

WROUGHT COPPER BASE ALLOYS FOR DESALINATION

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Summary

The principal copper alloys used in modern desalination plants include 90-10 copper nickel, C70600, 70-30 copper nickel, C71500, 2 per cent Fe, 2 per cent Mn modified copper nickel, C71640, aluminum brass, C68700, aluminum bronzes, C61300 and C61400, nickel aluminum bronze, C63000, naval brass, C46500, and C2800 Muntz metal. The composition and properties of these alloys are given in the Appendices. The three copper nickel alloys and aluminum brass are used as tubing. C70600 copper nickel and the aluminum bronze alloys are used for piping, water boxes and tubesheets. Naval brass and Muntz metal are used for tubesheets with aluminum brass tubes.

1. Corrosion Behavior in Clean Seawater

The corrosion resistance of copper base alloys depends upon formation of a protective film. Film formation is referred to sometimes as "passivation". The protective films formed on the different copper base alloys have general similarities, but differ considerably in composition, thickness and durability as well as in effectiveness. Film formation is affected by pH, time, aeration, velocity, temperature, pollution and other factors. There is generally an inner cuprous oxide film, Cu_2O , and an outer cupric oxide, CuO , film (Worth and Pryor 1970; Pourbaix 1974; Gilbert 1982). Although cuprous and cupric oxides are the principal components of the films, the lattice usually includes other metallic ions, iron, nickel, aluminum, calcium, sometimes silicon, and sometimes other species. Principal anions include chlorides, hydroxides and carbonates, bicarbonates and oxides. There is no fixed composition other than the dual cuprous-cupric oxide structure characterizing films on copper and copper base alloys in normal waters (Pourbaix 1974).

The inner film is normally reddish. The outer film may be greenish, brown or yellow-brown. Despite variations in composition, these oxide type films offer a high degree of protection, when formed under favorable conditions. In polluted waters, and in well water from shore side wells, the film is often a sulfide, rather than an oxide, type film.

Sulfide films are readily distinguished by their black color. Sulfide films, while protective, are thicker, more porous, and more easily damaged than oxide films.

Time is a major factor in film formation and a major factor in the degree of protection the film affords. Figure 1 shows the rate of film formation on C70600 in 60°F (16°C) seawater as measured by copper in the effluent (Tuthill 1987).

In 10 min copper in the effluent decreased tenfold; in 2 h a hundred-fold, but it was 3 months before the film became "mature" - mature in the sense that copper in the effluent was only slightly more than copper in the intake water. Efir and Anderson's data in Figure 2 show that corrosion rate, as measured by weight loss, continues to decrease in quiet and flowing seawater well beyond 3 months up to, at least, 7 years (INCO 1975).

The fact that the film becomes more protective with time accounts for the considerable variation in corrosion rates and durability of copper base alloys as reported by different investigators in the published literature. Data obtained in short term tests, before a fully mature film has formed, can be expected to overstate the corrosion rate and to understate the durability of copper alloys.

