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Seawater and Cooling Water Corrosion

COMPOSITION OF SUBSTITUTE OCEAN WATER

Stock Solution No. 1—Dissolve the indicated amounts of the following salts in water and dilute to a total volume of 7.0 L. Store in well stoppered glass containers.

$MgCl_2{\cdot}6H_2O$	3889.0 g (=555.6 g/L)
$CaCl_2$(anhydrous)	405.6 (-57.9 g/L)
$SrCl_2{\cdot}6H_2O$	14.8 g (=2.1 g/L)

Stock Solution No. 2—Dissolve the indicated amounts of the following salts in water and dilute to a total volume of 7.0 L or a convenient volume. Store in well stoppered amber glass containers.

KCl	486.2 g (=69.5 g/L)
$NaHCO_3$	140.7 g (=20.1 g/L)
KBr	70.4 g (=10.0 g/L)
$H3BO_3$	19.0 g (=2.7 g/L)
NaF	2.1 g (=0.3 g/L)

Stock Solution No. 3—Dissolve the indicated amounts of the following salts in water and dilute to a total volume of 10.0 L or a convenient volume. Store in well stoppered amber glass containers.

$Ba(NO_3)_2$	0.994 g
$Mn(NO_3)_2{\cdot}6H_2O$	0.546 g
$Cu(NO_3)_2{\cdot}3H_2O$	0.396 g
$Zn(NO_3)_2{\cdot}6H_2O$	0.151 g
$Pb(NO_3)_2$	0.066 g
$AgNO_3$	0.0049 g

Note—To make the addition of $AgNO_3$ in the above solution, dissolve 0.049 g of $AgNO_3$ in water and dilute to 1 L. Add 100 mL of this solution to Stock Solution No. 3 before diluting to 10.0 L.

1. Preparation of Substitute Ocean Water

1.1 To prepare 10.0 L of substitute ocean water, dissolve 245.34 g of sodium chloride and 40.94 g of anhydrous sodium sulfate in 8 to 9 L of water. Add 200 mL of Stock Solution No. 1 slowly with vigorous stirring and then 100 mL of Stock Solution No. 2. Dilute to 10.0 L. Adjust the pH to 8.2 with 0.1 N sodium hydroxide solution. Only a few milliliters of NaOH solution should be required.

Note—Prepare the solution and adjust the pH immediately prior to use.

2. Preparation of Substitute Ocean Water with Heavy Metals

2.1 Add 10 mL of Stock Solution No. 3 slowly and with vigorous stirring to 10.0 L of the substitute ocean water prepared as described in Section 1.

Chemical Composition of Substitute Ocean Water[A,B]

Compound	Concentration, g/L
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003
$Ba(NO_3)_2$	0.0000994
$Mn(NO_2)_2$	0.0000340
$Cu(NO_3)_2$	0.0000308
$Zn(NO_3)_2$	0.0000096
$Pb(NO_3)_2$	0.0000066
$AgNO_3$	0.00000049

[A] Chlorinity of this substitute ocean water is 19.38

[B] The pH (after adjustment with 0.1 *N* NaOH solution) is 8.2

The substitute ocean water prepared in accordance with Section 6 will have the composition shown above the line (upper half of the table). The substitute ocean water with heavy metals, prepared in accordance with Section 1, will have the complete composition shown.

Source: ASTM D1141-98, “Standard Practice for the Preparation of Substitute Ocean Water” (West Conshohocken, PA, USA: ASTM International, 2003). Reprinted with permission, copyright ASTM International.

