF MEXICO

Maximum Current Output   5.855 Amps

Maximum Current Demand   110 mA/m^2

Maximum Area Protected   5.855 A/(0.110 A/m^2) = 53.2m^2

If the structural member is relatively large, say 3 m diameter, then a single anode placed in the center of a 22 or 53 m^2 area will not be too far from the extremities of the cathode it is protecting. For smaller members, allowances have to be made for attenuation, and anode sizes must be selected to ensure that the anode protects half way to the next anode.

8.1.4 Sacrificial Anode Design Coated Structure

The effect of coating a structure on CP design can be seen by applying the DNV criteria to Example 1. It can be seen that significant savings in anode material can be achieved if a Category 2, 3 or 4 coating is used. The category 1 coatings are only helpful for short design life. This interpretation of the interaction between coatings and CP is still open to debate with many experts in the Oil Industry questioning the low performance criteria assigned to Category I coatings.

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Structure Area, m²:			63,000					
Allowance, Amps			220					
Piles, Amps:			120					
Zinc Anodes, Ah/kg			780		Cost, $/tonne, Feb 1995			1,025
Aluminum Anodes, Ah/kg			2,830		Cost, $/tonne, Feb 1995			2,000
CD mA/m²	tr, years	Category	k1	k2	f (ave)	f (final)	CP (ave) mA/m²	CP (final) mA/m²
North Sea								
90	35	1	0.1000	0.1000	1.8500	3.6000	90	90
90	35	1	0.1000	0.0500	0.9750	1.8500	88	90
90	35	2	0.0500	0.0300	0.5750	1.1000	52	90
90	35	2	0.0500	0.0200	0.4000	0.7500	36	68
90	35	3	0.0200	0.0150	0.2825	0.5450	25	49
90	35	3	0.0200	0.0120	0.2300	0.4400	21	40
90	35	4	0.0120	0.0120	0.2220	0.4320	20	39
90	35	4	0.0120	0.0120	0.2220	0.4320	20	39
Category			I	II	III	IV		
Total Current Demand, Amps			6,010	3,600	1,942	1,599		
Wt Aluminum, kg			723,465	433,387	233,745	192,451		
Cost Aluminum			1,446,931	866,774	467,490	384,903		
Number of Anodes			3,003	3,000	2,500	2,500		
Weight/Anode, kg			482	289	187	154		
Cost, $ / Anode			1,156	693	449	370		
Cost Installation $ / Anode			450	400	400	400		
Total Cost CP, $			**4,823,983**	**3,280,258**	**2,121,975**	**1,923,767**		
Gulf of Mexico								
60	35	1	0.1000	0.1000	1.8500	3.6000	60	60
60	35	1	0.1000	0.0500	0.9750	1.8500	59	60
60	35	2	0.0500	0.0300	0.5750	1.1000	35	60
60	35	2	0.0500	0.0200	0.4000	0.7500	24	45
60	35	3	0.0200	0.0150	0.2825	0.5450	17	33
60	35	3	0.0200	0.0120	0.2300	0.4400	14	26
60	35	4	0.0120	0.0120	0.2220	0.4320	13	26
60	35	4	0.0120	0.0120	0.2220	0.4320	13	26
Category			I	II	III	IV		
Total Current Demand			4,120	2,514	1,408	1,179		
Wt Aluminum			233,535	142,473	79,802	66,839		

8.1.5 Impressed Current Anode Design

Assuming the use of platinized titanium anodes with the following dimensions.

length = 1000 mm

diameter = 25 mm

Maximum driving potential = 9V

Then the surface area of the anode is:

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πdL   = 0.078m^2

	NORTH SEA	GULF OF MEXICO
Anode Resistance, Ohms	0.2277	0.1518
Maximum Anode Current Output, Amps	39.5	59.3
Maximum current density on anode surface, A/m^2	506	760
Number of anodes required	296	123

The distribution of the anodes is critical.

8.2 Ship Hull Protection

Ship Hulls require protection from both corrosion and the development of biofouling accumulations. The former is achieved by both coating and cathodic protection systems and the latter by antifouling coatings. In addition to the basic costs of the coating and cathodic protection systems, allowances must be made for dry dock costs, loss of revenue, and increased fuel consumption and lost performance due to the increase in skin friction drag caused by poor hull maintenance and biofouling.

SHIP HULL COATING

GRIT BLAST

NACE #1, with 1 - 2 mil anchor profile

BARRIER COAT

Hard Boiled Mastic, two component epoxy amine

Two coats, 3 mils D.F.T.

Coverage per one mil dry - 564 sq.ft./gal.

Cost, $23.00/gal.

Cost for 6 mils D.F.T. $0.24/sq.ft.