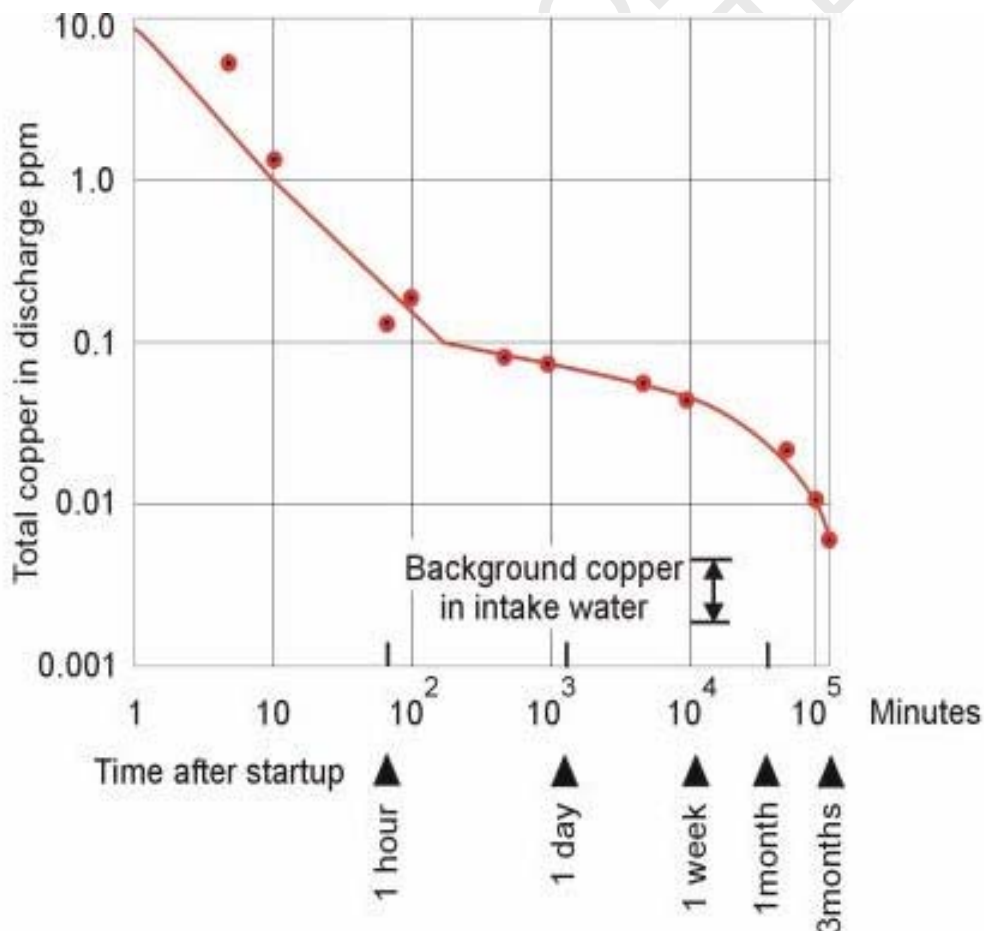


Figure 1. Formation rate of corrosion product film on Alloy C70600 in 60°F (16°C) seawater (Tuthill 1987).

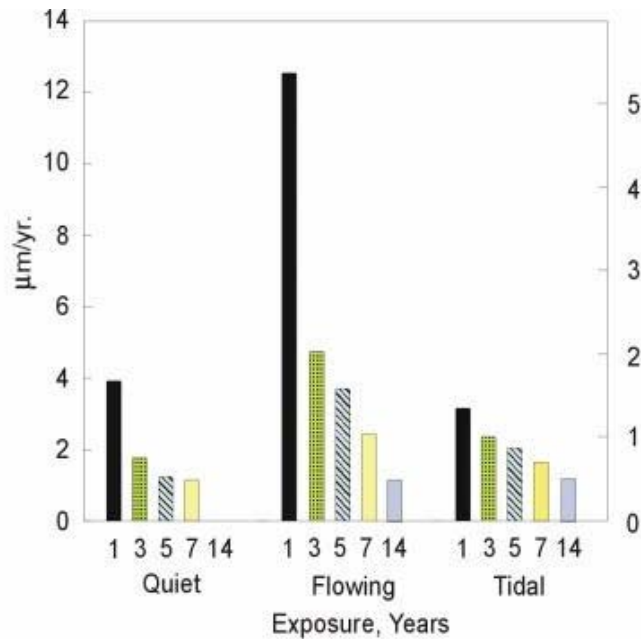


Figure 2. Corrosion rates for Alloy C70600 for long-term seawater exposure (INCO 1975).