WORLDWIDE SEAWATER EXPOSURE SITES: TYPICAL SEAWATER CHARACTERISTICS

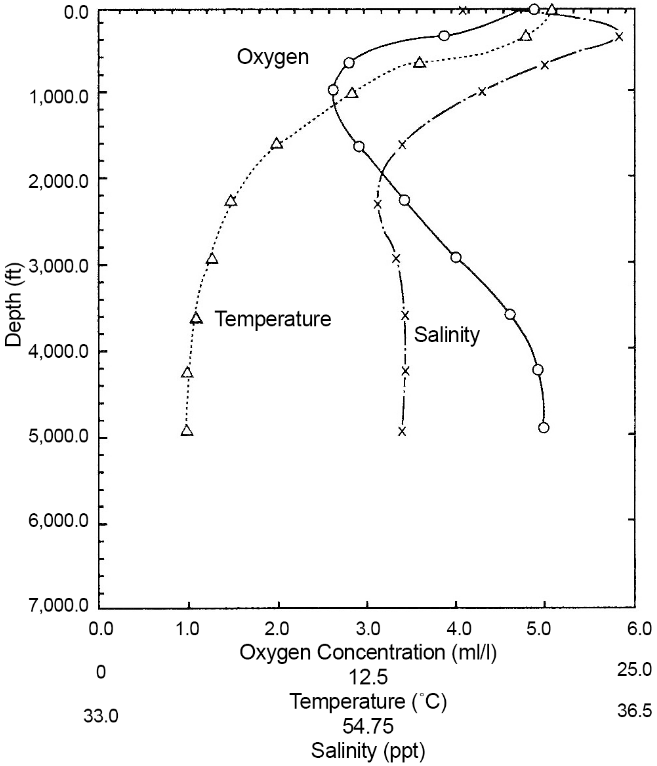
		Range of Environmental Constituents[a]			
Site	**Rack Location**	**Dissolved Oxygen, ppm**	**Salinity**	**Temperature °C**	**pH**
Ocean City, NJ	From raft 0.3 m below surface	5.2–11.7	31–34	1–29	7.5–8.2
Wrightsville Beach, NC Banks Channel	Fom wharf in channel	5.0–9.6	31.8–37.6	7–30	7.9 to 8.2
Key West, FL Fleming Key	Under pier	4–8	33–39	16–31	8.0–8.2
Freeport, TX	Intake flume	1.5–6.0	11.7–19.4[b]	15–27	7.5–8.6
Port Hueneme, CA Port Hueneme Harbor	From bulkhead	3.6–5.3	33	14–21	7.9–8.1
Talara, Peru	From pier, 180 m from shore	5–6	19.8[b]	18–22	8.2
KeAhole, Kona, HI	45 m from shore on pipe	6–14	34.6–35	24–28	8–8.3
Australia, Innisfail North Barnard Islands	From raft	5.1–6.5	31.7–37.2	23–30	8–8.5
Japan Sakata Harbor	Off docking pier	7.1–13	16.8–18.3[b]	2–28	8.4
Italy Genoa Harbor	From raft	4.5–6.0	35	11–25	8.1
Denmark, Sjaelland Kyndby Isefjord	From raft in Fjord	NA[c]	18–28	0–18	7.5–8.0
Sweden Studsvik (Baltic Sea)	From wooden bulkhead	6–10	7.8–8.1	2–20	7.4–7.6
Bohus-Malmon (North Sea)	From raft	6–10	21–28	2–20	8.0–8.2
England, Isle of Wight Langstone Harbor	From raft	88–118[d]	34–34.6	5–22	7.8–8.4

[a] compiled from information provided by participants
[b] chlorinity, g/L
[c] NA = not available
[d] reported as % saturation

Source: R. Kain, W. Young, eds., ASTM STP1300, Corrosion Testing in Natural Waters, vol. 2 (West Conshohocken, PA, USA: ASTM International, 1997), p. 37. Reprinted with permission, copyright ASTM.

ENVIRONMENT/DEPTH PROFILE IN THE GULF OF MEXICO

Ocean Environments in Gulf of Mexico (Galveston-Brownsville)



Source: S. Milligan.