CATHODIC PROTECTION DESIGN

SHIP	ORIANA
TYPE	PASSENGER
LENGTH, m	245
BREADTH, m	30
DRAFT, m	9.75
BLOCK COEFFICIENT, C_b	0.6
WETTED SURFACE AREA $(1.7xLxD)+(C_bxLxB)$ m^2	8,471
CURRENT DEMAND FOR HULL, $(@22mA/m^2)$ Amps	186
CURRENT DEMAND FOR RUDDERS, Amps	15
CURRENT DEMAND FOR PROPELLERS, Amps	35
TOTAL CURRENT DEMAND, AMPS	236

Sacrificial Anode Calculations

Current Output per Anode

Assume anode dimensions: 500mm x 115mm x 65mm

The current output, $I = \dfrac{V}{R}$

R =   the anode resistance calculated using Lloyds' Formula for plate anodes

Lloyds' Formula

$$R = \frac{\rho}{2S}$$

$$R = \frac{20\Omega - cm}{2(30.75cm)}$$

$$R = 0.325\Omega$$

Current output per anode,

$$I = \frac{V}{R}$$

$$I = \frac{0.25V}{0.325\Omega} = 0.769A$$

Number of anodes required to supply current,

$$\# \text{ of anodes needed} = \frac{\text{Total current required}}{\text{Current output per anode}}$$

$$\# \text{ of anodes needed} = \frac{236A}{0.384 \frac{A}{anode}} = 307 \text{ anodes}$$

The total current capacity for one anode is:

Volume of Anodes * Density * Capacity of Galvalum 1

$= 3.738 \times 10^{-3} \text{ m}^3 * 2,700 \text{ kg/m}^3 * 2,830 \text{ Ah/kg} = 28,558 \text{ Ah}$

The design life of the system will be

$= \dfrac{\underline{28,558 \text{ A hrs} * 307 \text{ anodes} * (0.9)}}{236 \text{ Amps}} = 33,435 \text{ hrs or 3.8 years}$

APPENDIX

Some Commonly Used Marine Materials

from Dexter, S.C. (1985), Handbook of Oceanographic Materials, Krieger Publishing, Malabar, FL.

Aluminum Alloys

Material	Composition	Density, ρ (lb/in^3)
Aluminum alloy 5052	97.25% Al, 2.5% Mg, 0.25% Cr	0.097
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
10 x 10^6	31 (H34)	38 (H34)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.92 to -1.1	Crevice and sometimes pitting attack.	Applications demanding good corrosion resistance and fatigue strength. These include fuel lines, tanks, and sheets.
Special Notes: Severe galvanic attack can occur when placed in contact with steel, stainless steel, copper alloys, nickel alloys, and titanium. Corrosion protection is desired for submerged applications.		

Material	Composition	Density, ρ (lb/in^3)
Aluminum alloy 6061	97.95% Al, 1.0% Mg, 0.6% Si, 0.25% Cu, 0.20% Cr	0.098
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
10 x 10^6	40 (T6)	45 (T6)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.72 to -1.07	Crevice and pitting attack. May also undergo intergranular attack and SCC.	Applications demanding adequate corrosion resistance and good mechanical properties. The most versatile aluminum alloy for marine use.
Special Notes: Severe galvanic attack can occur when placed in contact with steel, stainless steel, copper alloys, nickel alloys, and titanium. Cathodic protection and coating is desired for submerged applications.		

Material	Composition	Density, ρ (lb/in^3)
Aluminum alloy 7075	90% Al, 5.6% Zn, 2.5% Mg, 1.6% Cu, 0.3% Cr	0.101
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
10.4 x 10^6	73 (T6)	83 (T6)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.72 to -0.83	Severe crevice and pitting attack. Also susceptible to SCC and exfoliation.	Applications requiring high strength and low weight.
Special Notes: Severe galvanic attack can occur when placed in contact with steel, stainless steel, copper alloys, nickel alloys, and titanium. Must be anodized, coated, and cathodically protected for submerged applications.		

Copper and Copper alloys

Material	Composition	Density, ρ (lb/in^3)
Copper	99.9% Cu	0.322
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
17 x 10^6	50 (Fully hardened)	55 (Fully hardened)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.12 to -0.30	Uniform attack and sometimes localized attack as a result of metal ion concentration cells. Velocity effects can also be quite marked.	Electrical and architectural applications. Resists biofouling at corrosion rates > 1 mpy.
Special Notes: None		

Material	Composition	Density, ρ (lb/in^3)
Beryllium-Copper, CDA 172	97.9% Cu, 1.9% Be, 0.2% Co	0.298
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
18 x 10^6	150 - 190 (HT and 75% Cold Worked)	195 - 205 (HT and 75% Cold Worked)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.10 to -0.25	Uniform corrosion and slight crevice attack.	Applications requiring good corrosion resistance and high strength. These include springs, bearings, and bushings.
Special Notes: As in most copper alloys, metal ion concentration cells may form.		

Material	Composition	Density, ρ (lb/in^3)
Red Brass, CDA 230	85% Cu, 15% Zn	0.316
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
17 x 10^6	49 (50% Work Hardened)	57 - 72 (50% Work Hardened)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.20 to -0.40	Uniform corrosion and slight dezincification.	Applications requiring good corrosion resistance.
Special Notes: As in most copper alloys, metal ion concentration cells may form.		