Temperature has a major influence on the rate of film formation. At 60°F (16°C) it took slightly over one hour for the film to cover the surface and 3 months before a reasonably mature film reduced copper in the discharge close to the level of copper in the intake (Figure 1). At higher temperatures the film forms and matures faster. At lower temperatures, the film forms and matures more slowly. At 35°F (2°C) it took a week before a visible film completely covered specimens of C70600 in some work the author undertook. This corresponds roughly with the slightly over 1 h it took for full coverage to occur at 60°F (16°C), Figure 1. Although the film forms more slowly at low temperatures, it does form and become protective, even in Arctic and Antarctic waters, as demonstrated by the good performance of copper alloy tubed desalination plants at Prudhoe Bay, Alaska and McMurdo Sound, Antarctica. At 80°F (27°C), a common inlet temperature for MidEast desalination plants, rapid film formation and good protection can be expected within a day or two.

Oxygen is very important in film formation on copper alloys. Oxygen reduction is the primary cathodic reaction supporting corrosion, and film formation, of copper alloys in seawater. In the complete absence of oxygen, there would be no film formation and no corrosion of copper alloys in most waters. The feed from the heat reject section to the heat recovery section of many MSF desalination plants is deaerated, hence corrosion in the heat recovery section was not originally expected. However, the flash chambers of heat recovery sections are under vacuum and air is sucked in. In actual practice, there seems always to be sufficient oxygen present, due to the residual oxygen content of heat recovery section feed and to in-leakage of air, to support some corrosion of copper alloys as well as substantial corrosion of carbon steel.

Another major factor influencing film formation is pH. Ross and Anderson (Ross and Anderson 1975; Ross 1977) studied film formation on C70600, C71500, and C68700 in

seawater and found no film formation below pH 6 even though there was adequate oxygen, 5.5-7.5 mg l⁻¹, present. The unfilmed corrosion rates were high, on the order of 35 mpy (0.89 mm y⁻¹). At higher pH's, where some oxygen was present, corrosion rates were low and normal.

Velocity has several effects. At velocities below 3 fps (0.9 mps), sediment settles out readily in horizontal runs of pipe and tubing. Unless removed periodically, under-sediment corrosion, as evidenced by a general pitting attack, may occur. Slime layers also build up at low velocities, providing a good habitat for biofouling organisms to attach and grow. At normal design velocities of 5-8 fps (1.5-2.4 mps), turbulence around debris lodged in copper alloy tubes, partially blocking flow, has led to pinhole type failures of copper alloy tubing downstream of such lodgments (Newton and Bickett 1968; Ridgeway and Heath 1969). At higher velocities the protective film itself may be damaged or even stripped away, allowing the unfilmed areas to corrode at the high rates characteristic of initial exposure of unfilmed material.

Efird (1975) has studied the critical velocity at which the film is stripped away from copper alloys and the tube-wall-to-flowing-seawater shear stresses that exist at the inlet end, 5 diameters down the tube, and around obstructions. The critical velocity at which the protective film is stripped away by flow for the tube alloys is shown in Table 1. The somewhat higher critical shear stress for C70600 as compared to C71500 alloy is probably due to the higher water temperature at which the measurement was made, 27°C for C70600 versus 12°C for C71500. The film forms faster at the higher temperature and was probably more mature than the one formed at the lower temperature. The tube-wall-to-flowing-seawater shear stresses are shown in Table 2. The very high stresses shown downstream of partial lodgments explain why pinhole type penetrations occur downstream of debris in systems with poorly maintained screens.

Alloy	Critical velocity		Temp. °C	Critical shear stress, (Mpa)
	(m s ⁻¹)	(ft s ⁻¹)		
C12200 (copper)	1.3	4.4	17	9.6
C68700 (aluminum bars)	2.2	7.3	12	19.2
C70600 (90/10-Cu/Ni)	4.5	14.7	27	43.1
C71500 (70/30 Cu/Ni)	4.1	13.5	12	47.9
C72200 (Cu-16Ni-0.5Cr)	12.0	39.4	27	296.9

Table 1. Critical velocity and shear stress for copper-base alloys in seawater (Efird 1975).

Design Velocity		Tube wall shear stress (Mpa)		
(m s ⁻¹)	(ft s ⁻¹)	Inlet	>5 L/D Down tube	Around a 90% blockage
2.0	6.5	18.4	10.8	264.6
2.5	8.1	28.0	<18.0	
2.75	9.0	33.0	20.0	
3.0	9.8	37.4	22.0	

Table 2. Shear stresses developed in condenser tubes in seawater (Efird 1975).