SPECIFIC CONDUCTANCE OF SEAWATER AS A FUNCTION OF TEMPERATURE AND CHLORINITY

Conductance: $\Omega^{-1} \cdot cm^{-1}$

Chlorinity	Temperature, ˚C (˚F)					
%	0 (32)	5 (40)	10 (50)	15 (60)	20 (70)	25 (75)
1	0.001839	0.002134	0.002439	0.002763	0.003091	0.003431
2	0.03556	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

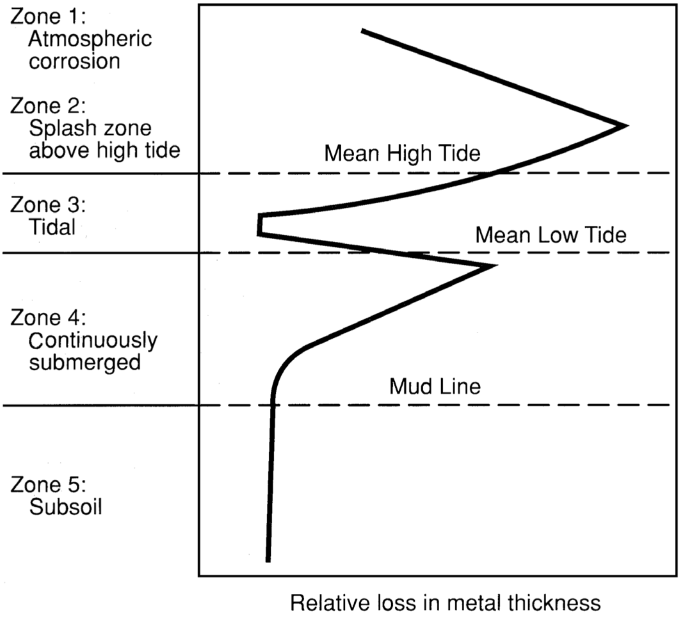
Source: L.J. Korb, *Metals Handbook,* 9th ed., vol. 13 (Materials Park, OH, USA: ASM International, 1987), p. 896. Reprinted with permission from ASM International.

CORROSION FACTORS FOR CARBON STEEL IN SEAWATER

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% chloride.)
Electrical Conductivity	High conductivity makes it possible for anodes and cathodes to operateover 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, for the most part, is cathodically controlled. 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 the 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 the 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.

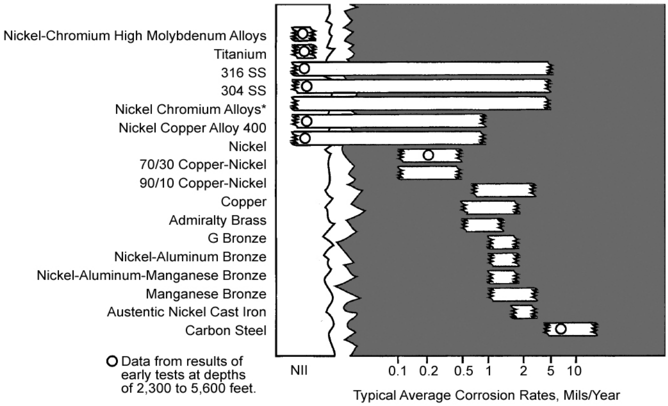
Source: F.W. Fink, et al., "Corrosion of Metals in Marine Environments," Battelle Memorial Institute DMIC Report 254, NTIS AD-712 5B5-S, 1970, pp. 7, 13. Reprinted with permission from Battelle Memorial Institute.

ZONES OF CORROSION FOR STEEL PILING IN SEAWATER



Source: F.L. LaQue, *Marine Corrosion Cause and Prevention* (Hoboken, NJ, USA: John Wiley & Sons, 1975), p. 116. Reprinted with permission from The Electrochemical Society.