Material	Composition	Density, ρ (lb/in^3)
Inhibited Admiralty Brass	71% Cu, 28% Zn, 1% Sn, 0.6% As, Sb, or Pb	0.308
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
16 x 10^6	72 (Fully Hardened)	88 - 97 (Fully Hardened)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.16 to -0.25	Uniform corrosion and crevice attack. Erosion corrosion at velocities > 6 fps.	Heat exchanger and condenser tubes and plates.
Special Notes: As in most copper alloys, metal ion concentration cells may form.		

Appendix: Material Properties - 2

Material	Composition	Density, ρ (lb/in^3)
Naval Brass	60% Cu, 39% Zn, 1% Sn	0.304
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
15 x 10^6	66 (Hard-Drawn)	88 (Hard-Drawn)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.20 to -0.27	Uniform corrosion and dezincification (not completely eliminated with CP).	Condenser plates, prop shafts, fasteners.
Special Notes: Dezincification of this alloy may be severe, and, therefore, should be used with caution in submerged applications.		

Material	Composition	Density, ρ (lb/in^3)
Aluminum Bronze D, CDA 614	91% Cu, 7% Al, 2% Fe	0.281
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
18 x 10^6	40 - 55 (Hardened)	75 - 85 (Hardened)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.09 to -0.26	Uniform corrosion and some dezincification and crevice corrosion	Corrosion resistant tubing, tanks, fasteners, and sheathing.
Special Notes: As in most copper alloys, metal ion concentration cells may form.		

Material	Composition	Density, ρ (lb/in^3)
High Silicon Bronze A, CDA 655	94.8% Cu, 3.3% Si, 1.5% Mn, < 1.5% Fe and Zn	0.308
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
15 x 10^6	45 - 57 (Half-Hard)	78 - 98 (Half-Hard)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.17 to -0.23	Uniform corrosion and crevice corrosion.	Marine hardware, fasteners, shafting, and heat exchanger tubing.
Special Notes: As in most copper alloys, metal ion concentration cells may form.		

Material	Composition	Density, ρ (lb/in^3)
90-10 Copper-Nickel	88.7% Cu, 10% Ni, 1.3% Fe	0.323
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
18 x 10^6	57 (Light Drawn)	60 (Light Drawn)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.15 to -0.30	Uniform corrosion and some surface attack.	Excellent resistance to marine fouling if allowed to freely corrode. Used for seawater tubing and boat hulls.
Special Notes: Susceptible to sulfide attack. Velocity effects at velocities > 10 fps.		

Appendix: Material Properties - 3

Material	Composition	Density, ρ (lb/in^3)
70-30 Copper-Nickel	68.9% Cu, 30% Ni, 0.5% Fe, 0.6% Mn	0.323
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
22 x 10^6	79 (Cold Drawn)	85 (Cold Drawn)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.17 to -0.23	Uniform corrosion and some surface attack.	Good strength. Used in heat exchangers with high water velocities.
Special Notes: Susceptible to sulfide attack. Velocity effects at velocities > 15 fps.		

Material	Composition	Density, ρ (lb/in^3)
Cast Silicon Brass and Bronze	82 - 91% Cu, 5 - 14% Zn, 4% Si	0.302
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
15 x 10^6 - 18 x 10^6	22 - 35 (As Cast)	55 - 70 (As Cast)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
~ -0.27	Uniform corrosion.	Bearings, impellers, gears, props, pumps, fittings.
Special Notes: None		

Material	Composition	Density, ρ (lb/in^3)
Cast Aluminum Bronze	81 - 88% Cu, 9 - 13% Al, 1 - 5% Fe, others	0.272 - 0.281
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
14 x 10^6 - 20 x 10^6	40 - 80 (Heat Treated)	80 - 124 (Heat Treated)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.3 to -0.4	Uniform corrosion and dealloying.	Pump housings, bearings, impellers, gears, props, fittings.
Special Notes: None		

Appendix: Material Properties - 4

Nickel Alloys

Material	Composition	Density, ρ (lb/in³)
Monel 400	66.25% Ni, 31.5% Cu, 1.35% Fe, 0.9% Mn	0.319
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
26×10^6	90 - 130 (Fully Hardened)	100 - 140 (Fully Hardened)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.04 to -0.14	Uniform corrosion, pitting, and crevice attack.	Valves, pumps, prop shafts, fixtures, fasteners.
Special Notes: Resists erosion corrosion to high velocities. May cause severe galvanic attack of less noble metals when coupled.		

Material	Composition	Density, ρ (lb/in³)
Inconel 625	65.3% Ni, 18.6% Cr, 9% Mo, 4% Cb, 3% Fe, 0.05% C	0.305
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
29.8×10^6	201 (70% Cold Worked)	219 (70% Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.04 to +0.10	Highly resistant to most forms of attack.	Wire rope, propeller blades, fittings, springs, fasteners. Parts where little to no corrosion can be accepted.
Special Notes: Resists erosion corrosion to high velocities.		