2. Corrosion Behavior in Modified Seawater

There have been a number of studies on the effect that pollution and sulfides have on corrosion behavior of copper alloys; results have varied considerably. Syrett has published one of the better and most thorough studies on the effect of sulfides (Syrett 1981).

Figure 3 from Syrett's paper presents a large amount of useful information and is worth reviewing in some detail. The upper line AB represents the anodic reaction in aerated water and traces normal film formation. The initial section of line AB represents corrosion of unfiled metal. The next, nearly vertical section, depicts the initial film forming stage where cuprous oxide is forming.

The intersection with the oxygen reduction line (EF) identifies the steady state corrosion current i_2 at the normal potential, E_2 . The steady state corrosion current i_2 corresponds to the steady state corrosion rate, which is normally less than 1 mpy (0.025 mm y^{-1}) for this copper alloy.

Line CD represents the anodic reaction in deaerated waters where sulfide is present. The cathodic reaction is shown by the hydrogen reduction line IJ; the corrosion potential is E_1 , and the steady state corrosion current is i_1 , point $\frac{1}{4}$. The film that forms in fully deaerated, sulfide-bearing waters is black, more porous, less adherent, and more easily damaged than the oxide type films previously described.

The corrosion current is much lower than in aerated waters, which would mean lower corrosion rates in sulfide infested waters, were it not for the more porous, more easily damaged nature of the sulfide film.

It should be noted that in deaerated waters in the absence of sulfides, hydrogen reduction does not occur, since copper will not displace hydrogen from water. It is only in deaerated sulfide bearing waters that the potential is depressed sufficiently for hydrogen reduction to occur.

When air is present in waters containing hydrogen sulfide, as can be the case with air in-leakage into the flash chambers which operate under a vacuum, the corrosion of copper alloys is greatly accelerated.

The intersection of the anodic line CD with the oxygen reduction line GH, point \downarrow , identifies the condition where air and sulfides coexist in seawater. The corrosion current at point \downarrow is two orders of magnitude greater than i_2 , the corrosion current in normal aerated seawater, and at least three orders of magnitude greater than the i_1 , the corrosion current in deaerated sulfide-bearing waters.

Air and hydrogen sulfide do not coexist at equilibrium, as oxygen reacts with hydrogen sulfide to produce sulfur and water. However, there is abundant evidence that oxygen and hydrogen do coexist under transitory, non-equilibrium conditions. Corrosion can be quite severe when these conditions exist. For example, May and Weldon (1964) found that 3 ppm of H_2S continuously added to clean aerated seawater increased the corrosion

rate of these copper alloys 4 to 10-fold.

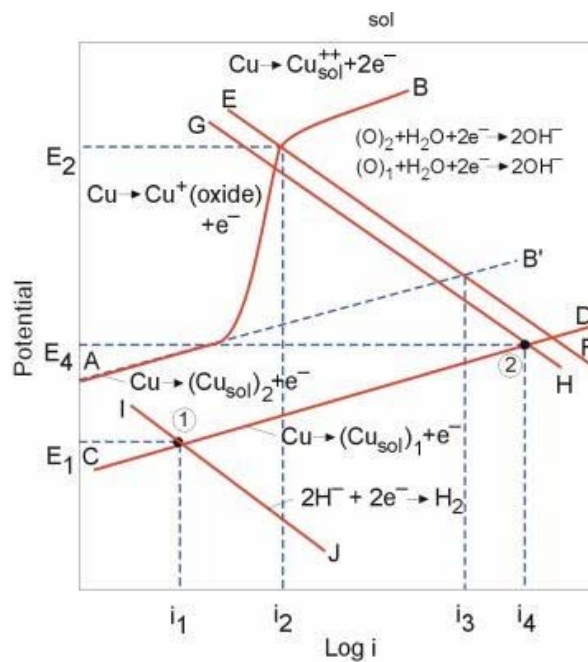


Figure 3. Influence of sulfide and oxygen on the corrosion current in a copper-nickel alloy exposed to flowing seawater (Pourbaix 1974).