RATES OF GENERAL WASTAGE OF METALS IN QUIET SEAWATER



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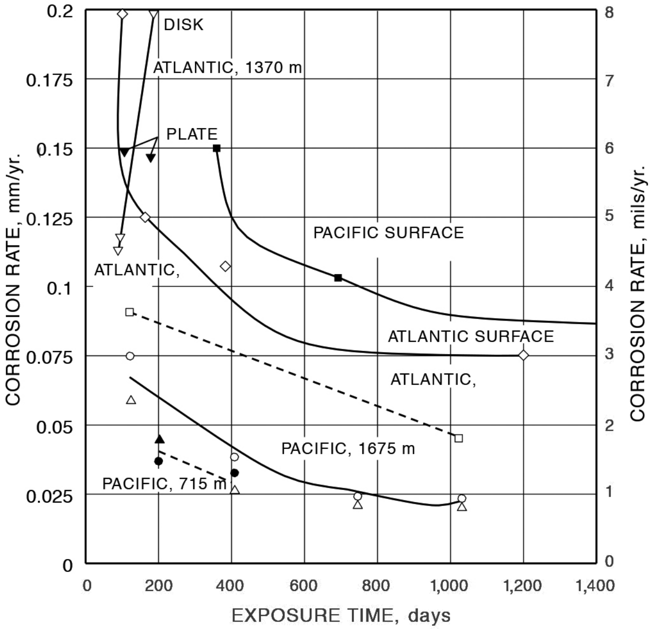
*Nickel chromium alloys designate a family of nickel base alloys with substantial chromium contents with or without alloying elements all of which, except those with high molybdenum contents, have related seawater corrosion characteristics.

Source: F.L. LaQue, *Marine Corrosion Cause and Prevention* (Hoboken, NJ, USA: John Wiley & Sons, 1975), p. 146. Reprinted with permission from The Electrochemical Society.

CORROSION RATES OF LOW CARBON STEEL AT VARYING DEPTHS OF SEAWATER



Source: Manual 20, *Corrosion Tests and Standards: Application and Interpretation* (West Conshohocken, PA, USA: ASTM International, 1995), p. 309. Reprinted with permission, copyright ASTM.

EFFECT OF VELOCITY ON THE CORROSION OF METALS IN SEAWATER

		Average Corrosion Rate (mm, y^{-1})		
			Flowing Seawater	
Alloy	**Deepest Pit (mm)**	**Quiet Seawater**	**8.2 m s^{-1}**	**35-42 m s^{-1}**
Carbon steel	2.0	0.075	–	4.5
Grey cast iron (graphitized)	4.9	0.55	4.4	13.2
Admiralty gunmetal	0.25	0.027	0.9	1.07
85/5/5/5 Cu Zn Pb Zn	0.32	0.017	1.8	1.32
Ni resist cast iron type 1B	nil	0.02	0.2	0.97
Ni Al bronze	1.12	0.055	0.22	0.97
70/30 Cu Ni + Fe	0.25	< 0.02	0.12	1.47
Type 316 stainless steel	1.8	0.02	< 0.02	< 0.01
6% Mo stainless steel	nil	0.01	< 0.02	< 0.01
Ni-Cu alloy 40	1.3	0.02	< 0.01	0.01

Source: P. Roberge, *Corrosion Basics,* 2nd ed. (Houston, TX, USA: NACE International, 2006), p. 389.

SUGGESTED VELOCITY LIMITS FOR CONDENSER TUBE ALLOYS IN SEAWATER

Alloy	Design Velocity That Should Not Be Exceeded (ft./s)	(m/s)
Copper	3(a)	0.9(a)
Silicon bronze	3(a)	0.9(a)
Admiralty brass	5(a)	1.5(a)
Aluminum brass	8(a)	2.4(a)
90-10 copper nickel	10(a)	3.0(a)
70-30 copper nickel	12(a)	3.7(a)
Ni-Cu alloy 400	No maximum velocity limit(b)	
Type 316 stainless steel	No maximum velocity limit(b)	
Ni-Cr-Fe-Mo alloys 825 and 20Cb3	No maximum velocity limit(b)	
Ni-Cr-Mo alloys 625 and C-276	No velocity limits	
Titanium	No velocity limits	

(a) In deaerated brines encountered in the heat recovery heat exchangers in desalination plants the critical velocities can be increased from 1 to 2 ft./s (0.3 to 0.6 m/s).