Material	Composition	Density, ρ (lb/in³)
Incoloy 825	41.8% Ni, 21.5% Cr, 30% Fe, 3% Mo, 1.8% Cu, 1% Ti, 0.03% C	0.294
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28×10^6	35 - 45 (Cold Drawn)	85 - 101 (Cold Drawn)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.03 to +0.05	Crevice corrosion and pitting.	Components in desalination plants and heat exchangers.
Special Notes: Resistant to chloride SCC.		

Iron and Steels

Material	Composition	Density, ρ (lb/in^3)
Ductile Cast Iron	3.3 - 4.0% C, 2 - 3% Si, 0.2 - 0.6% Mn, < 2.5% Ni, > 0.15% total P and Mg, remainder Fe	0.257
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
23 x 10^6 - 25 x 10^6	40 - 150	60 - 175
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.60 to -0.72	Mostly uniform with some shallow pitting.	General machinery parts, props, piping.
Special Notes: Cathodic protection is needed for longer term submerged exposure.		

Material	Composition	Density, ρ (lb/in^3)
AISI 1040 Steel	99.6% Fe, 0.4% C	0.283
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
30 x 10^6	86 (Heat Treated)	113 (Heat Treated)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.60 to -0.70	Mostly uniform with slight crevice corrosion.	Multiple structural and mechanical uses.
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Material	Composition	Density, ρ (lb/in^3)
AISI 1080 Steel	99.2% Fe, 0.8% C	0.283
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
30 x 10^6	142 (Heat Treated)	190 (Heat Treated)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.60 to -0.70	Mostly uniform with slight crevice corrosion. Also susceptible to SCC and hydrogen embrittlement.	Multiple structural and mechanical uses.
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Material	Composition	Density, ρ (lb/in^3)
HY-80 Steel	2 - 3.25% Ni, 1 - 1.8% Cr, 0.2% - 0.6% Mo, 0.15 - 0.35% Si, <0.25% P and S, 0.1 - 0.4% Mn, 0.18% C, remainder Fe	0.284
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
30 x 10^6	80 - 100 (Quenched and Tempered)	103 (Quenched and Tempered)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.63	Mostly uniform.	Hull plating, offshore platforms, tanks pressure vessels, cranes, booms
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Material	Composition	Density, ρ (lb/in^3)
HY-100 Steel	2.25 - 3.5% Ni, 1 - 1.8% Cr, 0.2% - 0.6% Mo, 0.15 - 0.35% Si, <0.25% P and S, 0.1 - 0.4% Mn, 0.2% C, remainder Fe	0.284
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
30 x 10^6	100 - 105 (Quenched and Tempered)	110 - 118 (Quenched and Tempered)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.63	Mostly uniform. Some tendency towards SCC and hydrogen embrittlement.	Hull plating, offshore platforms, tanks pressure vessels, cranes, booms
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Material	Composition	Density, ρ (lb/in^3)
Low Alloy-High Strength Steels (ASTM A-242 and A-441)	0.18 - 0.22% C, 0.5 - 1.5% (each) Mn, Ni, Cr, ~0.25% (each) P, Si, S, Cu, remainder Fe	0.283
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
30 x 10^6	40 - 60 (Annealed)	60 - 80 (Annealed)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.57 to -0.63	Mostly uniform with some crevice corrosion and pitting.	Structural sections and members.
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Appendix: Material Properties - 7

Material	Composition	Density, ρ (lb/in³)
Maraging 300 Steel	18 - 19 % Ni, 8.5 - 9.5% Co, 4.7 - 5.2% Mo, 0.5 - 0.7% Ti, 0.05 - 0.15% Al, < 0.03% C, remainder Fe	0.290
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
29×10^6	295 - 303 (Heat Treated)	297 - 306 (Heat Treated)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.57 to -0.58	Uniform, SCC, and hydrogen embrittlement. SCC and embrittlement can be controlled with cathodic protection.	High strength weldable structural pieces.
Special Notes: Coatings and/or cathodic protection is needed for marine use. Galvanic attack may occur if this alloy is immersed in seawater and in contact with copper alloys, nickel alloys, stainless steels, or titanium alloys.		

Titanium and Titanium Alloys

Material	Composition	Density, ρ (lb/in³)
Unalloyed Titanium	98.9 - 99.5% Ti	0.163
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
15×10^6	up to 90 (Cold Worked)	up to 100 (Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.05 to +0.06	None.	Structural members, marine parts requiring immunity, impressed current anodes.
Special Notes: SCC is possible if titanium contains higher levels of oxygen.		

Material	Composition	Density, ρ (lb/in³)
Titanium 6Al-4V	5.5 - 6.5% Al, 3.5 - 4.5% V, <0.25% Fe, remainder Ti	0.160
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
16.5×10^6	155 (Age Hardened)	165 - 170 (Age Hardened)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.05 to +0.06	None, except some tendency for SCC.	Pumps, impellers, structural members, marine hardware and parts requiring immunity.
Special Notes: None		

Stainless Steels

Material	Composition	Density, ρ (lb/in³)
302 Stainless Steel	70.85 - 74.85% Fe, 17 - 19% Cr, 8 - 10% Ni, 0.15% C	0.290
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28 x 10⁶	75 (Quarter Hard)	125 (Quarter Hard)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.05 to -0.10 (passive) -0.45 to -0.57 (active)	Crevice and pitting corrosion. Susceptible to local attack in areas covered by fouling	General purpose in non-submerged applications.
Special Notes: Local attack minimized in water velocities > 5 fps, but not generally recommended for submerged use due to pitting.		