Ammonia is sometimes encountered in the seawater feed to desalination plants. Ammonia may come from agricultural runoff or from industrial plant discharges near desalination plant intakes. Ammonia affects different copper alloys differently. In the presence of air and ammonia, aluminum brass is subject to stress corrosion cracking. Aluminum bronze is more resistant and copper nickels are highly resistant to ammonia stress corrosion cracking, as Thompson has shown, Table 3. Ammonia also tends to increase the general corrosion rates of copper alloys. Quantitative data for the increase in corrosion rate due to ammonia contamination is not yet available. However, Figure 4, from Michaels et al. (1979), shows the copper nickel alloys to be three orders of magnitude more resistant than aluminum brass to general corrosion in spray and fog tests with 1000-2000 ppm ammonia present.

Alloy		Time to 50% relaxation (h)
C44300		0.30
C2800		0.35
C46500		0.50
C26000		0.51
C68700		0.60
C60600		4.08
C61400		5.94
C70600		234
C14200	PDO copper	312
C71500		2000

Table 3. Ammoniacal stress corrosion resistance of brasses, aluminum bronzes, and copper-nickel alloys (Thompson 1961).

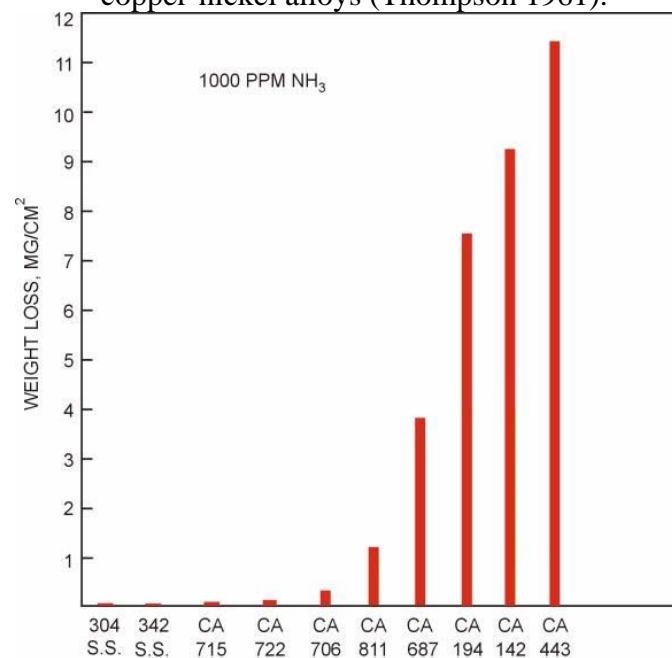


Figure 4. Weight losses of various alloys after testing for 10 days in 1000 ppm NH₃ contaminated condensate at 38°C (100°F) (Michaels 1979).

Chlorine is a common additive to seawater to control biofouling. Chlorination practices vary, especially since different governments regulate the residual chlorine allowed in the effluent differently. Chlorine also controls slime and is beneficial in preventing corrosion that might occur in time under adherent biofouling. The effect of chlorine residuals in the 0.5 to 3.0 ppm range on the three tubing alloys is shown in Table 4 (Anderson 1966). The corrosion rate for the 70-30 copper nickel alloy, C71500, appears to decrease slightly for chlorine residuals up to 3 ppm. For C70600, some concentrations resulted in slight decreases in corrosion rate, others in increases. For C68700, some chlorine concentrations had little effect on corrosion rate, others increased the corrosion rate. Overdosing beyond 3 ppm, which unfortunately occurs from time to time in a number of desalination plants, can be detrimental to performance of copper alloy tubing. Tubing in the heat reject stage is affected by overdosing. Tubing in the heat recovery stage, downstream of the heat reject stage, is less affected by overdosing, as the residual chlorine is consumed rapidly. Chlorine reacts rapidly with organic material and oxidizable species in seawater.