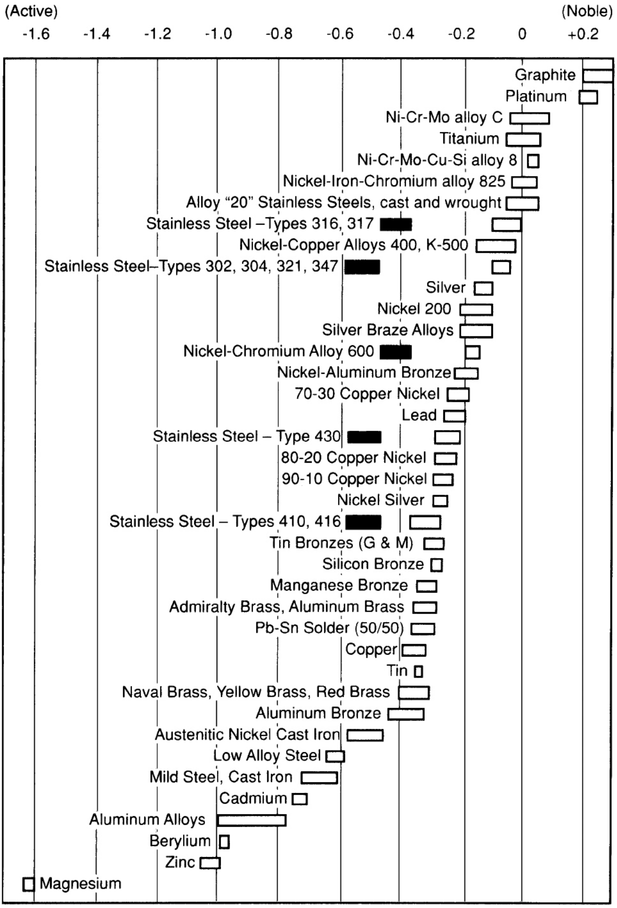
(b) Minimum velocity 5 ft./s (1.5 m/s).

Source: F.L. LaQue, *Marine Corrosion Cause and Prevention* (Hoboken, NJ, USA: John Wiley & Sons, 1975), p. 267. Reprinted with permission from The Electrochemical Society.

GALVANIC SERIES IN SEAWATER

Flowing Seawater at 2.4 to 4.0 m/s for 5 to 15 days at 5 to 30 ˚C

Volts vs Saturated Calomel Reference Electrode



Note: Dark boxes indicate active behavior of active-passive alloys.

Source: ASTM G82, “Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance” (West Conshohocken, PA, USA: ASTM International, 1998). Reprinted with permission, copyright ASTM.

CORROSION OF STEEL IN AERATED WATER

Oxygen Content (ml O_2 /1,000 ml H_2O)	Corrosion Rate (mpy)	Temperature (˚ F)	pH
0	0.00	77	7.0
2	4.93	77	7.0
6 (Airsaturation)	9.86	77	7.0
10	11.87	77	7.0
13	12.42	77	7.0
15	10.59	77	7.0
17	5.48	77	7.0
20	2.19	77	7.0
25	1.46	77	7.0
6	9.86	77	7.0
6 (Closed system)	20.00	132	7.0
6 (Open system)	18.00	132	7.0
6 (Closed system)	30.00	187	7.0
6 (Open system)	10.00	187	7.0
6	9.86	77	7.0
6	9.86	77	4.0
6	15.00	77	3.0
6	+40.00	77	2.6
6	9.86	77	10.0
6	3.00	77	12.0
6	5.00	77	14.0
6	13.00	77	16.0

Source: H.H. Uhlig, *Corrosion and Corrosion Control,* 2nd ed. (Hoboken, New Jersey, USA: John Wiley & Sons, 1971), pp. 94–95, 99. Reprinted with permission, copyright John Wiley & Sons, Inc.

CALCULATION OF CALCIUM CARBONATE SATURATION INDEX (LANGELIER INDEX)