Material	Composition	Density, ρ (lb/in³)
303 Stainless Steel	17 - 19% Cr, 8 - 10% Ni, > 0.15% S or Se, 0.15% C, remainder Fe	0.290
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28 x 10⁶	75 (Cold Worked)	110 (Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.05 to -0.10 (passive) -0.45 to -0.57 (active)	Severe crevice and pitting corrosion. Susceptible to local attack in areas covered by fouling	Generally not recommended for seawater application.
Special Notes: This grade may be substituted for others by suppliers with devastating consequences. Non-magnetic, austenitic alloy.		

Material	Composition	Density, ρ (lb/in³)
304 Stainless Steel	67.92 - 72.92% Fe, 18 - 20% Cr, 9 - 12% Ni, 0.08% C	0.290
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28 x 10⁶	75 (Cold Worked)	110 (Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.09 to -0.15 (passive) -0.20 to -0.57 (active)	Crevice and pitting corrosion. Susceptible to local attack in areas covered by fouling. Heat effected zones may be sensitized.	Topside wire rope and general purpose submerged use where velocities are > 5 fps.
Special Notes: Cathodic protection is necessary for submerged structural applications when exposure is greater than two months. Non-magnetic, austenitic alloy.		

Material	Composition	Density, ρ (lb/in³)
316 Stainless Steel	64.92 - 71.92% Fe, 16 - 18% Cr, 10 - 14% Ni, 2 - 3% Mo, 0.08% C	0.290
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28×10^6	30 - 42 (Annealed)	80 - 90 (Annealed)
Potential in Seawater, ref. S.C.E. and Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.00 to -0.15 (passive) -0.35 to -0.60 (active)	Crevice and pitting corrosion. Susceptible to local attack especially in areas covered by fouling. Heat effected zones may be sensitized.	Topside wire rope and general purpose where velocities are > 5 fps.

Special Notes: Cathodic protection is necessary for submerged structural applications when exposure is greater than six months. This is the most corrosion resistant 300 series stainless. Non-magnetic, austenitic alloy.

Material	Composition	Density, ρ (lb/in³)
17-4 PH Stainless Steel	16.5% Cr, 4% Ni, 4% Cu, 0.3% Nb and Ta, 0.07% C, remainder Fe	0.280 - 0.282
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
28.5×10^6	178 - 185 (Hardened)	200 (Hardened)
Potential in Seawater, ref. Ag-AgCl (V)	**Corrosion Types Suffered**	**Uses**
-0.10 to -0.20 (passive) -0.20 to -0.40 (active)	Crevice and pitting corrosion. Weld bead attack.	Parts with moderate corrosion resistance and high strength to weight ratio.

Special Notes: Cathodic protection should be from impressed current or mild steel sacrificial anodes. Problems arise with aluminum, zinc, and magnesium anodes. Cathodic protection may lead to hydrogen embrittlement and cracking.

Material	Composition	Density, ρ (lb/in³)
410 Stainless Steel	85.35 - 87.35% Fe, 11.5 - 13.5% Cr, 1% Mn, 0.15% C	0.280
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
29×10^6	140 - 145 (Heat Treated)	180 - 190 (Heat Treated)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.24 to -0.35 (passive) -0.45 to -0.57 (active)	Severe crevice and pitting corrosion.	Applications where a high strength alloy is important. Submerged applications require cathodic protection to prevent localized attack.

Special Notes: Magnetic, martensitic alloy.

Other Metals

Material	Composition	Density, ρ (lb/in^3)
Commercially Pure Magnesium	99.98% Mg	0.063
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
5.7×10^6 - 6.5×10^6	3 (As Cast)	13 (As Cast)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-1.60 to -1.63	Rapid uniform corrosion. Severe galvanic effects when coupled with all common marine metals.	Sacrificial anodes and corrosive links.
Special Notes: Not suitable for structural applications in seawater.		

Material	Composition	Density, ρ (lb/in^3)
Zinc	99.92% Zn, 0.08% Pb	0.258
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
----	----	19 - 23 (Hot Rolled)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.98 to -1.03	Uniform corrosion with some pitting in anaerobic conditions.	Galvanizing, sacrificial anodes and corrosive links.
Special Notes: None.		

Material	Composition	Density, ρ (lb/in^3)
Lead	----	0.410
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
2.0×10^6	----	2.0 (As Cast)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.19 to -0.25	Uniform corrosion.	Galvanizing, sacrificial anodes and corrosive links.
Special Notes: None.		

Material	Composition	Density, ρ (lb/in^3)
Gold	99.5 - 99.99% Au	0.698
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
10.8×10^6 - 11.6×10^6	30 (60% Cold Worked)	32 (60% Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
----	Completely resistant to marine corrosion.	Specialty applications and electrical contacts.
Special Notes: None.		