Chlorine residual	C68700	C70600	C71500
0.0 ppm	<1.0 (<0.03)	<1.0 (<0.03)	<1.0 (<0.03)
0.5 ppm continuous	2.9 (0.073)	1.6 (0.04)	0.4 (0.01)
0.5 ppm 2 h on, 2 h off	3.1 (0.08)	0.7 (0.02)	-
Ppm 1 h on, 5 h off	0.9 (0.023)	3.2 (0.08)	0.5 (0.013)
Ppm 2 h on, 2 h off	0.9 (0.023)	0.5 (0.013)	0.1 (0.003)
Ppm 2 h on, 2 h off	2.4 (0.06)	0.3 (0.008)	0.2 (0.005)

Table 4. The effects of chlorination on copper tubing alloys - mpy (mm y⁻¹) (Anderson

1966).

Sand is common in seawater from open channels in shallow waters. High sand loadings can be detrimental to copper alloy tubing. Sato and Nagata (1977) have developed some useful guidelines on the effect of sand. High sand loadings can damage the protective film, exposing bare metal to high unfiltered corrosion rates. For any given sand loading, damage increases with the size and sharpness of the sand present.

The general order of copper alloy resistance to sand follows.

1. C68700 - least resistance
2. C70600 - more resistance
3. C71500 - more resistance
4. C71640 - outstanding resistance

Sand is not always detrimental. Fine beach sands, which are the most likely to be encountered, are less damaging than larger angular particles encountered in some estuaries. Rough guidelines follow.

1. Up to 200 ppm of sand - Unlikely to be a problem
2. 200-1000 ppm of sand - Increasing potential for damage. Good performance from the less resistant alloys has been reported after a mature film forms under favorable conditions.
3. >1000 ppm of sand - resistance of the first three alloys listed above is often inadequate. C71640 is usually resistant.

Intermittent exposure to even the higher sand loadings is not necessarily damaging, particularly when fully mature films have formed. Spikes are not as damaging as steady state loadings.

Corrosion behavior in brackish and higher salinity waters is quite similar to performance in seawater. Experience indicates that velocity and turbulence damage may be a little less in brackish waters than in seawater, but there have been few studies made in fresh or low salinity waters.

Copper alloys seem to perform much the same in low as well as high chloride waters. The other factors discussed above, not chloride ion concentration, appear to control performance.

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Bibliography and Suggestions for further study