A			C		D	
Total Solids mg/L		**A**	**Calcium Hardness mg/L $CaCO_3$**	**C**	**M.O. Alkalinity mg/L $CaCO_3$**	**D**
	50–300	0.1	10–11	0.6	10–11	1.0
	400–1000	0.2	12–13	0.7	12–13	1.1
			14–17	0.8	14–17	1.2
B			18–22	0.9	18–22	1.3
Temperature			23–27	1.0	23–27	1.4
°C	**°F**	**B**	28–34	1.1	28–35	1.5
0-1	32-34	2.6	35–43	1.2	36–44	1.6
2-6	36–42	2.5	44–55	1.3	45–55	1.7
7-9	44–48	2.4	56–69	1.4	56–69	1.8
10–13	50–56	2.3	70–87	1.5	70–88	1.9
14–17	58–62	2.2	88–110	1.6	89–110	2.0
18–21	64–70	2.1	111–138	1.7	111–139	2.1
22–27	72–80	2.0	139–174	1.8	140–176	2.2
28–31	82–88	1.9	175–220	1.9	177–220	2.3
32–37	90–98	1.8	230–270	2.0	230–270	2.4
38–43	100–110	1.7	280–340	2.1	280–350	2.5
44–50	112–122	1.6	350–430	2.2	360–440	2.6
51–55	124–132	1.5	440–550	2.3	450–550	2.7
56–64	134–146	1.4	560–690	2.4	560–690	2.8
65–71	148–160	1.3	700–870	2.5	700–880	2.9
72–81	162–178	1.2	880–1,000	2.6	890–1,000	3.0

(1) Obtain values of A, B, C, and D from above table.
(2) pHs = (9.3 + A + B) − (C + D).
(3) Saturation index = pH − pHs.

NOTE: Roberge describes the usefulness of this index in *Corrosion Basics*, 2nd ed. (Houston, TX, USA: NACE International, 2006), p. 133. However, care must be taken in use of this index.

WATER ANALYSIS CONVERSION FACTORS

	$CaCO_3$ ppm	$CaCO_3$ grains/US gal.	English degree	French degree	German degree
$CaCO_3$, ppm	1.0	0.058	0.07	0.10	0.056
$CaCO_3$, grains/ US gal.	17.1	1.0	1.2	1.71	0.958
English degree	14.3	0.833	1.0	1.43	0.800
French degree	10.0	0.583	0.7	1.0	0.560
German degree	17.9	1.04	1.24	1.79	1.0

1 English degree = 1 grain $CaCO_3$/Imperial gallon.
1 French degree = 10 ppm $CaCO_3$.
1 German degree = 10 ppm CaO.

Source: Courtesy of H.P. Godard.

COMMON GROUPS OF ALGAE

	Temperature Range			
Group	˚C	˚F	pH Range	Examples
Green Algae	30–35	86–95	5.5–8.9	Chlorella—common unicellular Ulothrix(1)—filamentous Spirogyra—filamentous
Blue-Green Algae (Contain Blue Pigment)	35–40	95–104	6.0–8.9	Anacystis—unicellular slime former Phormidium—filamentous(1) Oscillatoria(2) causes the most severe problems
Diatoms (Brown Pigment and Silica in CellWall)	18–85	64–186	5.5–8.9	Fragilaria Cyclotella Diatoms(1)

(a) These algae may occur in cooling water with as much as 120 ppm chromate present.
(b) Oscillatoria will grow at 186 ˚F and at pH 9.5.

COMMON TYPES OF BACTERIA CAUSING SLIME PROBLEMS

Type	Example	pH Range	Problems Caused
Aerobic Capsulated	Aerobacter aerogenes Flavobacterium Proteus vulgaris Pseudomonas aeroginosa Serratia Alcaligenes	4.0–8.0 Optimum pH 7.5	Major slime forming bacteria. May produce green, yellow, and pink slimes in addition to usual grey or brown slime.
Aerobic Spore-Forming	Bacilus mycoides (in other Bacillus) species	5.0–8.0	Add to slime problem. Spores are more difficult to destroy.
Iron Bacteria	Crenothrix Leptothrix Gallionella	7.4–9.5	Precipitate ferric hydroxide in sheath- like coating around cell-forms bulking slime deposits.

NOTE: All of the above bacteria live in a temperature range of 68 to 104 ˚F with some species growing at 40 to 158 ˚F.

Source: NACE TPC Publication No. 1, "Cooling Water Treatment Manual" (Houston, TX, USA: NACE International, 1971).