Material	Composition	Density, ρ (lb/in³)
Platinum	99.85% Pt	0.775
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
$21 \times 10^6 - 25 \times 10^6$	27 (50% Cold Worked)	28 - 30 (50% Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
+0.20 to +0.35	Completely resistant to marine corrosion.	Impressed current anodes and electrical contacts.
Special Notes: None.		

Material	Composition	Density, ρ (lb/in³)
Silver	99.9% Ag	0.379
Elastic Modulus, E (psi)	**Yield Strength, σ_y (ksi)**	**Tensile Strength, σ_u (ksi)**
$10.3 \times 10^6 - 11.3 \times 10^6$	44 (50% Cold Worked)	up to 54 (50% Cold Worked)
Potential in Seawater, ref. S.C.E. (V)	**Corrosion Types Suffered**	**Uses**
-0.09 to -0.14	Slight uniform corrosion. Increased tarnish with sulfur compounds present.	Electrical conductors and radar applications. Solder when alloyed.
Special Notes: None.		

Appendix: Material Properties - 12

Polymers, Rubbers, and Elastomers

Material	Description	Specific Gravity
ABS, Medium Impact	Thermoplastic (acrylonitrile butadiene styrene)	1.05 - 1.07
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
3.0×10^5 - 4.1×10^5	0.2 - 0.45% in 24 hrs.	5.9 - 8.0
Behavior in the Marine Environment		**Uses**
Slight yellowing and embrittlement in direct sunlight. No chemical degradation in seawater. Not attacked by borers unless in contact with wood.		Multiple structural uses. Pipe, tubing, instrument housings, bearings.

Material	Description	Specific Gravity
Acetal, Standard Homopolymer	Thermoplastic (tradenames - Delrin, Celcon)	1.43
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
5.2×10^5	0.25% in 24 hrs.	10.0
Behavior in the Marine Environment		**Uses**
Slight chalking in sunlight. No chemical degradation in seawater. Usually not attacked by borers unless in contact with wood or tape. It is attacked by strong acids and bases. Excellent resistance to many organic solvents.		Gears, bushings, levers, shafts, springs, hardware.

Material	Description	Specific Gravity
Cast Acrylics	Polymethyl methacrylate (tradenames - Lucite, Perspex, Plexiglas)	1.17 - 1.28
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
2.7×10^5 - 5.0×10^5	0.2 - 0.5% in 24 hrs.	5.5 - 8.0 (High Impact Sheet)
Behavior in the Marine Environment		**Uses**
Usually not affected by sunlight. No chemical degradation in seawater. Usually not attacked by borers unless in contact with wood or tape. Water absorption can lead to a 10% reduction in hardness and up to a 30% reduction in tensile strength. It is attacked by strong acids and bases. Soluble in ketones, esters, and aromatic and chlorinated hydrocarbons. Excellent resistance to many organic solvents.		Lenses, windows, housings and many general purpose applications.

Material	Description	Specific Gravity
Epoxy	Diglycidal ether of bisphenol A	1.1 - 2.0
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
5×10^5 - 15×10^5	0.1 - 1.0% in 24 hrs.	5 - 15
Behavior in the Marine Environment		**Uses**
Resistant to sunlight with UV inhibitors. Usually not attacked by borers unless in contact with wood or tape. May be attacked by sulfuric and acetic acid. Some attack by stong bases. Resistant to organic solvents and weak acids and bases.		Potting material for electical components, castings, marine coatings, adhesives, patching compounds.

Material	Description	Specific Gravity
Nylon, Type 6	Thermoplastic, polyamide	1.14
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
3.8×10^5	1.3 - 1.9% in 24 hrs.	9.5 - 12.5
Behavior in the Marine Environment		**Uses**
Embrittled by prolonged exposure to sunlight. Usually not attacked by borers unless in contact with wood. May be attacked by strong acids, phenols, and formic acid. Resistant to bases, weak acids, and most common solvents. Water absorption and swelling may alter dimensions and mechanical properties		Bearings, gears, bushings, housings, rods, ropes, coatings.

Material	Description	Specific Gravity
Polycarbonate (unfilled)	Tradenames - Lexan, Merlon	1.19 - 1.25
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
3.0×10^5 - 4.5×10^5	0.12 - 0.19% in 24 hrs.	9.0 - 10.5
Behavior in the Marine Environment		**Uses**
Sunlight may lead to a slight color change and some embrittlement. No chemical degradation in seawater. Usually not attacked by borers unless in contact with wood. Low water absorption leads to good dimensional stability and retention of properties. It is attacked by strong acids and bases, organic solvents, and fuels. Resistance to weak acids, oils, and greases.		Lenses, windows, housings, impellers and parts requiring high impact resistance.

Material	Description	Specific Gravity
Polyethylene, High Density	Thermoplastic (Tradenames - Marlex, Norchem, Rulan)	0.95 - 0.96
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
3.0×10^5 - 4.5×10^5	< 0.01% in 24 hrs.	4.4
Behavior in the Marine Environment		**Uses**
Greatly degraded by sunlight if inhibitors are not used. Usually not attacked by borers unless in contact with wood. Generally shows excellent resistance to the marine environment. Good chemical resistance. Slowly attacked by strong acids.		Wire and cable insulation, pipe, housings.