- Aluminum Bronze Alloys Corrosion Resistance Guide. UK: Copper Development Association.
- Anderson D B (1966) Chlorination of Sea Water - Effects on Fouling and Corrosion. *Journal of Engineering for Power*, July.
- Ashbaugh W.G. (1986). Corrosion Failures. In *Metals Handbook. Failure analysis and prevention*. Vol. 11 (ed. K. Mills). pp.172-202. Metals Park, Ohio: ASM International. [Deals with corrosion failure analysis in detail. The same volume contains a special article on analysis of corrosion fatigue failures.]
- Bardal, E (2001): Corrosion in seawater – biological effects. www.desware.net. Oxford: EOLSS Publishers. [Main emphasis on corrosion resistant materials.]
- Birkett J D and Newton E H (1981) Survey of Service Behavior of Large Evaporative Desalting Plants, Cambridge, MA: A. D. Little Inc., April.
- CDA (1972) *Welding Handbook*. Copper Development Association US from Chapter 68 Sixth Edition of Vol. 4.
- Craig B. and Pohlman S.L. (1987). Forms of Corrosion. In *Metals Handbook. Corrosion*, Vol. 13 (ed. J. R. Davis), pp. 77-190. Metals Park, Ohio: ASM International. [A section with many articles by different authors, with description of corrosion forms.]
- Efird K D (1975) Corrosion/75 Paper No. 54. Houston, TX: NACE.
- Efird K. D. (1977). Effects of Fluid Dynamics on the Copper and Copper-Base Alloys in Seawater. *Corrosion* **33**(Jan), 3–8. [Determination of critical velocities for erosion corrosion of copper alloys.]
- Fontana M. G. and Greene N. (1978). Corrosion Forms. In *Corrosion Engineering*, pp. 28-115. New York: McGraw-Hill [Excellent and comprehensive description of various corrosion forms.]
- George P F (1973) Copper Alloys in the Desalting Environment. November, 1970 through November, Dow Chemical Company, Texas Division, Freeport Texas, for the Copper Development Association, 260 Madison Ave. NY, NY 10016.
- Gilbert P T (1982) A Review of Recent Work on Corrosion Behavior of Copper Alloys in Sea Water. MP Feb., pp. 47-53.
- Harding K and Bridle D A (1978) Corrosion of Ampco Alloys 8, 483 and 280 in an operating acid dosed seawater distiller. Chemistry Group, AEE Winfith (Unpublished).
- INCO (1975) Corrosion Resistance of Wrought 90-10 Copper-Nickel-Iron Alloy in Marine Environments. INCO TP A-1222.
- INCO (1979) Guide to the welding of copper-nickel alloys. INCO Europe Ltd.
- Lees D. J. (1982). Characteristics of Stress-Corrosion Fracture Initiation and Protection. *Metallurgist and Materials Technologist*, **14** (1), 29-38 [Comprehensive review of stress corrosion cracking.]
- May T P and Weldon B A (1964) Copper-nickel alloys for service in seawater. 24th International Congress on Fouling and Marine Corrosion, Cannes, France.
- Michaels H T (1979) The Influence of Corrosion and Fouling on Steam Condenser Performance. *Journal of Materials for Energy Systems* 1, Dec.
- Newton E H and Birkett J D (1968) *Survey of Materials Behavior in Multi-Stage Flash Distillation Plants*. Cambridge, MA: A. D. Little Inc., August.
- Newton E H, Birkett, J D and Ketteringham J M (1972) Cambridge, MA: A. D. Little Inc., March.
- North R F and Pryor M J (1970) *Corrosion Science* 10, 197.
- Perkins A. (1996). Corrosion monitoring. *Corrosion Engineering Handbook*, (ed. P. A. Schweitzer), pp. 623–652. New York: Marcel Dekker. [Description of various corrosion monitoring methods]
- Pourbaix M (1974) Atlas of Electrochemical Equilibria in Aqueous Solutions. Houston, TX: NACE.
- Ridgeway W F and Heath D J (1969) Lining mild steel components with 90/10 copper nickel alloy sheet.

Welding and Metal Fabrication, October, INCO London Publication 4210.

Ross W R (1977) The effect of seawater composition on corrosion of Cu-Ni-Fe alloys at elevated temperatures, *Corrosion/77*, Paper No. 94, San Francisco, March.

Ross W R and Anderson D B (1975) Hot Sea Water Corrosion of Copper-Base Alloys. *MP Sept.*, pp. 27-32.

Sato S and Nagata K (1977) Factors affecting corrosion of condenser tubes of copper alloys and titanium. *Corrosion 77*. Toronto: NACE.

Syrett B C (1981) Sulfide Attack in Steam Surface Condensers. "Proceedings of Second Intl. Conference on Environmental Degradation of Engineering Materials in an Aggressive Environment", pp. 3-14.

Thompson D H (1961) *Materials Research Std* 1, 108.

Todd B (1976) Private Communication.

Tuthill A H, Moller G E and Hornburg D (1995) The Suitability of 6% Molybdenum Austenitic Stainless Steels for Desalination Plant Services. IDA World Congress on Desalination and Water Sciences, Abu Dhabi, November 1995, 412-430.

Tuthill A H (1987) Guidelines for the use of copper alloys in seawater. *MP* 26(9), 12-22.

Wood J.D. (1989). Guide to Nondestructive evaluation techniques. In *Metals Handbook. Non-destructive evaluation and quality control.*, Vol. 17 (ed. J. R. Davis), pp. 49-51. Metals Park, Ohio: ASM International. [This is an introduction that is followed by a series of articles by many different authors, with detailed description of inspection and monitoring methods.]