MICROORGANISMS COMMONLY IMPLICATED IN BIOLOGICAL CORROSION

Genus or Species	pH Range	Temperature Range ˚C	Oxygen Requirement	Metals Affected	Action
Bacteria					
Desulfovibrio Best known: *D. desulfuricans*	4–8	10–40	Anaerobic	Iron and steel, stainless steels, aluminum zinc, copper alloys	Utilize hydrogen in reducing SO^{2-} to S^{2-} and H_2S; promote formation of sulfide films
Desulfotomaculum Best known: *D. nigrificans* (also known as *Clostridium*)	6–8	10–40 (some 45–75)	Anaerobic	Iron and steel, stainless steels	Reduce SO^{2-} to S^{2-} and H_2S (spore formers)
Desulfomonas	...	10–40	Anaerobic	Iron and steel	Reduce SO^{2-} to S^{2-}
Thiobacillus thiooxidans	0.5–8	10–40	Aerobic	Iron and steel, copper alloys, concrete and H_2S	Oxidizes sulfur and sulfides to form H_2SO_4 : damages protective coatings corrodes concrete in sewers
Thiobacillus ferrooxidans	1–7	10–40	Aerobic	Iron and steel	Oxidizes ferrous to ferric
Gallionella	7–10	20–40	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous (and manganous) to ferric (and manganic): promotes tubercule formation
Sphaerotilus	7–10	20–40	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous (and manganous) to ferric (and manganic): promotes tubercule formation
S. natans	...	...	...	Aluminum alloys	
Pseudomonas	4–9	20–40	Aerobic	Iron and steel, stainless steels	Some strains can reduce ferric to ferrous
P. aeruginosa	4–8	20–40	Aerobic	Aluminum alloys	
Fungi					
Cladosporium resinae	3–7	10–45 (best at 30–35)	...	Aluminum alloys	Produces organic acids in metabolizing certain fuel constituents

Source: L.J. Korb, *Metals Handbook*, 9th ed., vol. 13 (Materials Park, OH, USA: ASM International, 1987), p. 118. Reprinted with permission from ASM International.

MICROBIOCIDES USED IN COOLING WATER SYSTEMS

	Effectiveness[(a)]			
Microbiocide	**Bacteria**	**Fungi**	**Algae**	**Comments**
Chlorine	E	E	E	Oxidizing: reacts with $-NH_2$ groups; effective at neutral pH; loses effectiveness at 0.1–0.2 mg/L continuous free residual; 0.5–1.0 mg/L
Chlorine dioxide	E	G	G	Oxidizing; pH insensitive; can be used in presence of $-NH_2$ groups. Use concentration: 0.1–1 mg/L. intermittent free high pH. Use concentration: residual
Bromine	E	S	E	Oxidizing; substitute for Cl_2 and ClO_2; effective over broad pH range. Use concentration: 0.05–0.1 mg/L continuous free residual; 0.2 to 0.4 mg/L intermittent free residual
Organo-bromide (DBNPA)	E	NA	S	Nonoxidizing; pH range 6-8.5. Use concentration: 0.5–24 mg/L intermittent feed
Methylene bisthiocyanate	E	S	S	Nonoxidizing; hydrolyzes above pH 8. Use concentration: 1.5-8 mg/L intermittent feed
Isothiazolinone	E	G	E	Nonoxidizing; pH insensitive; deactivated by HS^- and $-NH_2$ groups. Use concentration: 0.9–13 mg/L intermittent feed
Quaternary ammonium salts	E	G	E	Nonoxidizing; tendency to foam; surface active; ineffective in highly oil- or organic-fouled systems. Use concentration: 8–35 mg/L intermittent feed
Organo-tin/ quaternary ammonium salts	E	G	E	Nonoxidizing; tendency to foam; functions best in alkaline pH. Use concentration: 7–50 mg/L
Glutaraldehyde	E	E	E	Nonoxidizing; deactivated by $-NH_2$ groups; effective over broad pH range. Use concentration: 10–75 mg/L intermittent feed

(a) E: excellent; G: good; S: slight, NA: not applicable

Source: L.J. Korb, *Metals Handbook*, 9th ed., vol. 13 (Materials Park, OH, USA: ASM International, 1987), p. 493. Reprinted with permission from ASM International.