Material	Description	Specific Gravity
Polypropylene	General purpose and high impact thermoplastic	0.89 - 0.91
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
1.6×10^5 - 2.2×10^5	< 0.01 - 0.03% in 24 hrs.	4.3 - 5.5
Behavior in the Marine Environment		**Uses**
Greatly degraded by sunlight if inhibitors are not used. Usually not attacked by borers unless in contact with wood. Generally shows excellent resistance to the marine environment. Good chemical resistance. Slowly attacked by strong acids.		Wire and cable coatings, film, packaging, hinges housings.

Material	Description	Specific Gravity
Teflon, PTFE	Polytetrafluoroethylene (tradenames - Teflon, Fluon, Halon, Rulon)	2.1 - 2.3
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
0.38×10^5 - 0.65×10^5	0.01% in 24 hrs.	2.0 - 6.5
Behavior in the Marine Environment		**Uses**
Not degraded by sunlight. Usually not attacked by borers unless in contact with wood. Generally shows excellent resistance to the marine environment. Excellent chemical resistance. May be attacked by the alkali metals.		Pipes, valves, bearings, impellers, electrical insulators, non-stick coatings.

Material	Description	Specific Gravity
Polyvinyl Chloride, PVC	Polytetrafluoroethylene (tradenames - Teflon, Fluon, Halon, Rulon)	1.30 - 1.45
Elastic Modulus, E (psi)	**Water Absorption**	**Tensile Strength, σ_u (ksi)**
3.5×10^5 - 6.0×10^5	0.03 - 0.04% in 24 hrs.	5.5 - 9.0
Behavior in the Marine Environment		**Uses**
Sunlight produces minor effects. Generally shows good resistance to the marine environment. Attacked by strong acids, ketones, esters, and aromatic hydrocarbons. Resistant to alcohols, aliphatic hydrocarbons, oils, bases, and weak acids.		Pipes, tanks, molded and extruded parts, housings.

Material	Description	Specific Gravity
Butyl Rubber	Isobutylene-isoprene	0.90
Tear Resistance	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
Good	Good to Excellent	2.5 - 3.0
Behavior in the Marine Environment		**Uses**
Very good resistance to sunlight produces. Excellent resistance to swelling in water. Resistant to acids, oxidation and heat aging. Vulnerable to many solvents, oils, and fuels.		Flexible electrical insulation, hose, shock absorption, diaphragms.

Material	Description	Specific Gravity
Natural and Synthetic Rubber	Polyisoprene	0.93
Tear Resistance	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
Excellent	Excellent	2.5 - 4.5
Behavior in the Marine Environment		**Uses**
Fair to poor resistance to sunlight. Marine exposure may cause some swelling. Microorganisms and hydrogen sulfide may lead to severe cracking. Resistant to oxidation and heat aging. Vulnerable to many solvents, oils, and fuels. Shows fair to good resistance to organic acids.		Seals, gaskets, hose, chemical tank linings.

Material	Description	Specific Gravity
Neoprene Rubber	Chloroprene	1.25
Tear Resistance	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
Fair to Good	Good	3.0 - 4.0
Behavior in the Marine Environment		**Uses**
Very good resistance to sunlight. Marine exposure may cause some swelling. May be degraded by aromatic hydrocarbons. Good to excellent resistance to other organic solvents, oils, fuels, acids, and heat.		Seals, gaskets, chemical tank linings, wetsuits.

Material	Description	Specific Gravity
Fluorocarbon Elastomers	Trade names: Kel-F, Viton	1.40 - 1.95
Tear Resistance	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
Poor to Fair	Good	1.5 - 3.0
Behavior in the Marine Environment		**Uses**
Very good resistance to sunlight and swelling. May be degraded by alkalies, synthetic lubricants, hydraulic fluids containing phosphates. Excellent resistance to high temperature air and oils.		O-rings, seals, gaskets, hose, shaft seals.

Material	Description	Specific Gravity
Urethane Elastomers	Trade names: Adiprene, Cyanaprene, Elastothane, Roylar	1.07
Tear Resistance	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
Excellent	Superior	5.0 - 8.0
Behavior in the Marine Environment		**Uses**
Very good resistance to sunlight and swelling (except at high temperatures). May be degraded by acids, alkalies, oxygenated alcohols. Excellent resistance to hydrocarbon solvents, oils.		Components requiring superior abrasion resistance.

Concrete and Glass

Material	Composition	Density, ρ (lb/ft^3)
Concrete	Varied	140 - 150
Elastic Modulus, E (psi)	**Compressive Strength, (ksi)**	**Flexural Strength, (ksi)**
3×10^6 - 6×10^6	3.5 - 7.5	0.4 - 0.8
Porosity (% by volume)	**Marine Attack Suffered**	**Uses**
5 - 10	Water absorption up to 2.4% @ 550 ft head. Degraded by high sulfate waters, causing cracking and softening.	Large structural members (with and without steel reinforcement), ship hulls, moorings.
Special Notes: Deterioration of concrete can lead to lowering of pH at the rebar, causing corrosion and spalling of the concrete. For longer term durability concrete, it is desirable to use low permeability types with reduced alkalinity and low 3 CaO Al$_2$O$_3$ content.		

Material	Composition	Specific Gravity
Glass (Borosilicate and Soda Lime)	Trade names: Kimax, Pyrex	2.13 to 2.55
Elastic Modulus, E (psi)	**Abrasion Resistance**	**Tensile Strength, σ_u (ksi)**
7.4×10^6 - 10.0×10^6	Excellent	0.5 - 40.0
Refractive Index	**Behavior in Marine Environment**	**Uses**
1.468 - 1.525	Generally unaffected by weathering or marine exposure.	Containers, plates, buoyancy spheres, lenses, housings.
Special Notes: May be attacked by hydrofluoric acid and sodium hydroxide.		

Wood

Material	Moisture Content (%)	Specific Gravity
Hardwood, Seasoned Maple and Oak	12	0.63 to 0.68
Elastic Modulus in Bending (psi)	**Modulus of Rupture (ksi)**	**Behavior in Marine Environment**
1.8×10^6	15.8 (maple) 14.3 - 15.2 (oak)	Left untreated these woods can be severely damaged by marine borers in as little as six months exposure when placed within six feet of bottom sediments. The borer attack is generally most rapid in warm coastal and lower latitude waters.

Material	Moisture Content (%)	Specific Gravity
Teak and Mahogany	52 (teak)	0.50 (mahogany)
Elastic Modulus in Bending (psi)	**Modulus of Rupture (ksi)**	**Behavior in Marine Environment**
1.4×10^6 - 1.7×10^6	11.1 - 11.4	These woods are susceptible to borer attack.

Material	Moisture Content (%)	Specific Gravity
Softwood, Seasoned Cedar and Cypress	12	0.46 to 0.47
Elastic Modulus in Bending (psi)	**Modulus of Rupture (ksi)**	**Behavior in Marine Environment**
0.9×10^6 - 1.4×10^6	8.8 (cedar) 10.6 (cypress)	Left untreated these woods can be severely damaged by marine borers in as little as six months exposure when placed within six feet of bottom sediments. The borer attack is generally most rapid in warm coastal and lower latitude waters.

Material	Moisture Content (%)	Specific Gravity
Softwood, Seasoned Pine and Spruce	12	0.35 to 0.40
Elastic Modulus in Bending (psi)	**Modulus of Rupture (ksi)**	**Behavior in Marine Environment**
1.2×10^6 - 2.0×10^6	8.6 - 10.1 (pine) 10.2 (spruce)	Left untreated these woods can be severely damaged by marine borers in as little as six months exposure when placed within six feet of bottom sediments. The borer attack is generally most rapid in warm coastal and lower latitude waters.

Fiber Reinforced Plastics (FRP)

from Agarwal, B.D and L.J. Broutman (1990), <u>Analysis</u> <u>and</u> <u>Performance</u> <u>of</u> <u>Fiber</u> <u>Composites</u>, Wiley Publishing, New York.

Material	Composition	Specific Gravity
E-Glass Reinforced Epoxy	57% E-Glass, 43% Epoxy	1.97
Tensile Modulus, E (psi)	**Tensile Strength, σ_u (ksi)**	**Longitudinal Poisson's Ratio**
3.1×10^6	82.5	0.25
Uses:		
Applications demanding excellent corrosion resistance and high strength to weight ratio. These include structural members, boat hulls, tanks, specialty items.		
Special Notes: Can be degraded by sunlight if inhibitors or barrier coat protection is not used. May also be somewhat degraded by water absorption if not protected.		

Material	Composition	Specific Gravity
Kevlar 49 Reinforced Epoxy	60% Kevlar 49, 40% Epoxy	1.40
Tensile Modulus, E (psi)	**Tensile Strength, σ_u (ksi)**	**Longitudinal Poisson's Ratio**
5.8×10^6	94.3	0.34
Uses:		
Applications demanding excellent corrosion resistance and high strength to weight ratio. These include structural members, boat hulls, tanks, specialty items.		
Special Notes: Can be degraded by sunlight if inhibitors or barrier coat protection is not used. May also be somewhat degraded by water absorption if not protected.		

Material	Composition	Specific Gravity
Carbon Fiber Reinforced Epoxy	58% Carbon Fiber, 42% Epoxy	1.54
Tensile Modulus, E (psi)	**Tensile Strength, σ_u (ksi)**	**Longitudinal Poisson's Ratio**
12.0×10^6	55.1	0.38
Uses:		
Applications demanding excellent corrosion resistance and high strength to weight ratio. Excellent stiffness properties. Uses include structural members, boat hulls, tanks, specialty items.		
Special Notes: Can be degraded by sunlight if inhibitors or barrier coat protection is not used. May also be somewhat degraded by water absorption if not protected.		